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Nickel(II) complexes with novel nitron-type NHC ligands: synthesis and catalytic activity in the Suzuki–Miyaura coupling of aryl chlorides

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S1. General information and materials

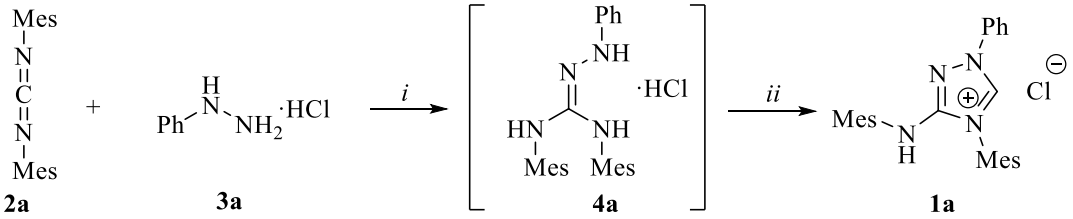
General Procedures. Solvents were purified and dried according to standard methods and stored over activated 3Å molecular sieves prior to use. Column chromatography was conducted on silica gel 60 (230−400 mesh, Merck).

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance Neo 300 (300 and 75 MHz, respectively) spectrometer. Chemical shifts are given relative to the residual signals of protons of chloroform-*d* or DMSO-d_6 (7.26 and 2.50 ppm for ^{1}H NMR, respectively) or carbon signals in chloroform-*d* or DMSO-d_6 (77.16 and 39.52 ppm for ^{13}C NMR, respectively). Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer. GC-MS analyses were accomplished using an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass-selective detector (EI, 70 eV) and an HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as the carrier gas at a flow rate of 1.0 ml·min^{-1}. Melting points were determined in a Thiele apparatus in open capillary tubes and were uncorrected.

Materials.

Starting compounds, *N*,*N'*-bis(2,4,6-trimethylphenyl)carbodiimide (**2a**),[S1] *N*,*N'*-bis[2,6-di(propan-2-yl)phenyl]carbodiimide (**2d**)[S1] were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

S2. Extended experimental data



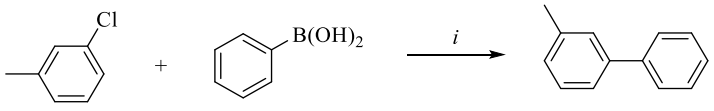
Scheme S1 *Reagents and conditions i*, **2a** (1.08 g, 3.88 mmol), **3a** (432 mg, 4 mmol), Et_3N (7.88 mg, 7.8 mmol), THF (15 ml), room temperature, 16 h. *ii*, See Table S1.

Table S1. Optimization of the cyclization step (*ii*, Scheme S1) in the synthesis of compound **1a**.[a]

Entry	Reagents	Solvent[b]	T (°C)	Time (h)	Yield of 1a (%)[c]
1.	HCOOH (10 eq)	neat	reflux	24	0
2.	1. CH_2O (40% aq. Solution, 2 ml) 2. Glacial CH_3COOH (1 g), $NaNO_2$ (0.5 g)[d]	1. *i*-PrOH 2. *i*-PrOH	1. 65 2. 65	1. 0.5 2. 2	0
3.	$HC(OMe)_3$ (3.3 eq),	EtOAc	reflux	24	0
4.	$HC(OMe)_3$ (3.3 eq),	neat	reflux	24	0
5.	$HC(OMe)_3$ (3.3 eq), HCl (1.5 eq, 35% aq. solution)	EtOAc	80	3	0
6.	$HC(OMe)_3$ (3.3 eq), HCl (1.5 eq, 10% dioxane solution)	EtOAc	80	3	32
7.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.5 eq)	EtOAc	80	3	74
8.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.1 eq)	EtOAc	80	3	72
9.	$HC(OMe)_3$ (5 eq), Me_3SiCl (1.1 eq)	EtOAc	80	3	71
10.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.1 eq)	EtOAc	60	3	49
11.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.1 eq)	EtOAc	80	1	52
12.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.1 eq)	Dioxane	80	3	57
13.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.1 eq)	THF	60	3	27
14.	$HC(OMe)_3$ (3.3 eq), Me_3SiCl (1.1 eq)	Toluene	80	3	37

[a] Residue formed after removing of volatiles by rotary evaporation in vacuum after the reaction of **2a** (1.08 g, 3.88 mmol), **3a** (432 mg, 4 mmol) and Et_3N (7.88 mg, 7.8 mmol) in THF (15 ml) at room temperature within 16 h was used as crude starting compound **4a**.
[b] Solvent (7 ml).
[c] Isolated yield.
[d] Formaldehyde and *i*-PrOH were removed by rotary evaporation in vacuum before the oxidation with NaO_2.

Table S2. Optimization of the Suzuki-Miyaura cross-coupling conditions[a]



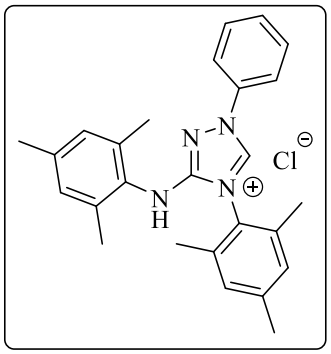
8a **9a** **10a**

Entry	**5a** loading, mol%	T, °C	Solvent	Time, h	Base	Yield of **10a**, %[b]
1	0.5	90	Toluene	5	K_3PO_4	45
2	1	90	Dioxane	5	K_3PO_4	88
3	1	90	Dioxane	3	K_3PO_4	70
4	0.5	90	Dioxane	3	K_3PO_4	63
5	0.5	90	Dioxane	5	K_3PO_4	85
6	0.5	90	Dioxane	16	K_3PO_4	87
7	0.5	60	Dioxane	5	K_3PO_4	57
8	0.5	120	Dioxane	5	K_3PO_4	75
9	0.5	90	MeCN	5	K_3PO_4	0
10	0.5	90	Xylene	5	K_3PO_4	70
11	0.5	90	DMA	5	K_3PO_4	0
12	0.5	90	Dioxane	5	K_2CO_3	0
13	0.5	90	Dioxane	5	Cs_2CO_3	0
14	0.5	90	Dioxane	5	KOH	10
15	0.5	90	Dioxane	5	t-BuOK	trace
16	0.5	90	Dioxane	5	t-BuONa	trace
17	0.5	90	Dioxane	5	without base	0

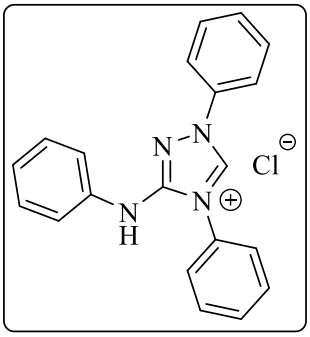
[a] *Reagents and conditions*: *i*, **8a** (0.1 mmol), **9a** (0.15 mmol), base (0.3 mmol), **5a** (0.5-1 mol%), solvent (1 ml), reaction time 3-16 h. [b] The yield was determined by GC-MS.

S3. Synthetic procedures and characterization of isolated compounds

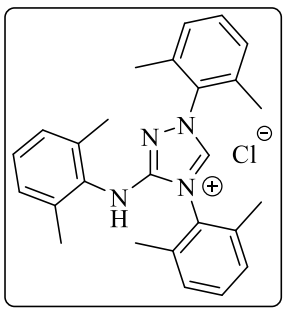
General procedure for the preparation of compounds 1a-i. A mixture of *N,N'*-diarylcarbodiimide **2a-d** (3.88 mmol), arylhydrazine hydrochloride **3a-d** (3.90 mmol) and Et_3N (788 mg, 7.8 mmol) in THF (15 ml) was stirred at 20 °C for 12 h. The THF was then rotary evaporated under vacuum at 25-30 °C and the resulting residue was dissolved in a mixture of EtOAc (7 ml) and trimethyl orthoformate (1.36 g, 12.80 mmol). While stirring, Me_3SiCl (922 mg, 8.54 mmol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 10 min and refluxed for 3 h. Upon cooling to 0-5 °C, the resulting precipitate was collected by filtration and recrystallized from CH_2Cl_2:EtOAc (1:4 vol.) mixture, then dried *in vacuo* at 50 °C overnight.



1-Phenyl-4-(2,4,6-trimethylphenyl)-3-[(2,4,6-trimethylphenyl)amino]-1*H*-1,2,4-triazol-4-ium chloride (1a). Yield 1209 mg (72 %), white powder, mp 279-281 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.19 (s, 6H), 2.26 (s, 3H), 2.30 (s, 6H), 2.39 (s, 3H), 6.99 (s, 2H), 7.27 (s, 2H), 7.53-7.64 (m, 3H), 7.89-7.92 (m, 2H), 9.07 (s, 1H), 11.04 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 17.3, 17.8, 20.5, 20.8, 120.1, 125.8, 129.1, 129.79, 129.83, 129.9, 131.4, 135.1, 135.4, 136.1, 136.9, 139.2, 141.4, 152.2. Anal. calcd. for $C_{26}H_{29}ClN_4$ (%): C, 72.12; H, 6.75; N, 12.94. Found (%): C, 71.87; H, 6.87; N, 12.84.

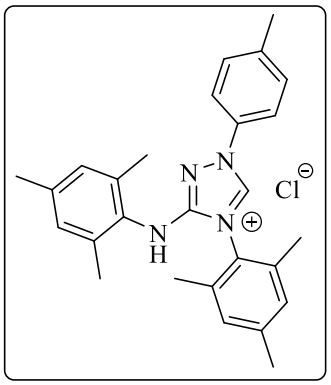


1,4-Diphenyl-3-(phenylamino)-1*H*-1,2,4-triazol-4-ium chloride (1b). Yield 796 mg (59%), white powder, mp 272-274 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.07-7.13 (m, 1H), 7.36-7.43 (m, 2H), 7.62-7.76 (m, 8H), 7.87-7.91 (m, 2H), 8.06-8.09 (m, 2H), 9.81 (s, 1H), 11.17 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 119.1, 120.0, 123.3, 126.8, 129.0, 130.06, 130.10, 130.14, 130.7, 131.2, 135.0, 138.5, 139.5, 150.5. Anal. calcd. for $C_{20}H_{17}ClN_4$ (%): C, 68.86; H, 4.91; N, 16.06. Found (%): C, 69.05; H, 4.76; N, 16.17.

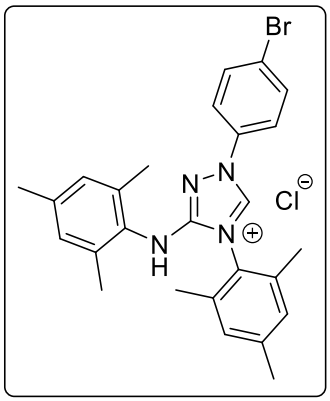


1,4-Bis(2,6-dimethylphenyl)-3-[(2,6-dimethylphenyl)amino]-1*H*-1,2,4-triazol-4-ium chloride (1c). Yield 756 mg (45 %), white powder, mp 296-298 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.24(s, 6H), 2.28 (s, 6H), 2.36 (s, 6H), 7.09-7.19 (m, 5H), 7.29-7.35 (m, 4H), 7.39-7.44 (m, 1H), 11.65 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 18.1, 18.4, 127.5, 128.6, 128.9, 129.0, 130.0, 131.4, 132.2, 132.9, 133.8, 135.2, 135.8,

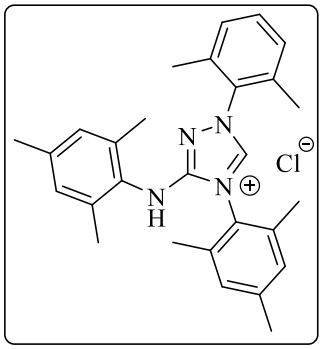
136.1, 143.3, 152.6. Anal. calcd. for $C_{26}H_{29}ClN_4$ (%): C, 72.12; H, 6.75; N, 12.94. Found (%): C, 72.34; H, 6.66; N, 12.78.



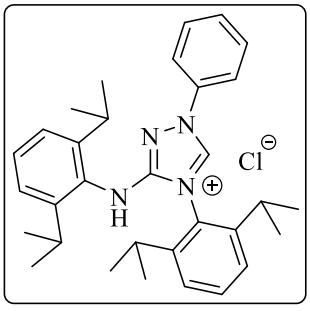
1-(4-Methylphenyl)-4-(2,4,6-trimethylphenyl)-3-[(2,4,6-trimethylphenyl)amino]-1*H*-1,2,4-triazol-4-ium chloride (1d). Yield 728 mg (42 %), white powder, mp 248-250 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.18 (s, 6H), 2.29-2.36 (m, 15H), 5.87 (s, 1H), 6.93 (s, 2H), 7.10 (s, 2H), 7.24-7.27 (m, 2H), 8.09-8.12 (m, 2H), 12.66 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.2, 18.3, 21.1, 21.3, 21.4, 120.1, 124.8, 129.7, 129.8, 130.4, 130.9, 132.9, 135.2, 135.9, 138.5, 139.3, 140.5, 142.8, 151.7. Anal. calcd. for $C_{27}H_{31}ClN_4$ (%): C, 72.55; H, 6.99; N, 12.53. Found (%): C, 72.37; H, 7.12; N, 12.65.



1-(4-Bromophenyl)-4-(2,4,6-trimethylphenyl)-3-[(2,4,6-trimethylphenyl)amino]-1*H*-1,2,4-triazol-4-ium chloride (1e). Yield 1013 mg (51%), white powder, mp >310 °C ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.17 (s, 6H), 2.26 (s, 3H), 2.29 (s, 6H), 2.39 (s, 3H), 6.98 (s, 2H), 7.26 (s, 2H), 7.83 (s, 4H), 9.08 (s, 1H), 11.01 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 17.3, 17.7, 20.5, 20.8, 122.2, 122.6, 125.7, 129.1, 129.8, 131.3, 132.7, 134.4, 135.4, 136.1, 136.9, 139.6, 141.4, 152.1. Anal. calcd. for $C_{26}H_{28}BrClN_4$ (%): C, 61.01; H, 5.51; N, 10.95. Found (%): C, 60.87; H, 5.63; N, 10.83.

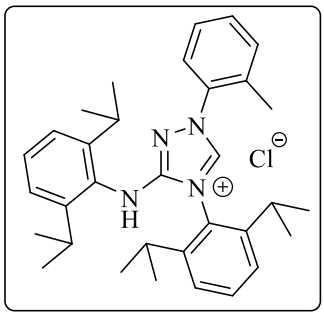


1,4-Bis(2,4,6-trimethylphenyl)-3-[(2,4,6-trimethylphenyl)amino]-1*H*-1,2,4-triazol-4-ium chloride (1f). Yield 966 mg (54%), white powder, mp >310 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (s, 6H), 2.24 (s, 3H), 2.26 (s. 6H), 2.37 (s, 9H), 5.99 (s, 1H), 6.90 (s, 2H), 7.11-7.13 (m, 4H), 7.25-7.30 (m, 1H), 12.32 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 18.1, 18.2, 21.1, 21.4, 124.7, 129.0, 129.7, 129.9, 130.9, 131.4, 133.9, 135.25, 135.30, 135.7, 138.8, 142.9, 144.1, 152.5. Anal. calcd. for $C_{28}H_{33}ClN_4$ (%): C, 72.94; H, 7.21; N, 12.15. Found (%): C, 73.12; H, 7.07; N, 12.19.

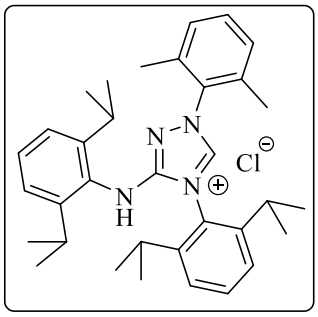


4-[2,6-Di(propan-2-yl)phenyl]-3-{[2,6-di(propan-2-yl)phenyl]amino}-1-phenyl-1*H*-1,2,4-triazol-4-ium chloride (1g). Yield 1244 mg (62%), white powder, mp 293-295 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.12-1.17 (m, 12H), 1.26 (d, J = 6.7 Hz, 6H), 1.38 (d, J = 6.8 Hz, 6H), 2.72 (hept, J = 6.7 Hz, 2H), 3.11 (hept, J = 6.8 Hz, 2H), 7.27-7.29 (m, 2H), 7.37-7.42 (m, 1H), 7.59-7.66 (m, 5H), 7.73-7.78 (m, 1H), 7.85-7.88 (m, 2H), 9.33 (s, 1H), 11.37 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz)

δ 22.5, 23.7, 25.0, 28.0, 28.7, 119.8, 123.8, 124.8, 125.3, 128.8, 130.0, 130.1, 130.8, 132.6, 135.0, 138.9, 146.3, 146.6, 154.1 (some C signals overlap). Anal. calcd. for $C_{32}H_{41}ClN_4$ (%): C, 74.32; H, 7.99; N, 10.83. Found (%): C, 74.17; H, 7.87; N, 11.06.

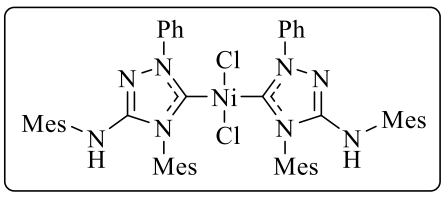


4-[2,6-Di(propan-2-yl)phenyl]-3-{[2,6-di(propan-2-yl)phenyl]amino}-1-(2-methylphenyl)-1*H*-1,2,4-triazol-4-ium chloride (1h). Yield 886 mg (43%), white powder, mp >310 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.12-1.17 (m, 12H), 1.27 (d, *J* = 6.7 Hz, 6H), 1.42 (d, *J* = 6.6 Hz, 6H), 2.27 (s, 3H), 2.69 (hept, *J* = 6.9 Hz, 2H), 3.10 (hept, *J* = 6.9 Hz, 2H), 7.22-7.25 (m, 2H), 7.31-7.36 (m, 1H), 7.45-7.63 (m, 6H), 7.74-7.79 (m, 1H), 9.43 (s, 1H), 11.00 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 16.6, 22.3, 23.4, 23.8, 24.9, 28.0, 28.9, 123.8, 124.7, 125.3, 126.5, 127.5, 128.8, 130.9, 131.5, 131.7, 132.6, 133.2, 134.1, 141.8, 146.2, 146.4, 154.3. Anal. calcd. for $C_{33}H_{43}ClN_4$ (%): C, 74.62; H, 8.16; N, 10.55. Found (%): C, 74.85; H, 8.03; N, 10.67.



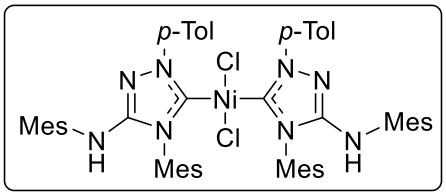
1-(2,6-Dimethylphenyl)-4-[2,6-di(propan-2-yl)phenyl]-3-{[2,6-di(propan-2-yl)phenyl]amino}-1*H*-1,2,4-triazol-4-ium chloride (1i). Yield 931 mg (44%), white powder, mp 308-311 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.19 (d, *J* = 6.9 Hz, 12H), 1.39-1.45(m, 12H), 2.20 (s, 6H), 2.68 (hept, *J* = 6.9 Hz, 2H), 3.06 (hept, *J* = 6.9 Hz, 2H), 6.39 (s, 1H), 7.11-7.19 (m, 4H), 7.28-7.36 (m, 2H), 7.44-7.46 (m, 2H), 7.62-7.67 (m, 1H), 12.65 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.3, 22.7, 23.9, 25.7, 29.0, 29.9, 124.3, 125.7, 129.1, 129.3, 129.9, 131.5, 133.4, 133.8, 135.1, 144.4, 146.5, 146.6, 154.2 (some C signals overlap). Anal. calcd. for $C_{34}H_{45}ClN_4$ (%): C, 74.90; H, 8.32; N, 10.28. Found (%): C, 74.76; H, 8.47; N, 10.06.

General procedure for the preparation of compounds 5a-e. The synthesis was carried out under an argon atmosphere. A mixture of azolium salt **1a,d-f,i** (0.1 mmol), $Ni(OAc)_2$ (9 mg, 0.05 mmol) and 1,4-dioxane (2 ml) was heated under reflux for 2 h. The reaction mixture was then cooled to room temperature, filtered through a short pad of celite and rotary evaporated to dryness in vacuo. The crude solid residue was dissolved in CH_2Cl_2 (1 ml) and purified by column chromatography using silica gel and CH_2Cl_2 as eluent.

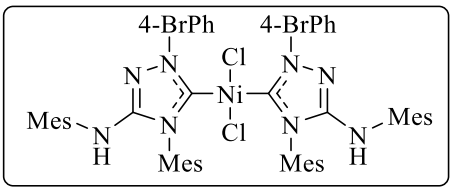


Dichloro(bis{2-phenyl-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene})nickel (5a). Yield 39.6 mg (86%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) (a mixture of rotamers): δ 2.04-2.05(m, 12H), 2.11 (s, 6H), 2.19 (s, 6H), 2.27 (s, 6H), 2.55 (s, 3H), 2.59(s, 3H), 4.69 (s,

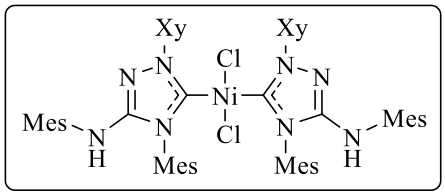
2H), 6.78 (s, 4H), 7.06 (s, 2H), 7.17-7.24 (m, 4H), 7.28-7.30 (m, 1H), 7.42-7.49 (m, 3H), 8.38-8.42 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) (a mixture of rotamers): δ 18.37, 18.40, 19.0, 19.2, 21.0, 21.5, 21.6, 124.7, 125.6, 127.0, 127.9, 128.7, 128.8, 129.4, 129.7, 130.2, 130.6, 131.5, 134.86, 134.89, 136.9, 137.0, 137.9, 138.1, 139.3, 140.0, 140.6, 140.7, 151.37, 151.44, 167.4. Anal. calcd. for $C_{52}H_{56}Cl_2N_8Ni$ (%): C, 67.69; H, 6.12; N, 12.14. Found (%): C, 67.86; H, 6.01; N, 12.23.



Dichloro(bis{2-(4-methylphenyl)-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene})nickel (5b). Yield 35 mg (73%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) (a mixture of rotamers): δ 2.04 (s, 9H), 2.11 (s, 6H), 2.19 (s, 6H), 2.27 (s, 6H), 2.31 (s, 3H), 2.46 (s, 3H), 2.47 (s, 3H), 2.56 (s, 3H), 2.59 (s, 3H), 4.64-4.66 (m, 2H), 6.78 (s, 4H), 6.91-7.05 (m, 4H), 7.13-7.23 (m, 4H), 8.23-8.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) (a mixture of rotamers): δ 18.37, 18.40, 19.0, 19.2, 21.0, 21.5, 21.6, 124.4, 125.4, 129.3, 129.4, 129.7, 129.8, 130.2, 130.4, 131.5, 134.8, 134.9, 136.4, 136.9, 137.4, 137.9, 138.3, 139.2, 139.8, 151.2, 151.3, 167.1. Anal. calcd. for $C_{54}H_{60}Cl_2N_8Ni$ (%): C, 68.22; H, 6.36; N, 11.79. Found (%): C, 68.34; H, 6.28; N, 11.91.

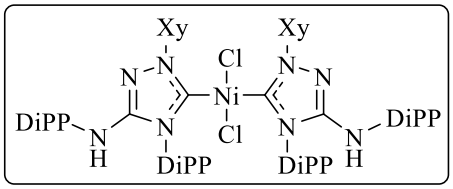


Bis{2-(4-bromophenyl)-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}(dichloro)nickel (5c) Yield 38 mg (71%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) (a mixture of rotamers): δ 2.02-2.03 (m, 12H), 2.09 (s, 3H), 2.19 (s, 6H), 2.25 (s, 9H), 2.58-2.61 (m, 6H), 4.67-4.68 (m, 2H), 6.78 (s, 4H), 7.04 (s, 1H), 7.22-7.27 (m, 6H), 7.56 (d, *J* = 8.7 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.37-8.41 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (a mixture of rotamers): δ 18.3, 18.37, 18.44, 18.9, 19.0, 21.0, 21.65, 21.68, 120.8, 121.9, 126.0, 127.4, 129.4, 129.5 130.3, 130.7, 130.8, 131.2, 131.8, 132.1, 134.9, 137.1, 137.8, 138.3, 139.5, 139.59, 139.64, 140.7, 151.6, 151.7, 167.9, 168.1. Anal. calcd. for $C_{52}H_{54}Br_2Cl_2N_8Ni$ (%): C, 57.81; H, 5.04; N, 10.37. Found (%): C, 58.03; H, 4.89; N, 10.51.



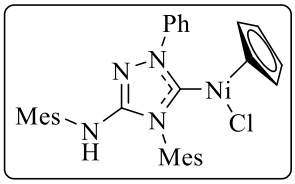
Dichloro(bis{2-(2,6-dimethylphenyl)-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene})nickel (5d). Yield 35 mg (72%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) (a mixture of rotamers): δ 2.02-2.04 (m, 24H), 2.15 (s, 18H), 2.54-2.58 (m, 6H), 4.76-4.78 (m, 2H), 6.75(s, 4H), 7.09-7.12(m, 8H), 7.28-7.33 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) (a mixture of rotamers): δ 18.2, 19.16, 19.20, 19.3, 21.0, 21.46, 21.54, 128.2, 128.4, 128.5, 128.6, 129.4, 129.7, 129.8, 129.9, 130.1, 131.6, 135.40, 135.43, 137.2, 137.4, 137.5, 137.8, 137.9, 138.5, 138.5, 138.6,

139.2, 139.3, 151.5, 151.6, 169.7, 169.8. Anal. calcd. for $C_{56}H_{64}Cl_2N_8Ni$ (%): C, 68.72; H, 6.59; N, 11.45. Found (%): C, 68.56; H, 6.74; N, 11.28.

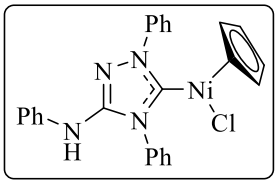


Dichloro{bis[2-(2,6-dimethylphenyl)-4-[2,6-di(propan-2-yl)phenyl]-5-{[2,6-di(propan-2-yl)phenyl]amino}-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene]}nickel (5e). Yield 37 mg (64%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) (a mixture of rotamers): δ 0.99 (d, *J* = 6.9 Hz, 12H), 1.11 (d, *J* = 6.9 Hz, 12H), 1.28-1.30 (m, 24H), 2.19 (s, 12H), 3.07 (hept, *J* = 6.9 Hz, 4H), 3.39 (hept, *J* = 6.9 Hz, 4H), 6.84 (s, 2H), 6.92-6.97 (m, 6H), 7.00-7.03 (m, 4H), 7.07-7.10 (m, 2H), 7.20-7.25 (m, 7H), 7.27-7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) (a mixture of rotamers): δ 20.5, 23.5, 23.6, 28.5, 28.8, 122.3, 122.6, 123.6, 128.1, 130.1, 132.0, 133.3, 135.4, 138.8, 145.1, 147.1, 147.4, 152.4, 165.5. Anal. calcd. for $C_{68}H_{88}Cl_2N_8Ni$ (%): C, 71.20; H, 7.73; N, 9.77. Found (%): C, 70.97; H, 7.68; N, 9.93.

General procedure for the preparation of compounds 6a-h. A mixture of azolium salt **1a-d,f-i** (0.5 mmol), $NiCp_2$ (142 mg, 0.75 mmol) and THF (5 ml) was stirred at 60 °C for 3 h under an argon atmosphere in a sealed high-pressure glass vial. The reaction mixture was then cooled to room temperature, filtered through a short pad of celite, and evaporated to dryness in vacuo. The crude solid residue was dissolved in CH_2Cl_2 (1 ml) and purified by column chromatography using silica gel and CH_2Cl_2 as eluent.

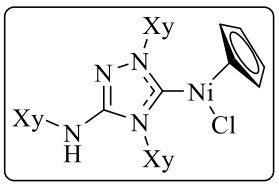


Chloro(η^5-cyclopentadienyl){2-phenyl-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}nickel (6a). Yield 216 mg (78%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.17 (s, 6H), 2.25 (s, 3H), 2.32 (s, 6H), 2.48 (s, 3H), 4.71 (s, 5H), 5.04 (s, 1H), 6.87 (s, 2H), 7.23(s, 2H), 7.40-7.45 (m, 1H), 7.51-7.56 (m, 2H), 8.68-8.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 18.7, 21.1, 21.5, 92.8, 125.0, 128.3, 128.6, 129.5, 130.2, 130.3, 131.3, 135.0, 137.3, 140.5, 141.0, 152.9, 168.0 (two C signals overlap). Anal. calcd. for $C_{31}H_{33}ClN_4Ni$ (%): C, 66.99; H, 5.99; N, 10.08. Found (%): C, 67.21; H, 5.93; N, 9.98.

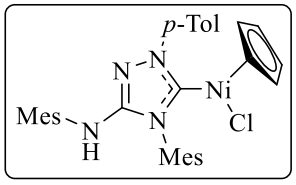


Chloro(η^5-cyclopentadienyl)[2,4-diphenyl-5-(phenylamino)-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene]nickel (6b). Yield 174 mg (74%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.65 (s, 5H), 6.04 (s, 1H), 7.02-7.08 (m, 1H), 7.29-7.41 (m, 4H), 7.50-7.55 (m, 1H), 7.62-7.67 (m, 2H), 7.76-7.83 (m, 3H), 7.88-8.09 (m, 2H), 8.84-8.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 92.5, 117.7, 123.3, 124.5, 128.6, 128.9, 129.5, 130.6, 130.9, 134.8, 137.9, 140.1, 150.8, 168.1 (two

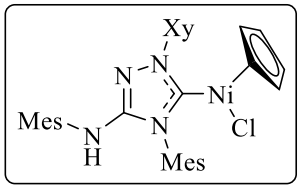
C signals overlap). Anal. calcd. for $C_{25}H_{21}ClN_4Ni$ (%): C, 63.67; H, 4.49; N, 11.88. Found (%): C, 63.46; H, 4.54; N, 12.03.



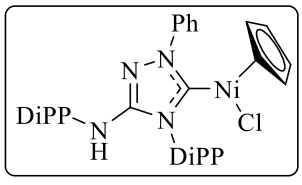
{2,4-Bis(2,6-dimethylphenyl)-5-[(2,6-dimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (6c). Yield 174 mg (63%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (s, 6H), 2.28 (s, 6H), 2.42 (s, 6H), 4.62 (s, 5H), 5.09 (s, 1H), 7.01-7.08 (m, 3H), 7.20-7.23 (m, 2H), 7.29-7.35 (m, 1H), 7.41-7.53 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.46, 18.51, 18.9, 92.6, 127.9, 128.5, 128.9, 129.6, 129.8, 130.9, 132.7, 133.9, 135.5, 136.9, 137.6, 139.1, 153.1, 170.1. Anal. calcd. for $C_{31}H_{33}ClN_4Ni$ (%): C, 66.99; H, 5.99; N, 10.08. Found (%): C, 66.73; H, 6.11; N, 10.21.



Chloro(η^5-cyclopentadienyl){2-(4-methylphenyl)-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}nickel (6d). Yield 204 mg (72%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.16 (s, 6H), 2.24 (s, 3H), 2.31 (s, 6H), 2.43 (s, 3H) 2.47 (s, 3H), 4.71 (s, 5H), 5.02 (s, 1H), 6.86 (s, 2H), 7.22 (s, 2H) 7.30-7.33 (m, 2H), 8.48-8.51 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 18.7, 21.1, 21.4, 21.5, 92.7, 124.9, 129.2, 129.5, 130.3, 131.4, 135.0, 137.3, 137.4, 138.1, 138.2, 141.0, 152.8, 160.1, 167.2. Anal. calcd. for $C_{32}H_{35}ClN_4Ni$ (%): C, 67.45; H, 6.19; N, 9.83. Found (%): C, 67.57; H, 6.06; N, 9.86.

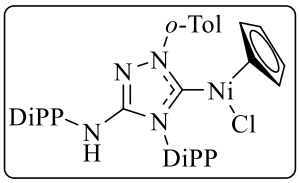


Chloro(η^5-cyclopentadienyl){2-(2,6-dimethylphenyl)-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}nickel (6e). Yield 251 mg (86%), dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.16 (s, 6H), 2.20 (s, 3H), 2.27 (s, 6H), 2.36 (s, 6H), 2.45 (s, 3H), 4.62 (s, 5H), 5.02 (s, 1H), 6.84 (s, 2H), 7.13-7.23 (m, 4H), 7.28-7.33 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.3, 18.5, 18.7, 21.1, 21.5, 92.6, 128.4, 129.6, 129.7, 130.1, 130.3, 131.3, 135.3, 137.0, 137.1, 137.6, 139.2, 140.7, 153.5, 169.8. Anal. calcd. for $C_{33}H_{37}ClN_4Ni$ (%): C, 67.89; H, 6.39; N, 9.60. Found (%): C, 68.07; H, 6.23; N, 9.52.

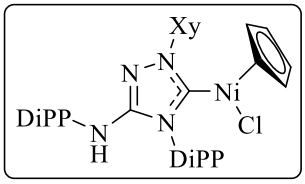


Chloro(η^5-cyclopentadienyl)(4-[2,6-di(propan-2-yl)phenyl]-5-{[2,6-di(propan-2-yl)phenyl]amino}-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)nickel (6f) Yield 259 mg (81%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.14 (d, *J* = 6.8, 12H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.51 (d, *J* = 6.6, 6H), 3.02 (m, 4H), 4.70 (s, 5H), 5.01-5.08 (m 1H), 7.14-7.17 (m, 2H), 7.40-7.56 (m, 6H), 7.68-7.70 (m, 1H), 8.52-8.54 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.3, 24.7, 26.0, 28.6, 28.8, 92.9, 124.2, 125.2, 125.6, 128.4, 131.1, 131.7, 141.0, 146.2, 148.5,

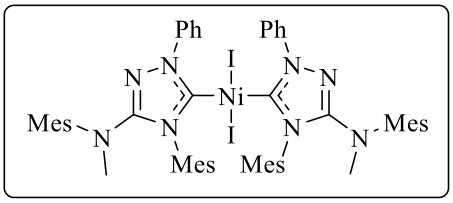
151.2, 154.5, 171.8. Anal. calcd. for $C_{37}H_{45}ClN_4Ni$ (%): C, 69.45; H, 7.09; N, 8.76. Found (%): C, 69.58; H, 6.96; N, 8.91.



Chloro(η^5-cyclopentadienyl){4-[2,6-di(propan-2-yl)phenyl]-5-{[2,6-di(propan-2-yl)phenyl]amino}-2-(2-methylphenyl)-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}nickel (6g). Yield 274 mg (84%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13 (d, *J* = 6.8 Hz, 12H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.52 (d, *J* = 6.6 Hz, 6H), 2.19 (s, 3H), 3.06 (hept, *J* = 7.1 Hz, 4H), 4.61 (s, 5H), 5.10 (s, 1H), 7.11-7.25 (m, 2H), 7.32-7.40 (m, 4H), 7.54-7.57 (m, 2H), 7.67-7.72 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.1, 24.2, 24.8, 26.0, 28.5, 28.8, 92.2, 124.2, 125.6, 126.1, 128.7, 129.7, 129.6, 129.9, 130.6, 131.2, 131.6, 135.8, 140.1, 146.3, 148.4, 154.8, 170.6. Anal. calcd. for $C_{38}H_{47}ClN_4Ni$ (%): C, 69.79; H, 7.24; N, 8.57. Found (%): C, 69.99; H, 7.07; N, 8.64.

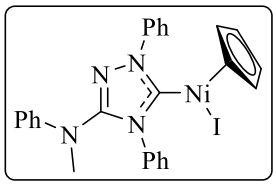


Chloro(η^5-cyclopentadienyl)[2-(2,6-dimethylphenyl)-4-[2,6-di(propan-2-yl)phenyl]-5-{[2,6-di(propan-2-yl)phenyl]amino}-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene]nickel (6h). Yield 290 mg (87%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (d, *J* = 6.8 Hz, 12H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.54-1.56 (m, 6H), 2.21(s, 6H), 3.07 (hept, *J* = 7.1 Hz, 4H), 4.58 (s, 5H), 5.05 (s, 1H), 7.11-7.17 (m, 4H), 7.22-7.25 (m, 1H), 7.27-7.30 (m, 1H), 7.53-7.56 (m, 2H), 7.67-7.72 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.7, 24.3, 24.7, 26.3, 28.5, 28.9, 92.7, 124.3, 125.6, 128.3, 128.6, 129.6, 131.1, 131.5, 136.8, 139.3, 146.2, 148.3, 155.1. Anal. calcd. for $C_{39}H_{49}ClN_4Ni$ (%): C, 70.12; H, 7.39; N, 8.39. Found (%): C, 69.98; H, 7.52; N, 8.25.



Diiodo(bis{2-phenyl-4-(2,4,6-trimethylphenyl)-5-[(2,4,6-trimethylphenyl)amino]-2,4-dihydro-3H-1,2,4-triazol-3-ylidene})nickel (7a). A mixture of complex **5a** (92 mg, 0.1 mmol), K_3PO_4 (85 mg, 0.4 mmol), KI (166 mg, 1 mmol) and CH_3I (37 mg, 0.26 mmol) in acetonitrile (2 ml) was stirred at room temperature in a sealed glass vial under an argon atmosphere for 12 h. The reaction mixture was then filtered through a short pad of celite, the filtrate was rotary evaporated to dryness under vacuum. The crude solid residue was dissolved in CH_2Cl_2 (1 ml) and purified by column chromatography on silica gel using CH_2Cl_2 as eluent. Yield 61 mg (54%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (s, 12H), 1.75 (s, 12H), 2.15 (s, 6H), 2.33 (s, 6H) 2.97 (s, 6H), 6.50 (s, 4H), 6.55 (s, 4H), 7.35-7.38 (m, 4H), 7.42-7.48 (m, 2H), 8.15-8.18 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 20.7, 20.9, 21.2, 40.2, 126.6, 127.9, 129.1, 129.6, 129.7, 132.0, 136.6, 136.7, 137.5, 137.9, 138.4, 141.0,

159.9, 179.6. Anal. calcd. for $C_{54}H_{60}I_2N_8Ni$ (%): C, 57.21; H, 5.34; N, 9.88. Found (%): C, 57.03; H, 5.41; N, 9.83.

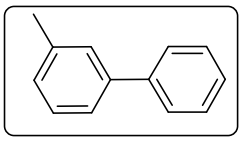


(η^5-Cyclopentadienyl)(iodo){5-[methyl(phenyl)amino]-2,4-diphenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}nickel (7b). A mixture of complex **6b** (47mg, 0.1 mmol), *t*-BuOK (13.4 mg, 0.12 mmol), KI (166 mg, 1 mmol) and CH_3I (37 mg, 0.26 mmol) in THF (2 ml) was stirred at room temperature in a sealed glass vial under an argon atmosphere for 12 h. The reaction mixture was then filtered through a short pad of celite, and the filtrate was rotary evaporated to dryness in vacuo. The crude solid residue was dissolved in CH_2Cl_2 (1 ml) and purified by column chromatography on silica gel using CH_2Cl_2 as eluent. Yield 42 mg (72%) dark red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.28 (s, 3H), 4.74 (s, 5H), 6.76-6.81 (m, 2H), 6.93-6.99 (m, 1H), 7.07-7.12 (m, 2H), 7.27-7.31 (m, 3H), 7.46-7.63 (m, 5H), 8.72-8.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.2, 92.6, 123.2, 124.7, 125.2, 128.5, 128.6, 128.8, 129.1, 129.4, 136.8, 140.2, 145.2, 157.0, 175.7 (two signals C overlap). Anal. calcd. for $C_{26}H_{23}I_2N_4Ni$ (%): C, 54.11; H, 4.02; N, 9.71. Found (%): C, 54.34; H, 3.96; N, 9.57.

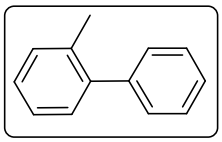
Catalytic activity study of complexes 5a-e, 6a-h, 7a,b and 11a-b, 12a-b in the Suzuki-Miyaura reaction. All experiments were conducted in 2 ml screw-capped high-pressure glass vials equipped with a magnetic stirrer under an argon atmosphere. Powdered K_3PO_4 (63.7 mg, 0.3 mmol) was added to a solution of *m*-chlorotoluene (12.7 mg, 0.1 mmol) and phenylboronic acid (18.3 mg, 0.15 mmol) in 1,4-dioxane (0.5 ml). Then, a dioxane solution containing corresponding complex **5a-e, 6a-h, 7a,b** or **11a-b, 12a-b** (0.5-1 μmol, 0.5-1 mol%) was added (10 μl). The resulting mixture was then stirred at 60-120 °C for 3-16 h (see Tables 1 and S2). Then, the reaction mixture was cooled to room temperature, and a solution of naphthalene (6.4 mg, 0.05 mmol) in acetonitrile (1 ml) was added as an internal GC-MS standard. An aliquot (3 μl) of the reaction mixture was taken by a syringe, dissolved in acetonitrile (1 ml) and subjected to GC-MS analysis (see Tables 1 and S1).

Synthesis of compounds 10a-m (general procedure). All experiments were conducted in 4 ml screw-capped high-pressure glass vials equipped with a magnetic stirrer under an argon atmosphere. A solution of complex **5a** (2.3 mg, 2.5 μmol, 0.5 mol%) in 1,4-dioxane (0.5ml) was added to a mixture of K_3PO_4 (318 mg, 1.5 mmol), aryl chloride **8a-i** (0.5 mmol) and arylboronic acid **9a-c** (0.7 mmol) in dioxane (2.5 ml). The resulting mixture was stirred at 90 °C for 5 h, cooled to room temperature and filtered through a short pad of Celite. The filtrate was then rotary

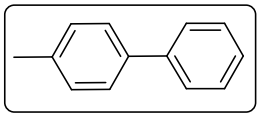
evaporated to give a crude product which was purified using silica gel column chromatography using a 1:1 hexane: methylene chloride eluent.



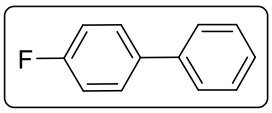
3-Methylbiphenyl (10a). Yield 66 mg (79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.46 (s, 3H), 7.18-7.22 (m, 1H), 7.34-7.40 (m, 2H), 7.42-7.50 (m, 4H), 7.60-7.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 124.4, 127.29, 127.31, 128.12, 128.13, 128.80, 128.83, 138.5, 141.4, 141.5. (^{1}H and ^{13}C NMR spectral data of compound **10a** are in good agreement with those published earlier).[S2]



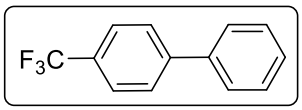
2-Methylbiphenyl (10b). Yield 72 mg (86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (s, 3H), 7.11-7.16 (m, 4H), 7.18-7.24 (m, 3H), 7.25-7.31 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6, 125.9, 126.9, 127.4, 128.2, 129.3, 129.9, 130.4, 135.5, 142.07, 142.10. (^{1}H and ^{13}C NMR spectral data of compound **10b** are in good agreement with those published earlier).[S3]



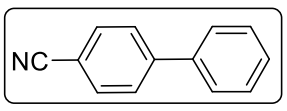
4-Methylbiphenyl (10c). Yield 74 mg (88%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.26 (s, 3H), 7.10-7.13 (m, 2H), 7.15-7.21 (m, 1H), 7.26-7.32 (m, 2H), 7.34-7.38 (m, 2H), 7.42-7.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 127.11, 127.14, 128.9, 129.6, 137.2, 138.5, 141.3 (two signals C overlap). (^{1}H and ^{13}C NMR spectral data of compound **10c** are in good agreement with those published earlier).[S3]



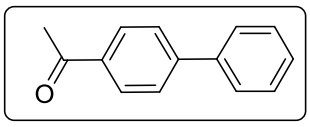
4-Fluorobiphenyl (10d). Yield 81 mg (94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.00-7.07 (m, 2H), 7.24-7.48 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 115.8 (d, J = 21.4 Hz), 127.6, 127.8, 129.3 (d, J = 8.1 Hz), 129.4, 137.90 (d, J = 3.3 Hz), 140.8, 163.03 (d, J = 246.3 Hz). (^{1}H and ^{13}C NMR spectral data of compound **10d** are in good agreement with those published earlier).[S2]



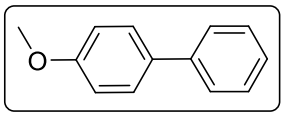
4-(Trifluoromethyl)biphenyl (10e). Yield 94 mg (92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.52 (m, 3H), 7.60-7.63 (m, 2H), 7.71 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 125.85 (q, J = 3.8 Hz), 127.4, 127,6, 128.3, 129.1, 139.9, 144.9 (some signals C is overlap). (^{1}H and ^{13}C NMR spectral data of compound **10e** are in good agreement with those published earlier).[S4]



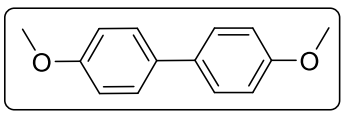
Biphenyl-4-carbonitrile (10f). Yield 65 mg (73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41-7.51 (m, 3H), 7.58-7.61 (m, 2H), 7.67-7.75 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 111.1, 119.1, 127.4, 127.9, 128.8, 129.3, 132.7, 139.3, 145.8. (^{1}H and ^{13}C NMR spectral data of compound **10f** are in good agreement with those published earlier).[S2]



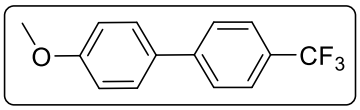
1-(Biphenyl-4-yl)ethanone (10g). Yield 90 mg (92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.64 (s, 3H), 7.40-7.51 (m, 3H), 7.62-7.71 (m, 4H), 8.02-8.06 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.8, 127.36, 127.41, 128.4, 129.05, 129.09, 136.0, 140.0, 145.9, 197.9. (^{1}H and ^{13}C NMR spectral data of compound **10g** are in good agreement with those published earlier).[S4]



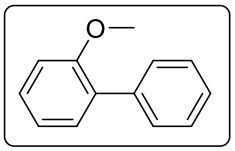
4-Methoxybiphenyl (10h). Yield 72 mg (78%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.86 (s, 3H), 6.96-7.01 (m, 2H), 7.28-7.34 (m, 1H), 7.39-7.45 (m, 2H), 7.52-7.58 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.5, 114.3, 126.8, 126.9, 128.3, 128.9, 133.9, 141.0, 159.3. (^{1}H and ^{13}C NMR spectral data of compound **10h** are in good agreement with those published earlier).[S5]



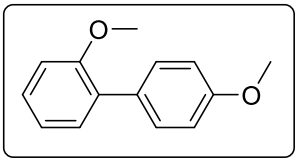
4,4'-Dimethoxybiphenyl (10i). Yield 73 mg (68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.85 (s, 6H), 6.93-6.98 (m, 4H), 7.45-7.50 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.5, 114.3, 127.9, 133.6, 158.8. (^{1}H and ^{13}C NMR spectral data of compound **10i** are in good agreement with those published earlier).[S4]



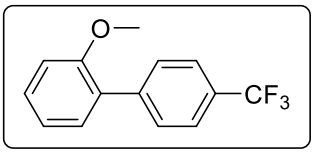
4-Methoxy-4'-(trifluoromethyl)biphenyl (10j). Yield 68 mg (54%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.87 (s, 3H), 6.99-7.02 (m, 2H), 7.53-7.56 (m, 2H), 7.66 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.5, 114.6, 125.82 (q, J = 3.8 Hz), 127.0, 128.5, 132.3, 144.5, 160.0 (some signals C overlap). (^{1}H and ^{13}C NMR spectral data of compound **10j** are in good agreement with those published earlier).[S5]



2-Methoxybiphenyl (10k). Yield 61 mg (66%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.90 (s, 3H), 7.08-7.18 (m, 2H), 7.41-7.47 (m, 3H), 7.50-7.56 (m, 2H), 7.65-7.69 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.6, 11.3, 120.9, 127.0, 128.1, 128.7, 129.6, 130.8, 131.0, 138.7, 156.6. (^{1}H and ^{13}C NMR spectral data of compound **10k** are in good agreement with those published earlier).[S6]



2,4'-Dimethoxybiphenyl (10l). Yield 87 mg (81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.83 (s, 3H), 3.86 (s, 3H), 6.96-7.06 (m, 4H), 7.28-7.34 (m, 2H), 7.47-7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.4, 55.7, 111.3, 113.6, 121.0, 128.3, 130.5, 130.7, 130.8, 131.0, 156.6, 158.8. (^{1}H and ^{13}C NMR spectral data of compound **10l** are in good agreement with those published earlier).[S7]



2-Methoxy-4'-(trifluoromethyl)biphenyl (10m). Yield 86 mg (68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.83 (s, 3H), 7.00-7.09 (m, 2H), 7.30-7.40 (m, 2H), 7.63-7.69 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.7, 11.5, 121.1, 125.0 (q, J = 3.8 Hz), 129.6, 130.0, 130.9, 142.4, 156.6 (some signals C is overlap). (^{1}H and ^{13}C NMR spectral data of compound **10m** are in good agreement with those published earlier).[S8]

S4. X-Ray structure determination

X-ray crystallographic data and refinement details.

A single crystal of compound **5a** was obtained from a solution in 2:1 CH_2Cl_2:1,4-dioxane mixture by a slow evaporation at room temperature. Single crystals of compounds **6e** and **6g** were obtained by a slow crystallization from 2:1 benzene/Et_2O solutions in hexane vapors. X-ray diffraction data for **5a**•$2CH_2Cl_2$, **6e** and **6g**•H_2O were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation (**5a**•$2CH_2Cl_2$, **6e** and **6g**•H_2O) or Mo K_α-radiation (**5a**•$2CH_2Cl_2$). The intensity data were integrated and analytically corrected for absorption and decay by the CrysAlisPro program (CrysAlisPro. Version 1.171.43. *Rigaku Oxford Diffraction*, **2023**). The structure was solved by direct methods using SHELXT[S9] and refined by the full-matrix least-squares minimization method on F^2 using SHELXL-2018[S10] in the OLEX2 program.[S11] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. A position of hydrogen atoms located at nitrogen or oxygen atoms (H4 at N4 in **5a**•$2CH_2Cl_2$, **6e**, **6g**•H_2O; atoms H1A and H1B in **6g**•H_2O) were found from the electron density-difference map; these atoms were refined with individual isotropic displacement parameters. All other H-atoms were positioned geometrically and refined as riding atoms with relative isotropic displacement parameters. In **6e**, a highly disordered non-coordinating molecule (presumably hexane) was removed by the Solvent Mask procedure implemented in the OLEX2 program.[S11]

Crystal data, data collection and structure refinement details for **5a**, **6e** and **6g** are summarized in Table S3. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2301724-2301727, correspondingly; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/structures/

Table S3. Crystal data and structure refinement for **5a, 6e** and **6g**

Identification code	**5a•2CH_2Cl_2**	**5a•2CH_2Cl_2**	**6e**	**6g•H_2O**
Empirical formula	$C_{54}H_{60}Cl_6N_8Ni$	$C_{54}H_{60}Cl_6N_8Ni$	$C_{33}H_{37}ClN_4Ni$	$C_{38}H_{49}ClN_4NiO$
Formula weight	1092.51	1092.51	583.82	671.97
Temperature, K	100.01(10)	100.00(10)	100.00(10)	100.00(10)
Wavelength, Å	0.71073	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	Pbcn	$P2_12_12_1$
a, Å	16.3057(3)	16.30763(10)	20.10910(10)	10.01462(8)
b, Å	14.41195(19)	14.41133(6)	18.39695(8)	17.91785(15)
c, Å	11.8836(2)	11.87970(7)	18.19766(8)	19.61513(15)
β, °	110.635(2)	110.6127(7)	90	90
Volume, $Å^3$	2613.45(8)	2613.17(3)	6732.15(5)	3519.75(5)
Z	2	2	8	4
Calculated density, $g·cm^{-3}$	1.388	1.388	1.152	1.268
Absorption coefficient, mm^{-1}	0.723	3.710	1.745	1.755
F(000)	1140	1140	2464	1432
Crystal size, mm	0.34×0.11×0.06	0.29×0.20×0.06	0.20×0.19×0.15	0.67×0.39×0.21
θ range for data collection, °	2.313-34.657	2.895-80.033	3.256-80.331	3.341-80.332
Index ranges	-25<=h<=24, -23<=k<=22, -17<=l<=18	-20<=h<=19, -17<=k<=18, -15<=l<=15	-25<=h<=25, -23<=k<=23, -23<=l<=19	-12<=h<=12, -22<=k<=22, -25<=l<=25
Reflections collected	47987	44665	55294	50676
Independent reflections [$R_{(int)}$]	10193 [0.0245]	5695 [0.0249]	7325 [0.0235]	7677 [0.0420]
Observed reflections (with I>2σ(I))	8944	5579	6974	7622
Completeness to $\theta_{full}/\theta_{max}$, °	0.999 / 0.911	1.000 / 0.998	1.000 / 0.993	1.000 / 0.996
T_{max} / T_{min}	0.744 / 1.000	1.000 / 0.238	1.000 / 0.568	1.000 / 0.194
Data / restraints / parameters	10193 / 0 / 323	5695 / 0 / 322	7325 / 19 / 386	7677 / 9 / 451
Goodness-of-fit on F^2	1.056	1.042	1.033	1.079
Final R1 / wR2 indices with I>2σ(I)	0.0311/0.0832	0.0295 / 0.0787	0.0277 / 0.0788	0.0296 / 0.0718
Final R1 / wR2 indices (all data)	0.0365/0.0854	0.0300 / 0.0791	0.0289 / 0.0798	0.0298 / 0.0719
Absolute structure parameter	-	-	-	0.002(6)
Largest diff, peak / hole, $ē·Å^3$	0.547/-0.603	0.362 / -0.395	0.248 / -0.294	0.194 / -0.239
CCDC deposition number	2301724	2301725	2301726	2301727

The structure of 5a.

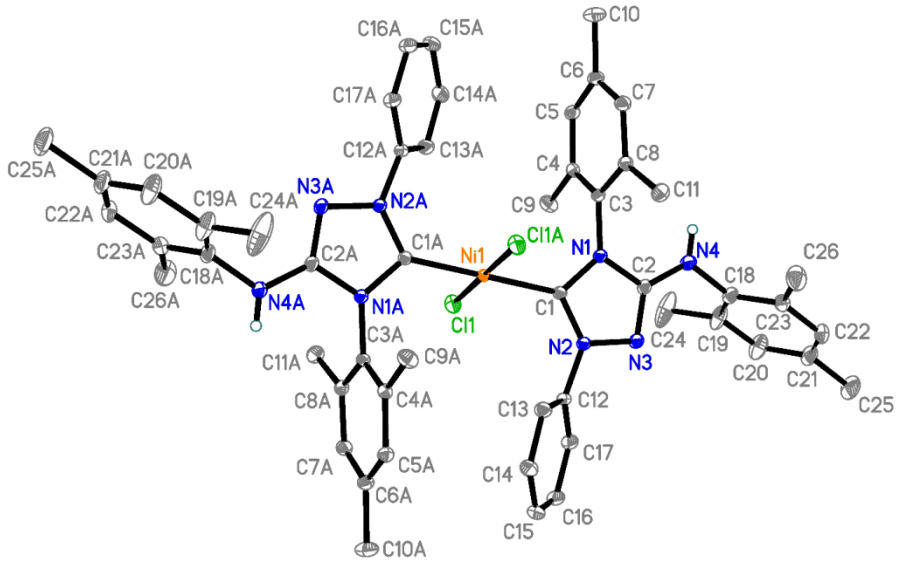


Figure S1. Molecular structure of compound **5a** (p=50%). Hydrogen atoms (except NH) are omitted.

The structure of **5a**•2CH_2Cl_2 contains one crystallographically non-equivalent lattice molecule of CH_2Cl_2 (not shown in figure above).

Table S4. Selected bond lengths in **5a**, Å.

	Cu Kα-radiation	Mo Kα-radiation		Cu Kα-radiation	Mo Kα-radiation
Ni1-Cl1	2.1840(3)	2.1847(2)	C6-C10	1.5069(17)	1.5074(13)
Ni1-C1	1.9256(12)	1.9214(9)	C7-C8	1.3940(17)	1.3965(13)
N1-C1	1.3741(15)	1.3755(11)	C8-C11	1.5075(17)	1.5065(13)
N1-C2	1.3794(15)	1.3808(11)	C12-C13	1.3890(17)	1.3904(13)
N1-C3	1.4416(15)	1.4384(11)	C12-C17	1.3880(17)	1.3921(12)
N2-N3	1.4034(14)	1.4008(11)	C13-C14	1.3931(17)	1.3954(13)
N2-C1	1.3319(15)	1.3381(11)	C14-C15	1.3864(19)	1.3907(15)
N2-C12	1.4310(15)	1.4258(11)	C15-C16	1.393(2)	1.3926(16)
N3-C2	1.3063(16)	1.3108(12)	C16-C17	1.3910(18)	1.3928(13)
N4-C2	1.3601(16)	1.3563(12)	C18-C19	1.395(2)	1.3938(16)
N4-C18	1.4359(16)	1.4353(13)	C18-C23	1.3947(19)	1.3961(15)
N4-H4	0.807(19)	0.80(2)	C19-C20	1.396(2)	1.3980(15)
C3-C4	1.3983(17)	1.3993(13)	C19-C24	1.505(2)	1.5030(17)
C3-C8	1.3986(17)	1.3989(13)	C20-C21	1.387(2)	1.3894(16)
C4-C5	1.3953(17)	1.3976(12)	C21-C22	1.388(2)	1.3907(17)
C4-C9	1.5024(17)	1.5022(14)	C21-C25	1.5065(19)	1.5066(15)
C5-C6	1.3896(18)	1.3920(14)	C22-C23	1.3956(19)	1.3958(14)
C6-C7	1.3987(18)	1.3974(14)	C23-C26	1.504(2)	1.5033(17)

The structure of 6e.

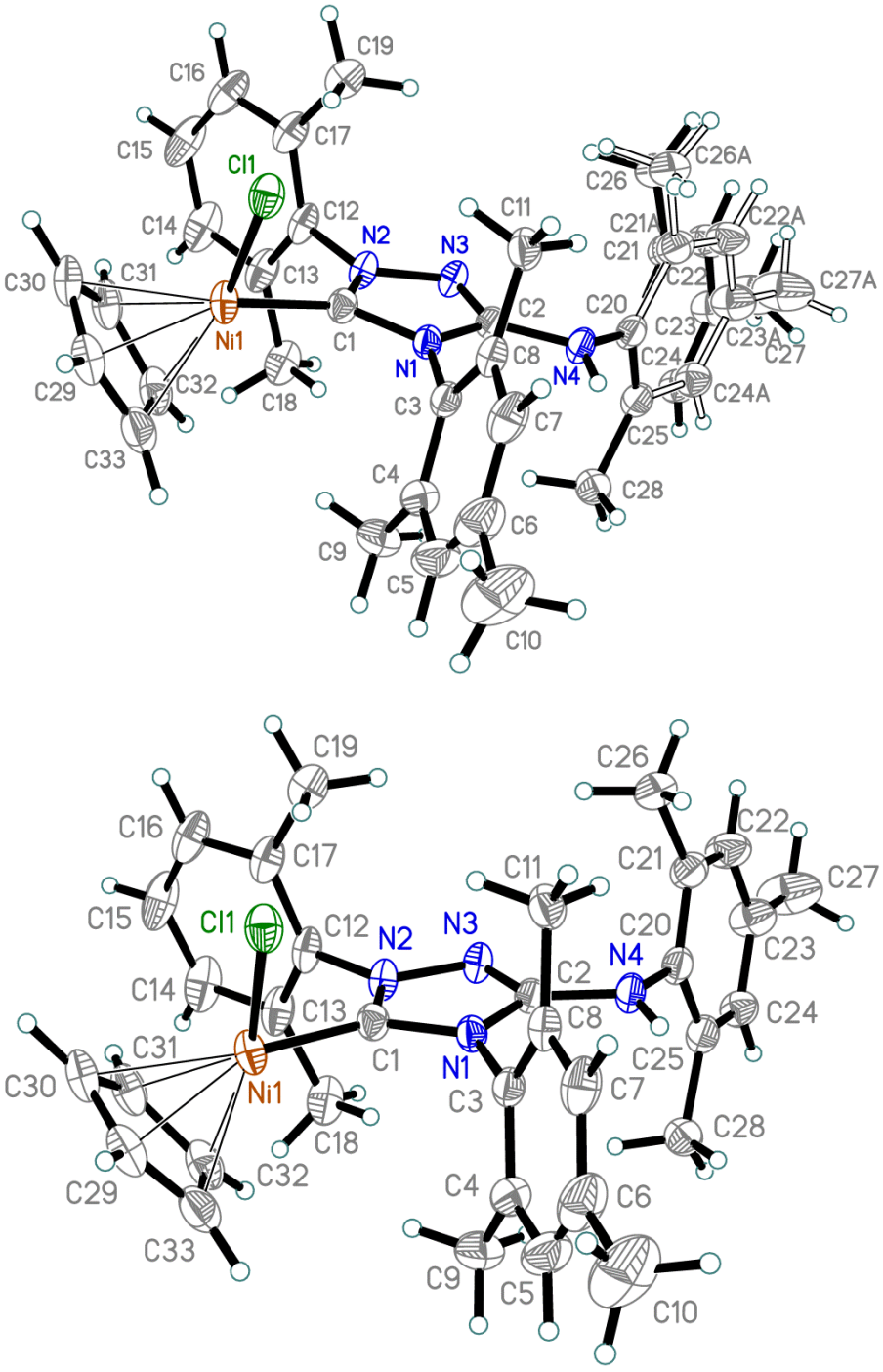


Figure S2. Molecular structure of compound **6e** (p=50%). A disorder ratio for one Mes-group (top figure) is 0.723(12):0.277(12) (the minor component is shown in open solid lines). The disorder is omitted in the bottom figure.

Table S5. Selected bond lengths in **6e**, Å.

Ni1-Cl1	2.1810(3)	C4-C5	1.3960(18)	C21-C26	1.511(4)
Ni1-C1	1.8765(11)	C4-C9	1.5086(18)	C22-C23	1.394(4)
Ni1-C29	2.1523(12)	C5-C6	1.385(2)	C23-C24	1.395(4)
Ni1-C30	2.1919(12)	C6-C7	1.392(2)	C23-C27	1.514(4)
Ni1-C31	2.1783(11)	C6-C10	1.5133(18)	C24-C25	1.400(4)
Ni1-C32	2.0378(12)	C7-C8	1.3917(16)	C25-C28	1.5068(16)
Ni1-C33	2.1361(13)	C8-C11	1.5018(16)	C25-C24A	1.410(11)
N1-C1	1.3776(13)	C12-C13	1.3906(17)	C21A-C22A	1.408(13)
N1-C2	1.3780(14)	C12-C17	1.3971(17)	C21A-C26A	1.512(13)
N1-C3	1.4410(13)	C13-C14	1.3989(16)	C22A-C23A	1.362(12)
N2-N3	1.3951(12)	C13-C18	1.5072(18)	C23A-C24A	1.389(12)
N2-C1	1.3284(14)	C14-C15	1.382(2)	C23A-C27A	1.532(12)
N2-C12	1.4403(13)	C15-C16	1.387(2)	C29-C30	1.4443(19)
N3-C2	1.3095(14)	C16-C17	1.3948(16)	C29-C33	1.392(2)
N4-H4	0.821(17)	C17-C19	1.5035(17)	C30-C31	1.3876(19)
N4-C2	1.3566(13)	C20-C21	1.383(5)	C31-C32	1.441(2)
N4-C20	1.4359(14)	C20-C25	1.3938(16)	C32-C33	1.4319(19)
C3-C4	1.3980(16)	C20-C21A	1.442(12)	Ni-$Cp_{centroid}$	1.7671(5)
C3-C8	1.3992(15)	C21-C22	1.388(5)		

The structure of 6g•H_2O.

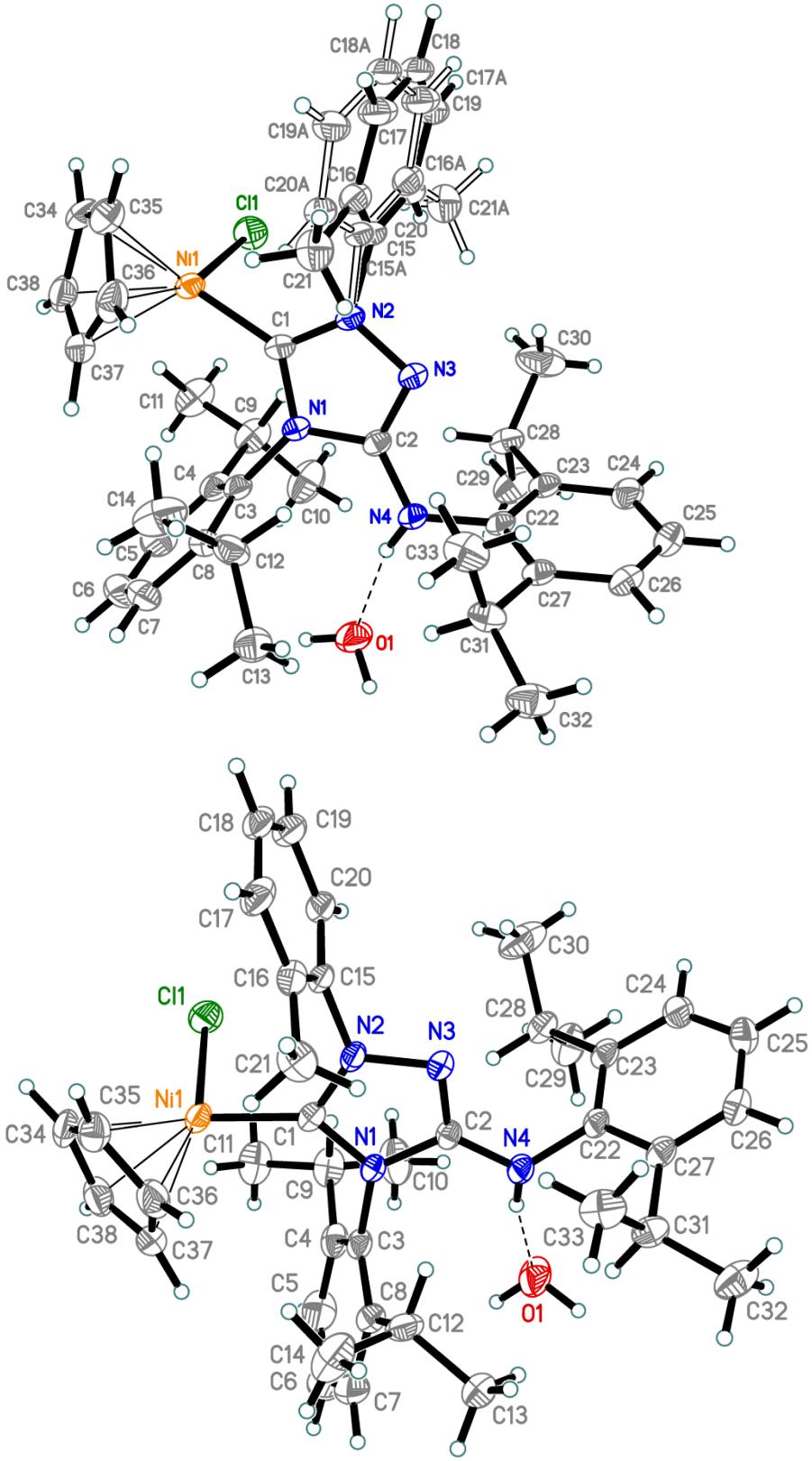


Figure S3. Molecular structure of compound **6g•H_2O** (p=50%). A disorder ratio for the 2-MeC_6H_4-group (top figure) is 0.635(3): 0.365(3) (the minor component is shown in open solid lines). The disorder is omitted in the bottom figure.

Table S6. Selected bond lengths in **6g**·H_2O, Å.

Ni1-Cl1	2.2017(7)	C4-C9	1.512(4)	C18A-C19A	1.403(10)
Ni1-C1	1.879(2)	C5-C6	1.383(5)	C19A-C20A	1.391(9)
Ni1-C34	2.140(2)	C6-C7	1.382(5)	C22-C23	1.402(3)
Ni1-C35	2.157(3)	C7-C8	1.394(3)	C22-C27	1.405(3)
Ni1-C36	2.037(3)	C8-C12	1.515(4)	C23-C24	1.396(3)
Ni1-C37	2.131(3)	C9-C10	1.531(4)	C23-C28	1.516(3)
Ni1-C38	2.183(3)	C9-C11	1.534(4)	C24-C25	1.380(4)
N1-C1	1.379(3)	C12-C13	1.535(3)	C25-C26	1.383(4)
N1-C2	1.390(3)	C12-C14	1.526(4)	C26-C27	1.394(3)
N1-C3	1.446(3)	C15-C16	1.384(6)	C27-C31	1.518(3)
N2-N3	1.397(2)	C15-C20	1.391(6)	C28-C29	1.523(3)
N2-C1	1.327(3)	C16-C17	1.398(6)	C28-C30	1.520(4)
N2-C15	1.432(7)	C16-C21	1.500(6)	C31-C32	1.534(4)
N2-C15A	1.479(12)	C17-C18	1.376(7)	C31-C33	1.534(3)
N3-C2	1.308(3)	C18-C19	1.385(7)	C34-C35	1.399(4)
N4-H4	0.88(3)	C19-C20	1.385(5)	C34-C38	1.429(4)
N4-C2	1.356(3)	C15A-C16A	1.390(12)	C35-C36	1.399(4)
N4-C22	1.447(3)	C15A-C20A	1.394(12)	C36-C37	1.446(5)
C3-C4	1.409(3)	C16A-C17A	1.379(11)	C37-C38	1.385(4)
C3-C8	1.405(3)	C16A-C21A	1.484(10)	O1-H1A	0.96(3)
C4-C5	1.393(4)	C17A-C18A	1.391(12)	O1-H1B	0.94(3)
Ni1-$Cp_{centroid}$	1.7596(12)				

Table S7. Hydrogen bonds for **6g**·H_2O, Å and °.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N4-H4...O1	0.88(3)	1.98(3)	2.843(3)	166(3)
O1-H1A...Cl1#1	0.96(3)	2.19(3)	3.147(2)	172(4)

Symmetry transformation to generate equivalent atoms: #1 -x+1/2, -y+1, z+1/2

S5. ^{1}H and ^{13}C NMR spectra

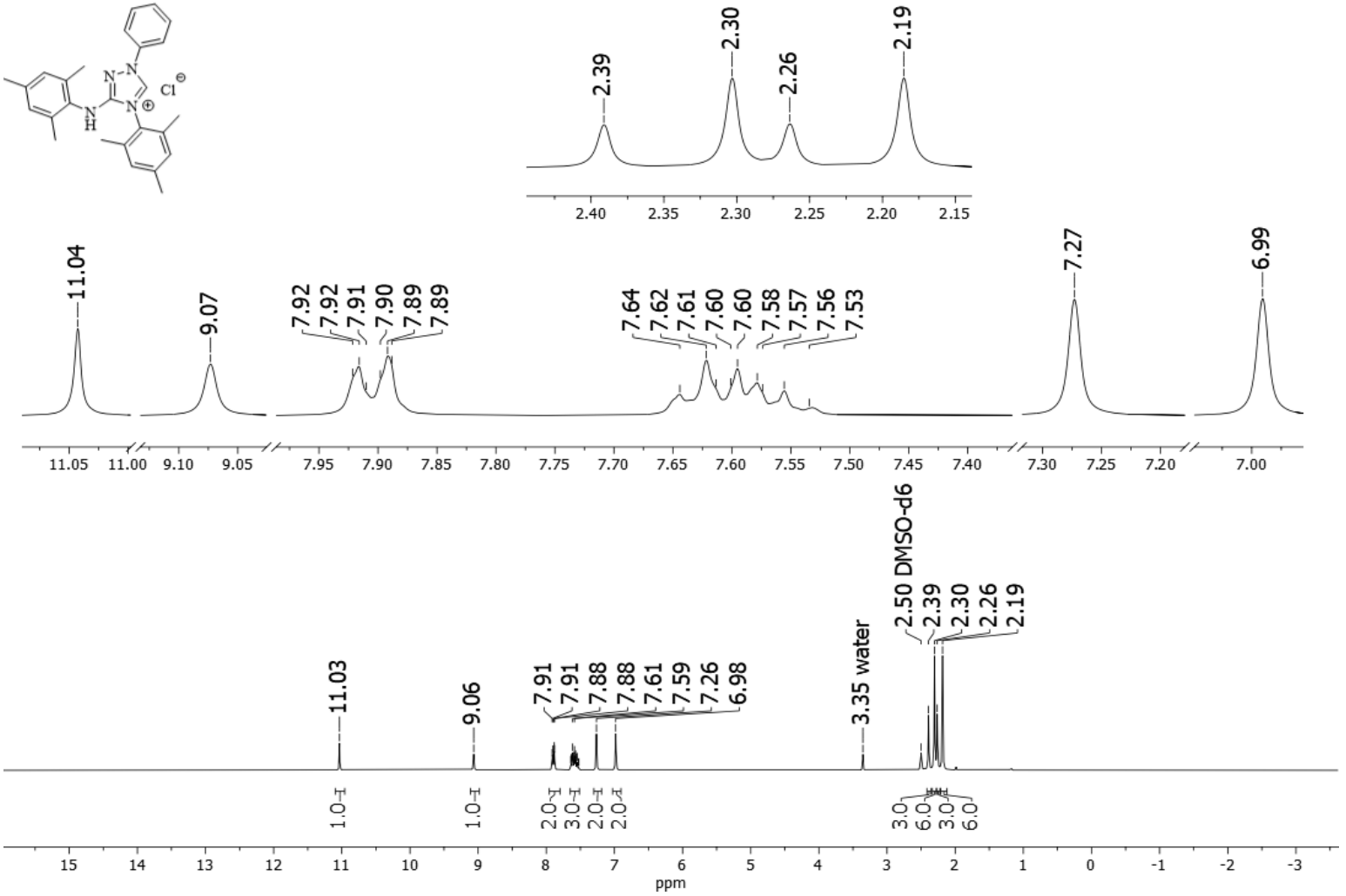


Figure S4. [1]H NMR spectrum of compound **1a** (DMSO-d_6, 300 MHz).

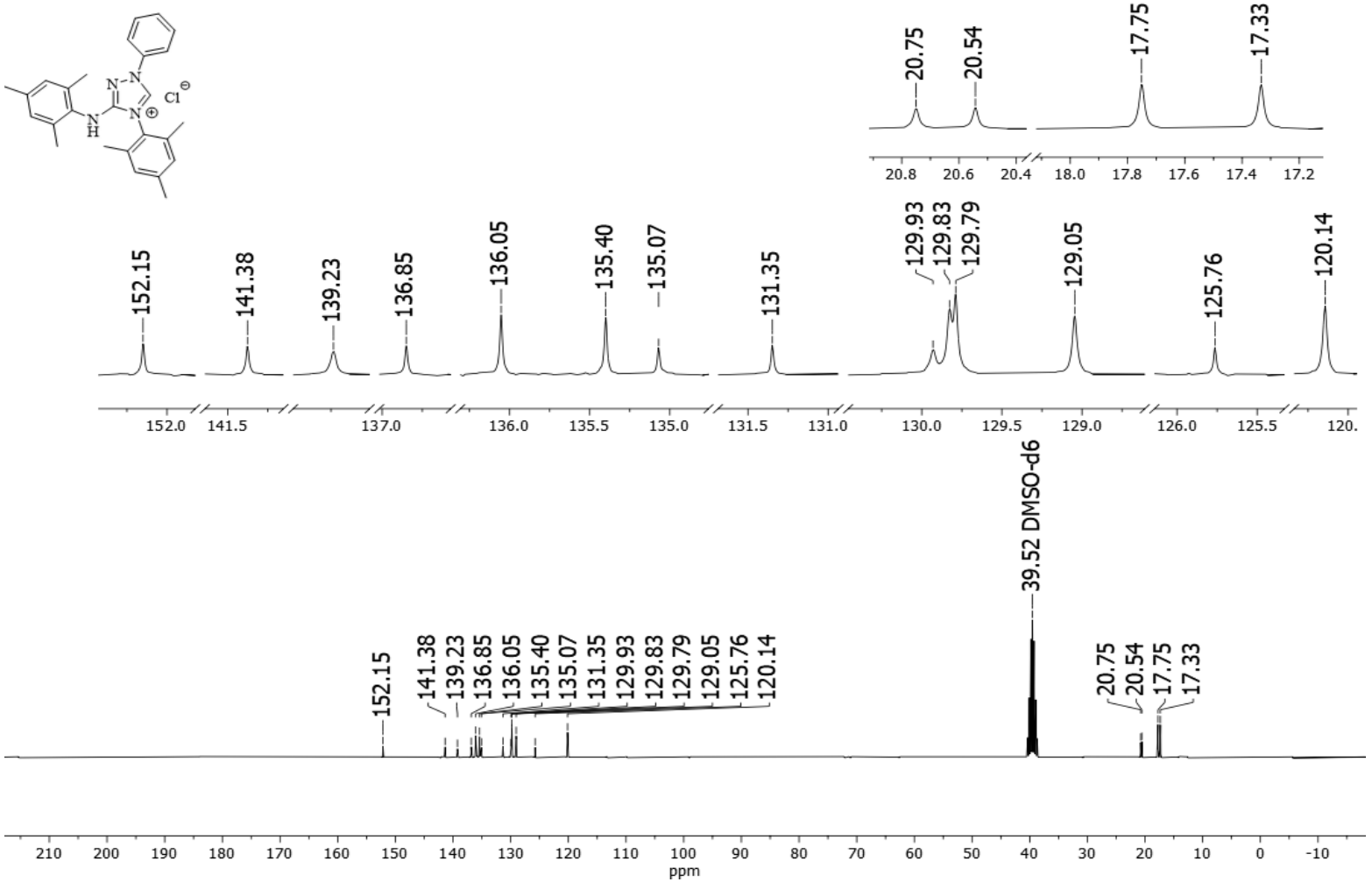


Figure S5. ^{13}C NMR spectrum of compound **1a** (DMSO-d_6, 75 MHz).

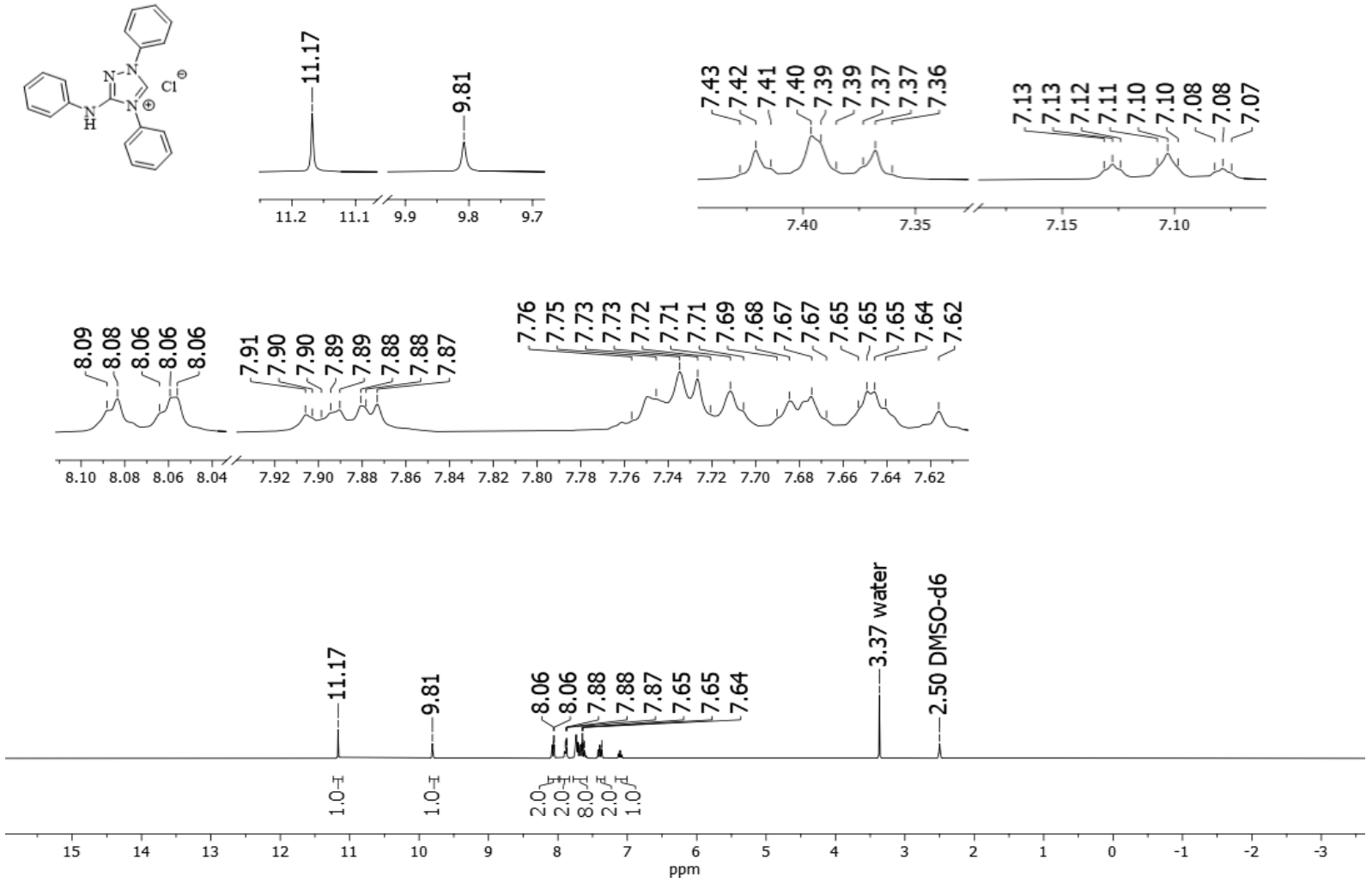


Figure S6. ^{1}H NMR spectrum of compound **1b** (DMSO-d_6, 300 MHz).

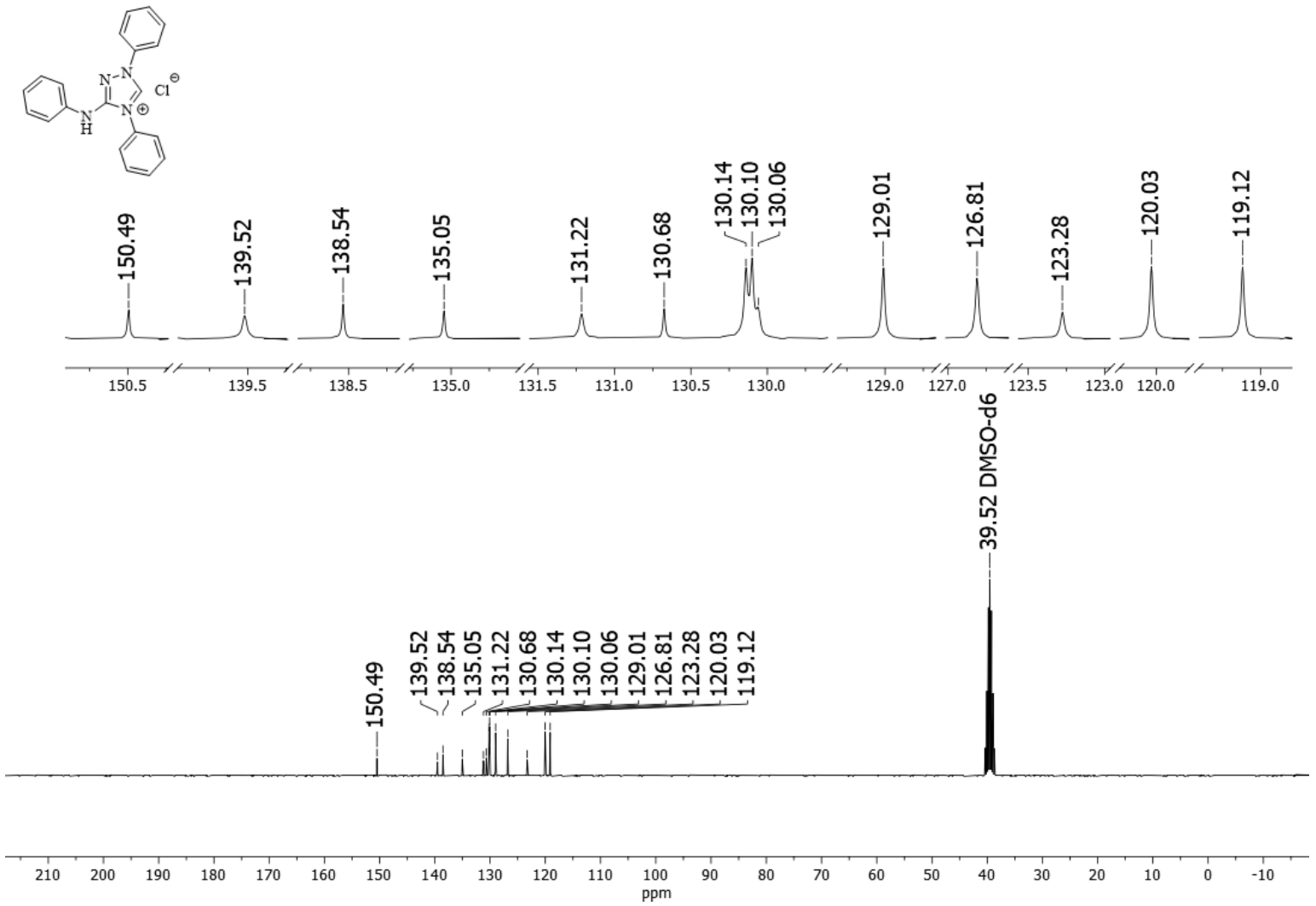


Figure S7. ^{13}C NMR spectrum of compound **1b** (DMSO-d_6, 75 MHz).

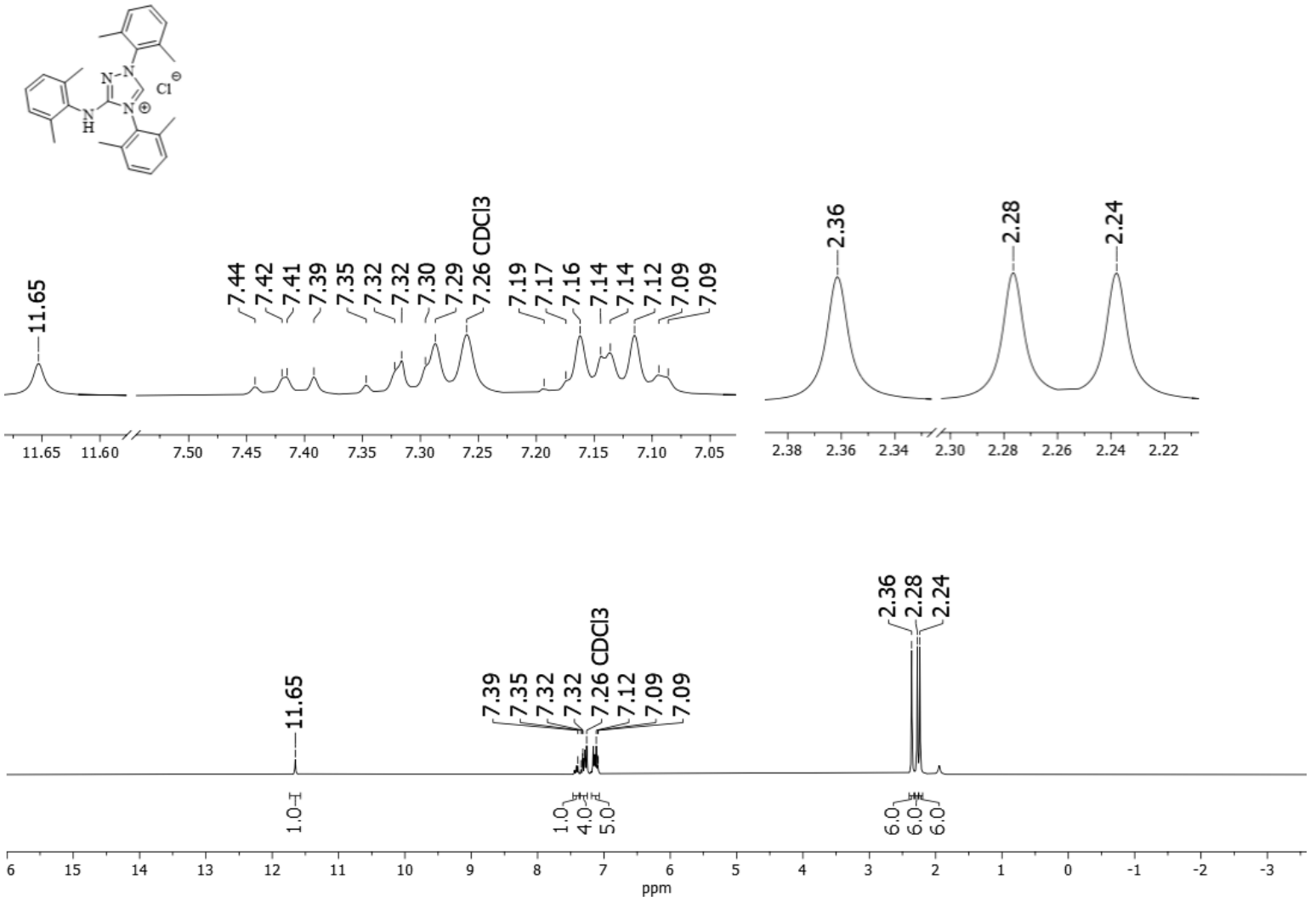


Figure S8. ^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 300 MHz).

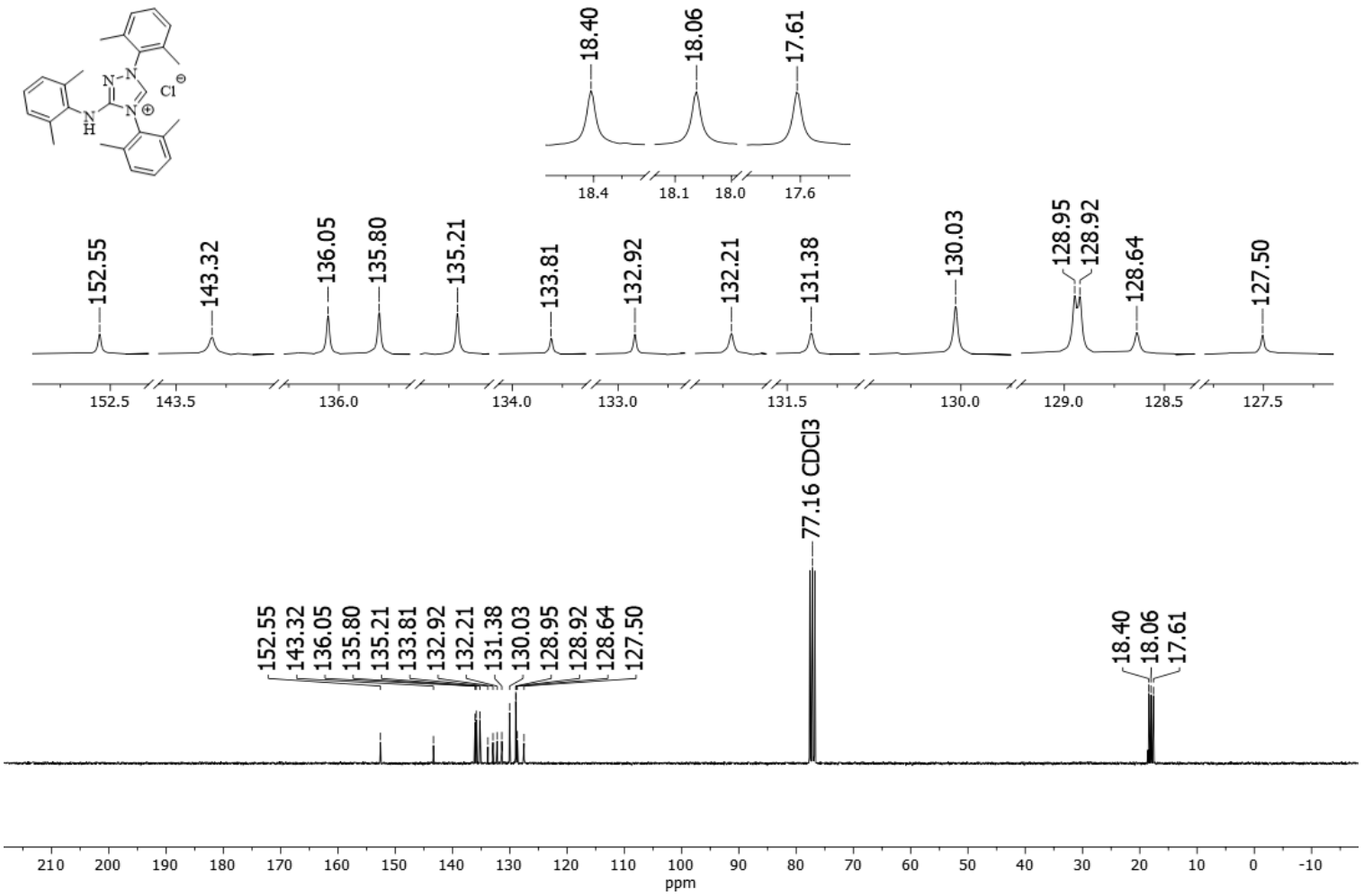


Figure S9. ^{13}C NMR spectrum of compound **1c** ($CDCl_3$, 75 MHz).

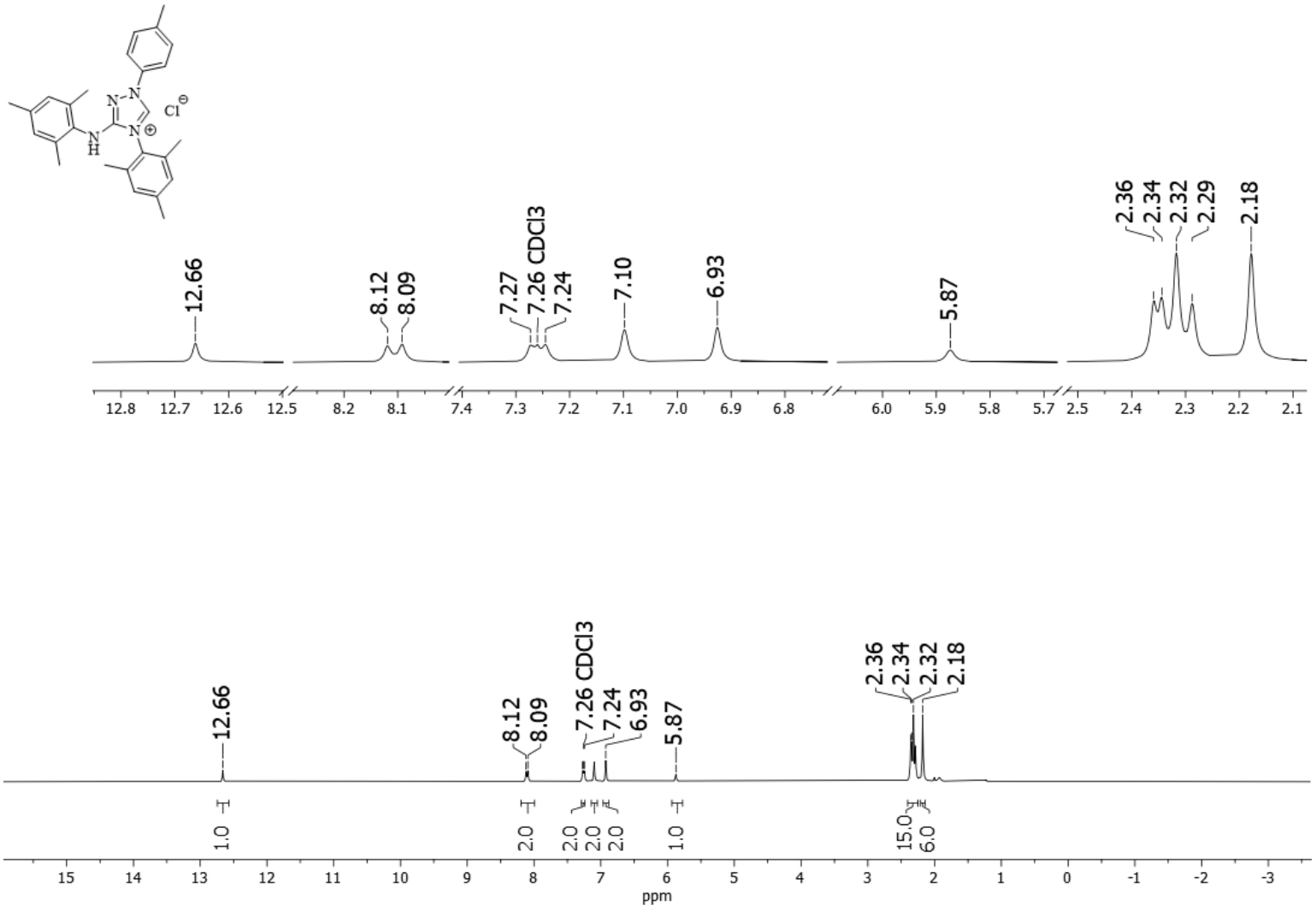


Figure S10. ^{1}H NMR spectrum of compound **1d** ($CDCl_3$, 300 MHz).

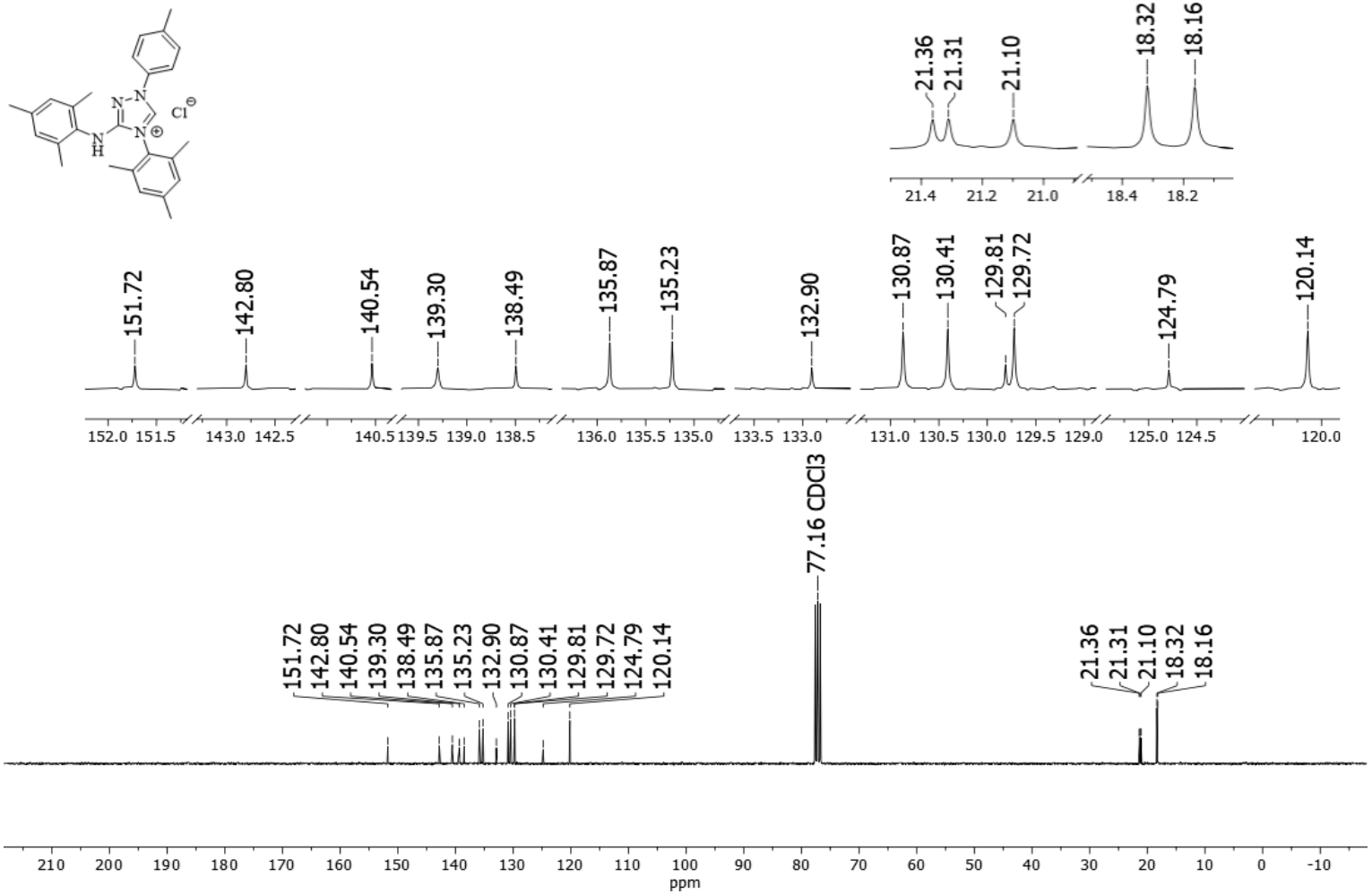


Figure S11. ^{13}C NMR spectrum of compound **1d** ($CDCl_3$, 75 MHz).

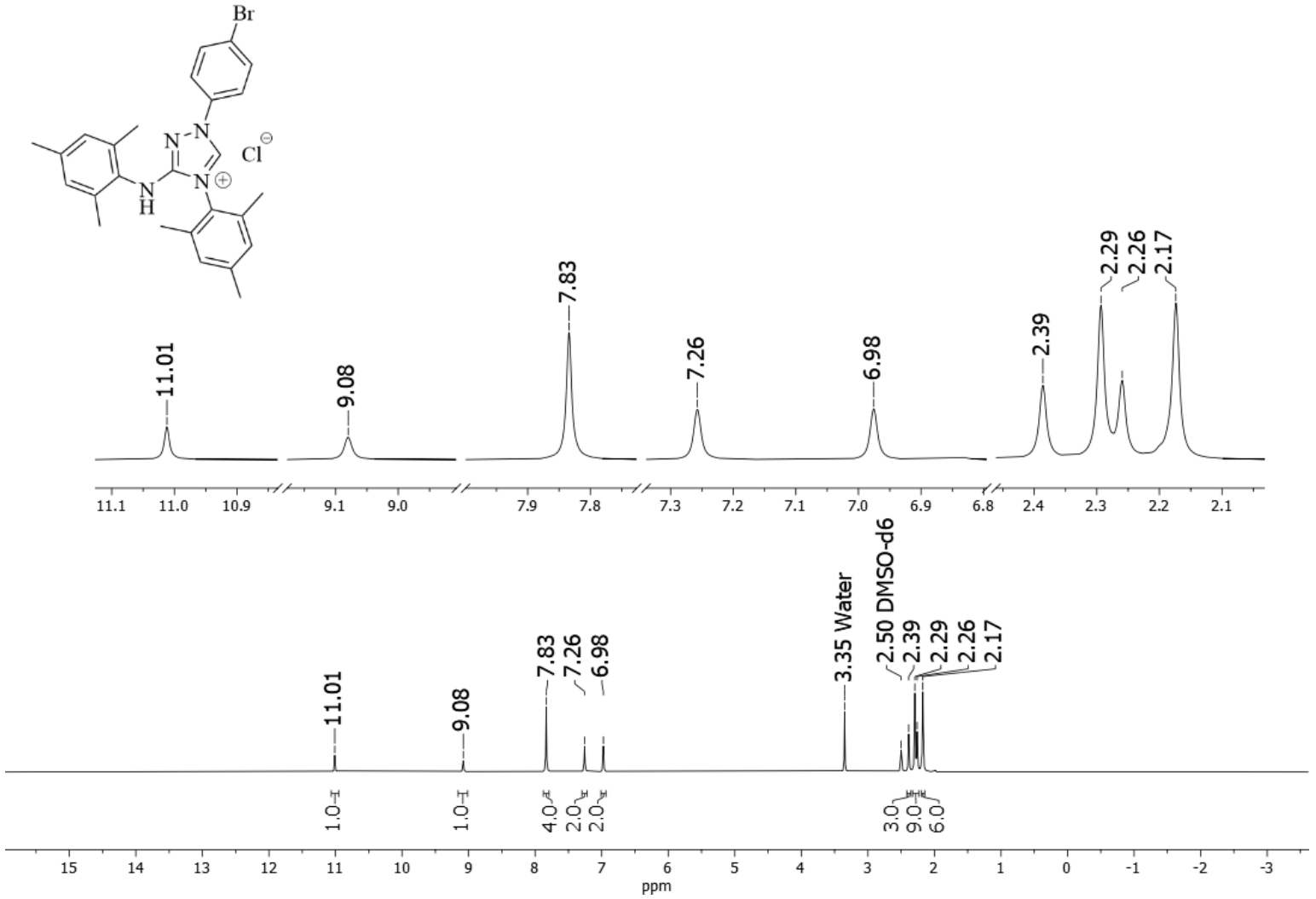


Figure S12. ^{1}H NMR spectrum of compound **1e** (DMSO-d_6, 300 MHz).

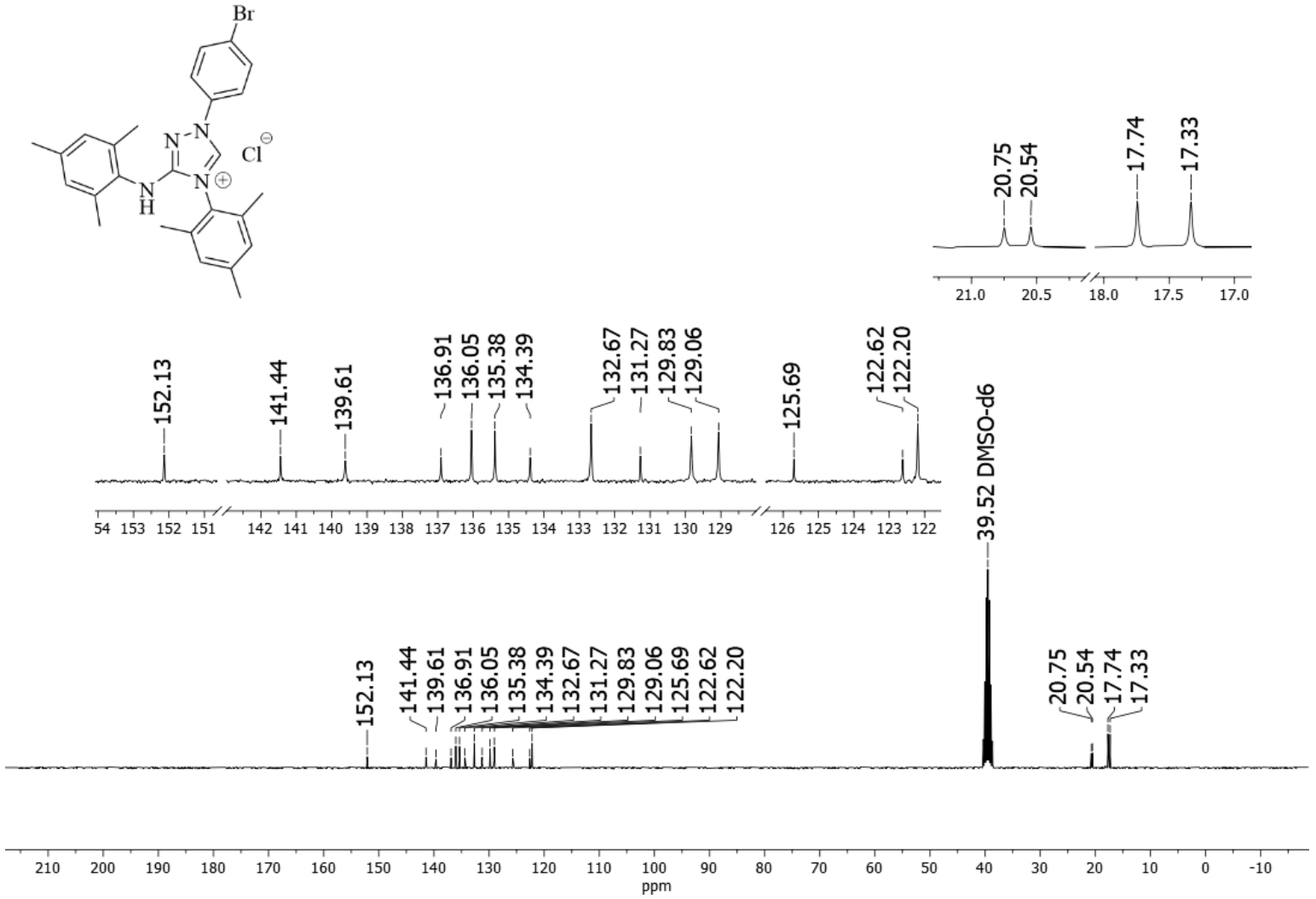


Figure S13. ^{13}C NMR spectrum of compound **1e** (DMSO-d_6, 75 MHz).

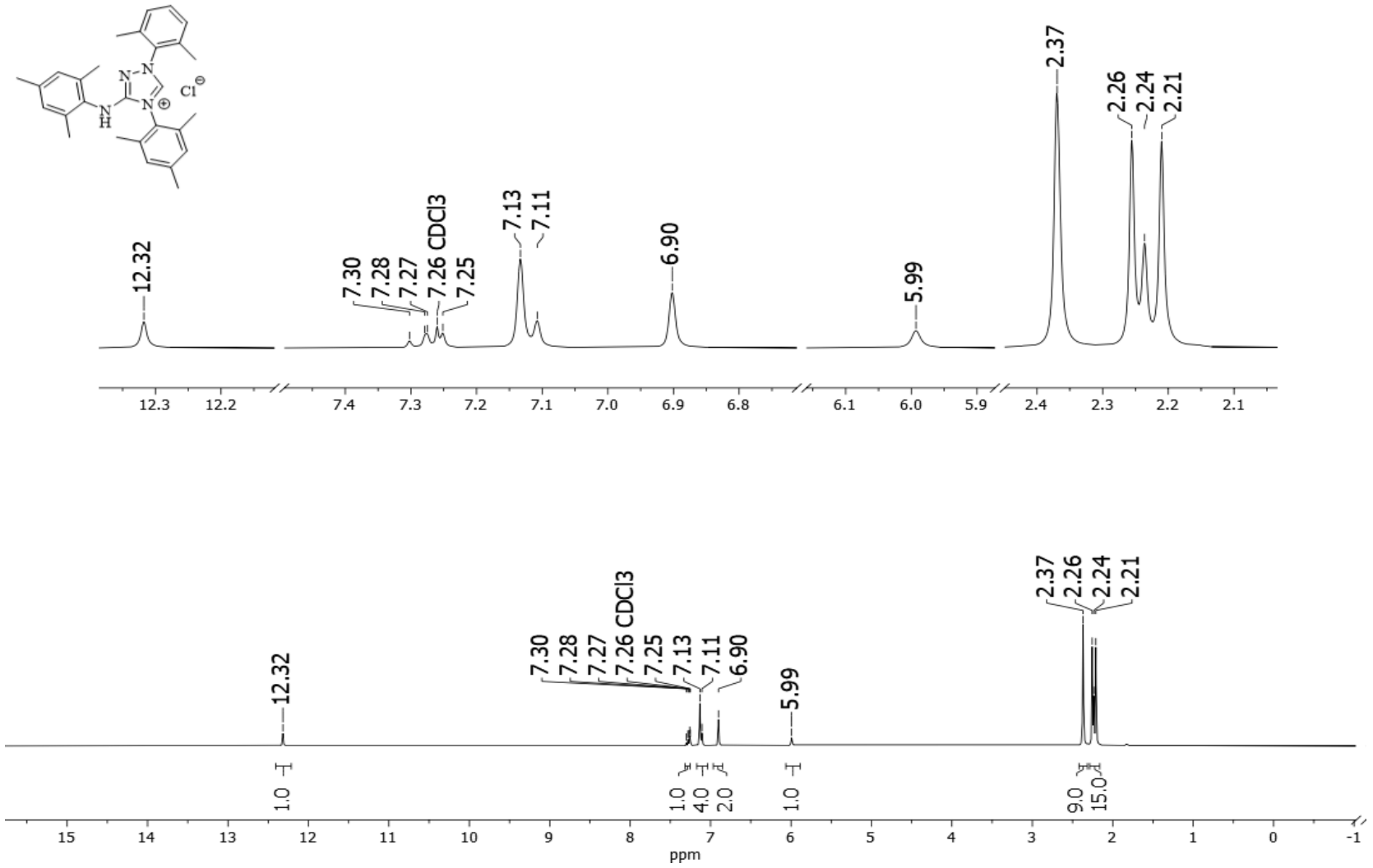


Figure S14. ^{1}H NMR spectrum of compound **1f** ($CDCl_3$, 300 MHz).

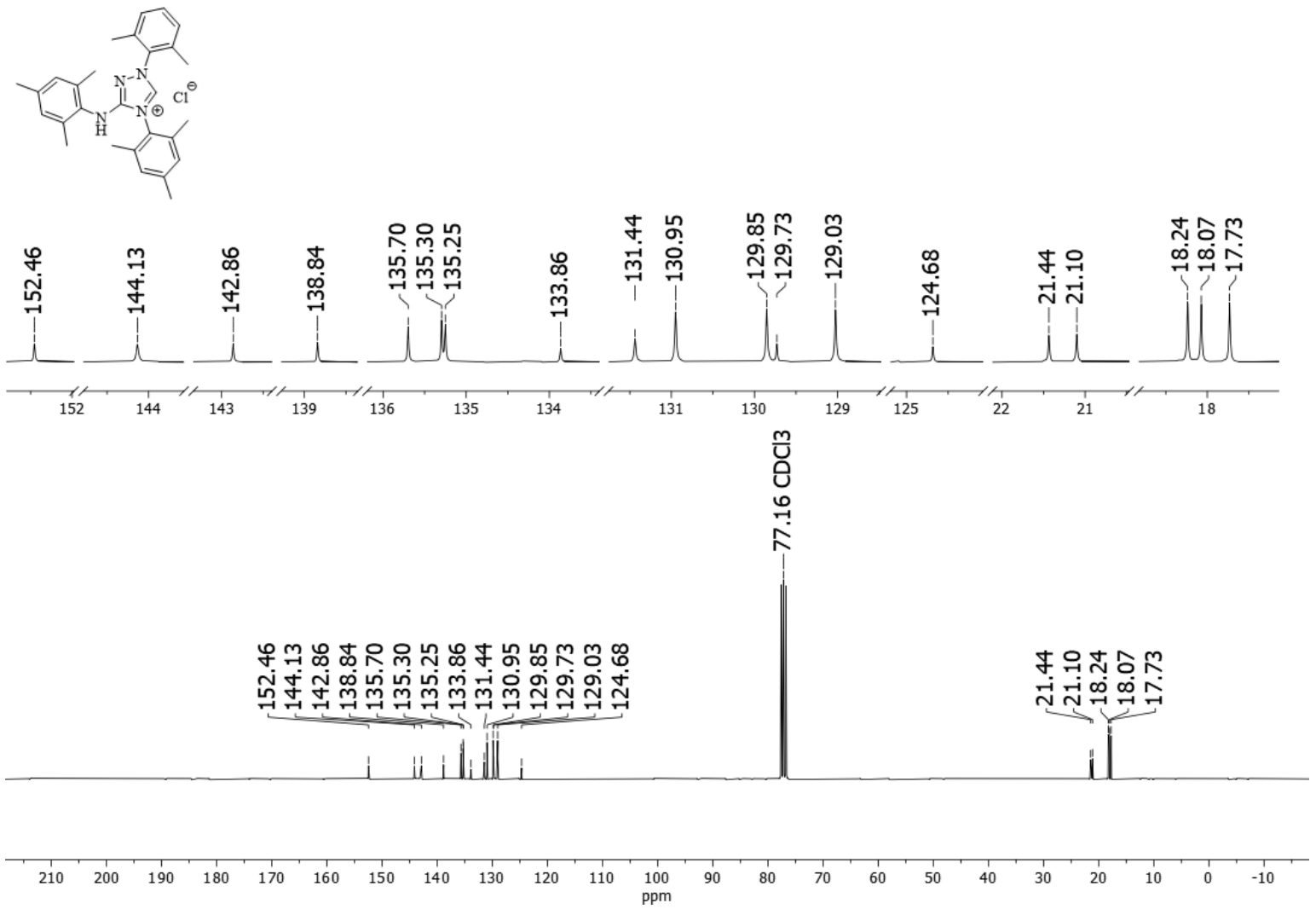


Figure S15. ^{13}C NMR spectrum of compound **1f** ($CDCl_3$, 75 MHz).

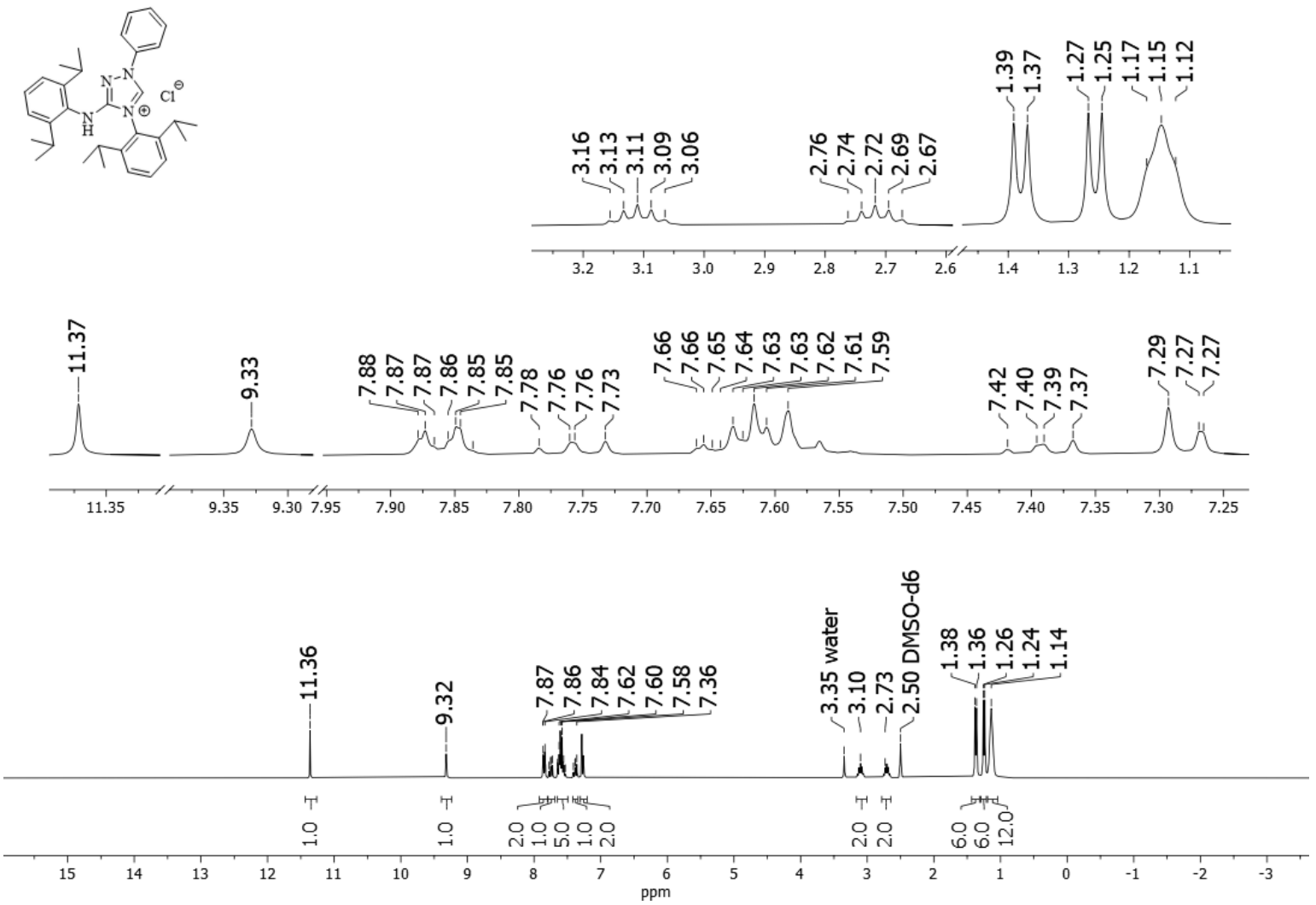


Figure S16. ^{1}H NMR spectrum of compound **1g** (DMSO-d_6, 300 MHz).

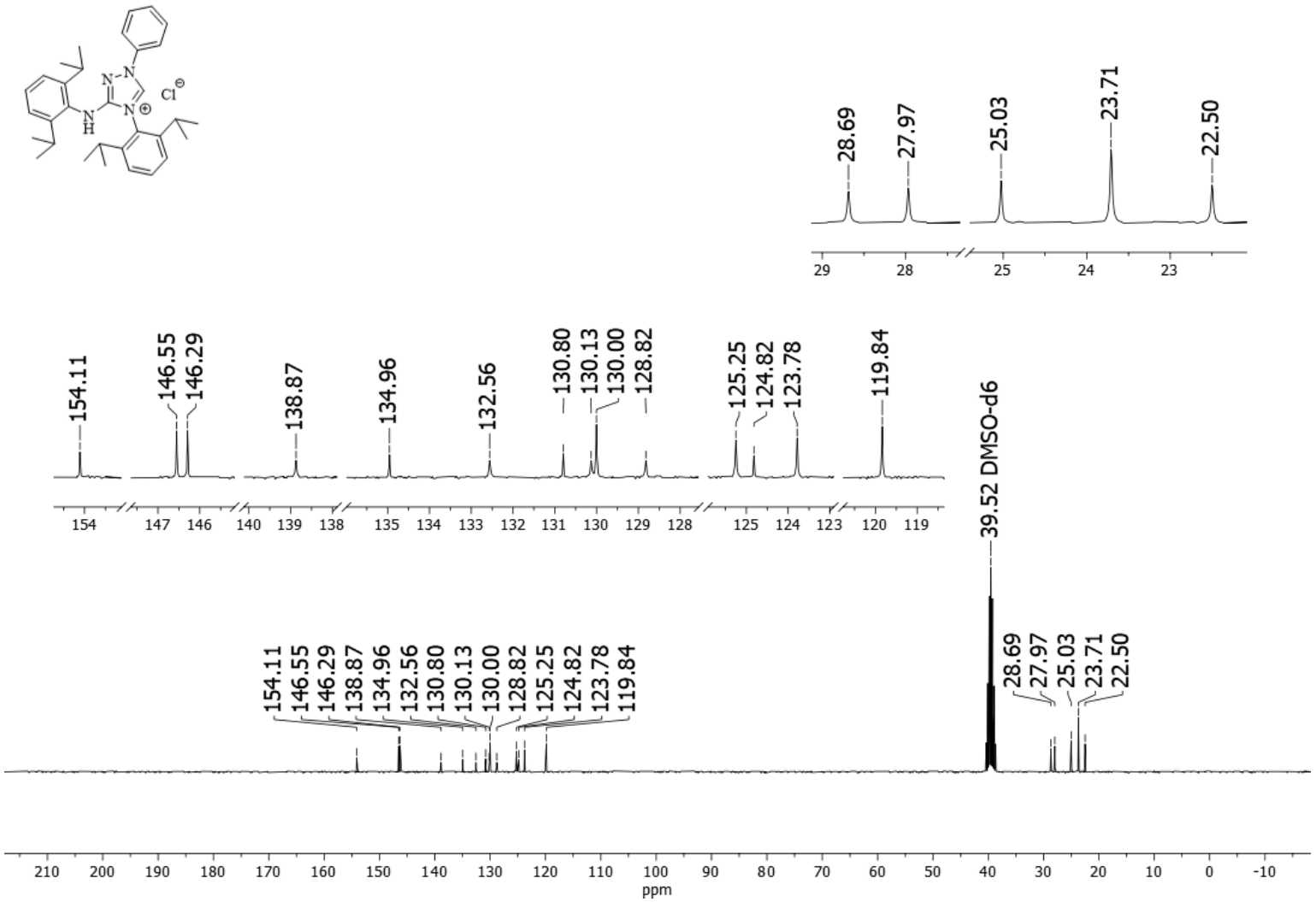


Figure S17. ^{13}C NMR spectrum of compound **1g** (DMSO-d_6, 75 MHz).

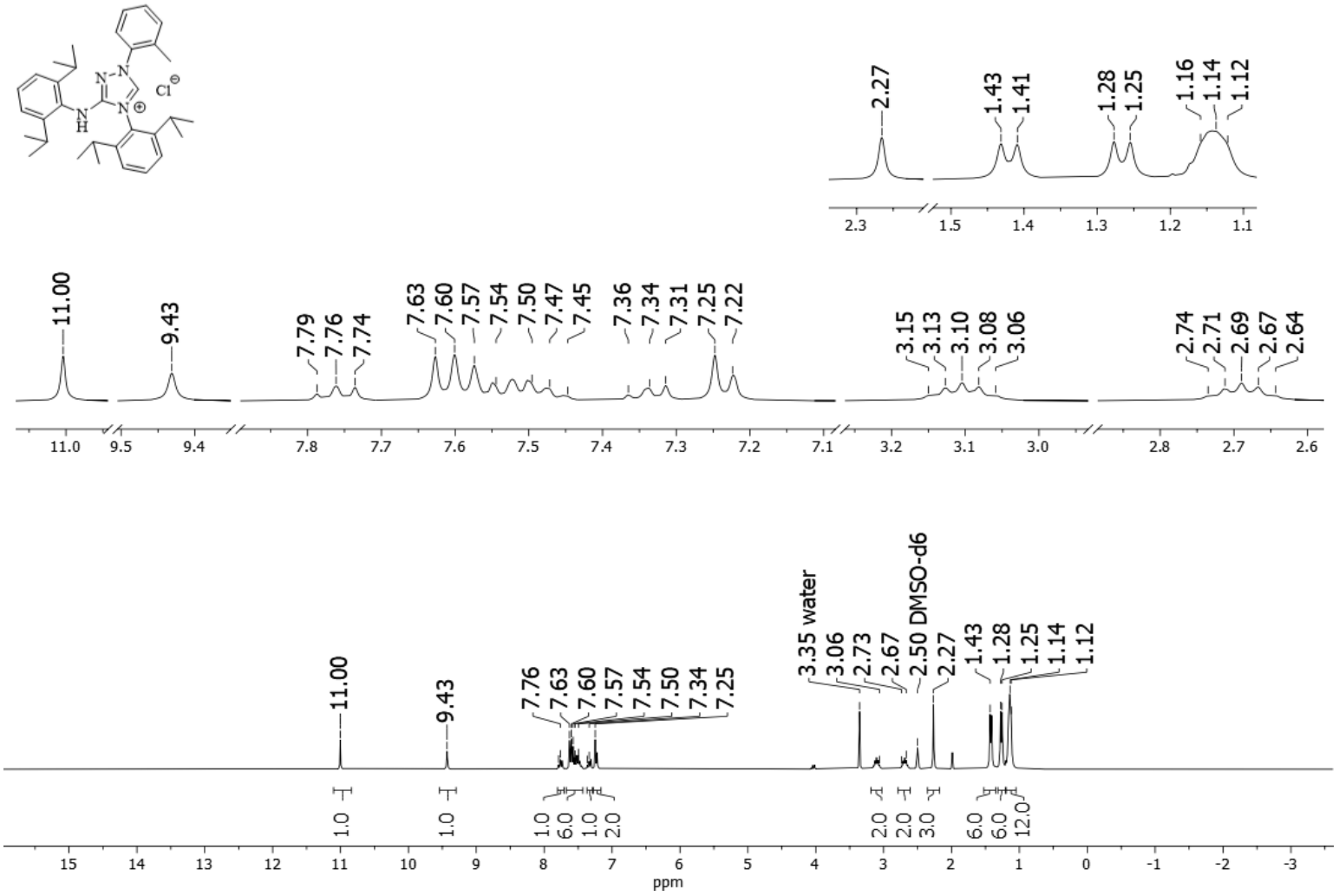


Figure S18. ^{1}H NMR spectrum of compound **1h** (DMSO-d_6, 300 MHz).

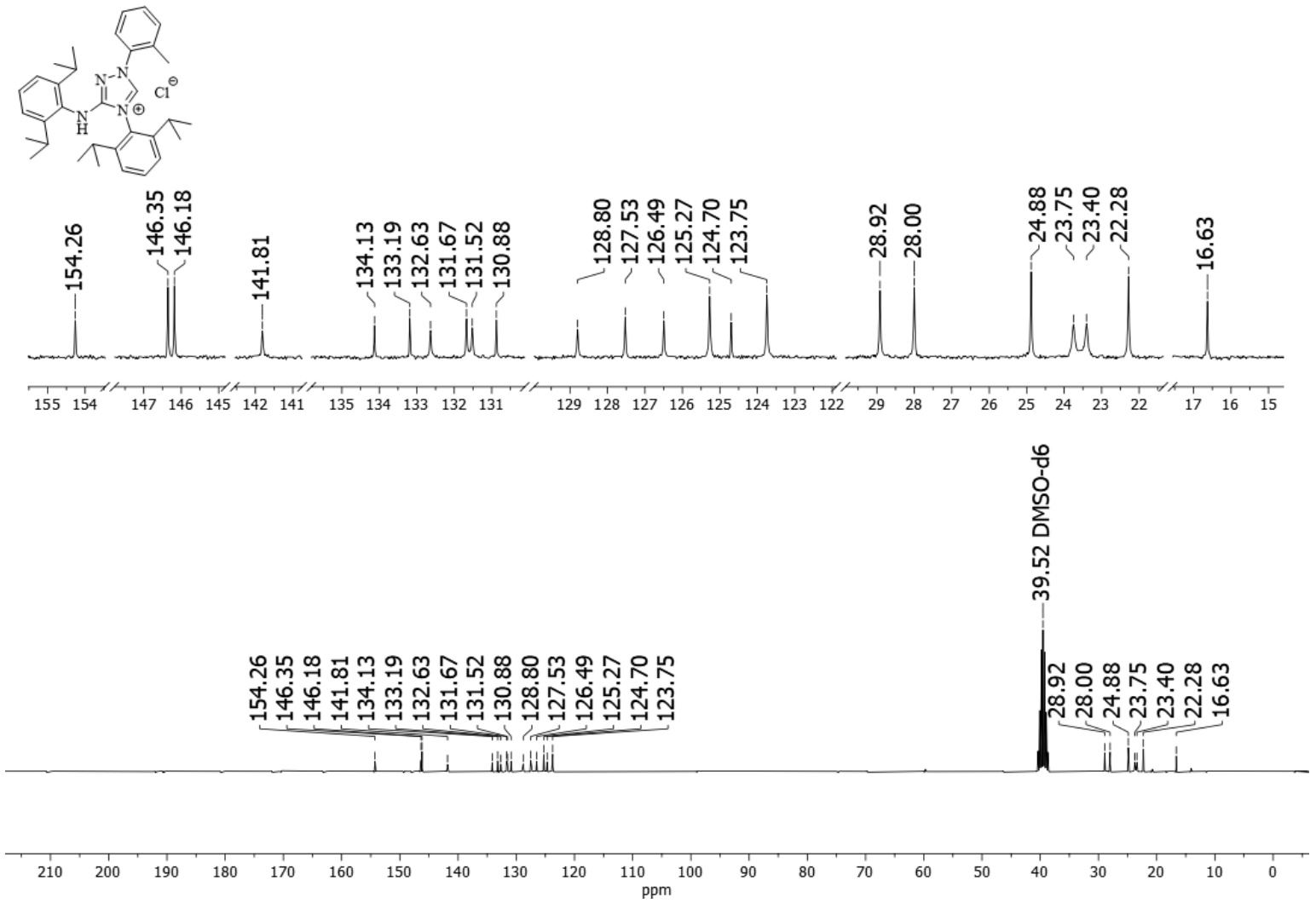


Figure S19. ^{13}C NMR spectrum of compound **1h** (DMSO-d_6, 75 MHz).

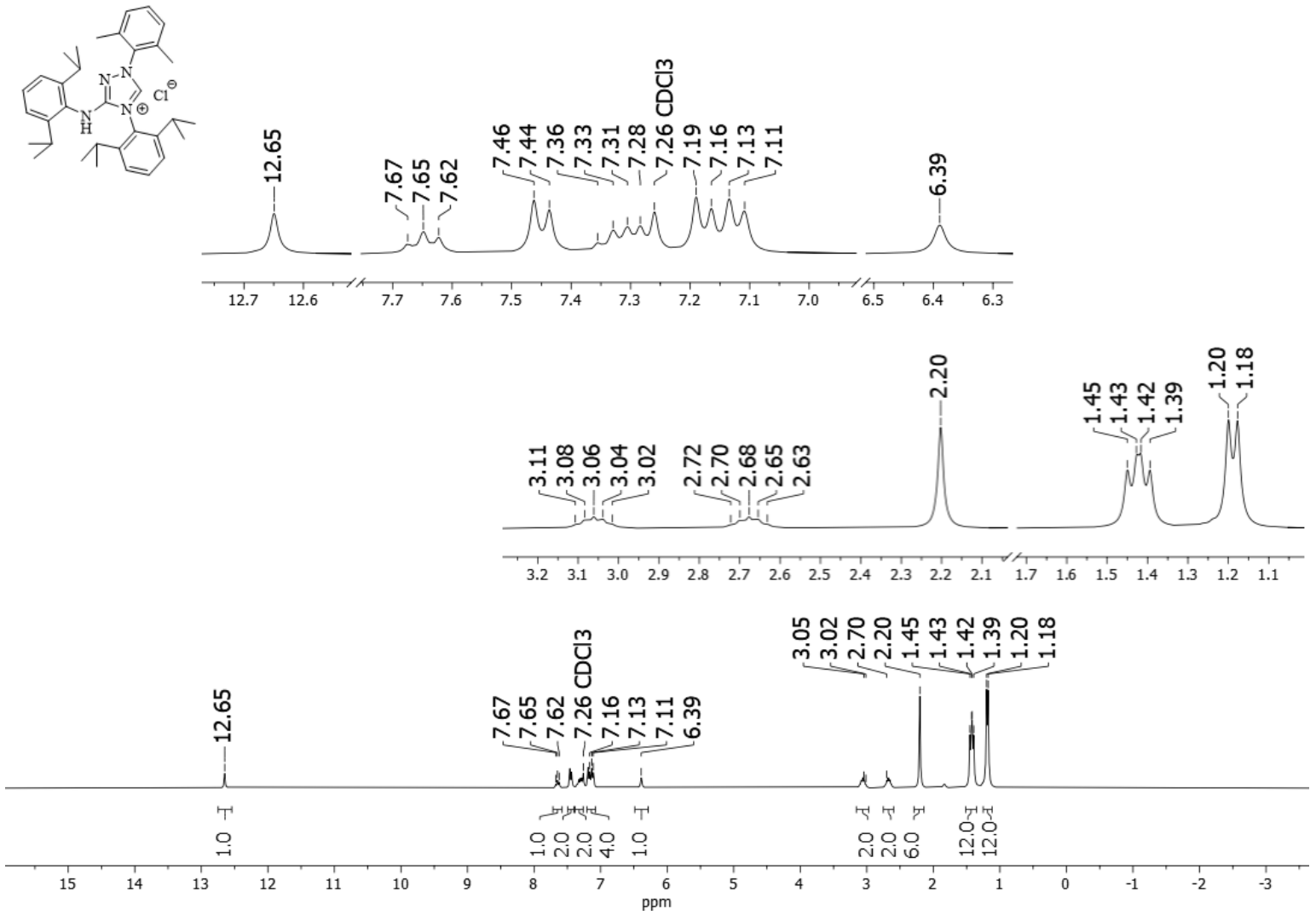


Figure S20. ^{1}H NMR spectrum of compound **1i** ($CDCl_3$, 300 MHz).

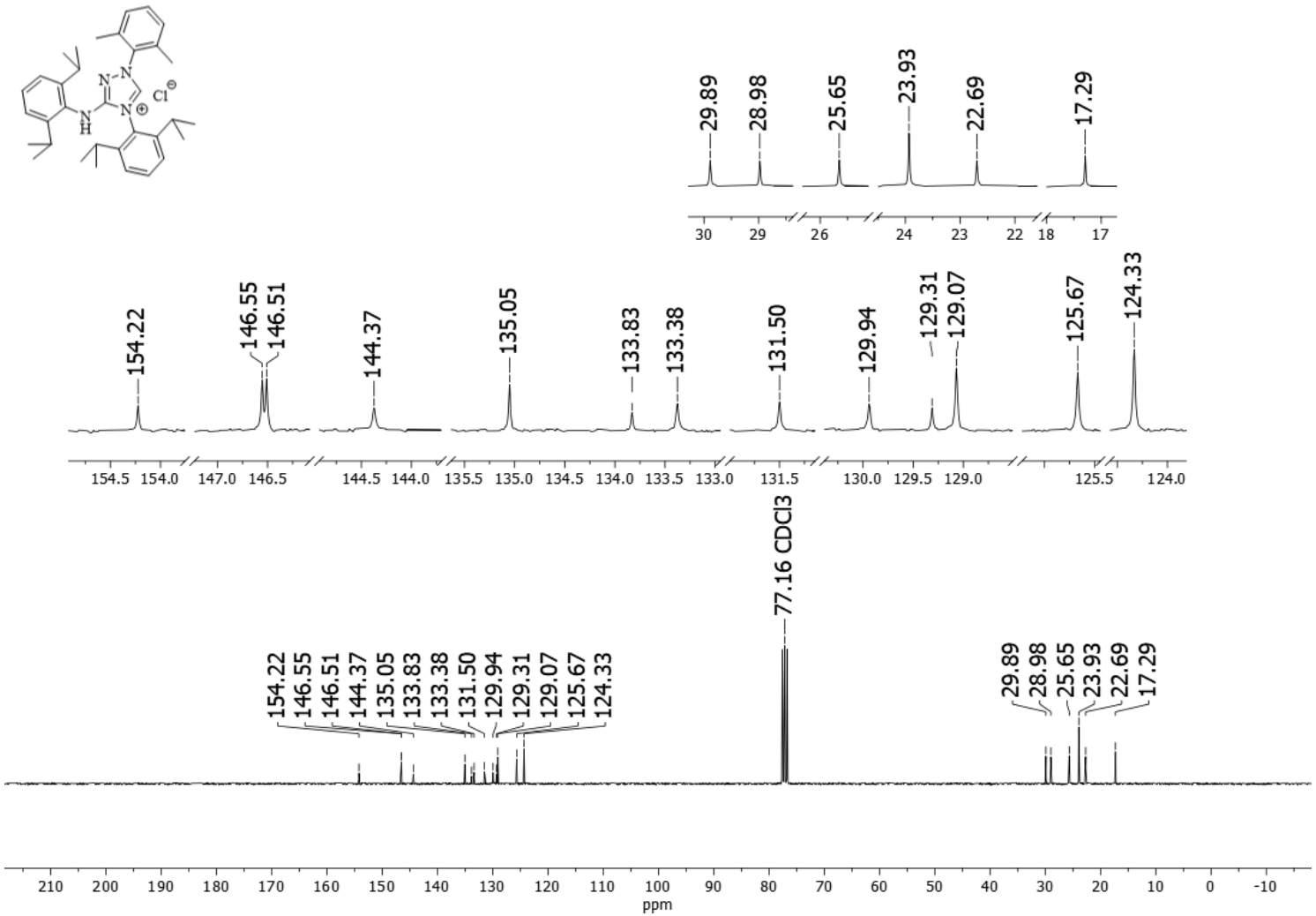


Figure S21. ^{13}C NMR spectrum of compound **1i** ($CDCl_3$, 75 MHz).

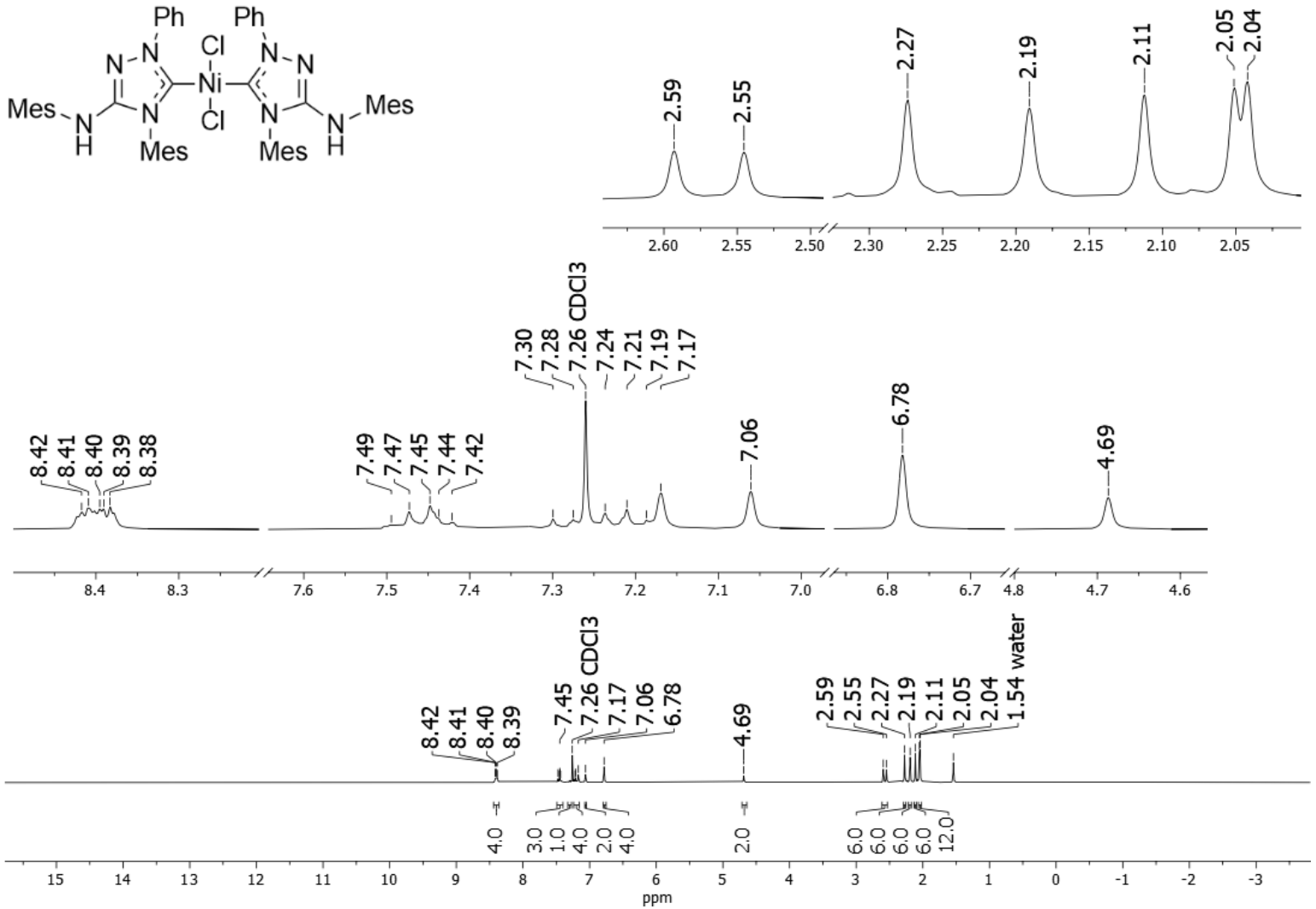


Figure S22. ^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 300 MHz).

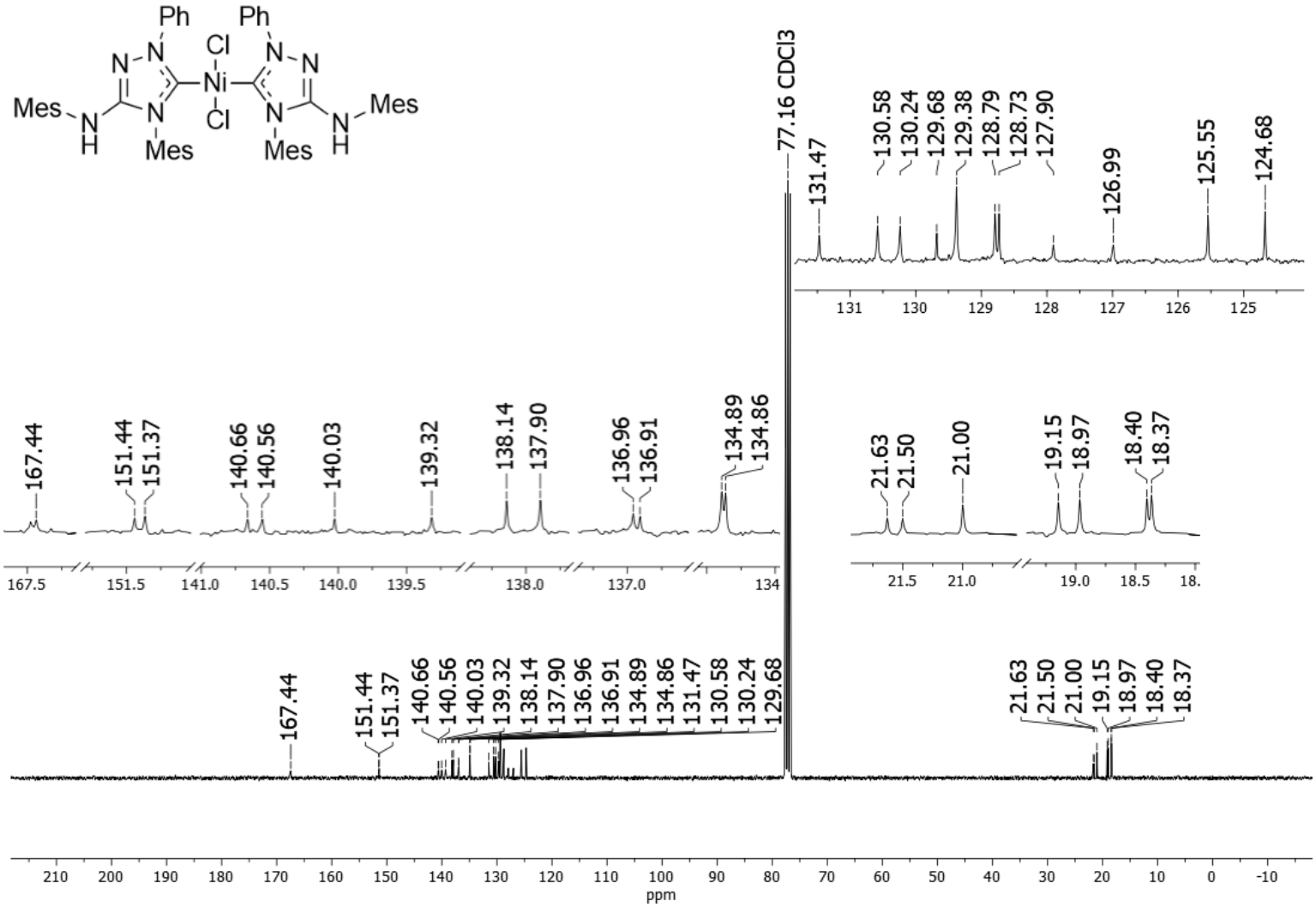


Figure S23. ^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 75 MHz).

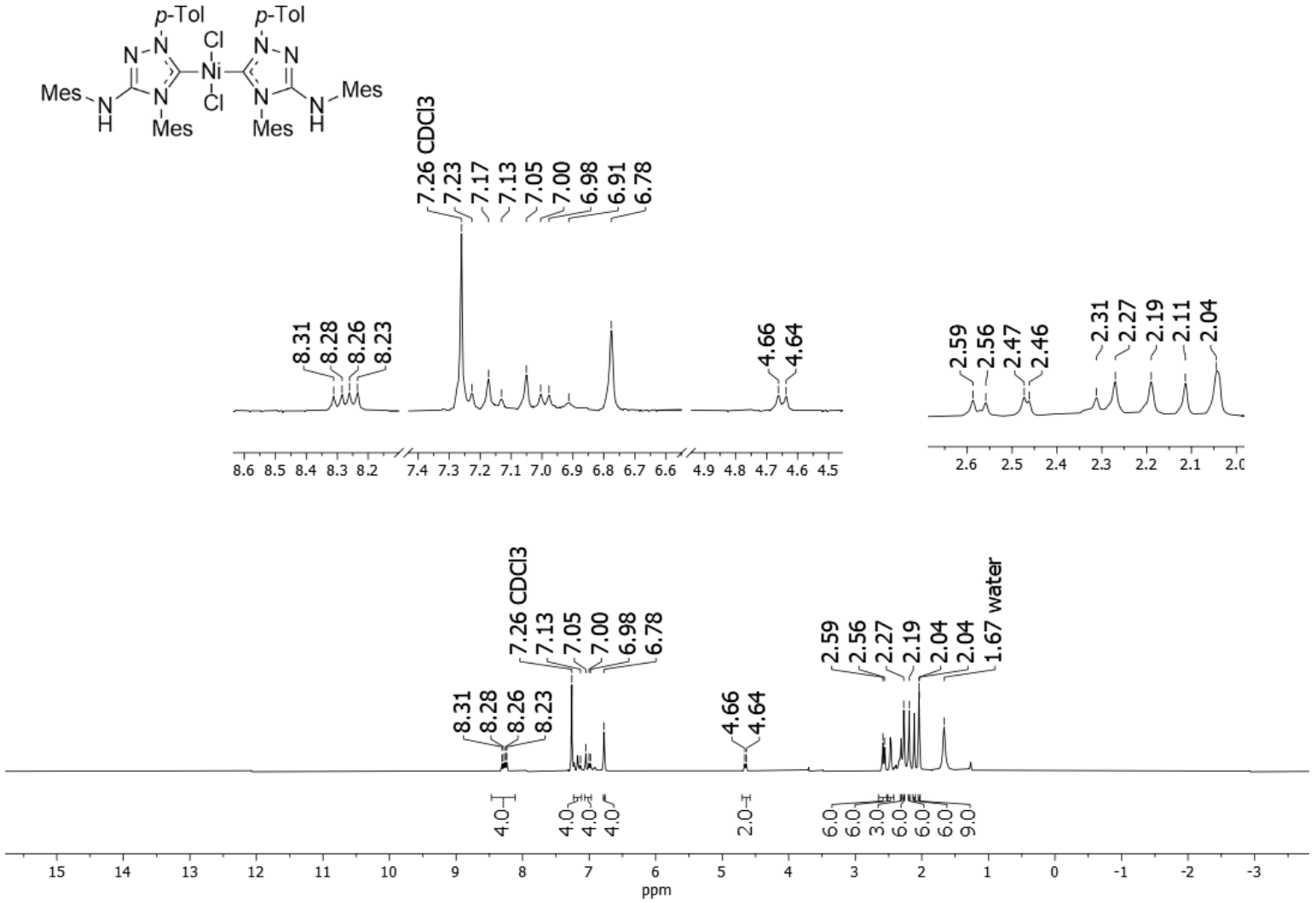


Figure S24. ^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 300 MHz).

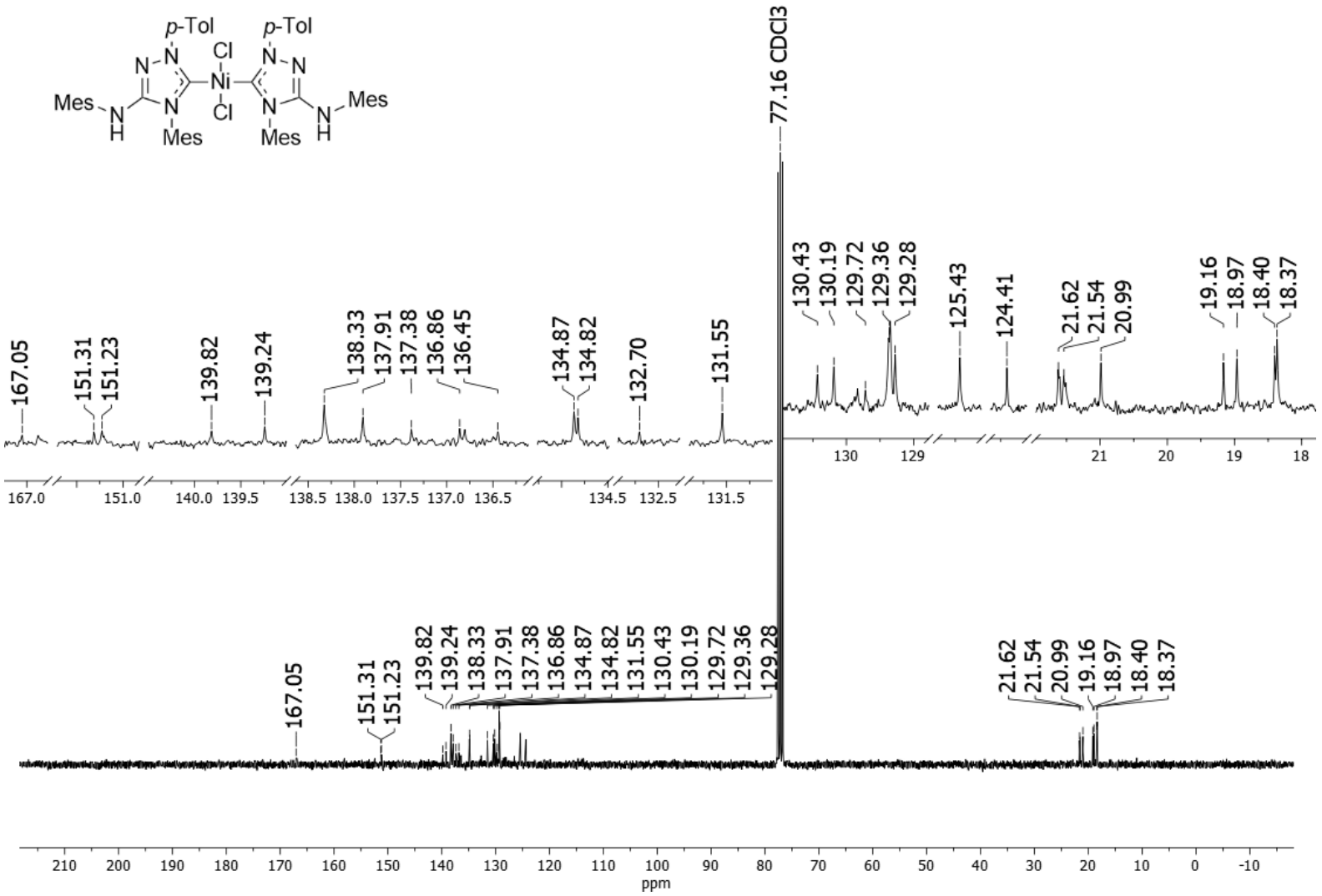


Figure S25. ^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 75 MHz).

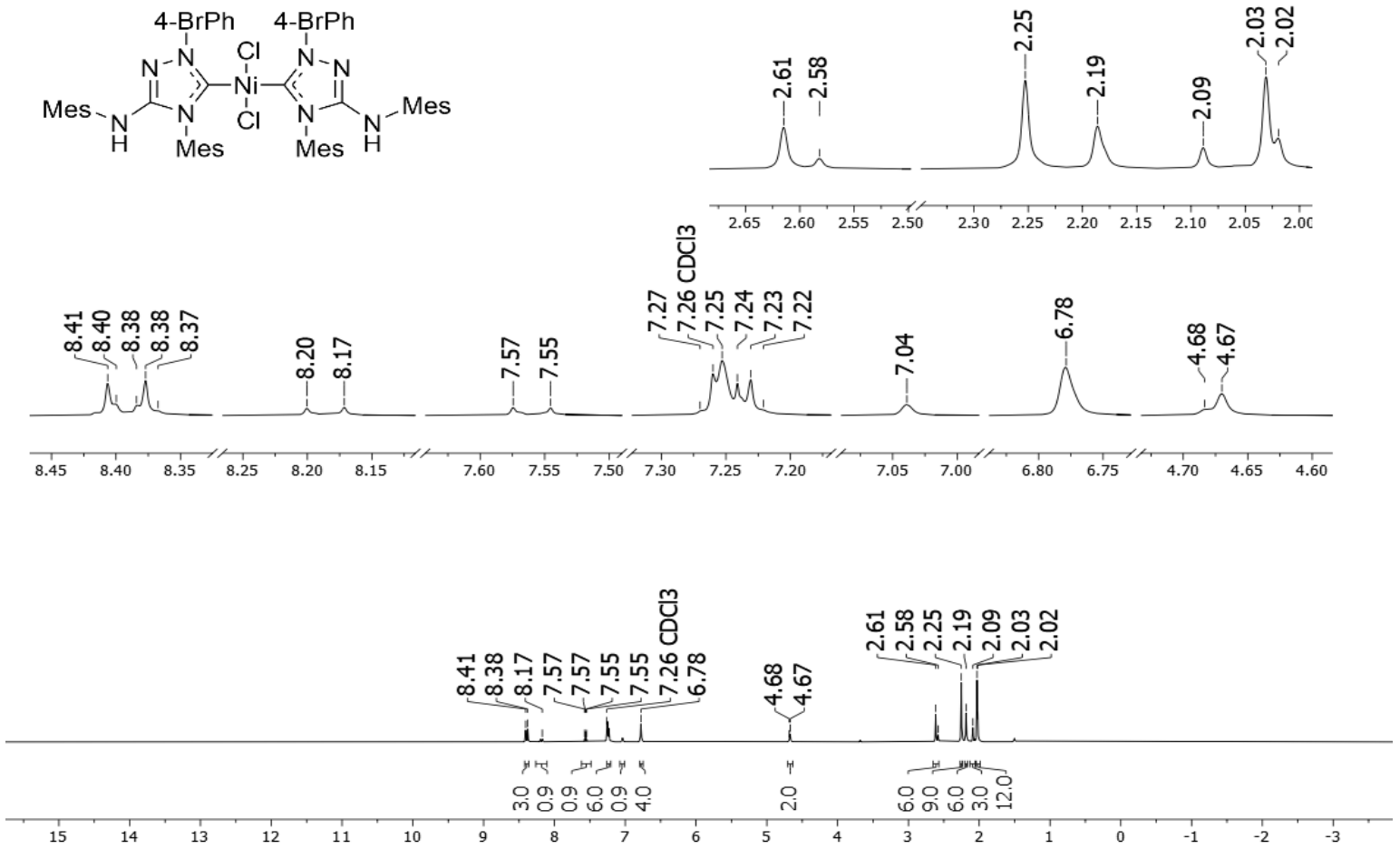


Figure S26. ^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 300 MHz).

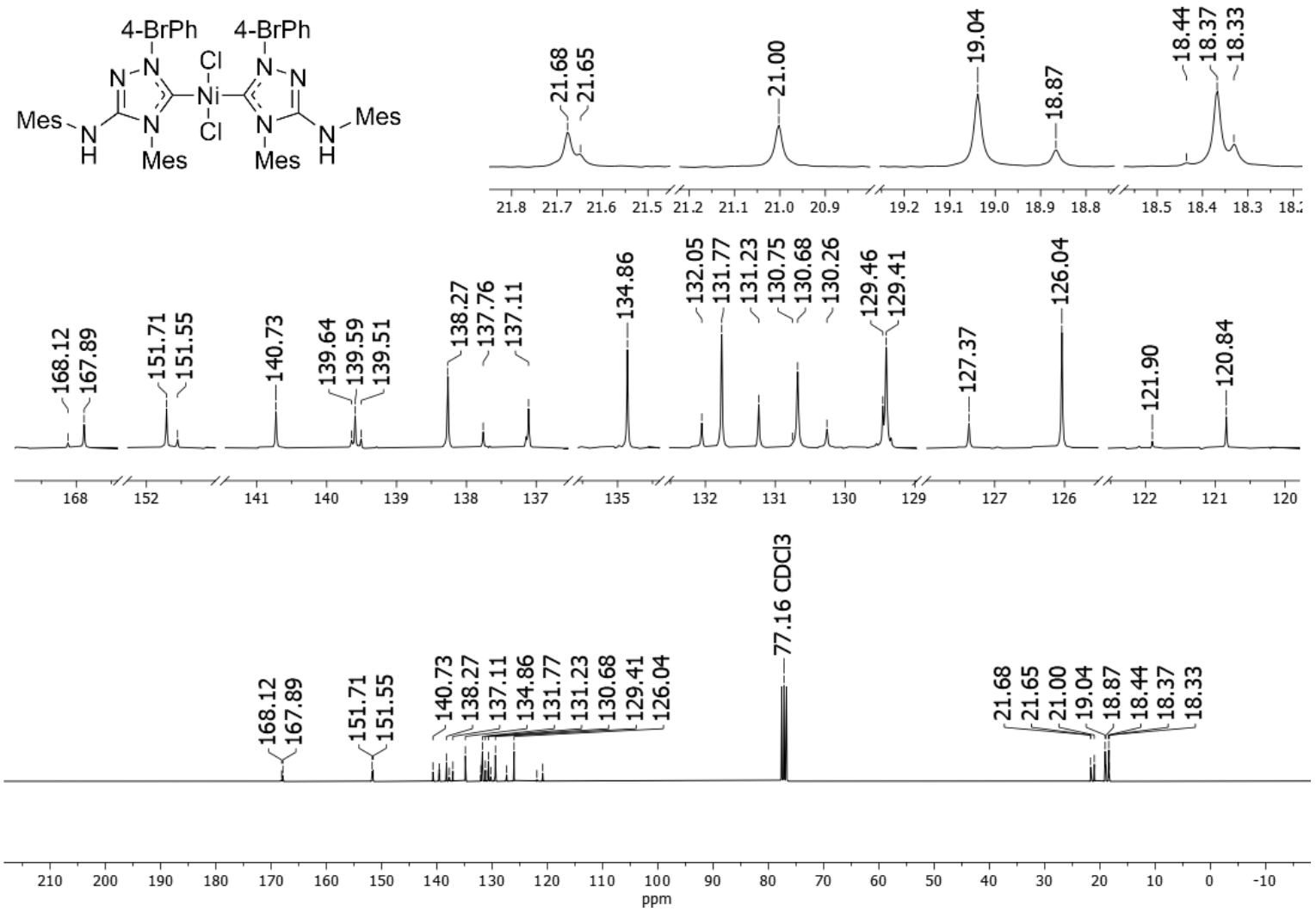


Figure S27. ^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 75 MHz).

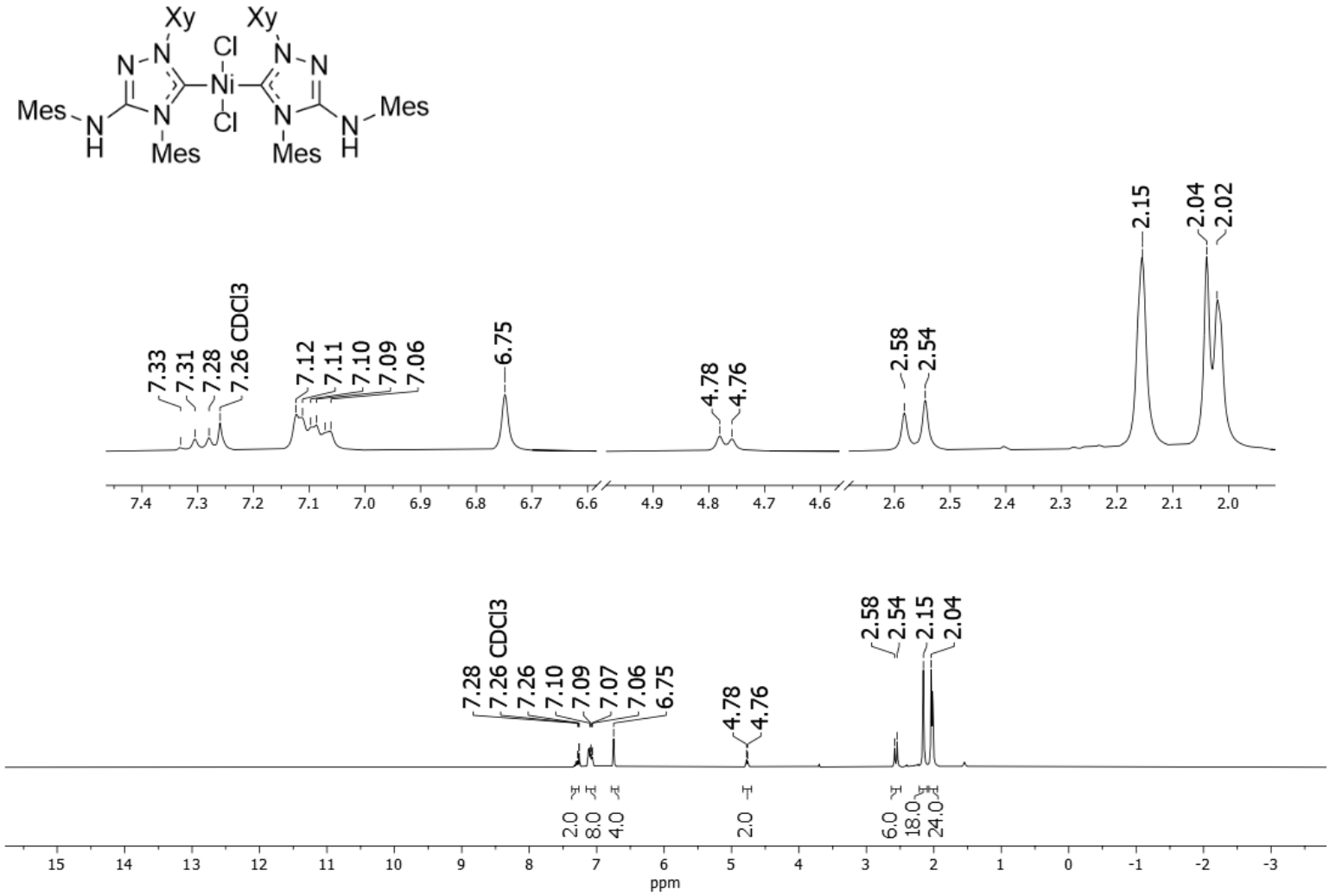


Figure S28. ^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 300 MHz).

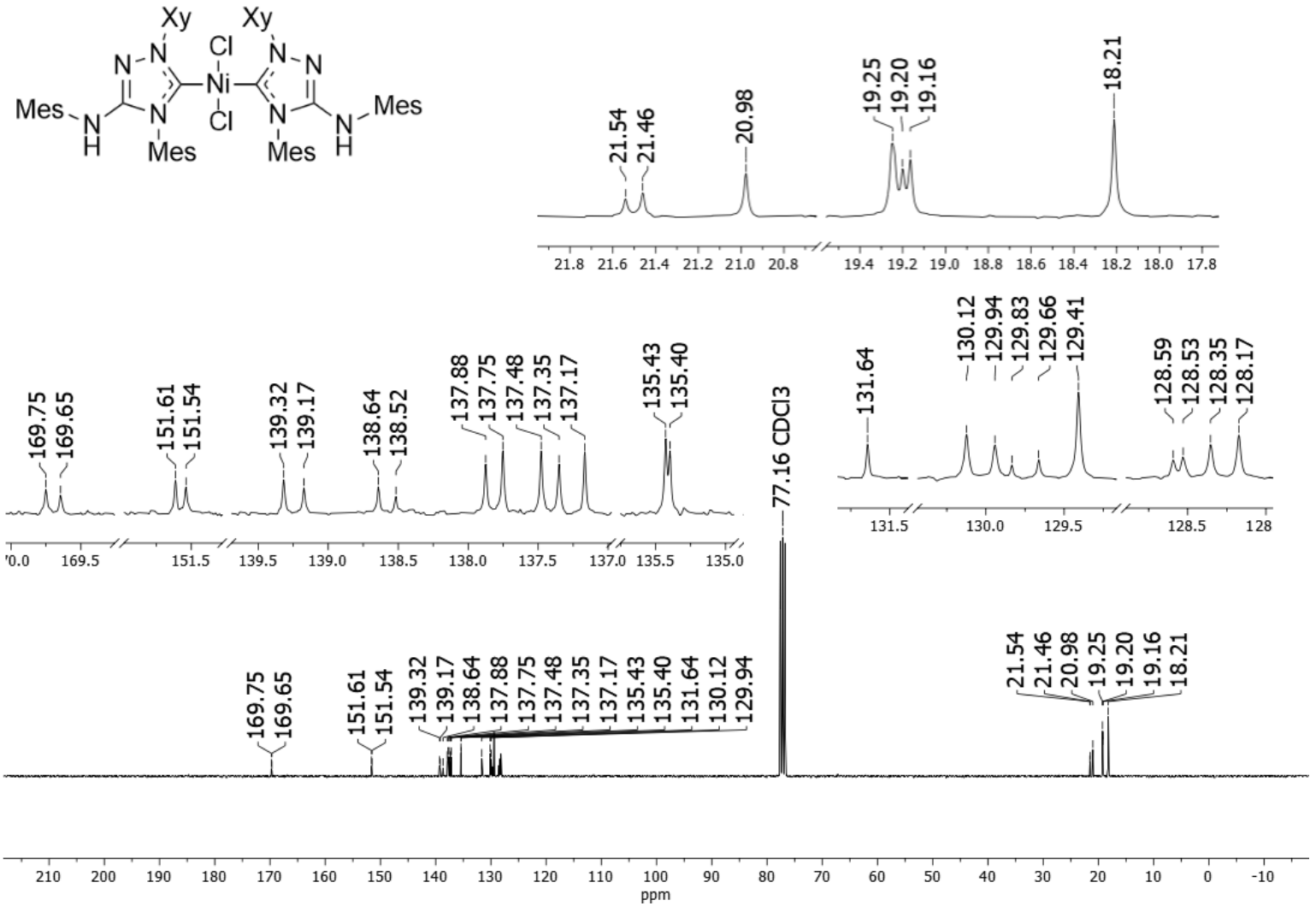


Figure S29. ^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 75 MHz).

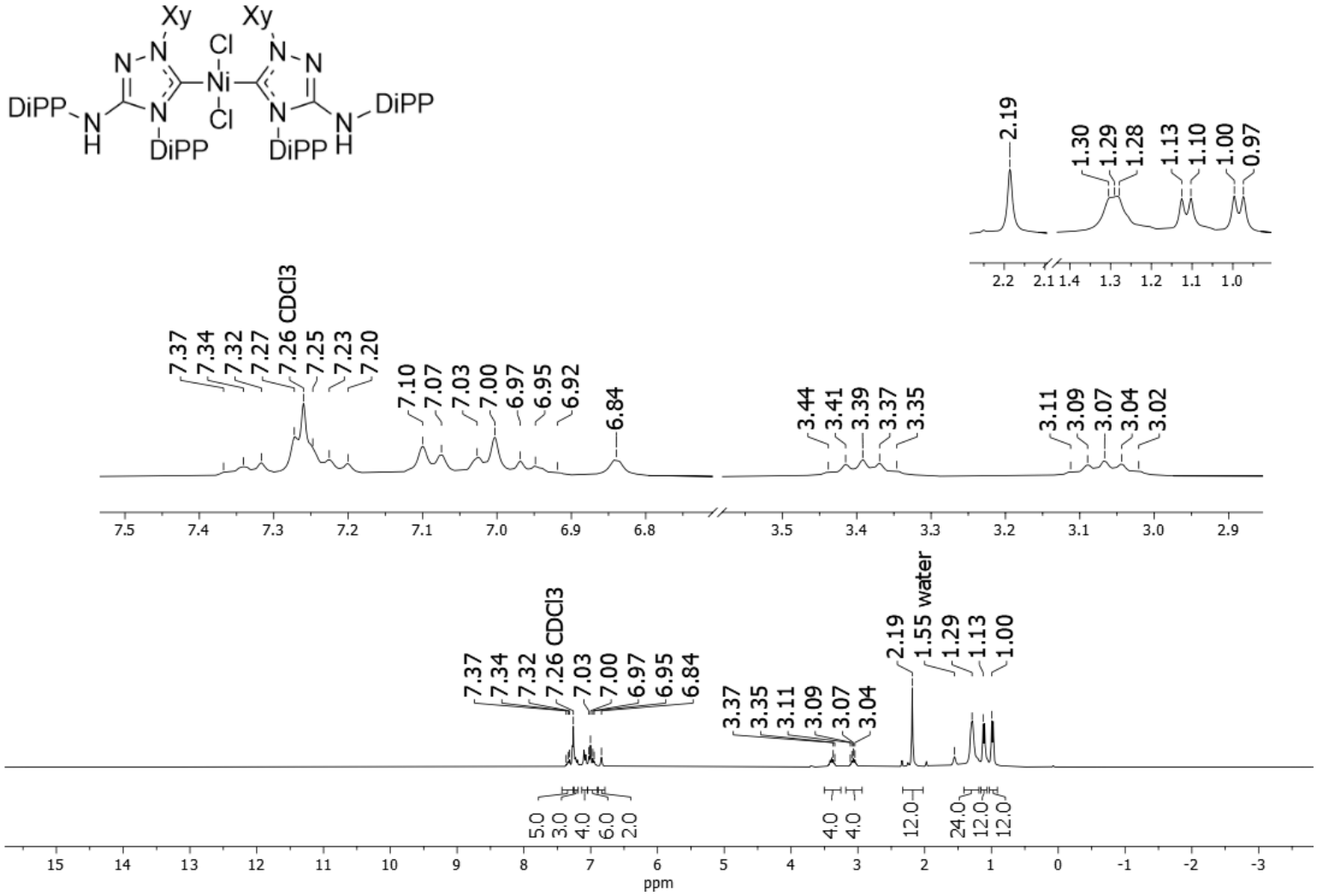


Figure S30. ^{1}H NMR spectrum of compound **5e** ($CDCl_3$, 300 MHz).

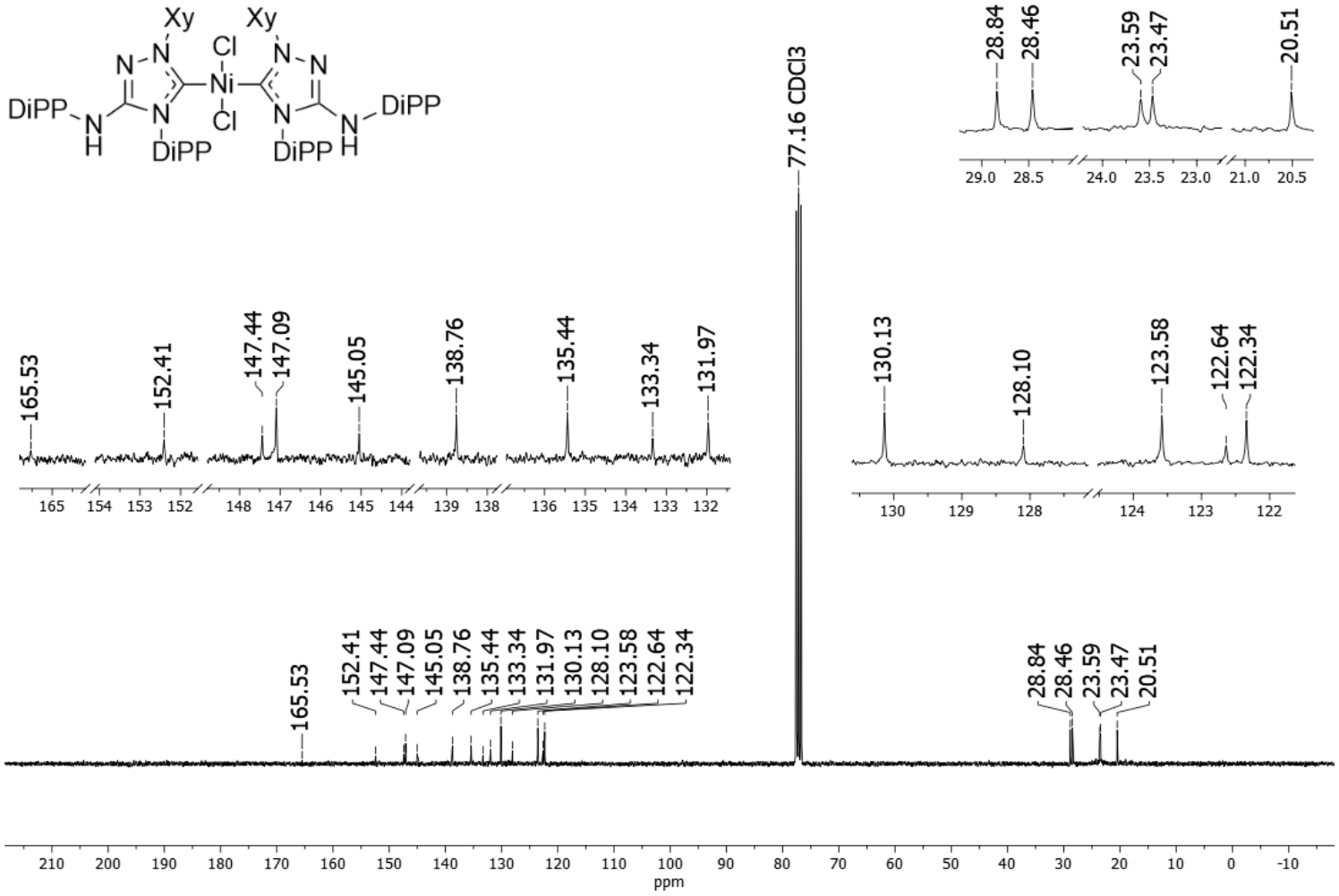


Figure S31. ^{13}C NMR spectrum of compound **5e** ($CDCl_3$, 75 MHz).

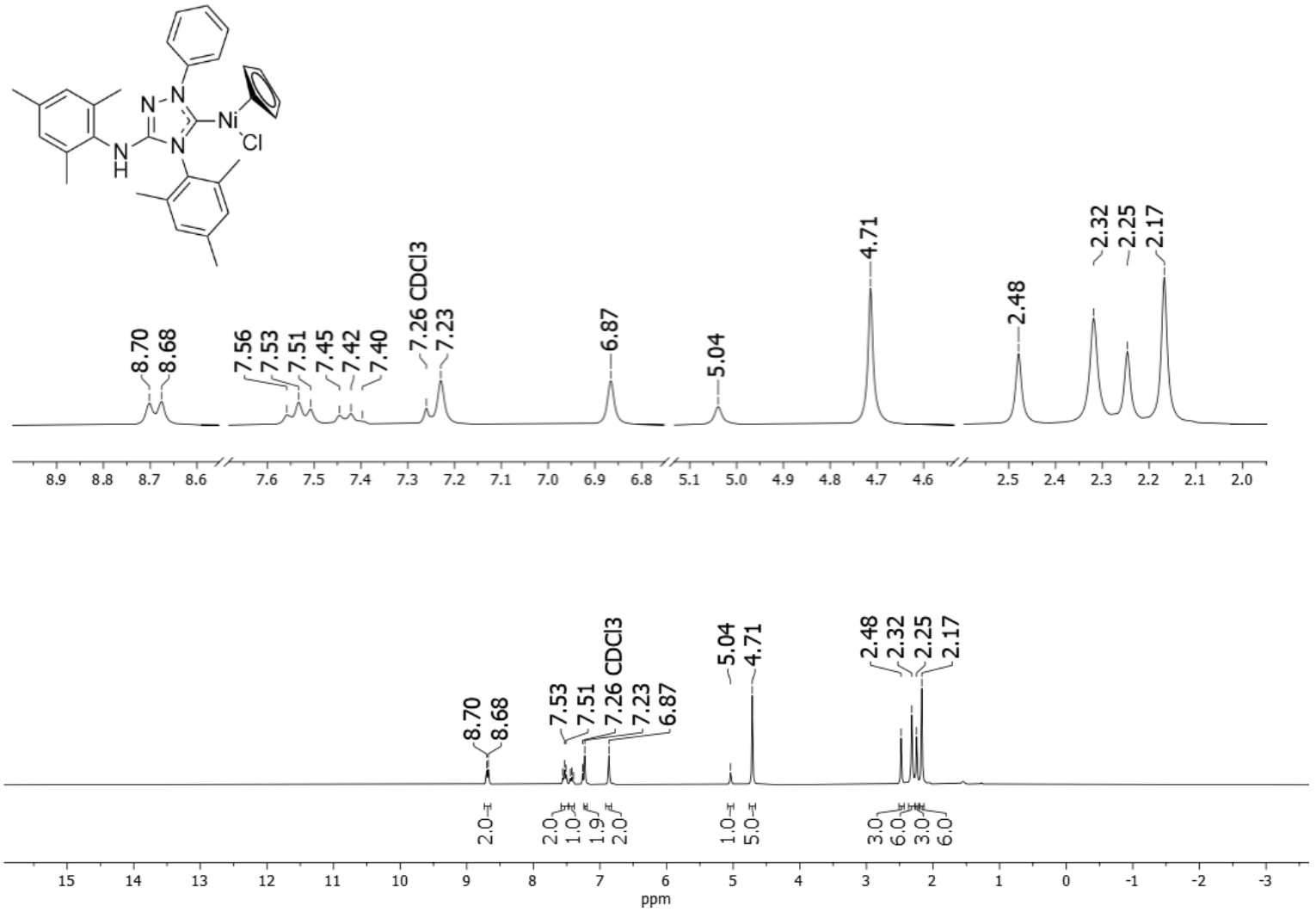


Figure S32. ^{1}H NMR spectrum of compound **6a** ($CDCl_3$, 300 MHz).

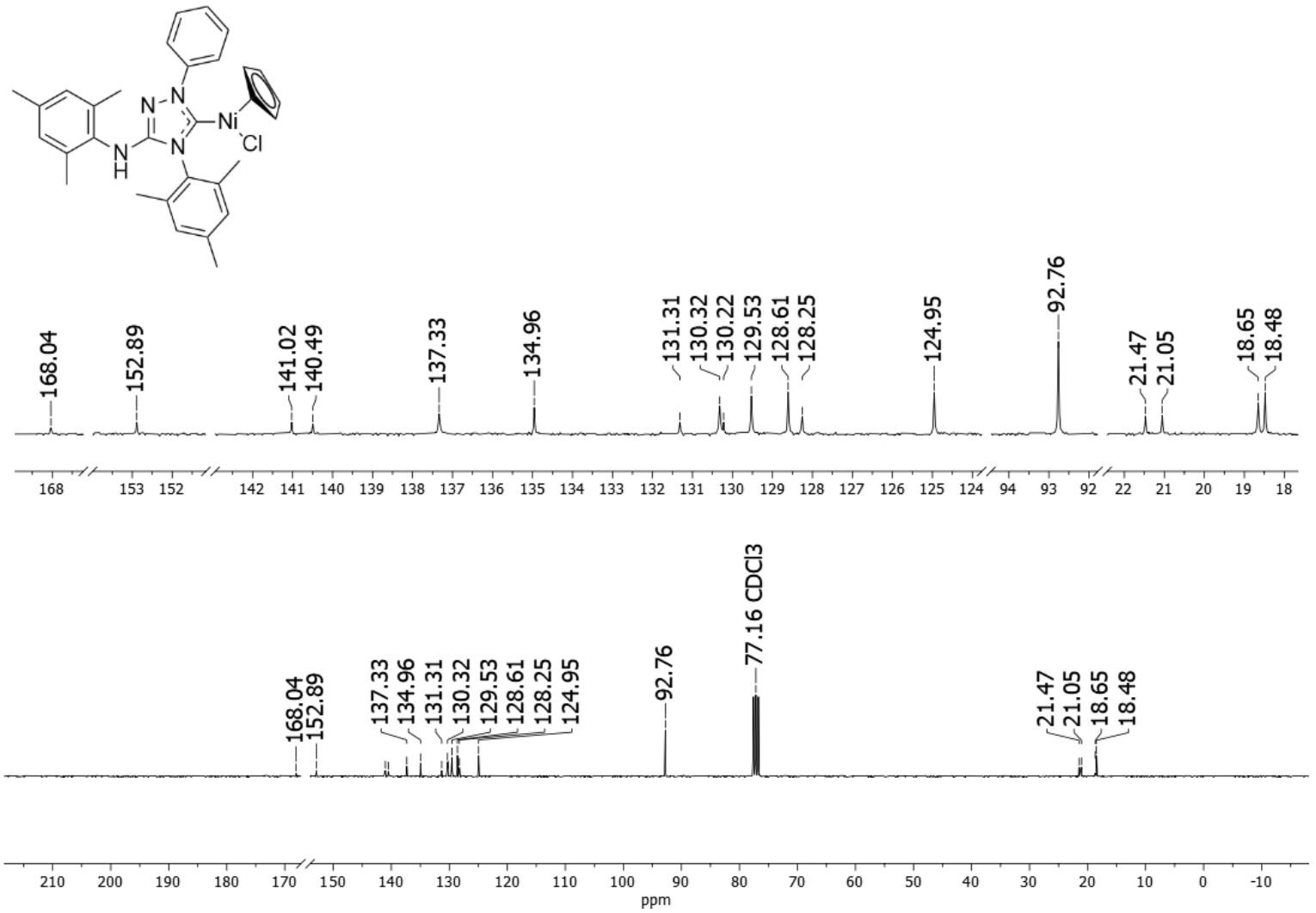


Figure S33. ^{13}C NMR spectrum of compound **6a** ($CDCl_3$, 75 MHz).

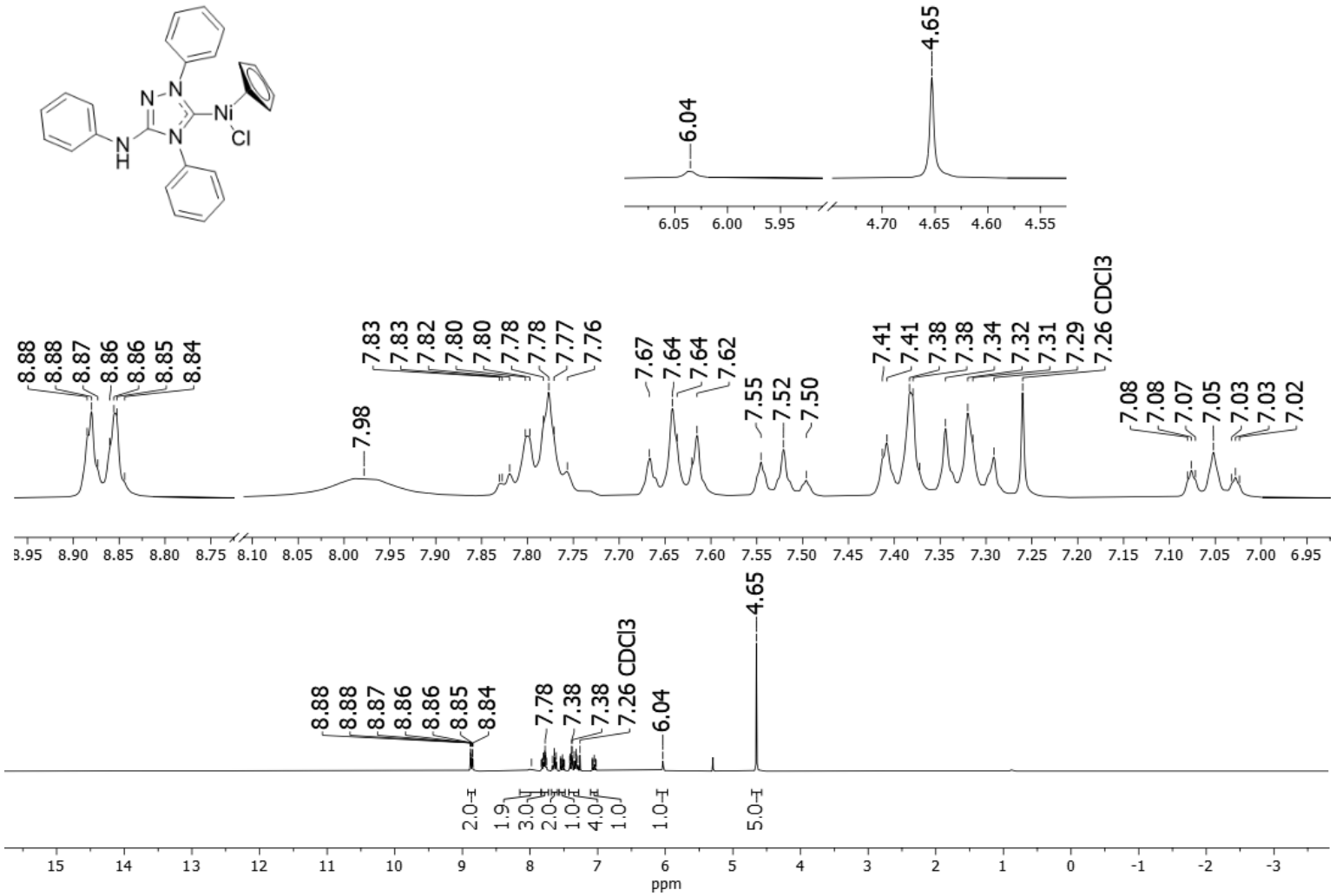


Figure S34. ^{1}H NMR spectrum of compound **6b** ($CDCl_3$, 300 MHz).

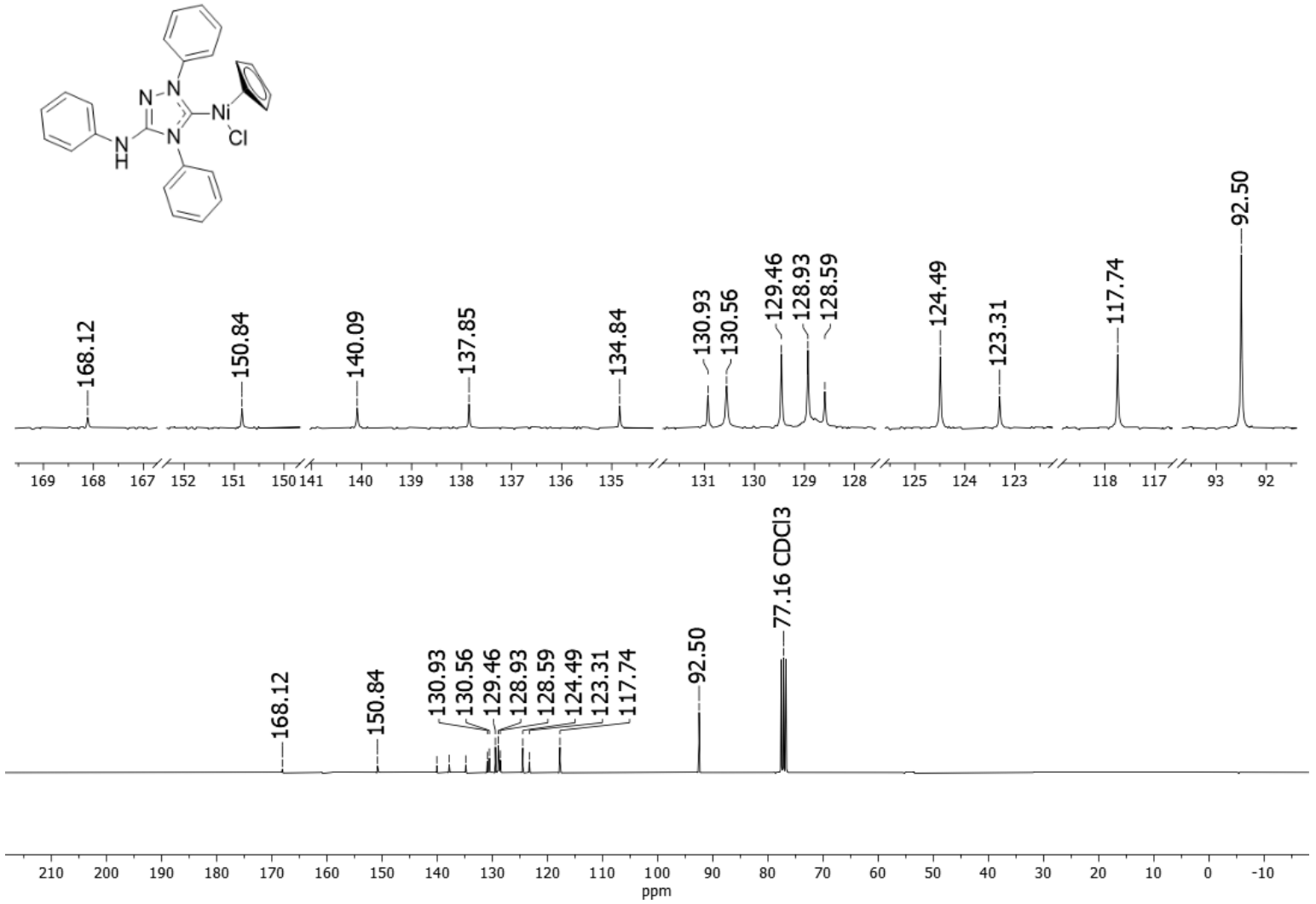


Figure S35. ^{13}C NMR spectrum of compound **6b** ($CDCl_3$, 75 MHz).

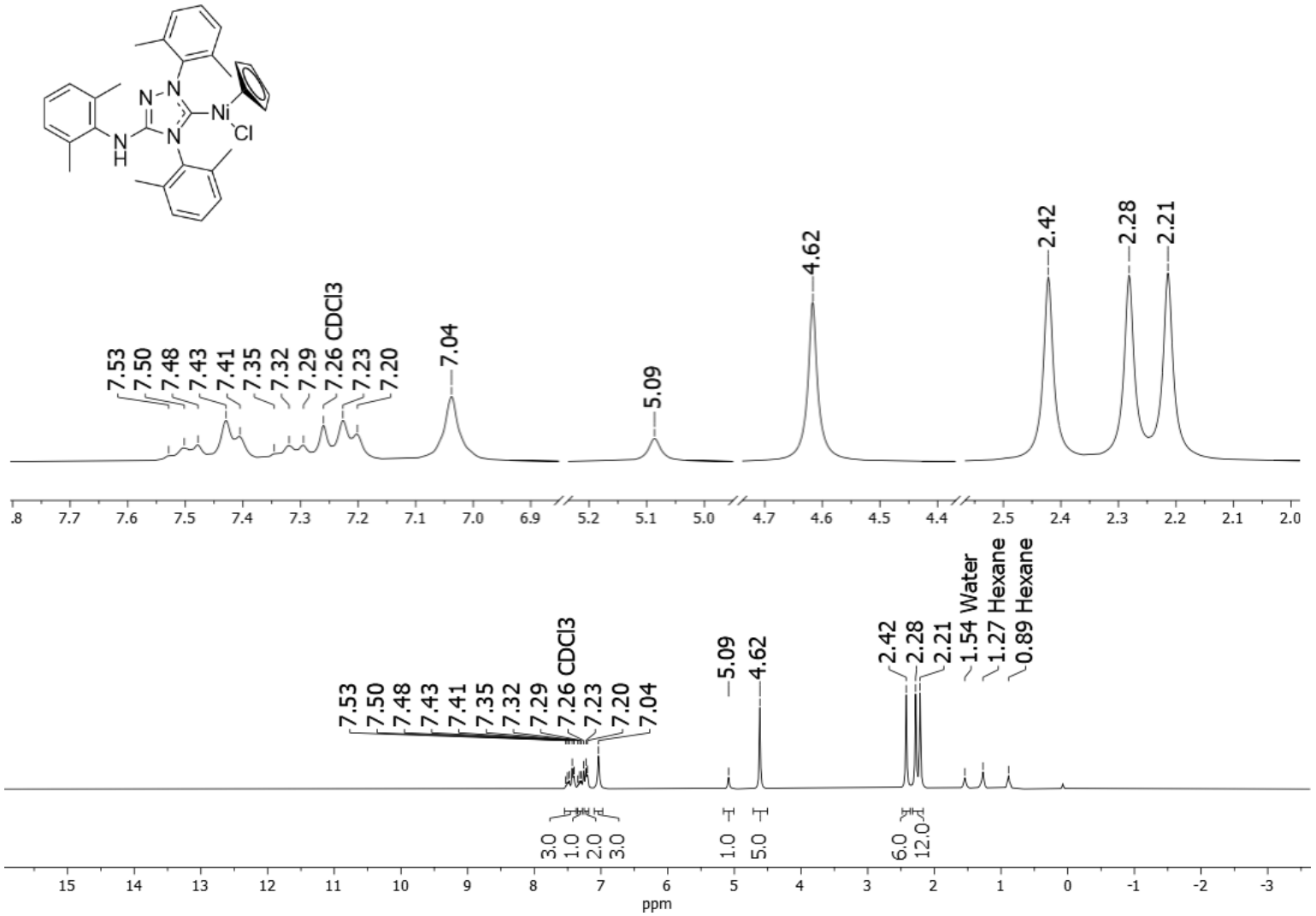


Figure S36. ^{1}H NMR spectrum of compound **6c** ($CDCl_3$, 300 MHz).

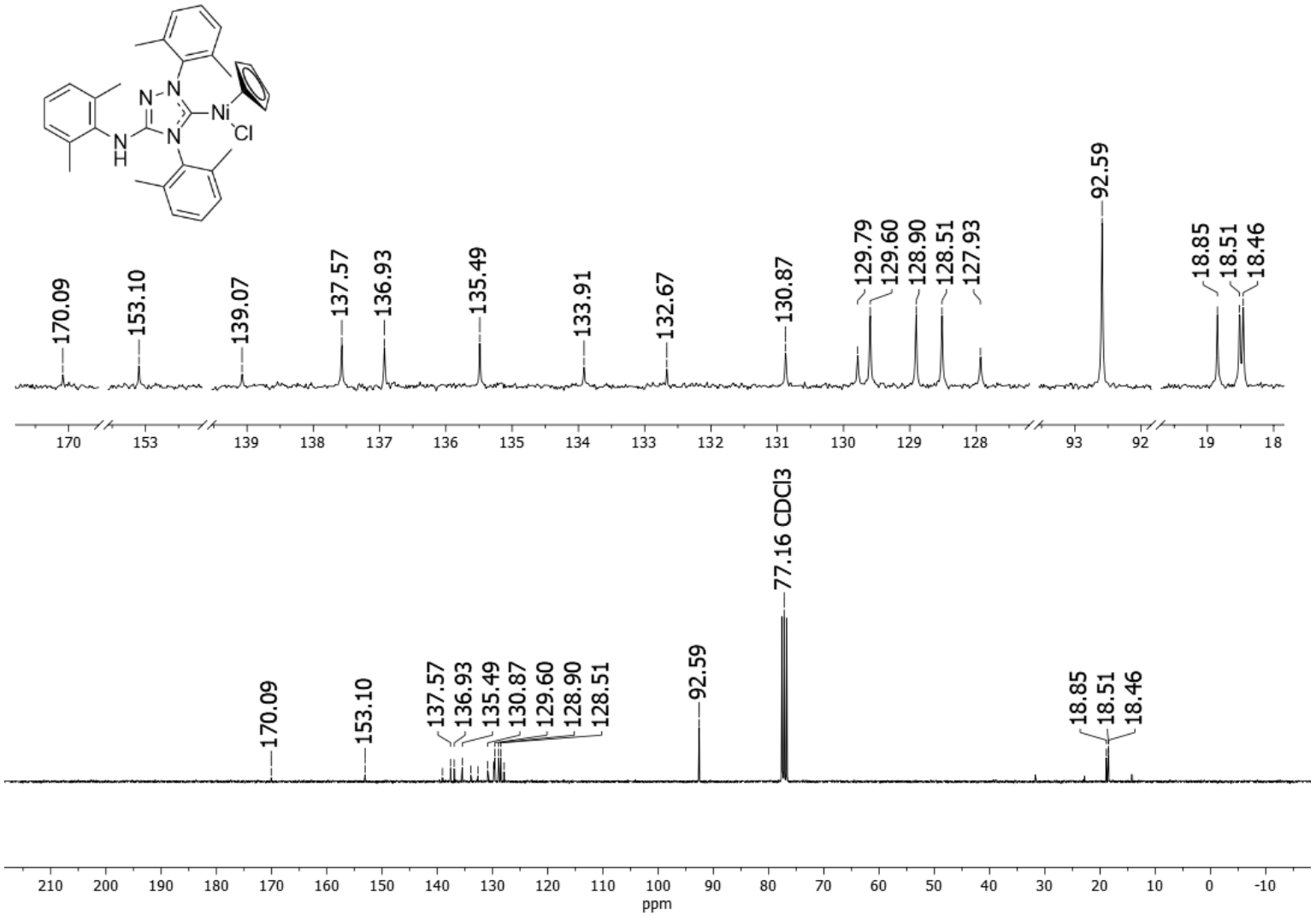


Figure S37. ^{13}C NMR spectrum of compound **6c** ($CDCl_3$, 75 MHz).

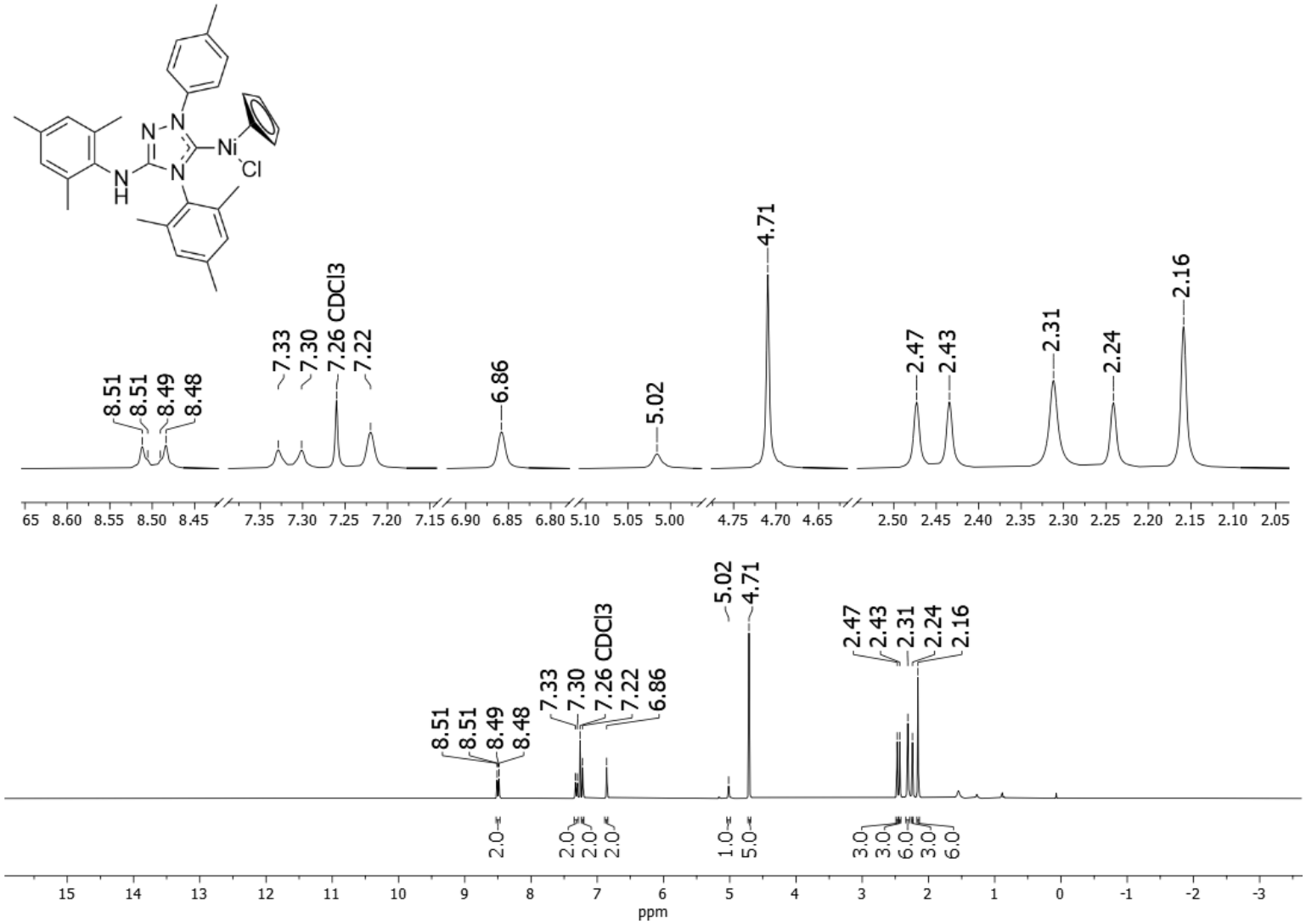


Figure S38. ^{1}H NMR spectrum of compound **6d** ($CDCl_3$, 300 MHz).

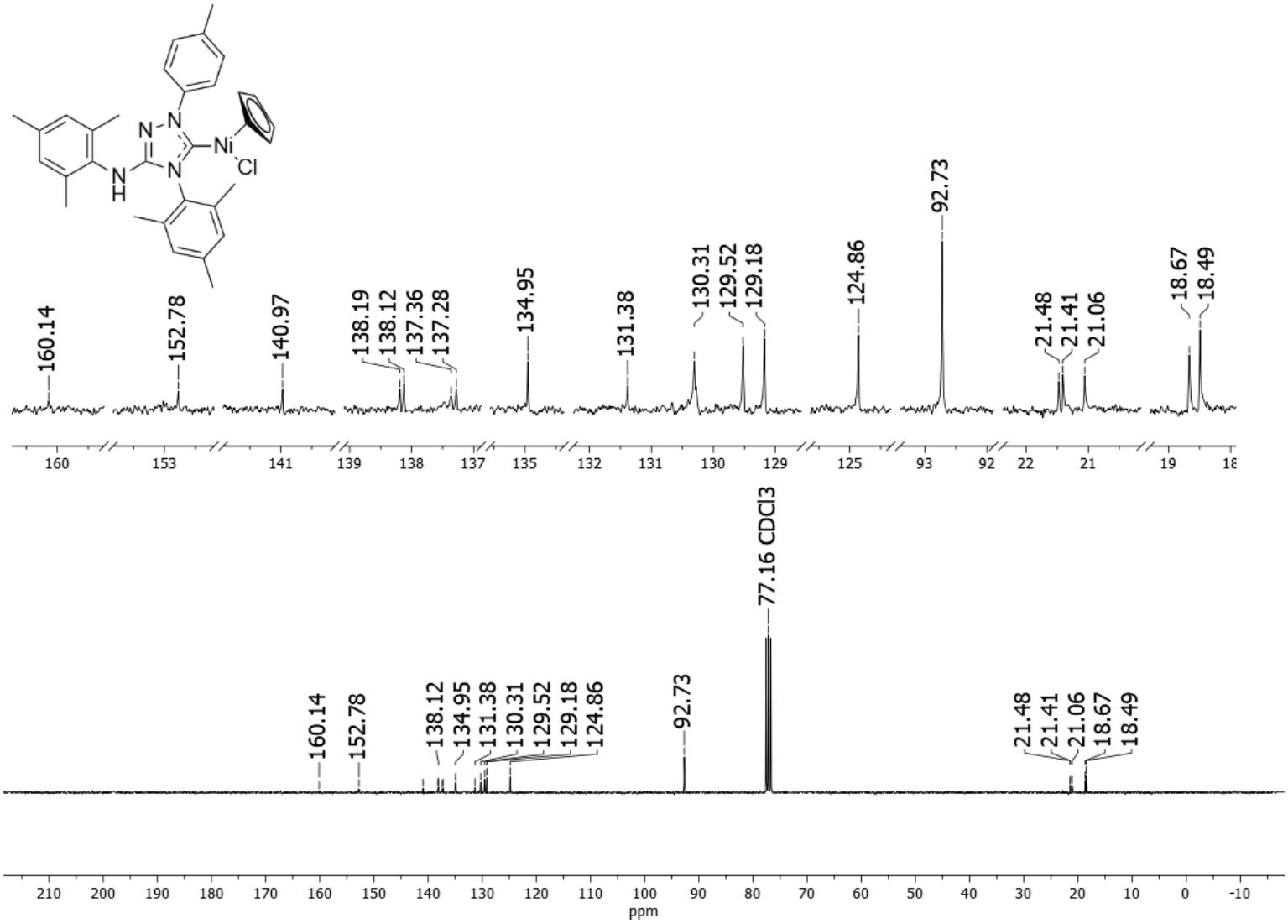


Figure S39. ^{13}C NMR spectrum of compound **6d** ($CDCl_3$, 75 MHz).

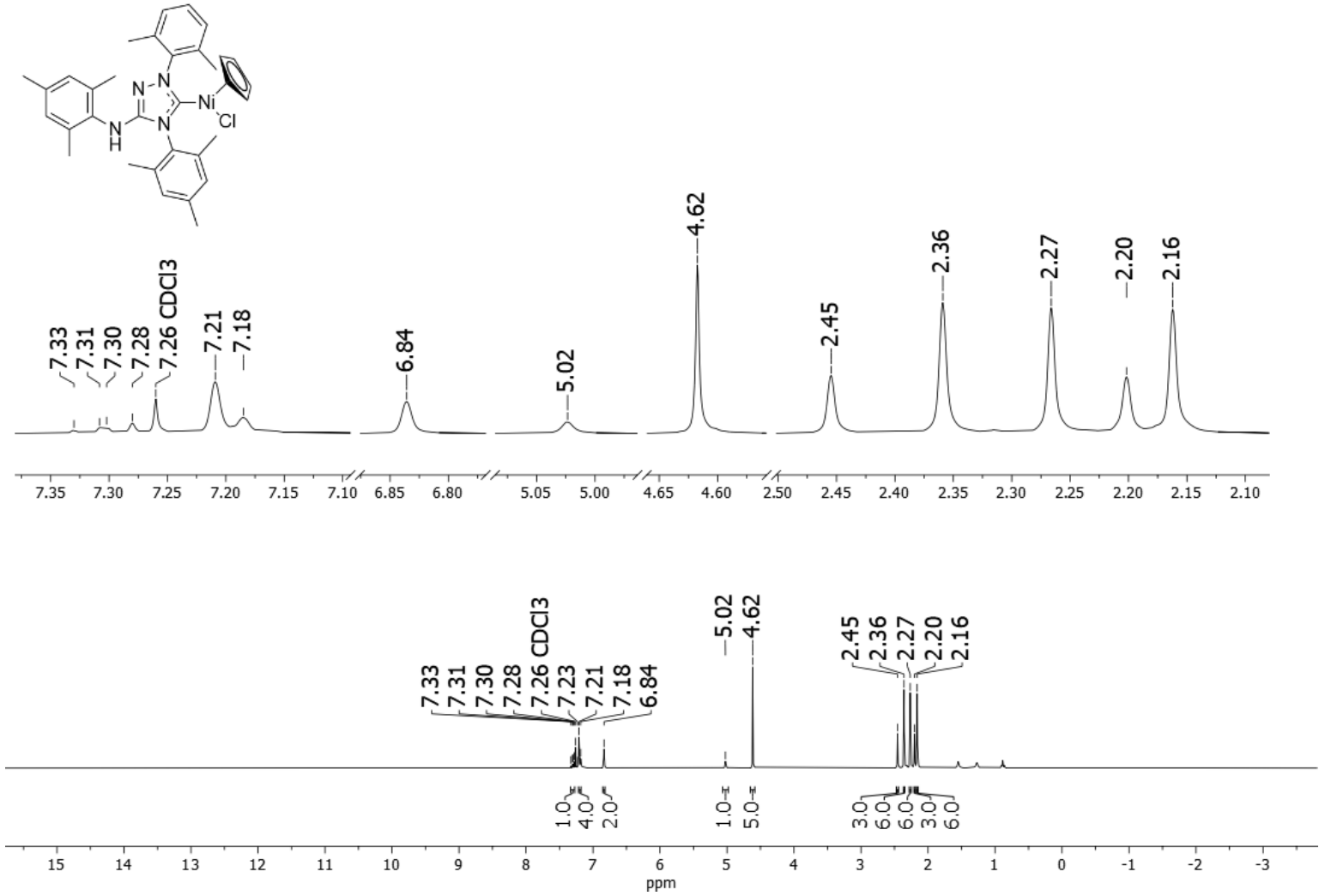


Figure S40. ^{1}H NMR spectrum of compound **6e** ($CDCl_3$, 300 MHz).

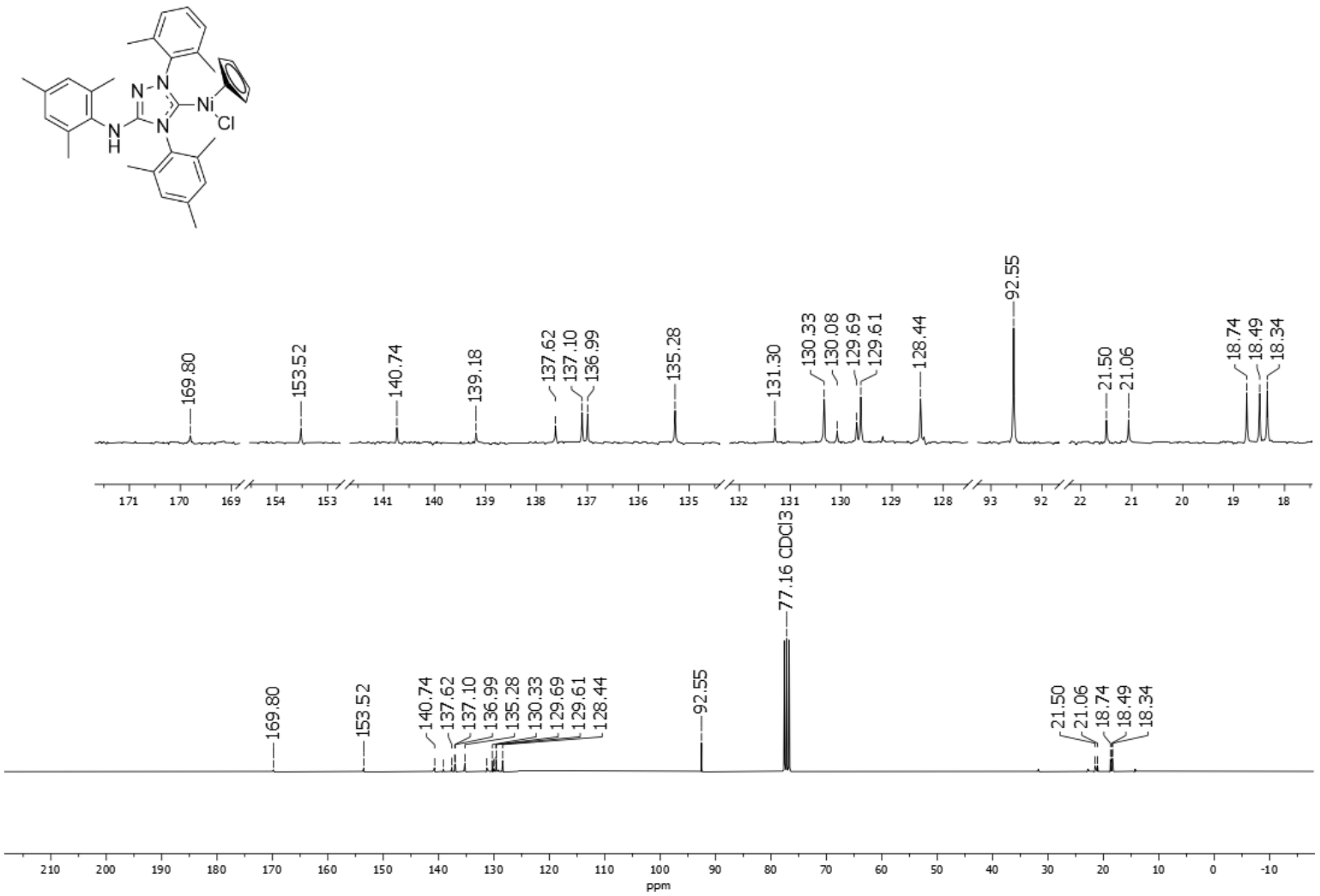


Figure S41. ^{13}C NMR spectrum of compound **6e** ($CDCl_3$, 75 MHz).

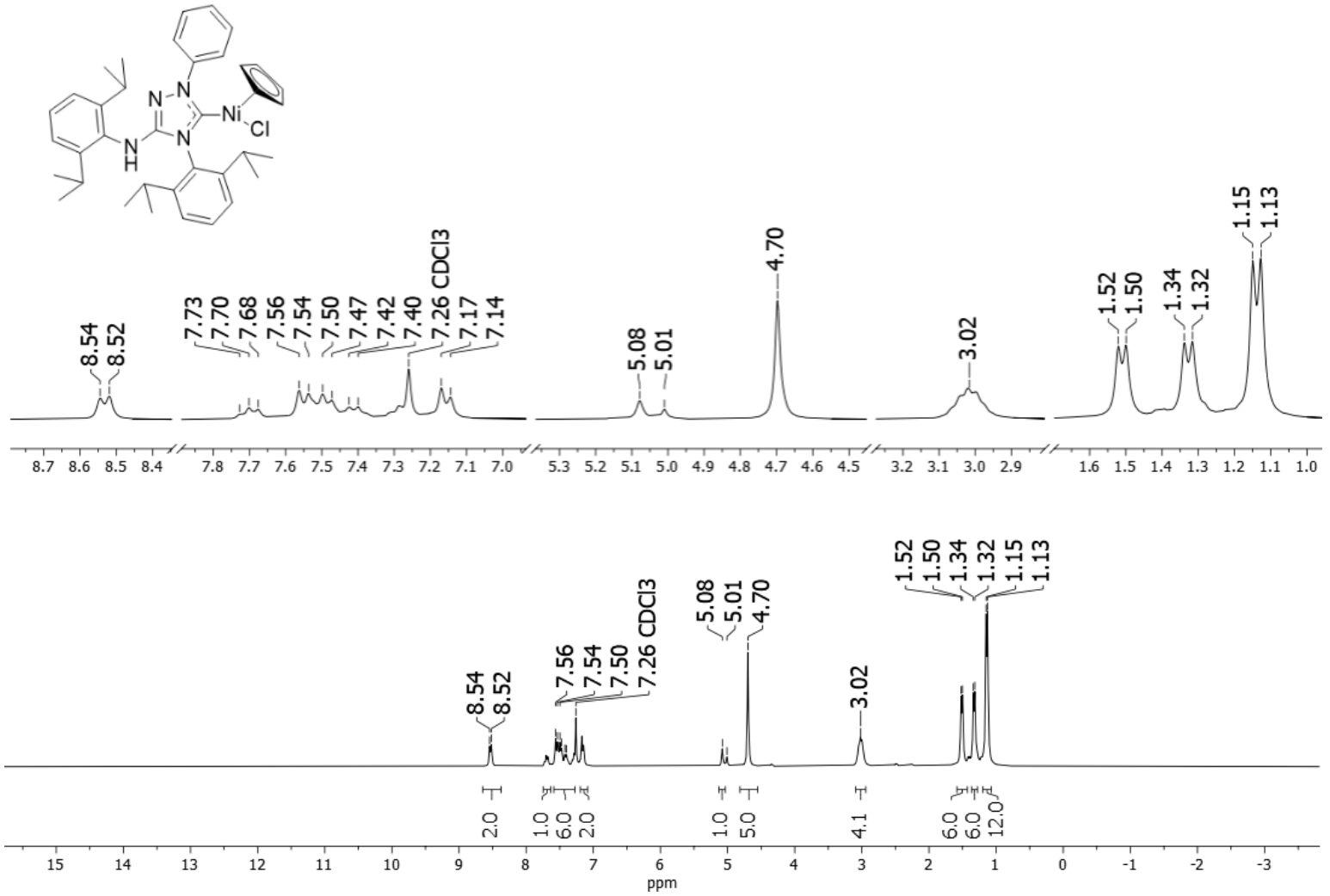


Figure S42. ^{1}H NMR spectrum of compound **6f** ($CDCl_3$, 300 MHz).

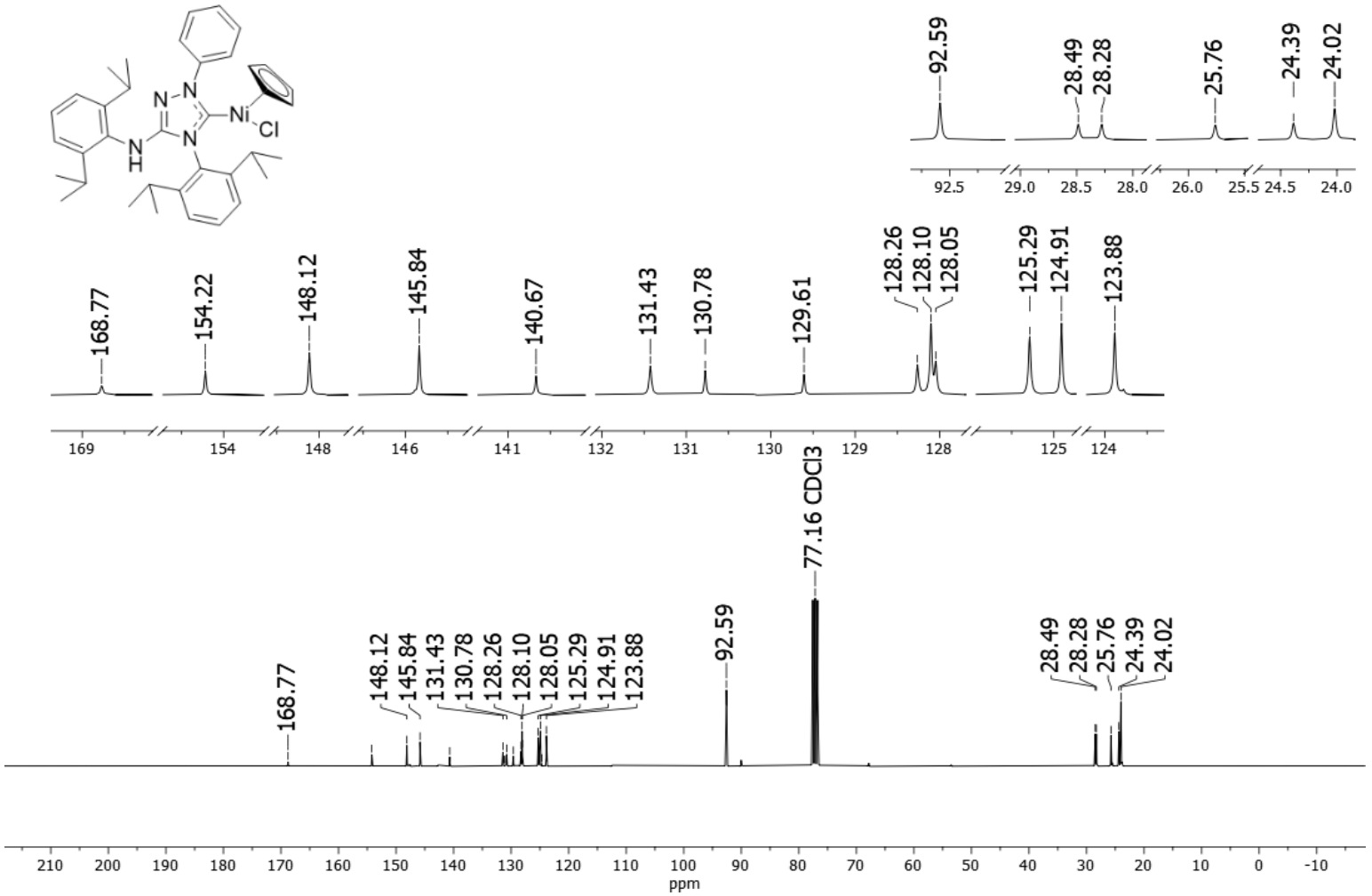


Figure S43. ^{13}C NMR spectrum of compound **6f** ($CDCl_3$, 75 MHz).

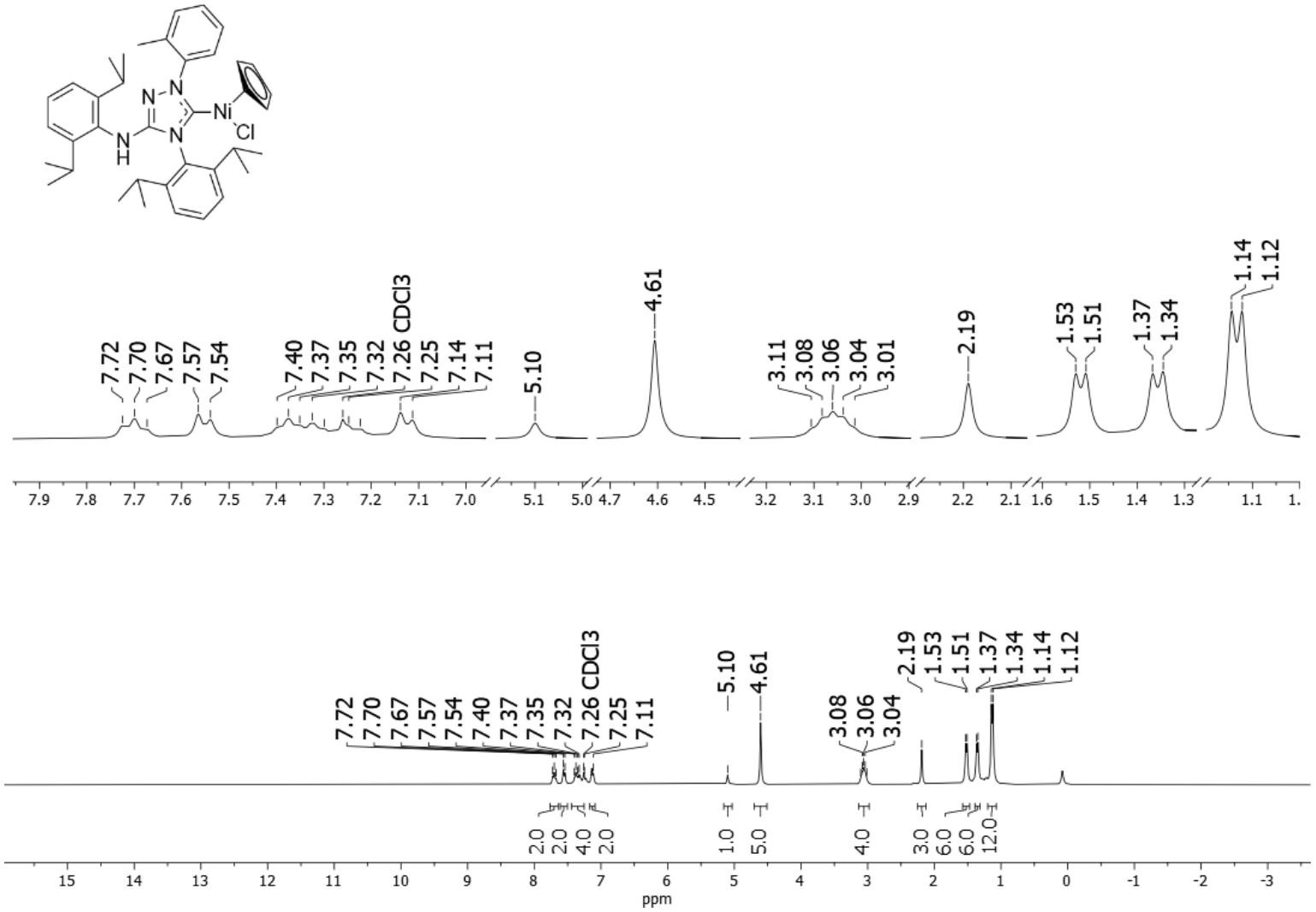


Figure S44. ^{1}H NMR spectrum of compound **6g** ($CDCl_3$, 300 MHz).

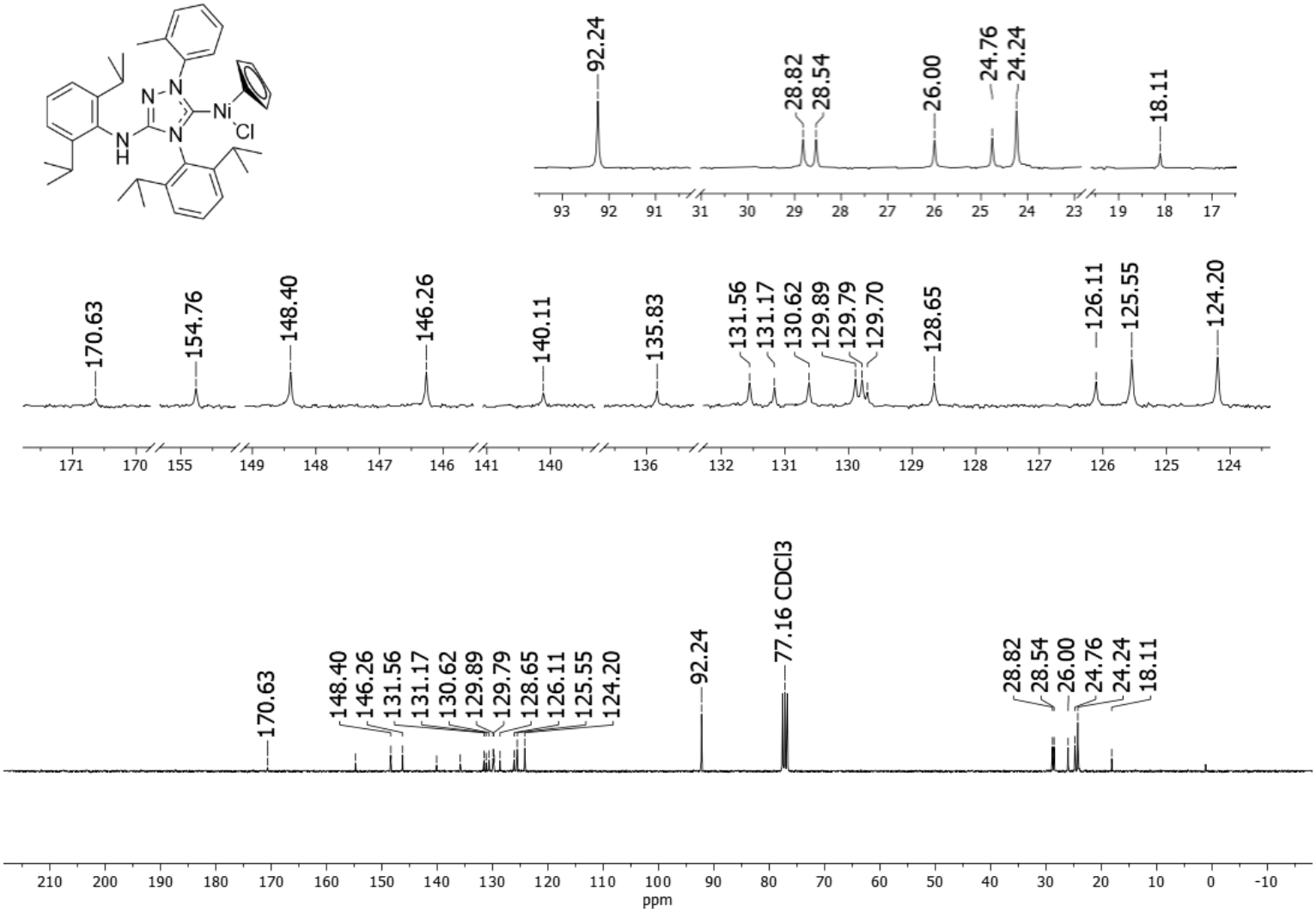


Figure S45. ^{13}C NMR spectrum of compound **6g** ($CDCl_3$, 75 MHz).

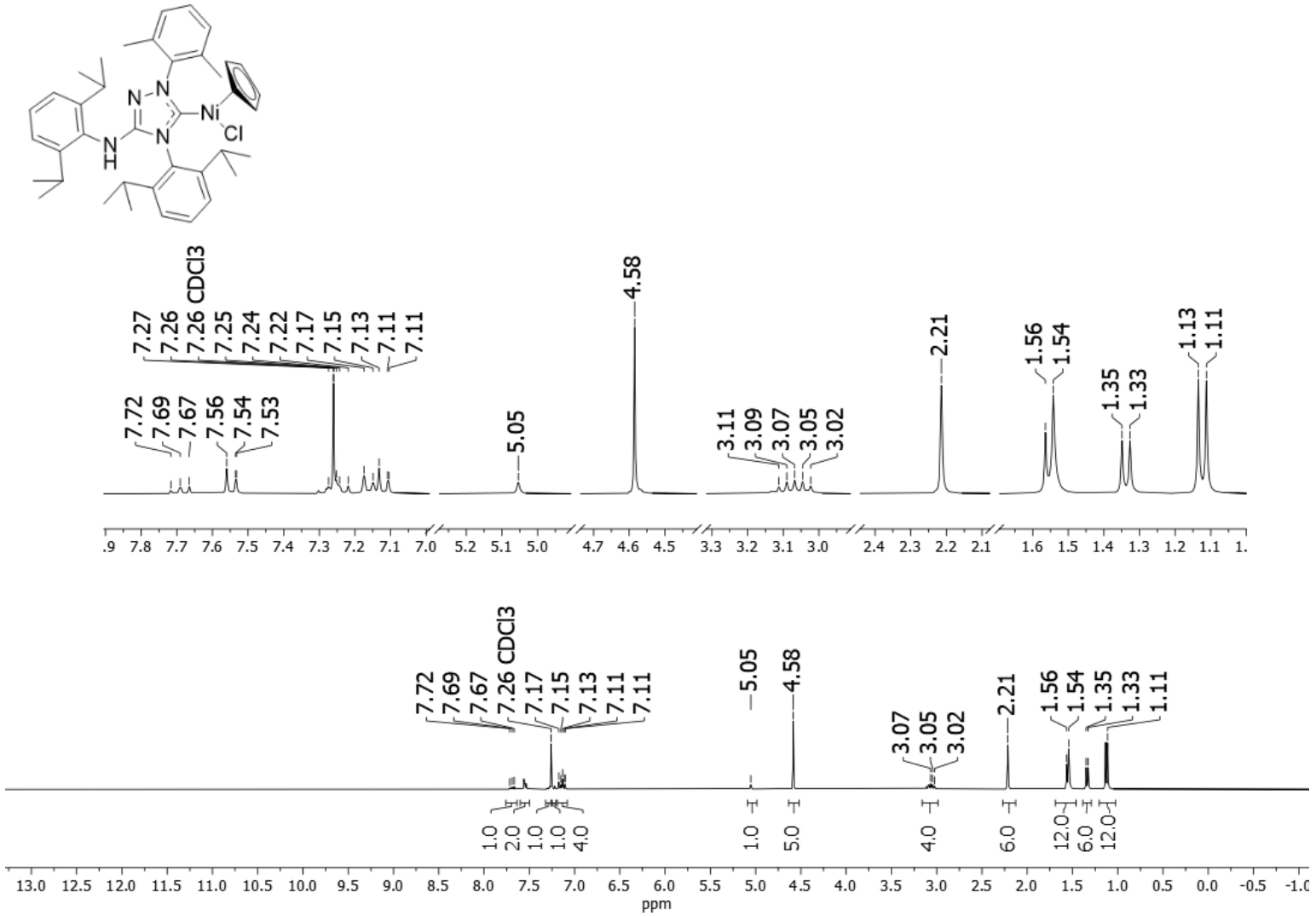


Figure S46. ^{1}H NMR spectrum of compound **6h** ($CDCl_3$, 300 MHz).

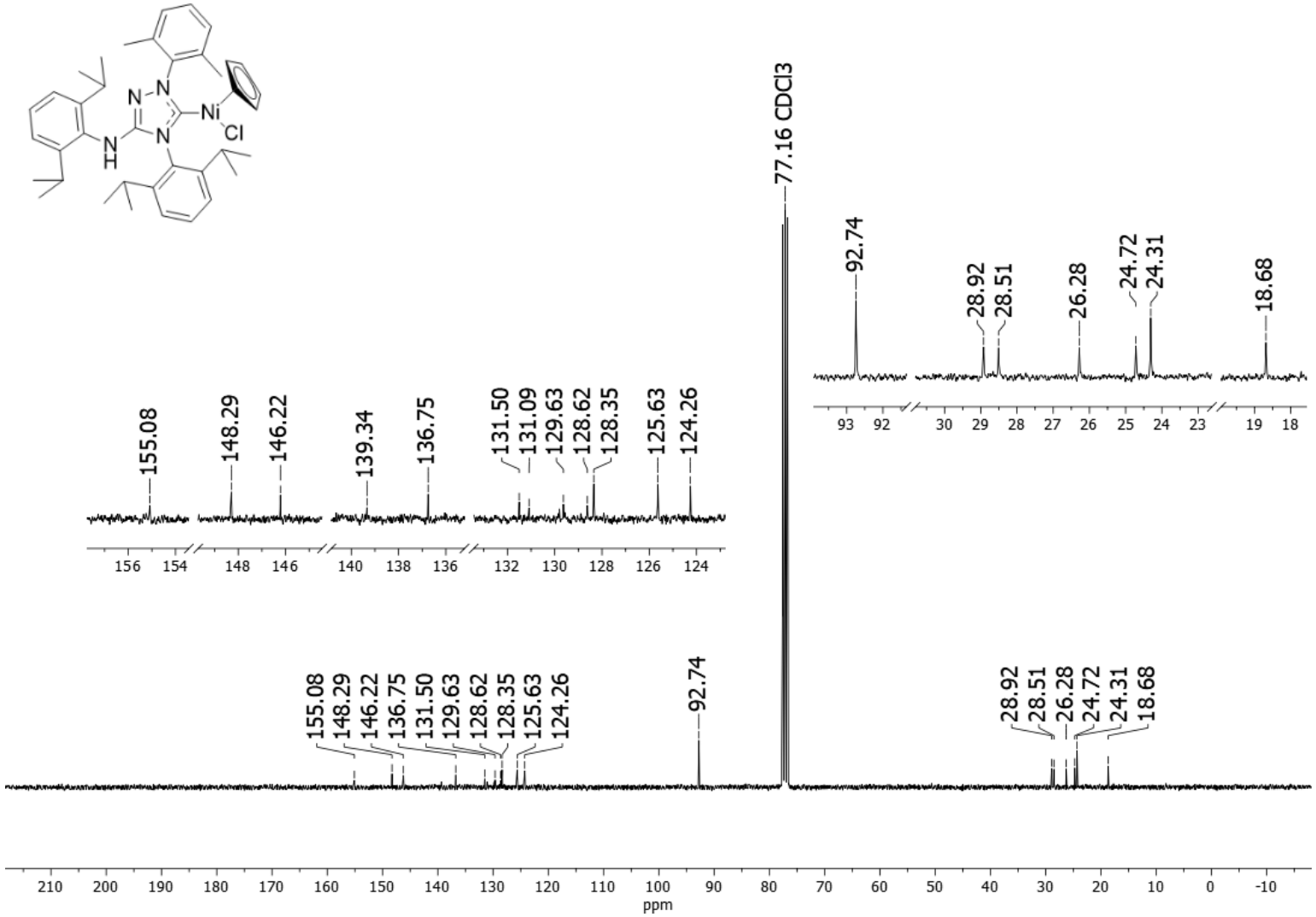


Figure S47. ^{13}C NMR spectrum of compound **6h** ($CDCl_3$, 75 MHz).

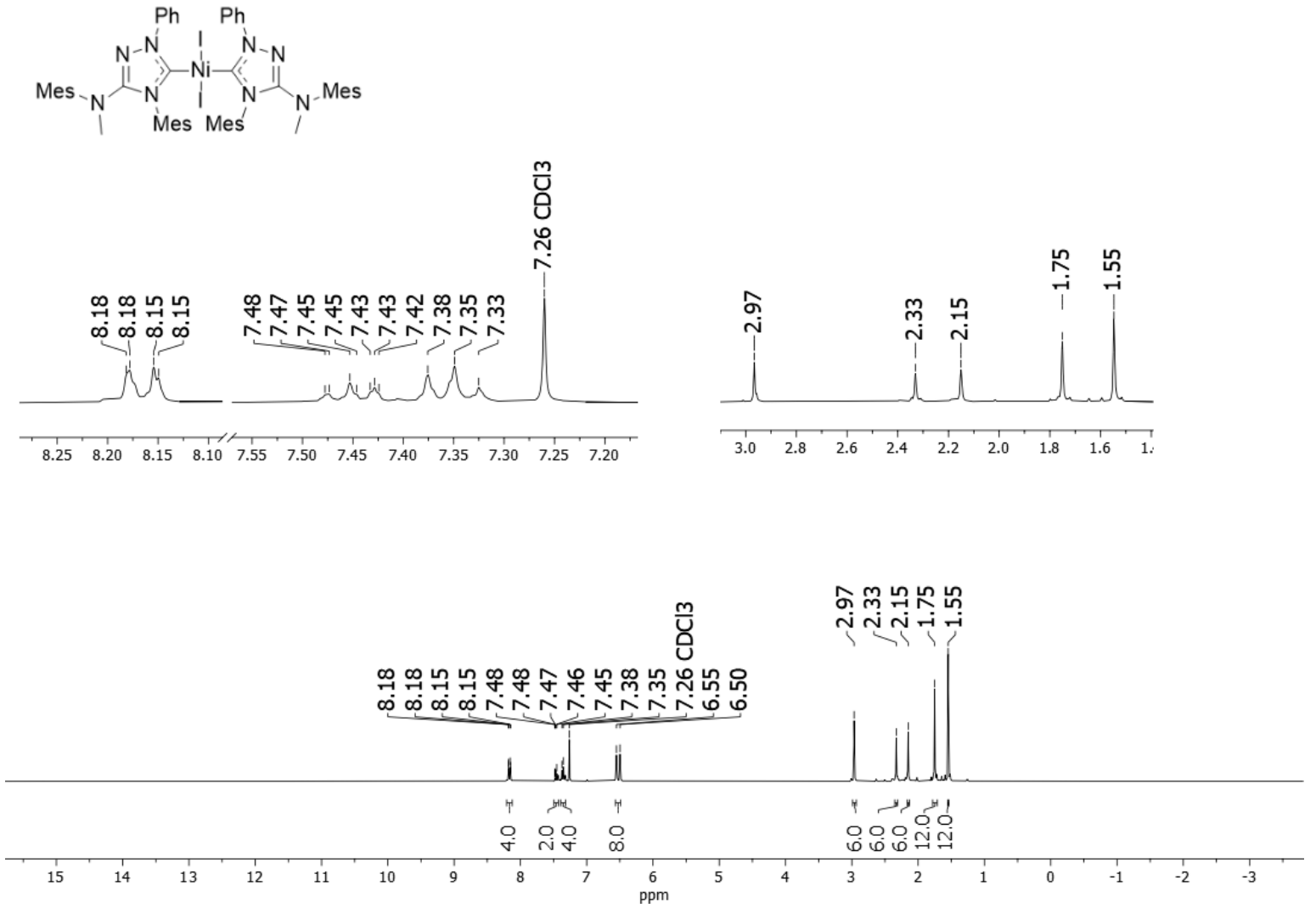


Figure S48. ^{1}H NMR spectrum of compound **7a** ($CDCl_3$, 300 MHz).

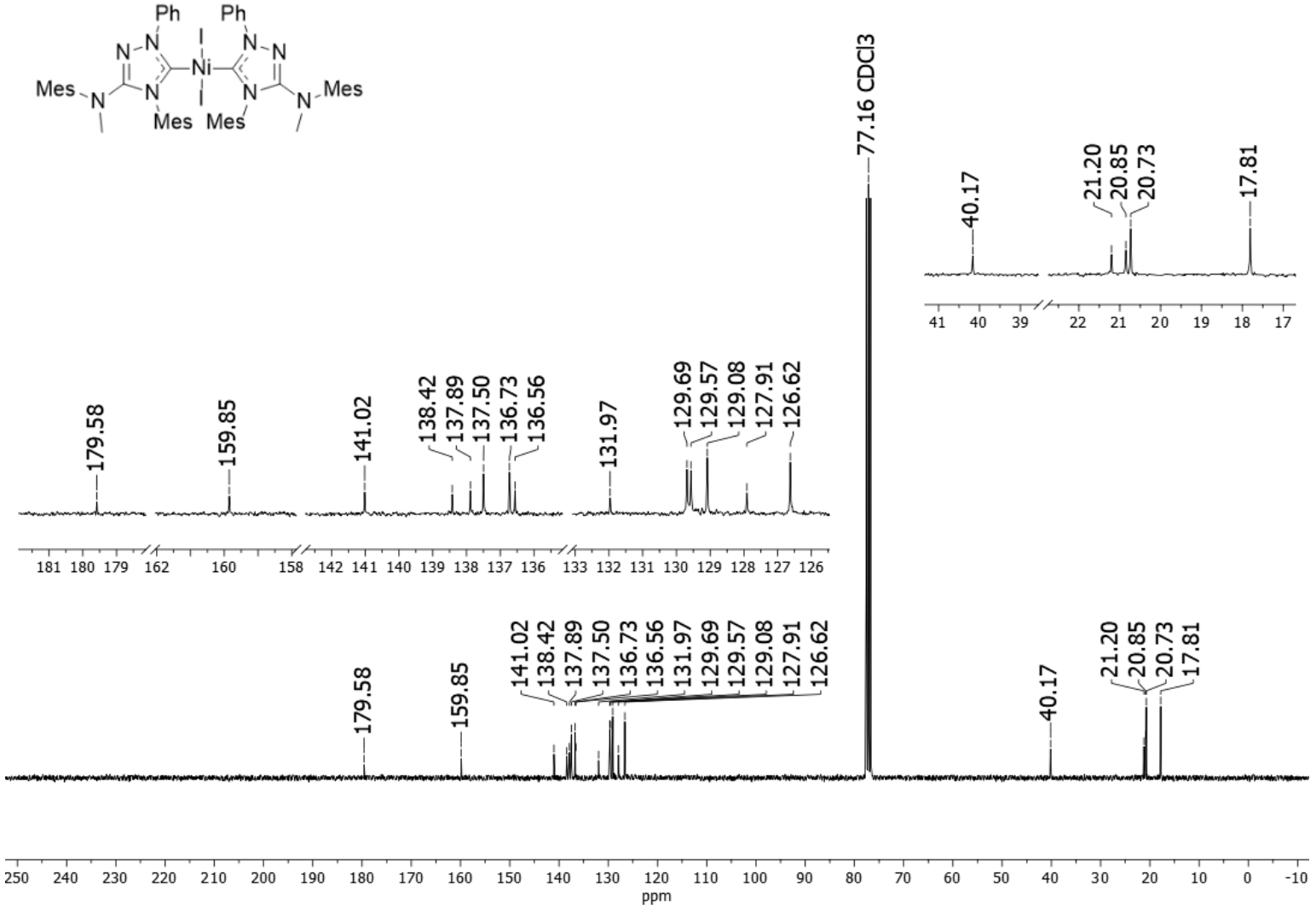


Figure S49. ^{13}C NMR spectrum of compound **7a** ($CDCl_3$, 75 MHz).

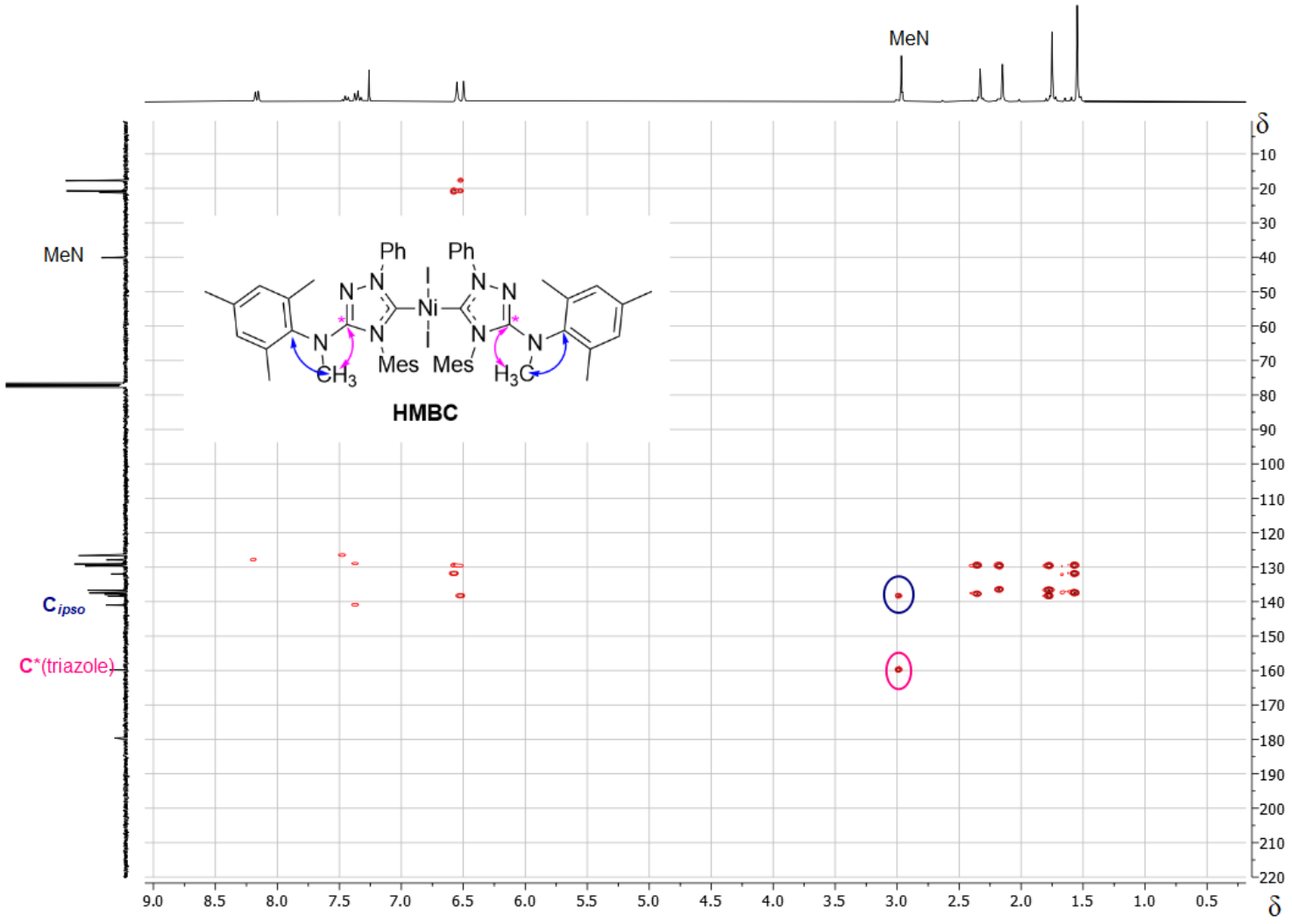


Figure S50. Fragment of ^{1}H-^{13}C-HMBC spectrum of compound **7a** ($CDCl_3$, δ, ppm).

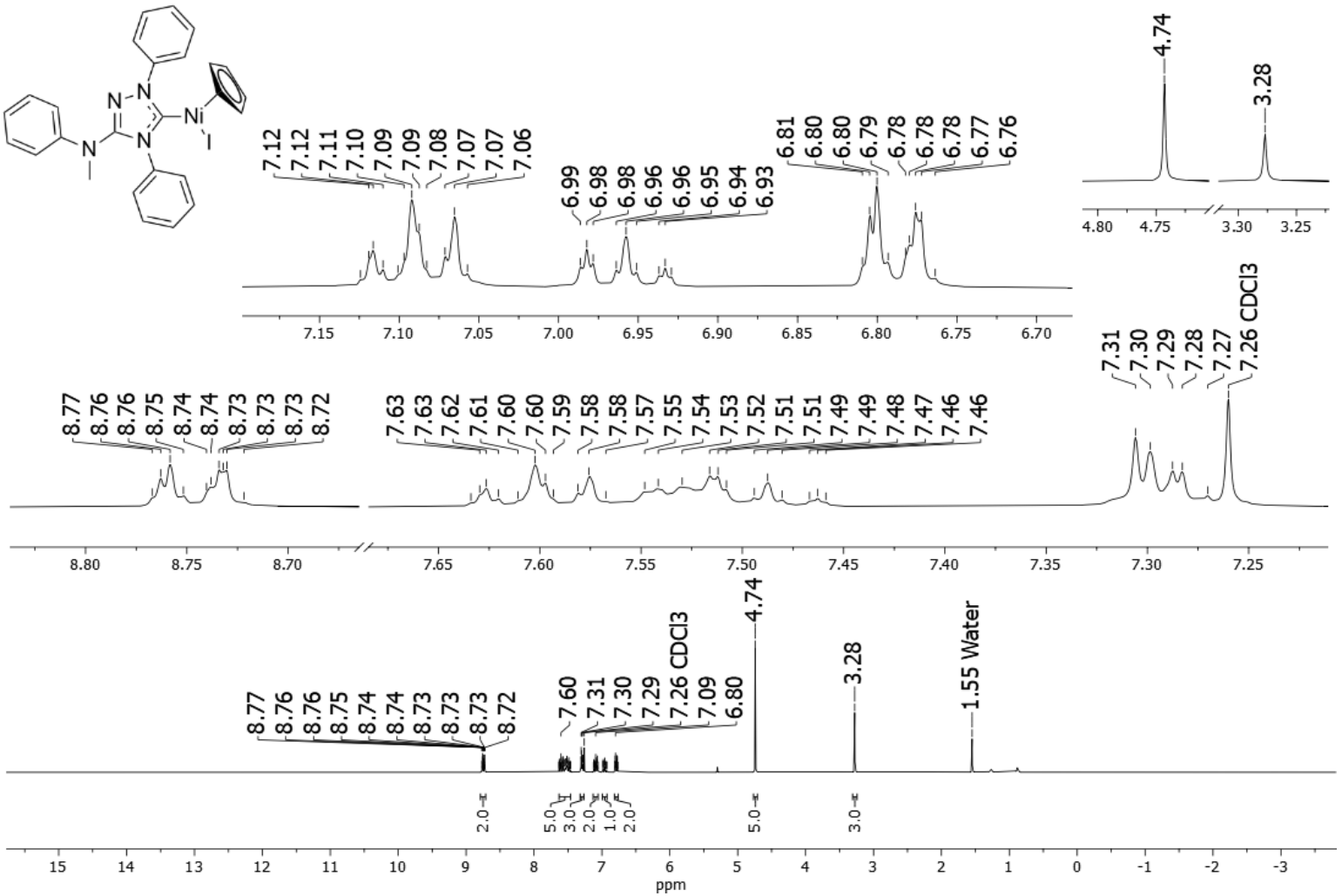


Figure S51. ^{1}H NMR spectrum of compound **7b** ($CDCl_3$, 300 MHz).

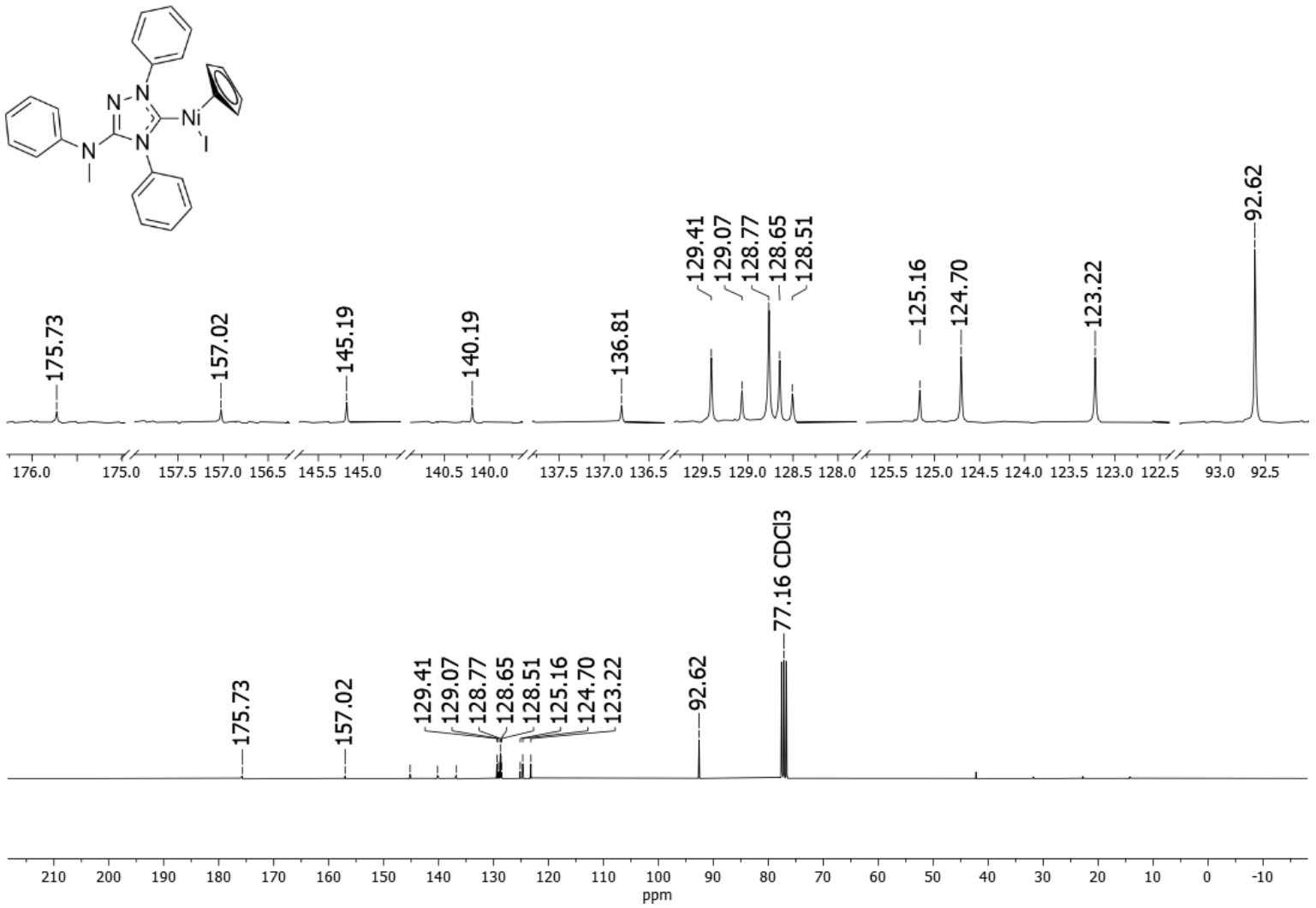


Figure S52. ^{13}C NMR spectrum of compound **7b** ($CDCl_3$, 75 MHz).

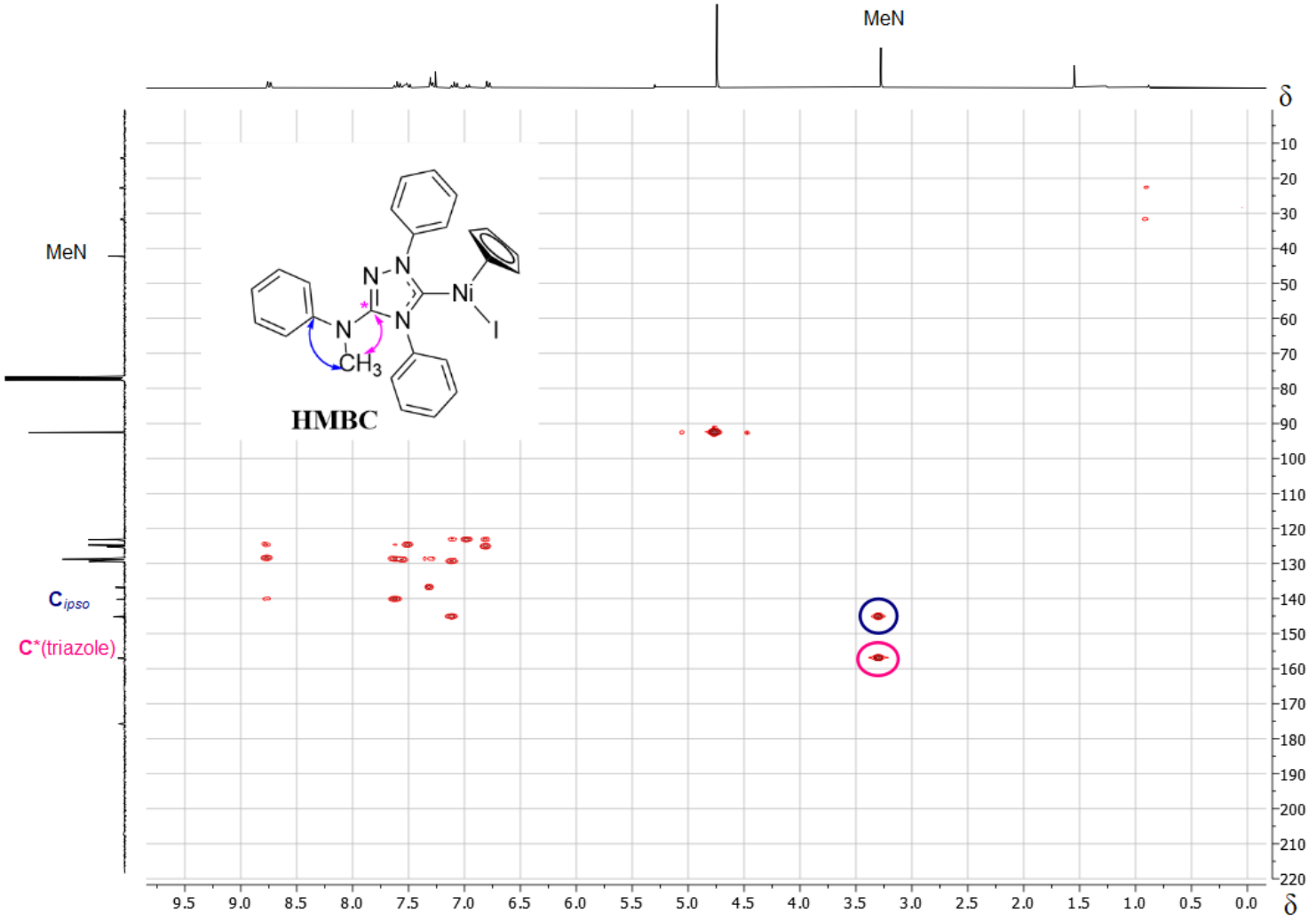


Figure S53. Fragment of ^{1}H-^{13}C-HMBC spectrum of compound **7b** ($CDCl_3$, δ, ppm).

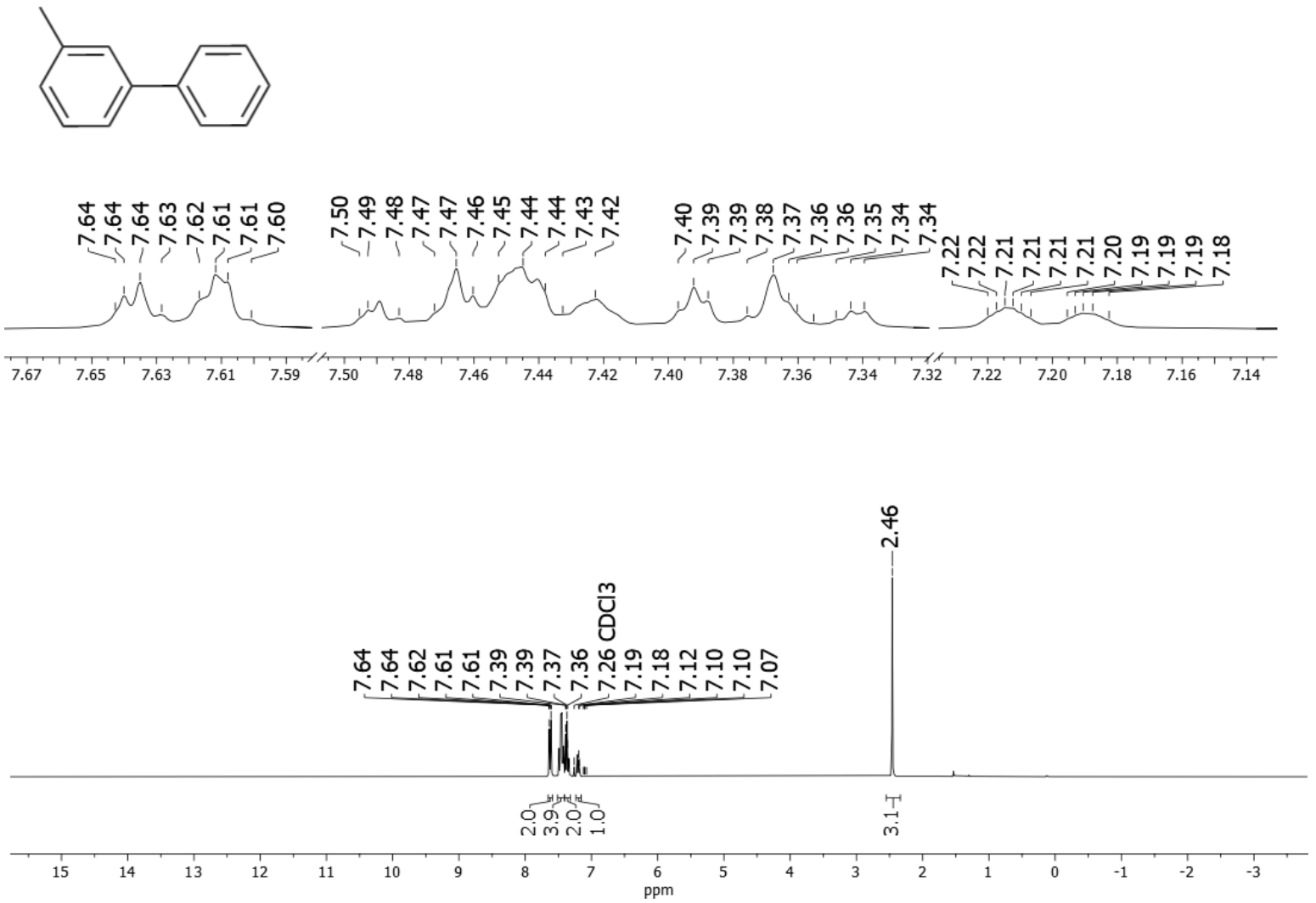


Figure S54. ^{1}H NMR spectrum of compound **10a** ($CDCl_3$, 300 MHz).

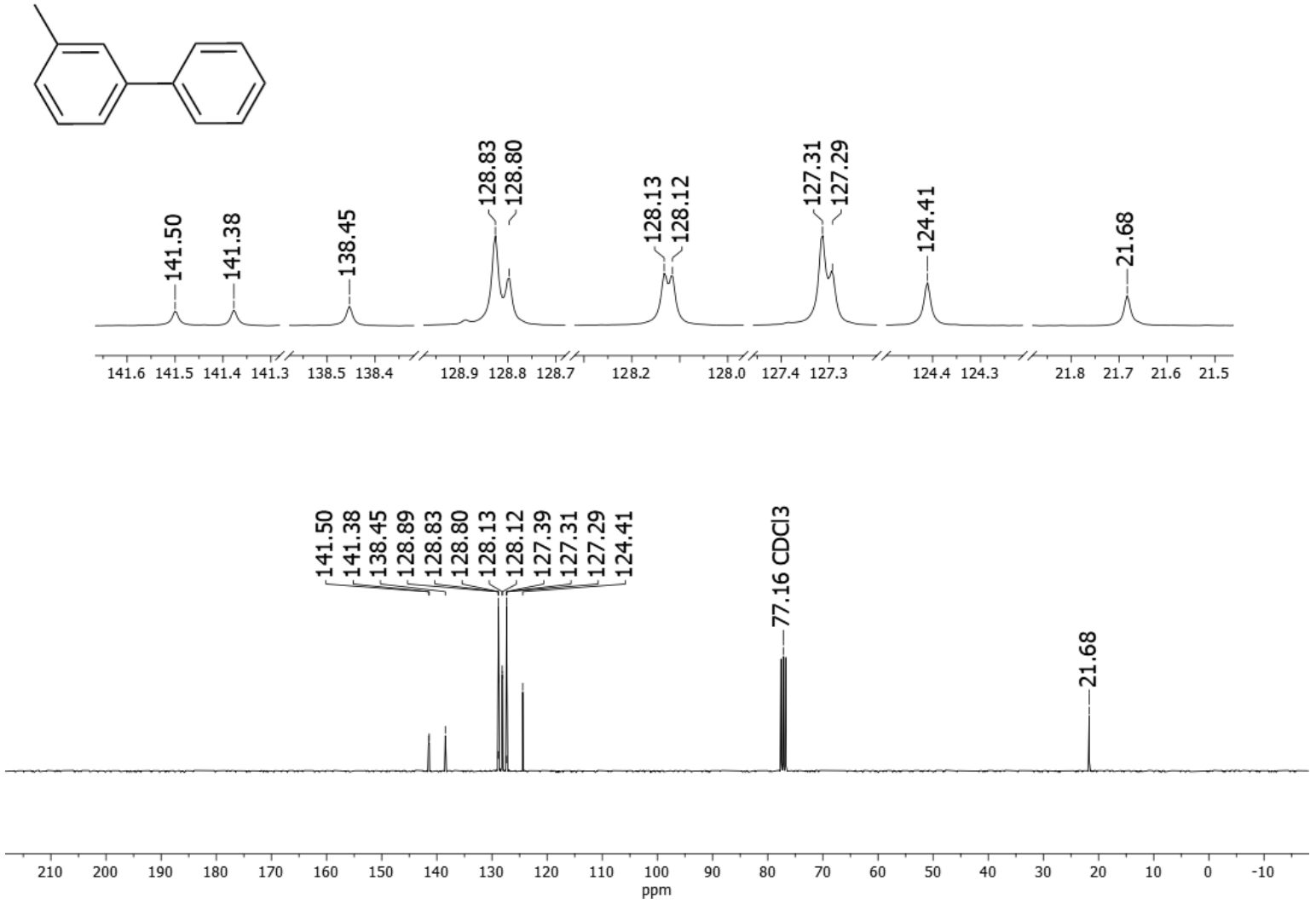


Figure S55. ^{13}C NMR spectrum of compound **10a** ($CDCl_3$, 75 MHz).

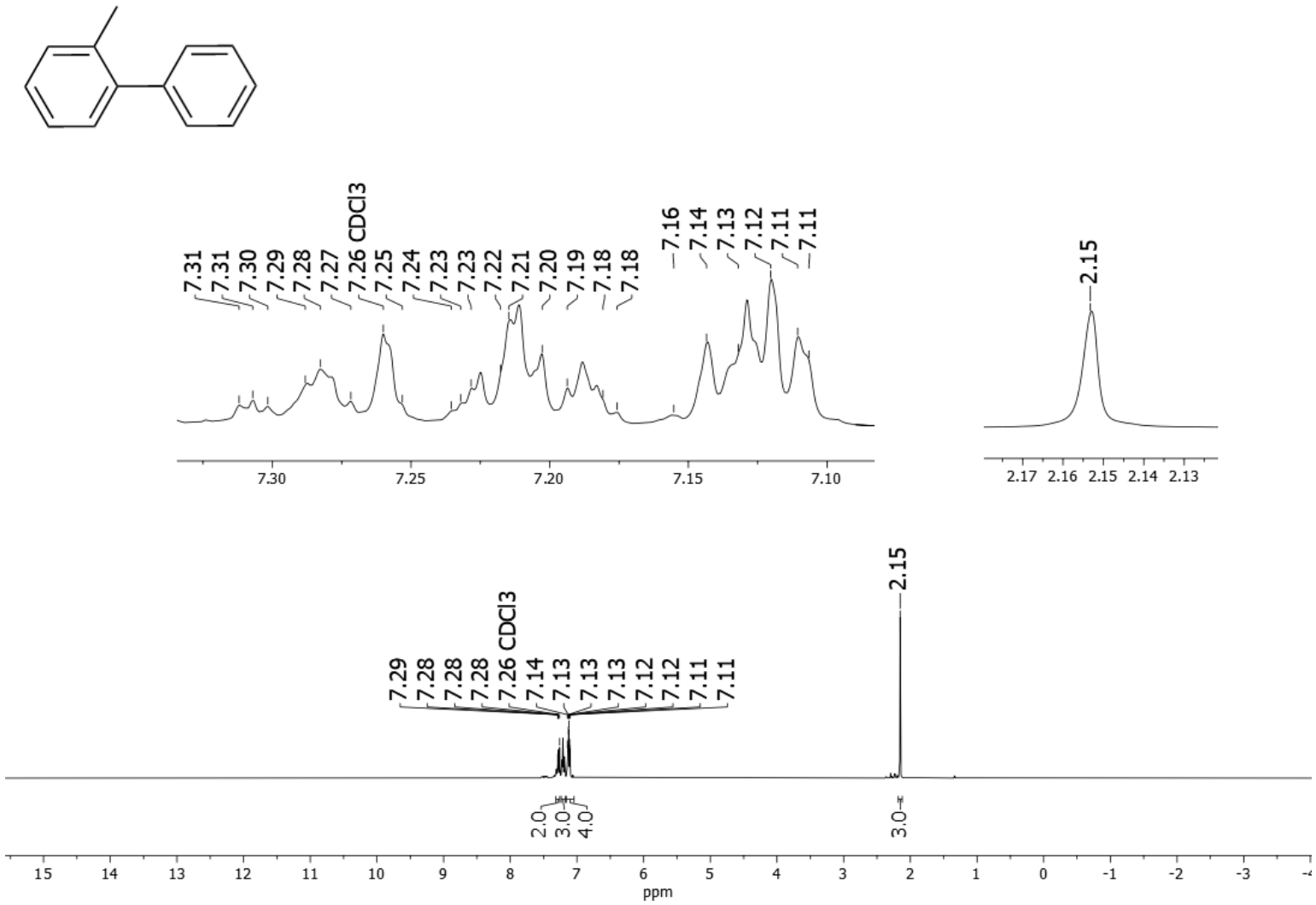


Figure S56. ^{1}H NMR spectrum of compound **10b** ($CDCl_3$, 300 MHz).

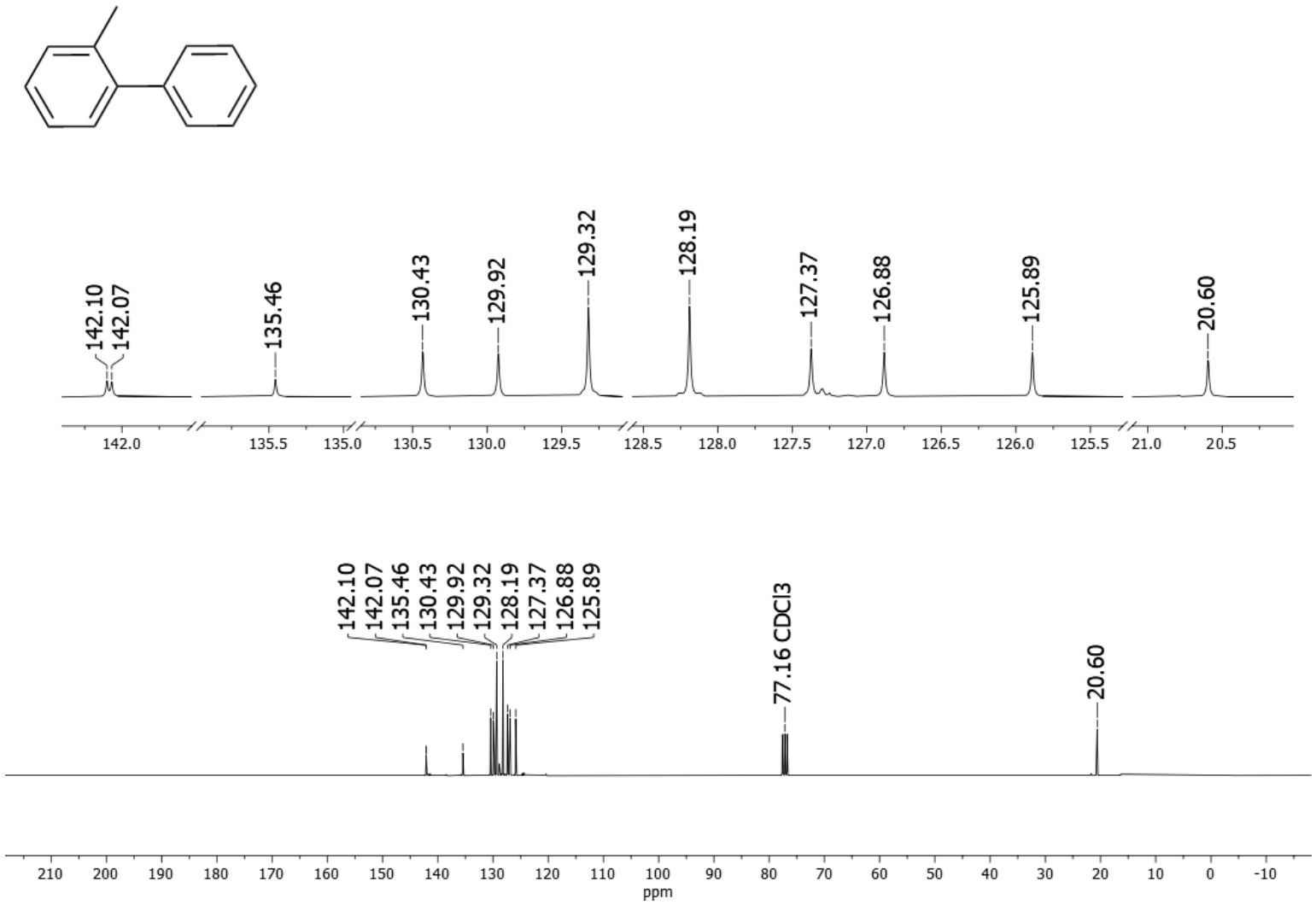


Figure S57. ^{13}C NMR spectrum of compound **10b** ($CDCl_3$, 75 MHz).

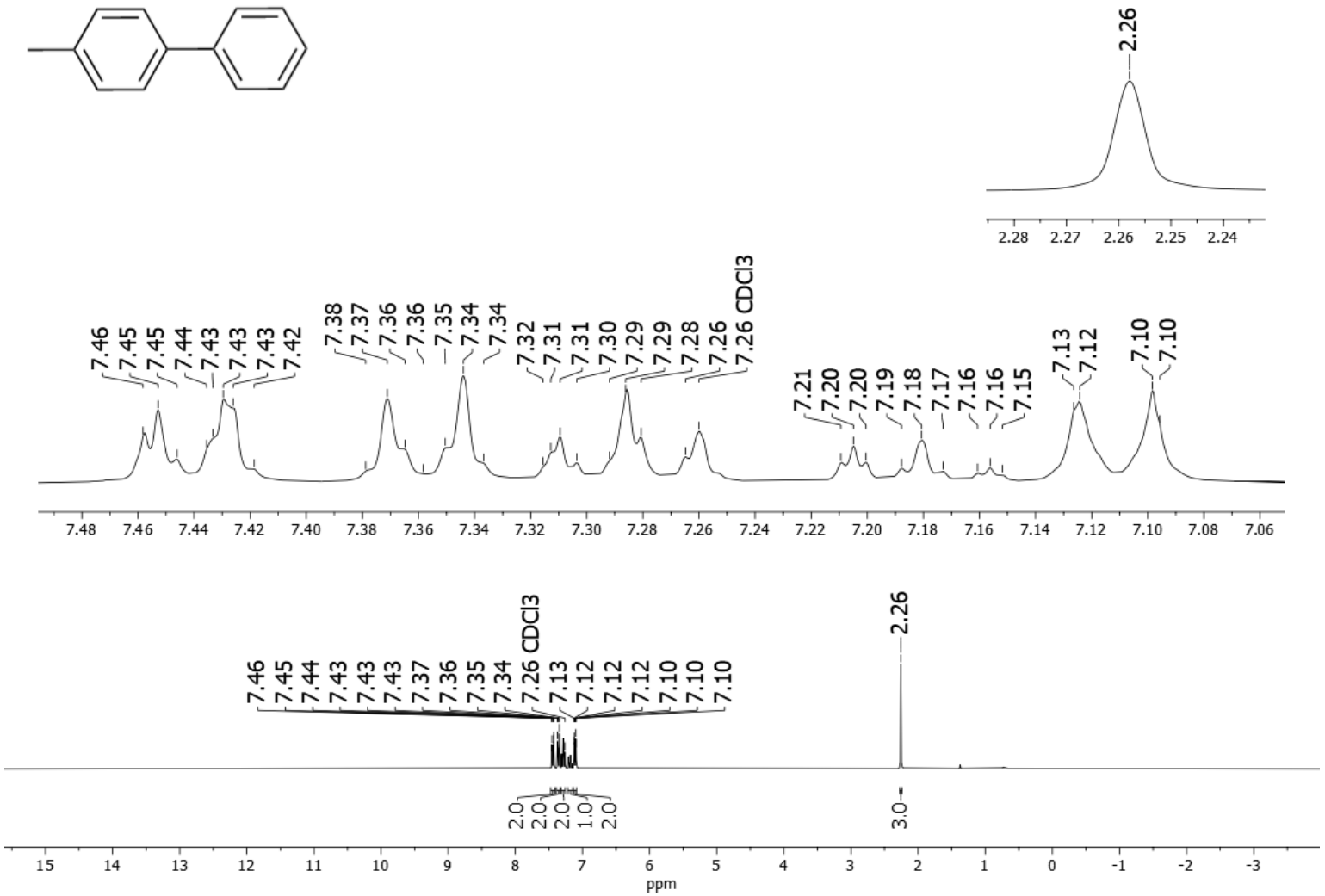


Figure S58. ^{1}H NMR spectrum of compound **10c** ($CDCl_3$, 300 MHz).

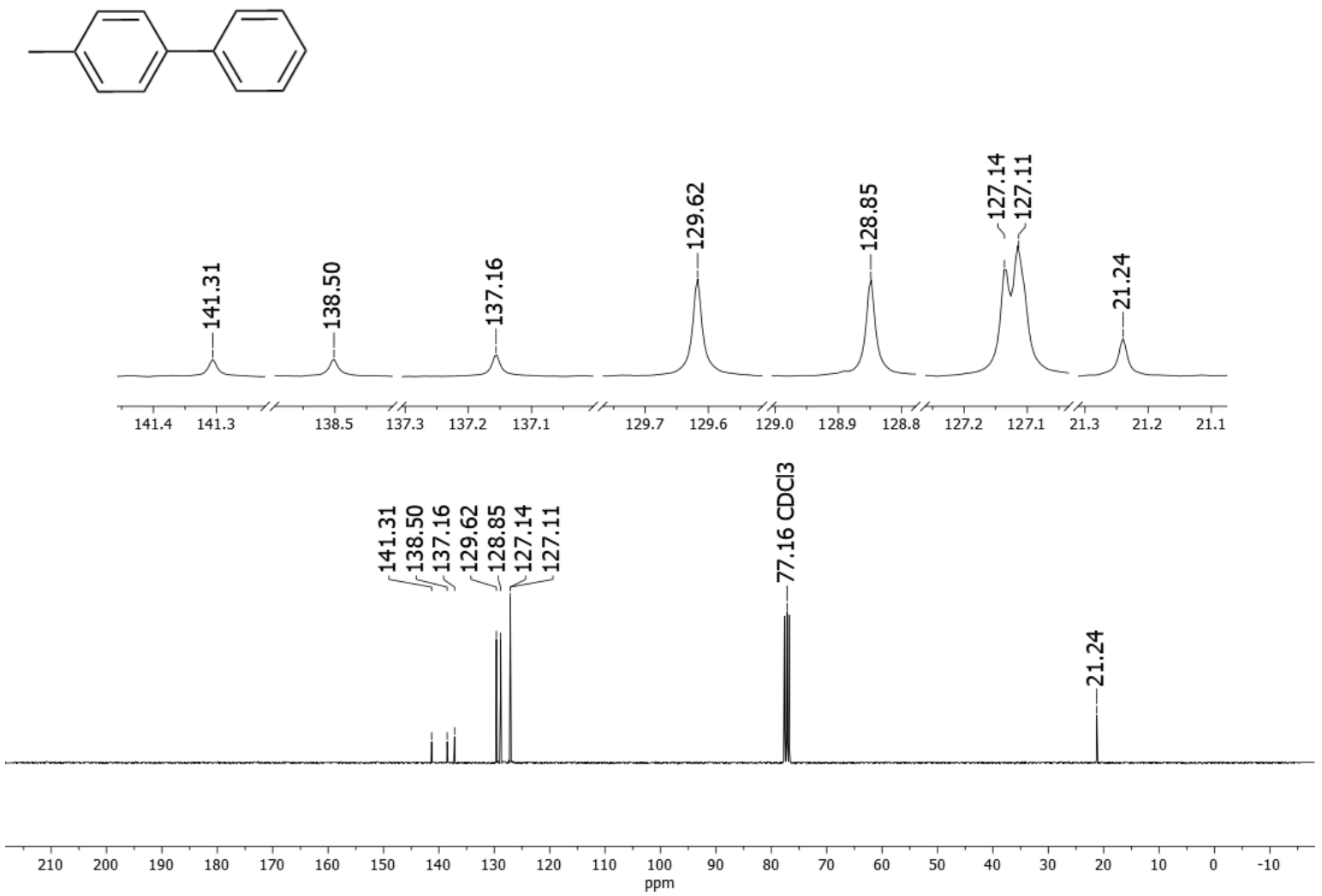


Figure S59. ^{13}C NMR spectrum of compound **10c** ($CDCl_3$, 75 MHz).

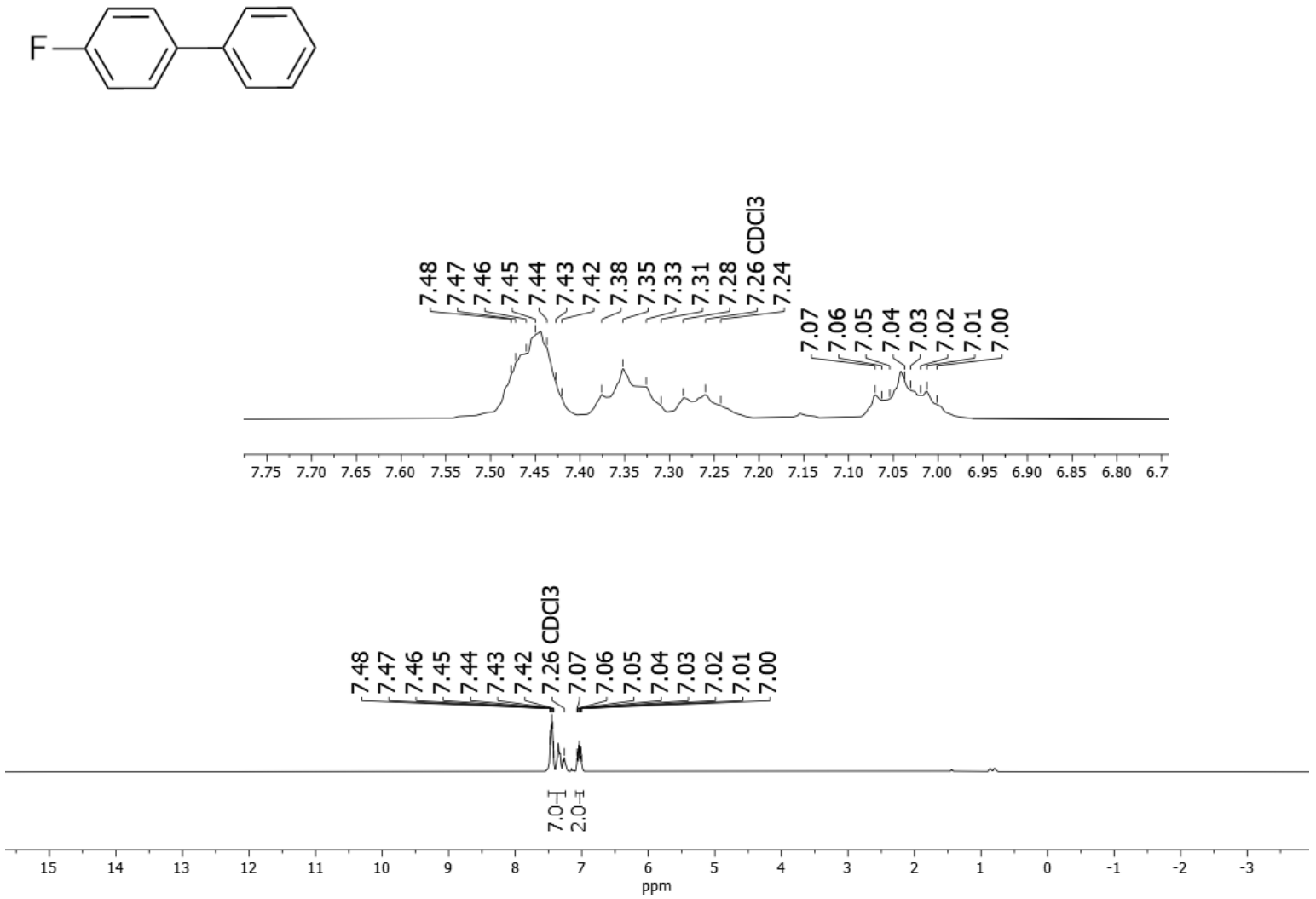


Figure S60. ^{1}H NMR spectrum of compound **10d** ($CDCl_3$, 300 MHz).

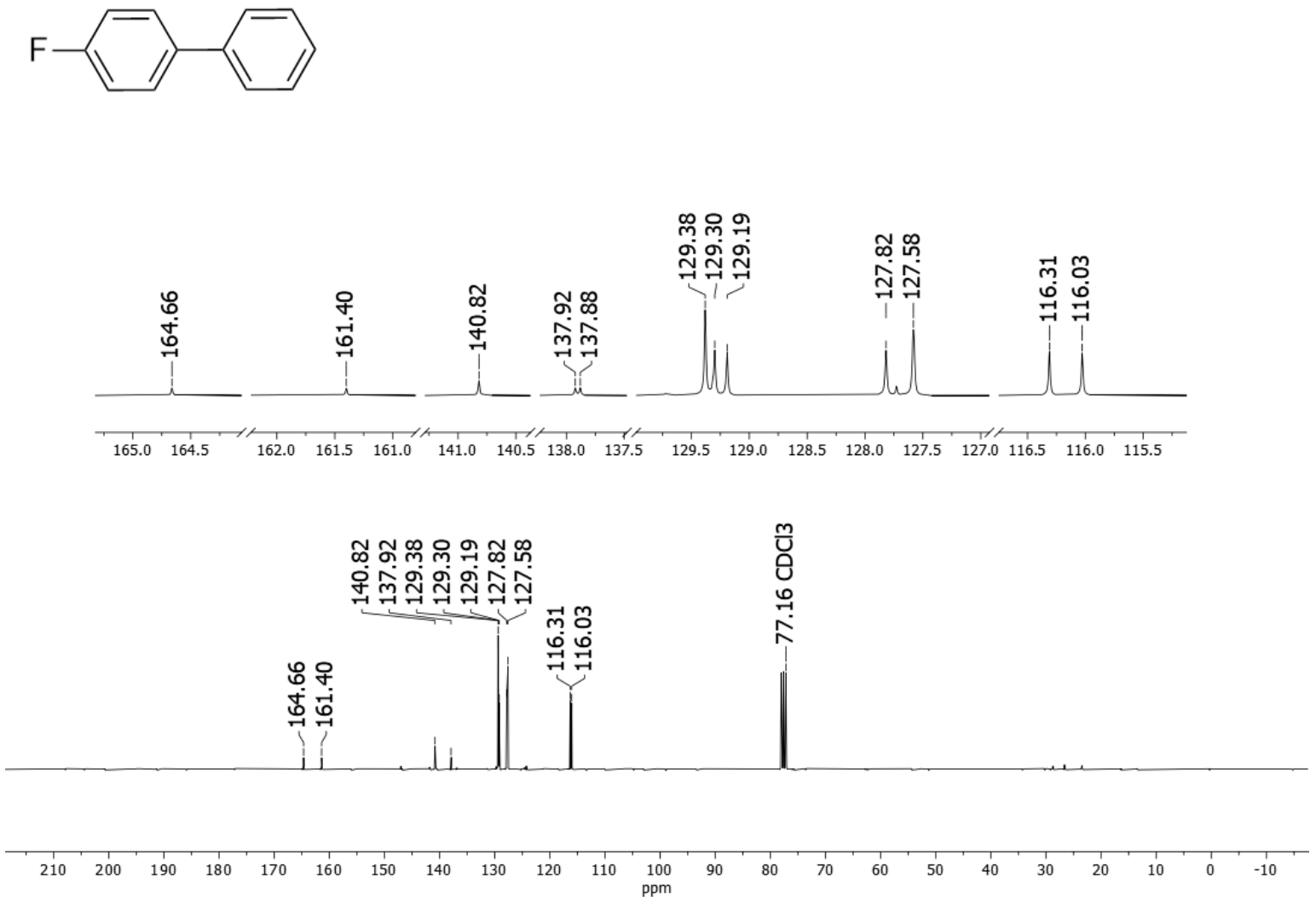


Figure S61. ^{13}C NMR spectrum of compound **10d** ($CDCl_3$, 75 MHz).

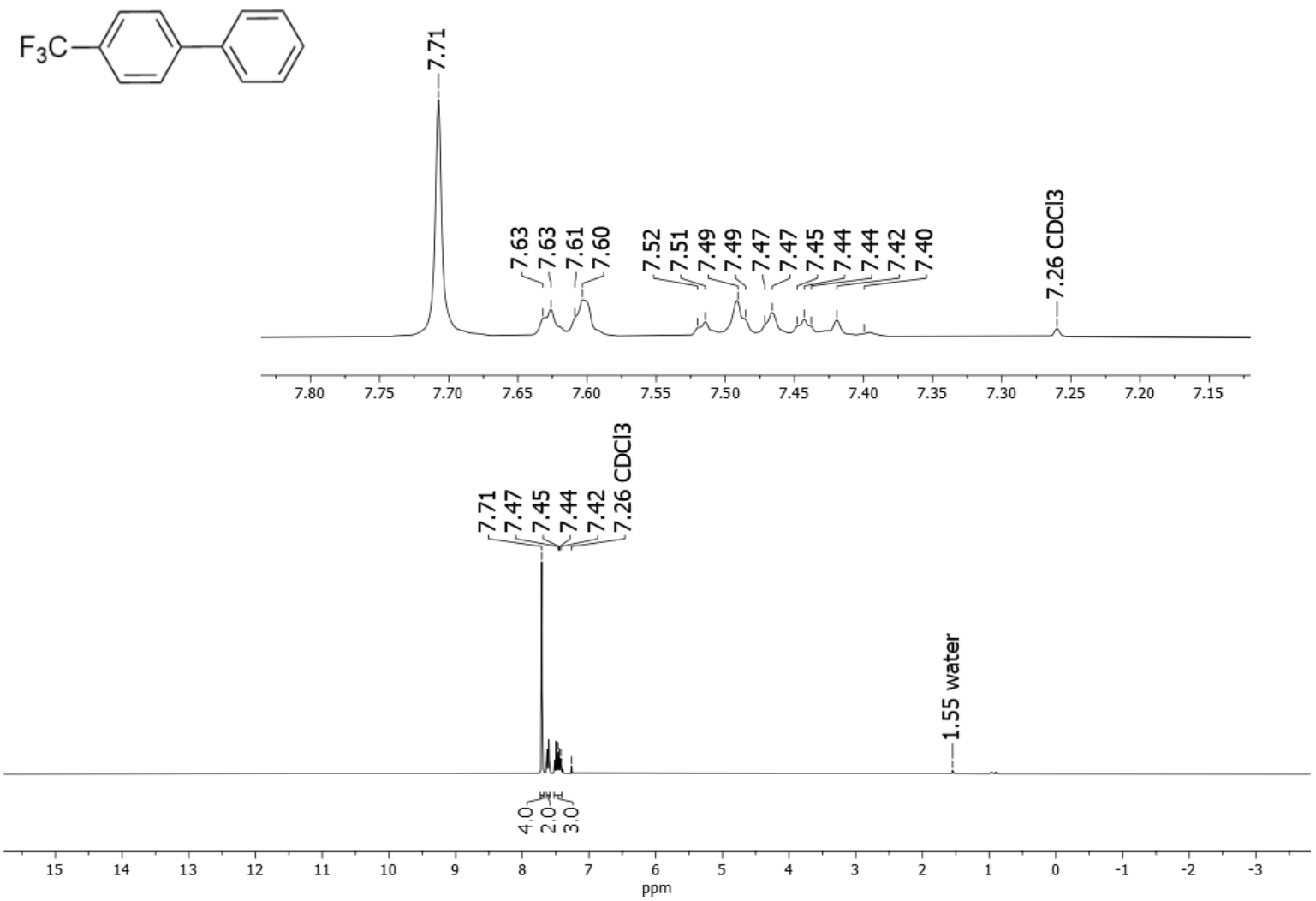


Figure S62. ^{1}H NMR spectrum of compound **10e** ($CDCl_3$, 300 MHz).

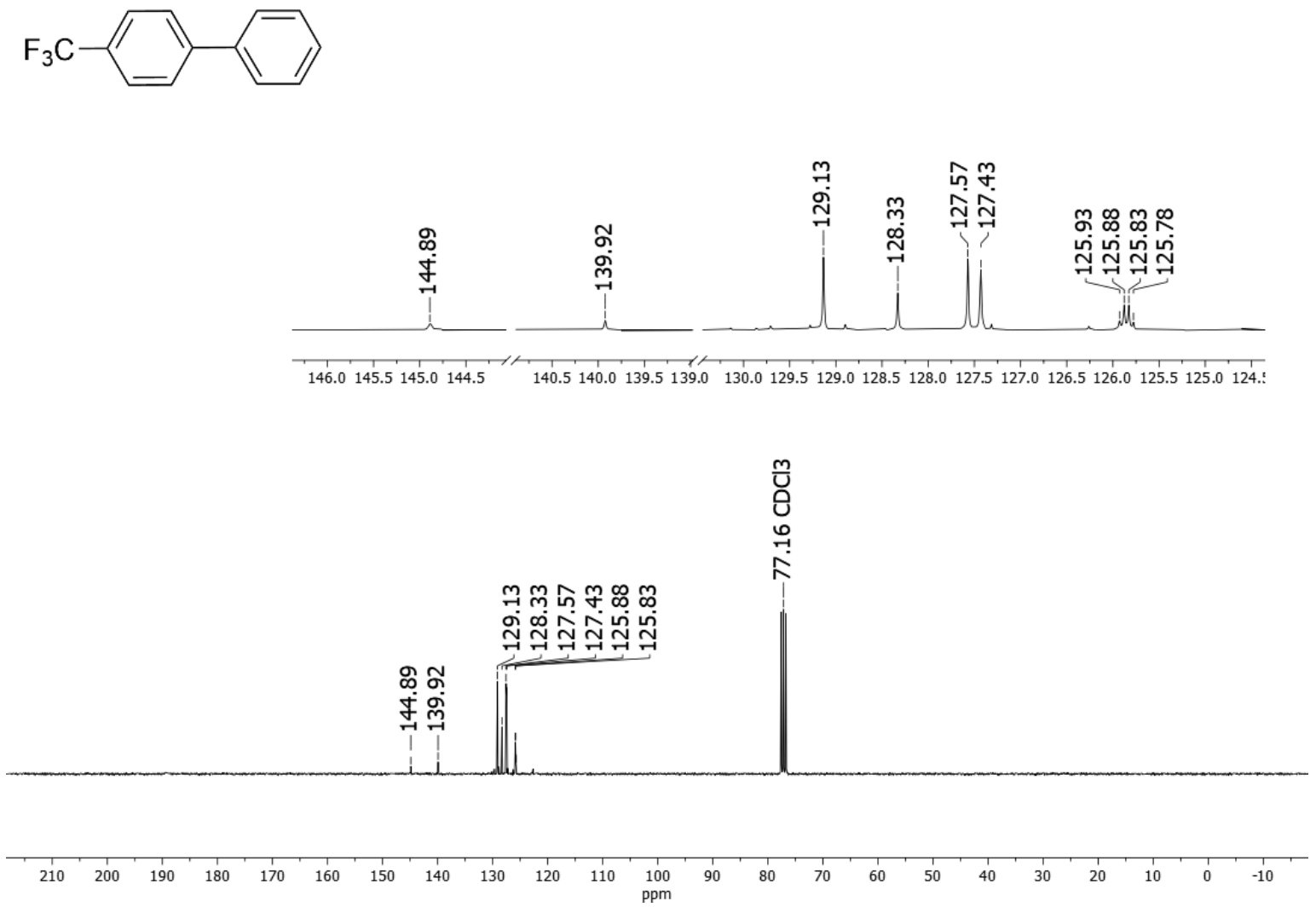


Figure S63. ^{13}C NMR spectrum of compound **10e** ($CDCl_3$, 75 MHz).

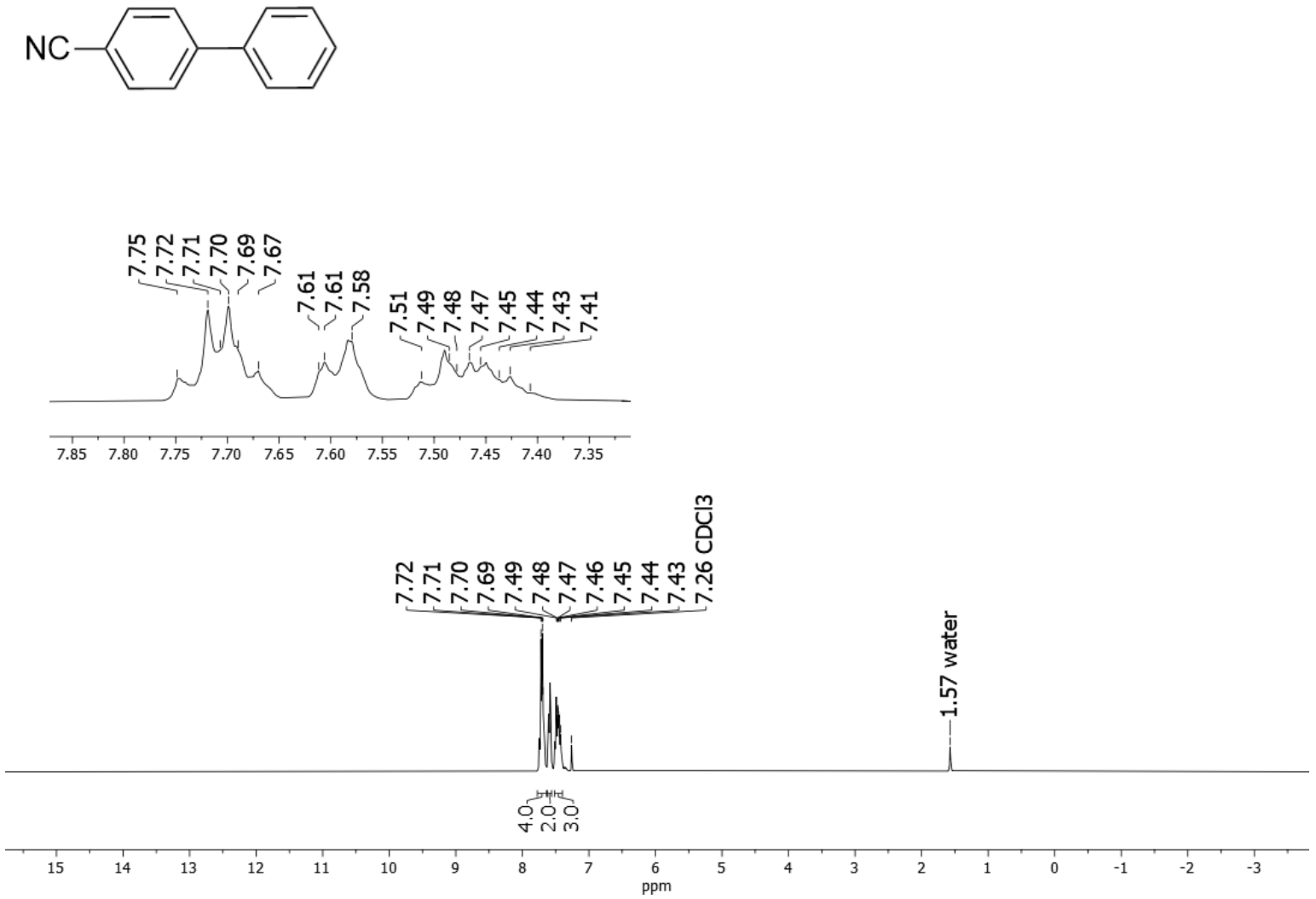


Figure S64. ^{1}H NMR spectrum of compound **10f** ($CDCl_3$, 300 MHz).

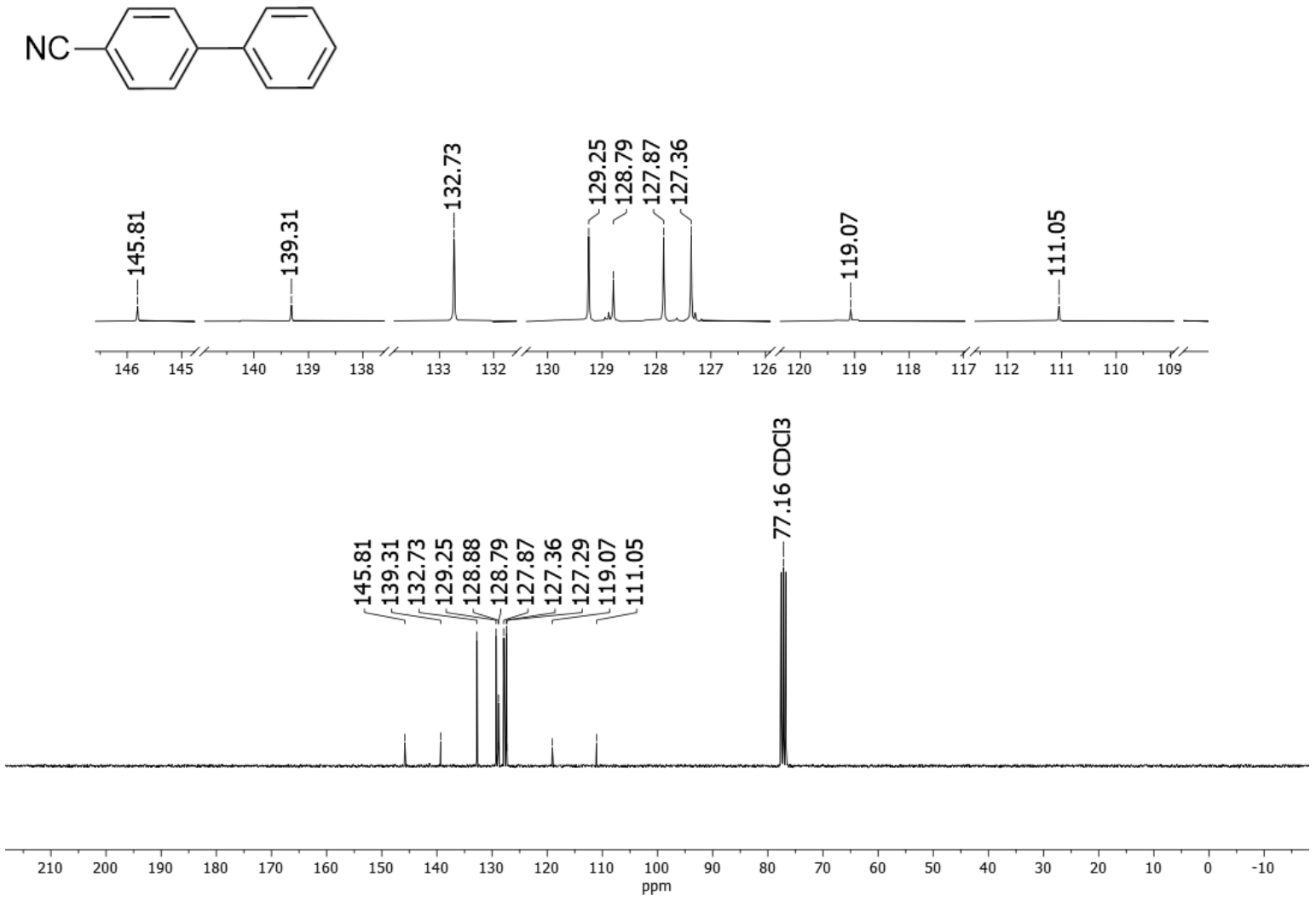


Figure S65. ^{13}C NMR spectrum of compound **10f** ($CDCl_3$, 75 MHz).

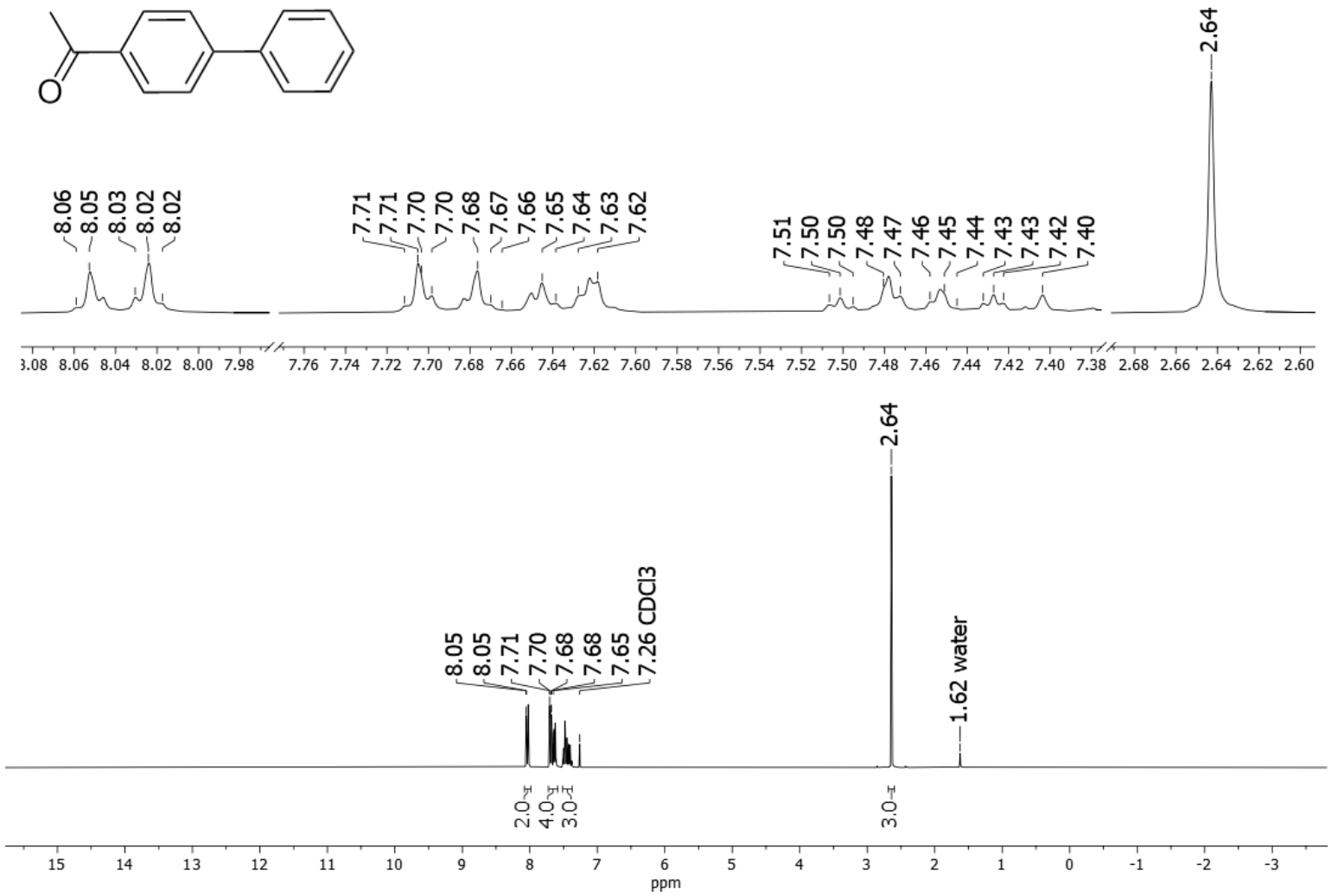


Figure S66. ^{1}H NMR spectrum of compound **10g** ($CDCl_3$, 300 MHz).

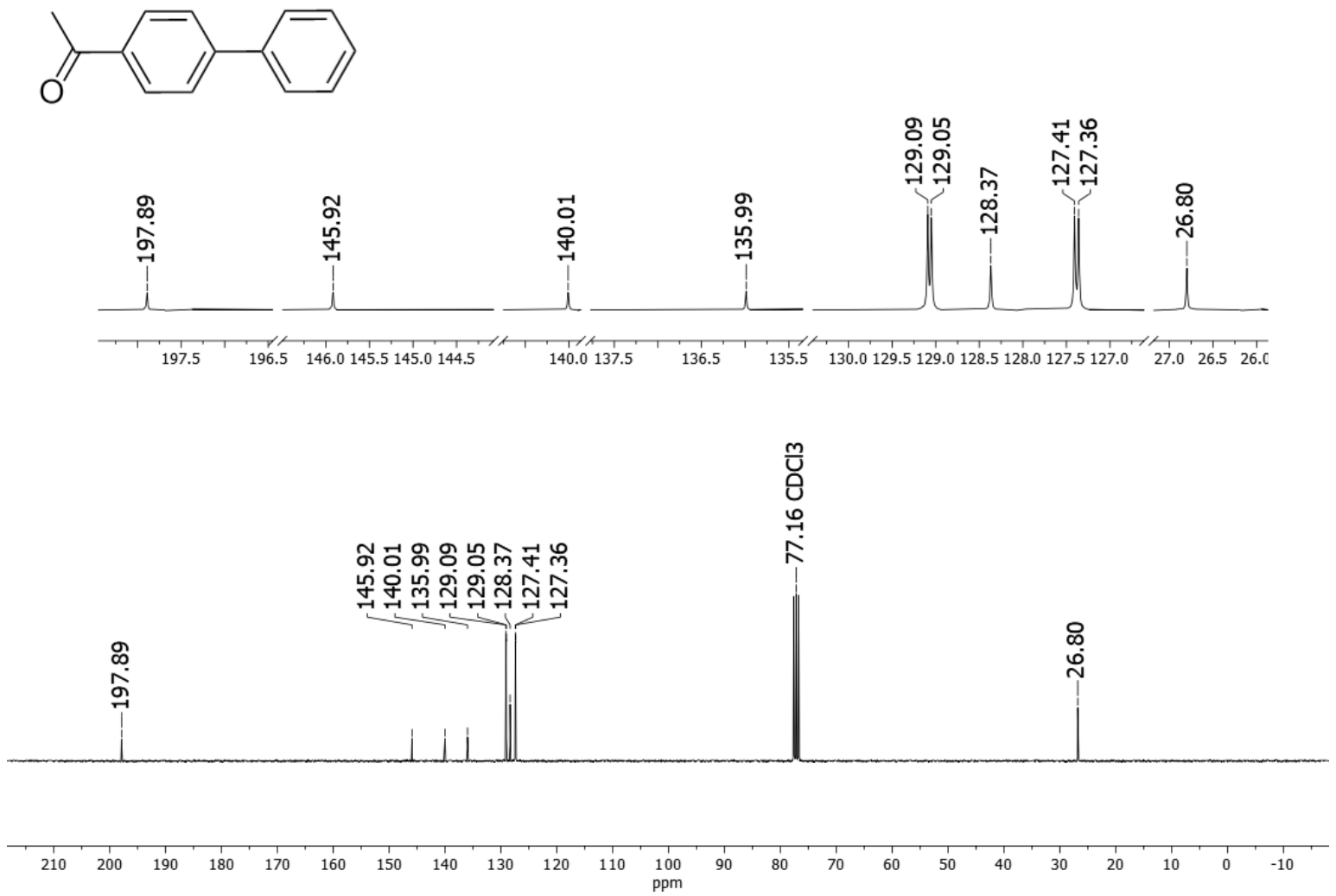


Figure S67. ^{13}C NMR spectrum of compound **10g** ($CDCl_3$, 75 MHz).

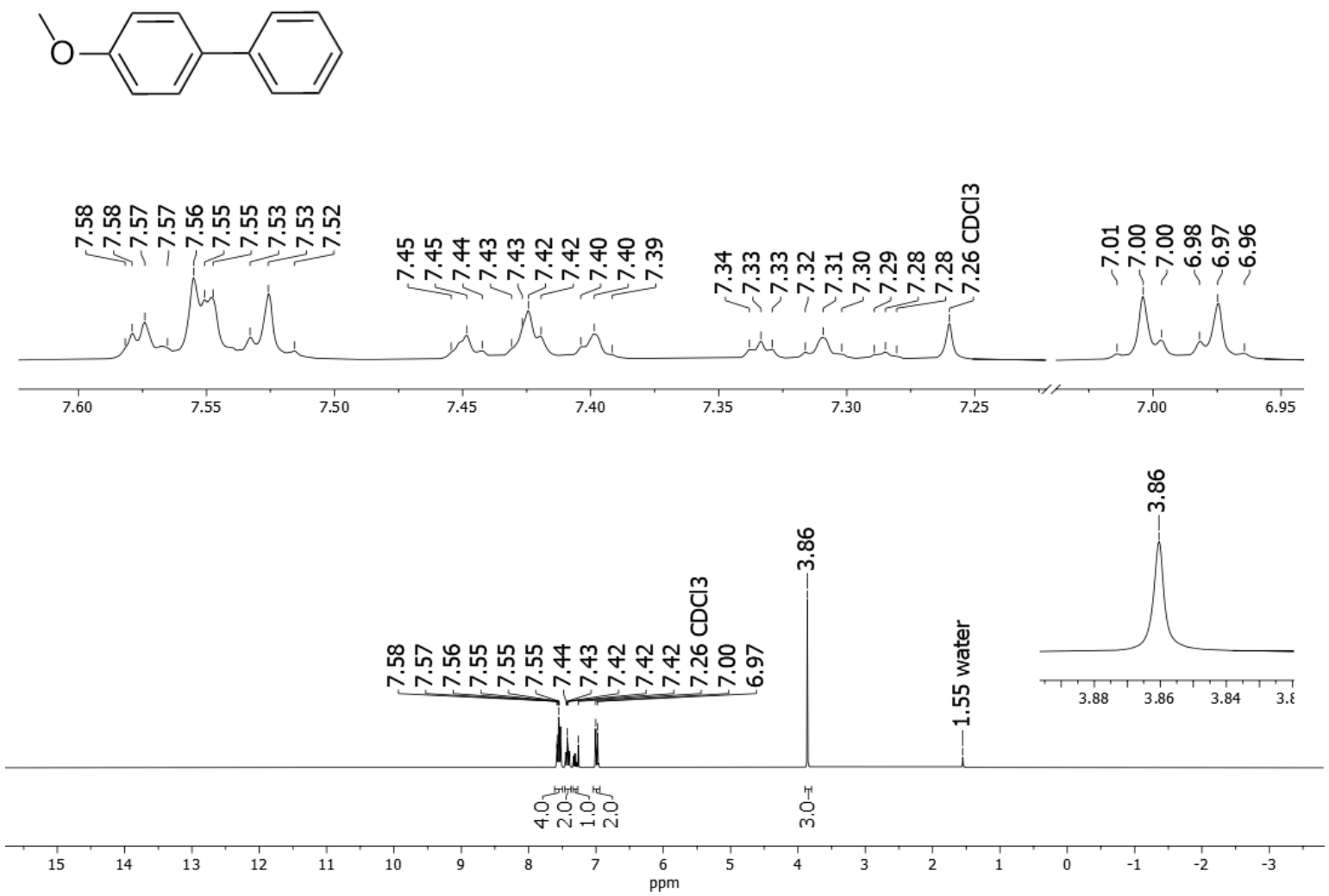


Figure S68. ^{1}H NMR spectrum of compound **10h** ($CDCl_3$, 300 MHz).

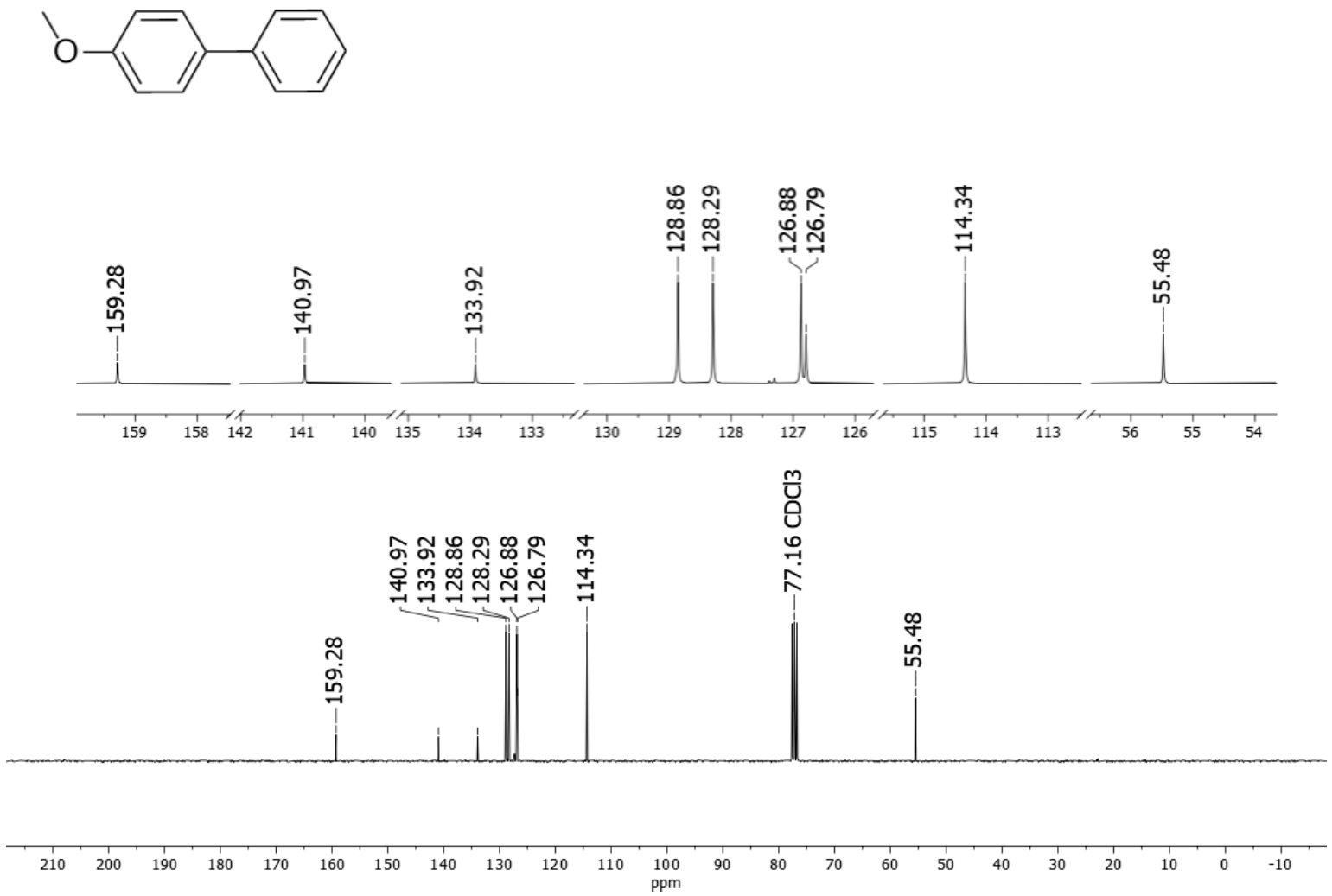


Figure S69. ^{13}C NMR spectrum of compound **10h** ($CDCl_3$, 75 MHz).

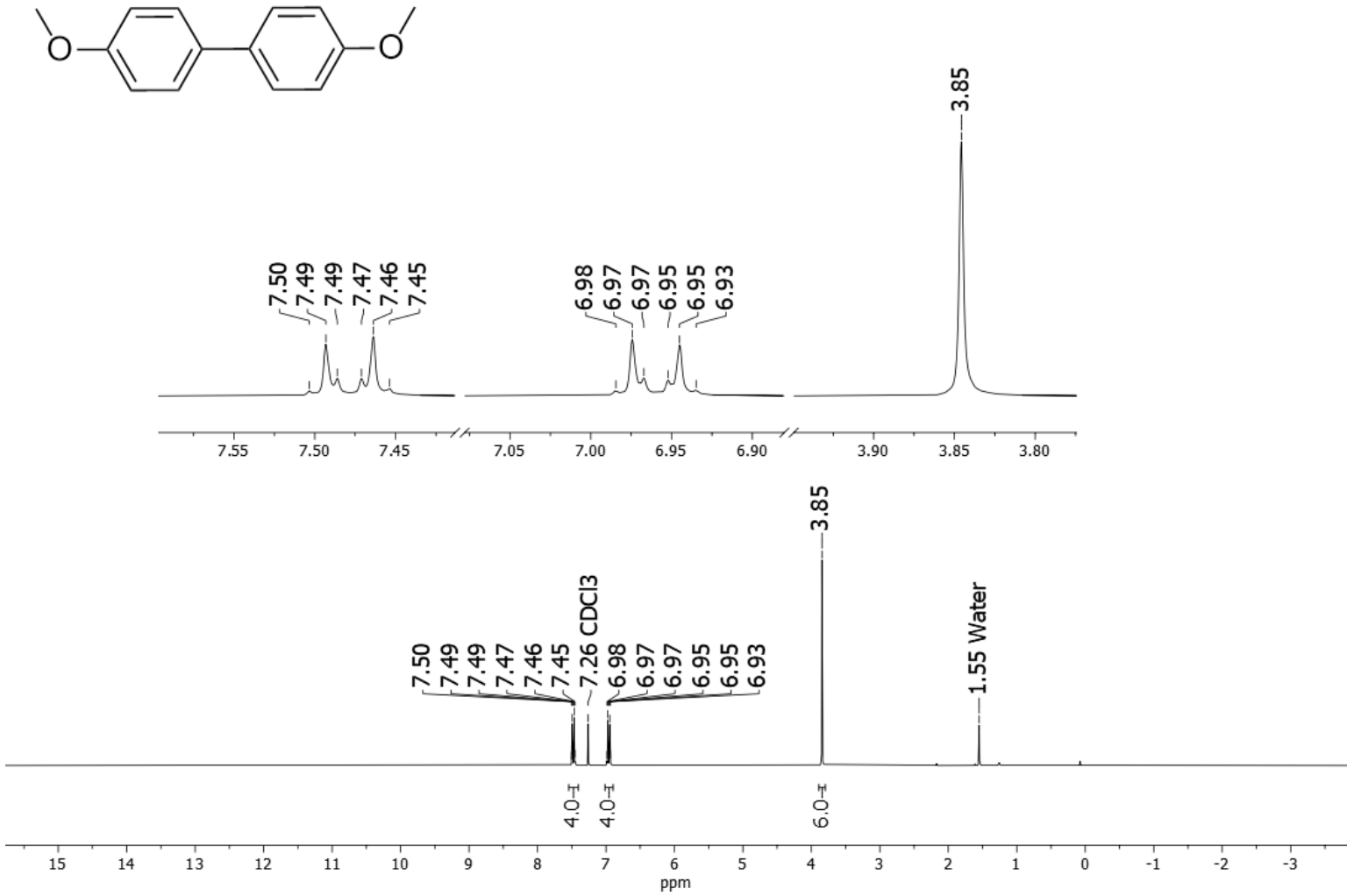


Figure S70. ^{1}H NMR spectrum of compound **10i** ($CDCl_3$, 300 MHz).

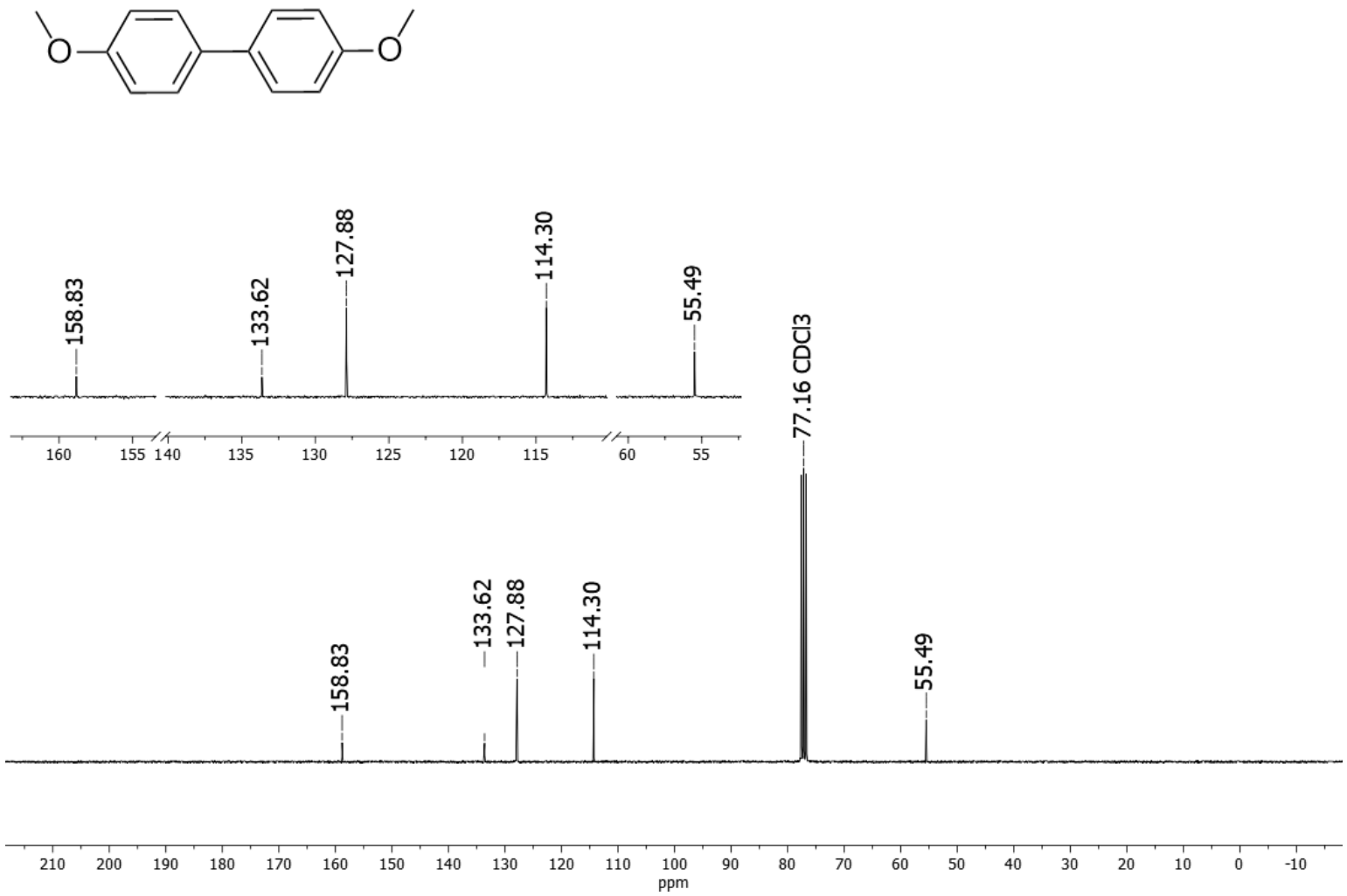


Figure S71. ^{13}C NMR spectrum of compound **10i** ($CDCl_3$, 75 MHz).

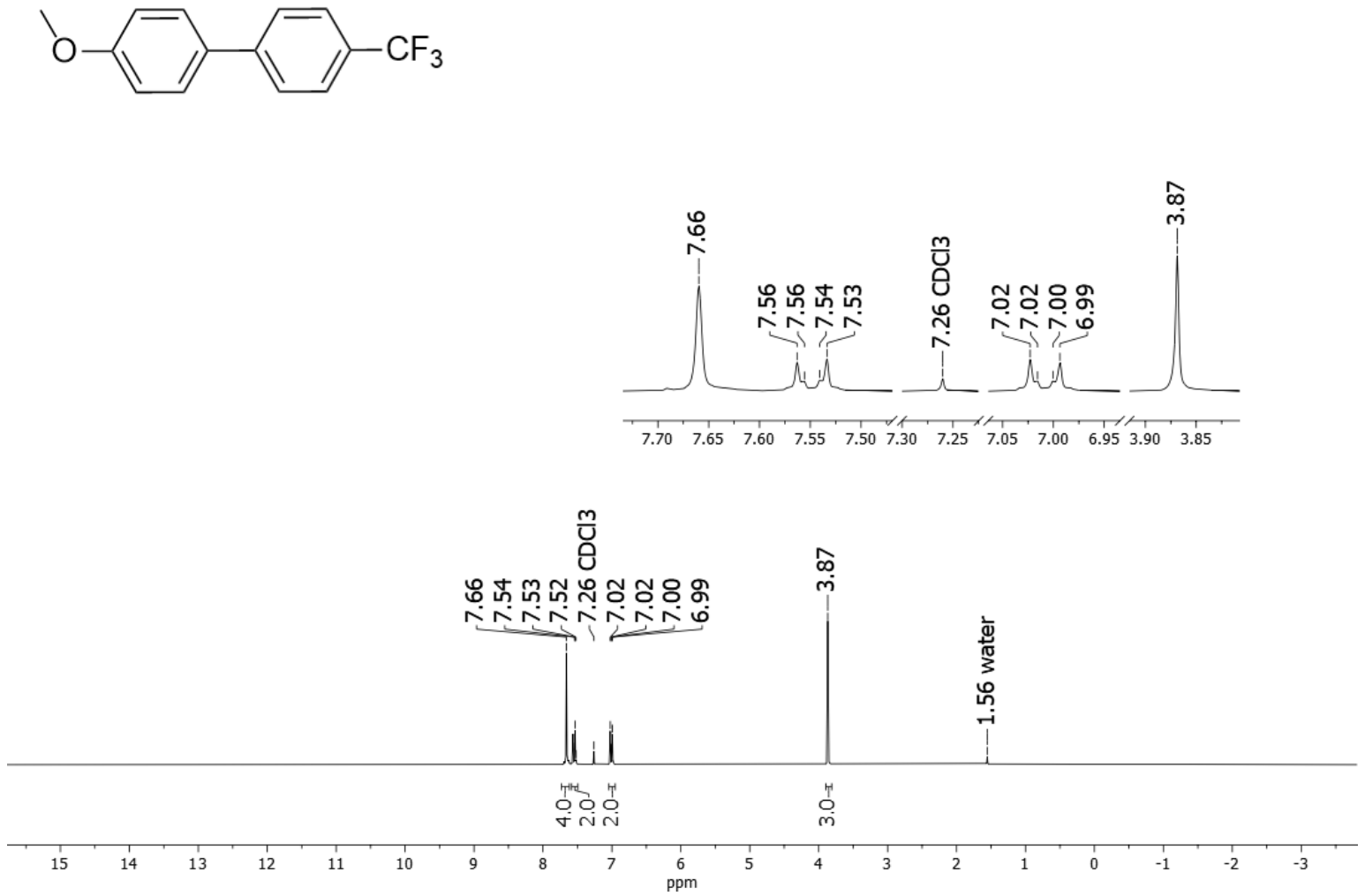


Figure S72. ^{1}H NMR spectrum of compound **10j** ($CDCl_3$, 300 MHz).

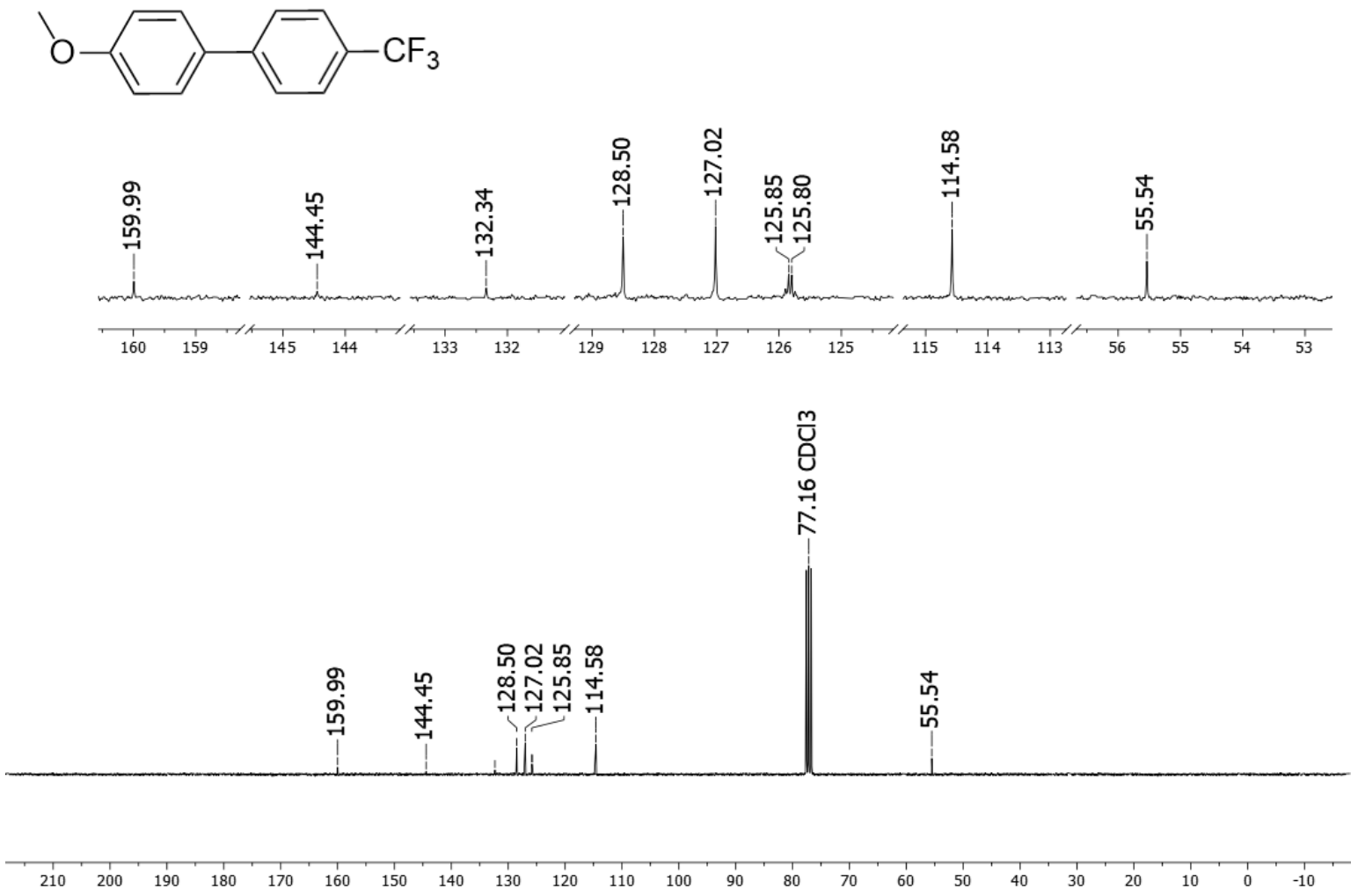


Figure S73. ^{13}C NMR spectrum of compound **10j** ($CDCl_3$, 75 MHz).

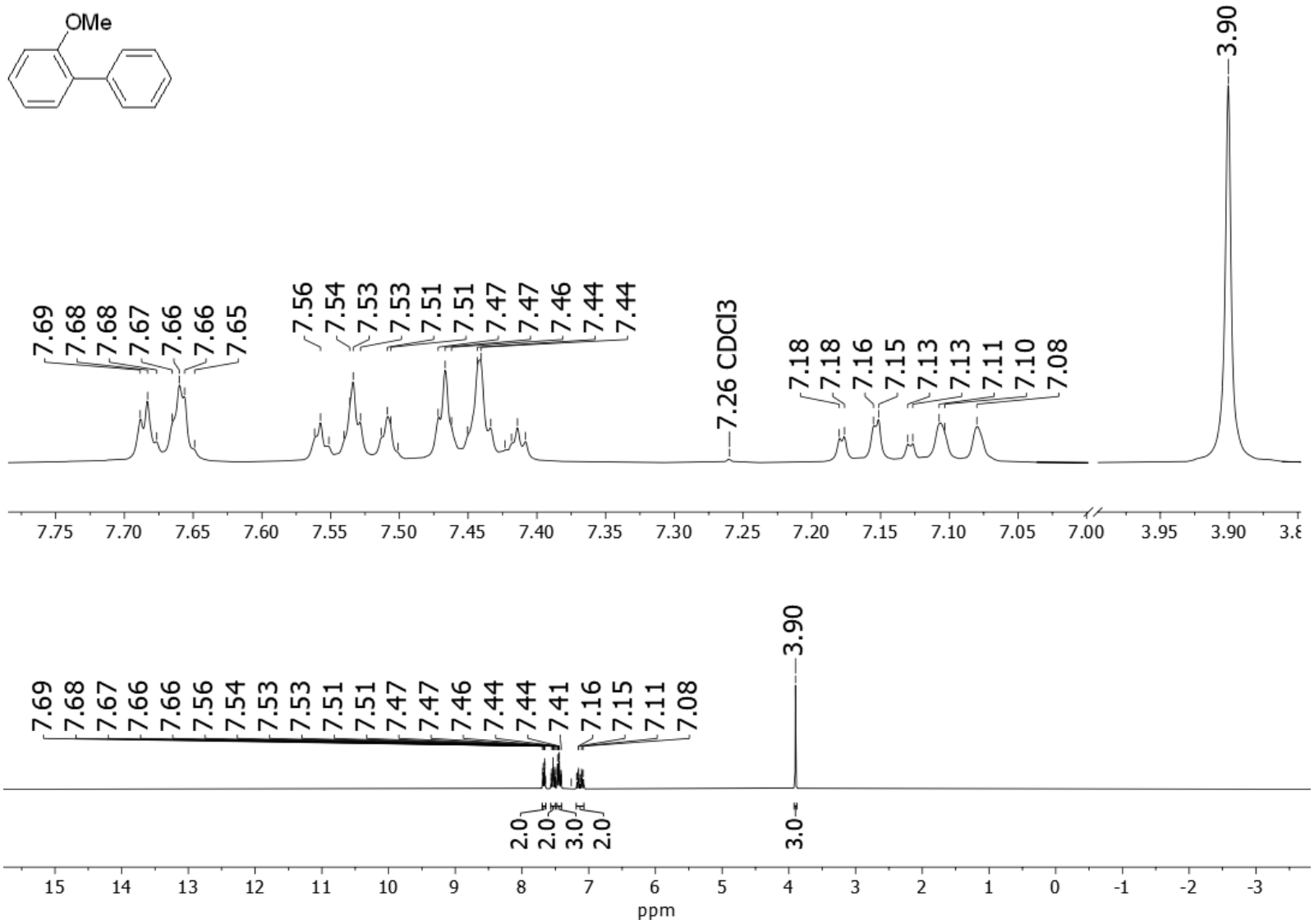


Figure S74. ^{1}H NMR spectrum of compound **10k** ($CDCl_3$, 300 MHz).

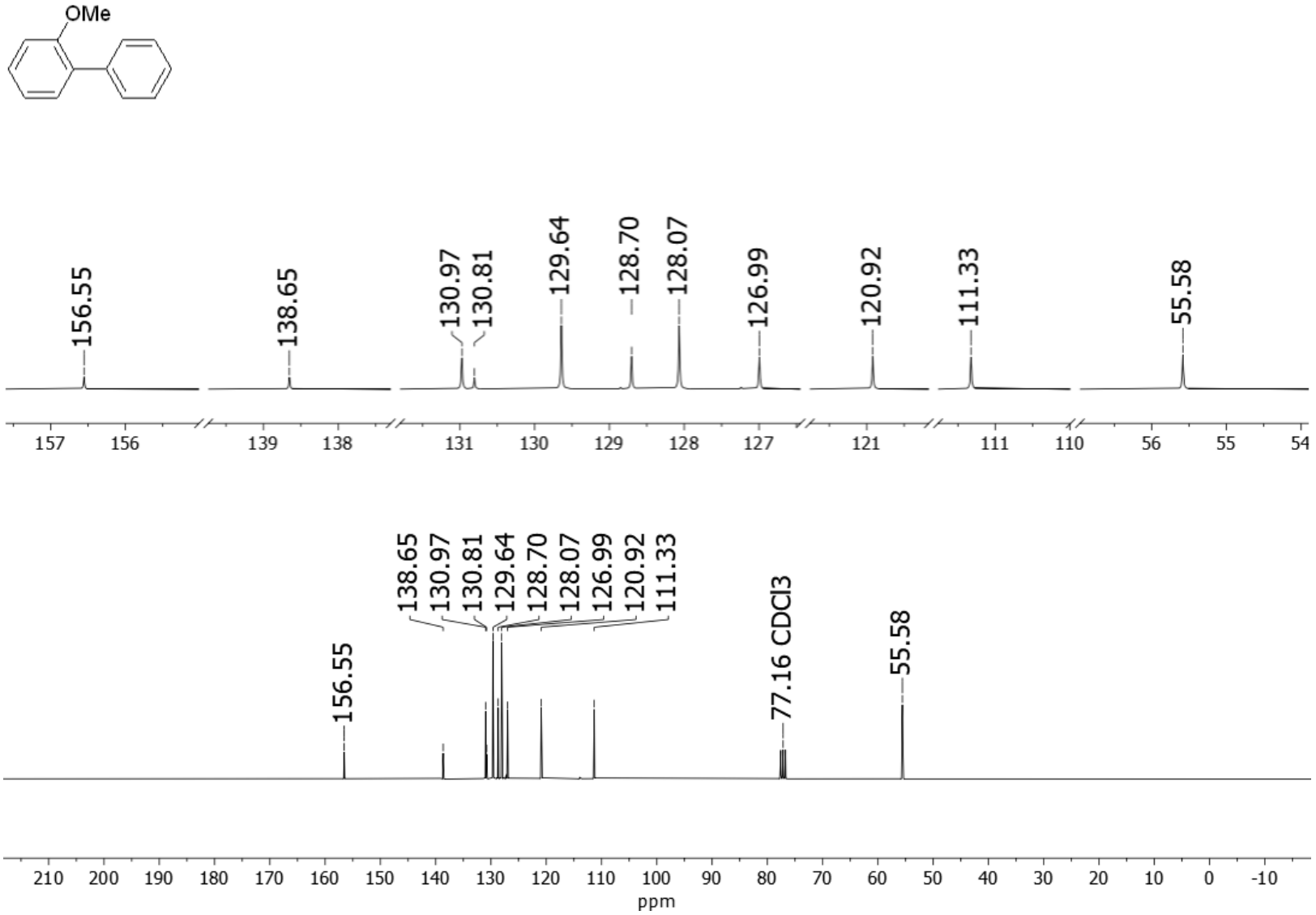


Figure S75. ^{13}C NMR spectrum of compound **10k** ($CDCl_3$, 75 MHz).

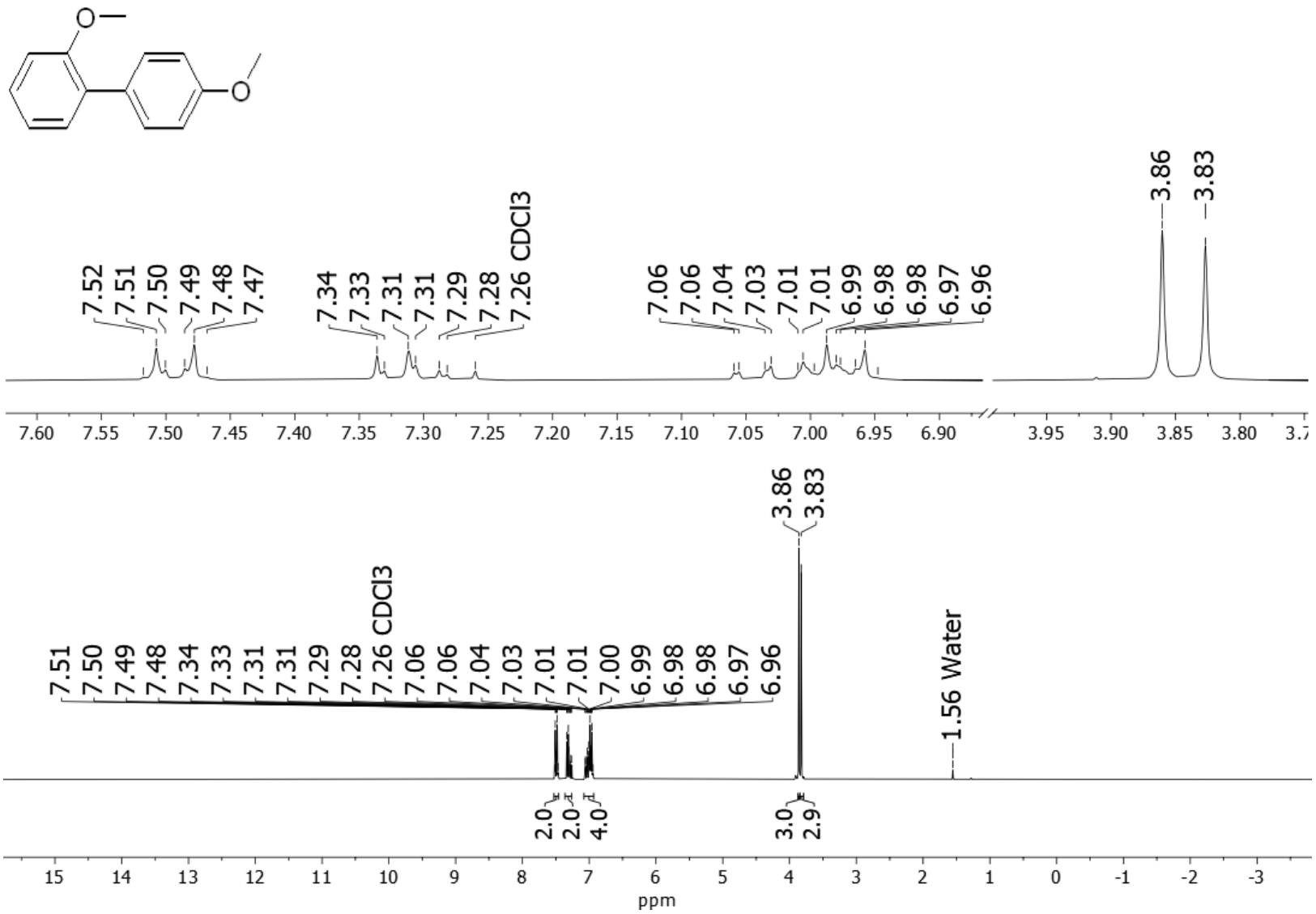


Figure S76. ^{1}H NMR spectrum of compound **10l** ($CDCl_3$, 300 MHz).

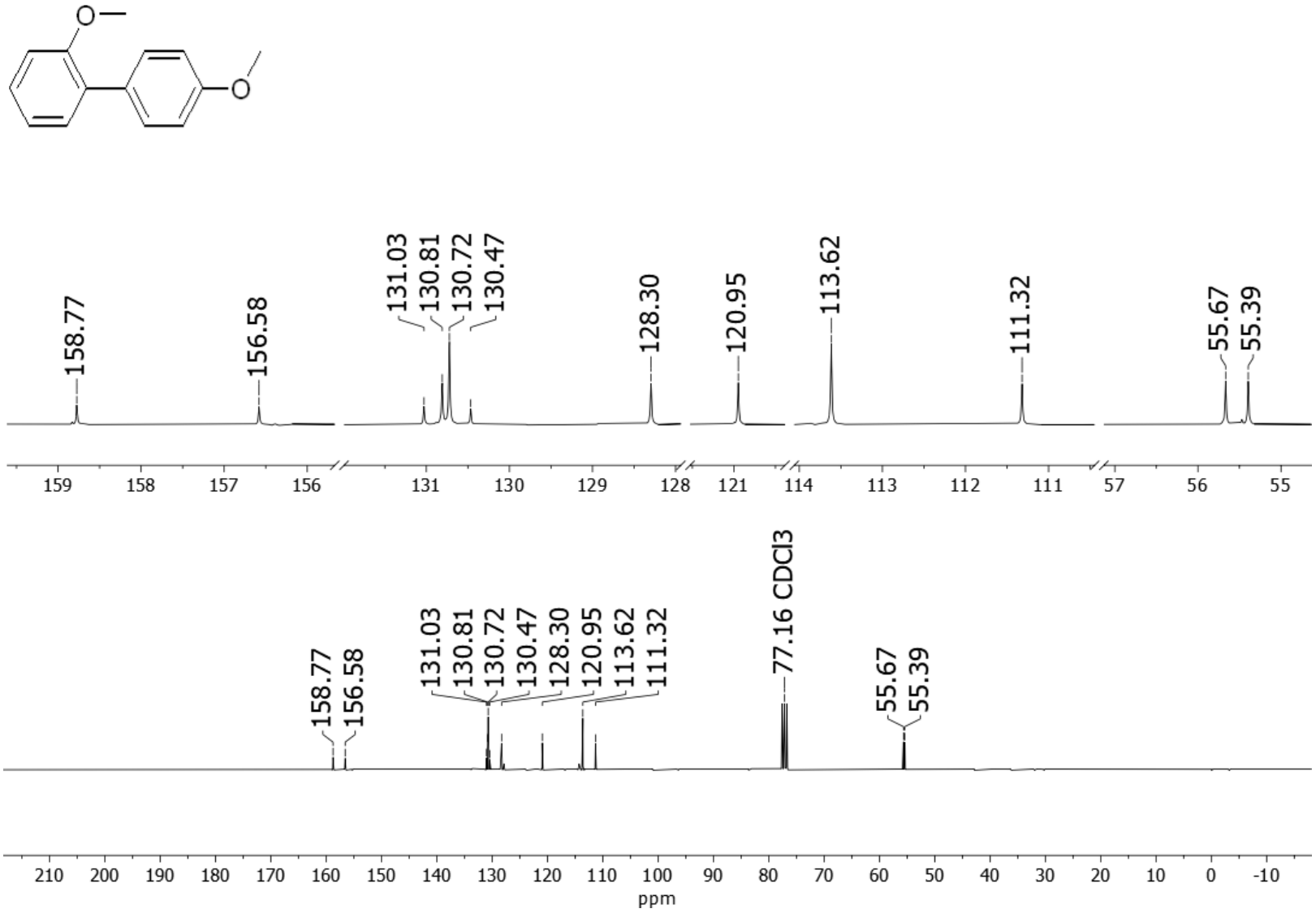


Figure S77. ^{13}C NMR spectrum of compound **10l** ($CDCl_3$, 75 MHz).

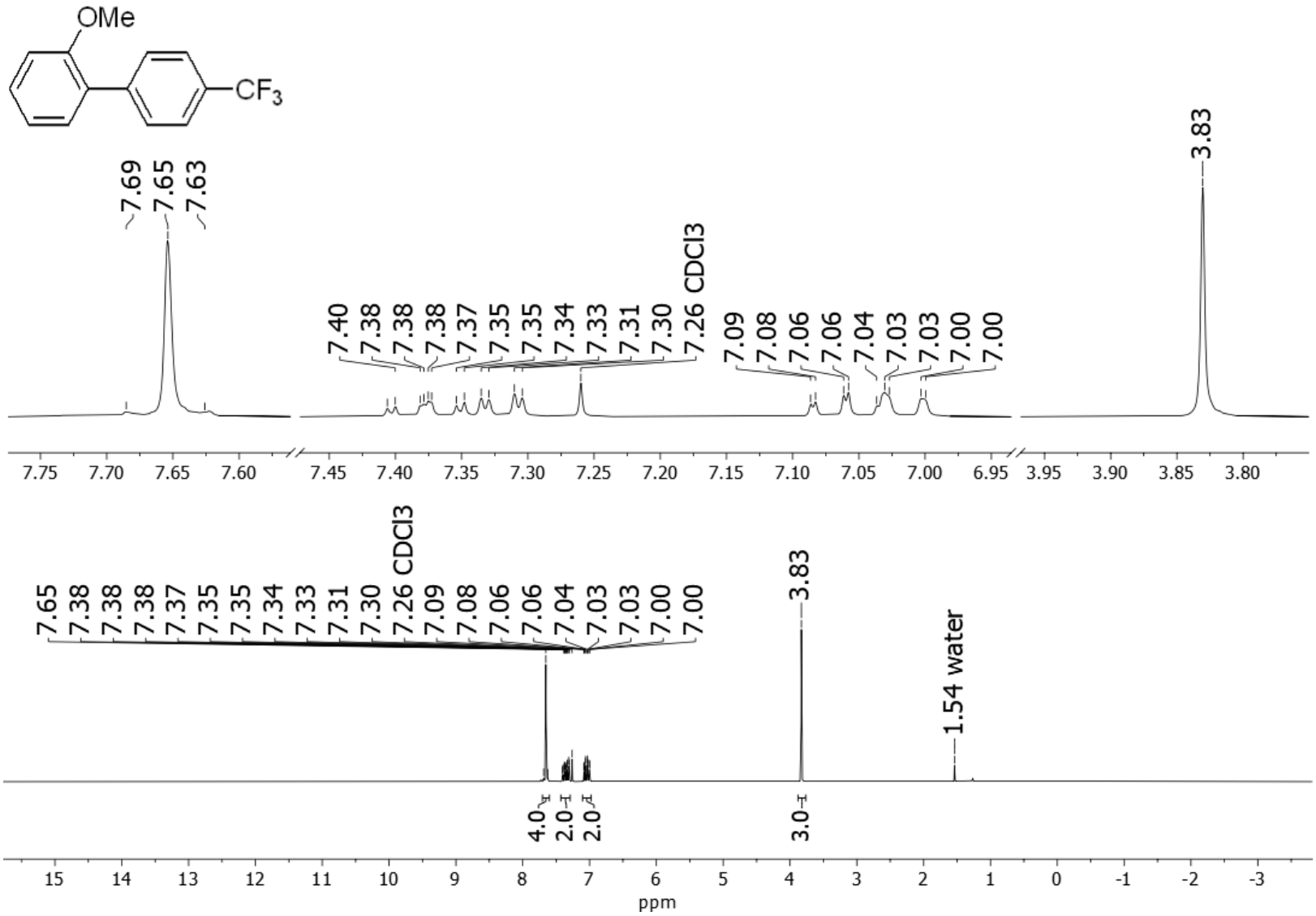


Figure S78. ^{1}H NMR spectrum of compound **10m** ($CDCl_3$, 300 MHz).

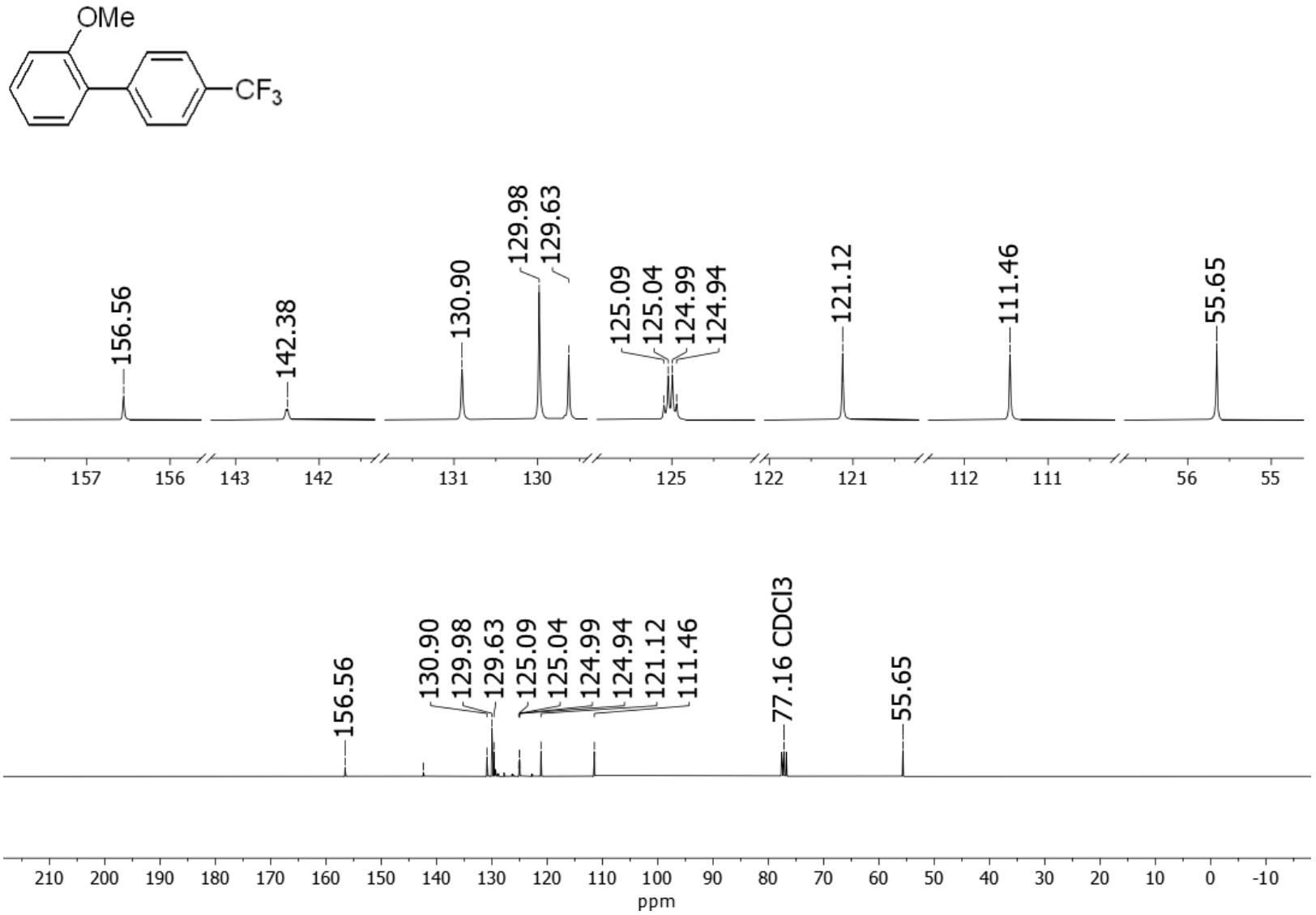


Figure S79. ^{13}C NMR spectrum of compound **10m** ($CDCl_3$, 75 MHz).

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