Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 67–69

(NHC)$NiCp_2$ complexes: new air-stable thermally activated precatalysts for olefin hydroheteroarylation

Oleg V. Khazipov and Victor M. Chernyshev

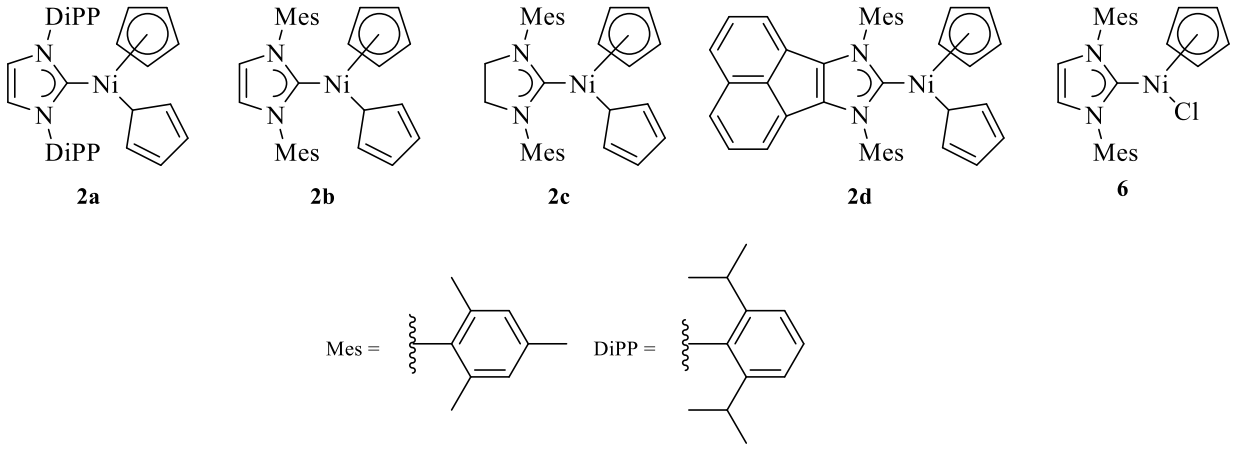
Table of contents:

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). Glassware was dried at 120 °C in an oven for at least 3 h before the use.

Instrumentation. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance NEO 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent signals as internal standards: δ 7.26 for ^{1}H, δ 77.2 for ^{13}C. Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer. GC-MS experiments were accomplished using an Agilent 7890A GC instrument equipped with an Agilent 5975C mass-selective detector (electron ionization, 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}.

Materials. 1,3-Bis[2,6-bis(prop-2-yl)phenyl]-1*H*-imidazol-3-ium chloride (**1a**),[S1] 1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium chloride (**1b**),[S1] 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**1c**),[S2] 7,9-bis(2,4,6-trimethylphenyl)-7*H*-acenaphtho[1,2-*d*]imidazol-9-ium chloride (**1d**),[S3] {1,3-bis[2,4,6-trimethylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)-(cyclopentadienyl)nickel (**6**)[S4] were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

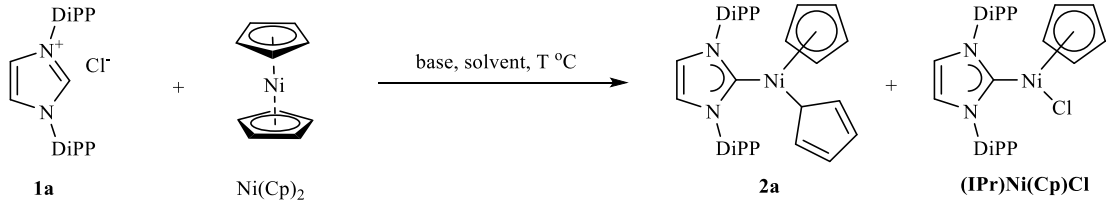


2a **2b** **2c** **2d** **6**

Figure S1. Overview of Ni/NHC complexes studied as precatalysts.

S2. Extended experimental data

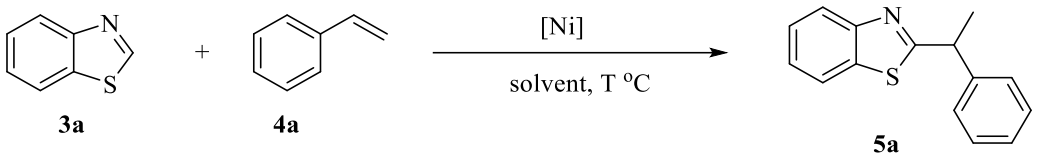
Table S1. Effect of reaction conditions on the yield of **2a** and **(IPr)Ni(Cp)Cl** complexes.[a]



Entry	Base (mol per 1 mol of IPr·HCl)	Solvent	Time, h	*T*, °C	Yield of **2a**, %[b]	Yield of **(IPr)Ni(Cp)Cl**, %[b]
1	Bu^tONa (1.05)	Toluene	1	25	79	trace
2	Bu^tONa (1.05)	Toluene	2	25	97	trace
3	Bu^tONa (1.05)	Dioxane	2	25	86	trace
4	Bu^tOK (1.05)	Toluene	1	25	73	trace
5	Cs_2CO_3 (1)	Toluene	1	25	1	2
6	Cs_2CO_3 (3)	Toluene	1	40	3	4
7	Cs_2CO_3 (3)	Toluene	1	80	20	25
8	Cs_2CO_3 (3)	Toluene	5	40	6	9
9	Cs_2CO_3 (3)	Dioxane	1	40	trace	trace
10	Cs_2CO_3 (3)	Dioxane	1	80	8	72
11	Cs_2CO_3 (3)	Dioxane	5	40	11	15
12	Cs_2CO_3 (3)	THF	1	40	3	26
13	Cs_2CO_3 (3)	THF	1	80	2	83
14	Cs_2CO_3 (3)	CH_2Cl_2	1	40	trace	trace
15	Cs_2CO_3 (3)	CH_3CN	1	40	21	36
16	Cs_2CO_3 (3)	acetone	1	40	54	30
17	K_3PO_4 (3)	toluene	1	25	trace	trace
18	K_3PO_4 (3)	acetone	1	40	27	25
19	NaOAc (3)	acetone	1	40	4	19
20	DIPEA (3)	acetone	1	40	0	0

[a] Reaction conditions: **1a** (0.105 mmol), $NiCp_2$ (0.1 mmol), base (1.05–3 equiv.), solvent (1 mL), 25-80 °C, 1-5 h. [b]Yields were determined by ^1H NMR spectroscopy using CH_3NO_2 as an internal standard.

Table S2. Optimization of the reaction conditions.[a]



Entry	Precatalyst (mol %)	*T*, °C	Solvent	Time, h	Yield of **5a**, %[b]
1	**2a** (10)	110	Toluene	5	trace
2	**2a** (10)	150	Xylene	5	2
3	**2b** (10)	110	Toluene	5	31
4	**2b** (10)	140	Xylene	5	78
5	**2b** (10)	150	Xylene	5	96
6	**2b** (10)	160	Xylene	5	95
7	**2b** (5)	150	Xylene	5	58
8	**2b** (15)	150	Xylene	5	97
9	**2b** (10)	150	Xylene	2	73
10	**2b** (10)	85	Xylene	20	2
11	**2b** (10)	110	Dioxane	5	26
12	**2b** (10)	85	Dioxane	20	trace
13	**2b** (10)	85	THF	20	0
14	**2b** (10)	85	CH_3CN	20	0
15	**2b** (10)	85	DMF	20	0
16	**2b** (10)	150	DMF	20	0
17	**2c** (10)	150	Xylene	5	46
18	**2d** (10)	150	Xylene	5	38
19	**6** (10)	150	Xylene	5	0
20	$NiCp_2$ (10)	150	Xylene	5	0

[a]*Reagents and conditions*: **3a** (0.25 mmol), **4a** (0.3 mmol), precatalyst **2a-d**, (IMes)Ni(Cp)Cl (**6**) or $NiCp_2$ (5-15 mol%), *o*-xylene (1 mL). [b]Yields were determined by CG-MS using 1,3-diisopropylbenzene as an internal standard.

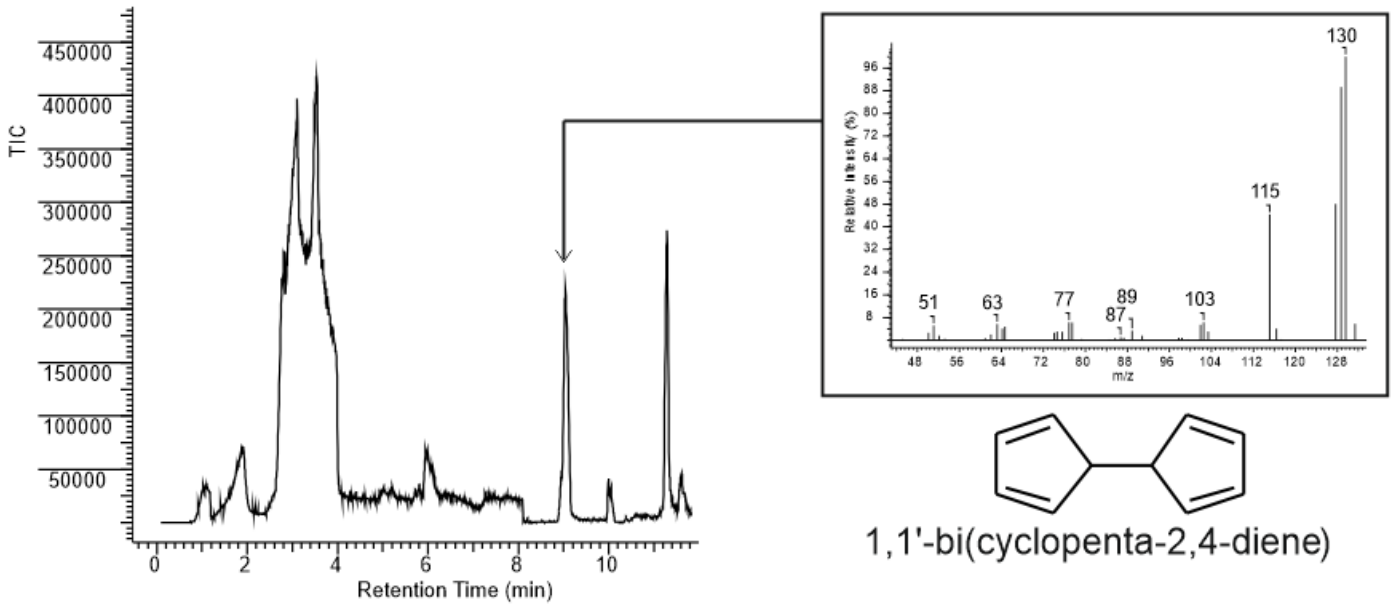
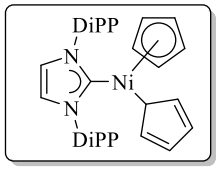


Figure S2. Observing the formation of 1,1'-bi(cyclopenta-2,4-diene) **7** at heating of complex **2b** at 150 °C in *o*-xylene. The mass spectra for the peak at ≈9 min is identical to the mass-spectrum of 1,1'-bi(cyclopenta-2,4-diene) presented in Wiley Mass-Spectra Electronic Database, John Wiley & Sons, Inc., Spectrum ID CAS2009_1_015749.

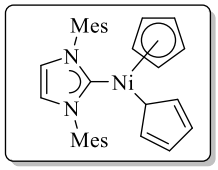
S3. Experimental procedures and characterization of synthesized compounds

Synthesis of complexes (NHC)NiCp$_2$.

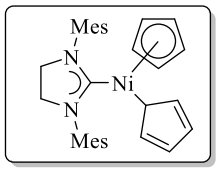
A mixture of azolium salt **1a-d** (0.55 mmol), $NiCp_2$ (95 mg, 0.5 mmol), Bu^{t}ONa (56 mg, 0.58 mmol) in toluene (4 mL) was stirred at 25 ^{o}C within 2 h. Then the reaction mixture was filtered through a short pad of celite, the volatiles were removed *in vacuo*. The crude product was washed with pentane and recrystallized from a toluene-pentane (~1:2) mixture.



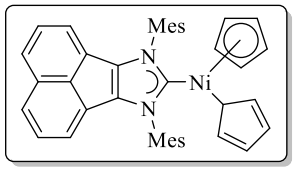
(IPr)NiCp$_2$ (2a). Yield 262 mg (91%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (d, *J* = 6.6 Hz, 12H), 1.34 (d, *J* = 6.6 Hz, 12H), 3.12 (sept, *J* = 6.6 Hz, 4H), 3.80 (s, 5H), 5.30 (s, 5H), 7.09 (s, 2H), 7.39-7.42 (m, 4H), 7.54-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.4, 25.7, 28.9, 92.0, 108.3, 124.1, 124.9, 129.9, 137.1, 145.9, 180.2. The spectral characteristics of the product obtained are similar to those described in the literature.[S5]



(IMes)NiCp$_2$ (2b). Yield 207 mg (84%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.24 (s, 12H), 2.49 (s, 6H), 3.90 (s, 5H), 5.44 (s, 5H), 7.06 (s, 2H), 7.16 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 21.3, 92.1, 108.0, 123.9, 129.3, 135.6, 137.0, 138.9, 176.9. Anal. calcd. for $C_{31}H_{34}N_2Ni$ (%): C, 75.48; H, 6.95; N, 5.68. Found (%): C, 75.43; H, 6.97; N, 5.77.



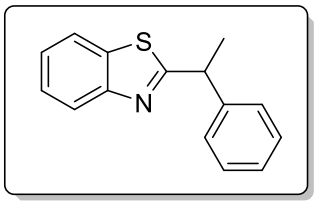
(SIMes)NiCp$_2$ (2c). Yield 220 mg (89%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.41 (s, 12H), 2.42 (s, 6H), 3.86 (s, 4H), 3.87 (s, 5H), 5.43 (s, 5H), 7.10 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 21.3, 51.4, 92.6, 108.5, 129.7, 136.5, 137.5, 138.1, 210.3. Anal. calcd. for $C_{31}H_{36}N_2Ni$ (%): C, 75.17; H, 7.33; N, 5.66. Found (%): C, 75.26; H, 7.35; N, 5.54.



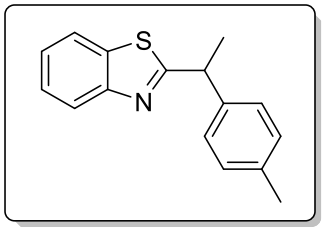
(IMes^{AN})NiCp$_2$ (2d). Yield 243 mg (79%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.32 (s, 12H), 2.54 (s, 6H), 3.98 (s, 5H), 5.51 (s, 5H), 6.92-6.94 (m, 2H), 7.18-7.28 (m, 4H), 7.34-7.39 (m, 2H), 7.69-7.72 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.6, 21.5, 92.5, 108.4, 120.3, 126.1, 127.6, 127.7, 128.4, 129.2, 129.7, 135.56, 135.64, 139.2, 139.3, 184.7. Anal. calcd. for $C_{41}H_{38}N_2Ni$ (%): C, 79.75; H, 6.20; N, 4.54. Found (%):C, C, 79.69; H, 6.24; N, 4.46.

Synthesis of hydroheteroarylation products 5a-l

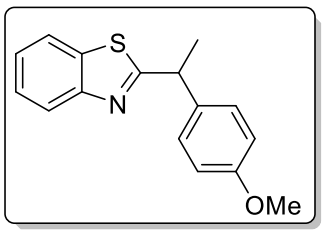
An oven-dried vial equipped with a magnetic stirring bar and a septum was charged in air with **2b** (12 mg, 0.025 mmol, 10 mol %), heterocyclic compound **3a-c** (0.25 mmol), alkene **4a-d** (0.3 mmol), and xylene (1 mL). Then the resulted mixture was purged with argon by syringe *via* septum and heated at 150 °C and vigorous stirring within 5 h (see Scheme 2 of the mail text). After cooling to room temperature, the mixture was diluted with xylene (4 mL) and filtered through a short pad of Celite. Then xylene was removed *in vacuo*, and the residue obtained was chromatographed on silica gel (elution with hexane, then with EtOAc).



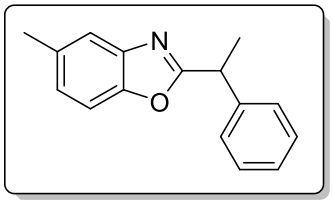
2-(1-Phenylethyl)-1,3-benzothiazole (5a). Yield 54 mg (91%), yellow powder, mp 34-36 °C (lit.[S6] mp 33-35 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.89 (d, *J*=7.2 Hz, 3H), 4.61 (q, *J*=7.2 Hz, 1H), 7.27-7.48 (m, 7H) 7.77-7.81 (m, 1H), 8.02-8.05 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 45.0, 121.6, 123.0, 124.8, 126.0, 127.4, 127.8, 128.9, 135.5, 143.2, 153.3, 176.4. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]



2-[1-(4-Methylphenyl)ethyl]-1,3-benzothiazole (5b). Yield 52 mg (82%), yellow powder, mp 31-33 °C (lit.[S6] mp 32-35 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.86 (d, *J*=7.0 Hz, 3H), 2.34 (s, 3H), 4.57 (q, *J*=7.0 Hz, 1H), 7.15-7.19 (m, 2H) 7.27-7.35 (m, 3H), 7.42-7.47 (m, 1H), 7.75-7.80 (m, 1H), 8.00-8.04 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2, 21.4, 44.6, 121.6, 122.9, 124.8, 126.0, 127.7, 129.6, 135.5, 137.1, 140.3, 153.2, 176.9. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]

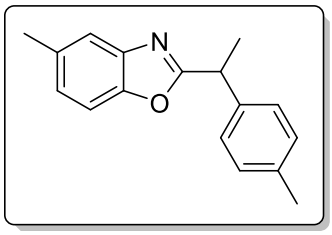


2-[1-(4-Methoxyphenyl)ethyl]-1,3-benzothiazole (5c). Yield 52 mg (78%), white powder, mp 59-61 °C (lit.[S6] mp 60-62 °C). ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.84 (d, *J*=7.3 Hz, 3H), 3.80 (s, 3H), 4.54 (q, *J*=7.3 Hz, 1H), 6.86-6.91 (m, 2H) 7.29-7.35 (m, 3H), 7.40-7.47 (m, 1H), 7.76-7.80 (m, 1H), 7.98-8.02 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 44.2, 55.4, 114.3, 121.6, 123.0, 124.8, 126.0, 128.9, 135.4, 135.5, 153.4, 158.9, 177.1. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]

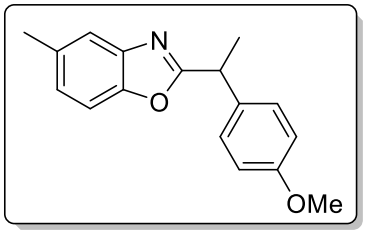


2-(1-Phenylethyl)-5-methyl-1,3-benzoxazole (5d). Yield 55 mg (93%), orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.82 (d, *J*=7.3 Hz, 3H), 2.45 (s, 3H), 4.39 (q, *J*=7.3 Hz, 1H), 7.05-7.11 (m, 1H), 7.22-7.30 (m, 2H), 7.31-7.39 (m, 4H, Ar), 7.48-7.51 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ^{13}C NMR (75 MHz, $CDCl_3$) δ

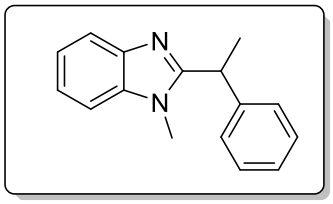
20.0, 21.6, 40.3, 110.0, 119.9, 125.8, 127.4, 127.6, 128.9, 134.0, 141.5, 141.5, 149.3, 169.0. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]



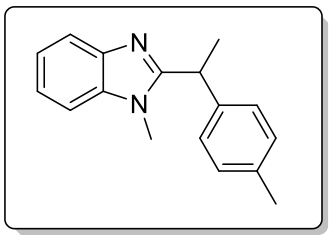
2-[1-(4-Methylphenyl)ethyl]-5-methyl-1,3-benzoxazole (5e). Yield 53 mg (84%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.80 (d, *J*=7.2 Hz, 3H), 2.32 (s, 3H), 2.45 (s, 3H), 4.36 (q, *J*=7.2 Hz, 1H), 7.06-7.10 (m, 1H, Ar), 7.13-7.16 (m, 2H), 7.23-7.27 (m, 2H), 7.29-7.32 (m, 1H), 7.49-7.50 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.0, 21.2, 21.6, 39.9, 110.0, 119.9, 125.8, 127.5, 129.6, 134.0, 137.0, 138.5, 141.5, 149.3, 169.2. The spectral characteristics of the product obtained are similar to those described in the literature.[6]



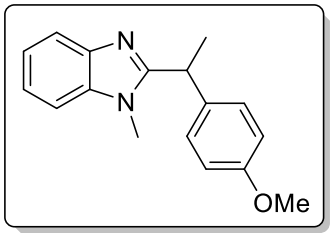
2-[1-(4-Methoxyphenyl)ethyl]-5-methyl-1,3-benzoxazole (5f). Yield 54 mg (81%), white powder, mp 73–75 °C (lit.[S6] mp 75-76 °C). ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.78 (d, *J*=7.2 Hz, 3H), 2.44 (s, 3H), 3.77 (s, 3H), 4.34 (q, *J*=7.2 Hz, 1H), 6.82-6.89 (m, 2H), 7.05-7.09 (m, 1H), 7.24-7.32 (m, 3H), 7.47-7.49 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.0, 21.6, 39.5, 55.4, 110.0, 114.3, 119.9, 125.7, 128.6, 133.6, 134.0, 141.5, 149.2, 158.9, 169.3. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]



2-(1-Phenylethyl)-1-methyl-1*H*-benzimidazole (5g). Yield 53 mg (89%), white powder, mp 88-91 °C (lit.[S6] mp 89-90 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88 (d, *J*=7.2 Hz, 3H), 3.49 (s, 3H), 4.36 (q, *J*=7.2 Hz, 1H), 7.19-7.33 (m, 8H), 7.83-7.88 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.8, 29.9, 39.1, 109.0, 119.8, 121.9, 122.4, 127.0, 127.5, 129.1, 136.3, 142.5, 143.0, 156.9. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]

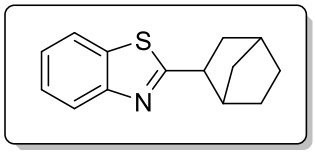


2-[1-(4-Methylphenyl)ethyl]-1-methyl-1*H*-benzimidazole (5h). Yield 53 mg (85%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (d, *J*=7.0 Hz, 3H), 2.30 (s, 3H), 3.48 (s, 3H), 4.31 (q, *J*=7.0 Hz, 1H), 7.07-7.10 (m, 4H), 7.27-7.27 (m, 3H), 7.81-7.87 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1, 21.9, 29.9, 38.7, 109.0, 119.7, 121.8, 122.3, 127.3, 129.7, 136.3, 136.6, 140.0, 142.5, 157.1. The spectral characteristics of the product obtained are similar to those described in the literature.[S6]

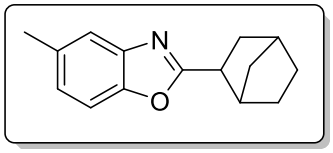


2-[1-(4-Methoxyphenyl)ethyl]-1-methyl-1*H*-benzimidazole (5i). Yield 56 mg (76%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (d, *J*=7.1 Hz, 3H), 3.50 (s, 3H), 3.78 (s, 3H), 4.32 (q, *J*=7.1 Hz, 1H), 6.81-6.86 (m, 2H), 7.11-7.16 (m,

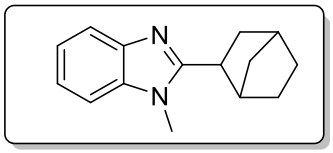
2H), 7.25-7.29 (m, 3H), 7.82-7.88 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.9, 29.9, 38.3, 55.4, 109.0, 114.4, 119.7, 121.8, 122.3, 128.5, 135.1, 136.2, 142.4, 157.2, 158.6. The spectral characteristics of the product obtained are similar to those described in the literature.[6]



2-(2-Norbornyl)-1,3-benzothiazole (5j). Yield 48 mg (84%), orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25-1.35 (m, 2H), 1.41-1.50 (m, 1H), 1.54-1.72 (m, 3H), 1.83-1.94 (m, 1H), 2.09-2.18 (m, 1H), 2.42-2.45 (m, 1H), 2.62-2.64 (m, 1H), 3.16-3.22 (m, 1H), 7.29-7.35 (m, 1H), 7.40-7.46 (m, 1H), 7.81-7.84 (m, 1H), 7.95-7.98 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.9, 29.9, 36.6, 36.7, 38.4, 44.4, 47.3, 121.5, 122.7, 124.6, 125.9, 135.0, 153.3, 177.7. The spectral characteristics of the product obtained are similar to those described in the literature.[6]



2-(2-Norbornyl)-5-methyl-1,3-benzoxazole (5k). Yield 49 mg (86%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.22-1.34 (m, 2H), 1.37-1.45 (m, 1H), 1.55-1.70 (m, 3H), 1.72-1.78 (m, 1H), 2.11-2.20 (m, 1H), 2.40-2.44 (m, 1H), 2.45 (s, 3H), 2.65-2.69 (m, 1H), 2.94-3.00 (m, 1H), 7.06-7.10 (m, 1H), 7.30-7.36 (m, 1H), 7.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 28.9, 29.7, 35.6, 36.4, 36.6, 41.8, 42.2, 77.2, 109.7, 119.6, 125.4, 133.8, 141.6, 149.2, 170.8. The spectral characteristics of the product obtained are similar to those described in the literature.[6]



2-(2-Norbornyl)-1-methyl-1*H*-benzimidazole (5l). Yield 45 mg (79%), white powder, mp 90-92 °C (lit[6] mp 89-90 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.21-1.27 (m, 1H), 1.30-1.38 (m, 1H), 1.40-1.48 (m, 1H), 1.59-1.82 (m, 4H), 2.29-2.37 (m, 1H), 2.43-2.49 (m, 1H), 2.52-2.57 (m, 1H), 2.87-2.94 (m, 1H), 3.73 (s, 3H), 7.19-7.24 (m, 2H), 7.27-7.30 (m, 1H), 7.73-7.77 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.2, 29.8, 30.0, 35.8, 36.3, 36.5, 40.1, 42.0, 108.8, 119.4, 121.7, 122.0, 136.4, 142.4, 158.8. The spectral characteristics of the product obtained are similar to those described in the literature.[6]

S4. ^{1}H and ^{13}C NMR spectra

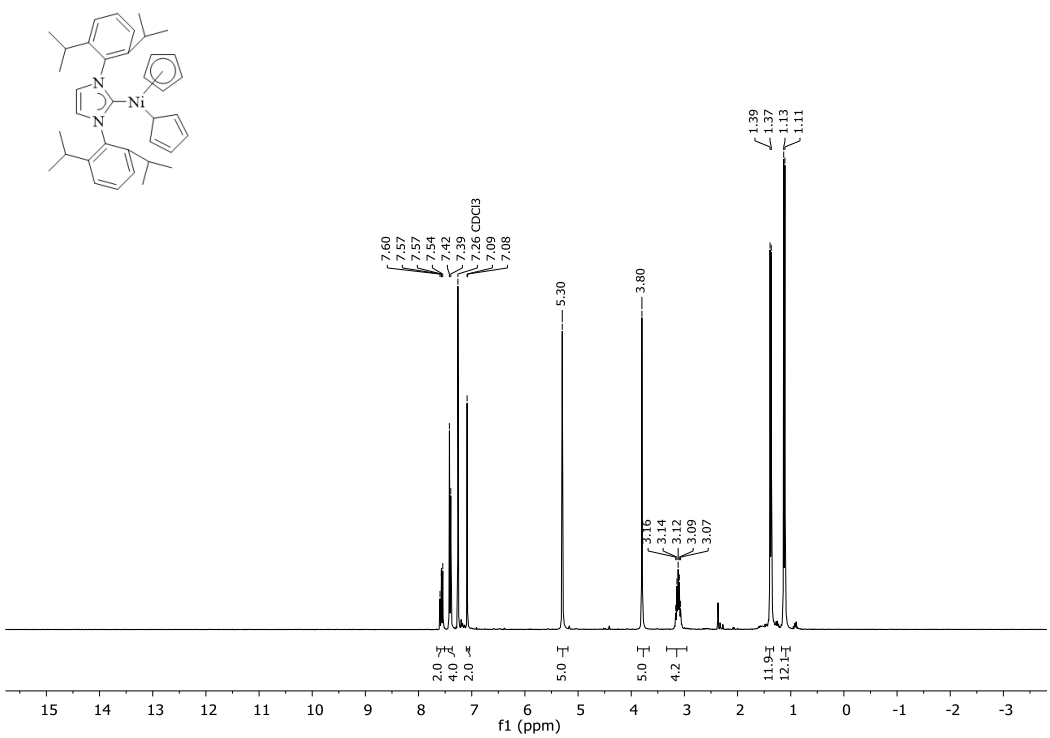


Figure S3. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 300 MHz).

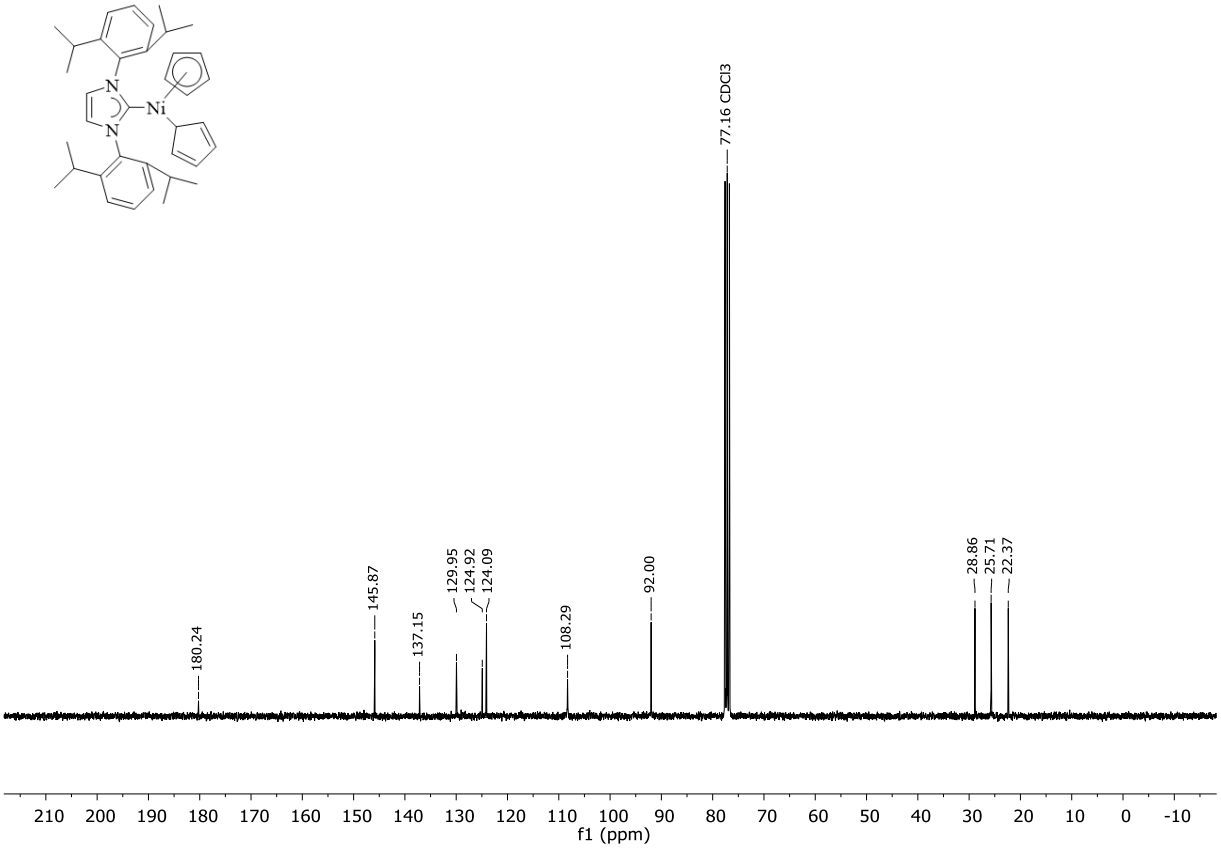


Figure S4. ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 75 MHz).

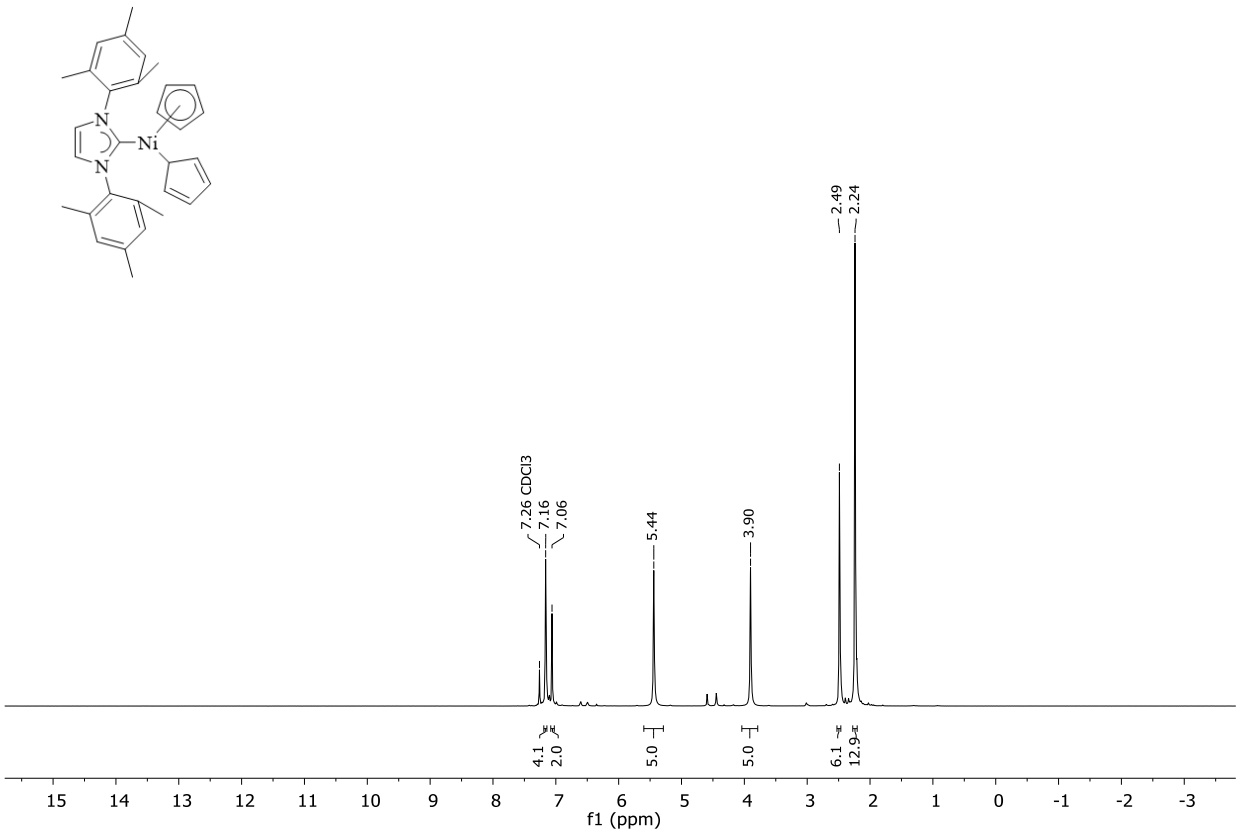


Figure S5. ^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 300 MHz).

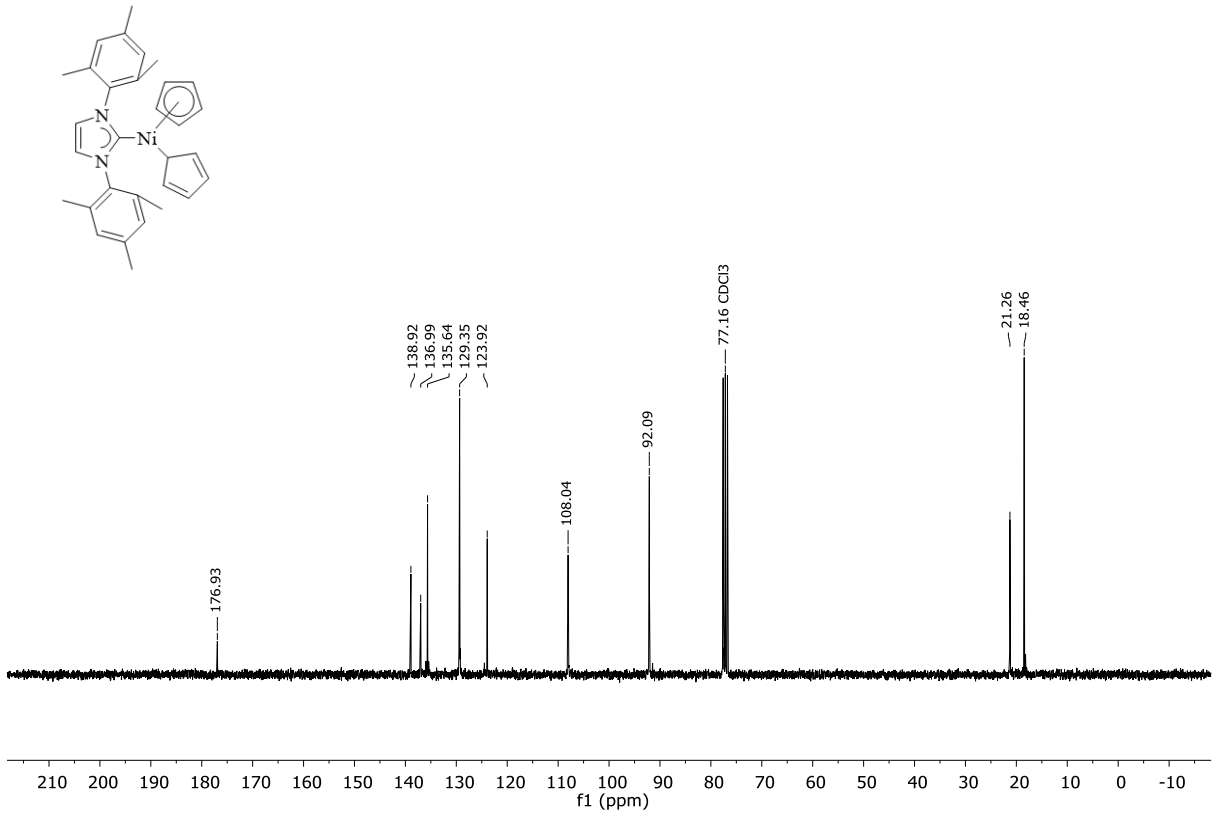


Figure S6. ^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 75 MHz).

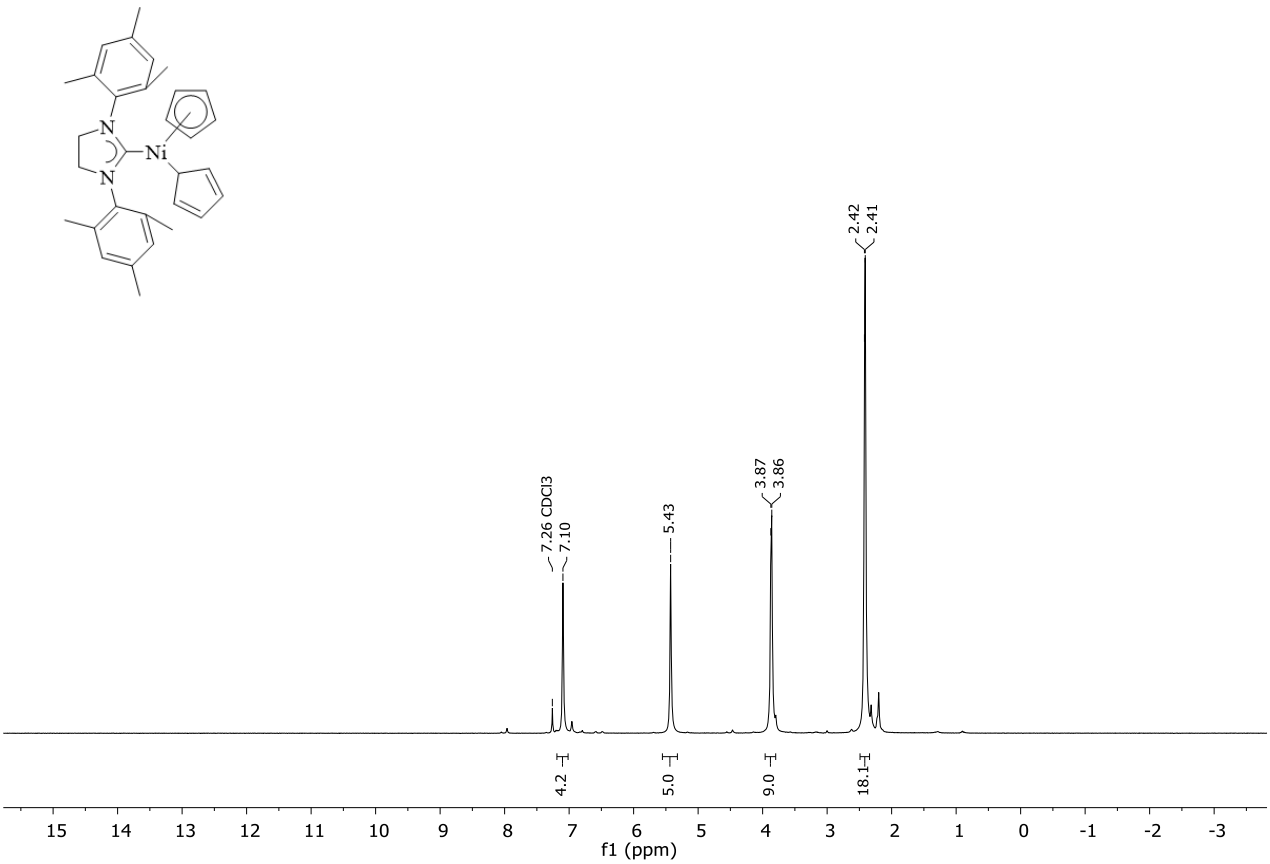


Figure S7. ^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 300 MHz).

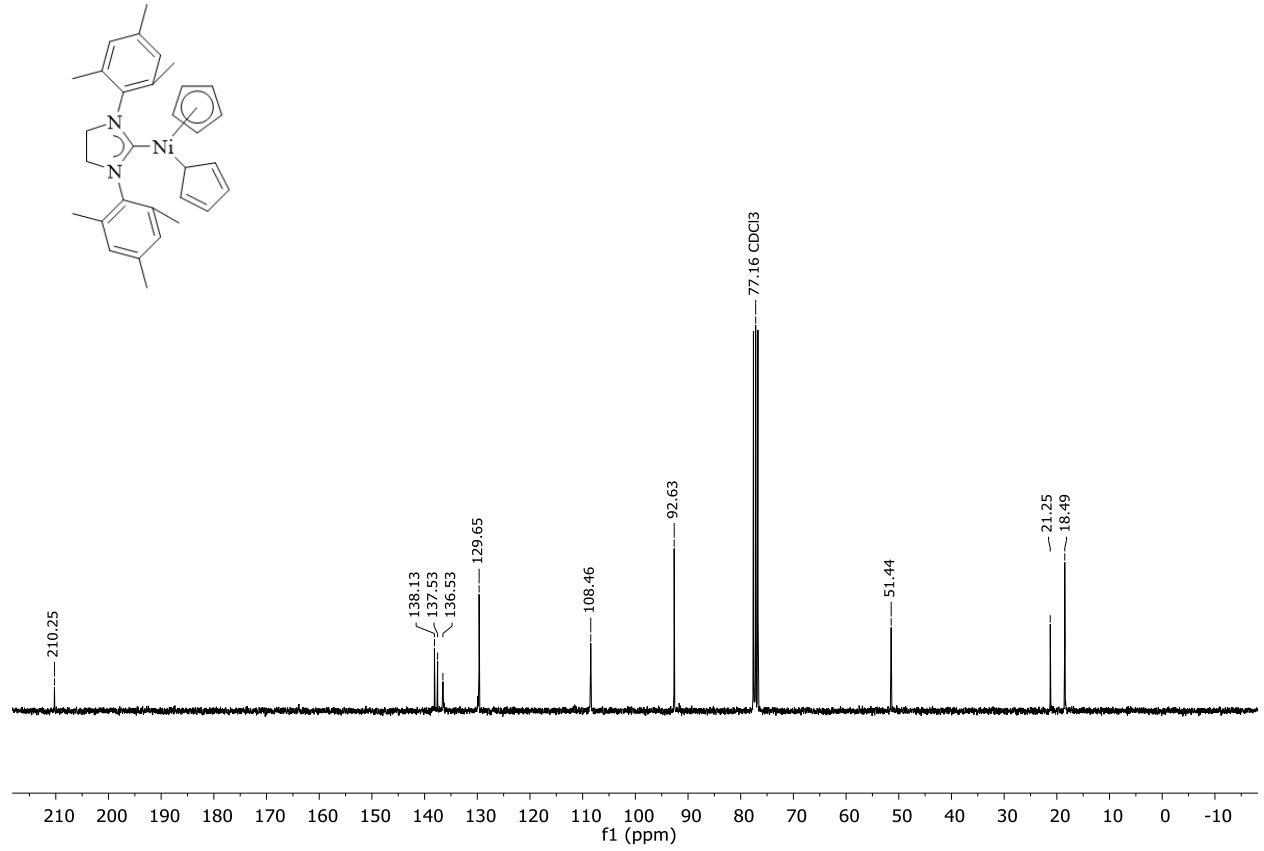


Figure S8. ^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 75 MHz).

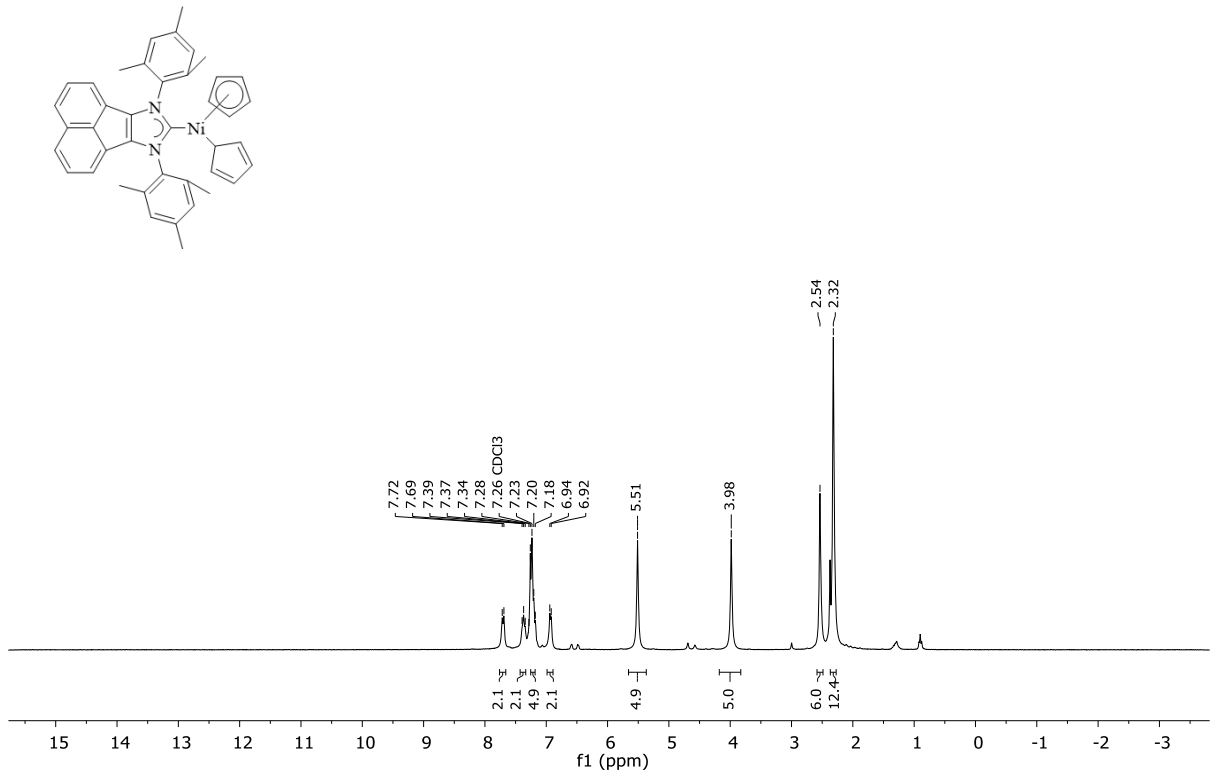


Figure S9. ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 300 MHz).

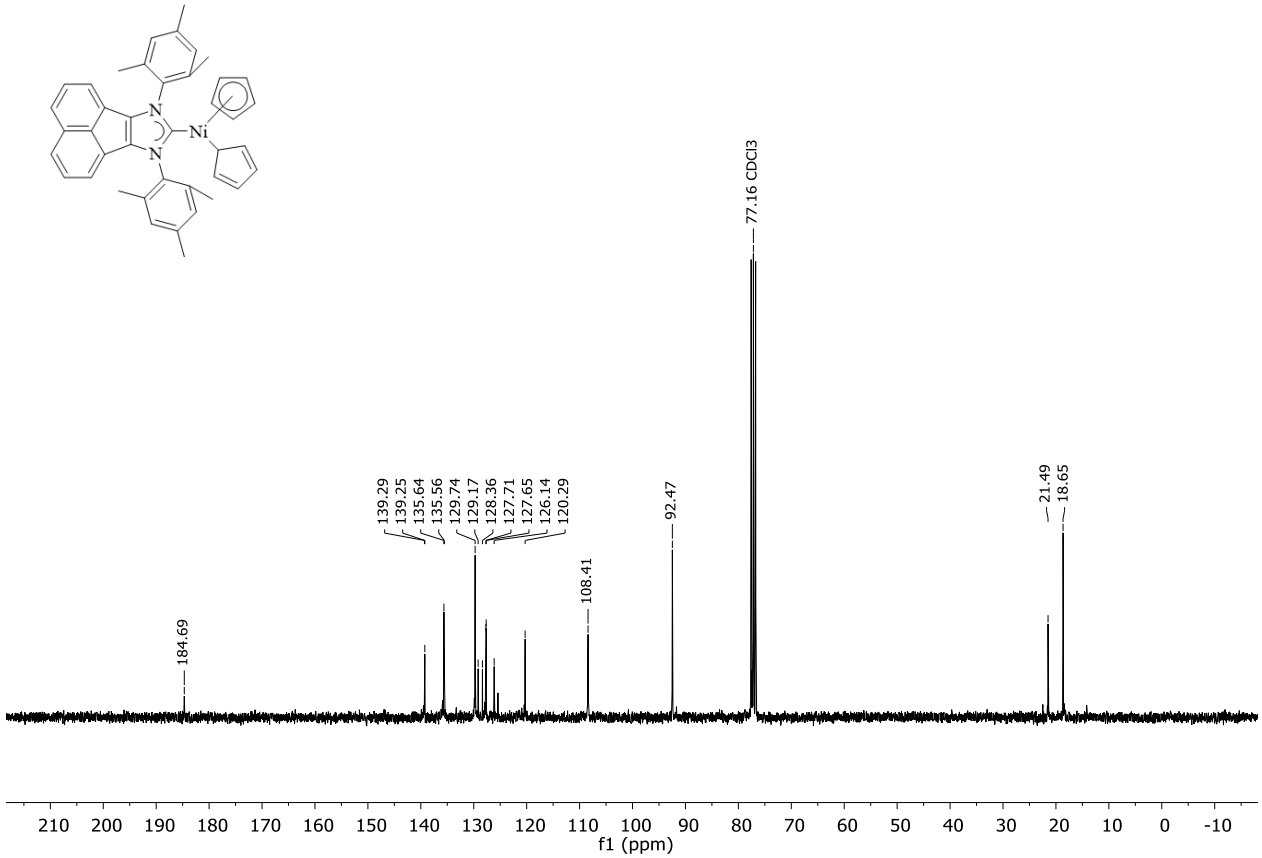


Figure S10. ^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 75 MHz).

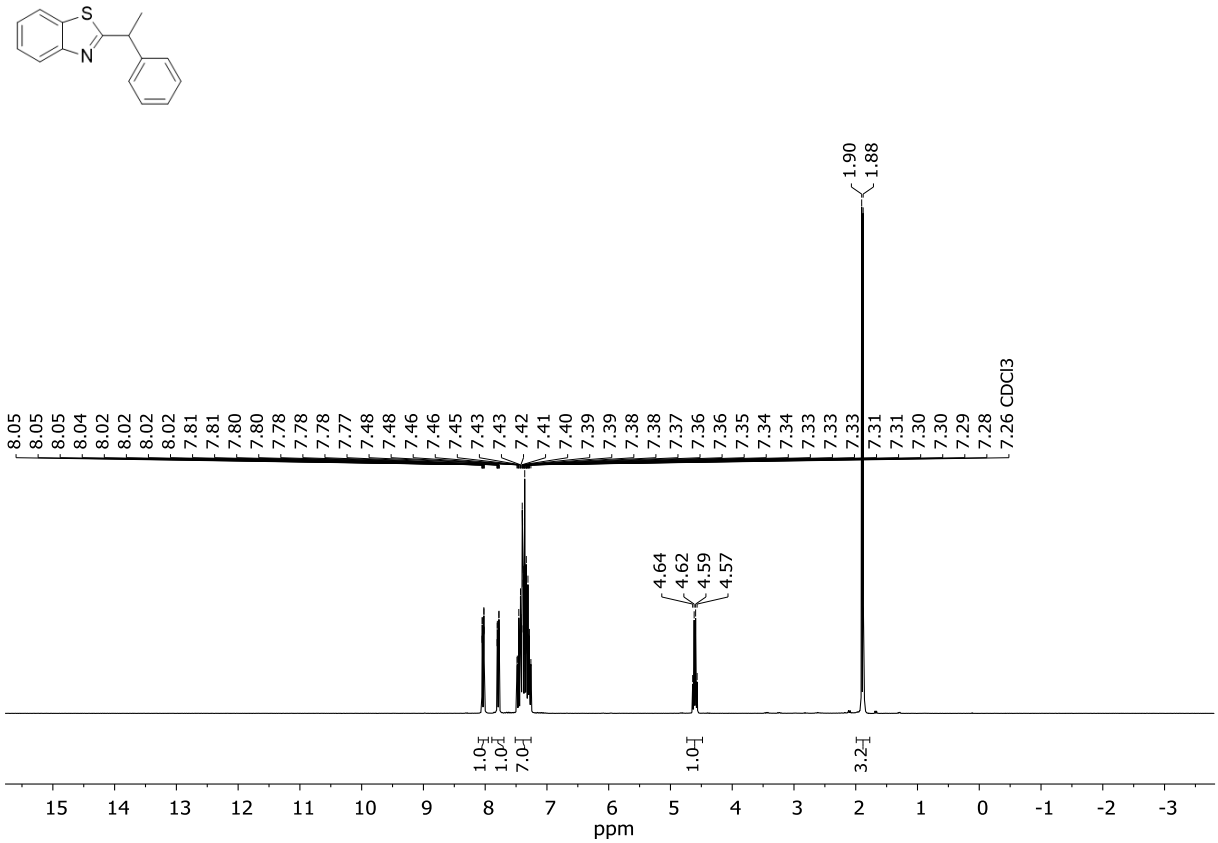


Figure S11. ^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 300 MHz).

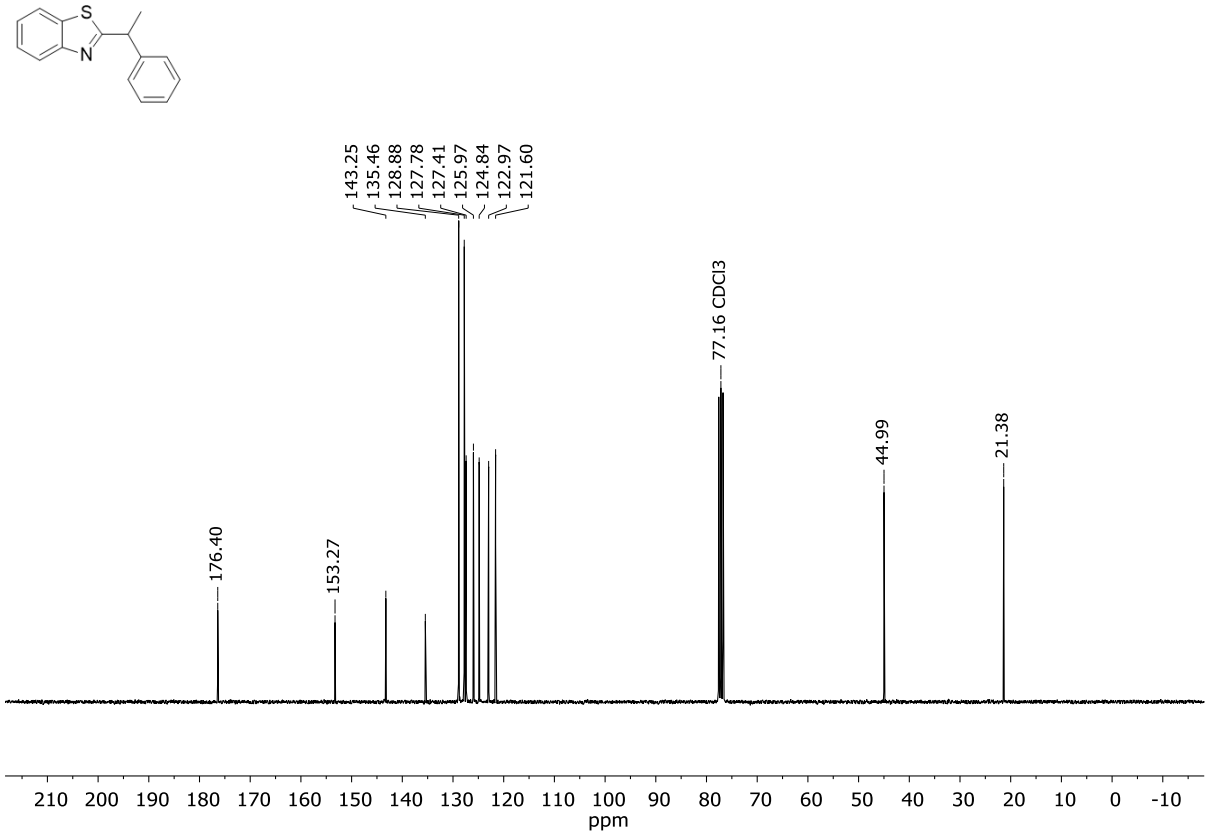


Figure S12. ^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 75 MHz).

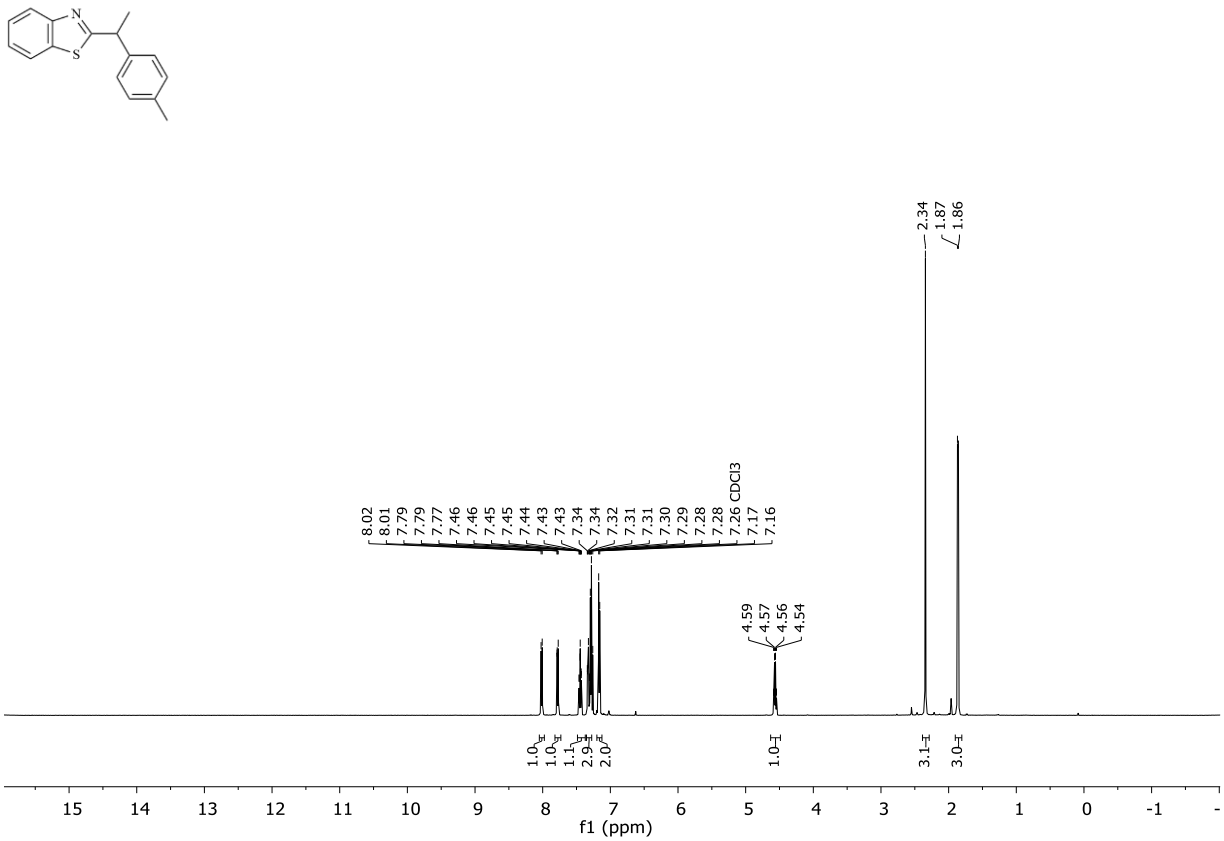


Figure S13. ^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 300 MHz).

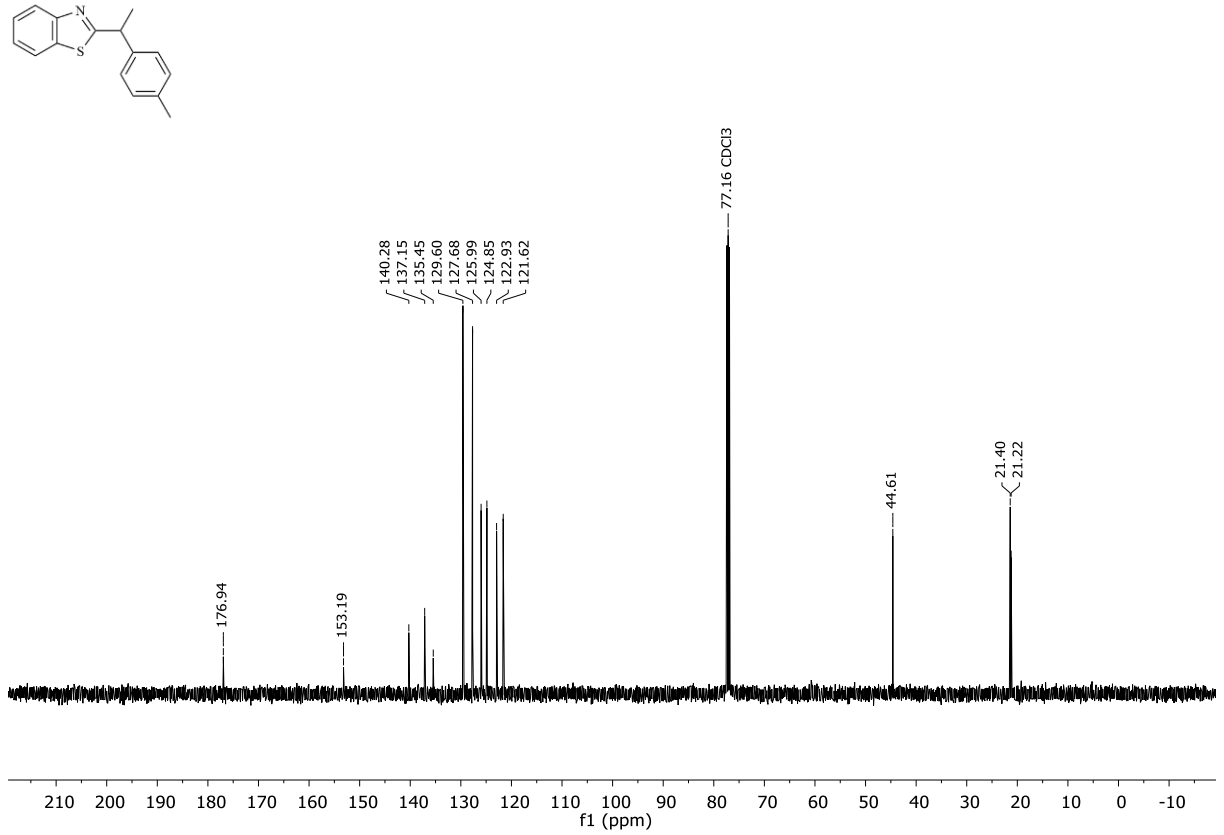
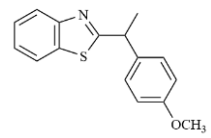


Figure S14. ^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 75 MHz).



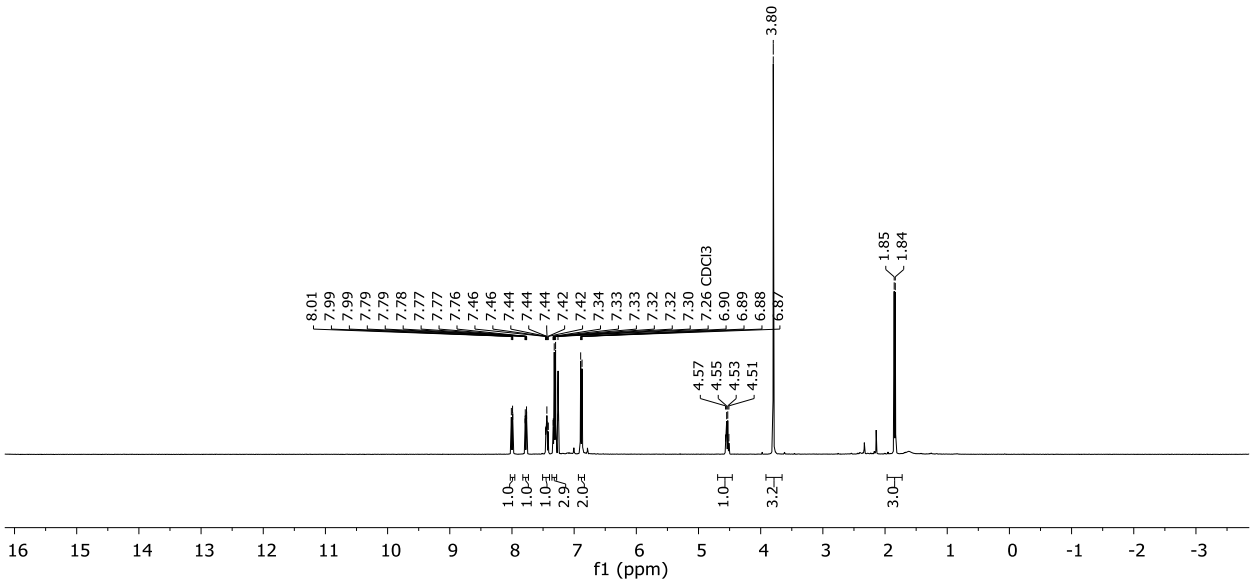
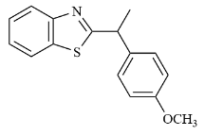


Figure S15. ^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 300 MHz).



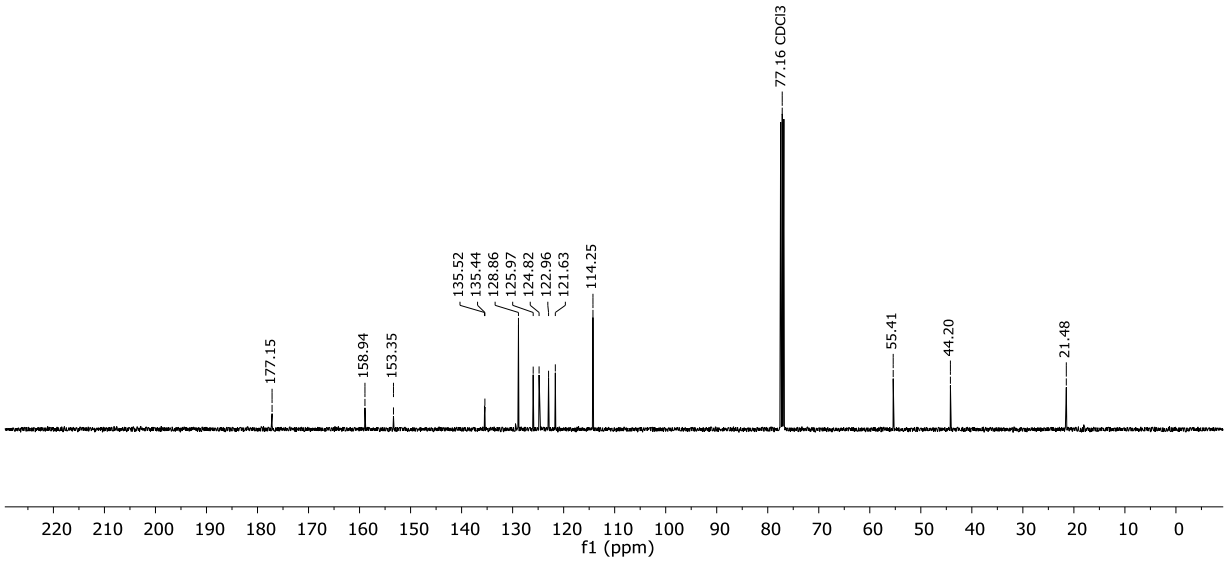
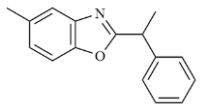


Figure S16. ^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 75 MHz).



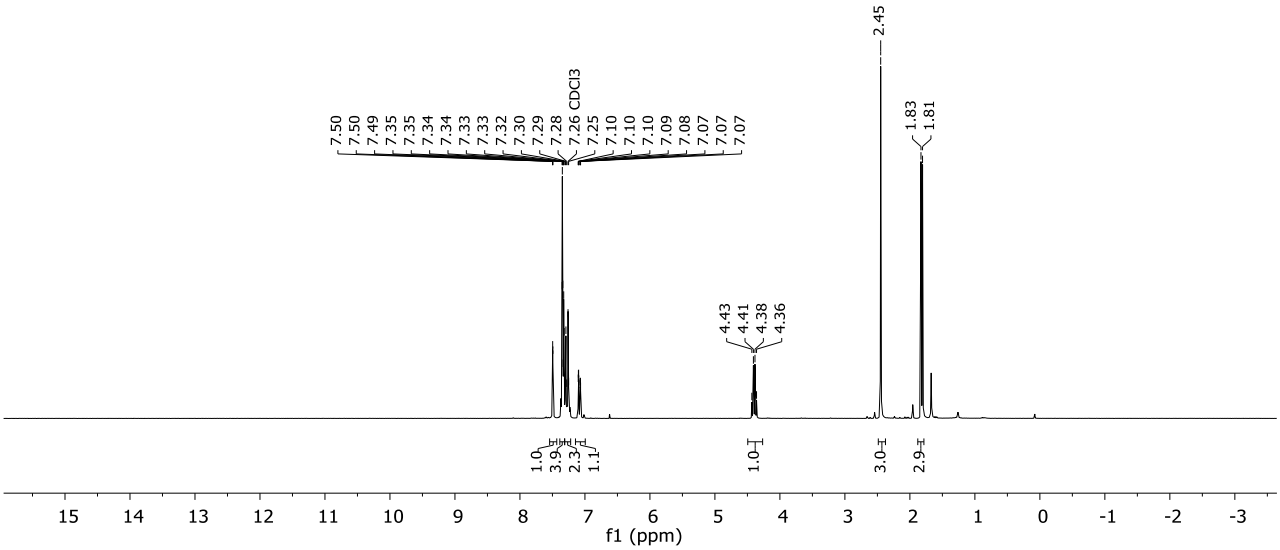
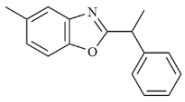


Figure S17. ^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 300 MHz).



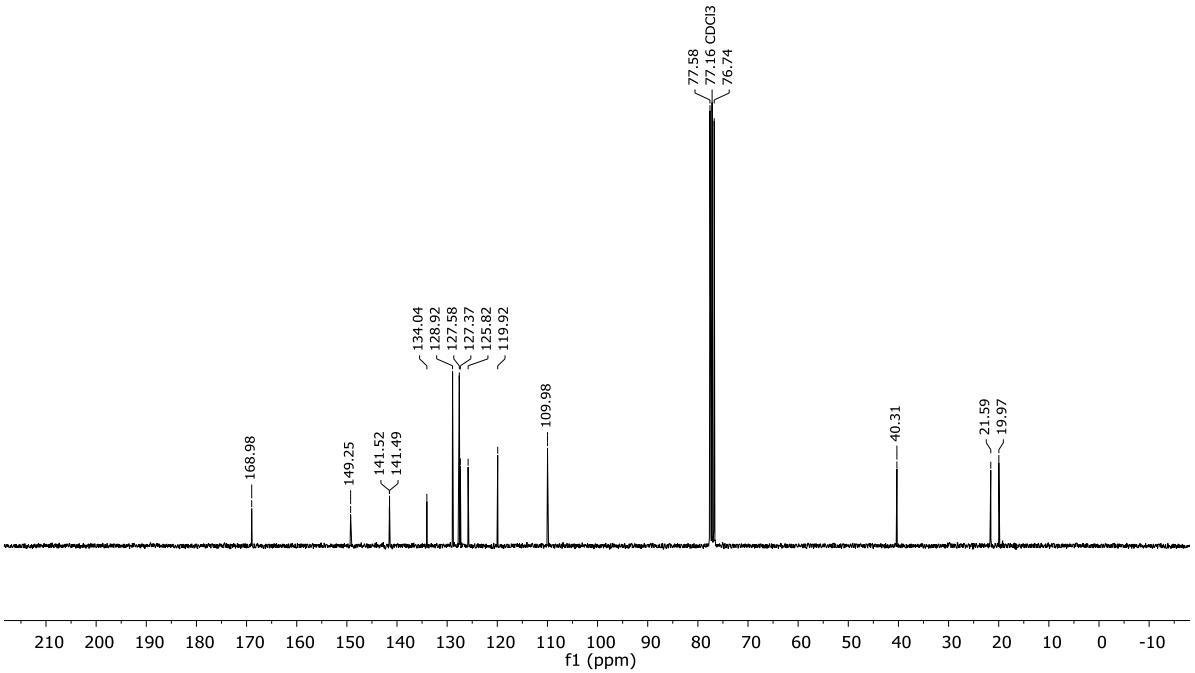


Figure S18. ^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 75 MHz).

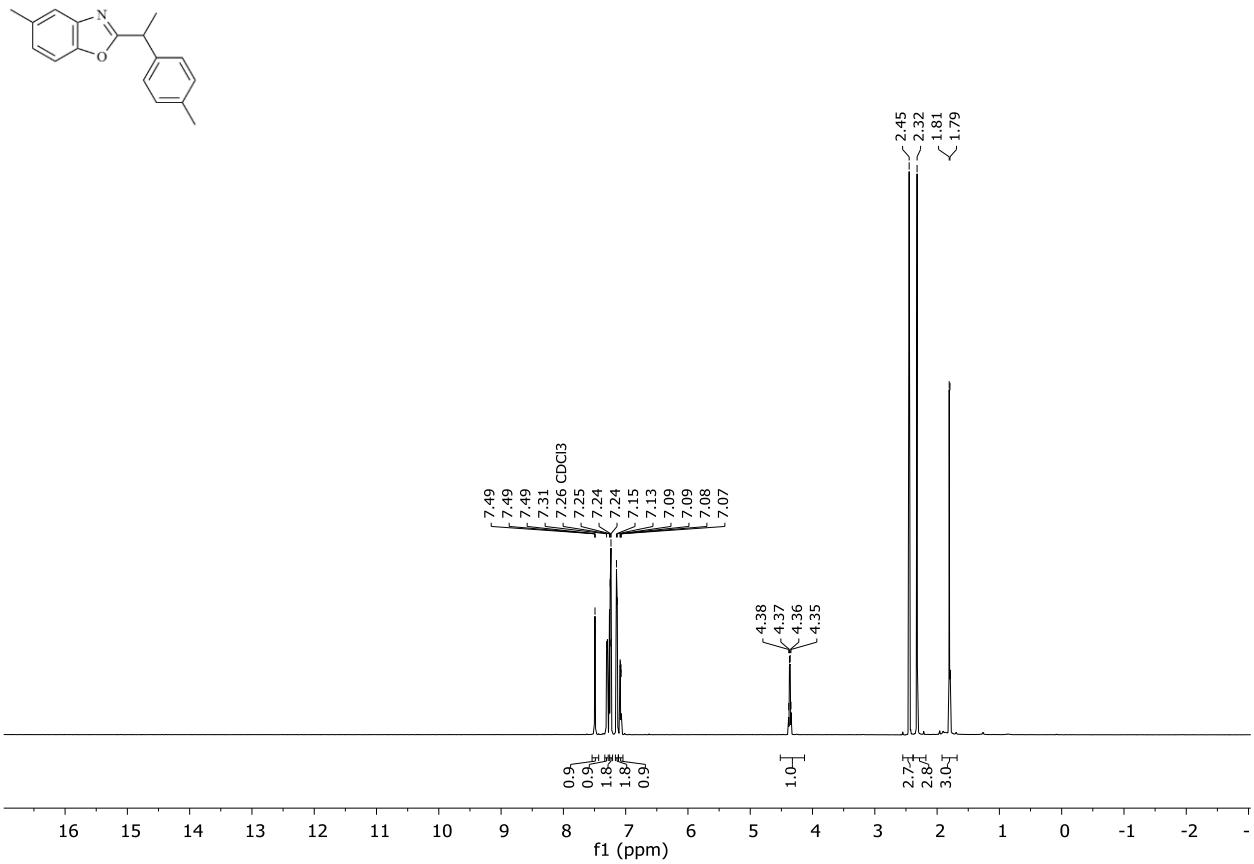


Figure S19. ^{1}H NMR spectrum of compound **5e** ($CDCl_3$, 300 MHz).

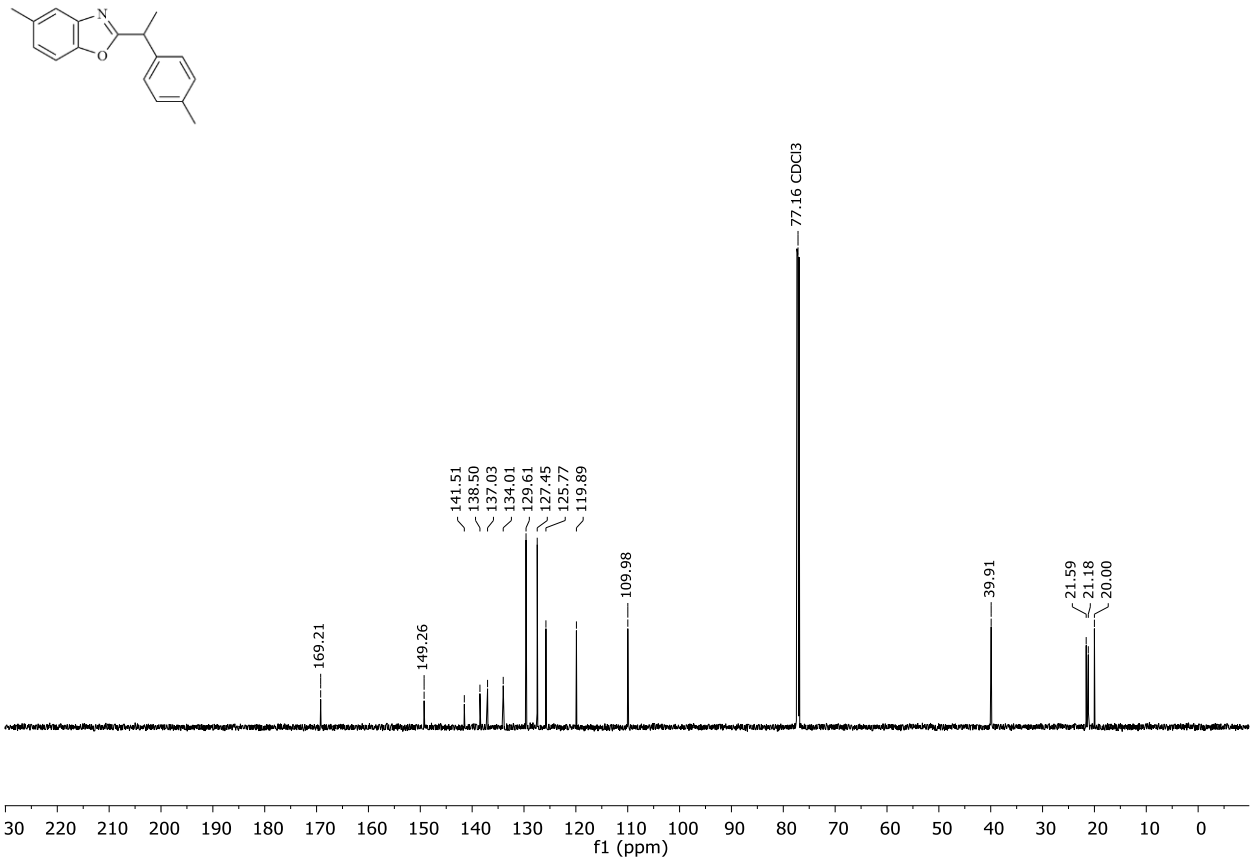


Figure S20. ^{13}C NMR spectrum of compound **5e** ($CDCl_3$, 75 MHz).

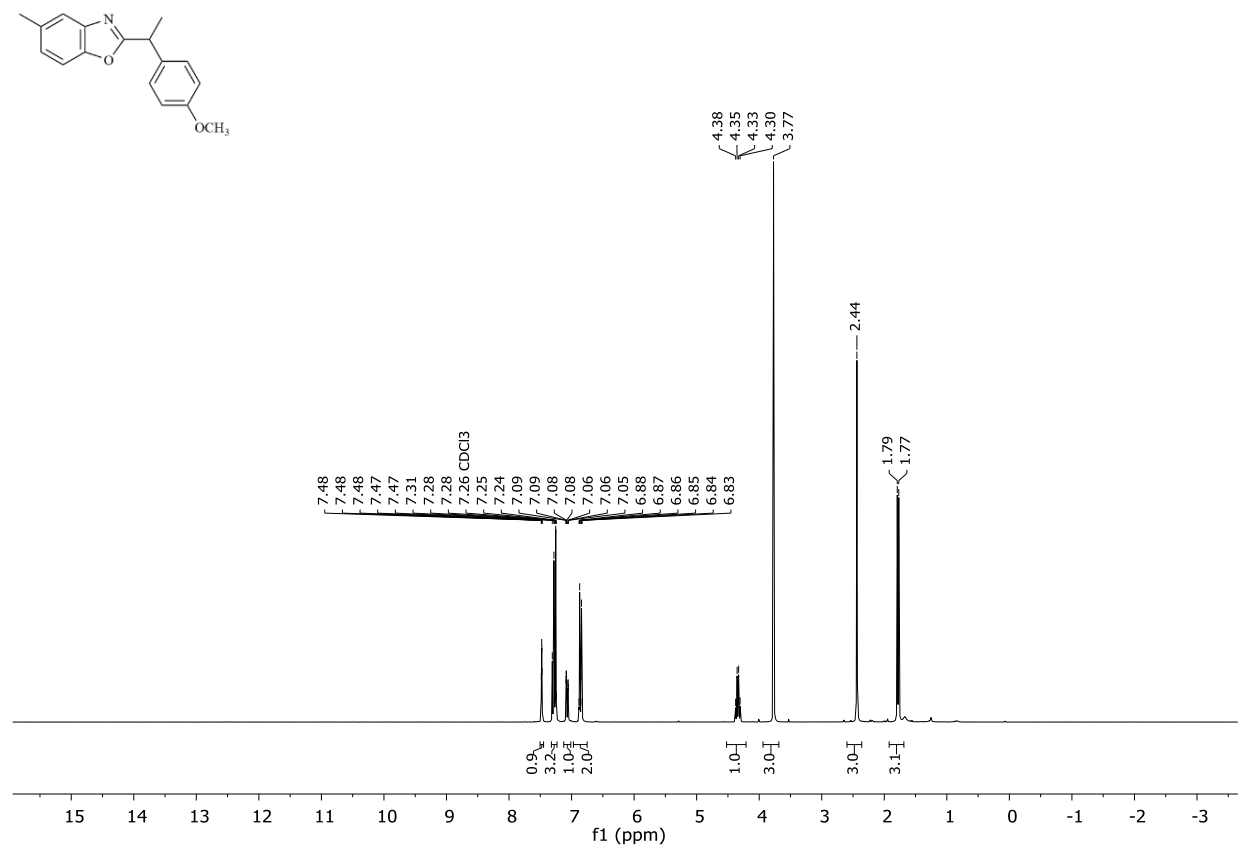


Figure S21. ^{1}H NMR spectrum of compound **5f** ($CDCl_3$, 300 MHz).

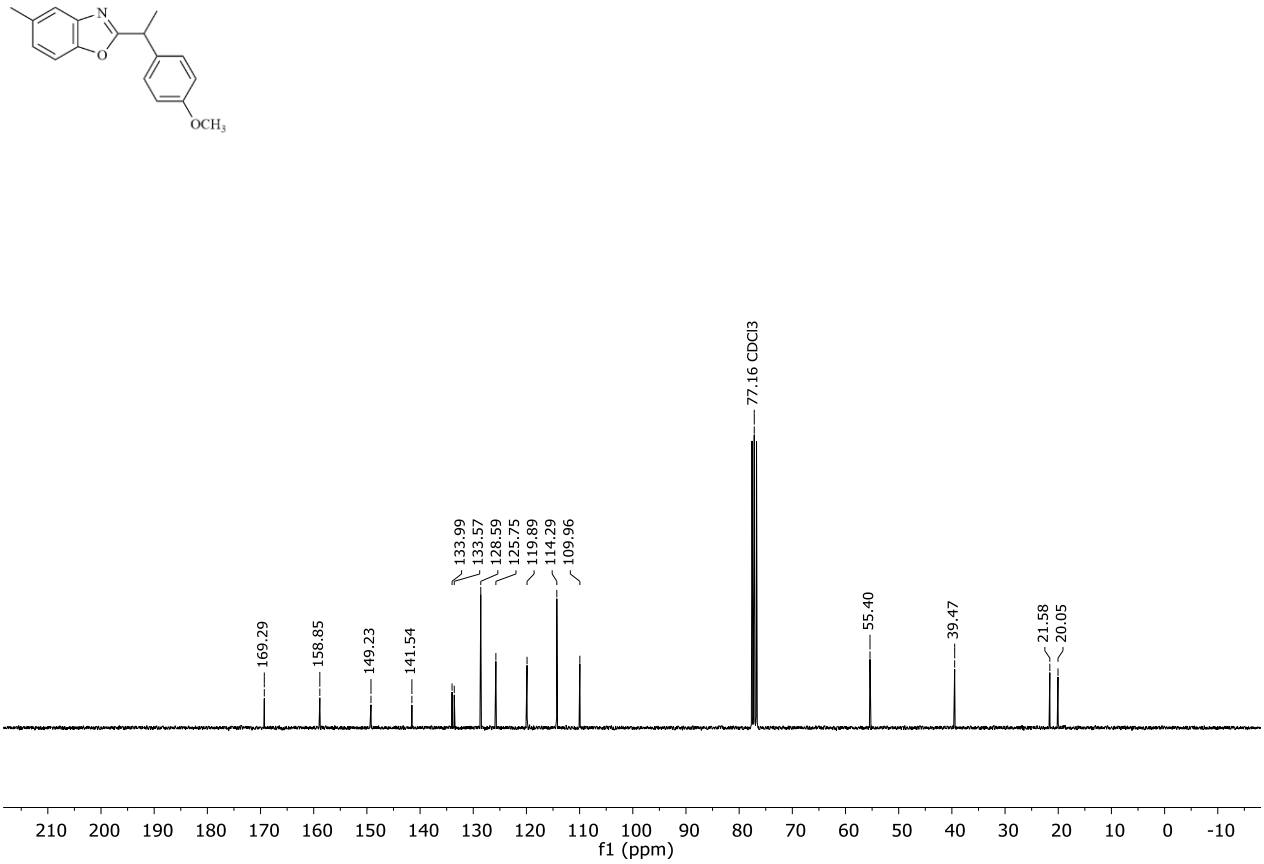


Figure S22. ^{13}C NMR spectrum of compound **5f** ($CDCl_3$, 75 MHz).

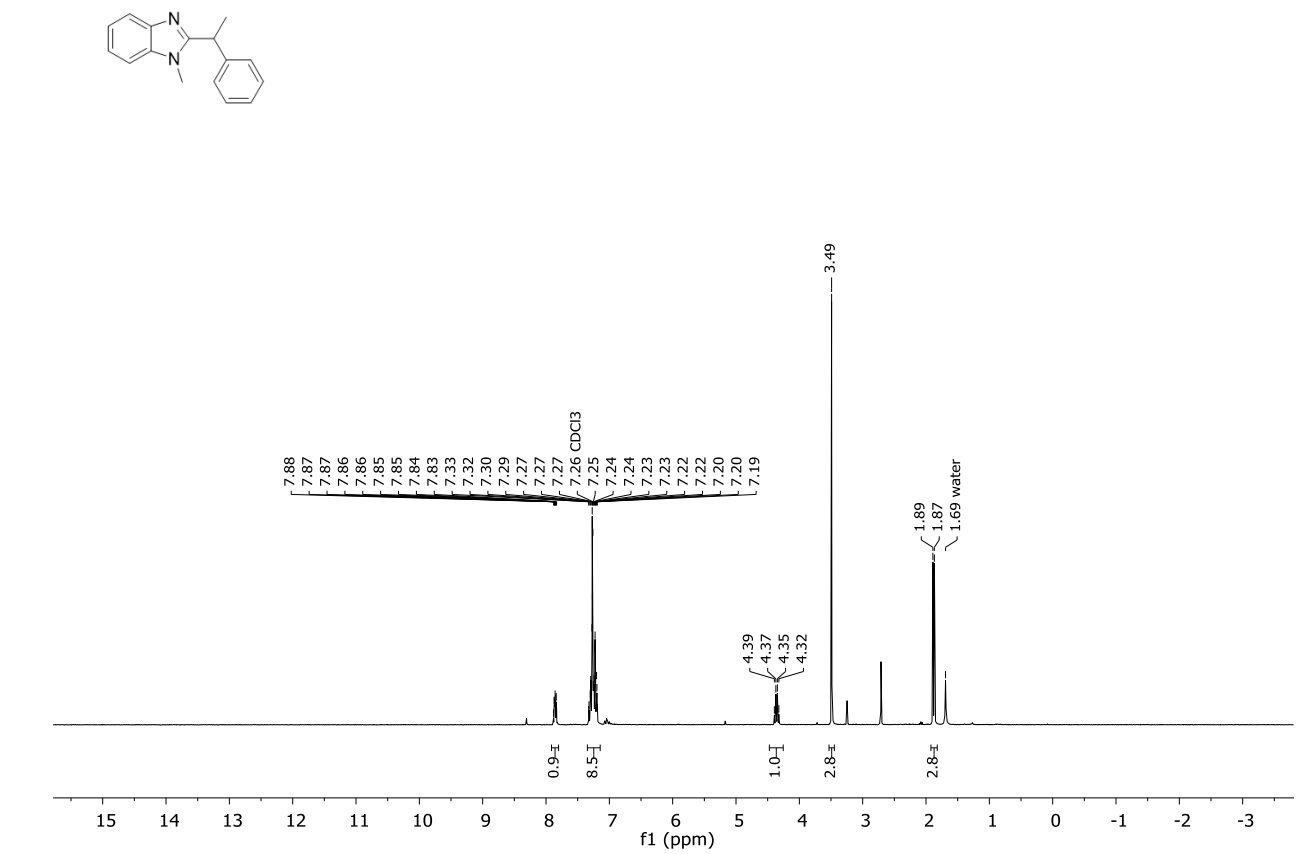


Figure S23. ^{1}H NMR spectrum of compound **5g** ($CDCl_3$, 300 MHz).

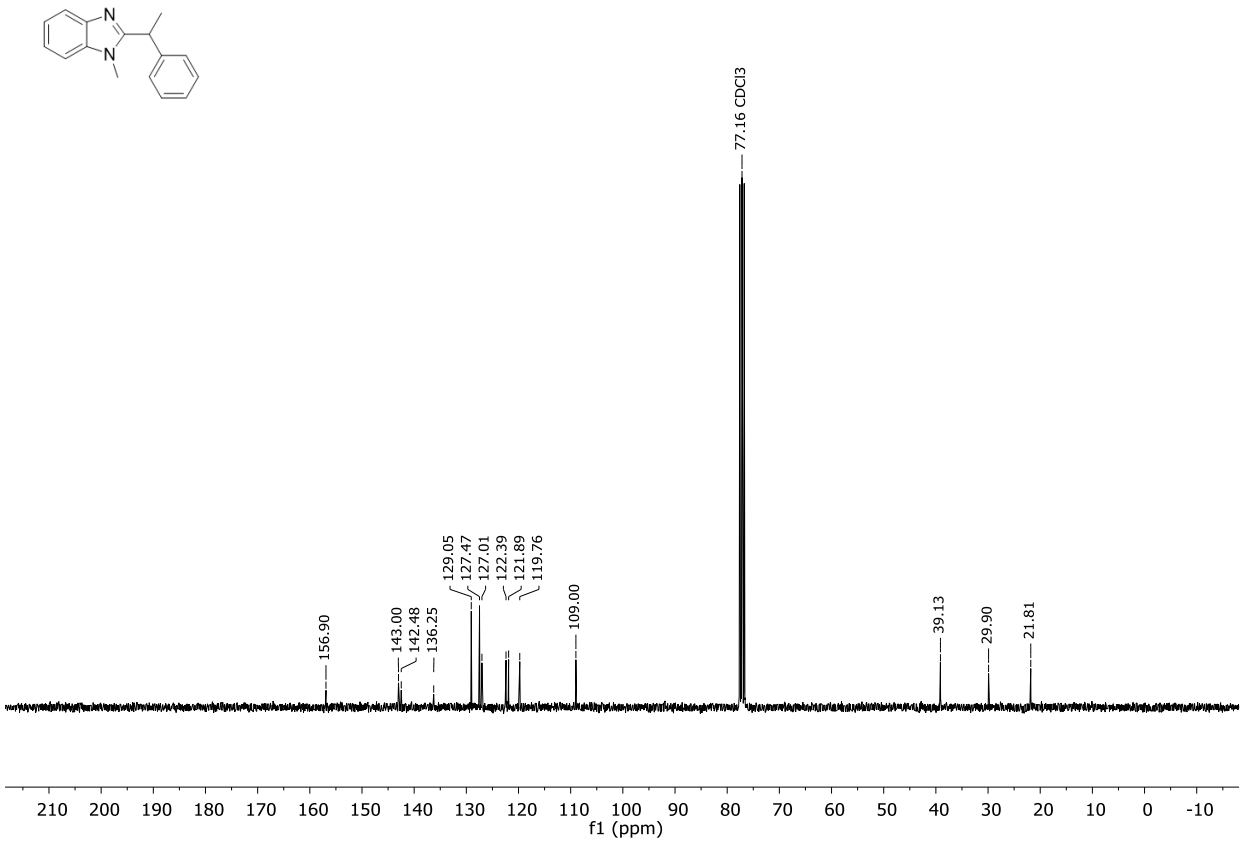


Figure S24. ^{13}C NMR spectrum of compound **5g** ($CDCl_3$, 75 MHz).

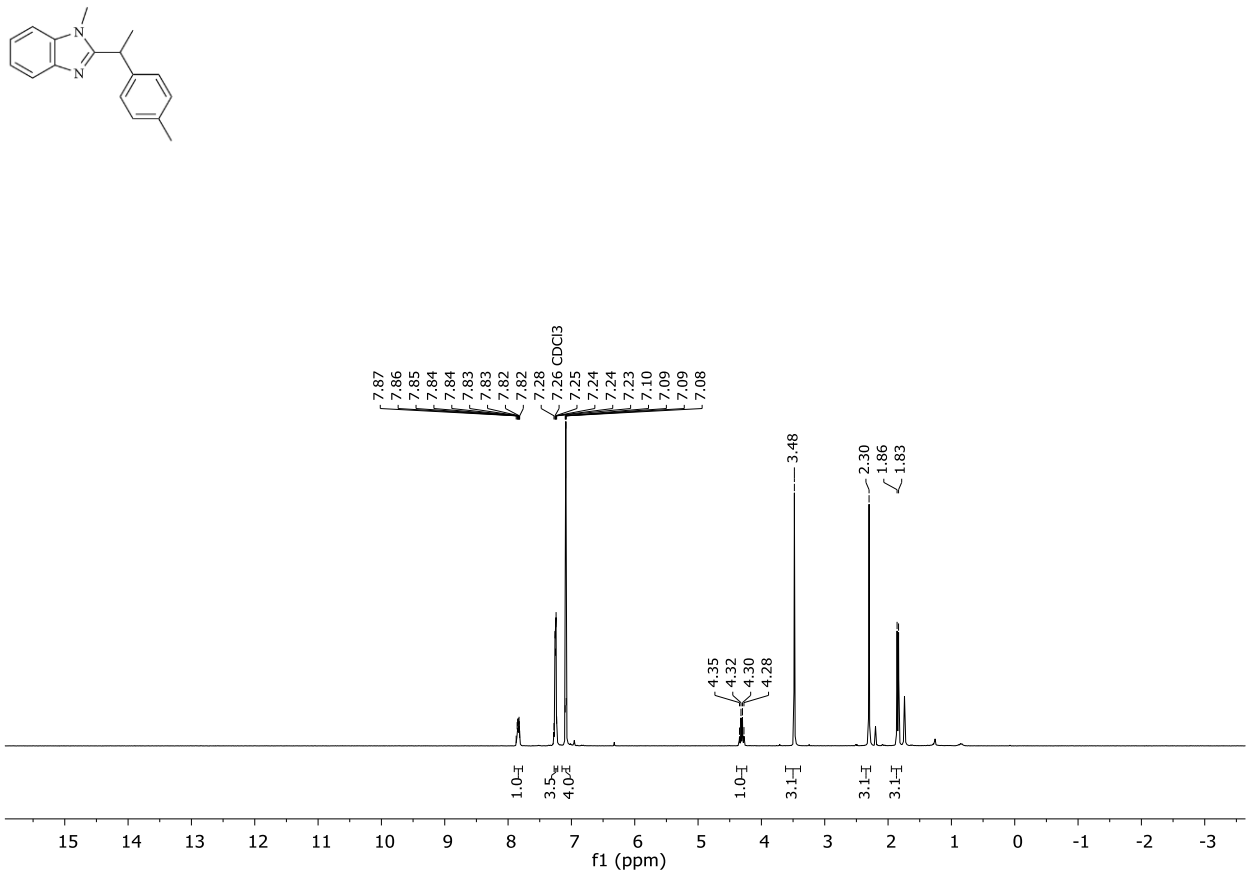


Figure S25. ^{1}H NMR spectrum of compound **5h** ($CDCl_3$, 300 MHz).

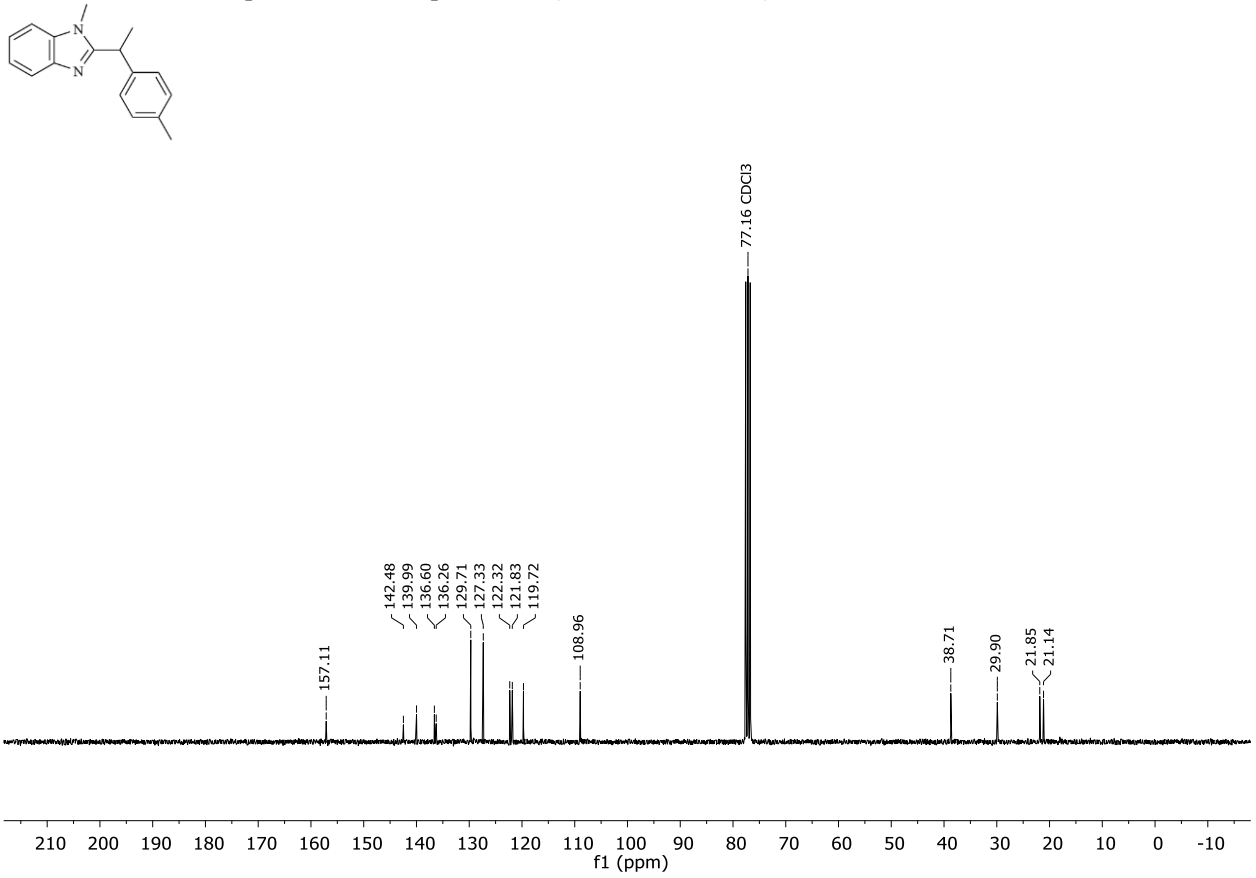


Figure S26. ^{13}C NMR spectrum of compound **5h** ($CDCl_3$, 75 MHz).

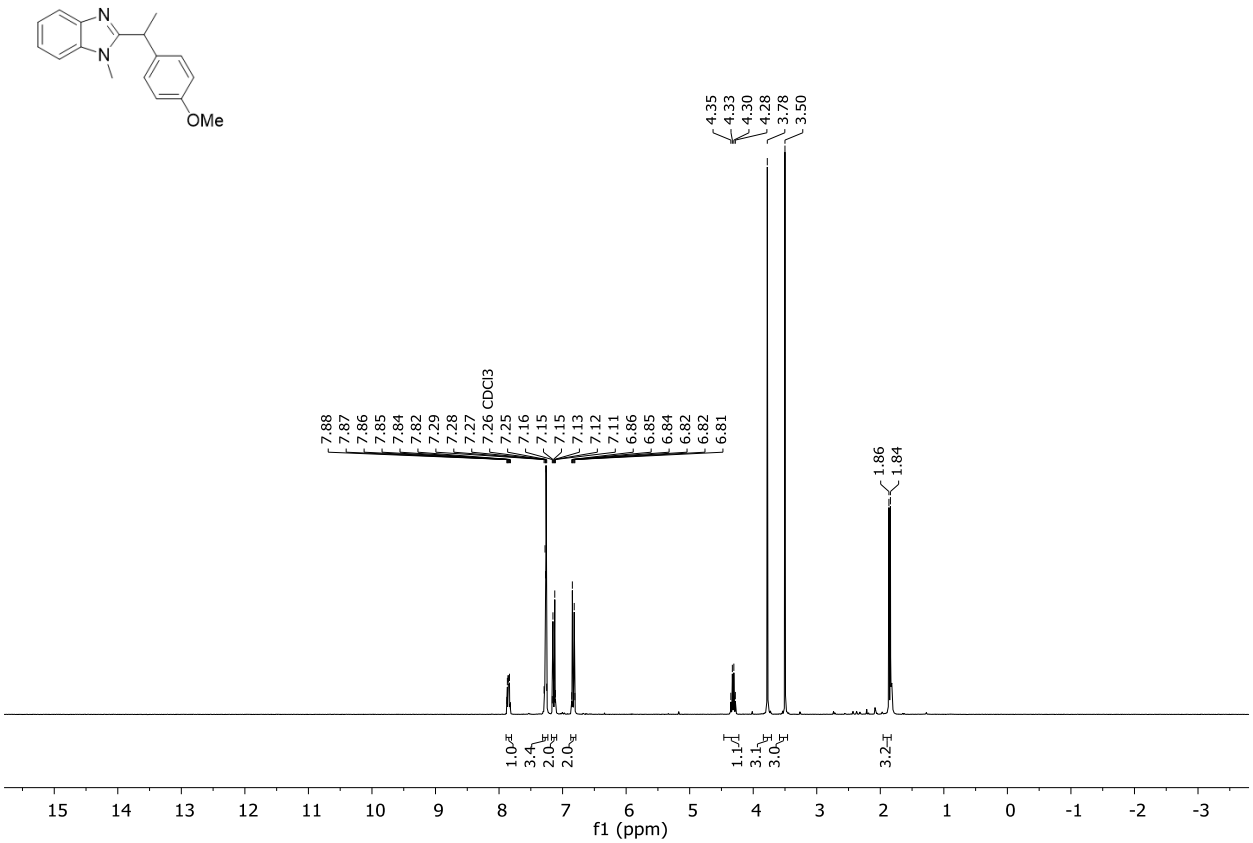


Figure S27. ^{1}H NMR spectrum of compound **5i** ($CDCl_3$, 300 MHz).

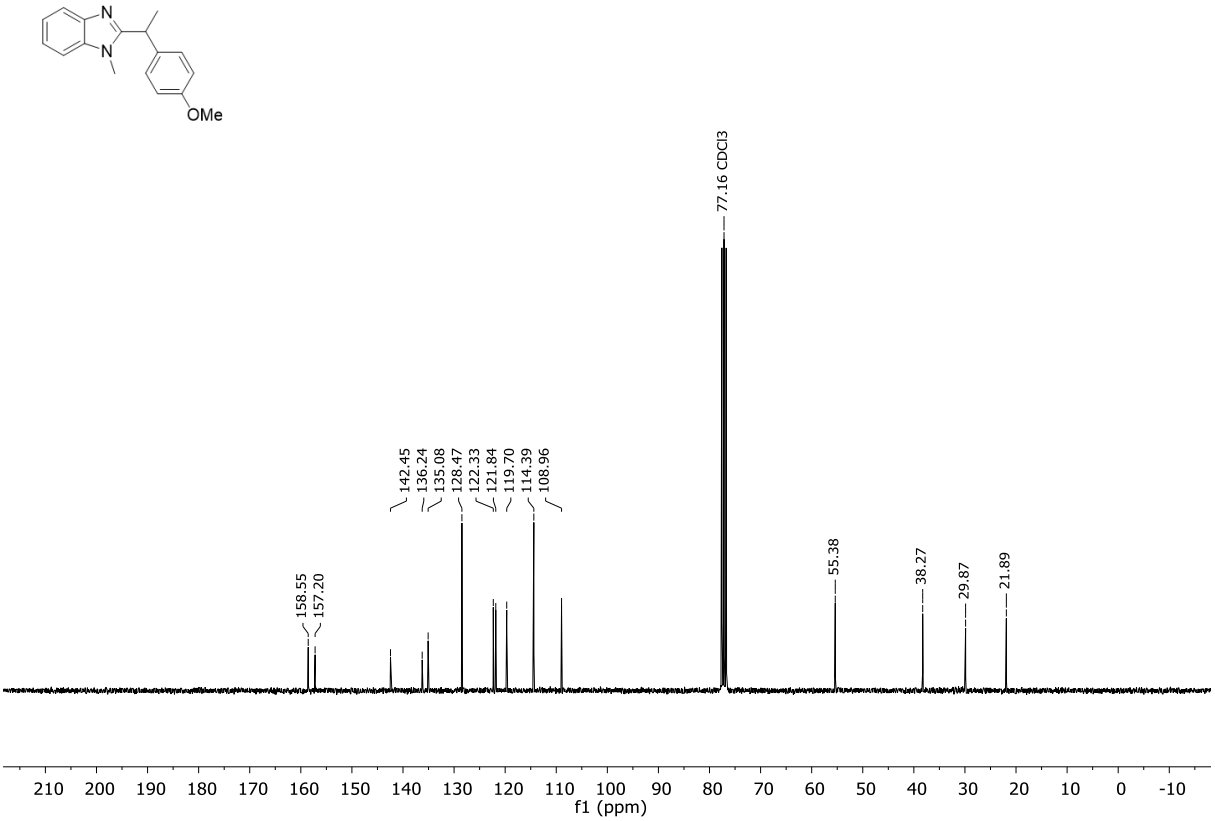


Figure S28. ^{13}C NMR spectrum of compound **5i** ($CDCl_3$, 75 MHz).

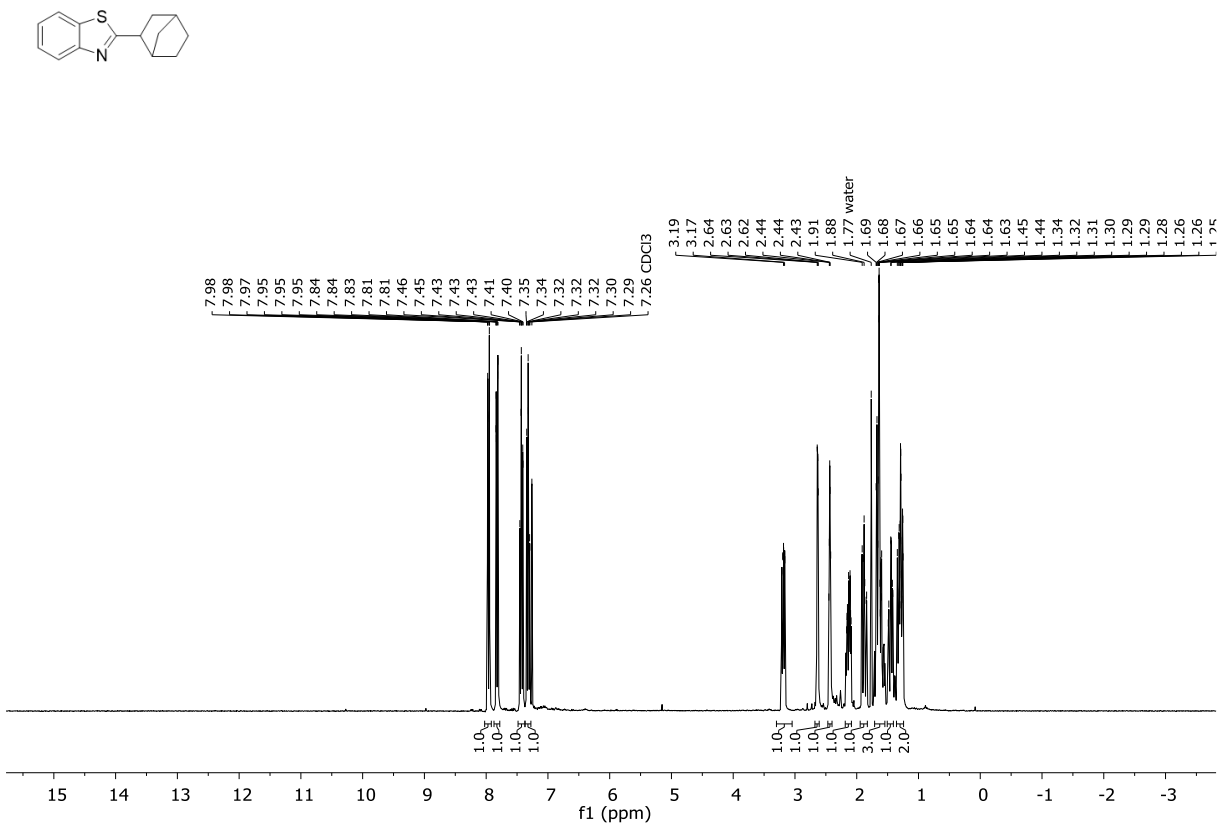


Figure S29. ^{1}H NMR spectrum of compound **5j** ($CDCl_3$, 300 MHz).

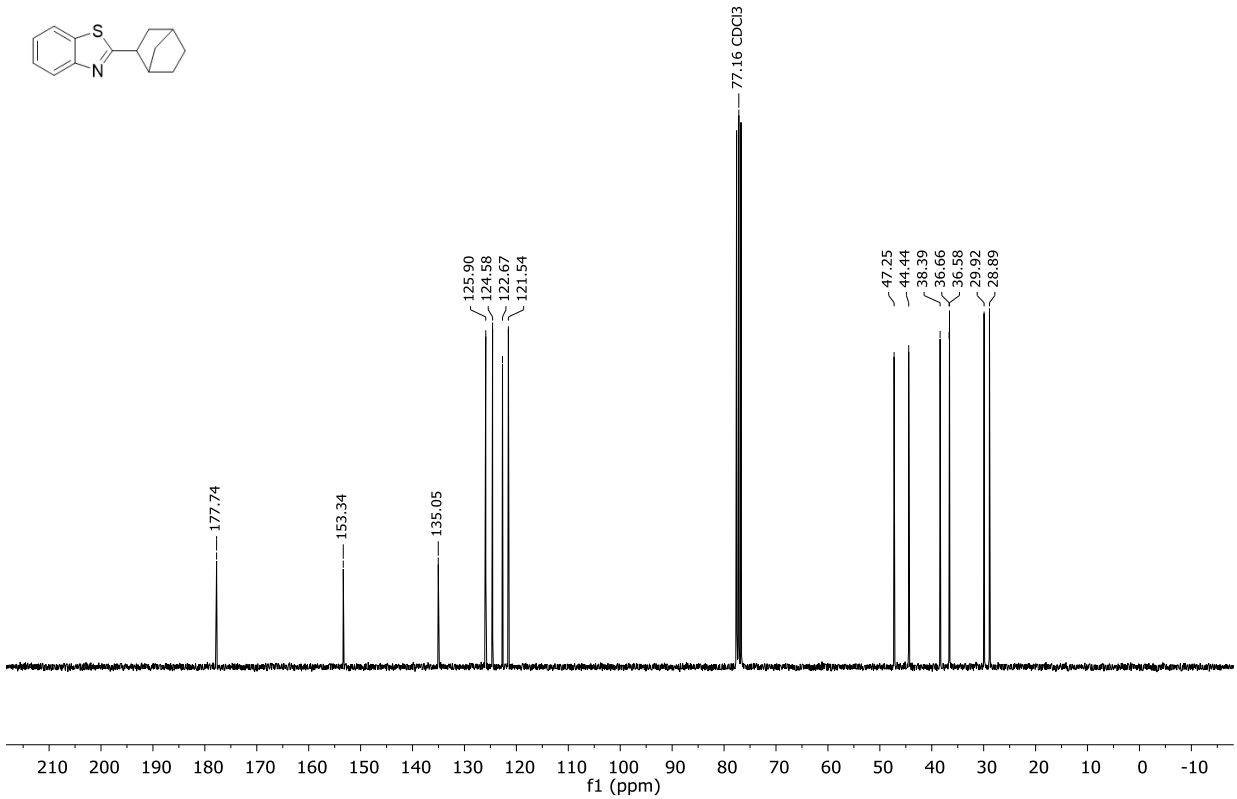
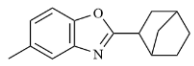


Figure S30. ^{13}C NMR spectrum of compound **5j** ($CDCl_3$, 75 MHz).



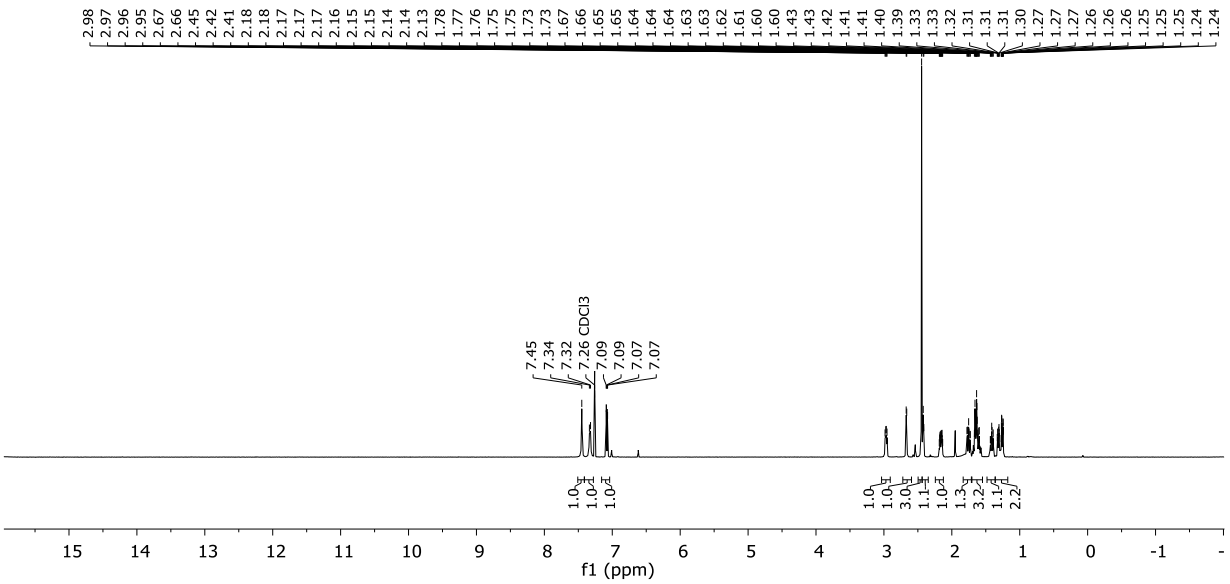
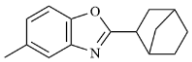


Figure S31. ^{1}H NMR spectrum of compound **5k** ($CDCl_3$, 300 MHz).



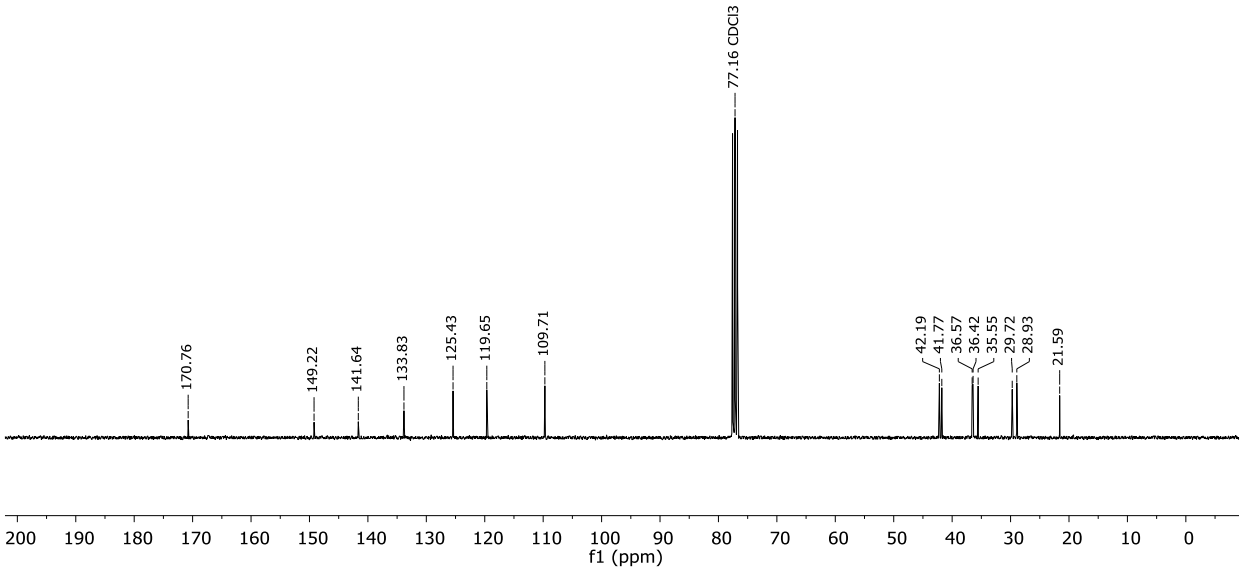


Figure S32. ^{13}C NMR spectrum of compound **5k** ($CDCl_3$, 75 MHz).

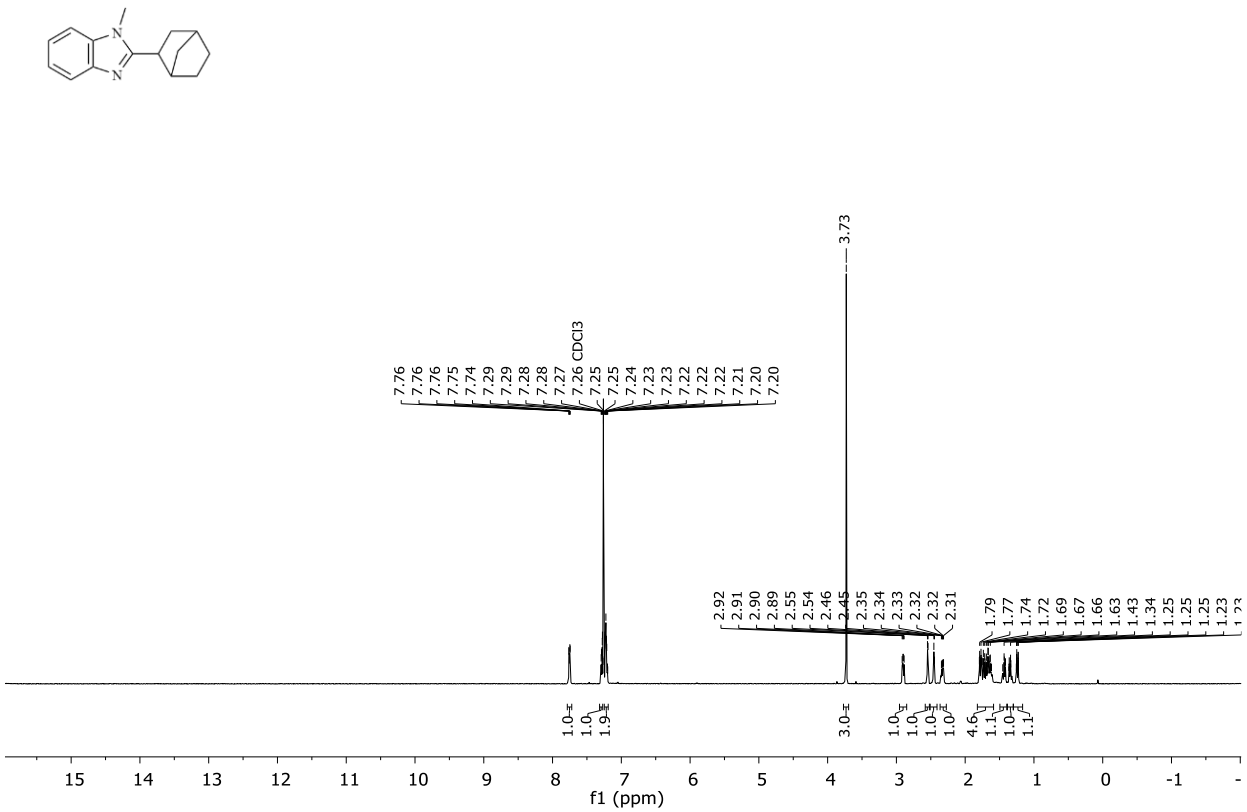


Figure S33. ^{1}H NMR spectrum of compound **5l** ($CDCl_3$, 300 MHz).

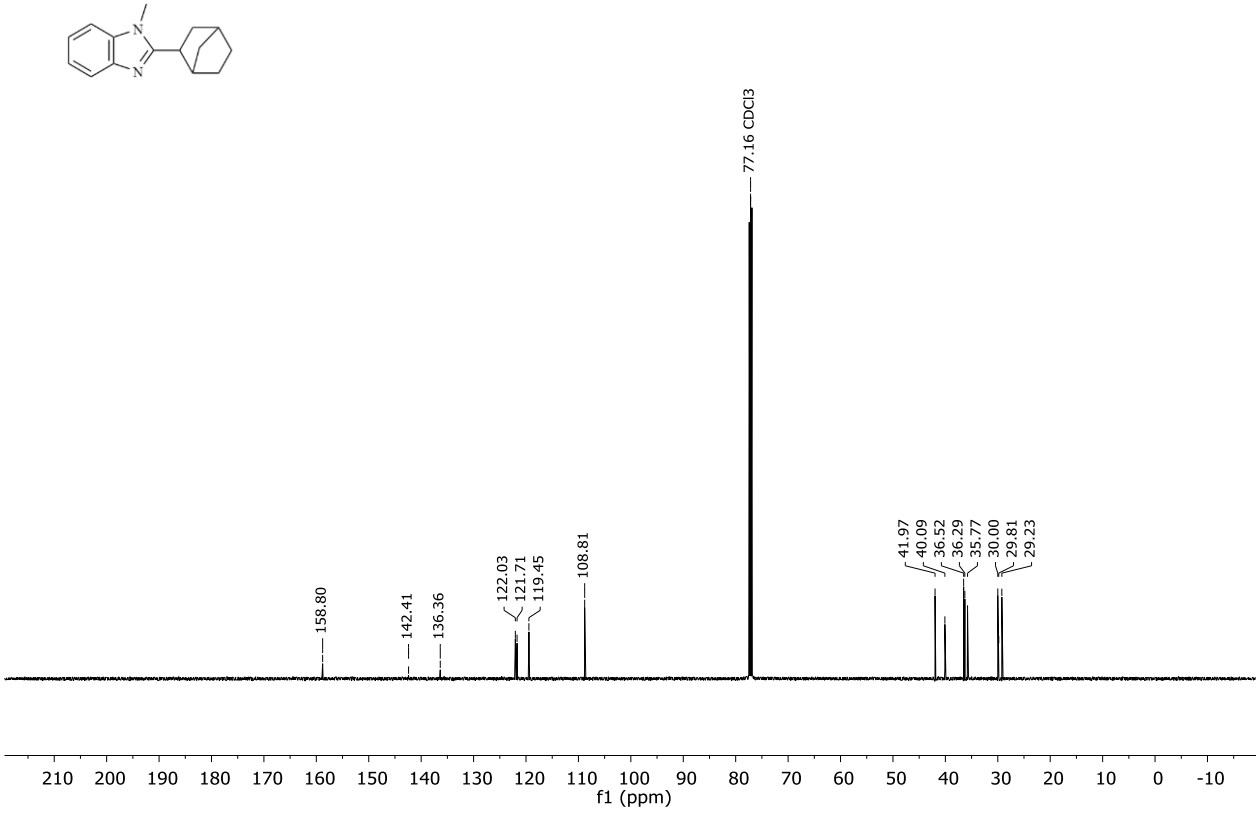


Figure S34. ^{13}C NMR spectrum of compound **5l** ($CDCl_3$, 75 MHz).

S5. References

S1 L. Hintermann, *Beilstein J. Org. Chem.*, 2007, **3**, 22.

S2 A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez and F. Lamaty, *New J. Chem.*, 2017, **41**, 1057.

S3 K. A. Crawford, A. H. Cowley and S. M. Humphrey, *Catal. Sci. Technol.*, 2014, **4**, 1456.

S4 C. D. Abernethy, A.H. Cowley and R. A. Jones, *J. Organomet. Chem.*, 2000, **596**, 3.

S5 E. A. Bielinski, W. Dai, L. M. Guard, N. Hazari and M. K. Takase, *Organometallics*, 2013, **32**, 4025.

S6 O. V. Khazipov, K. E. Shepelenko, D. V. Pasyukov, V. V. Chesnokov, S. B. Soliev, V. M. Chernyshev and V. P. Ananikov, *Org. Chem. Front.*, 2021, **8**, 2515.