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One-pot two step synthesis of unsymmetrically substituted indenes from 3,4-diarylbutadiene sulfones

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Contents

General information.

3,4-Diaryl butadiene sulfones were obtained from corresponding 3-arylbutadiene sulfones by Heck-Matsuda reaction using literature procedure[S1]. $BF_3 \cdot Et_2O$ was purchased from Aldrich. Silica gel chromatography purifications were performed by flash chromatography using EM Science silica gel 60 (230-400 mesh). All other reagents were commercially available and were used without further purification. Analytical methods: All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and High Resolution Mass Spectrometry (HRMS) spectroscopy. Chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a

Bruker "Ascend™ 400" (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F). NOESY NMR spectrum was acquired at 298 K (mixing time value D8 = 800 ms, relaxation time D1 = 1.93 s). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ''s", ''d", "t" or ''m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation ''br" is given for broadened signals. High Resolution Mass Spectrometry spectra were carried out using AB Sciex TripleTOF 5600+ supported TurboV ESI ionization source. FT-IR spectra were obtained in a Bruker "Alpha-T" FTIR (KBr).

General procedure for 3,4-diaryl butadiene sulfone synthesis

An oven-dried screw-cap tube was cooled to room temperature under argon pressure and charged with aryldiazonium salt (1.5 mmol), 3-arylbutadiene sulfone (1 mmol), $Pd(OAc)_2$ (5 mol %) and MeOH (2 ml/mmol). The tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 1 h. The reaction mixture was allowed to cool to room temperature followed by evaporation of the solvent. Then crude was dissolved in 1,4-dioxane (5 ml/mmol), and DBN (0.2 ml/mmol) was added followed by reflux with stirring for 6-24 h. The resulting solution was washed with 10% citric acid, dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel (eluent: from CH_2Cl_2/petroleum ether=1:1 to CH_2Cl_2).

Required 3,4-diarylbutadiene sulfones for the preparation of compounds **1a–i** were synthesized according to the literature procedure.[S1] 3-(3-Chlorophenyl)-4-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide was synthesized for the first time from 3-(3-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide.

3-(3-Chlorophenyl)-4-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide

Yield 294 mg (88%); white solid, m.p. 124-126 °C (from CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 1H, Ar), 7.20 – 7.15 (m, 1H, Ar), 7.12 (t, J = 1.7 Hz, 1H, Ar), 7.04 – 6.94 (m, 3H, Ar), 6.81 – 6.73 (m, 2H, Ar), 4.26 (d, *J* = 8.1 Hz, 2H), 3.78 (s, 3H, OCH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.9, 137.1, 134.8, 132.0, 130.1, 129.9, 128.6, 128.5, 128.3, 126.9, 126.4, 114.3, 61.1, 61.0, 55.4.

HRMS calc. for $C_{17}H_{16}ClO_3S$ $[M+H]^+$ 335.0503; found 335.0506.

General Procedure

3,4-Diarylbutadiene sulfone (1 mmol) was heated in *o*-dichlorobenzene (5 ml/mmol; 10 ml/mmol for methoxy-substituted indenes **1a-d**,**i**,**j**) in a round-bottom flask under inert atmosphere

for 5 hours. After that the reaction mixture was cooled to 65 °C, and $BF_3 \cdot Et_2O$ (0.2 mmol) was added. The mixture was stirred for 2 hours at 65 °C, allowed to cool to room temperature, quenched with methanol (2 ml), and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: CH_2Cl_2/hexane = from 3:1 to 1:1 by volume).

*6-Methoxy-3-methyl-2-(4-nitrophenyl)-1H-indene (**1a**)*

Yield 219 mg (78%); orange solid, m.p. 155-157 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.1 Hz, 2H, Ar), 7.60 (d, *J* = 9.1 Hz, 2H, Ar), 7.34 (d, *J* = 8.3 Hz, 1H, Ar indene), 7.09 (d, *J* = 2.3 Hz, 1H), 6.93 (dd, *J* = 8.3, 2.2 Hz, 1H, Ar indene), 3.87 (s, 3H, OCH_3), 3.78 (s, 2H, CH_2), 2.38 (s, 3H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 145.8, 144.5, 144.5, 140.1, 139.0, 135.7, 128.3, 123.9, 120.6, 112.6, 110.1, 55.7, 40.6, 12.7.

HRMS calc. for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.1130; found 282.1128.

FT-IR (KBr, cm^{-1}): 2968, 2918, 2832, 1728, 1589, 1562, 1503, 1460, 1340, 1255, 1236, 1125, 1063, 1024, 892, 850, 750, 691.

*6-Methoxy-3-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indene (**1b**)*

Yield 237 mg (78%); beige solid, m.p. 100-102 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H, Ar), 7.55 (d, *J* = 8.1 Hz, 2H, Ar), 7.30 (d, *J* = 8.3 Hz, 1H, Ar indene), 7.09 (d, *J* = 2.5 Hz, 1H, Ar indene), 6.92 (dd, *J* = 8.3, 2.3 Hz, 1H, Ar indene), 3.86 (s, 3H, OCH_3), 3.73 (q, *J* = 2.3 Hz, 1H, CH_2), 2.31 (t, *J* = 2.1 Hz, 3H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 144.4, 141.5 – 141.2 (m), 140.4, 136.7, 136.6, 128.2 (q, *J* = 32.4 Hz), 128.2, 125.4 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 271.7 Hz), 120.1, 112.3, 110.1, 55.7, 40.8, 12.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.31.

HRMS calc. for $C_{18}H_{15}F_3O$ $[M]^+$ 304.1075; found 304.1069.

FT-IR (KBr, cm^{-1}): 2936, 2918, 2896, 2837, 2360, 1559, 1589, 1483, 1460, 1434, 1411, 1332, 1291, 1231, 1168, 1115, 1074, 1024, 864, 833, 807, 597.

*2-(4-Chlorophenyl)-6-methoxy-3-methyl-1H-indene (**1c**)*

Yield 181 mg (67%); beige solid, m.p. 82-84 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H, Ar), 7.24 (s, 1H, Ar indene), 7.05 (d, *J* = 2.2 Hz, 1H, Ar indene), 6.88 (dd, *J* = 8.3, 2.2 Hz, 1H, Ar indene), 3.84 (s, 3H, OCH_3), 3.65 (q, *J* = 2.3 Hz, 2H, CH_2), 2.26 (t, *J* = 2.1 Hz, 3H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 144.2, 140.7, 136.9, 136.3, 135.2, 132.2, 129.4, 128.7, 119.8, 112.2, 110.2, 55.8, 40.9, 12.3.

HRMS calc. for $C_{17}H_{16}ClO$ $[M+H]^+$ 271.0890; found 271.0885.

FT-IR (KBr, cm^{-1}): 2960, 2939, 2910, 2834, 2360, 1604, 1575, 1484, 1451, 1399, 1379, 1339, 1287, 1227, 1145, 1108, 1091, 1070, 1026, 926, 825, 718, 429.

*2-(4-tert-Butylphenyl)-6-methoxy-3-methyl-1H-indene (**1d**)*

Yield 222 mg (76%); white solid, m.p. 75-77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H, Ar), 7.26 (d, *J* = 8.2 Hz, 1H, Ar indene overlapping with residual $CHCl_3$), 7.08 (d, J = 2.3 Hz, 1H, Ar indene), 6.89 (dd, *J* = 8.2 Hz, 2.3 Hz, 2H, Ar indene), 3.86 (s, 3H, OCH_3), 3.71 (q, *J* = 2.0 Hz, 2H, CH_2), 2.30 (t, *J* = 1.9 Hz, 3H, CH_3), 1.36 (s, 9H, $C(CH_3)_3$).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.1, 149.4, 144.3, 141.2, 138.1, 135.0, 134.0, 127.9, 125.4, 119.4, 112.0, 110.1, 55.8, 40.9, 34.7, 31.4, 12.3.

HRMS calc. for $C_{21}H_{25}O$ $[M+H]^+$ 293.1905; found 293.1903.

FT-IR (KBr, cm^{-1}): 2953, 2902, 2864, 2831, 1606, 1577, 1509, 1484, 1480, 1450, 1347, 1289, 1229, 1142, 1148, 1110, 1068, 1027, 918, 574.

*3,6-Dimethyl-2-(4-nitrophenyl)-1H-indene (**1e**)*

Yield 212 mg (80%); yellow solid, m.p. 131-133 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.17 (m, 2H, Ar), 7.66 – 7.56 (m, 2H, Ar), 7.33 (m, 2H, Ar indene), 7.19 (d, *J* = 7.9 Hz, 1H, Ar indene), 3.75 (q, *J* = 2.2 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.37 (t, *J* = 2.0 Hz, 3H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.0, 144.6, 144.4, 142.9, 139.1, 136.9, 136.1, 128.5, 127.7, 124.6, 123.9, 119.7, 40.5, 21.7, 12.6.

HRMS calc. for $C_{17}H_{16}NO_2$ $[M+H]^+$ 266.1181; found 266.1178.

FT-IR (KBr, cm^{-1}): 3436, 2924, 1585, 1559, 1506, 1448, 1377, 1333, 1288, 1204, 1107, 1075, 843, 815, 751, 693, 531.

*Ethyl 4-(3,6-dimethyl-1H-inden-2-yl)benzoate (**1f**)*[S2]

Yield 269 mg (92%); white solid, m.p. 77-79 °C; lit.[S2] data: m.p. 53-58 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H, Ar), 7.54 (d, *J* = 8.4 Hz, 2H, Ar), 7.30 (d, *J* = 8.0 Hz, 2H, Ar indene), 7.17 (d, *J* = 7.8 Hz, 1H, Ar indene), 4.41 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.73 (q, *J* = 2.3 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.36 – 2.32 (m, 3H), 1.42 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 148.9, 144.8, 142.6, 142.4, 138.7, 136.9, 129.8, 128.3, 128.0, 123.7, 120.8, 119.1, 61.0, 40.9, 34.9, 31.8, 14.5, 12.4.

FT-IR (KBr, cm^{-1}): 2981, 2909, 2863, 1713, 1603, 1553, 1445, 1365, 1272, 1182, 1103, 1019, 853, 809, 771, 703 cm.

HRMS calc. for $C_{20}H_{21}O_2$ $[M+H]^+$ 293.1542; found 293.1540.

NMR, IR and HRMS are in agreement with lit. data[S2].

6-tert-Butyl-2-(2-fluorophenyl)-3-methyl-1H-indene (***1g***)

Yield 214 mg (75%); yellow solid, m.p. 41-43 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 1H), 7.48 – 7.24 (m, 4H, Ar,), 7.23 – 7.09 (m, 2H, Ar indene), 3.75 (q, *J* = 2.3 Hz, 2H, CH_2), 2.17 (q, *J* = 2.0 Hz, 3H, CH_3), 1.39 (s, 9H, $(CH_3)_3$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1 (d, *J* = 247.2 Hz), 148.4 , 144.3 , 143.3 , 137.3 , 134.7 , 131.3 (d, *J* = 4.3 Hz), 128.6 (d, *J* = 8.1 Hz), 125.6 (d, *J* = 15.4 Hz), 124.0 (d, *J* = 3.4 Hz), 123.5 , 120.7 , 118.8 , 116.0 (d, *J* = 22.7 Hz), 41.7 (d, *J* = 3.0 Hz), 34.9 , 31.8 , 12.0 (d, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2.

HRMS calc. for $C_{10}H_{22}F$ $[M+H]^+$ 281.1706; found 281.1704.

FT-IR (KBr, cm^{-1}): 3469, 3078, 2960, 2908, 2863, 2360, 2340, 1616, 1573, 1482, 1440, 1394, 1361, 1263, 1215, 1175, 1111, 872, 820, 756, 631.

*Ethyl 4-(6-tert-butyl-3-methyl-1H-inden-2-yl)benzoate (**1h**)*

Yield 227 mg (68%); yellow solid, m.p. 74-76 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.03 (m, 2H, Ar), 7.56 – 7.50 (m, 3H, Ar), 7.41 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar indene), 7.35 (d, *J* = 8.0 Hz, 1H, Ar indene), 4.40 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.76 (q, *J* = 2.2 Hz, 2H, CH_2), 2.33 (t, *J* = 2.1 Hz, 3H, CH_3), 1.41 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.38 (s, 9H, $C(CH_3)_3$).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 148.9, 144.8, 142.6, 142.4, 138.7, 136.9, 129.8, 128.3, 128.0, 123.7, 120.8, 119.1, 61.0, 40.9, 34.9, 31.8, 14.5, 12.4.

HRMS calc. for $C_{23}H_{27}O_2$ $[M+H]^+$ 335.2011; found 335.2010.

FT-IR (KBr, cm^{-1}): 2964, 2902, 2865, 1711, 1603, 1475, 1440, 1364, 1276, 1182, 1106, 1026, 819, 771, 704 cm.

*2-(2-Fluorophenyl)-6-methoxy-3-methyl-1H-indene (**1i**)*

Yield 175 mg (69%); orange solid, m.p. 44-46 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.37 (m, 3H, Ar overlapping with residual $CHCl_3$), 7.07-7.20 (m, 3H, Ar), 6.90 (dd, *J* = 8.3 Hz, 2.3 Hz, 1H, Ar indene), 3.86 (s, 3H, OCH_3), 3.72 (d, *J* = 1.8 Hz, 2H, CH_2), 2.15 (q, *J* = 1.8 Hz, 3H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1 (d, *J* = 247.2 Hz), 158.3 , 145.1 , 140.1 , 137.0 , 133.1 , 131.2 (d, *J* = 4.4 Hz), 128.5 (d, *J* = 8.2 Hz), 125.6 (d, *J* = 15.0 Hz), 124.0 (d, *J* = 3.6 Hz), 119.8 , 116.0 (d, *J* = 22.8 Hz), 112.1 , 110.0 , 55.8 , 41.6 (d, *J* = 3.6 Hz), 12.0 (d, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3.

HRMS calc. for $C_{17}H_{16}FO$ $[M+H]^+$ 255.1185; found 255.1181.

FT-IR (KBr, cm^{-1}): 2961, 2906, 2865, 1607, 1576, 1483, 1448, 1390, 1272, 1231, 1143, 1103, 1067, 1025, 925, 912, 833, 753.

*2-(3-Chlorophenyl)-6-methoxy-3-methyl-1H-indene (**1j**)*

Yield 173 mg (64%); beige solid, m.p. 41-43 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 1H, Ar), 7.37 – 7.27 (m, 3H, Ar), 7.25 – 7.20 (m, 1H, Ar), 7.08 (d, *J* = 2.4 Hz, 1H, Ar indene), 6.91 (dd, *J* = 8.3, 2.3 Hz, 1H, Ar indene)
3.86 (s, 3H, OCH_3), 3.68 (q, *J* = 1.8 Hz, 2H, CH_2), 2.29 (t, *J* = 2.1 Hz, 3H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 144.3, 140.6, 139.7, 136.7, 135.8, 134.4, 129.7, 128.1, 126.4, 126.3, 123.4, 119.9, 112.3, 110.1, 55.8, 40.8, 12.3.

HRMS calc. for $C_{17}H_{16}ClO$ $[M+H]^+$ 271.0890; found 271.0886.

FT-IR (KBr, cm^{-1}): 2954, 2902, 2865, 1711, 1603, 1475, 1443, 1364, 1276, 1182, 1106, 1074, 1026, 874, 819, 771, 704.

References

S1. O. V. Shurupova, S. A. Rzhevskiy, L. I. Minaeva, M. A. Topchiy and A. F. Asachenko, *RSC Adv.*, 2022, **12**, 5517-5521.

S2. D. Eom, S. Park, Y. Park, T. Ryu and P. H. Lee, *Org. Lett.*, 2012, **14**, 5392-5395.

NMR and HRMS spectra pictures

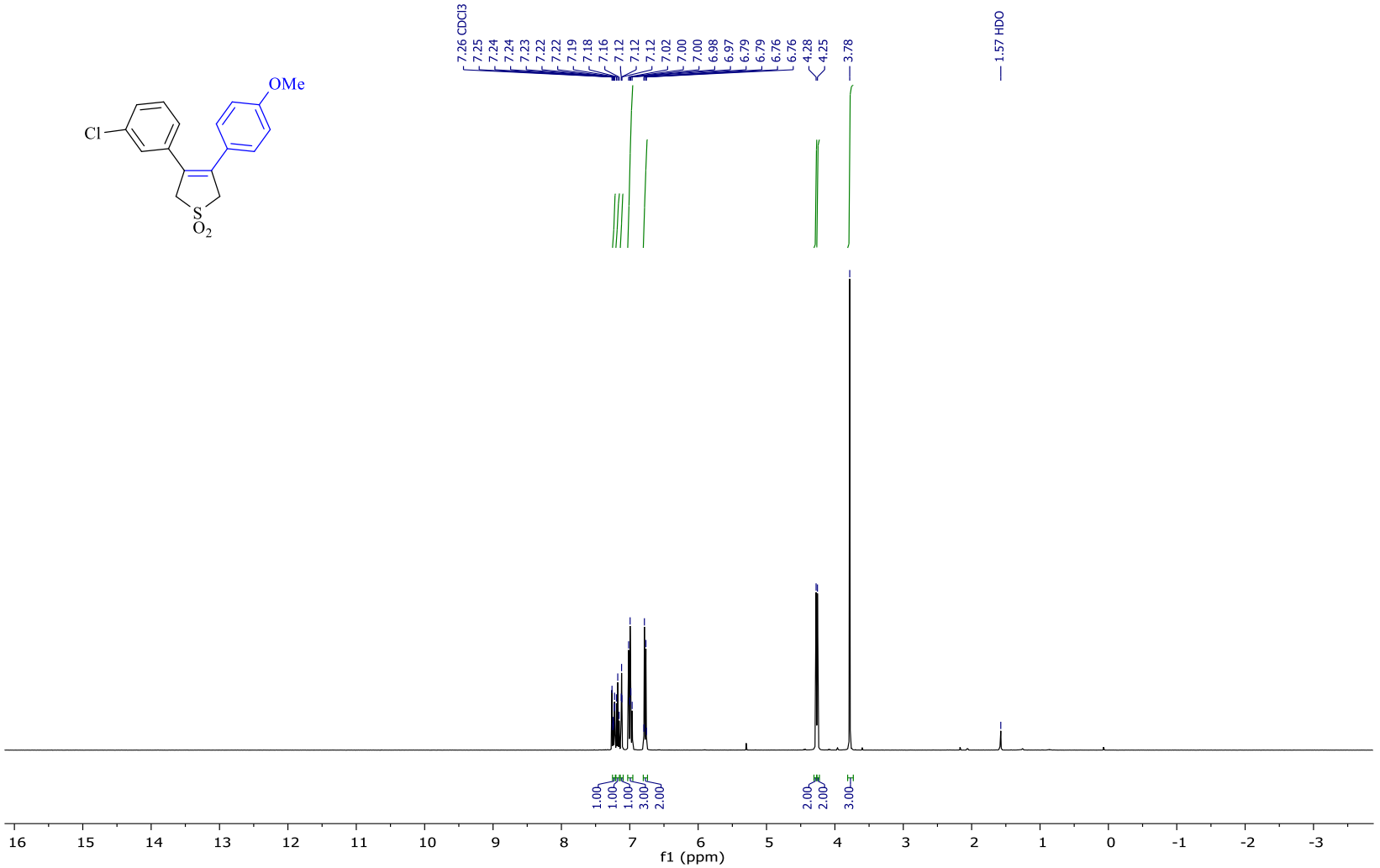

Figure S1. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3-(3-chlorophenyl)-4-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide.

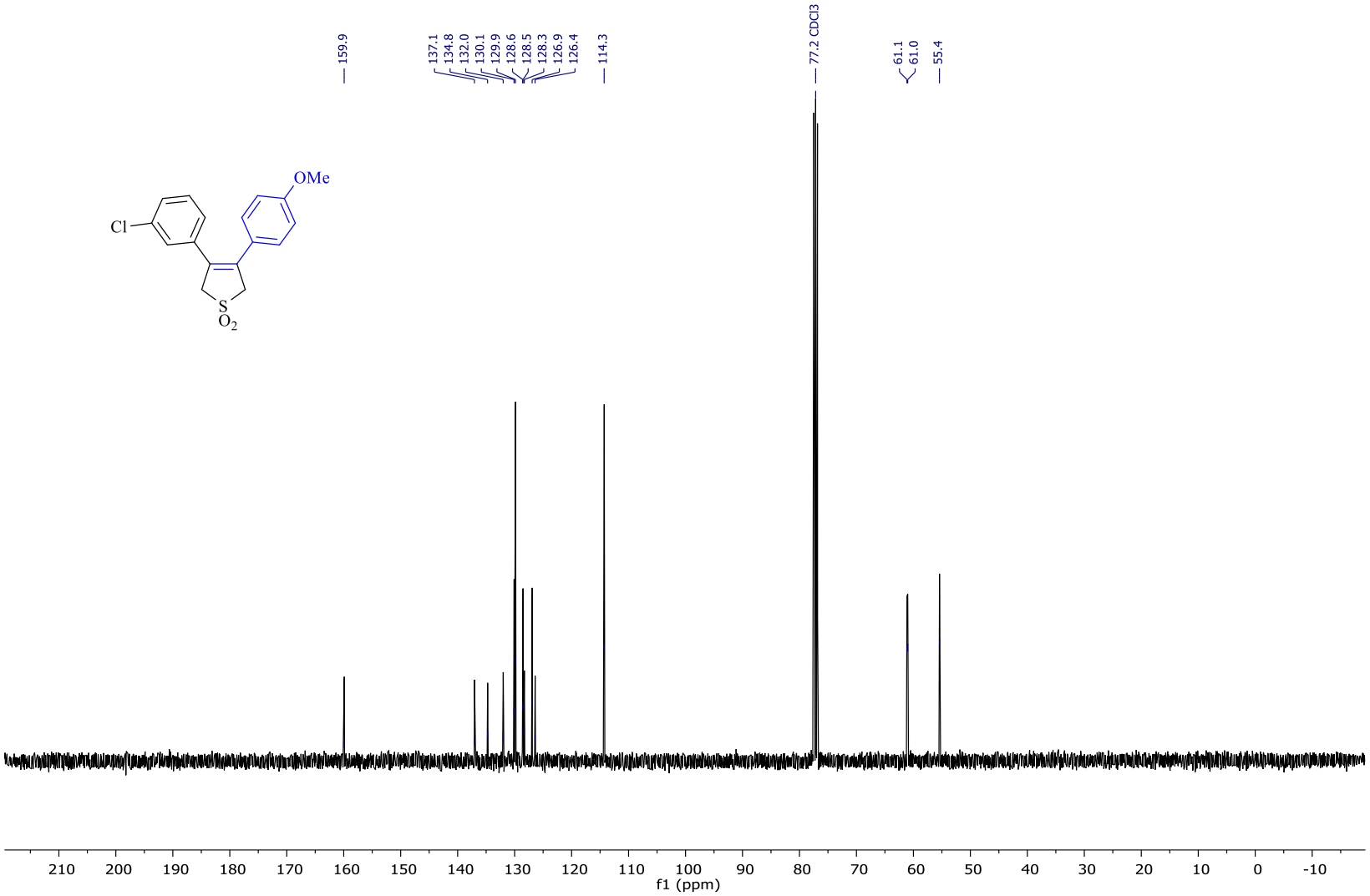

Figure S2. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 3-(3-chlorophenyl)-4-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide.

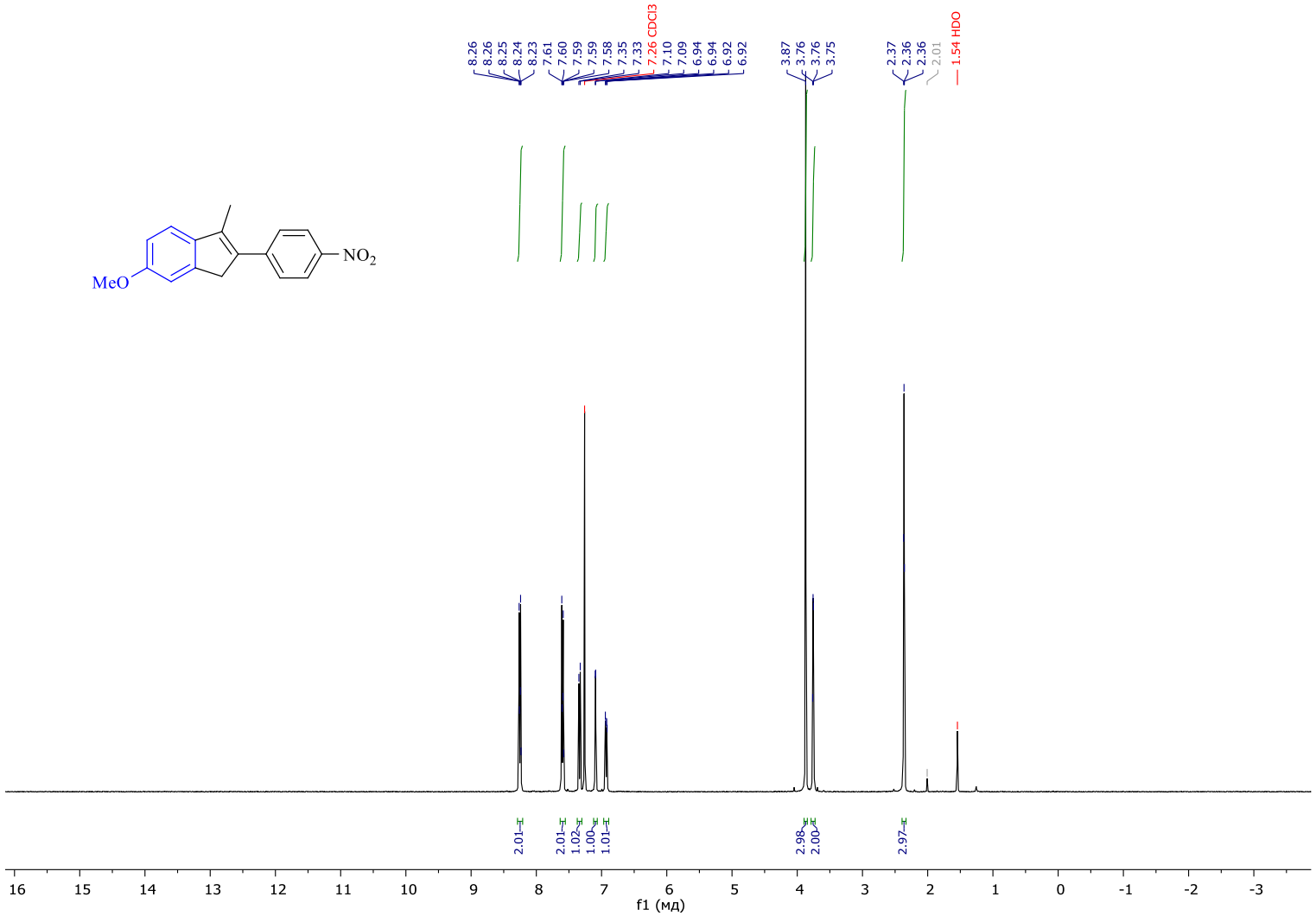

Figure S3. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 6-methoxy-3-methyl-2-(4-nitrophenyl)-1*H*-indene (1a).

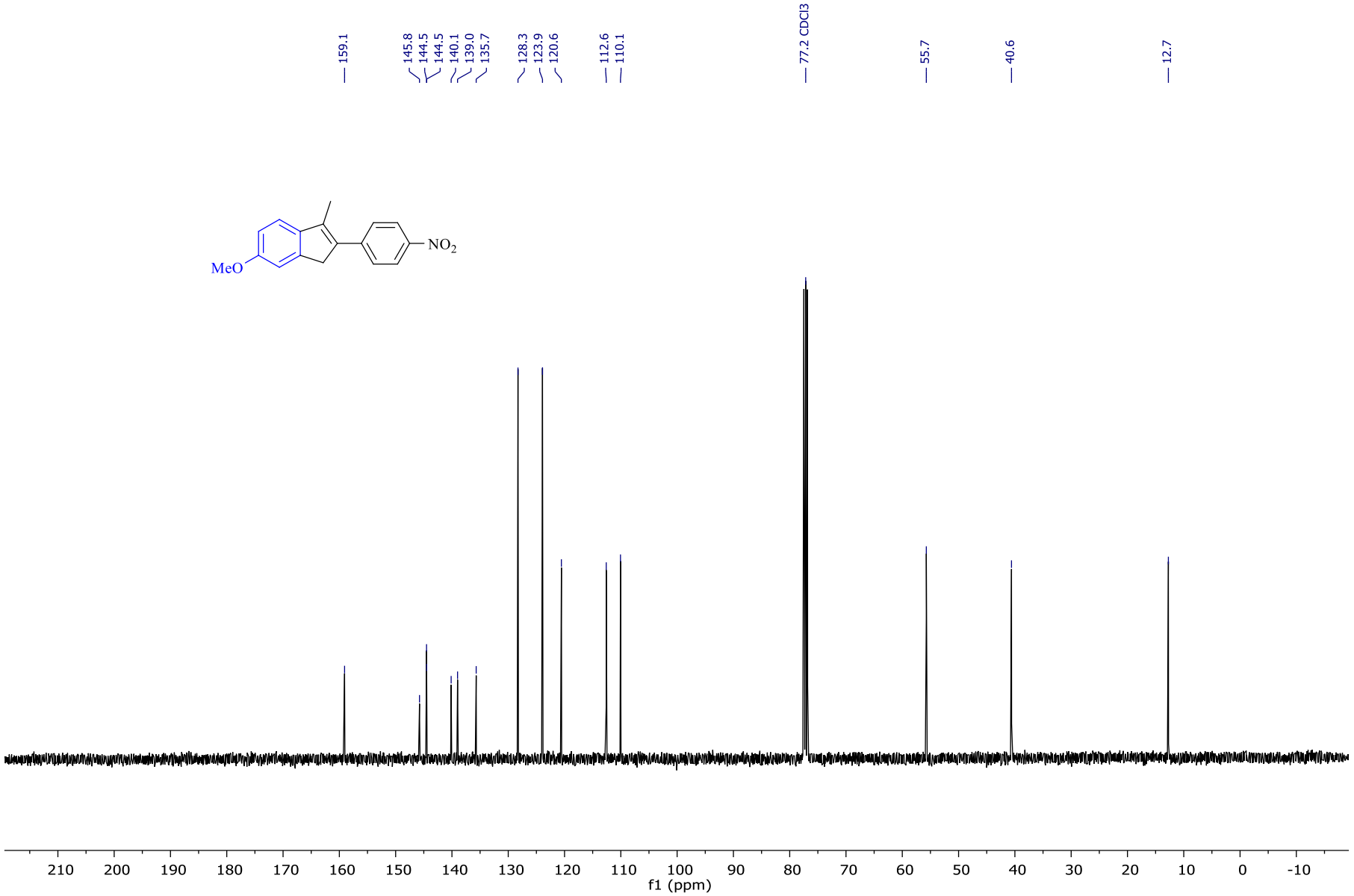

Figure S4. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 6-methoxy-3-methyl-2-(4-nitrophenyl)-1*H*-indene (1a).

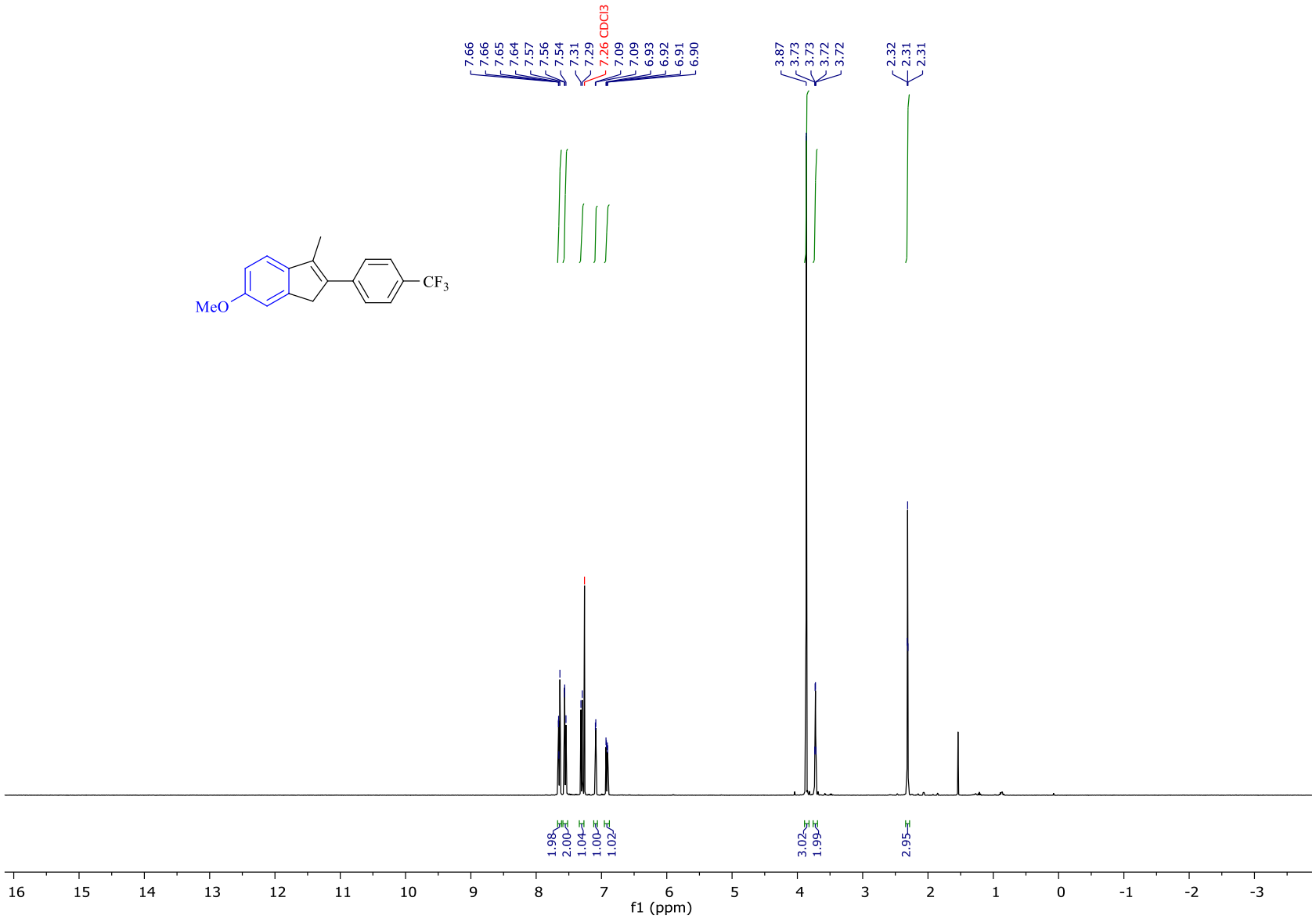

Figure S5. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 6-methoxy-3-methyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indene (1b)

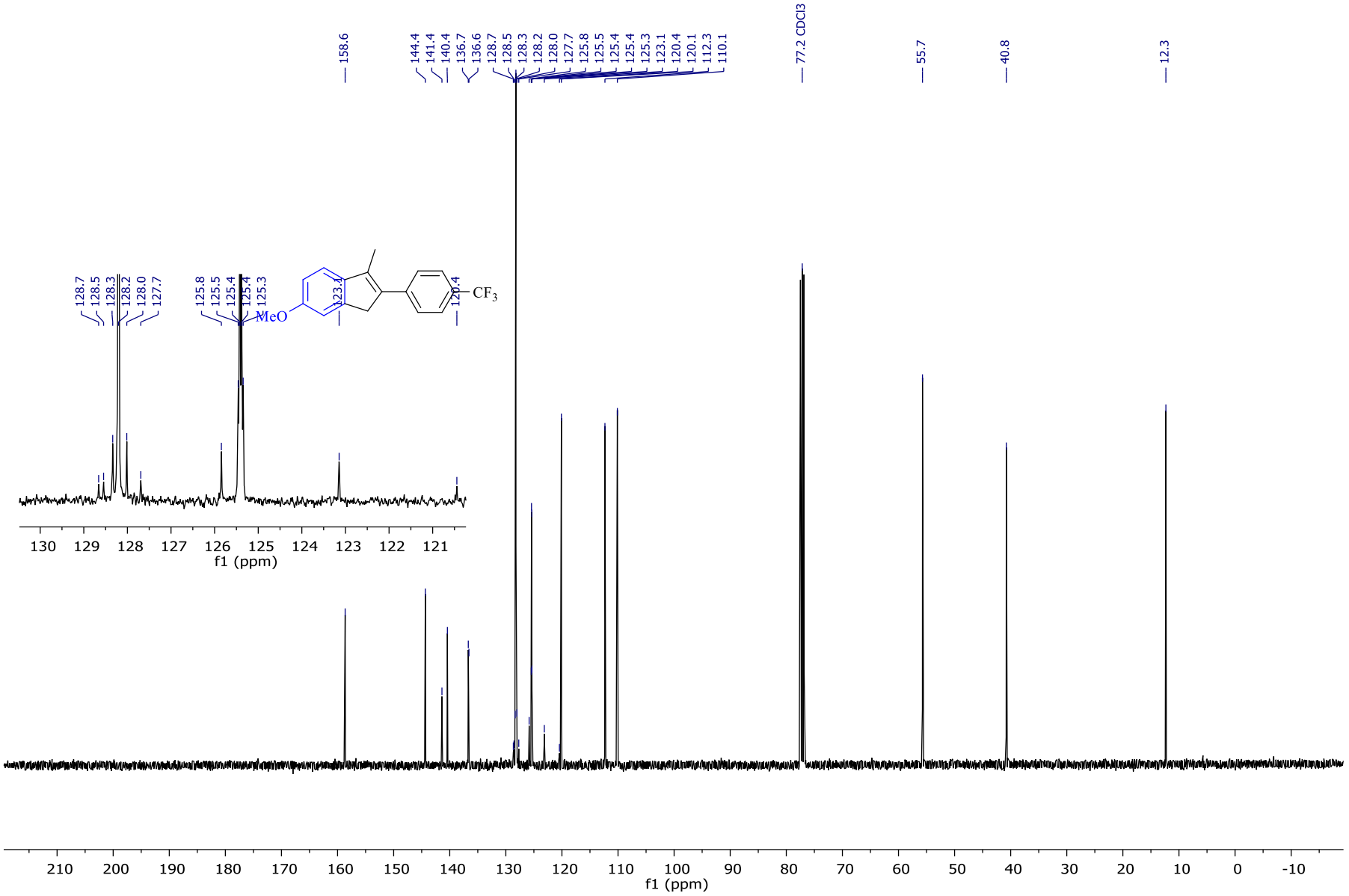

Figure S6. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 6-methoxy-3-methyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indene (1b).

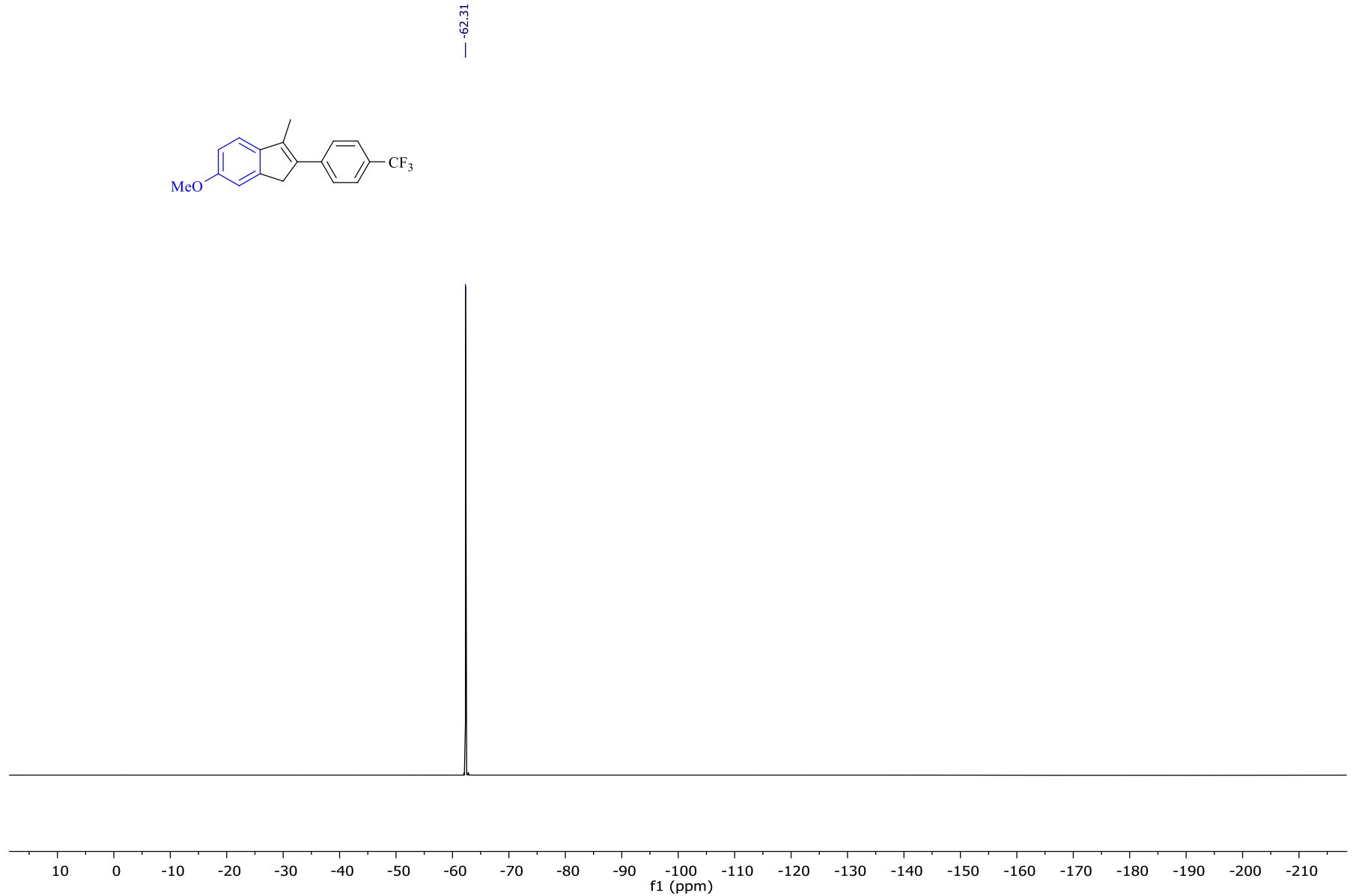

Figure S7. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 6-methoxy-3-methyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indene (1b).

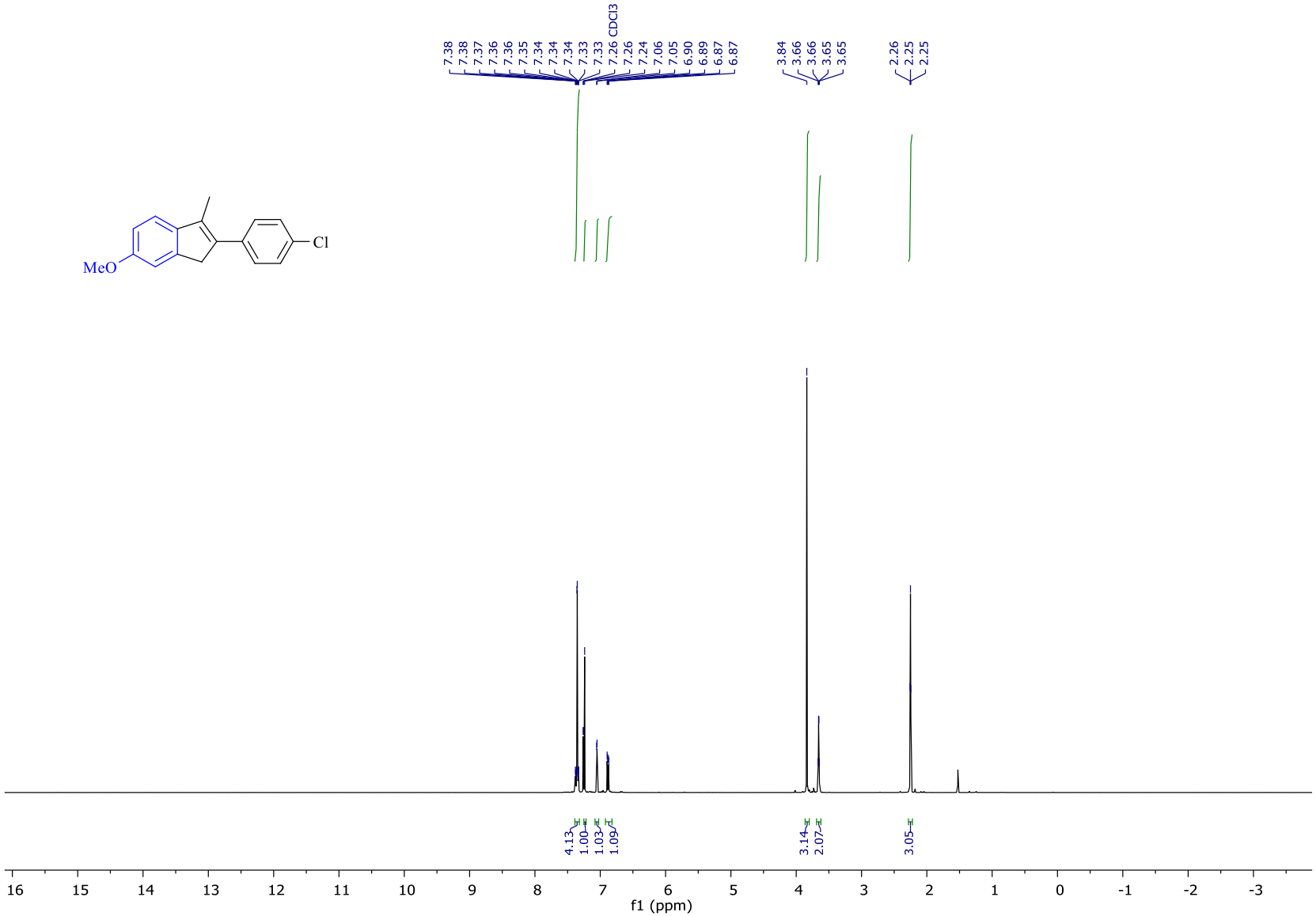

Figure S8. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 2-(4-chlorophenyl)-6-methoxy-3-methyl-1*H*-indene (1c)

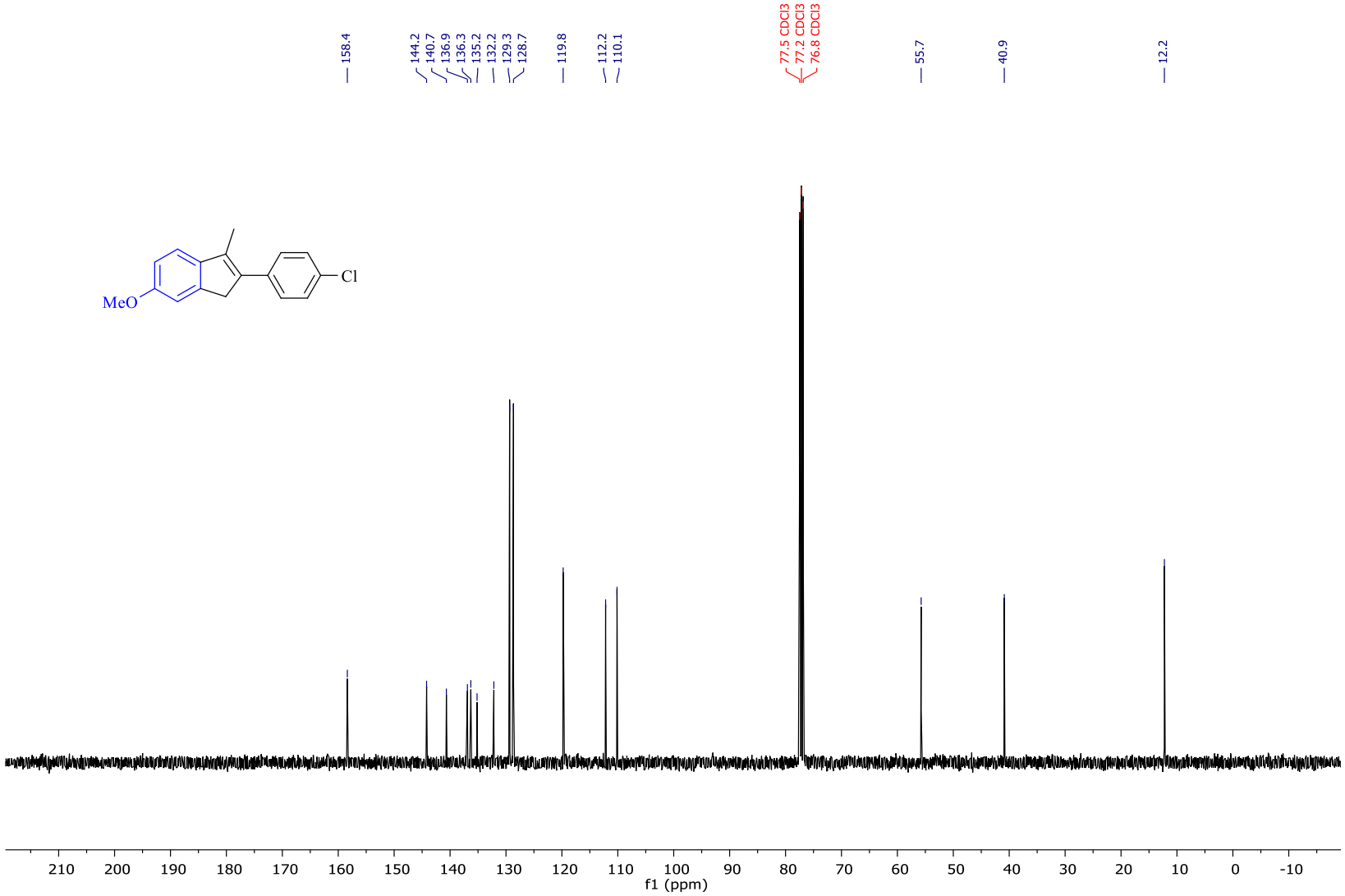

Figure S9. $^{13}C\{^{1}H\}$ NMR (101MHz, $CDCl_3$) spectrum of 2-(4-chlorophenyl)-6-methoxy-3-methyl-1*H*-indene (1c)

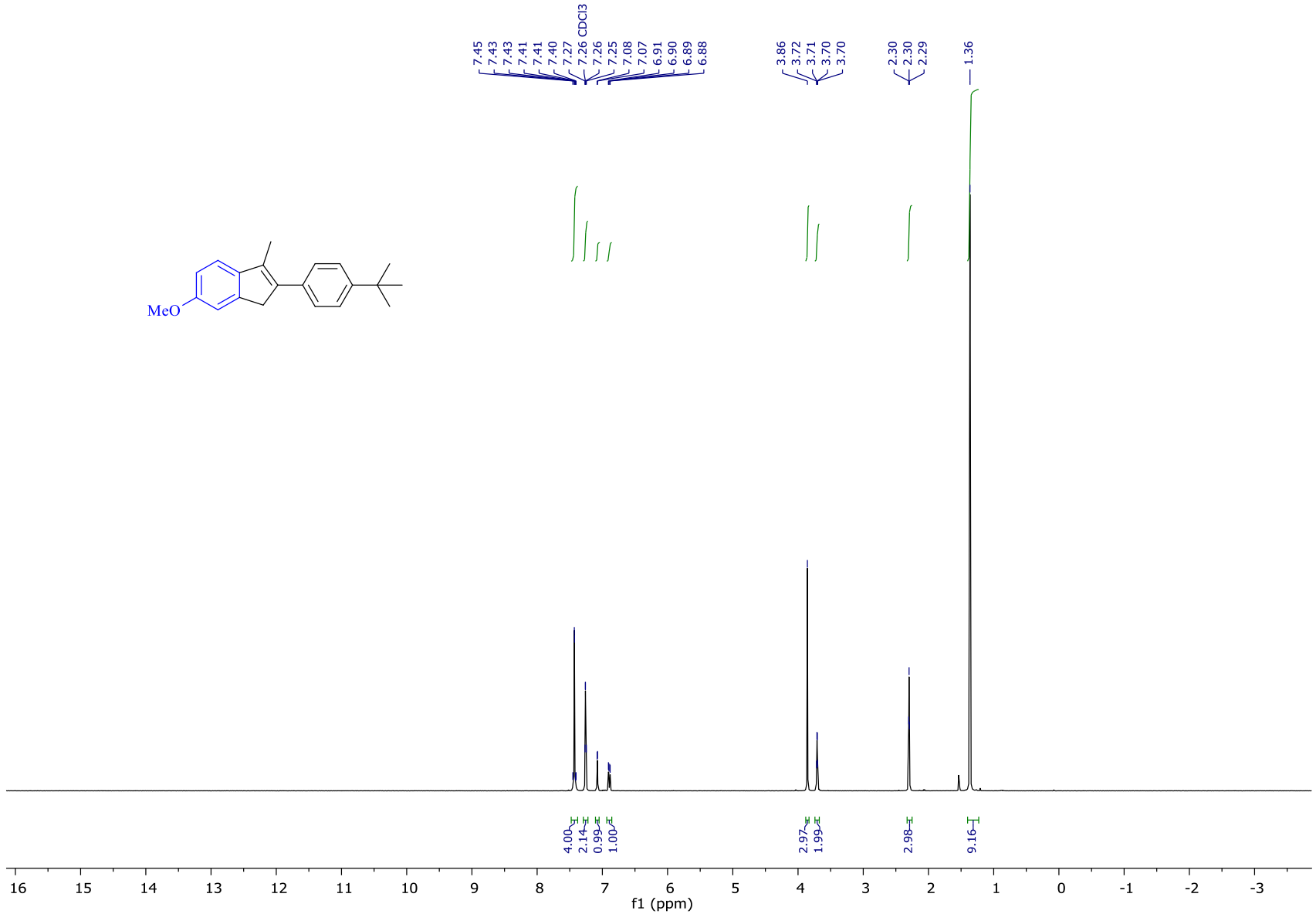

Figure S10. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 2-(4-*tert*-butylphenyl)-6-methoxy-3-methyl-1*H*-indene (1d)

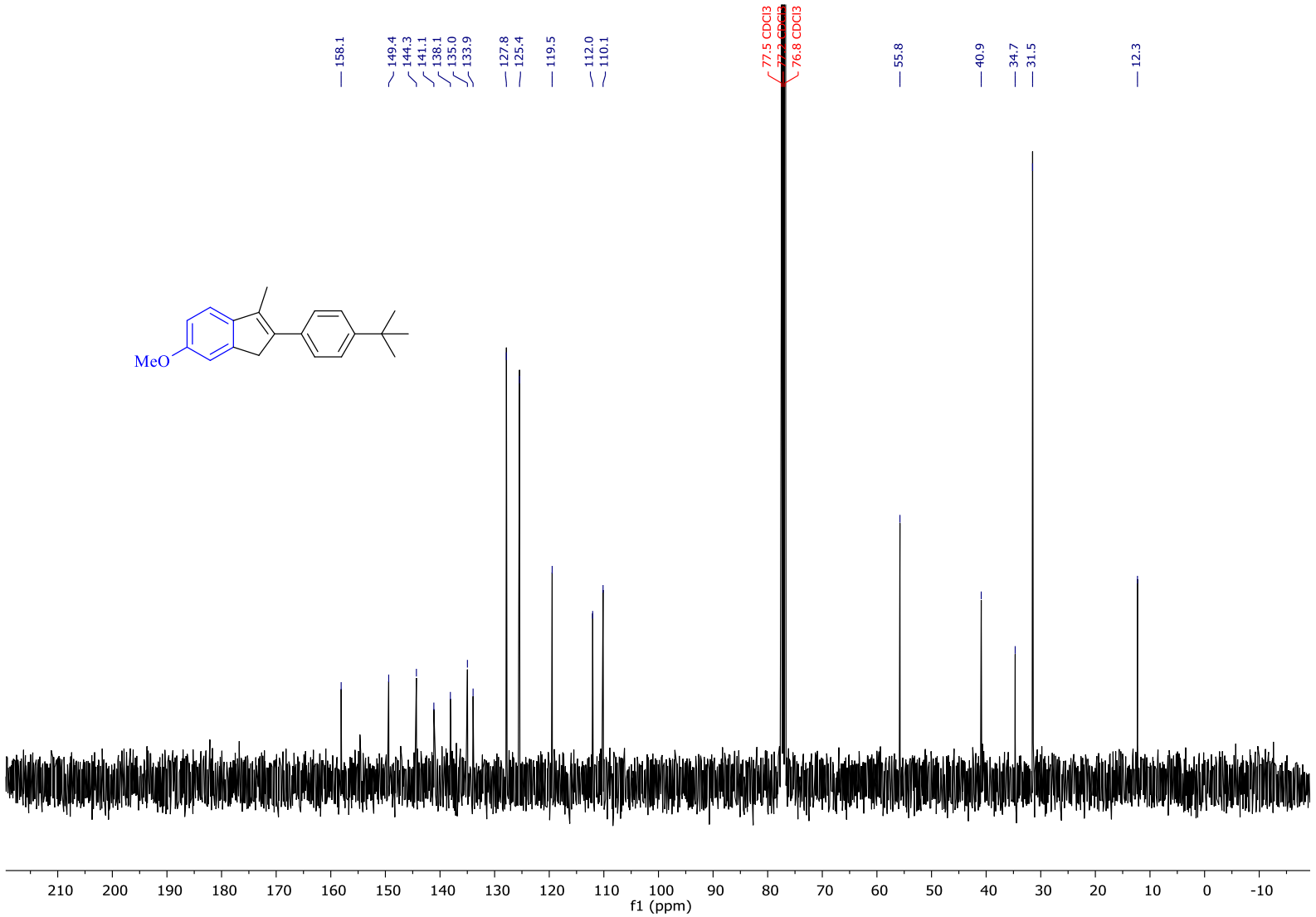

Figure S11. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 2-(4-*tert*-butylphenyl)-6-methoxy-3-methyl-1*H*-indene (1d).

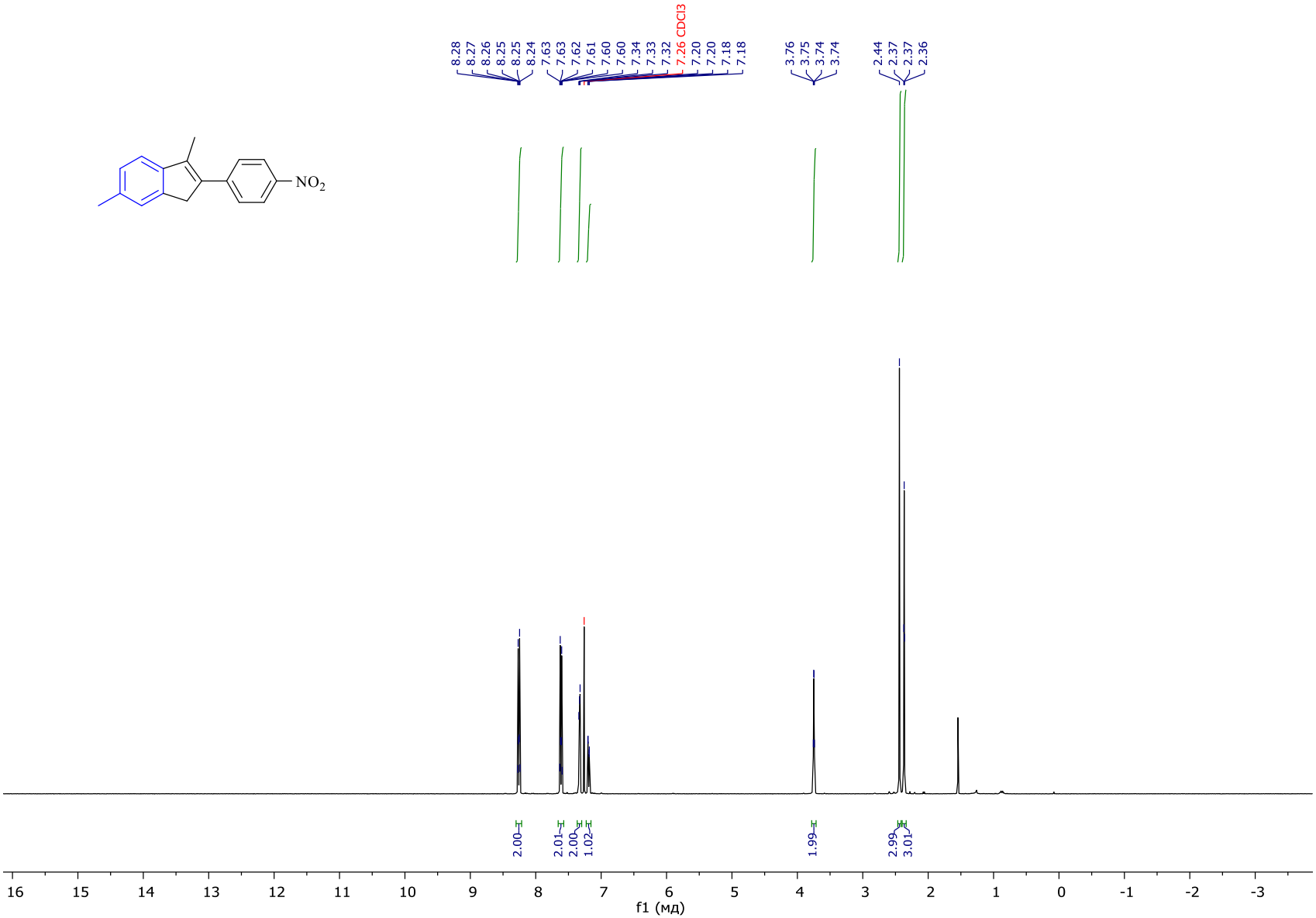

Figure S12. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3,6-dimethyl-2-(4-nitrophenyl)-1*H*-indene (1e).

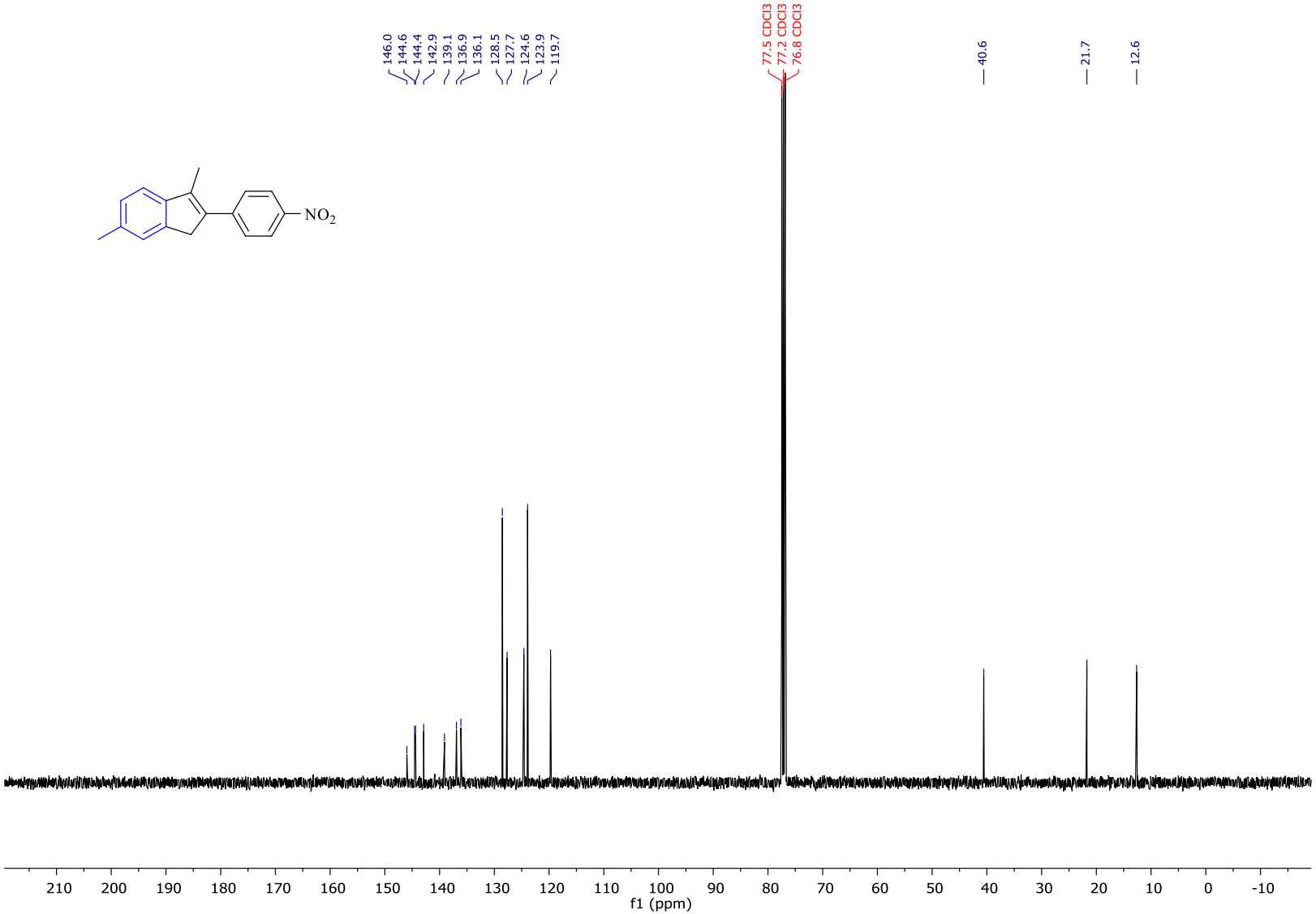

Figure S13. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 3,6-dimethyl-2-(4-nitrophenyl)-1*H*-indene (1e).

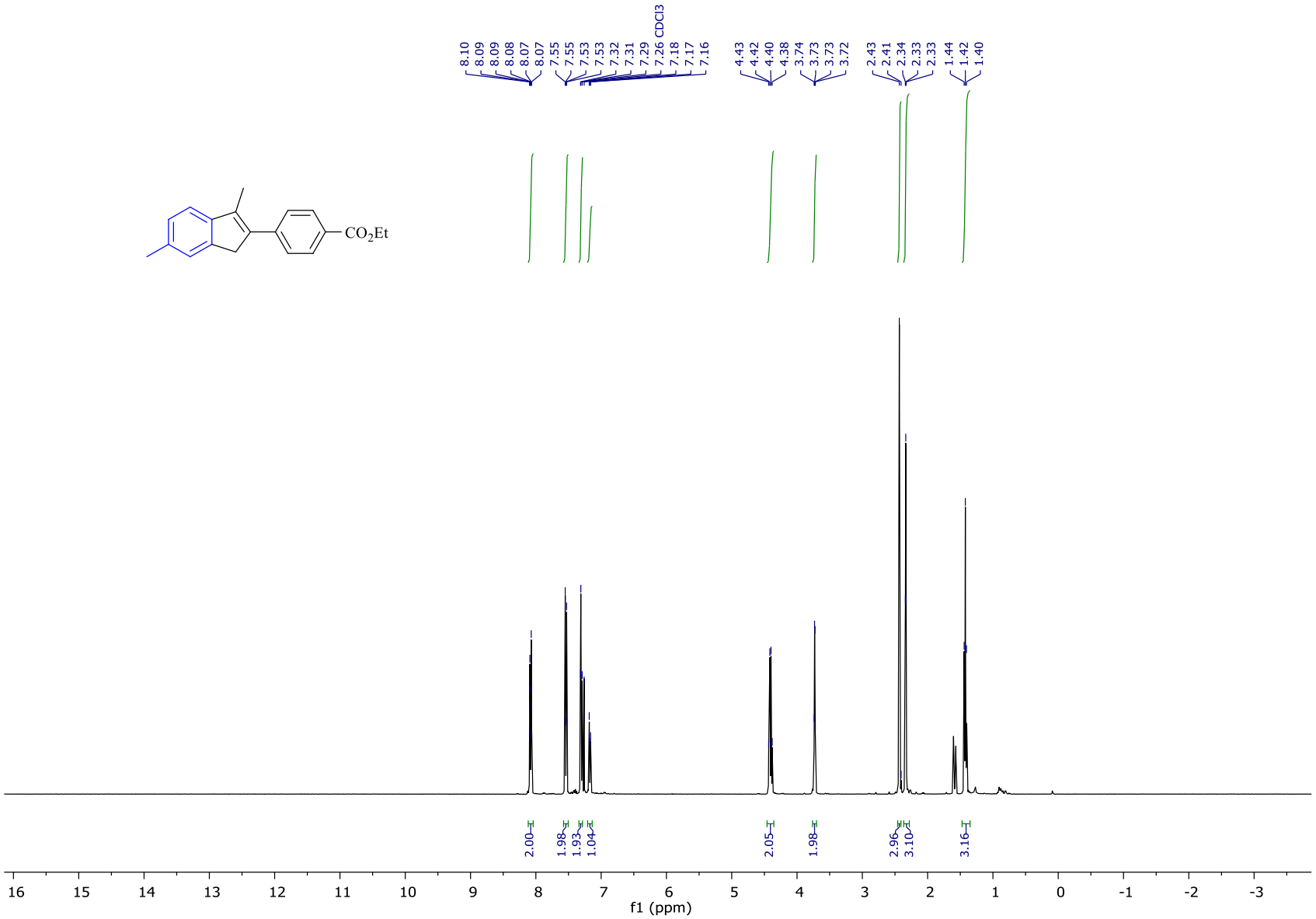

Figure S14. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of ethyl 4-(3,6-dimethyl-1*H*-inden-2-yl)benzoate (1f).

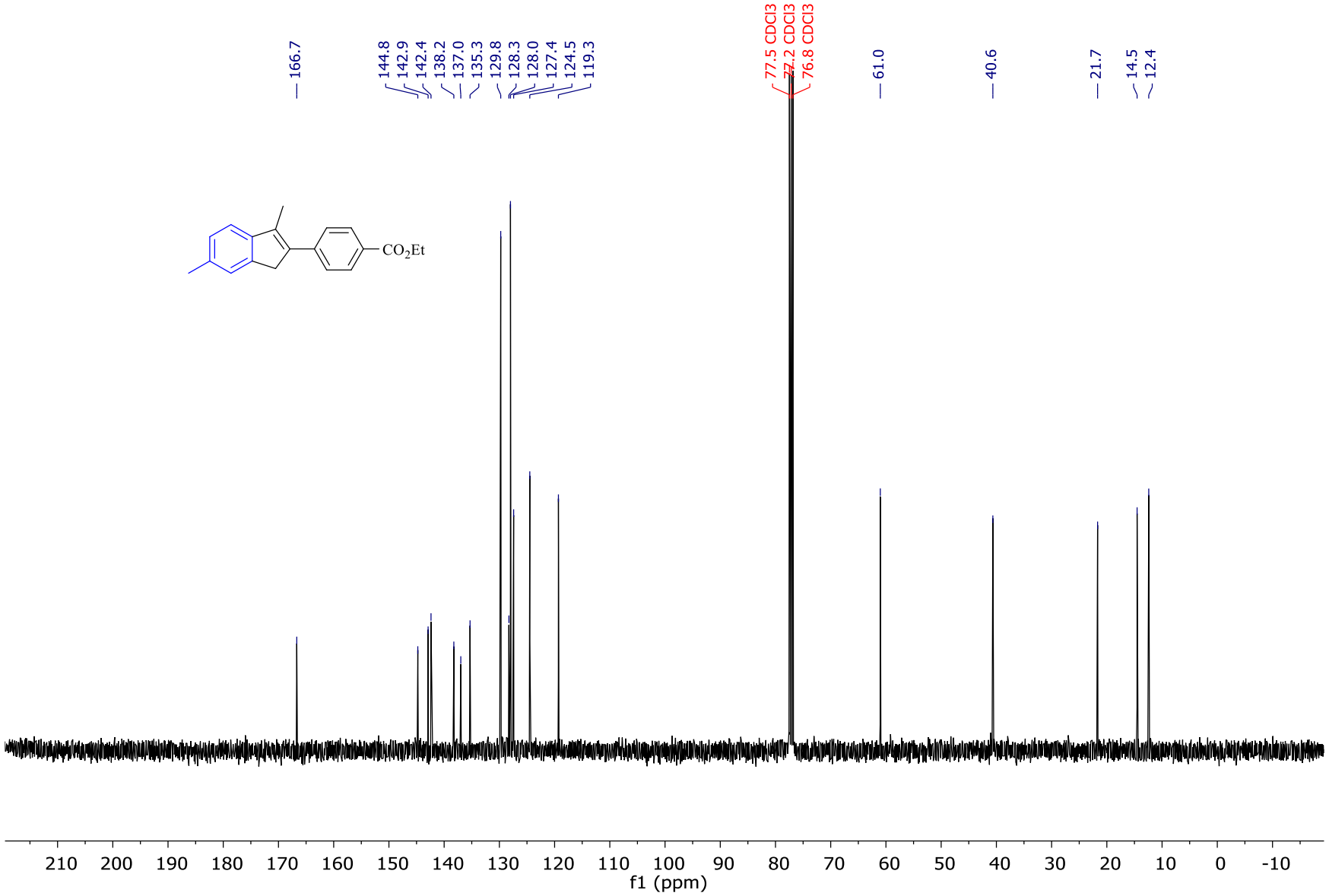

Figure S15. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of ethyl 4-(3,6-dimethyl-1*H*-inden-2-yl)benzoate (1f).

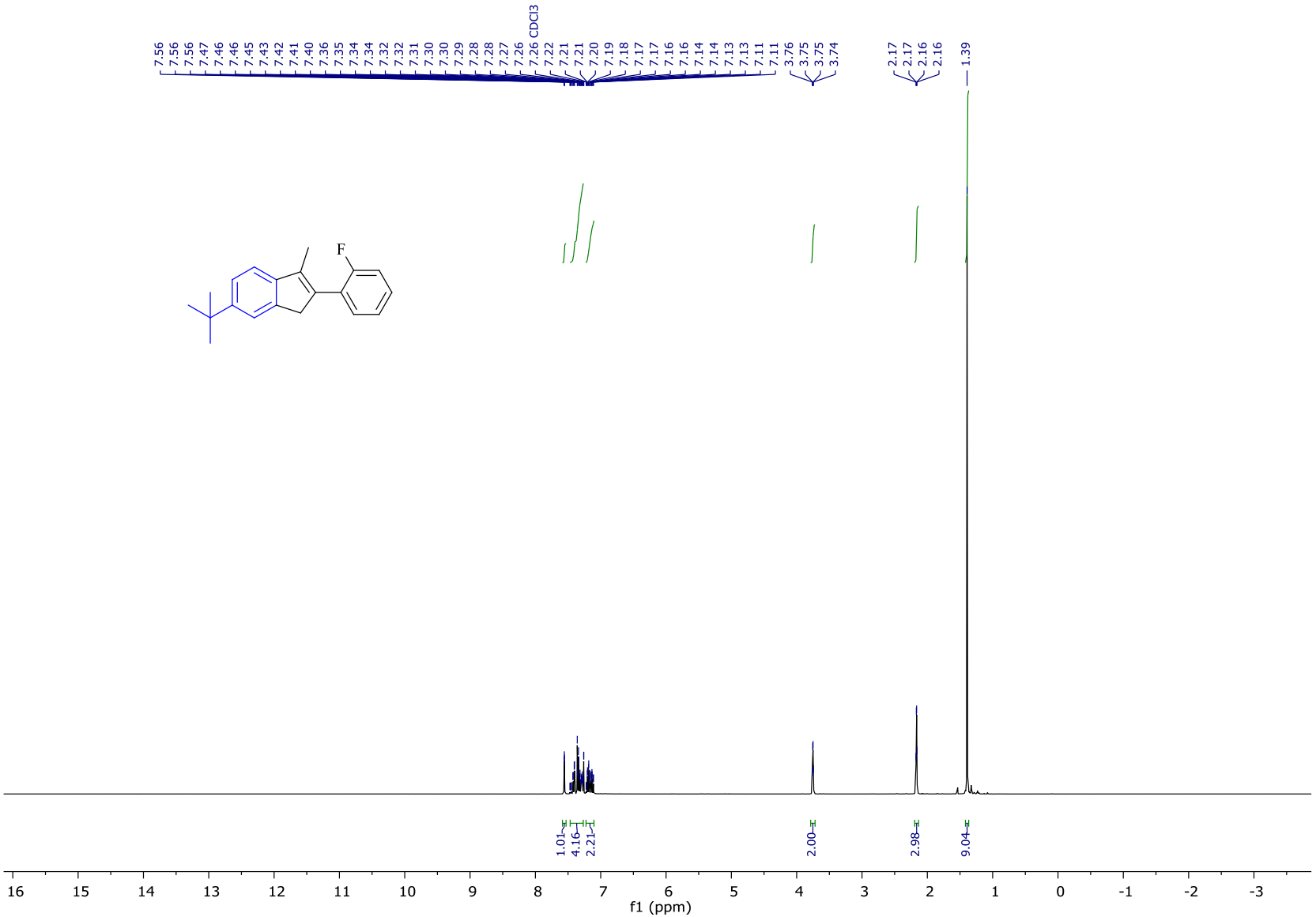

Figure S16. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 6-*tert*-butyl-2-(2-fluorophenyl)-3-methyl-1*H*-indene (1g).

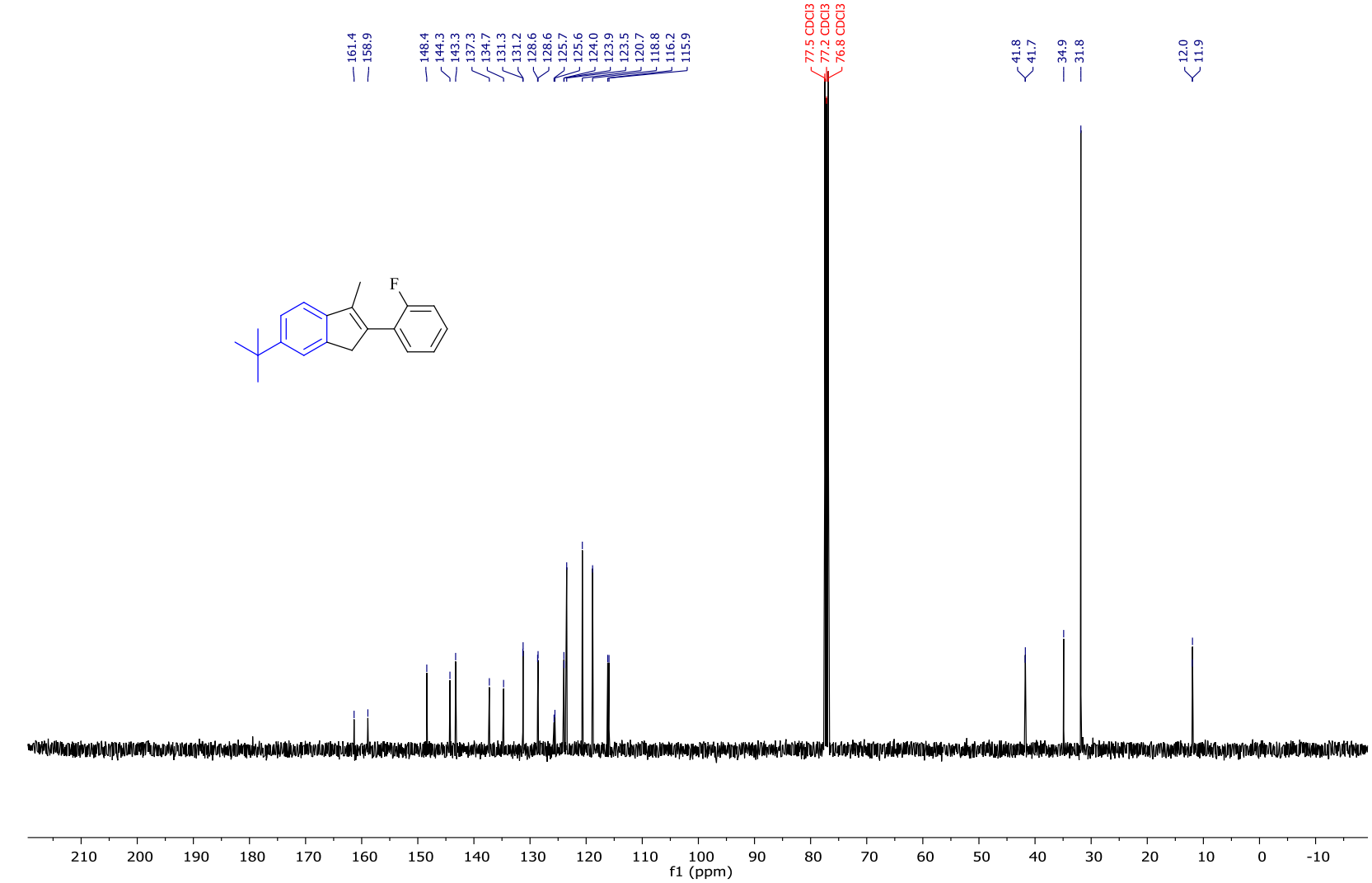

Figure S17. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 6-*tert*-butyl-2-(2-fluorophenyl)-3-methyl-1*H*-indene (1g).

Figure S18. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 6-*tert*-butyl-2-(2-fluorophenyl)-3-methyl-1*H*-indene (1g).

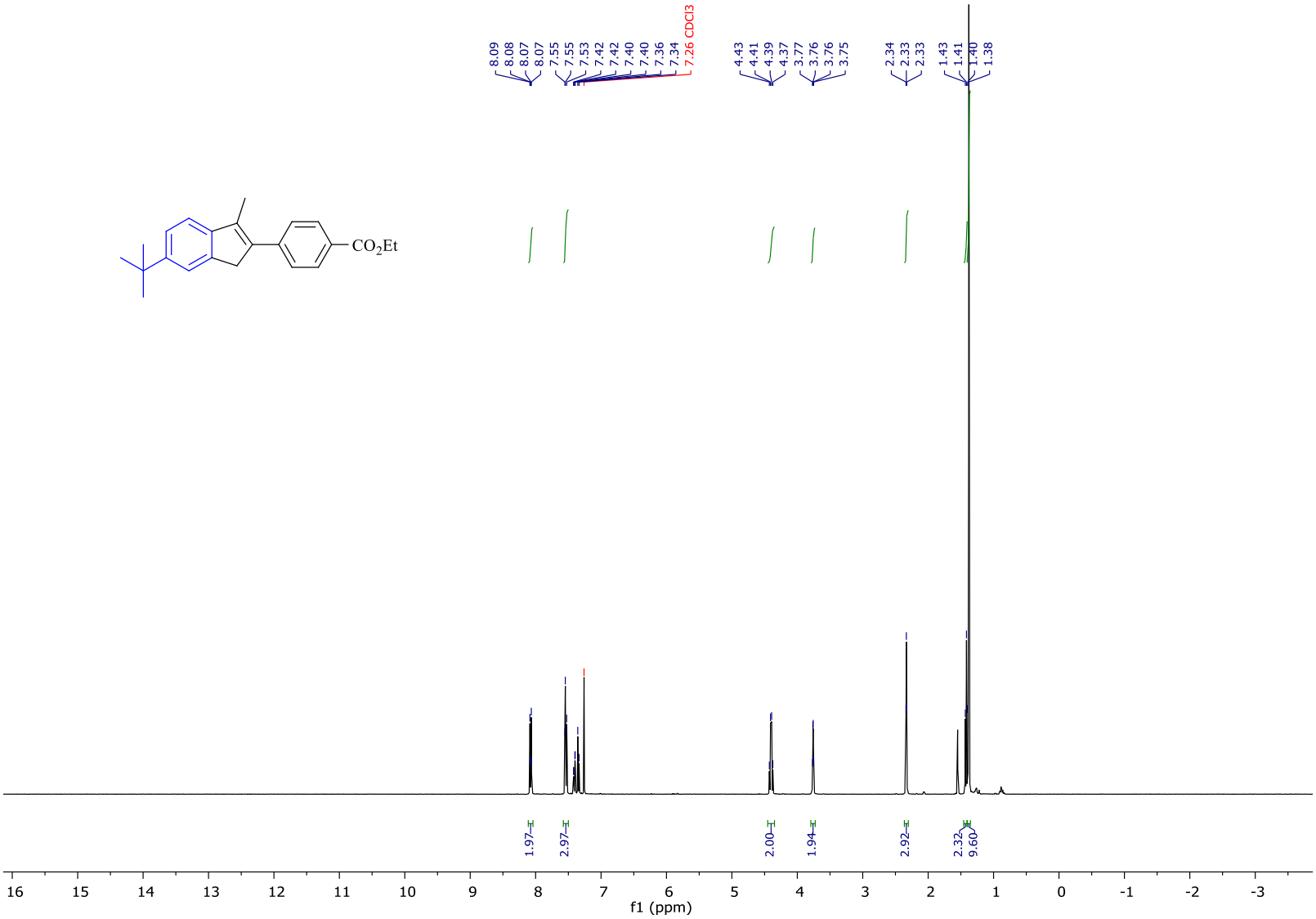

Figure S19. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of ethyl 4-(6-*tert*-butyl-3-methyl-1*H*-inden-2-yl)benzoate (1h)

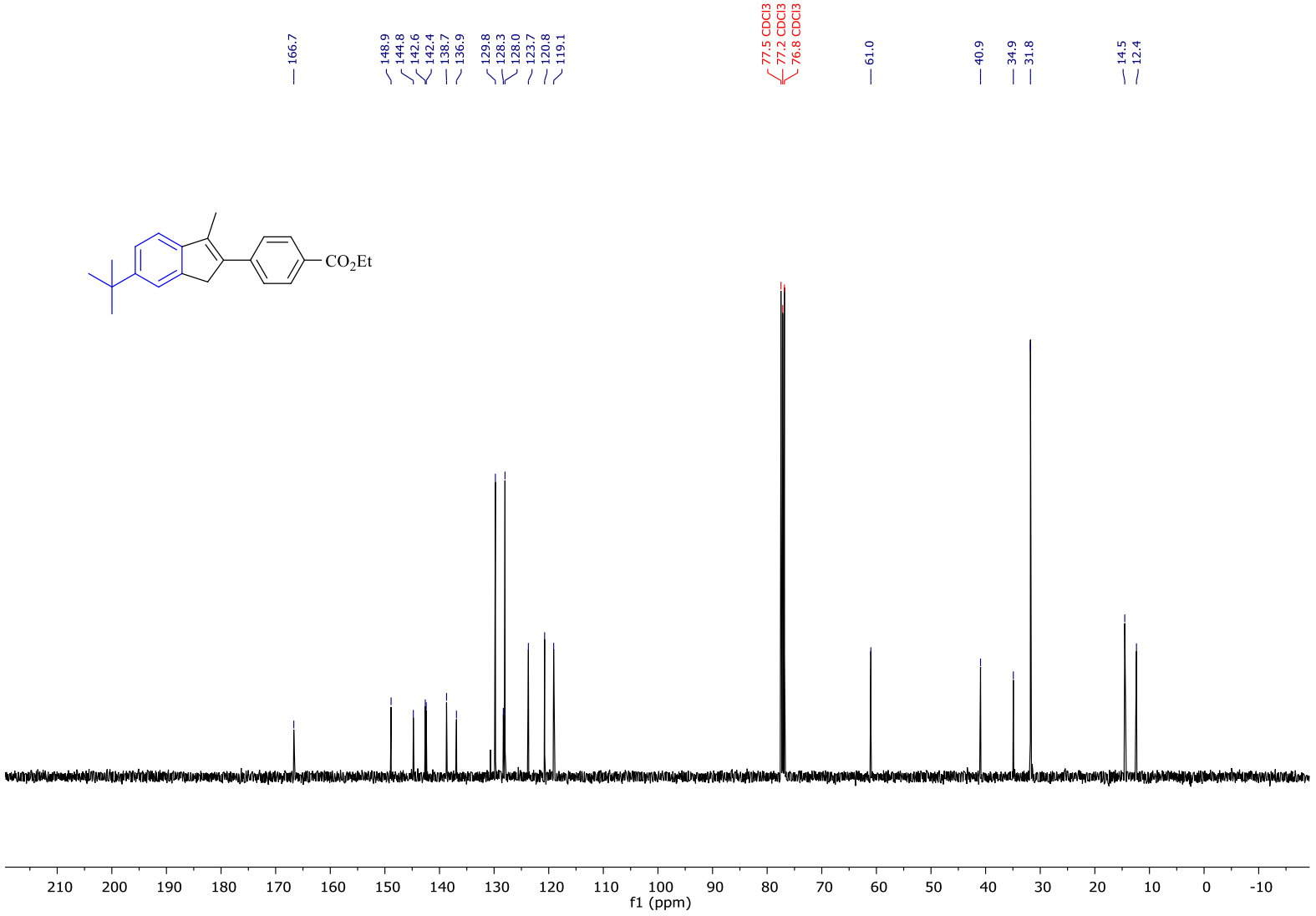

Figure S20. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of ethyl 4-(6-*tert*-butyl-3-methyl-1*H*-inden-2-yl)benzoate (1h).

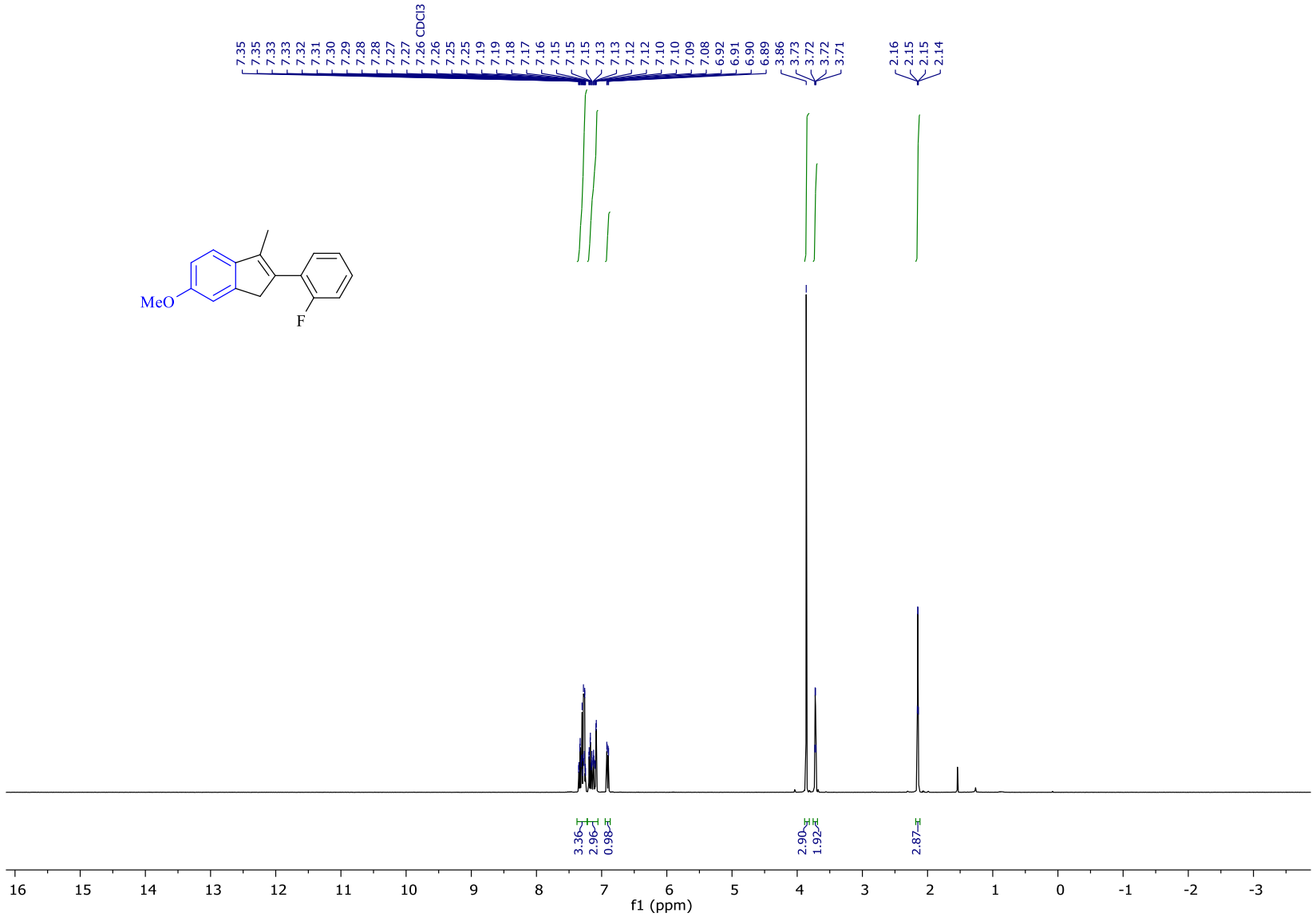

Figure S21. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 2-(2-fluorophenyl)-6-methoxy-3-methyl-1*H*-indene (1i).

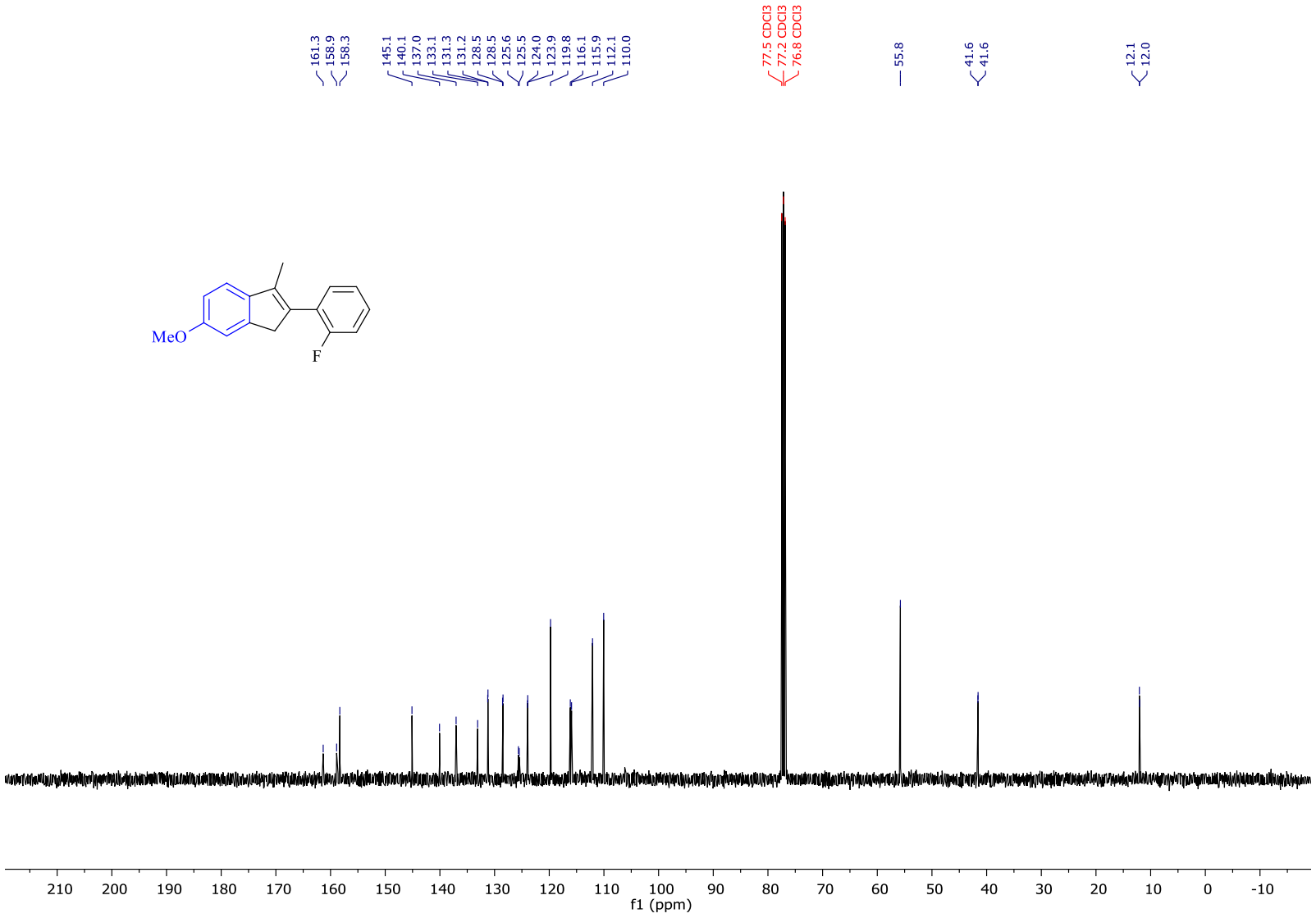

Figure S22. ^{13}C {^{1}H} NMR (101MHz, $CDCl_3$) spectrum of 2-(2-fluorophenyl)-6-methoxy-3-methyl-1*H*-indene (1i).

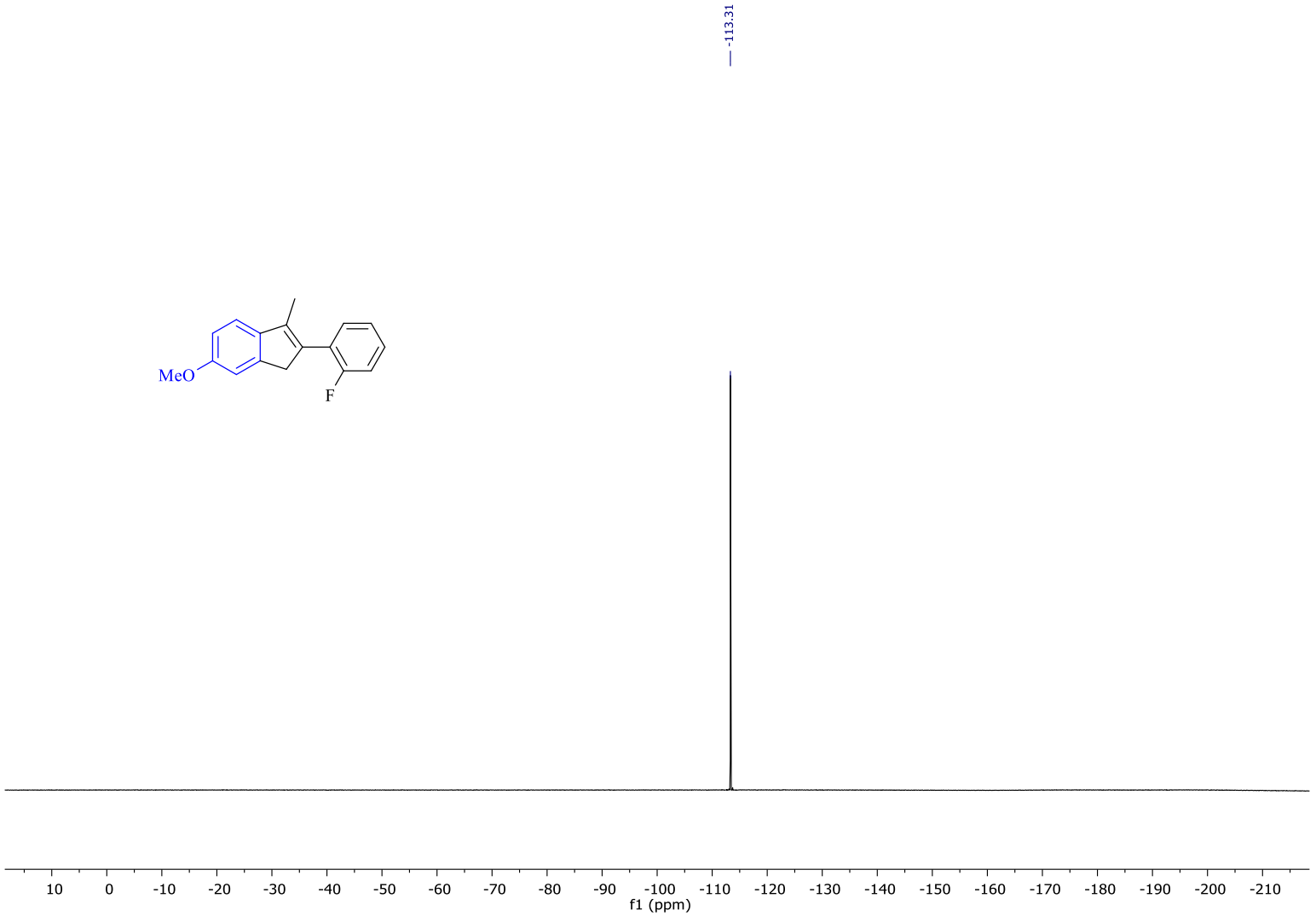

Figure S23. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(2-fluorophenyl)-6-methoxy-3-methyl-1*H*-indene (1i).

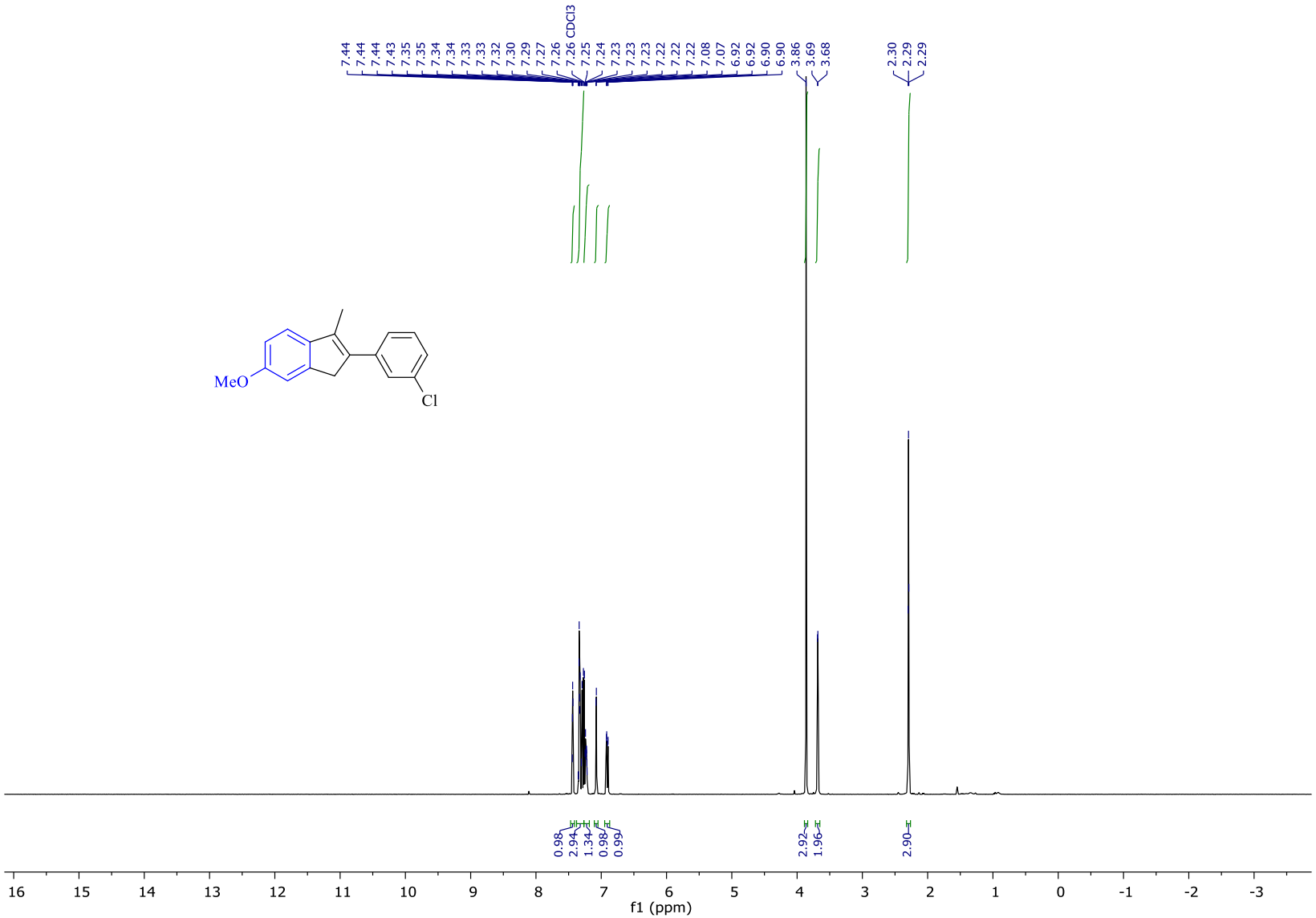

Figure S24. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 2-(3-chlorophenyl)-6-methoxy-3-methyl-1*H*-indene (1j).

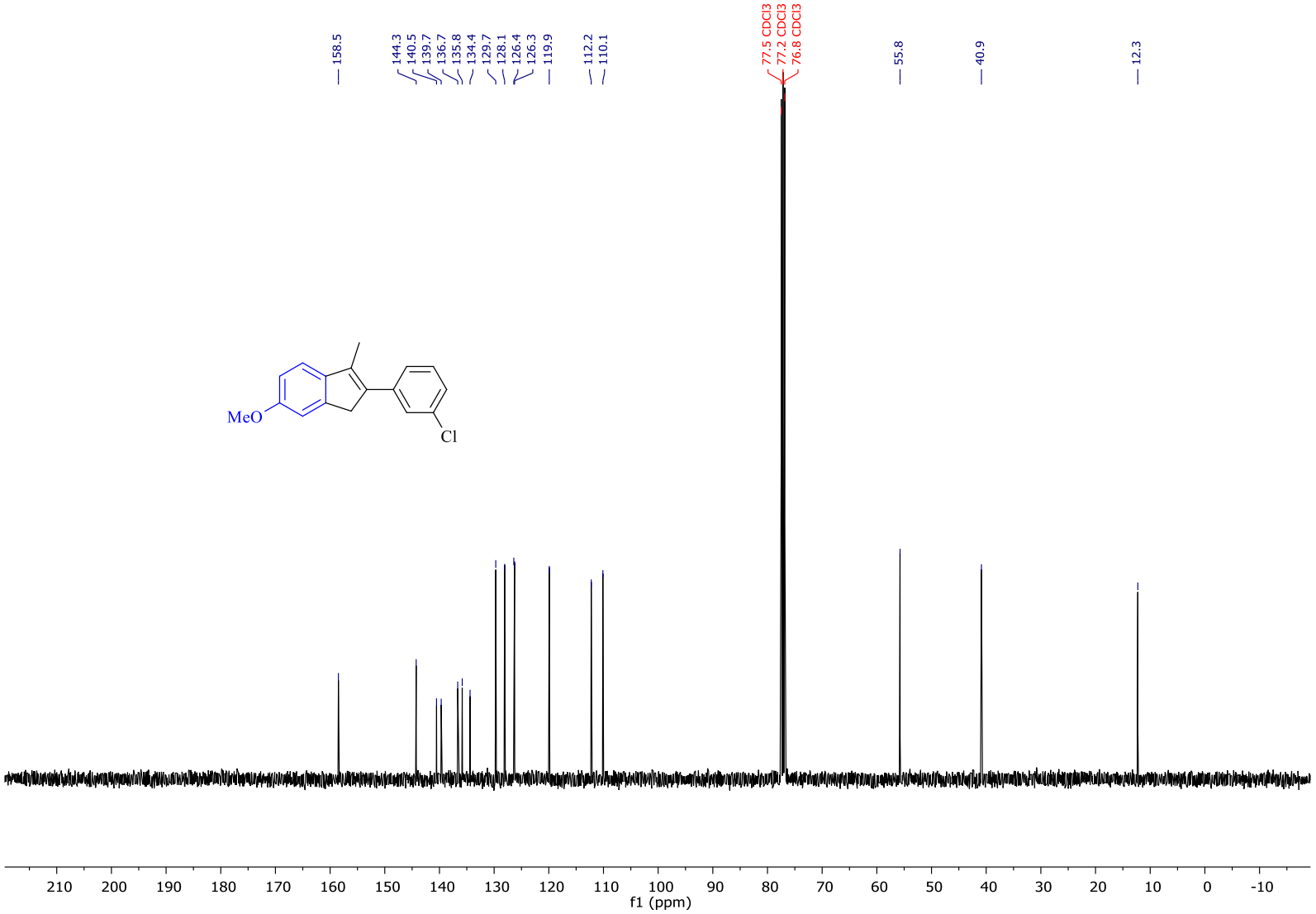

Figure S25. $^{13}C\{^{1}H\}$ NMR (101MHz, $CDCl_3$) spectrum of 2-(3-chlorophenyl)-6-methoxy-3-methyl-1*H*-indene (1j).

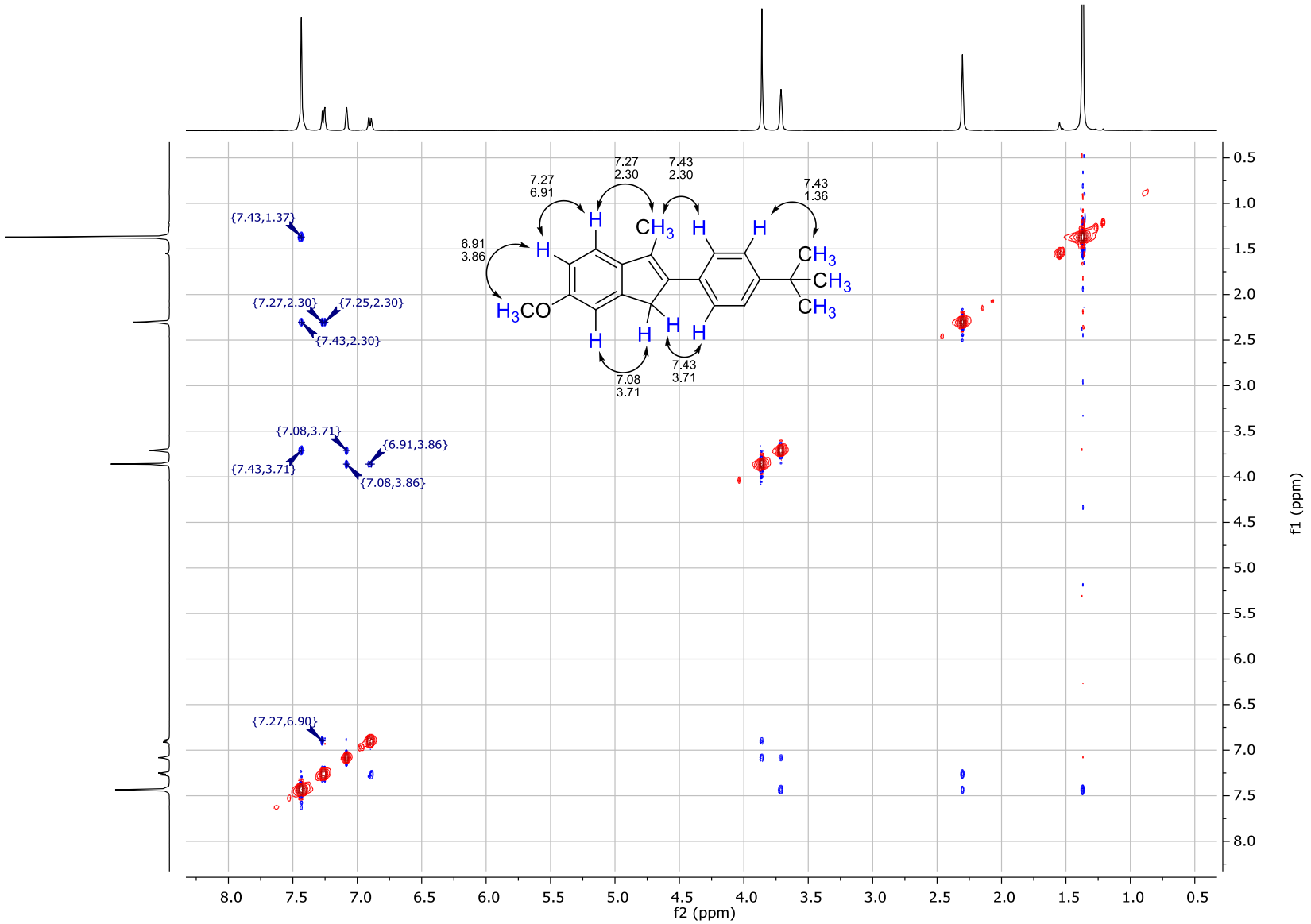

Figure S26. ^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-*tert*-butylphenyl)-6-methoxy-3-methyl-1*H*-indene (1d).

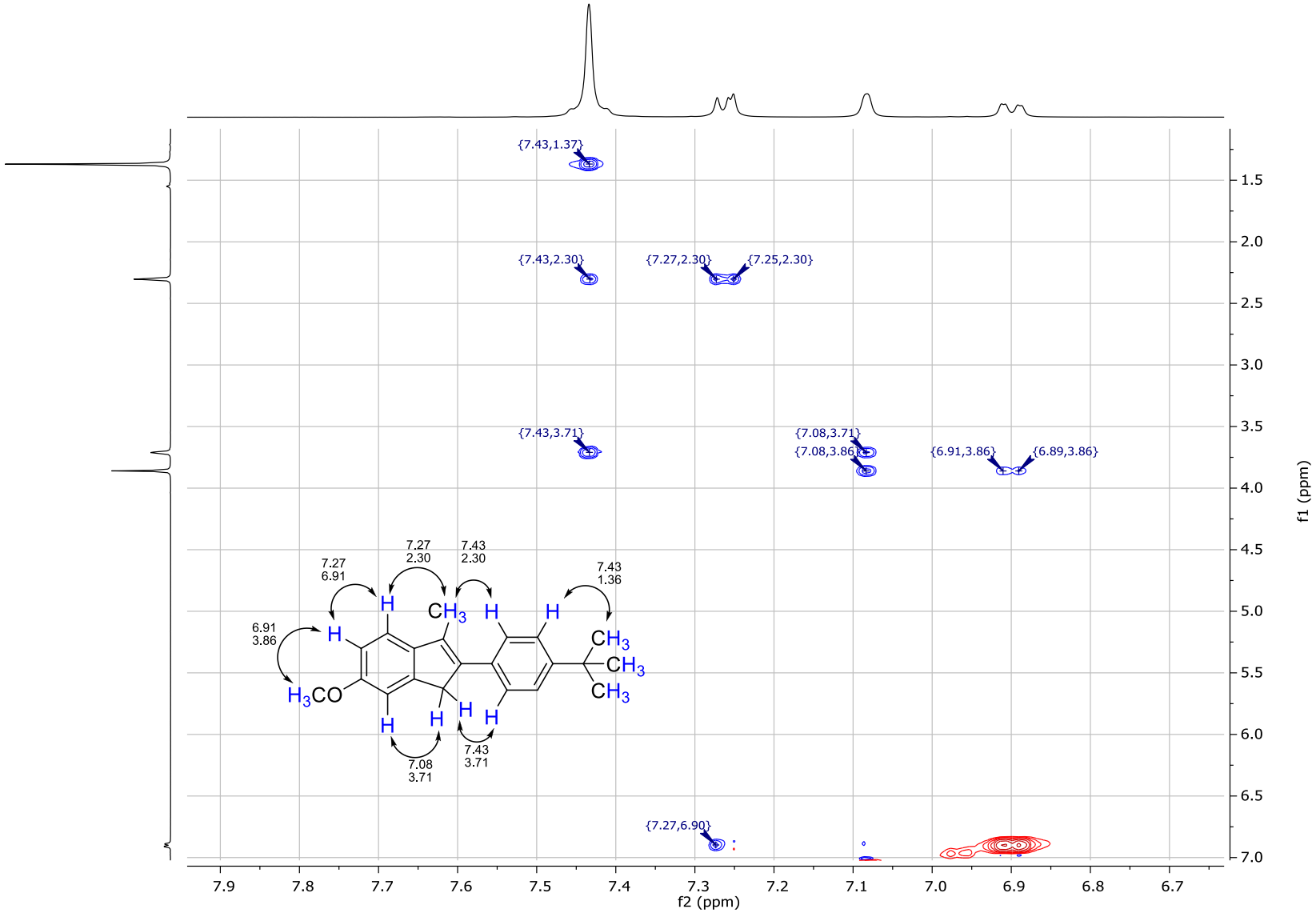

Figure S27. ^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-*tert*-butylphenyl)-6-methoxy-3-methyl-1*H*-indene (1d). Expanded region.