

PIFA-Mediated Cyclization of Methyl(2-(1-phenylvinyl)phenyl)sulfane for the Concise, Flexible, and Scalable De Novo Synthesis of C3-Arylated Benzo[b]thiophenes

Xinya Liu,^a Olivier Provot,^a Christine Tran^a Jean François Soulé,^b and Abdallah Hamze^a

a CNRS, BioCIS, Université Paris-Saclay, 91400 Orsay, France

b Chimie ParisTech, CNRS, Institute of Chemistry for Life and Health Sciences, PSL University, 75005 Paris, France

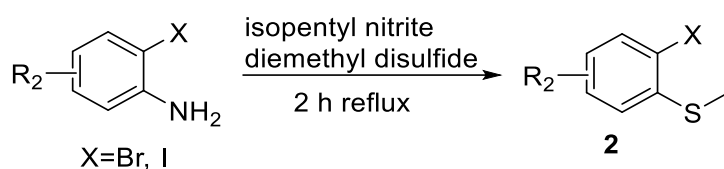
Contents

1. General information	2
2. General procedure A for the preparation of starting materials 2. ²	2
3. General procedure B for the preparation of (methyl)sulfane compounds 3.	3
4. Analytical data Characterization of compounds 3	4
5. General procedure C for the preparation of thiophenes 4.	12
6. Analytical data Characterization of compounds 4	12
7. Derivatization of benzothiophene 4 C2-arylation	20
8. Skeletal editing	21
9. Mechanism study: Control experiment.....	22
10. References.....	26
9. ¹ H, ¹³ C, ¹⁹ F NMR Spectra	27

1. General information

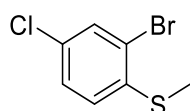
Solvent peaks were used as reference values, with CDCl₃ at 7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR. Chemical shifts δ are given in ppm, and the following abbreviations are used: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), multiplet (m), and broad singlet (bs). In the ¹³C NMR spectra, signals corresponding to C, CH, CH₂, or CH₃ were assigned from the JMOD sequence. Reaction courses and product mixtures were routinely monitored by TLC on silica gel, and compounds were visualized under a UVP Mineralight UVGL-58 lamp (254 nm) and with phosphomolybdic acid/heating, anisaldehyde/ heating, or vanillin/ heating. Flash chromatography was performed using silica gel 60 (40–63 mm, 230–400 mesh) at medium pressure (200 mbar). Dioxane, dichloromethane, cyclohexane, and tetrahydrofuran were dried using the procedures described in D. Perrin Purification of Laboratory Chemicals.¹ Organic extracts were, in general, dried over MgSO₄ or Na₂SO₄. High-resolution mass spectra were recorded with the aid of a MicrOTOF-Q II. A positive ion mass spectrum for the known product was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source.

2. General procedure A for the preparation of starting materials 2.²



To a flask under Ar was added dimethyl disulfide (200 mmol, 20.0 equiv.) and isopentyl nitrite (30 mmol, 3.0 equiv.). 2-haloaniline derivatives (10 mmol, 1.0 equiv.) were then slowly added, and the reaction was allowed to reflux at 70 °C for 2 h. The reaction was then concentrated under reduced pressure. The crude mixture was then extracted with EtOAc and washed with H₂O and brine. The combined organic phases were then dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was then purified on a silica plug (Pentane to Pentane/EtOAc: 9/1).

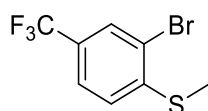
(2-Bromo-4-chlorophenyl)(methyl)sulfane (2w)²



Yellow liquid; ¹H NMR (200 MHz, CDCl₃) δ 7.79 (s, 1H), 7.48 – 7.28 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H).

Data are consistent with the literature.

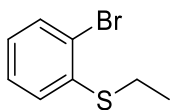
(2-Bromo-4-(trifluoromethyl)phenyl)(methyl)sulfane(2y)³



Yellow liquid; ¹H NMR (200 MHz, CDCl₃) δ 8.01 (s, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 2.51 (s, 3H).

Data are consistent with the literature.

(2-Bromophenyl)(ethyl)sulfane(2ad)⁴

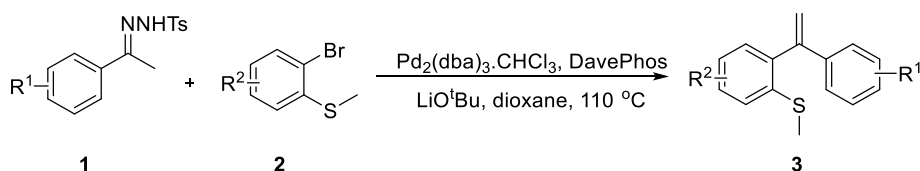


(2-Bromophenyl)(ethyl)sulfane was synthesized by the addition of iodoethane (0.81 mL, 10 mmol) to a solution containing 2-bromobenzenethiol (0.75 g, 4 mmol) and cesium carbonate (1.31 g, 4 mmol) in DMF (3 mL). The reaction mixture was stirred at room temperature, resulting in a notable exothermic reaction and immediate precipitation of a white solid. The progress of the reaction was monitored by TLC, showing completion within 2 hours. The mixture was then extracted twice with ethyl acetate (2 × 100 mL) and water. The combined organic layers were dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure, yielding (2-Bromophenyl)(ethyl)sulfane (0.87 g, 100%) as a yellow oil.

Yellow liquid (1.1 g, quant.); ¹H NMR (200 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.20 (m, 2H), 7.13 – 6.92 (m, 1H), 3.08 – 2.87 (q, *J* = 6.2 Hz, 2H), 1.39 (t, *J* = 6.2 Hz, 3H).

Data are consistent with the literature.

3. General procedure B for the preparation of (methyl)sulfane compounds 3.

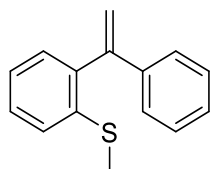


To a sealed tube under Ar, *N*-tosylhydrazone **1** (2.75 mmol) Pd₂(dba)₃·CHCl₃ (5 mol%), DavePhos (10 mol%), lithium *tert*-butoxide (5.5 mmol) were solubilized in dioxane (10 mL) in a sealed tube. Sulfane **2** (2.5 mmol, 1.0 equiv.) was slowly added, and the reaction was allowed to heat at 100 °C for 2.5 h. The crude reaction mixture was then allowed to reach room temperature, taken up in dichloromethane, and filtered through Celite®. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane to Pentane/EtOAc: 9/1).

4. Analytical data Characterization of compounds 3

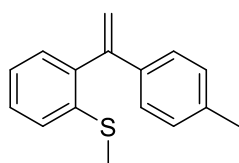
All the compounds **3** were prepared according to general procedure B.

Methyl(2-(1-phenylvinyl)phenyl)sulfane (**3a**)⁵



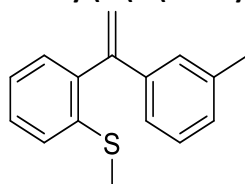
Yellow oil (481 mg, 85%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3053, 2918, 1712, 1612, 1583, 1492, 1467, 1433, 1359, 1321, 1255, 1219, 1155, 1126, 1072, 1053, 1037, 1026. ¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.27 (m, 7H), 7.28 – 7.17 (m, 2H), 5.89 (s, 1H), 5.34 (s, 1H), 2.39 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.1 (C), 140.8 (C), 139.9 (C), 137.7 (C), 130.2 (CH), 128.2 (2 CH), 128.1 (CH), 127.7 (CH), 126.6 (2 CH), 125.3 (CH), 124.6 (CH), 116.1 (CH₂), 15.9 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₅H₁₅S calcd. 227.0889, found 227.0890.

Methyl(2-(1-(*p*-tolyl)vinyl)phenyl)sulfane (**3b**)⁶



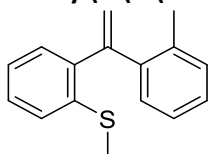
Yellow oil (420 mg, 70%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2918, 1610, 1583, 1510, 1465, 1433, 1321, 1303, 1255, 1186, 1181, 1085, 1055, 1035, 1018. ¹H NMR (300 MHz, CDCl₃) δ 7.43 – 7.31 (m, 1H), 7.32 – 7.18 (m, 5H), 7.14 (d, J = 8.4 Hz, 2H), 5.84 (s, 1H), 5.27 (s, 1H), 2.39 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 147.9 (C), 140.9 (C), 137.5 (2 C), 137.0 (C), 130.2 (CH), 129.0 (2 CH), 128.0 (CH), 126.4 (2 CH), 125.1 (CH), 124.5 (CH), 115.1 (CH₂), 21.1 (CH₃), 15.9 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₇S calcd. 241.1045, found 241.1052.

Methyl(2-(1-(*m*-tolyl)vinyl)phenyl)sulfane (**3c**)⁶



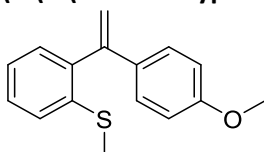
Yellow oil (450 mg, 75%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2918, 1598, 1581, 1487, 1465, 1433, 1315, 1257, 1126, 1055, 1037. ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.00 (m, 8H), 5.82 (s, 1H), 5.26 (s, 1H), 2.35 (s, 3H), 2.32 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.2 (C), 140.9 (C), 139.9 (C), 137.7 (2 C), 130.2 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 125.3 (CH), 124.6 (CH), 123.9 (CH), 115.9 (CH₂), 21.5 (CH₃), 15.9 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₇S calcd. 241.1045, found 241.1047.

Methyl(2-(1-(*o*-tolyl)vinyl)phenyl)sulfane (3d)



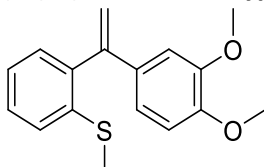
Yellow oil (432 mg, 72%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3053, 2918, 1612, 1583, 1487, 1460, 1433, 1313, 1159, 1041. ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.28 (m, 4H), 7.27 – 7.21 (m, 3H), 7.17 (m, 1H), 5.70 (d, *J* = 1.6 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 2.44 (s, 3H), 2.30 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 151.2 (C), 144.6 (C), 144.3 (C), 140.1 (C), 138.9 (C), 133.4 (CH), 132.8 (2 CH), 130.8 (CH), 130.4 (CH), 129.2 (CH), 128.4 (CH), 127.4 (CH), 123.1 (CH₂), 23.6 (CH₃), 19.1 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₆H₁₇S calcd. 241.1045, found 241.1046.

(2-(1-(4-Methoxyphenyl)vinyl)phenyl)(methyl)sulfane (3e)⁶



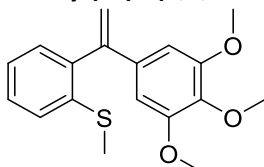
Yellow oil (512 mg, 80%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm⁻¹): 2835, 1712, 1604, 1570, 1508, 1463, 1431, 1359, 1319, 1292, 1246, 1178, 1149, 1116, 1083, 1055, 1029. ¹H NMR (300 MHz, CDCl₃) δ 7.36 (m, 1H), 7.30 – 7.17 (m, 5H), 6.92 – 6.79 (m, 2H), 5.76 (s, 1H), 5.20 (s, 1H), 3.82 (s, 3H), 2.38 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 159.3 (C), 147.5 (C), 140.9 (C), 137.6 (C), 132.5 (C), 130.1 (CH), 128.0 (CH), 127.7 (2 CH), 125.1 (CH), 124.5 (CH), 114.1 (CH₂), 113.6 (2 CH), 55.2 (CH₃), 15.9 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₆H₁₇OS calcd. 257.0995, found 257.0989.

(2-(1-(3,4-Dimethoxyphenyl)vinyl)phenyl)(methyl)sulfane (3f)



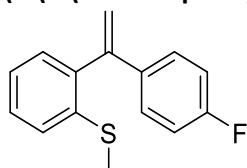
Pink solid (522 mg, 73%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 90/10). mp: 66-68 °C; IR (film, cm⁻¹): 2833, 1600, 1579, 1512, 1463, 1433, 1415, 1259, 1228, 1180, 1138, 1026. ¹H NMR (300 MHz, CDCl₃) δ 7.43 – 7.30 (m, 1H), 7.30 – 7.14 (m, 3H), 6.96 (d, *J* = 1.7 Hz, 1H), 6.91 – 6.66 (m, 2H), 5.77 (d, *J* = 1.0 Hz, 1H), 5.22 (d, *J* = 1.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.37 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 149.0 (C), 148.9 (C), 147.7 (C), 140.8 (C), 137.7 (C), 132.8 (C), 130.1 (CH), 128.1 (CH), 125.2 (CH), 124.5 (CH), 119.6 (CH), 114.3 (CH₂), 110.8 (CH), 109.6 (CH), 55.8 (2 CH₃), 15.9 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₇H₁₉O₂S calcd. 287.1100, found 287.1103.

Methyl(2-(1-(3,4,5-trimethoxyphenyl)vinyl)phenyl)sulfane (3g)



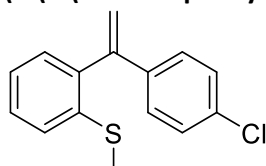
White solid (300 mg, 38%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 90/10). mp: 108-110 °C; IR (film, cm⁻¹): 2935, 2835, 1579, 1504, 1433, 1411, 1342, 1234, 1186, 1124, 1058, 1002. ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.31 (m, 1H), 7.27 (m, 1H), 7.24 – 7.09 (m, 2H), 6.53 (s, 2H), 5.80 (s, 1H), 5.27 (s, 1H), 3.86 (s, 3H), 3.79 (s, 6H), 2.38 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 153.0 (2 C), 147.9 (C), 140.5 (C), 138.1 (C), 137.8 (C), 135.6 (C), 130.1 (CH), 128.2 (CH), 125.3 (CH), 124.5 (CH), 115.6 (CH₂), 104.2 (2 CH), 60.8 (CH₃), 56.1 (2 CH₃), 16.0 (CH₃). HRMS (ESI) *m/z*: (M + Na)⁺ C₁₈H₂₀O₃SNa calcd. 339.1025, found 339.1028.

(2-(1-(4-Fluorophenyl)vinyl)phenyl)(methyl)sulfane (3h)



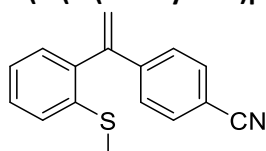
Yellow oil (531 mg, 87%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2920, 1600, 1583, 1504, 1465, 1433, 1319, 1298, 1255, 1220, 1157, 1101, 1083, 1055, 1012. ^1H NMR (300 MHz, CDCl_3) δ 7.41 – 7.31 (m, 1H), 7.33 – 7.16 (m, 5H), 7.08 – 6.90 (m, 2H), 5.79 (s, 1H), 5.29 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 162.5 (d, $J = 246$ Hz, C), 147.2 (C), 140.5 (C), 137.6 (C), 136.1 (C), 130.2 (2 CH), 128.3 (d, $J = 6$ Hz, CH), 128.2 (CH), 125.3 (CH), 124.7 (2 CH), 115.87 (CH_2), 115.1 (d, $J = 30$ Hz, CH), 15.88 (CH_3). ^{19}F NMR (188 MHz, CDCl_3) δ -114.64. HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{15}\text{H}_{14}\text{FS}$ calcd. 245.0795, found 245.0798.

(2-(1-(4-Chlorophenyl)vinyl)phenyl)(methyl)sulfane (3i)⁶



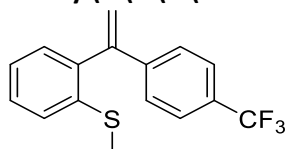
Yellow oil (507 mg, 78%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2918, 1614, 1583, 1489, 1465, 1431, 1394, 1317, 1253, 1091, 1055, 1035, 1010. ^1H NMR (300 MHz, CDCl_3) δ 7.37 (m, 1H), 7.31 – 7.16 (m, 7H), 5.83 (s, 1H), 5.33 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.1 (C), 140.2 (C), 138.4 (C), 137.6 (C), 133.5 (C), 130.2 (CH), 128.4 (2 CH), 128.3 (CH), 127.9 (2 CH), 125.4 (CH), 124.7 (CH), 116.5 (CH_2), 15.9 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{15}\text{H}_{14}\text{ClS}$ calcd. 261.0499, found 261.0501.

4-(1-(2-(Methylthio)phenyl)vinyl)benzotrile (3j)



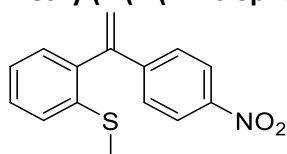
Yellow oil (446 mg, 71%); Rf = 0.35 (Cyclohexane/Ethyl acetate = 96/4). IR (film, cm^{-1}): 2920, 2225, 1712, 1602, 1583, 1504, 1465, 1433, 1402, 1321, 1255, 1180, 1118, 1083, 1055, 1039, 1016. ^1H NMR (300 MHz, CDCl_3) δ 7.63 – 7.53 (m, 2H), 7.44 – 7.32 (m, 3H), 7.29 – 7.18 (m, 3H), 5.92 (s, 1H), 5.45 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 146.9 (C), 144.5 (C), 139.3 (C), 137.6 (C), 132.1 (2 CH), 130.2 (CH), 128.7 (CH), 127.1 (2 CH), 125.6 (CH), 124.9 (CH), 119.1 (CH_2), 118.9 (CH_2), 111.1 (C), 15.9 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{16}\text{H}_{14}\text{NS}$ calcd. 252.0841, found 252.0841.

Methyl(2-(1-(4-(trifluoromethyl)phenyl)vinyl)phenyl)sulfane (3k)



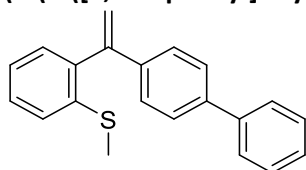
Yellow oil (522 mg, 71%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2922, 1616, 1510, 1465, 1435, 1406, 1321, 1255, 1163, 1112, 1087, 1064, 1039, 1014. ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.40 (m, 3H), 7.33 – 7.20 (m, 3H), 5.93 (s, 1H), 5.44 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.1 (C), 143.5 (C), 139.9 (C), 137.7 (C), 130.2 (CH), 129.3 (C), 128.5 (CH), 126.8 (2 CH), 125.5 (2 CH), 125.2 (q, $J = 4$ Hz, CH), 124.8 (CH), 124.2 (q, $J = 270$ Hz, CF), 118.2 (CH_2), 15.9 (CH_3). ^{19}F NMR (377 MHz, CDCl_3) δ -62.44. HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{16}\text{H}_{14}\text{F}_3\text{S}$ calcd. 295.0763, found 295.0764.

Methyl(2-(1-(4-nitrophenyl)vinyl)phenyl)sulfane (3l)



Yellow solid (203 mg, 30%); mp: 88-89 °C; Rf = 0.3 (Petroleum ether = 100). IR (film, cm^{-1}): 2920, 1593, 1512, 1490, 1465, 1431, 1338, 1288, 1255, 1182, 1109, 1083, 1055, 1039, 1012. ^1H NMR (300 MHz, CDCl_3) δ 8.24 – 8.02 (m, 2H), 7.50 – 7.33 (m, 3H), 7.28 (d, J = 4.6 Hz, 1H), 7.23 (m, 2H), 5.96 (s, 1H), 5.50 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.2 (C), 146.7 (C), 146.5 (C), 139.3 (C), 137.6 (C), 130.3 (CH), 128.8 (CH), 127.3 (2 CH), 125.7 (CH), 125.0 (CH), 123.6 (2 CH), 119.9 (CH_2), 15.9 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{15}\text{H}_{14}\text{NO}_2\text{S}$ calcd. 272.0740, found 272.0738.

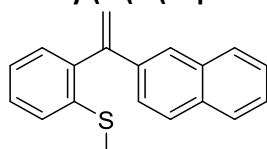
(2-(1-([1,1'-Biphenyl]-4-yl)vinyl)phenyl)(methyl)sulfane (3m)



Yellow oil (513 mg, 68%); Rf = 0.6 (Petroleum ether = 100). IR (film, cm^{-1}): 3028, 2918, 1581, 1516, 1485, 1463, 1433, 1402, 1319, 1155, 1122, 1085, 1055, 1037, 1006. ^1H NMR (300 MHz, CDCl_3) δ 7.68 – 7.51 (m, 4H), 7.52 – 7.32 (m, 6H), 7.29 (m, 2H), 7.25 – 7.18 (m, 1H), 5.92 (d, J = 1.2 Hz, 1H), 5.33 (d, J = 1.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.6 (C), 140.8 (C), 140.7 (C), 140.5 (C), 138.9 (C), 137.8 (C), 130.3 (CH), 128.7 (3 CH), 128.2 (CH), 127.2 (CH), 127.0 (5 CH), 125.3 (CH), 124.7 (CH), 116.1 (CH_2), 15.9 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{21}\text{H}_{19}\text{S}$ calcd. 303.1202, found 303.1200.

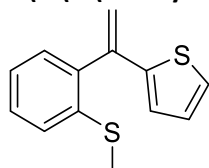
Gram-scale reaction for 3m. was prepared using the same procedure B. starting from (Z)-N'--(1-([1,1'-biphenyl]-4-yl)ethylidene)-4-methylbenzenesulfonohydrazide (3.36 g, 9.24 mmol), and (2-bromophenyl)(methyl)sulfane (1.68 g, 8.4 mmol). After purification by flash chromatography on silica gel (Pentane to Pentane/EtOAc: 9/1). Compound **3m** was obtained as a yellow oil (1.97 g, 78%).

Methyl(2-(1-(naphthalen-2-yl)vinyl)phenyl)sulfane (3n)



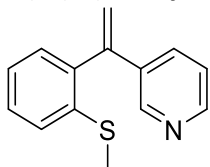
Yellow oil (524 mg, 76%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 3053, 2918, 1583, 1504, 1463, 1431, 1315, 1271, 1238, 1199, 1120, 1076, 1053, 1018. ^1H NMR (300 MHz, CDCl_3) δ 7.78 (m, J = 16.3, 2.9 Hz, 3H), 7.60 (s, 2H), 7.52 – 7.35 (m, 3H), 7.27 (m, J = 12.8, 6.7 Hz, 3H), 5.99 (s, 1H), 5.40 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.1 (C), 140.7 (C), 137.8 (C), 137.3 (C), 133.4 (C), 133.0 (C), 130.3 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.6 (CH), 126.0 (CH), 125.9 (2 CH), 125.4 (CH), 124.7 (CH), 124.5 (CH), 116.6 (CH_2), 15.9 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{19}\text{H}_{17}\text{S}$ calcd. 277.1045, found 277.1046.

2-(1-(2-(Methylthio)phenyl)vinyl)thiophene (3o)



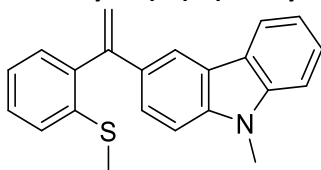
Yellow oil (365 mg, 63%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2918, 1610, 1583, 1465, 1433, 1342, 1313, 1255, 1224, 1122, 1083, 1064, 1053, 1022. ^1H NMR (300 MHz, CDCl_3) δ 7.38 (m, 1H), 7.33 – 7.29 (m, 1H), 7.27 – 7.16 (m, 3H), 6.94 (dd, J = 5.1, 3.6 Hz, 1H), 6.71 (dd, J = 3.6, 1.1 Hz, 1H), 5.83 (s, 1H), 5.16 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.6 (C), 141.7 (C), 140.0 (C), 137.7 (C), 129.8 (CH), 128.4 (CH), 127.4 (CH), 125.9 (CH), 125.5 (CH), 125.1 (CH), 124.6 (CH), 114.5 (C), 16.1 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{13}\text{H}_{13}\text{S}_2$ calcd. 233.0453, found 233.0454.

3-(1-(2-(Methylthio)phenyl)vinyl)pyridine (3p)



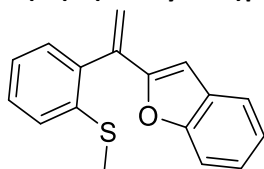
Yellow oil (482 mg, 85%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 90/10). IR (film, cm^{-1}): 2920, 1616, 1583, 1564, 1471, 1433, 1413, 1311, 1257, 1192, 1126, 1089, 1056, 1037, 1022. ^1H NMR (300 MHz, CDCl_3) δ 8.49 (d, J = 1.8 Hz, 1H), 8.41 (dd, J = 4.8, 1.6 Hz, 1H), 7.54 – 7.39 (m, 1H), 7.32 – 7.23 (m, 1H), 7.20 – 7.07 (m, 4H), 5.78 (s, 1H), 5.31 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.6 (CH), 148.1 (CH), 145.5 (C), 139.5 (C), 137.6 (C), 135.6 (C), 133.7 (CH), 130.2 (CH), 128.6 (CH), 125.6 (CH), 124.9 (CH), 123.0 (CH), 117.8 (CH_2), 15.9 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{14}\text{H}_{14}\text{NS}$ calcd. 228.0841, found 228.0844.

9-Methyl-3-(1-(2-(methylthio)phenyl)vinyl)-9H-carbazole (3q)



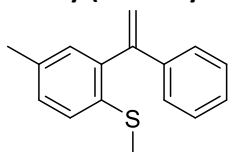
Yellow oil (452 mg, 55%); Rf = 0.4 (Cyclohexane/Ethyl acetate = 98/2). IR (film, cm^{-1}): 2922, 2848, 1597, 1469, 1431, 1359, 1321, 1276, 1244, 1155, 1122, 1053, 1020. ^1H NMR (300 MHz, CDCl_3) δ 8.14 (m, 2H), 7.58 (dd, J = 8.5, 1.8 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.27 (m, 7H), 6.02 (s, 1H), 5.42 (s, 1H), 3.80 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 149.0 (C), 141.6 (C), 141.6 (C), 140.9 (C), 138.0 (C), 131.4 (C), 130.5 (CH), 128.2 (CH), 125.9 (CH), 125.3 (CH), 125.0 (CH), 124.7 (CH), 123.1 (C), 122.1 (C), 120.6 (CH), 119.1 (CH), 118.8 (CH), 114.3 (CH_2), 108.6 (CH), 108.3 (CH), 29.1 (CH_3), 16.0 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{22}\text{H}_{20}\text{NS}$ calcd. 330.1311, found 330.1314.

2-(1-(2-(methylthio)phenyl)vinyl)benzofuran (3r)



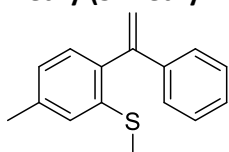
Yellow oil (399 mg, 60%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2918, 1616, 1583, 1550, 1465, 1450, 1433, 1301, 1255, 1174, 1107, 1078, 1051, 1037, 1006. ^1H NMR (300 MHz, CDCl_3) δ 7.61 – 7.39 (m, 3H), 7.38 – 7.19 (m, 5H), 6.30 (s, 1H), 6.29 (s, 1H), 5.43 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 155.4 (C), 155.1 (C), 138.1 (C), 137.9 (C), 137.3 (C), 130.0 (CH), 129.0 (C), 128.7 (CH), 125.7 (CH), 124.7 (2 CH), 122.7 (CH), 121.4 (CH), 116.5 (CH_2), 111.1 (CH), 105.5 (CH), 16.2 (CH_3). HRMS (ESI) m/z : ($\text{M} + \text{H}$) $^+$ $\text{C}_{17}\text{H}_{15}\text{OS}$ calcd. 267.0838, found 267.0840.

Methyl(4-methyl-2-(1-phenylvinyl)phenyl)sulfane (3s)



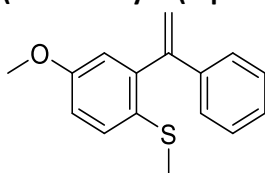
Yellow oil (420 mg, 70%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2918, 1614, 1573, 1492, 1465, 1319, 1255, 1211, 1155, 1138, 1074, 1049, 1026. ^1H NMR (300 MHz, CDCl_3) δ 7.41 – 6.92 (m, 8H), 5.83 (s, 1H), 5.28 (s, 1H), 2.4 (3H), 2.34 (3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.3 (C), 143.8 (C), 141.1 (C), 140.1 (C), 134.6 (C), 131.1 (CH), 128.9 (CH), 128.2 (2 CH), 127.6 (CH), 126.6 (2 CH), 126.2 (CH), 115.8 (CH_2), 20.7 (CH_3), 16.5 (CH_3). HRMS (ESI) m/z: (M + H)⁺ $\text{C}_{16}\text{H}_{17}\text{S}$ calcd. 241.1045, found 241.1048.

Methyl(5-methyl-2-(1-phenylvinyl)phenyl)sulfane (3t)



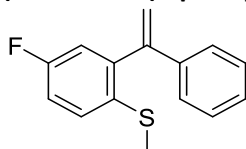
Yellow oil (486 mg, 81%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2918, 1597, 1573, 1492, 1481, 1319, 1261, 1217, 1153, 1072, 1051, 1028. ^1H NMR (300 MHz, CDCl_3) δ 7.38 – 7.24 (m, 5H), 7.18 – 7.05 (m, 2H), 7.04 – 6.94 (m, 1H), 5.83 (d, J = 1.1 Hz, 1H), 5.30 (d, J = 1.1 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.1 (C), 138.1 (C), 137.9 (C), 137.3 (C), 130.2 (CH), 129.2 (C), 128.2 (2 CH), 127.6 (CH), 126.6 (2 CH), 126.1 (CH), 125.5 (CH), 116.0 (CH_2), 21.3 (CH_3), 16.0 (CH_3). HRMS (ESI) m/z: (M + H)⁺ $\text{C}_{16}\text{H}_{17}\text{S}$ calcd. 241.1045, found 241.1050.

(4-Methoxy-2-(1-phenylvinyl)phenyl)(methyl)sulfane (3u)



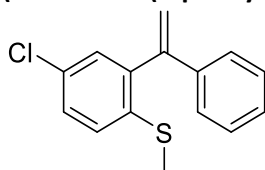
Yellow oil (390 mg, 61%); Rf = 0.5 (Petroleum ether = 100). IR (film, cm^{-1}): 2833, 1591, 1562, 1492, 1463, 1440, 1413, 1321, 1286, 1257, 1222, 1182, 1151, 1130, 1053, 1028. ^1H NMR (300 MHz, CDCl_3) δ 7.30 (m, 5H), 7.26 (d, J = 1.9 Hz, 1H), 6.90 (m, 1H), 6.83 (m, 1H), 5.82 (s, 1H), 5.27 (s, 1H), 3.81 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 157.9 (C), 148.5 (C), 143.6 (C), 140.0 (C), 133.8 (C), 129.7 (CH), 128.2 (2 CH), 127.6 (CH), 126.5 (2 CH), 116.2 (CH), 115.6 (CH_2), 113.9 (CH), 55.4 (CH_3), 17.8 (CH_3). HRMS (ESI) m/z: (M + H)⁺ $\text{C}_{16}\text{H}_{17}\text{OS}$ calcd. 257.0995, found 257.0996.

(4-Fluoro-2-(1-phenylvinyl)phenyl)(methyl)sulfane (3v)



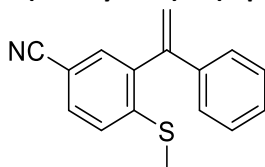
Yellow oil (336 mg, 55%); Rf = 0.55 (Petroleum ether = 100). IR (film, cm^{-1}): 2920, 1595, 1573, 1492, 1462, 1411, 1319, 1301, 1282, 1253, 1203, 1141, 1074, 1047, 1028. ^1H NMR (300 MHz, CDCl_3) δ 7.37 – 7.22 (m, 6H), 7.13 – 6.93 (m, 2H), 5.87 (s, 1H), 5.32 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 146.9 (C), 143.3 (C), 140.5 (2 C), 139.0 (C), 128.4 (2 CH), 128.0 (CH), 126.6 (d, J = 4 Hz, CH), 126.5 (2 CH), 124.8 (d, J = 4 Hz, CH), 124.2 (CH), 117.1 (CH_2), 15.4 (CH_3). ^{19}F NMR (377 MHz, CDCl_3) δ -118.23. HRMS (ESI) m/z: (M + H)⁺ $\text{C}_{15}\text{H}_{14}\text{FS}$ calcd. 245.0795, found 245.0796.

(4-Chloro-2-(1-phenylvinyl)phenyl)(methyl)sulfane (3w)



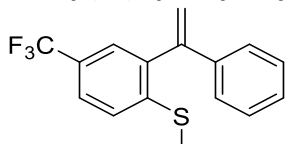
Yellow solid (403 mg, 62%); R_f = 0.5 (Petroleum ether = 100). mp: 44-46 °C; IR (film, cm⁻¹): 2918, 1712, 1614, 1575, 1550, 1492, 1458, 1435, 1390, 1315, 1253, 1219, 1159, 1101, 1047, 1026. ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.25 (m, 6H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 5.86 (s, 1H), 5.31 (s, 1H), 2.34 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 147.1 (C), 139.3 (C), 130.5 (C), 130.0 (CH), 128.4 (2 CH), 128.1 (CH), 127.9 (CH), 126.7 (CH), 126.5 (2 CH), 123.6 (C), 121.3 (C), 116.7 (CH₂), 16.1 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₅H₁₄ClS calcd.261.0499, found 261.0495.

4-(Methylthio)-3-(1-phenylvinyl)benzonitrile (3x)



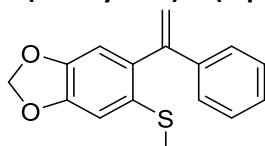
White solid (439 mg, 70%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 98/2). mp: 99-101 °C; IR (film, cm⁻¹): 3055, 2918, 2223, 1710, 1616, 1587, 1492, 1462, 1431, 1321, 1257, 1193, 1134, 1091, 1076, 1049, 1026. ¹H NMR (300 MHz, CDCl₃) δ 7.61 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.39 – 7.21 (m, 6H), 5.91 (s, 1H), 5.34 (s, 1H), 2.40 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 146.2 (C), 145.7 (C), 140.6 (C), 138.6 (C), 132.8 (CH), 131.4 (CH), 128.5 (2 CH), 128.2 (CH), 126.4 (2 CH), 124.1 (CH), 118.9 (CN), 117.6 (CH₂), 107.5 (C), 15.2 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₄NS calcd.252.0841, found 252.0843.

Methyl(2-(1-phenylvinyl)-4-(trifluoromethyl)phenyl)sulfane (3y)



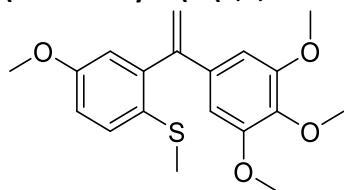
Yellow solid (456 mg, 62%); R_f = 0.5 (Petroleum ether = 100). mp: 41-43 °C; IR (film, cm⁻¹): 2922, 1604, 1494, 1366, 1313, 1273, 1257, 1174, 1153, 1120, 1095, 1082, 1051, 1028. ¹H NMR (300 MHz, CDCl₃) δ 7.63 – 7.54 (m, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.27 (m, 6H), 5.90 (s, 1H), 5.33 (s, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.1 (C), 143.4 (C), 140.6 (C), 139.1 (C), 128.6 (2 CH), 128.2 (CH), 126.8 (q, *J* = 4 Hz, CH), 126.6 (2 CH), 126.5 (C), 124.9 (q, *J* = 4 Hz, CH), 124.4 (q, *J* = 273 Hz, CF), 124.3 (CH), 117.3 (CH₂), 15.52 (CH₃). ¹⁹F NMR (377 MHz, CDCl₃) δ -62.07. HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₄F₃S calcd. 295.0763, found 295.0764.

5-(Methylthio)-6-(1-phenylvinyl)benzo[d][1,3]dioxole (3z)



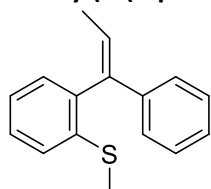
Yellow oil (304 mg, 45%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1573, 1498, 1473, 1444, 1330, 1226, 1114, 1035. ¹H NMR (200 MHz, CDCl₃) δ 7.32 (s, 5H), 6.88 (s, 1H), 6.76 (s, 1H), 6.00 (s, 2H), 5.82 (s, 1H), 5.27 (s, 1H), 2.28 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.1 (C), 147.7 (C), 145.8 (C), 140.3 (C), 135.6 (C), 129.6 (C), 128.2 (2 CH), 127.6 (CH), 126.6 (2 CH), 116.1 (CH₂), 110.8 (CH), 108.4 (CH), 101.3 (CH₂), 17.7 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₅O₂S calcd. 271.0787, found 271.0782.

(4-Methoxy-2-(1-(3,4,5-trimethoxyphenyl)vinyl)phenyl)(methyl)sulfane (3aa)



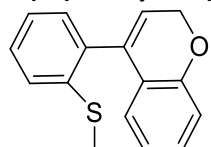
Yellow oil (649 mg, 75%); R_f = 0.35 (Cyclohexane/Ethyl acetate = 85/15). IR (film, cm⁻¹): 1579, 1506, 1463, 1413, 1338, 1290, 1234, 1126, 1028, 1006. ¹H NMR (200 MHz, CDCl₃) δ 7.28 (d, *J* = 6.9 Hz, 1H), 6.97 – 6.77 (m, 2H), 6.53 (s, 2H), 5.77 (s, 1H), 5.24 (s, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.79 (s, 6H), 2.30 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 157.8 (C), 153.0 (2 C), 148.2 (C), 143.4 (C), 138.2 (C), 135.7 (C), 129.7 (CH), 128.2 (C), 116.1 (CH), 115.2 (CH₂), 114.0 (CH), 104.2 (2 CH), 60.8 (CH₃), 56.1 (2 CH₃), 55.4 (CH₃), 17.9 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₉H₂₃O₄S calcd. 347.1312, found 347.1317.

Methyl(2-(1-phenylprop-1-en-1-yl)phenyl)sulfane (3ab)



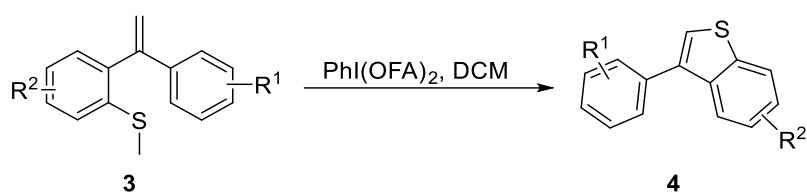
Yellow oil (396 mg, 66%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2918, 1492, 1435, 1064, 1037. ¹H NMR (300 MHz, CDCl₃) δ 7.37 (m, 1H), 7.32 – 7.20 (m, 7H), 7.13 (m, 1H), 6.38 (q, *J* = 6.9 Hz, 1H), 2.36 (s, 3H), 1.68 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 140.8 (C), 140.3 (C), 138.3 (C), 138.1 (C), 130.3 (CH), 128.2 (2 CH), 127.8 (CH), 126.7 (CH), 126.1 (2 CH), 125.7 (CH), 124.6 (CH), 124.5 (CH), 15.4 (CH₃), 15.2 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₆H₁₇S calcd. 241.1045, found 241.1045.

3-(2-(Methylthio)phenyl)-2H-chromene (3ac)



Yellow oil (527 mg, 83%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 98/2). R_f=0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2920, 1710, 1639, 1602, 1583, 1483, 1462, 1448, 1431, 1342, 1267, 1220, 1147, 1114, 1064, 1012. ¹H NMR (300 MHz, CDCl₃) δ 7.46 – 7.34 (m, 1H), 7.34 – 7.25 (m, 1H), 7.24 – 7.08 (m, 3H), 6.97 – 6.75 (m, 2H), 6.66 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.78 (t, *J* = 3.7 Hz, 1H), 5.03-4.92 (m, 2H), 2.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 154.1 (C), 138.3 (C), 136.7 (C), 135.3 (C), 129.9 (CH), 129.3 (CH), 128.5 (CH), 125.5 (CH), 125.1 (CH), 124.6 (CH), 123.2 (C), 121.7 (CH), 121.1 (CH), 116.0 (CH), 65.4 (CH₂), 15.8 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₆H₁₅OS calcd. 255.0838, found 255.0842.

5. General procedure C for the preparation of thiophenes 4.

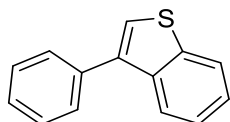


To a solution of the corresponding compound **3** (0.2 mmol, 1.0 equiv.) and $\text{PhI}(\text{OFA})_2$ (0.6 mmol, 3.0 equiv.), 2 mL of dry DCM was added, and the resulting mixture was stirred at room temperature for 10 mins. The mixture was added to a saturated sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution and stirred at room temperature, which was extracted with DCM three times. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane to Pentane/EtOAc: 9/1).

6. Analytical data Characterization of compounds 4

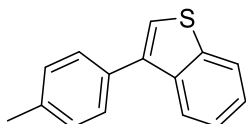
All the compounds **4** were prepared according to general procedure C.

3-Phenylbenzo[*b*]thiophene (**4a**)⁷



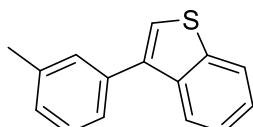
Yellow oil (35 mg, 82%); $R_f = 0.5$ (Petroleum ether = 100). IR (film, cm^{-1}): 3057, 1598, 1523, 1483, 1458, 1440, 1425, 1348, 1305, 1259, 1211, 1143, 1072, 1060. ^1H NMR (300 MHz, CDCl_3) δ 8.06 – 7.85 (m, 2H), 7.62 (m, 2H), 7.52 (m, 2H), 7.47 – 7.31 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 140.7 (C), 138.1 (C), 138.0 (C), 136.1 (C), 128.7 (2 CH), 127.6 (2 CH), 124.4 (CH), 124.3 (CH), 123.4 (CH), 122.9 (3 CH). HRMS (ESI) m/z : $(\text{M} + \text{H})^+$ $\text{C}_{14}\text{H}_{11}\text{S}$ calcd. 211.0576, found 211.0575.

3-(*p*-Tolyl)benzo[*b*]thiophene (**4b**)⁸



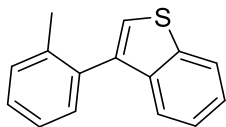
White oil (37 mg, 82%); $R_f = 0.5$ (Petroleum ether = 100). IR (film, cm^{-1}): 1531, 1494, 1425, 1342, 1058, 1020. ^1H NMR (300 MHz, CDCl_3) δ 7.93 (m, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.35 (m, 3H), 7.31 (d, $J = 7.8$ Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 140.7 (C), 138.1 (C), 138.0 (C), 137.3 (C), 133.1 (C), 129.4 (2 CH), 128.6 (2 CH), 124.3 (CH), 124.2 (CH), 122.9 (CH), 122.9 (CH), 122.9 (CH), 21.2 (CH_3). HRMS (ESI) m/z : $(\text{M} + \text{H})^+$ $\text{C}_{15}\text{H}_{13}\text{S}$ calcd. 225.0732, found 225.0732.

3-(*m*-Tolyl)benzo[*b*]thiophene (**4c**)⁸



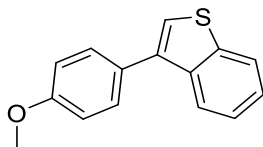
White oil (38 mg, 84%); $R_f = 0.5$ (Petroleum ether = 100). IR (film, cm^{-1}): 1604, 1583, 1521, 1456, 1427, 1377, 1261, 1240, 1165, 1141, 1091, 1060, 1022. ^1H NMR (300 MHz, CDCl_3) δ 8.42 – 7.82 (m, 2H), 7.45 (m, 6H), 7.37 – 7.19 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 140.7 (C), 138.4 (C), 138.3 (C), 138.0 (C), 136.0 (C), 129.5 (CH), 128.6 (CH), 128.3 (CH), 125.8 (CH), 124.0 (CH), 124.3 (CH), 123.2 (CH), 123.0 (CH), 122.9 (CH), 21.5 (CH_3). HRMS (ESI) m/z : $(\text{M} + \text{H})^+$ $\text{C}_{15}\text{H}_{13}\text{S}$ calcd. 225.0732, found 225.0734.

3-(*o*-Tolyl)benzo[*b*]thiophene (4d)⁸



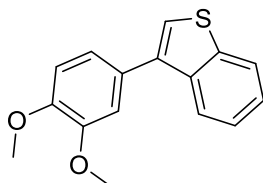
White oil (35 mg, 79%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3059, 1525, 1477, 1454, 1109, 1056, 1045, 1018. ¹H NMR (300 MHz, CDCl₃) δ 8.04 – 7.92 (m, 1H), 7.59 – 7.49 (m, 1H), 7.49 – 7.30 (m, 7H), 2.25 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 140.0 (C), 139.1 (C), 137.6 (C), 137.1 (C), 135.5 (C), 130.5 (CH), 130.3 (CH), 127.9 (CH), 125.7 (CH), 124.3 (CH), 124.2 (CH), 123.7 (CH), 123.2 (CH), 122.7 (CH), 20.2 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₅H₁₃S calcd. 225.0732, found 225.0732.

3-(4-Methoxyphenyl)benzo[*b*]thiophene (4e)⁸



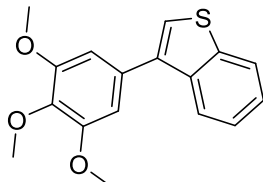
White oil (37 mg, 77%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2833, 1710, 1610, 1573, 1527, 1492, 1438, 1425, 1346, 1303, 1286, 1244, 1176, 1107, 1058, 1031. ¹H NMR (300 MHz, CDCl₃) δ 8.06 – 7.80 (m, 2H), 7.63 – 7.48 (m, 2H), 7.47 – 7.36 (m, 2H), 7.34 (s, 1H), 7.11 – 6.97 (m, 2H), 3.89 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 159.2 (C), 140.7 (C), 138.1 (C), 137.7 (C), 129.8 (2 CH), 128.5 (C), 124.3 (CH), 124.2 (CH), 122.9 (2 CH), 122.5 (CH), 114.2 (2 CH), 55.4 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₅H₁₃OS calcd. 241.0682, found 241.0689.

3-(3,4-Dimethoxyphenyl)benzo[*b*]thiophene (4f)⁹



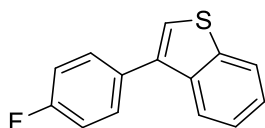
White oil (46 mg, 85%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 94/6). IR (film, cm⁻¹): 2997, 2883, 1604, 1583, 1527, 1496, 1462, 1425, 1354, 1311, 1253, 1236, 1197, 1172, 1163, 1138, 1060, 1026. ¹H NMR (300 MHz, CDCl₃) δ 8.02 – 7.86 (m, 2H), 7.41 (m, 3H), 7.22 – 7.08 (m, 2H), 6.98 (s, 1H), 3.96 (s, 3H), 3.94 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 149.2 (C), 148.7 (C), 140.7 (C), 138.1 (C), 137.9 (C), 128.9 (C), 124.4 (CH), 124.3 (CH), 122.9 (CH), 122.9 (CH), 122.7 (CH), 121.1 (CH), 112.1 (CH), 111.5 (CH), 56.0 (2 CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₅O₂S calcd 271.0787, found 271.0791.

3-(3,4,5-Trimethoxyphenyl)benzo[*b*]thiophene (4g)¹⁰



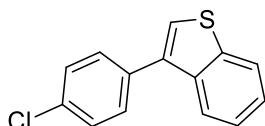
Yellow oil (46 mg, 76%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 98/2). IR (film, cm⁻¹): 1583, 1496, 1413, 1354, 1236, 1126, 1010. ¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.88 (m, 2H), 7.47 – 7.35 (m, 3H), 6.80 (s, 2H), 3.94 (s, 3H), 3.92 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 153.5 (2 C), 140.7 (C), 138.1 (C), 137.9 (C), 131.6 (C), 124.5 (CH), 124.4 (CH), 123.2 (CH), 122.9 (CH), 122.9 (CH), 106.1 (2 CH), 61.0 (CH₃), 56.3 (2 CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₇H₁₇O₃S calcd 301.0893, found 301.0895.

3-(4-Fluorophenyl)benzo[*b*]thiophene (4h)⁸



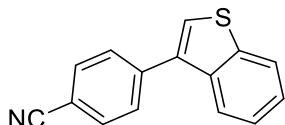
White oil (33 mg, 72%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1606, 1556, 1529, 1490, 1456, 1425, 1408, 1342, 1317, 1296, 1220, 1157, 1093, 1058, 1014. ¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.80 (m, 2H), 7.55 (m, 2H), 7.46 – 7.33 (m, 3H), 7.24 – 7.13 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 162.4 (d, *J* = 245 Hz, C), 140.6 (2 C), 137.9 (C), 137.0 (C), 130.2 (d, *J* = 8 Hz, 2 CH), 124.5 (d, *J* = 6 Hz, 2 CH), 123.4 (CH), 122.9 (CH), 122.7 (CH), 115.8 (CH), 115.5 (CH). ¹⁹F NMR (377 MHz, CDCl₃) δ -114.52. HRMS (ESI) *m/z*: (M + H)⁺ C₁₄H₁₀FS calcd 229.0482, found 229.0481.

3-(4-Chlorophenyl)benzo[*b*]thiophene (4i)¹¹



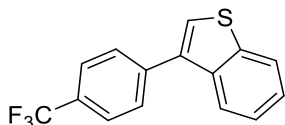
White oil (35 mg, 72%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1519, 1481, 1425, 1400, 1342, 1315, 1296, 1261, 1211, 1143, 1089, 1058, 1014. ¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.82 (m, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.31 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 144.7 (C), 140.7 (C), 136.8 (C), 134.4 (C), 133.5 (C), 129.9 (2 CH), 128.9 (2 CH), 124.5 (CH), 124.5 (CH), 123.7 (CH), 122.9 (CH), 122.6 (CH). HRMS (ESI) *m/z*: (M + H)⁺ C₁₄H₁₀ClS calcd 245.0186, found 245.0181.

4-(Benzo[*b*]thiophen-3-yl)benzonitrile (4j)¹¹



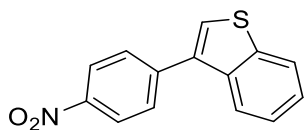
White oil (26 mg, 56%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2922, 1710, 1361, 1219. ¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.90 (m, 1H), 7.90 – 7.82 (m, 1H), 7.81 – 7.74 (m, 2H), 7.74 – 7.64 (m, 2H), 7.50 (s, 1H), 7.48 – 7.38 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 140.8 (C), 140.6 (C), 137.0 (C), 136.1 (C), 132.6 (2 CH), 129.2 (2 CH), 125.3 (CH), 124.9 (CH), 124.8 (CH), 123.1 (CH), 122.3 (CH), 118.8 (C), 111.2 (C). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₀NS calcd. 236.0528, found 236.0533.

3-(4-(Trifluoromethyl)phenyl)benzo[*b*]thiophene (4k)¹⁰



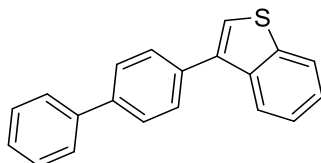
Yellow solid (34 mg, 62%); R_f = 0.5 (Petroleum ether = 100). mp: 45-48 °C, IR (film, cm⁻¹): 1712, 1618, 1458, 1425, 1409, 1319, 1213, 1161, 1118, 1105, 1066, 1018. ¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.84 (m, 2H), 7.81 – 7.65 (m, 4H), 7.48 (s, 1H), 7.46 – 7.38 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 142.0 (C), 140.7 (C), 139.6 (C), 137.4 (C), 136.6 (C), 128.9 (2 CH), 126.7 (q, *J* = 272 Hz, CF), 125.7 (q, *J* = 4 Hz, CH), 124.7 (CH), 124.6 (2 CH), 123.1 (2 CH), 122.6 (CH). ¹⁹F NMR (377 MHz, CDCl₃) δ -62.43. HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₀F₃S calcd 279.0450, found 279.0448.

3-(4-Nitrophenyl)benzo[*b*]thiophene (**4l**)¹⁰



Yellow oil (36 mg, 70%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1597, 1510, 1456, 1425, 1342, 1217, 1107, 1058. ¹H NMR (300 MHz, CDCl₃) δ 8.43 – 8.25 (m, 2H), 8.03 – 7.83 (m, 2H), 7.82 – 7.68 (m, 2H), 7.56 (s, 1H), 7.52 – 7.40 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 147.1 (C), 142.5 (C), 140.8 (C), 137.0 (2 C), 129.2 (2 CH), 125.7 (CH), 124.9 (CH), 124.9 (CH), 124.1 (2 CH), 123.1 (CH), 122.3 (CH). HRMS (ESI) m/z: (M + H)⁺ C₁₄H₁₀NO₂S calcd 256.0427, found 256.0426.

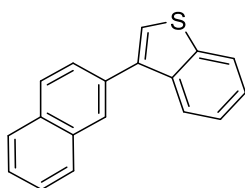
3-([1,1'-Biphenyl]-4-yl)benzo[*b*]thiophene (**4m**)¹²



White solid (43 mg, 76%); mp: 89-91 °C; R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3028, 1529, 1483, 1446, 1425, 1404, 1344, 1259, 1060, 1006. ¹H NMR (300 MHz, CDCl₃) δ 8.08 – 7.91 (m, 2H), 7.82 – 7.64 (m, 6H), 7.58 – 7.35 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 140.8 (C), 140.7 (C), 140.4 (C), 137.9 (C), 137.7 (C), 135.0 (C), 129.1 (2 CH), 128.9 (2 CH), 127.4 (3 CH), 127.1 (2 CH), 124.5 (CH), 124.4 (CH), 123.5 (CH), 123.0 (2 CH). HRMS (ESI) m/z: (M + H)⁺ C₂₀H₁₅S calcd 287.0889, found 287.0885.

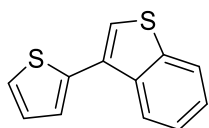
Gram-scale reaction for 4m. To a solution of **3m** (1.97 g, 6.5 mmol, 1.0 equiv.) and PhI(OFA)₂ (8.3 g, 19.5 mmol, 3.0 equiv.), 44 mL of dry DCM was added, and the resulting mixture was stirred at room temperature for 10 mins. The mixture was added saturated sodium thiosulfate (Na₂S₂O₃) and stirred at room temperature, which was extracted with DCM. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane to Pentane/EtOAc: 9/1). The expected product **4a** was obtained in 80% yield, 5.2 mmol, 1.49 g.

3-(Naphthalen-2-yl)benzo[*b*]thiophene (**4n**)¹³



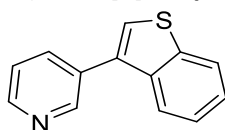
White oil (35 mg, 68%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3051, 1629, 1598, 1523, 1504, 1456, 1425, 1311, 1259, 1246, 1205, 1143, 1132, 1058, 1020. ¹H NMR (300 MHz, CDCl₃) δ 8.16 – 7.87 (m, 6H), 7.76 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.64 – 7.51 (m, 3H), 7.51 – 7.37 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 140.8 (C), 138.1 (2 C), 133.6 (C), 133.5 (C), 132.8 (C), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.0 (CH), 126.4 (CH), 126.1 (CH), 124.5 (CH), 124.5 (CH), 123.8 (CH), 123.0 (2 CH). HRMS (ESI) m/z: (M + H)⁺ C₁₈H₁₃S calcd 261.0732, found 261.0730.

3-(Thiophen-2-yl)benzo[*b*]thiophene (4o)⁸



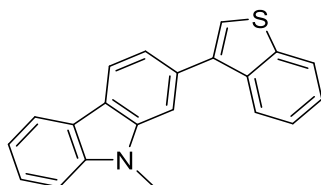
Yellow oil (26 mg, 60%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1456, 1435, 1415, 1369, 1338, 1309, 1257, 1228, 1141, 1122, 1076, 1056, 1022. ¹H NMR (300 MHz, CDCl₃) δ 8.20 – 8.08 (m, 1H), 7.96 – 7.86 (m, 1H), 7.52 (s, 1H), 7.49 – 7.33 (m, 4H), 7.17 (dd, *J* = 5.1, 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 140.7 (C), 137.5 (2 C), 130.7 (C), 127.7 (CH), 125.3 (CH), 124.9 (CH), 124.8 (CH), 124.7 (CH), 124.0 (CH), 123.1 (CH), 123.0 (CH). HRMS (ESI) *m/z*: (M + H)⁺ C₁₂H₉S₂ calcd 217.0140, found 217.0142.

3-(Benzo[*b*]thiophen-3-yl)pyridine (4p)



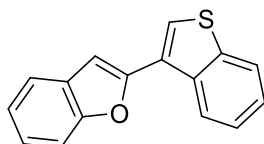
Yellow oil (24 mg, 57%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 80/20). IR (film, cm⁻¹): 1507, 1517, 1467, 1458, 1425, 1406, 1350, 1313, 1261, 1222, 1186, 1145, 1126, 1103, 1062, 1024. ¹H NMR (300 MHz, CDCl₃) δ 8.91 – 8.80 (m, 1H), 8.65 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.00 – 7.77 (m, 3H), 7.47 (s, 1H), 7.46 – 7.38 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 149.6 (CH), 148.8 (CH), 140.8 (C), 137.6 (C), 136.0 (CH), 134.5 (C), 132.0 (C), 124.9 (CH), 124.8 (CH), 124.8 (CH), 123.7 (CH), 123.2 (CH), 122.5 (CH). HRMS (ESI) *m/z*: (M + H)⁺ C₁₃H₁₀NS calcd 212.0528, found 212.0524.

2-(Benzo[*b*]thiophen-3-yl)-9-methyl-9H-carbazole (4q)



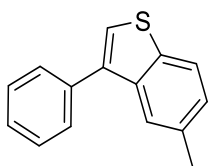
White solid (40 mg, 64%); R_f = 0.5 (Petroleum ether = 100). mp: 137-139 °C; IR (film, cm⁻¹): 2922, 2852, 1602, 1325, 1246, 1122, 1064, 1020. ¹H NMR (300 MHz, CDCl₃) δ 8.20 (d, *J* = 1.3 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.95 – 7.80 (m, 2H), 7.60 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.36 – 7.26 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 1H), 3.79 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 141.4 (C), 140.7 (C), 140.5 (C), 138.9 (2 C), 138.5 (C), 126.9 (C), 126.7 (CH), 126.0 (CH), 124.3 (CH), 124.2 (CH), 123.1 (CH), 122.9 (CH), 122.8 (C), 122.6 (2 CH), 120.5 (CH), 120.4 (CH), 119.2 (CH), 108.6 (CH), 29.2 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₂₁H₁₆NS calcd 314.0998, found 314.0993.

2-(Benzo[*b*]thiophen-3-yl)benzofuran (4r)



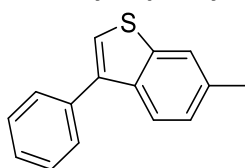
White solid (29 mg, 58%); R_f = 0.5 (Petroleum ether = 100). mp: 78-80 °C; IR (film, cm⁻¹): 1598, 1448, 1421, 1301, 1257, 1190, 1060. ¹H NMR (300 MHz, CDCl₃) δ 8.33 (d, *J* = 7.6 Hz, 1H), 8.21 – 7.73 (m, 2H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.51 (m, 3H), 7.31 (m, 2H), 7.12 (s, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 154.3 (C), 140.6 (2 C), 136.0 (C), 128.9 (2 C), 125.1 (CH), 124.9 (CH), 124.8 (CH), 124.4 (CH), 123.2 (2 CH), 123.0 (CH), 121.0 (CH), 111.0 (CH), 102.4 (CH). HRMS (ESI) *m/z*: (M + H)⁺ C₁₆H₁₁OS calcd 251.0525, found 251.0524.

5-Methyl-3-phenylbenzo[*b*]thiophene (4s)¹²



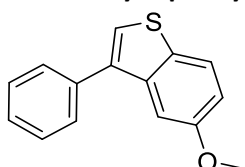
White oil (34 mg, 75%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1600, 1523, 1485, 1436, 1338, 1296, 1263, 1219, 1195, 1155, 1128, 1072, 1056, 1028. ¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.77 (s, 1H), 7.64 (m, 2H), 7.60 – 7.43 (m, 3H), 7.41 (s, 1H), 7.31 – 7.23 (m, 1H), 2.52 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 138.3 (C), 137.9 (C), 137.8 (C), 136.2 (C), 134.1 (C), 128.8 (2 CH), 128.7 (2 CH), 127.5 (CH), 126.2 (CH), 123.6 (CH), 122.8 (CH), 122.5 (CH), 21.6 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₃S calcd. 225.0732, found 225.0735.

6-Methyl-3-phenylbenzo[*b*]thiophene (4t)



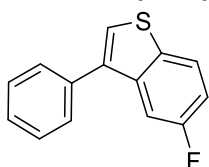
White oil (35 mg, 78%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2918, 1600, 1521, 1483, 1440, 1344, 1263, 1207, 1157, 1072, 1051, 1029. ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 0.7 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.59 – 7.37 (m, 3H), 7.36 (s, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 2.56 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 141.1 (C), 137.9 (C), 136.3 (C), 135.8 (C), 134.4 (C), 128.7 (4 CH), 127.5 (CH), 126.1 (CH), 122.7 (CH), 122.6 (CH), 122.3 (CH), 21.5 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₃S calcd. 225.0732, found 225.0731.

5-Methoxy-3-phenylbenzo[*b*]thiophene (4u)¹⁴



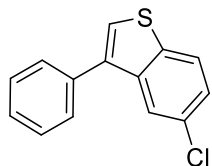
Yellow oil (37 mg, 78%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 2829, 1597, 1556, 1519, 1485, 1450, 1431, 1301, 1263, 1226, 1209, 1178, 1141, 1128, 1060, 1024. ¹H NMR (300 MHz, CDCl₃) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.35 (m, 3H), 7.10 – 7.03 (m, 1H), 3.85 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 157.8 (C), 139.0 (C), 136.2 (2 C), 133.1 (C), 128.8 (2 CH), 128.6 (2 CH), 127.5 (CH), 124.7 (CH), 123.5 (CH), 114.6 (CH), 105.3 (CH), 55.6 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₃OS calcd. 241.0682, found 241.0702.

5-Fluoro-3-phenylbenzo[*b*]thiophene (4v)



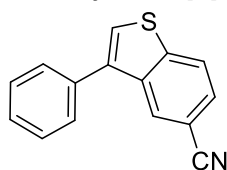
White oil (36 mg, 78%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1600, 1560, 1525, 1485, 1436, 1336, 1298, 1274, 1251, 1193, 1134, 1114, 1074, 1028. ¹H NMR (300 MHz, CDCl₃) δ 7.84 (dd, *J* = 8.8, 4.9 Hz, 1H), 7.66 – 7.37 (m, 7H), 7.17 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 162.7 (C), 159.5 (C), 138.0 (C), 137.6 (d, *J* = 243 Hz, C), 135.0 (C), 128.8 (2 CH), 128.5 (2 CH), 127.8 (CH), 125.7 (CH), 124.0 (d, *J* = 6 Hz, CH), 113.3 (d, *J* = 24 Hz, CH), 108.5 (d, *J* = 23 Hz, CH). ¹⁹F NMR (188 MHz, CDCl₃) δ -118.41. HRMS (ESI) *m/z*: (M + H)⁺ C₁₄H₁₀FS calcd. 229.0482, found 229.0483.

5-Chloro-3-phenylbenzo[*b*]thiophene (4w)¹²



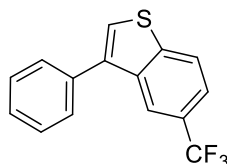
White oil (39 mg, 80%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1602, 1579, 1546, 1519, 1485, 1444, 1427, 1332, 1247, 1211, 1178, 1145, 1076, 1029. ¹H NMR (300 MHz, CDCl₃) δ 7.90 (dd, *J* = 2.1, 0.6 Hz, 1H), 7.83 (dd, *J* = 8.6, 0.6 Hz, 1H), 7.62 – 7.40 (m, 6H), 7.37 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 139.2 (C), 138.8 (C), 137.7 (C), 135.4 (C), 130.9 (C), 128.9 (2 CH), 128.6 (2 CH), 127.8 (CH), 125.2 (CH), 124.9 (CH), 123.9 (CH), 122.6 (CH). HRMS (ESI) *m/z*: (M + H)⁺ C₁₄H₁₀ClS calcd. 245.0186, found 245.0186.

3-Phenylbenzo[*b*]thiophene-5-carbonitrile (4x)



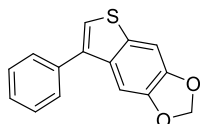
White solid (37 mg, 78%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 98/2). mp: 125-127 °C; IR (film, cm⁻¹): 2222, 1543, 1429, 1336, 1207, 1078, 1056. ¹H NMR (300 MHz, CDCl₃) δ 8.20 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.38 (m, 7H). ¹³C NMR (75 MHz, CDCl₃) δ 144.8 (C), 138.2 (C), 137.9 (C), 134.6 (C), 129.0 (2 CH), 128.6 (2 CH), 128.3 (CH), 127.7 (CH), 126.3 (CH), 125.6 (CH), 123.9 (CH), 119.4 (C), 108.2 (C). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₀NS calcd. 236.0528, found 236.0527.

3-Phenyl-5-(trifluoromethyl)benzo[*b*]thiophene (4y)



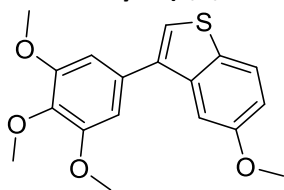
White oil (37 mg, 67%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 1606, 1525, 1489, 1448, 1429, 1346, 1315, 1298, 1257, 1170, 1147, 1112, 1070, 1029. ¹H NMR (400 MHz, CDCl₃) δ 8.21 – 8.13 (m, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.63 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.60 – 7.51 (m, 5H), 7.49 – 7.43 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.9 (C), 138.7 (C), 137.8 (C), 135.3 (C), 129.1 (2 CH), 128.8 (2 CH), 128.2 (CH), 125.4 (CH), 127.3 (q, *J* = 32 Hz, C), 124.8 (q, *J* = 273 Hz, C), 123.6 (CH), 120.9 (q, *J* = 2 Hz, CH), 120.3 (q, *J* = 2 Hz, CH). ¹⁹F NMR (188 MHz, CDCl₃) δ -61.43. HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₀F₃S calcd 279.0450, found 279.0449.

7-Phenylthieno[2',3',4,5]benzo[1,2-*d*][1,3]dioxole (4z)



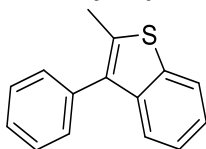
White oil (29 mg, 57%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 98/2). IR (film, cm⁻¹): 2893, 1600, 1519, 1498, 1483, 1463, 1444, 1274, 1246, 1207, 1107, 1074, 1039. ¹H NMR (300 MHz, CDCl₃) δ 7.44 (m, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.25 (m, 1H), 7.16 (m, 3H), 5.91 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 147.0 (C), 146.8 (C), 137.8 (C), 136.2 (C), 134.2 (C), 132.7 (C), 128.7 (2 CH), 128.6 (2 CH), 127.5 (CH), 121.6 (CH), 101.8 (CH), 101.8 (CH), 101.4 (CH₂). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₁O₂S calcd 255.0474, found 255.0472.

5-Methoxy-3-(3,4,5-trimethoxyphenyl)benzo[*b*]thiophene (4aa)



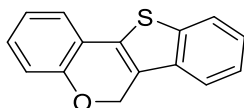
White oil (42 mg, 63%); R_f = 0.5 (Cyclohexane/Ethyl acetate = 92/8). IR (film, cm⁻¹): 2933, 2829, 1597, 1581, 1523, 1496, 1458, 1421, 1408, 1348, 1325, 1257, 1234, 1220, 1180, 1166, 1120, 1068, 1043, 1026, 1006. ¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.39 (m, 2H), 7.05 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.80 (s, 2H), 3.94 (s, 3H), 3.91 (s, 6H), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 157.8 (C), 153.5 (2 C), 139.0 (C), 137.7 (C), 133.0 (C), 131.7 (2 C), 124.5 (CH), 123.6 (CH), 114.7 (CH), 105.9 (2 CH), 105.2 (CH), 60.9 (CH₃), 56.2 (2 CH₃), 55.5 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₈H₁₉O₄S calcd. 331.0999, found 331.1002.

2-Methyl-3-phenylbenzo[*b*]thiophene (4ab)¹⁴



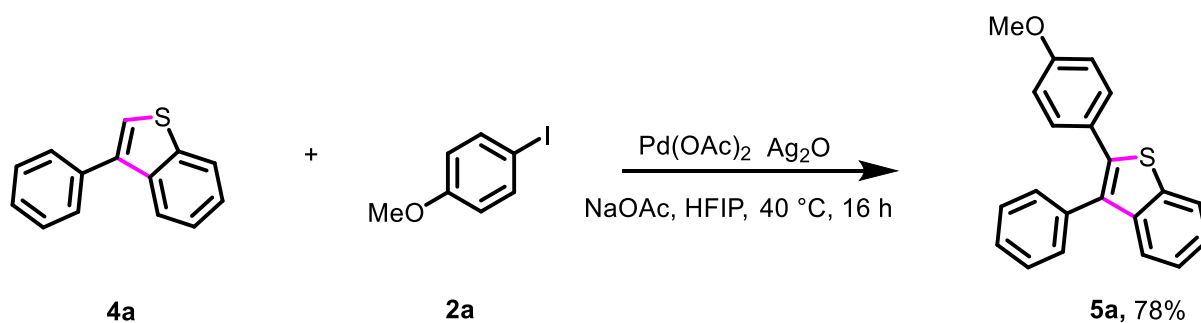
White oil (34 mg, 76%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3055, 2916, 1600, 1489, 1456, 1433, 1379, 1350, 1195, 1147, 1064, 1018. ¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.77 (m, 1H), 7.62 – 7.36 (m, 6H), 7.36 – 7.28 (m, 2H), 2.55 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 140.4 (C), 138.3 (C), 136.1 (C), 135.4 (C), 133.9 (C), 130.1 (2 CH), 128.5 (2 CH), 127.3 (CH), 124.1 (CH), 123.8 (CH), 122.5 (CH), 121.9 (CH), 14.5 (CH₃). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₃S calcd 225.0732, found 225.0732.

6*H*-Benzo[4,5]thieno[3,2-*c*]chromene (4ac)

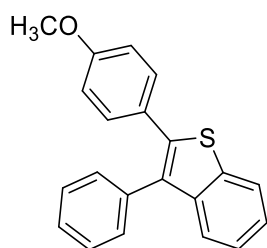


White oil (29 mg, 61%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3059, 2841, 1718, 1583, 1535, 1489, 1444, 1429, 1361, 1288, 1220, 1190, 1153, 1101, 1064, 1041, 1024, 1006. ¹H NMR (200 MHz, CDCl₃) δ 8.29 (d, *J* = 8.1 Hz, 1H), 8.09 – 7.79 (m, 2H), 7.57 – 7.35 (m, 2H), 7.31 – 7.07 (m, 3H), 5.36 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.3 (C), 139.6 (C), 135.9 (C), 132.5 (C), 128.3 (CH), 126.2 (C), 125.1 (CH), 124.4 (CH), 123.4 (CH), 123.2 (CH), 122.7 (CH), 122.5 (CH), 122.3 (C), 117.3 (CH), 65.3 (CH₂). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₁OS calcd 239.0525, found 239.0521.

7. Derivatization of benzothiophene 4 C2-arylation



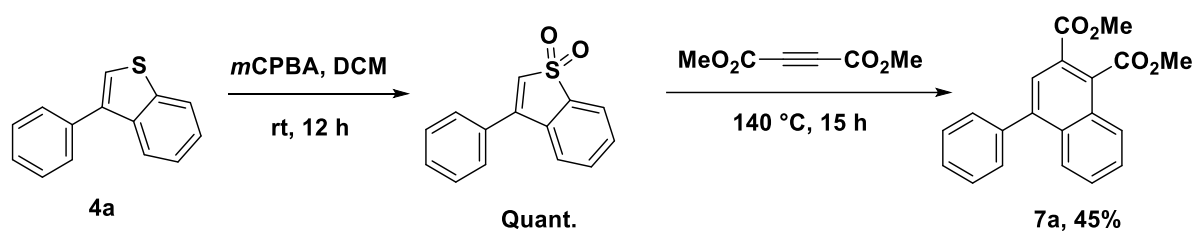
Compound **5a** was synthesized following the Larrosa protocol.¹⁵ A mixture of $\text{Pd}(\text{OAc})_2$ (0.8 mol %), silver oxide (1 equiv, 0.196 mmol), NaOAc (0.5 equiv., 0.098 mmol), 4-iodoanisole (2.0 equiv, 0.392 mmol) and 3-(*p*-tolyl)benzo[*b*]thiophene (1.0 equiv, 0.196 mmol) was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol [1M] at $40\text{ }^\circ\text{C}$ for 16 hours. Subsequently, the resulting mixture was diluted with EtOAc and filtered through a silica plug. The filtrate was then evaporated to dryness under reduced pressure. The crude product was purified by column chromatography using silica gel, EtOAc in hexane: EtOAc = 98:2.



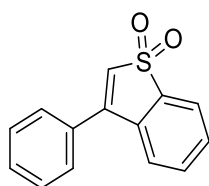
2-(4-methoxyphenyl)-3-phenylbenzo[*b*]thiophene (**5a**)¹⁶

White solid (48.3 mg, 78%); $R_f = 0.4$ (Petroleum ether/Ethyl acetate = 98/2). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.81 – 7.68 (m, 1H), 7.47 (m, 1H), 7.36 – 7.19 (m, 7H), 7.19 – 7.15 (m, 1H), 7.14 – 7.11 (m, 1H), 6.74 – 6.61 (m, 2H), 3.66 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 159.2 (C), 141.1 (C), 139.5 (C), 138.6 (C), 135.8 (C), 132.4 (C), 130.8 (2 CH), 130.5 (2 CH), 128.7 (2 CH), 127.3 (CH), 126.7 (C), 124.4 (CH), 124.3 (CH), 123.2 (CH), 122.0 (CH), 113.9 (2 CH), 55.3 (CH₃). HRMS (ESI) m/z : ($\text{M} + \text{H}$)⁺ $\text{C}_{21}\text{H}_{16}\text{SO}$ calcd 317.0995, found 317.0991.

8. Skeletal editing



3-Phenylbenzo[*b*]thiophene 1,1-dioxide¹⁷



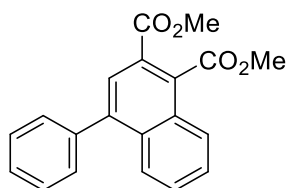
To a solution of 3-phenylbenzo[*b*]thiophene (40 mg, 0.19 mmol, 1.0 equiv.) in DCM (1.2 mL), *m*CPBA 77w% (119 mg, 0.53 mmol, 2.8 equiv.) was added portionwise. The reaction mixture was stirred at room temperature for 12 h. The white suspension was then quenched with an aqueous solution of Na₂CO₃ (5 w%), and extracted with DCM three times. The organic phase was washed with brine, dried over MgSO₄, filtered, and concentrated over reduced pressure. The residue was purified by chromatography on silica gel (Cyclohexane/DCM: 9/1 to Cyclohexane/DCM: 8/2). The desired product was obtained as a white solid (55 mg, quant.).

¹H NMR (300 MHz, CDCl₃) δ 7.83 – 7.78 (m, 1H), 7.62 – 7.44 (m, 8H), 6.64 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 146.0, 138.3, 133.8, 133.4, 132.1, 131.2 (2 C), 130.7, 130.6, 129.3, 128.1, 125.9, 124.4, 121.7.

Data are consistent with the literature.

Dimethyl 4-phenylnaphthalene-1,2-dicarboxylate (7a)¹⁸



To a solution of 3-phenylbenzo[*b*]thiophene 1,1-dioxide (27 mg, 0.11 mmol, 1.0 equiv.) in diphenyl ether (306 μL), dimethyl acetylenedicarboxylate (300 μL, 2.5 mmol, 22.0 equiv.) was added. The reaction mixture was stirred at 140 °C for 15 h. The crude residue was then purified by chromatography on silica gel (Cyclohexane/EtOAc: 9/1 to Cyclohexane/EtOAc: 8/2). Finally, the excess of dimethyl acetylenedicarboxylate was removed by bulb-to-bulb distillation, providing the expected compound as a colorless oil (16 mg, 45%).

¹H NMR (300 MHz, CDCl₃) δ 7.98 (s, 1H), 7.97 – 7.92 (m, 2H), 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 5H), 4.11 (s, 3H), 3.96 (s, 3H).

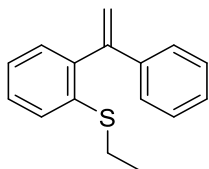
¹³C NMR (75 MHz, CDCl₃) δ 166.4 (2 C), 142.3, 139.6, 134.4, 133.7, 130.1 (2 C), 130.0, 129.3, 128.7, 128.6, 128.1, 128.1, 127.7, 126.6, 126.0, 124.4, 53.1, 52.8.

Data are consistent with the literature.

9. Mechanism study: Control experiment

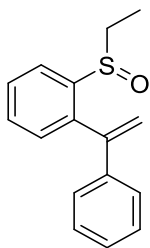
Ethyl(2-(1-phenylvinyl)phenyl)sulfane (**6a**)¹⁹

Was prepared according to the general method B from (Z)-4-methyl-N'-(1-phenylethylidene)benzenesulfonohydrazide NTH (**1**) and (2-bromophenyl)(ethyl)sulfane.

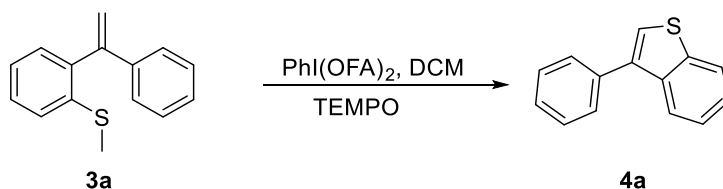


Yellow liquid (390 mg, 65%); R_f = 0.5 (Petroleum ether = 100). IR (film, cm⁻¹): 3053, 2918, 1712, 1612, 1583, 1492, 1467, 1433, 1359, 1321, 1255, 1219, 1155, 1126, 1072, 1053, 1037, 1026. ¹H NMR (300 MHz, CDCl₃) δ 7.59 (m, 1H), 7.58 – 7.47 (m, 7H), 7.46 – 7.41 (m, 1H), 6.08 (s, 1H), 5.52 (s, 1H), 3.06 (q, J = 7.4 Hz, 2H), 1.44 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.3 (C), 144.0 (C), 140.2 (C), 136.1 (C), 130.5 (CH), 128.2 (2 CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 126.6 (2 CH), 125.2 (CH), 115.8 (CH₂), 27.2 (CH₂), 13.9 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₇S calcd. 241.1045, found 241.1042.

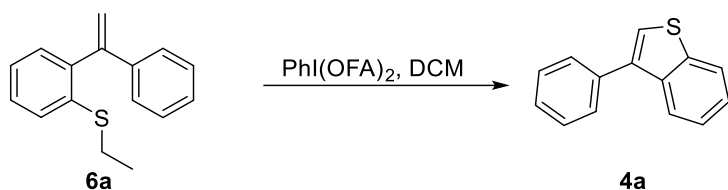
1-(Ethylsulfinyl)-2-(1-phenylvinyl)benzene (**7a**)¹⁹



Compound **7a** was prepared according to the method of Harpold²⁰ by adding a solution of 178 mg (0.83 mmol) of sodium metaperiodate in 5 ml of water to a stirred mixture of 197 mg (0.82 mmol) of compound **6a** in 12 ml of methanol. The temperature was maintained at 0-5°C throughout the 0.5-hour addition and for 3 hours following the addition. At this point, 4 ml of methanol was added, and stirring continued for 5 hours without cooling. The resulting mixture was then added to saturated brine and was extracted three times with AcOEt. The solvents were evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel. Yellow liquid (155 mg, 74%); ¹H NMR (300 MHz, CDCl₃) δ 8.03 (dd, J = 7.8, 1.4 Hz, 1H), 7.60 (td, J = 7.6, 1.4 Hz, 1H), 7.51 (td, J = 7.4, 1.4 Hz, 1H), 7.38 – 7.20 (m, 6H), 5.84 (s, 1H), 5.34 (s, 1H), 2.81 – 2.46 (m, 2H), 1.10 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.5 (C), 146.3 (C), 142.1 (C), 139.3 (C), 130.6 (CH), 130.5 (CH), 128.7 (CH), 128.6 (2 CH), 128.4 (CH), 126.7 (2 CH), 124.6 (CH), 117.3 (CH₂), 48.3 (CH₂), 6.1 (CH₃). HRMS (ESI) m/z: (M + H)⁺ C₁₆H₁₇OS calcd. 257.0095, found 257.0092.

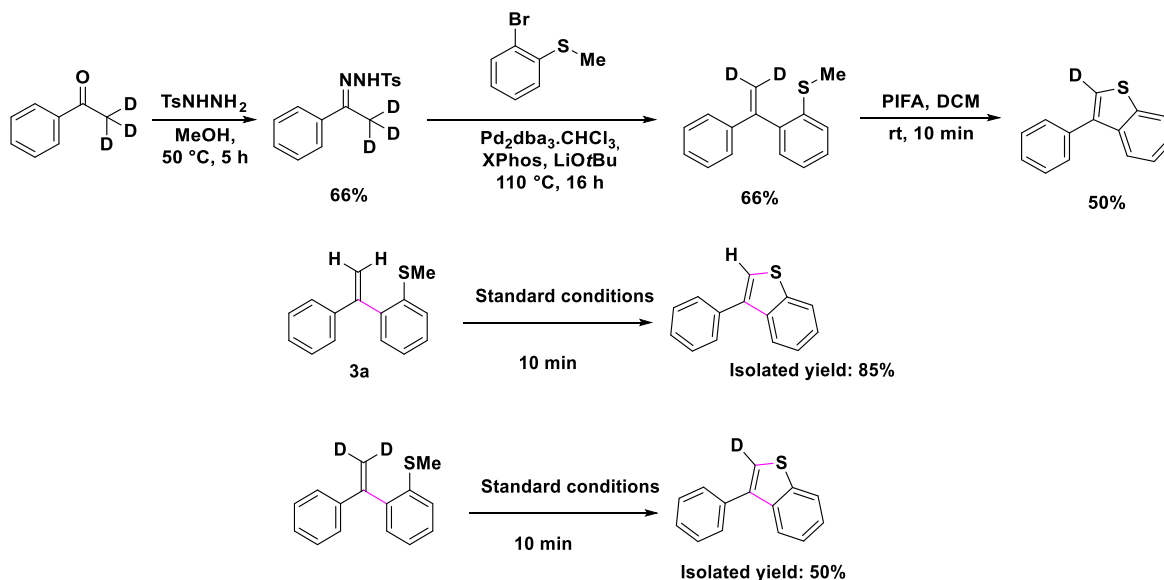


To a solution of the corresponding compound **3a** (0.2 mmol, 1.0 equiv.) and PhI(OFA)_2 (0.6 mmol, 3.0 equiv.) and TEMPO (0.6 mmol, 3.0 equiv.), 2 mL of dry DCM was added, and the resulting mixture was stirred at room temperature for 10 mins. The mixture was added saturated sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and stirred at room temperature, which was extracted with DCM. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane to Pentane/EtOAc: 9/1). The yield of the expected product **4a** was obtained in 74%.

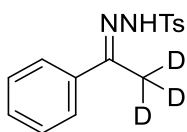


To a solution of the corresponding compound **5a** (48 mg, 0.2 mmol, 1.0 equiv.) and PhI(OFA)_2 (0.6 mmol, 3.0 equiv.), 2 mL of dry DCM was added, and the resulting mixture was stirred at room temperature for 10 mins. The mixture was added saturated sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and stirred at room temperature, which was extracted with DCM. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane to Pentane/EtOAc: 9/1). The expected product **4a** was obtained with a 67% yield.

Kinetic isotopic effect

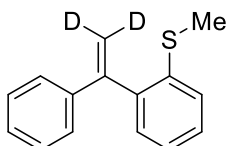


(Z)-4-Methyl-*N'*-(1-phenylethylidene-2,2,2-*d*₃)benzenesulfonylhydrazide (1a-D)



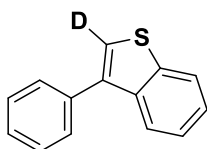
In a 100 mL round-bottom flask, *p*-toluenesulfonyl hydrazide (3.0 g, 16 mmol, 1.0 equiv.) was dissolved in MeOH (32 mL). The solution was heated at 50 °C for 5 min. Acetophenone- β,β,β -*d*₃ (1.9 mL, 16 mmol, 1.0 equiv.) was then added slowly to the reaction mixture, which was stirred at 50 °C for 5 h. The generated white solid was filtered and dried under *vacuo*, giving the corresponding compound as a white solid (3.1 g, 66%). *R*_f = 0.1 (Cyclohexane/EtOAc: 9/1); m.p.: 147-149 °C; IR (film, cm⁻¹): 3221, 1597, 1493, 1408, 1335, 1317, 1163, 1092, 1038, 1020, 1007; ¹H NMR (300 MHz, CDCl₃) δ 8.30 (s, 1H), 8.01 – 7.95 (m, 2H), 7.69 – 7.63 (m, 2H), 7.39 – 7.31 (m, 5H), 2.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 152.9, 144.2, 137.4, 135.6, 129.7 (2 C), 129.6, 128.4 (2 C), 128.2 (2 C), 126.4 (2 C), 21.6, 13.95 – 11.85 (m). HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₄D₃N₂O₂S calcd. 292.1199, found 292.1193.

Methyl(2-(1-phenylvinyl-2,2-*d*₂)phenyl)sulfane (3a-D)



A sealed tube under Ar atmosphere was charged with (Z)-4-methyl-*N'*-(1-phenylethylidene-2,2,2-*d*₃)benzenesulfonylhydrazide (500 mg, 1.7 mmol, 1.3 equiv.), (2-bromophenyl)(methyl)sulfane (176 μ L, 1.3 mmol, 1.0 equiv.), Xphos (62 mg, 0.13 mmol, 10 mol%), Pd₂(dba)₃.CHCl₃ (67 mg, 0.07 mmol, 5 mol%). The reaction mixture was solubilized in dioxane (6.5 mL) and stirred at room temperature for 5 min. Lithium *tert*-butoxide (229 mg, 2.9 mmol, 2.2 equiv.) was then added, and the reaction was heated at 110 °C for 16 h. The crude reaction mixture was cooled to room temperature, taken up in dichloromethane and filtered through Celite®. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Cyclohexane to Cyclohexane/EtOAc: 95/5). The product was obtained as a yellow oil (196 mg, 66%). *R*_f = 0.8 (Cyclohexane/EtOAc: 9/1); IR (film, cm⁻¹): 3055, 2918, 1582, 1491, 1431, 1317, 1254, 1128, 1070, 1038; ¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.27 (m, 7H), 7.27 – 7.18 (m, 2H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 148.0, 140.8, 140.0, 137.8 (2 C), 130.3, 128.4, 128.3, 128.2, 127.7, 126.7, 125.4, 124.7, 115.6 (p, *J* = 23.8 Hz), 16.0. HRMS (ESI) *m/z*: (M + H)⁺ C₁₅H₁₃D₂S calcd. 229.1020, found 229.1015.

3-Phenylbenzo[*b*]thiophene-2-*d* (4a-D)



To a solution of the methyl(2-(1-phenylvinyl-2,2-*d*₂)phenyl)sulfane (46 mg, 0.2 mmol, 1.0 equiv.) in DCM (2 mL), PhI(OTFA)₂ (258 mg, 0.6 mmol, 3.0 equiv.) was added. The resulting mixture was stirred at room temperature for 10 min. The mixture was quenched with an aqueous solution of saturated sodium thiosulfate and extracted with DCM three times. The organic phase was washed with brine, dried over MgSO₄, filtered, and concentrated over reduced pressure. The residue was purified by chromatography on silica gel (Cyclohexane or Pentane). The product was obtained as a yellow oil (21

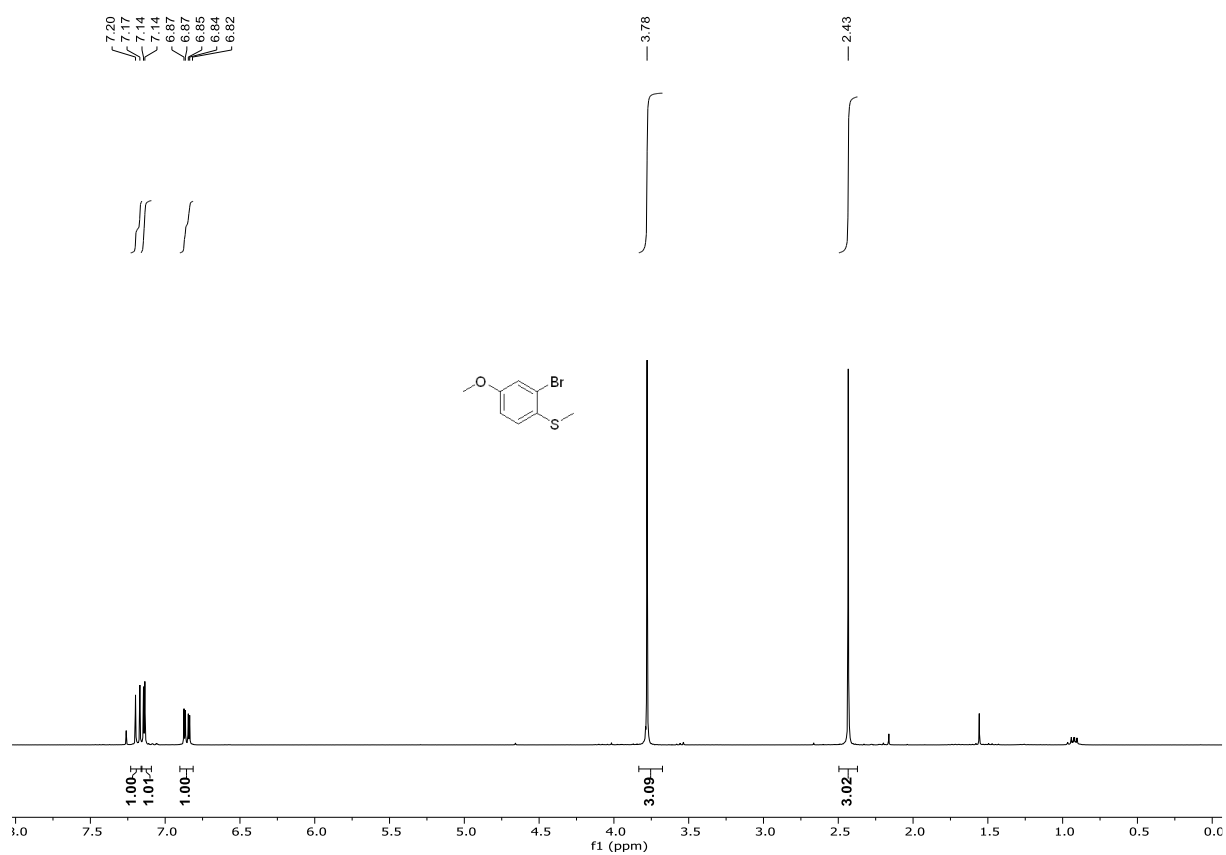
mg, 50%). Rf = 0.73 (Cyclohexane/EtOAc: 9/1); IR (film, cm^{-1}): 3055, 1601, 1516, 1479, 1456, 1441, 1420, 1344, 1306, 1260, 1179, 1159, 1070, 1020; ^1H NMR (300 MHz, CDCl_3) δ 8.03 – 7.89 (m, 2H), 7.68 – 7.56 (m, 2H), 7.60 – 7.46 (m, 2H), 7.46 – 7.35 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.8, 138.2, 138.1, 136.2, 128.9 (2 C), 127.7 (2 C), 124.6 (2 C), 124.5 (2 C), 123.3 (t, $J = 28.0$ Hz), 123.1. HRMS (ESI) m/z : (M + H)⁺ $\text{C}_{14}\text{H}_{10}\text{DS}$ calcd. 212.0644, found 213.0705.

10. References

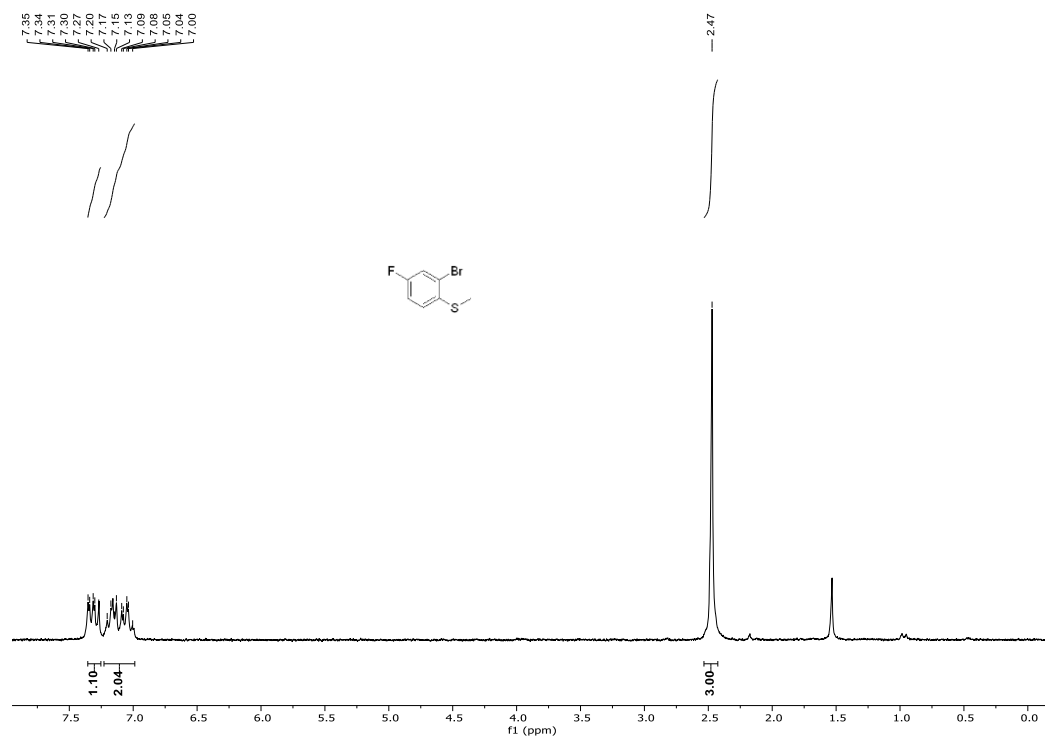
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9. ^1H , ^{13}C , ^{19}F NMR Spectra

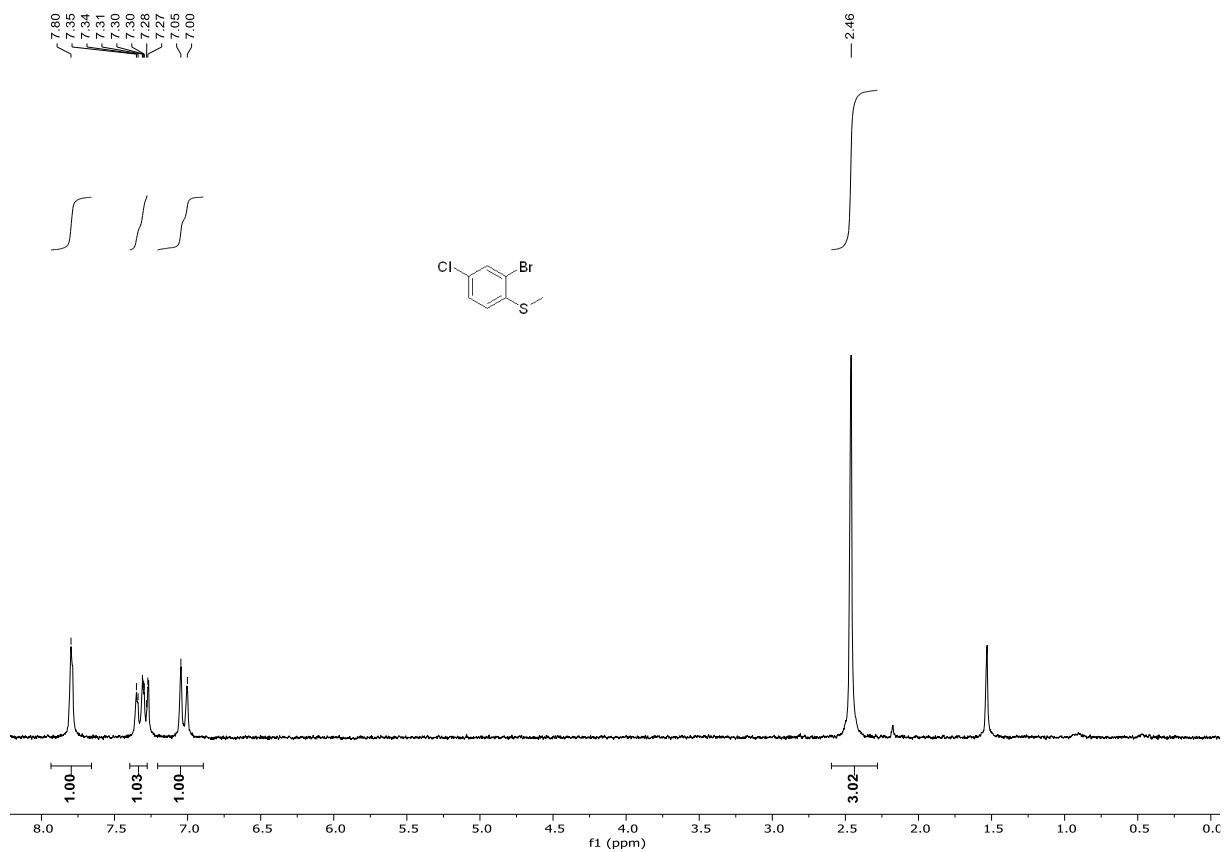
^1H NMR (300 MHz, CDCl_3) of (2-bromo-4-methoxyphenyl)(methyl)sulfane



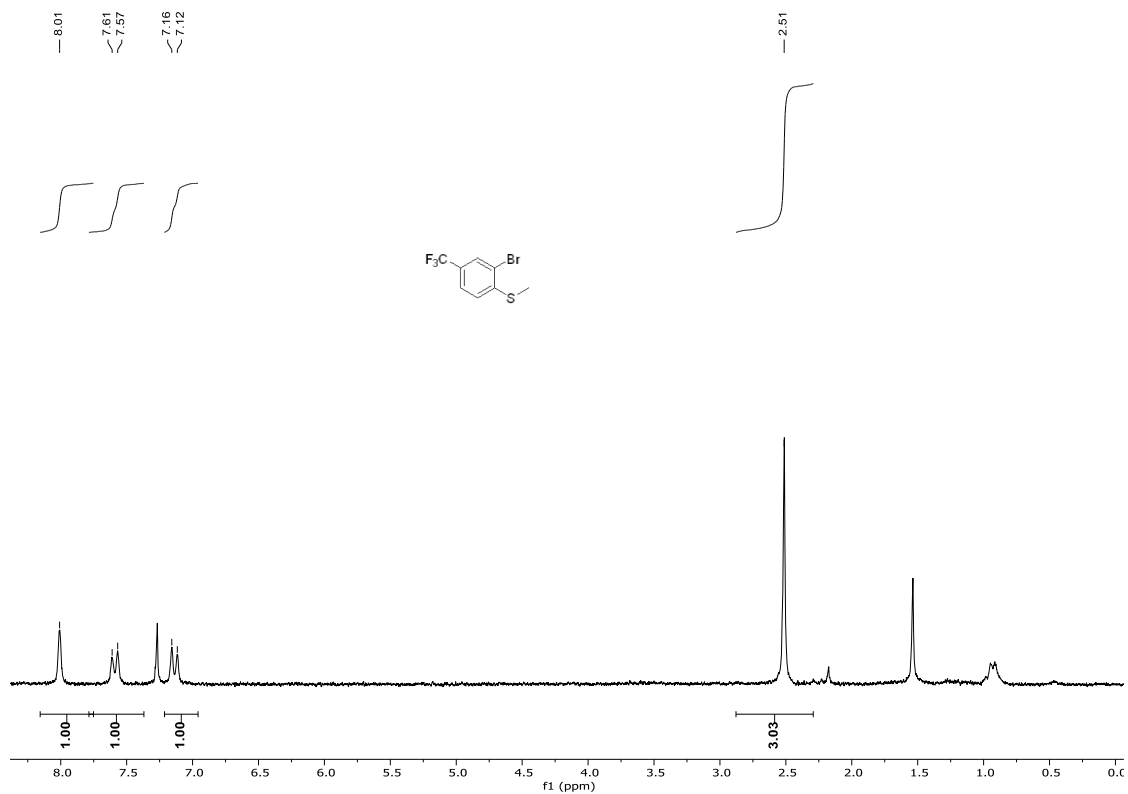
^1H NMR (200 MHz, CDCl_3) of (2-bromo-4-fluorophenyl)(methyl)sulfane



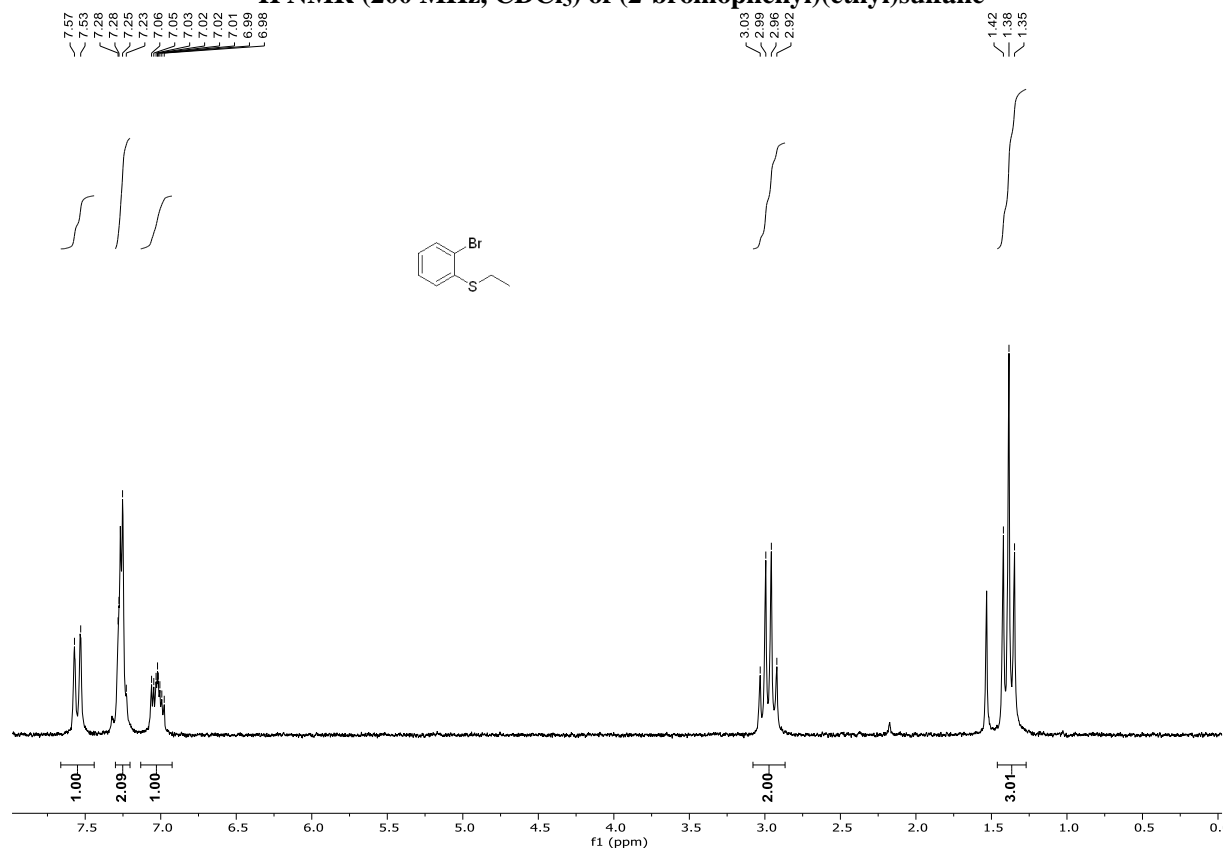
¹H NMR (200 MHz, CDCl₃) of (2-bromo-4-chlorophenyl)(methyl)sulfane



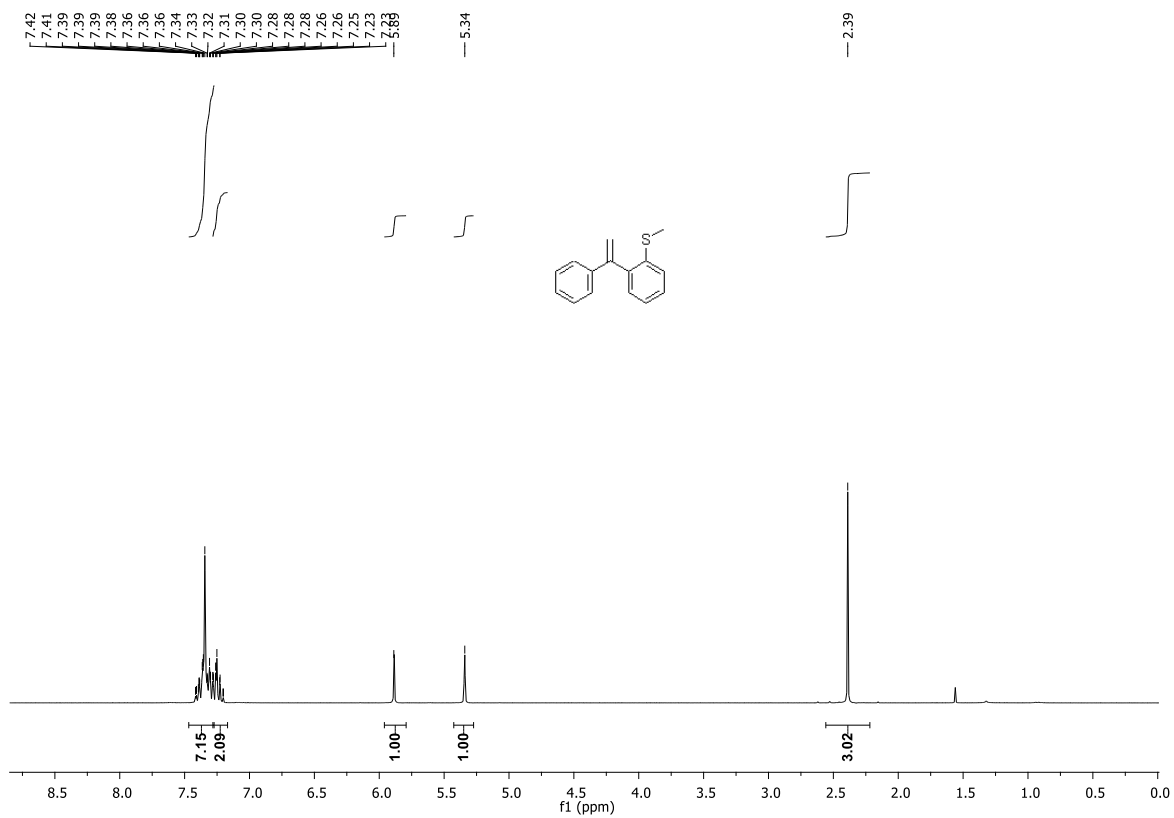
¹H NMR (200 MHz, CDCl₃) of (2-bromo-4-(trifluoromethyl)phenyl)(methyl)sulfane



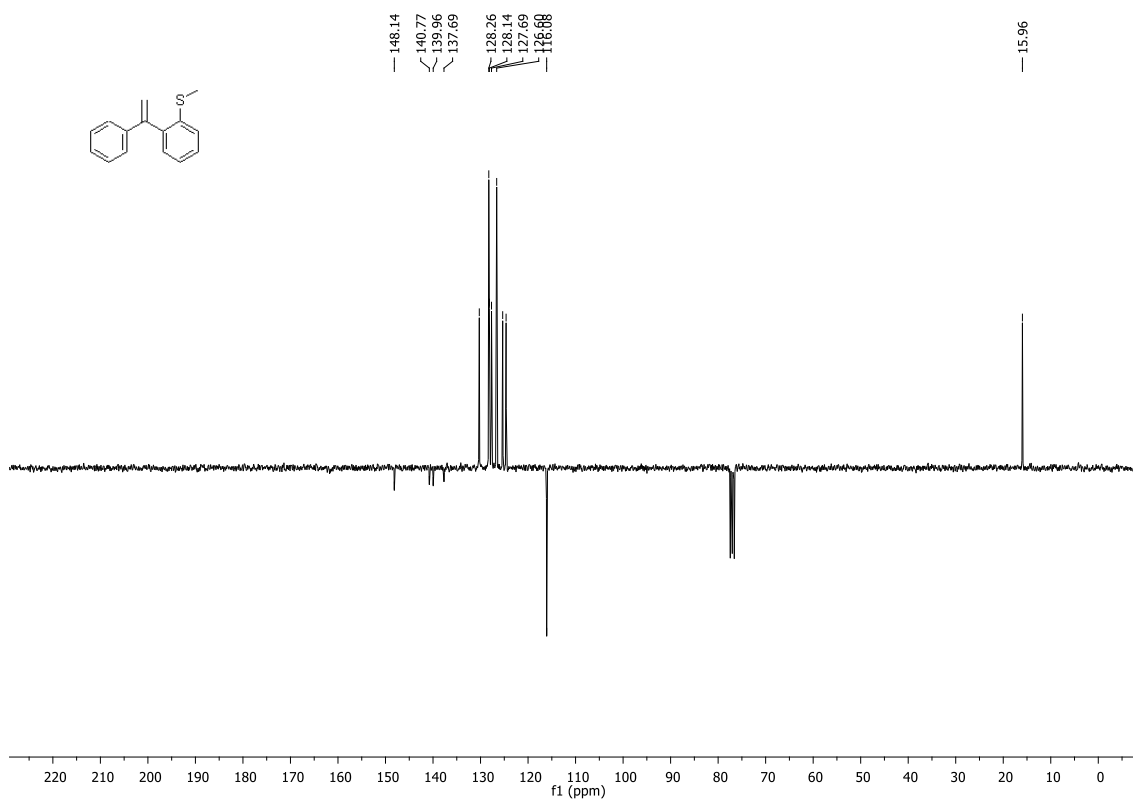
¹H NMR (200 MHz, CDCl₃) of (2-bromophenyl)ethylsulfane



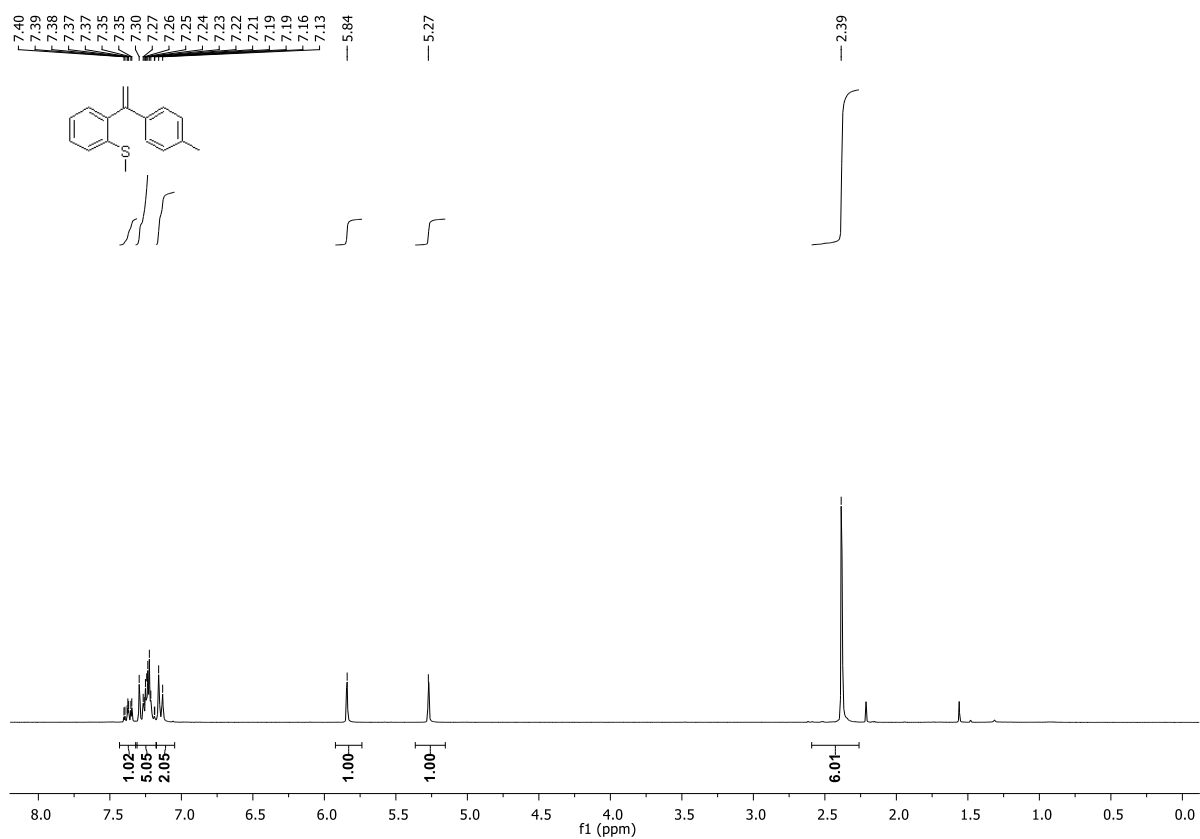
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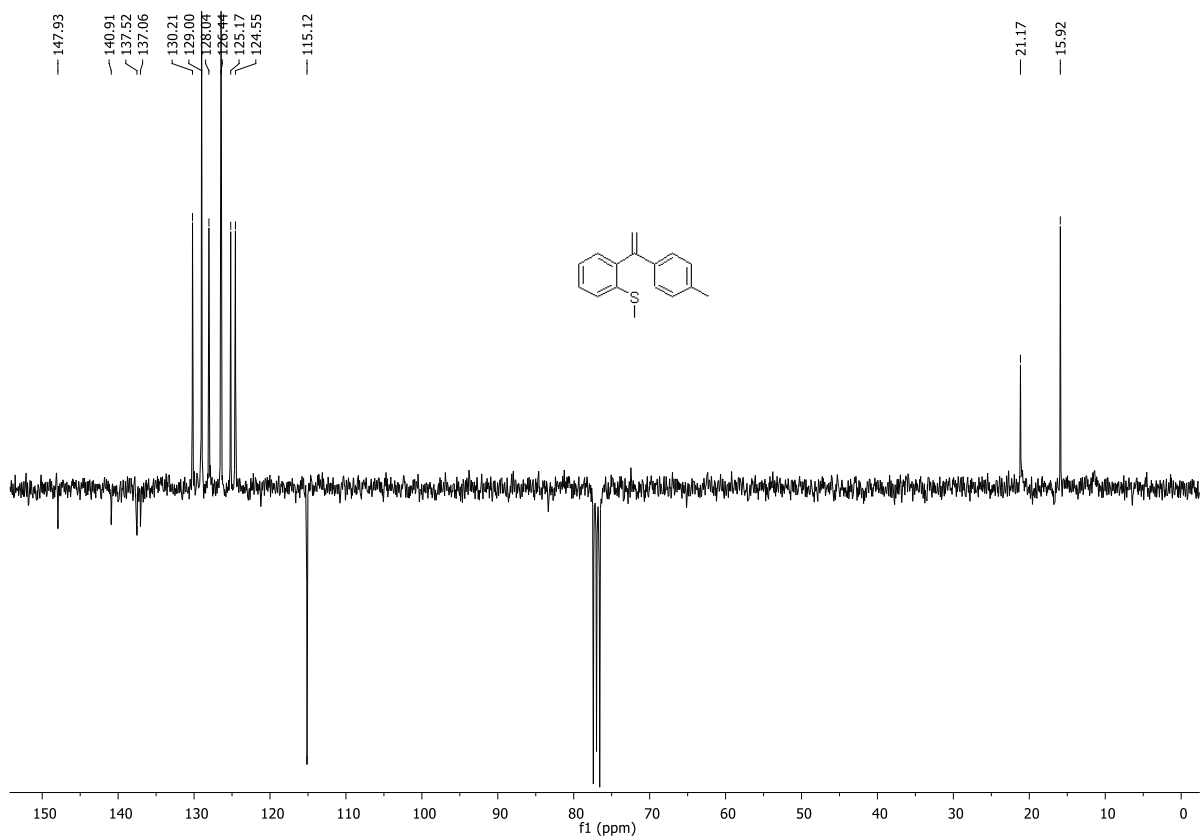
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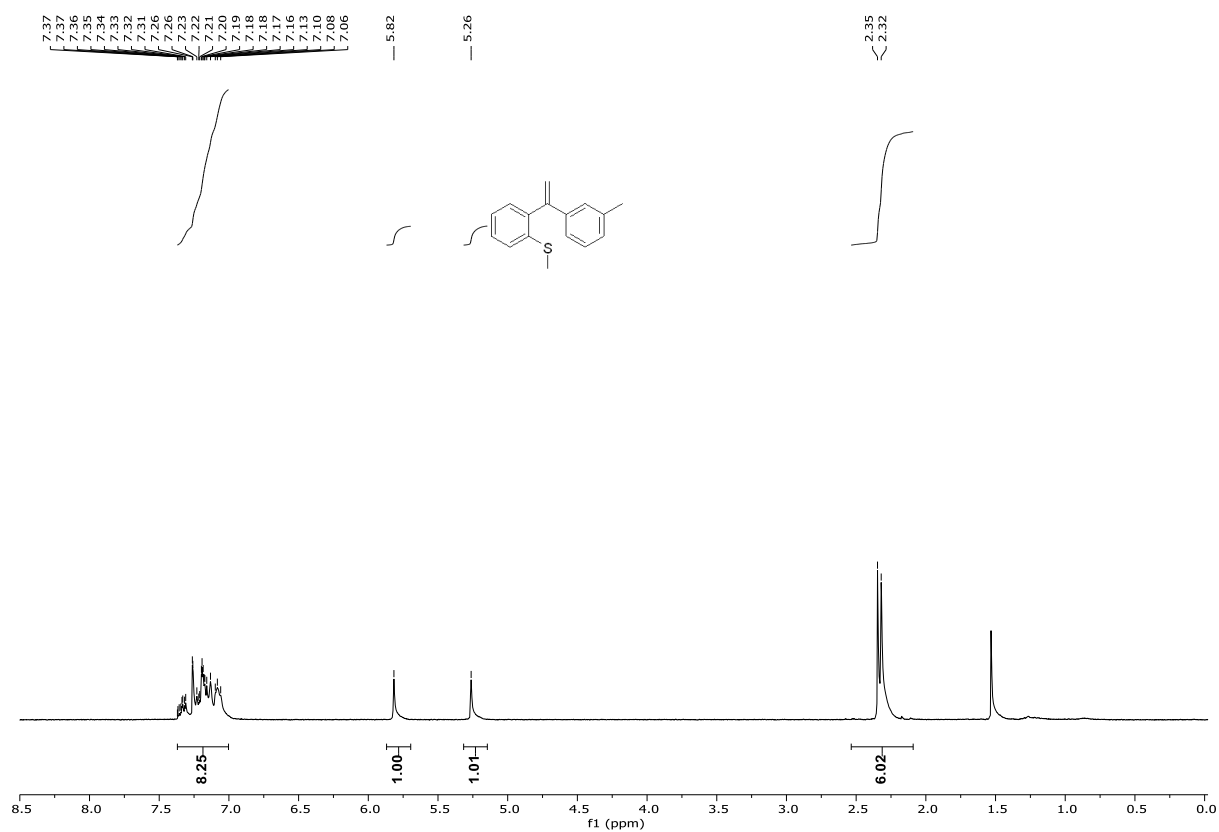
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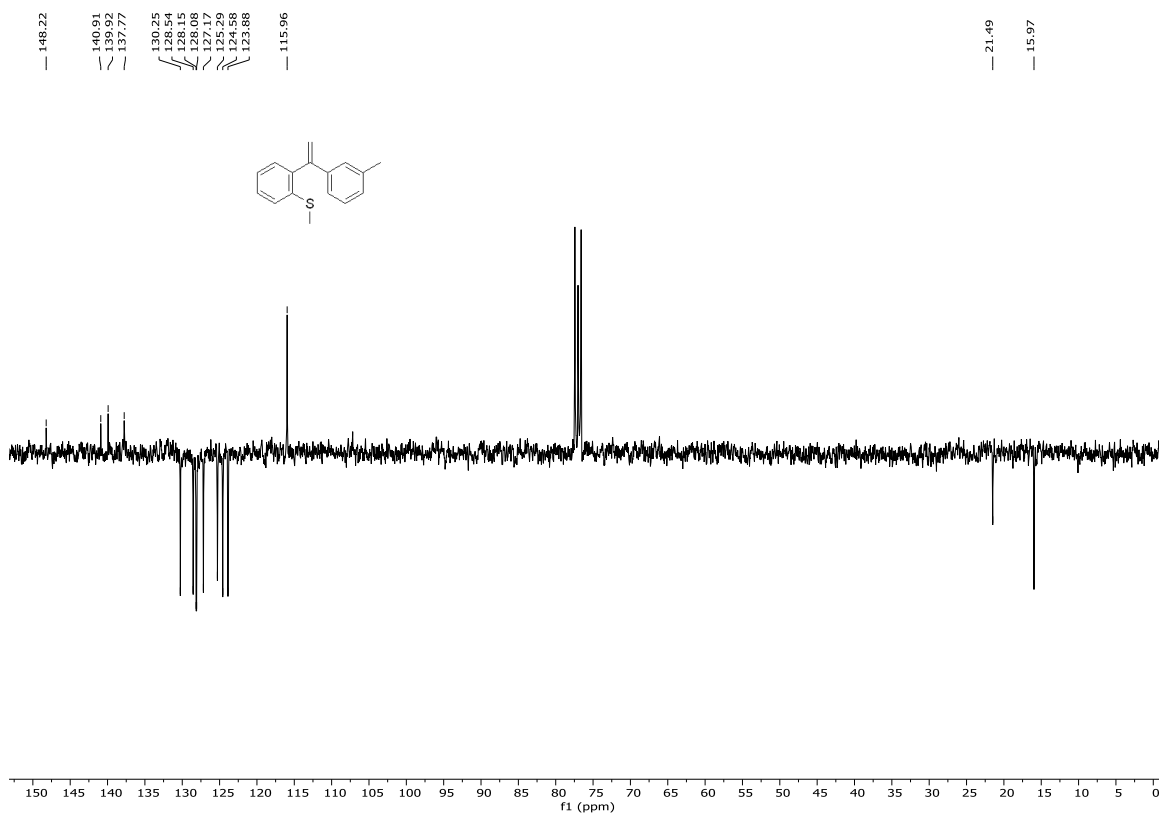
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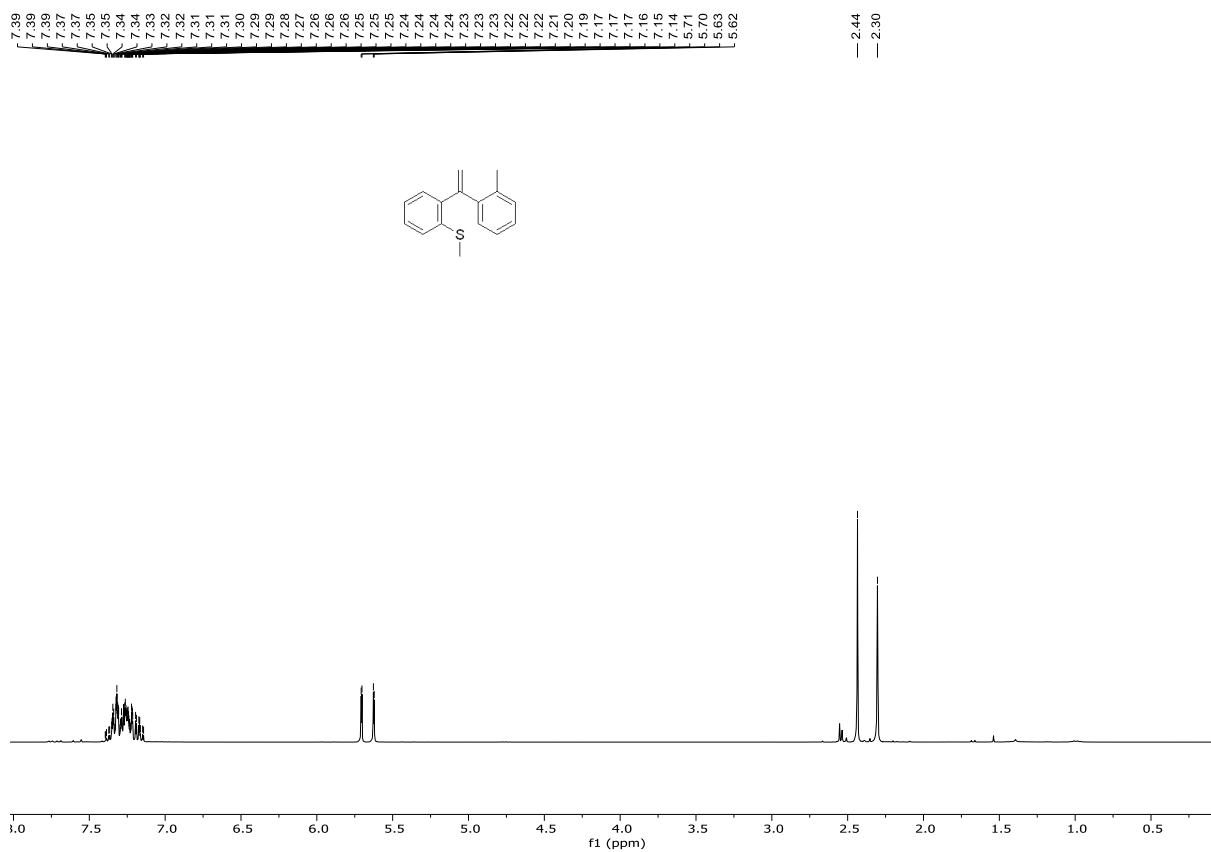
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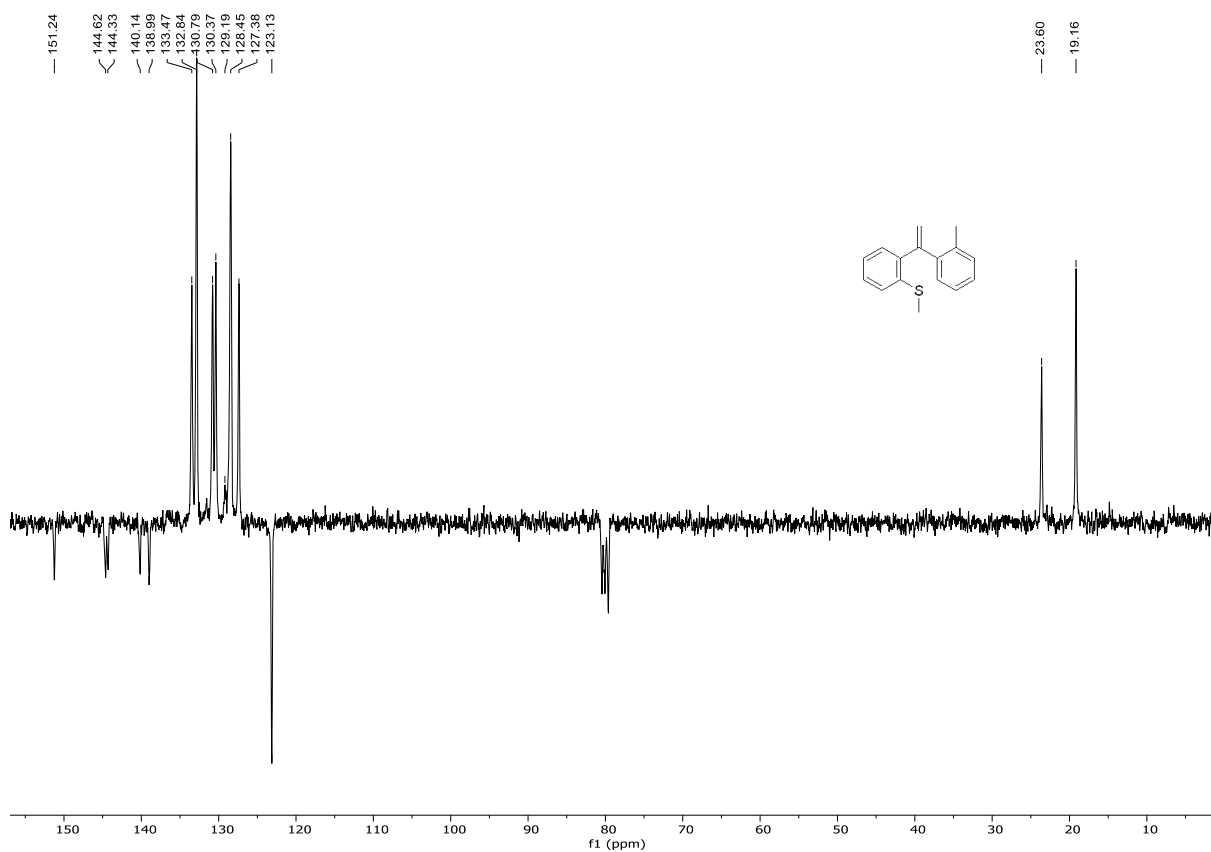
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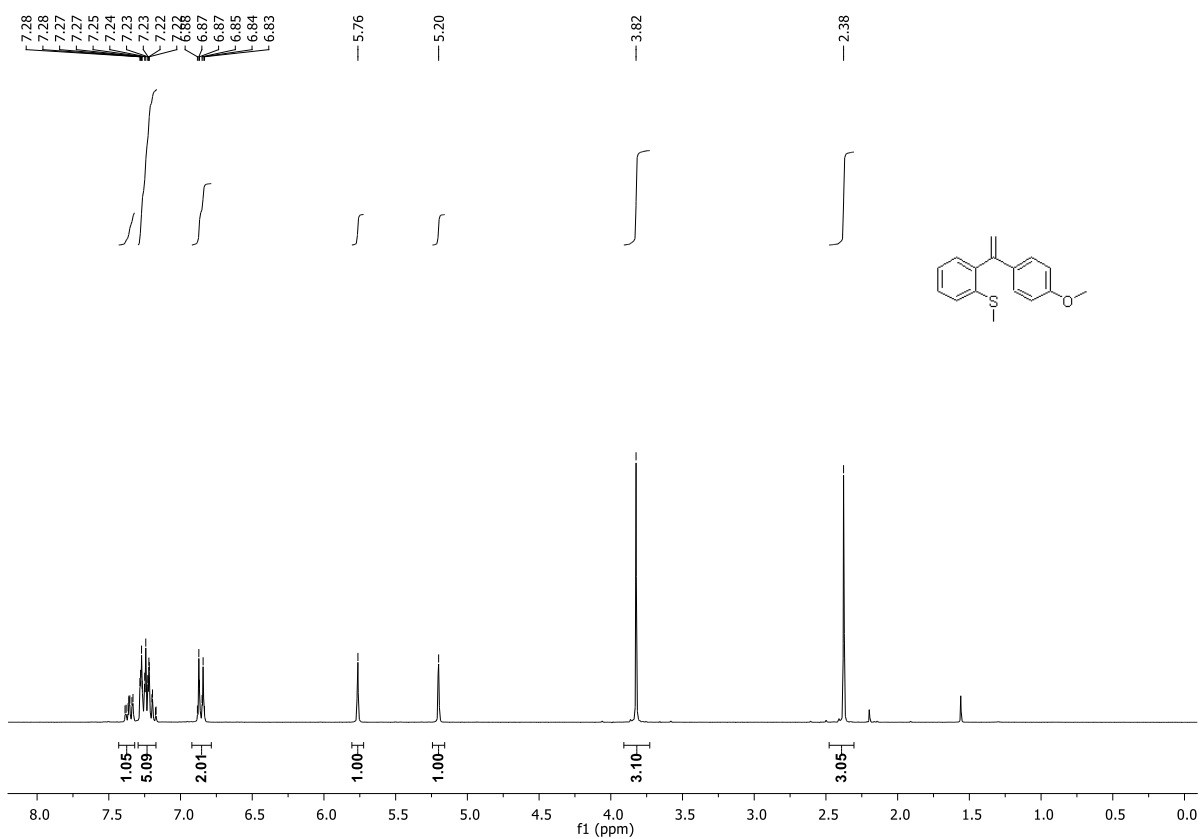
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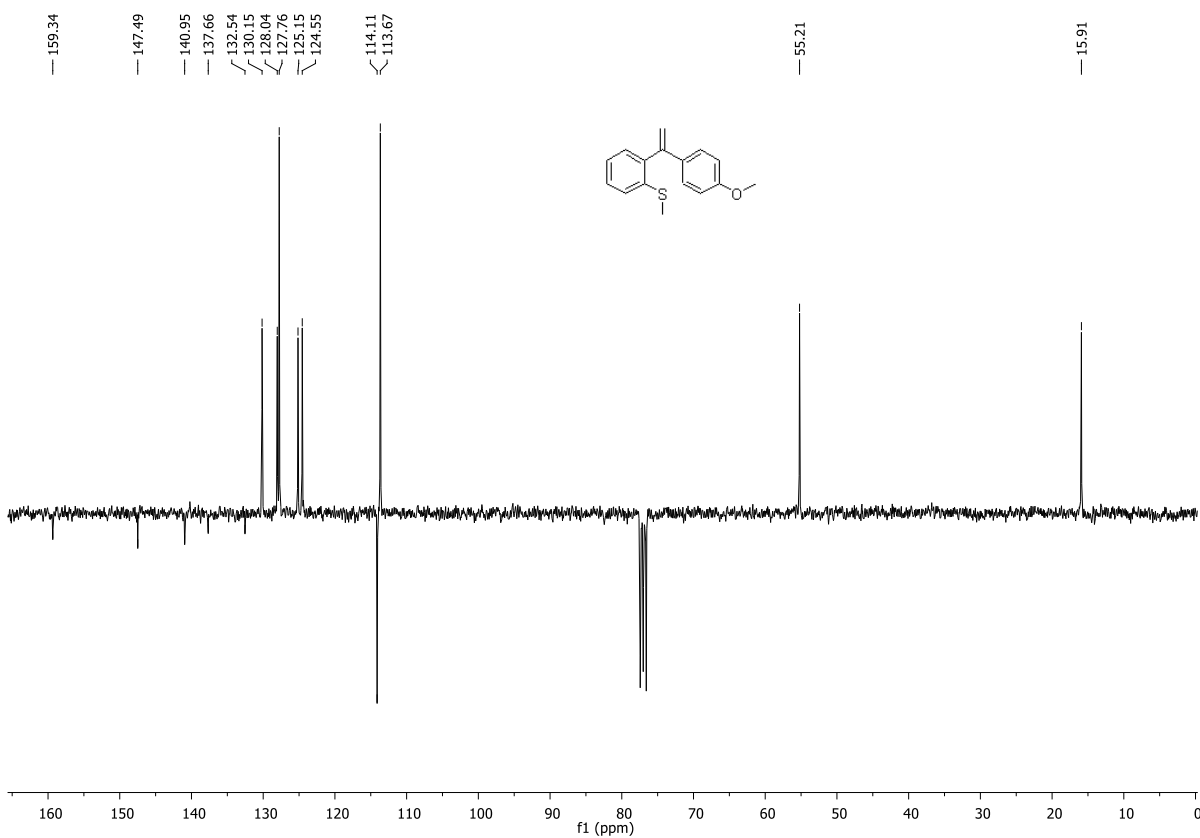
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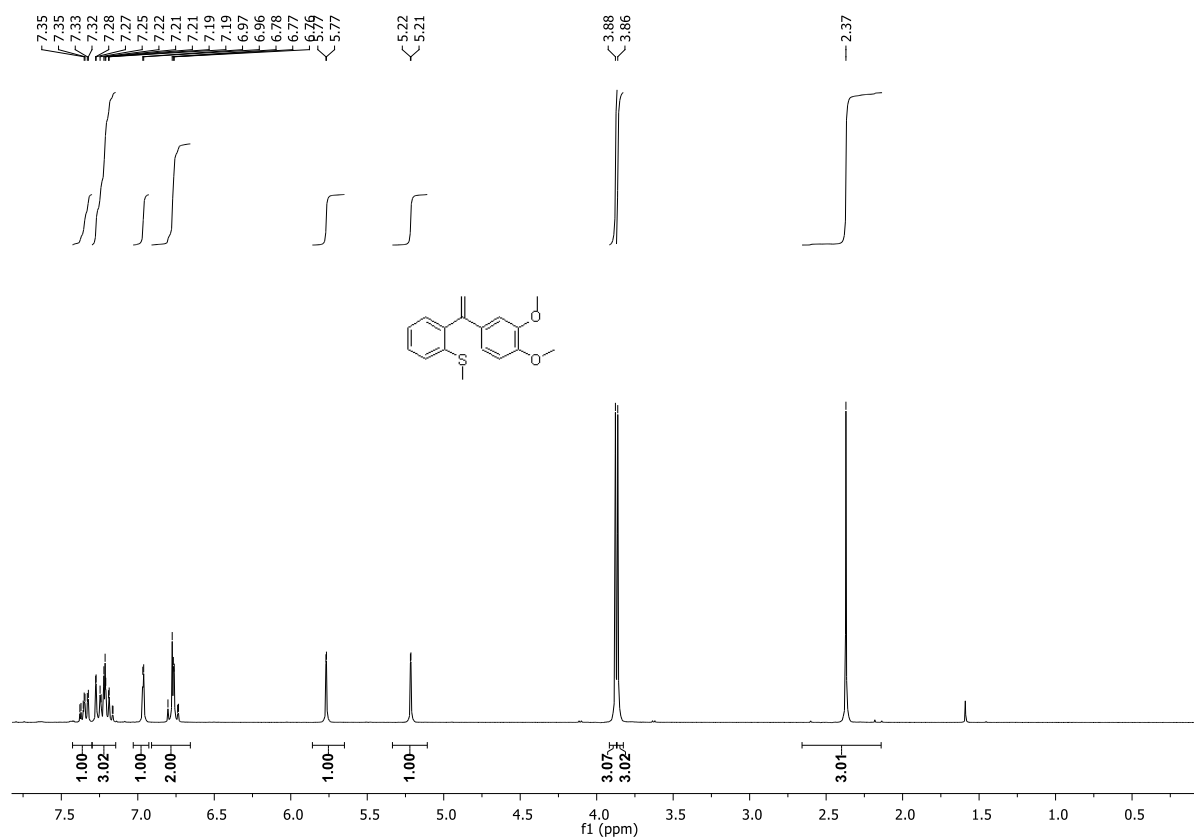
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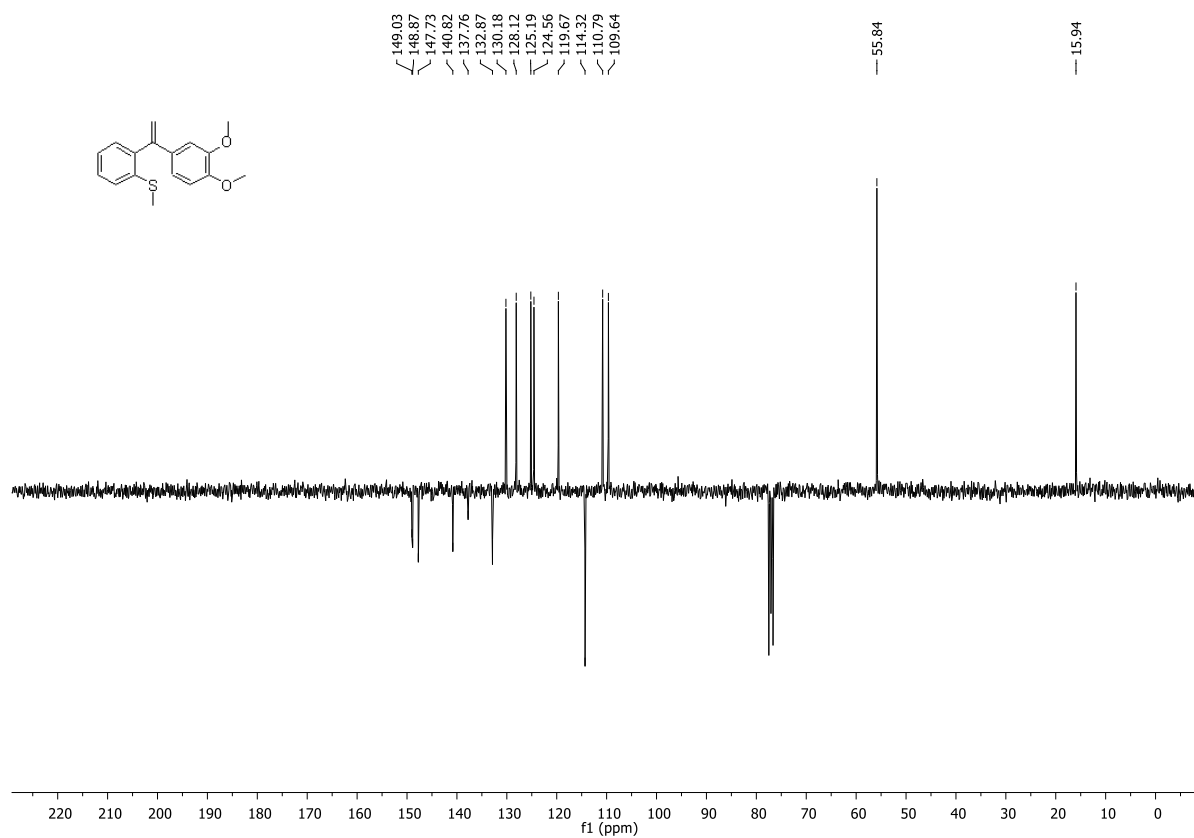
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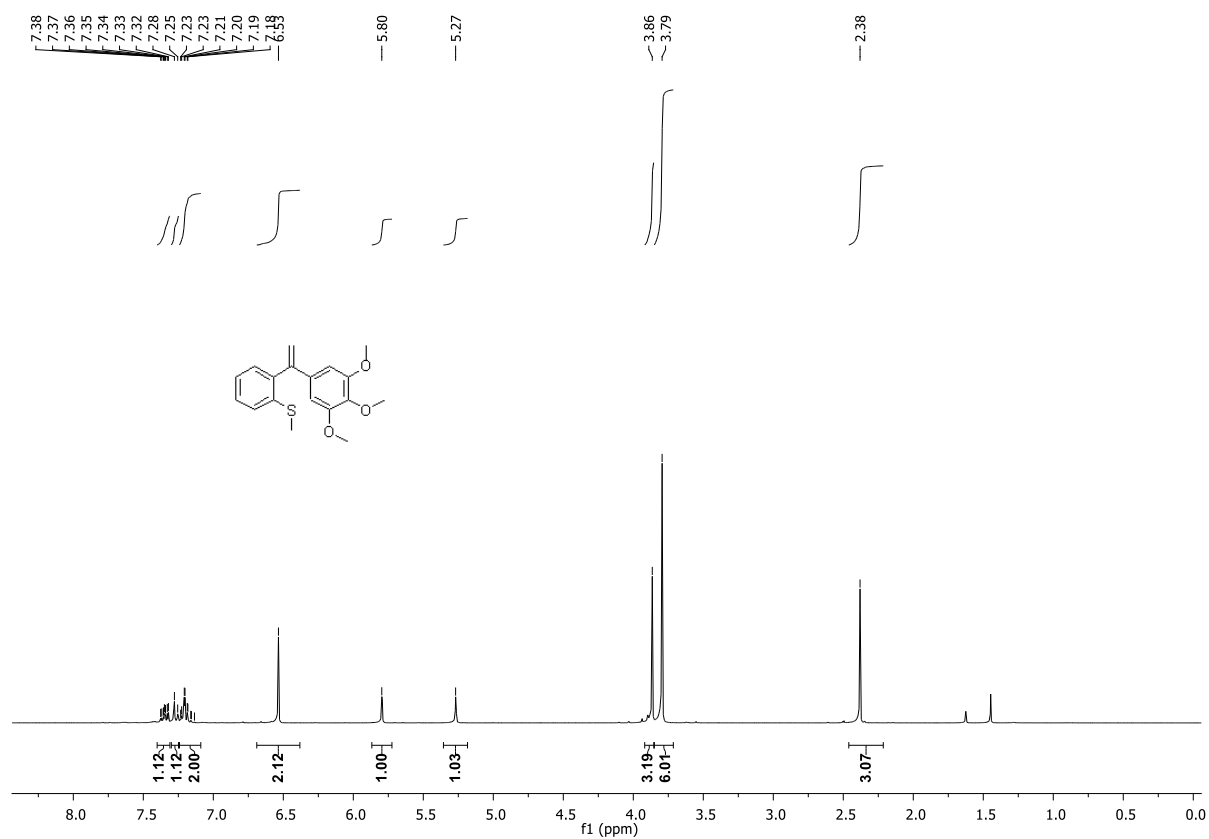
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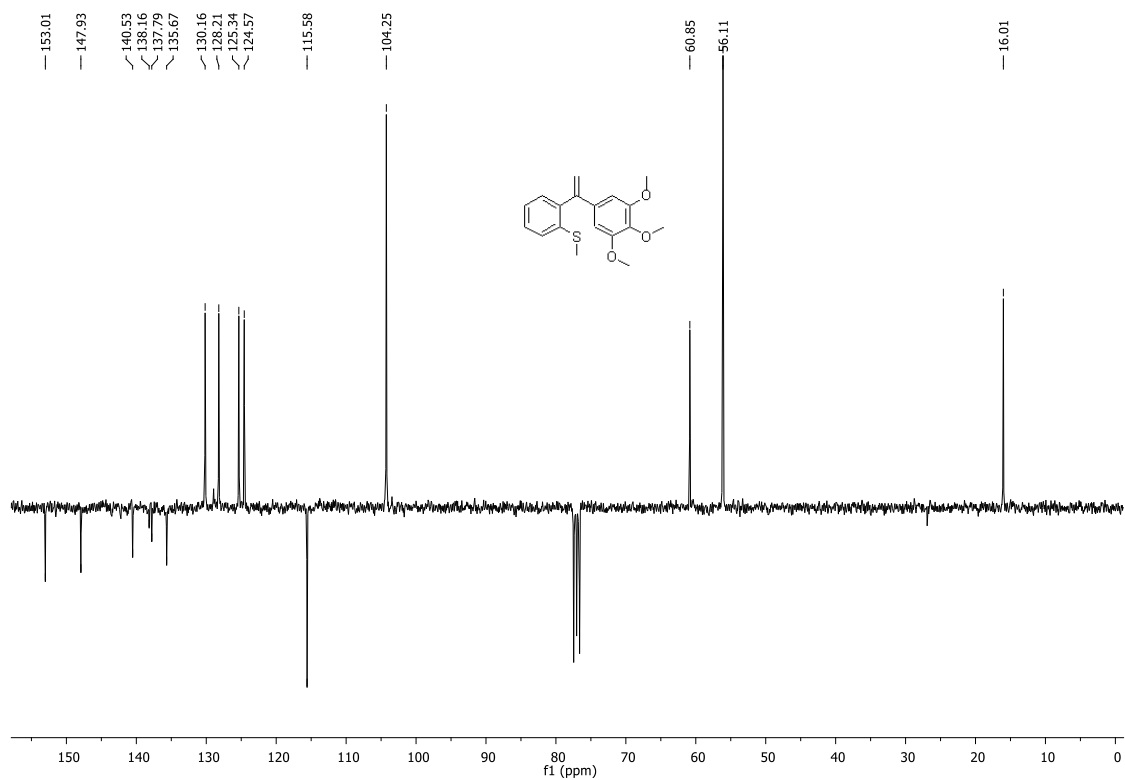
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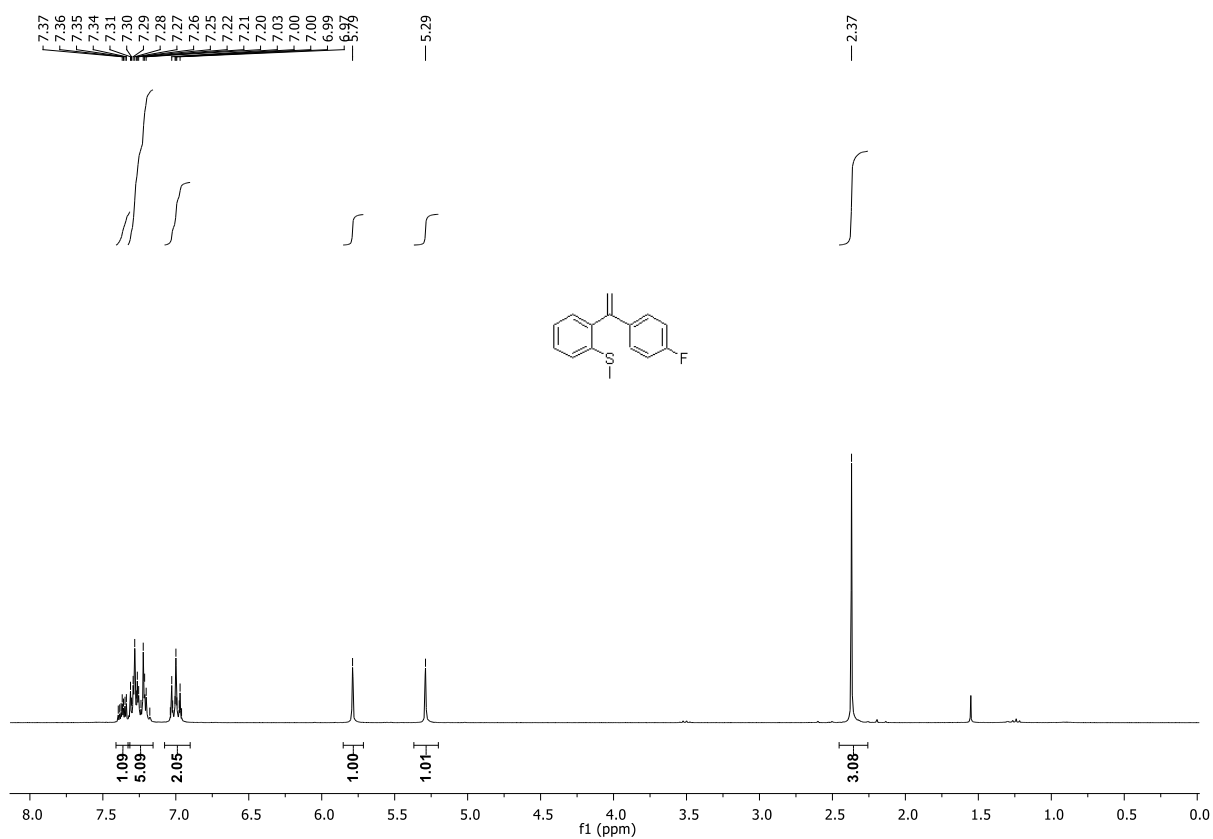
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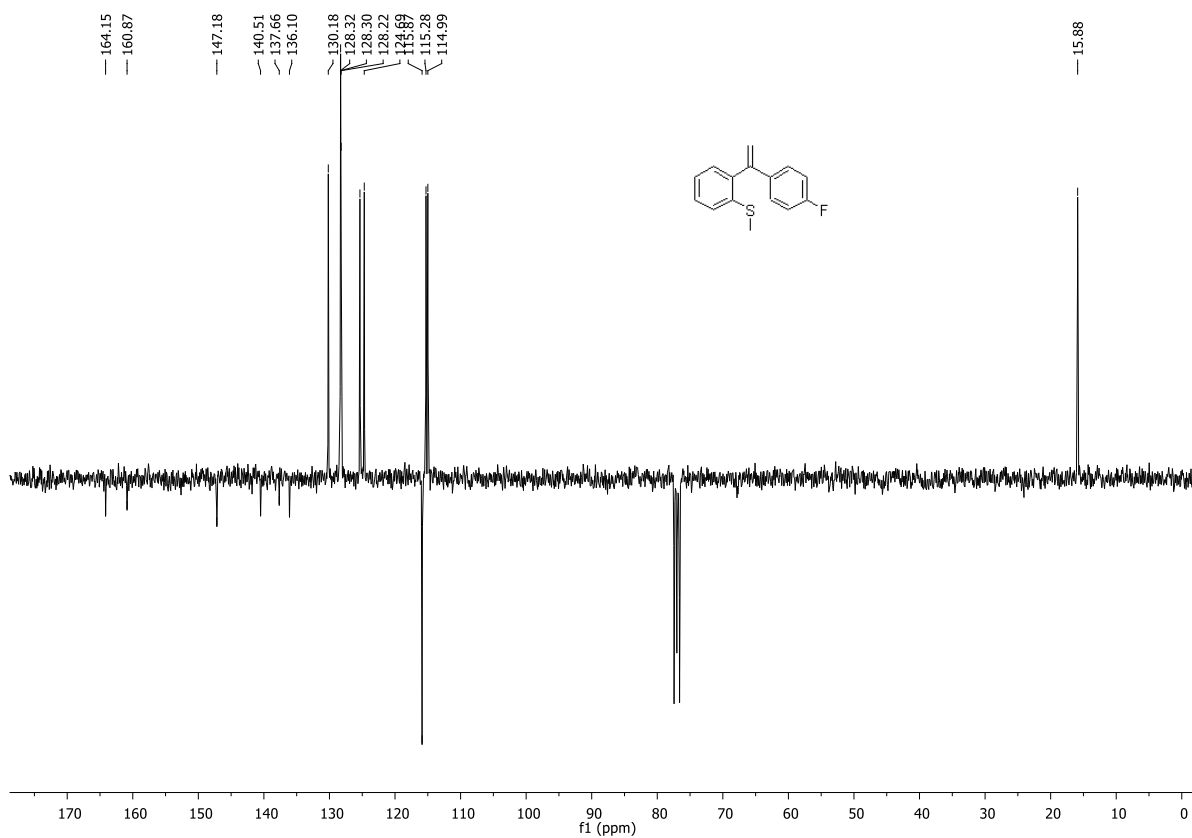
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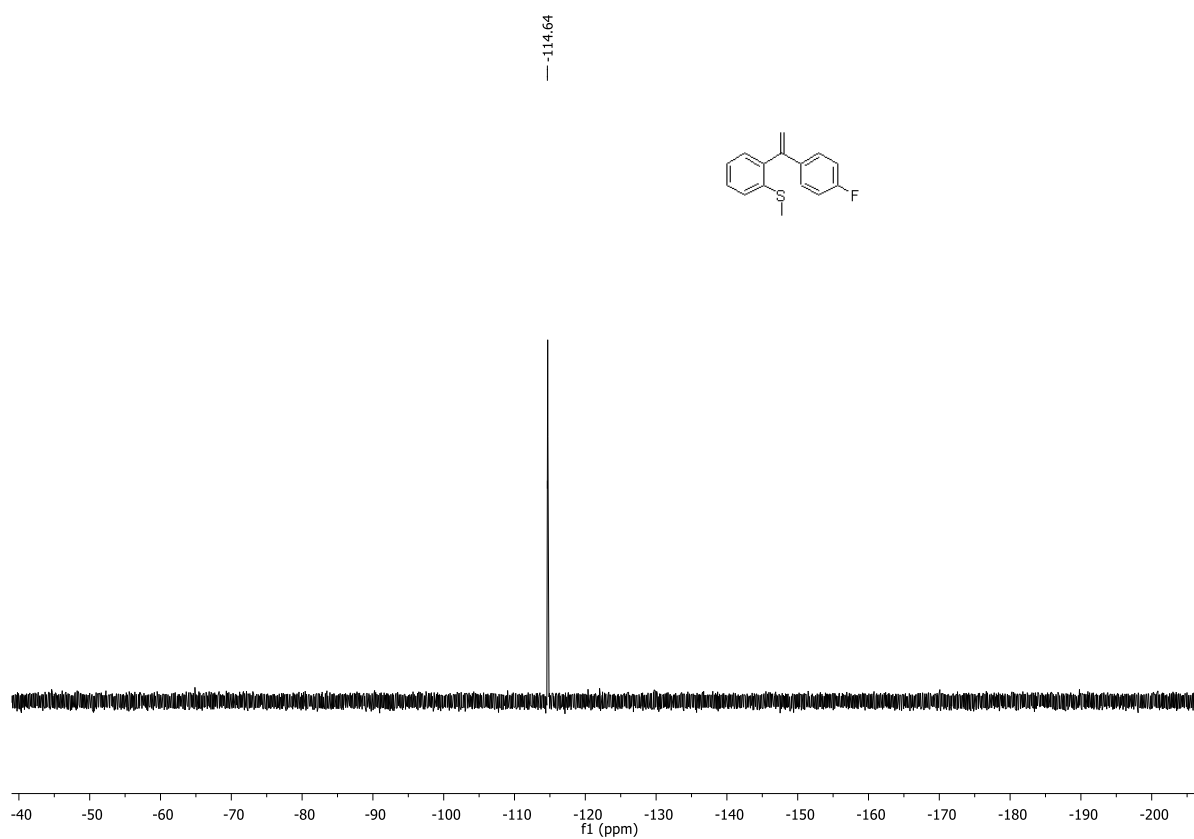
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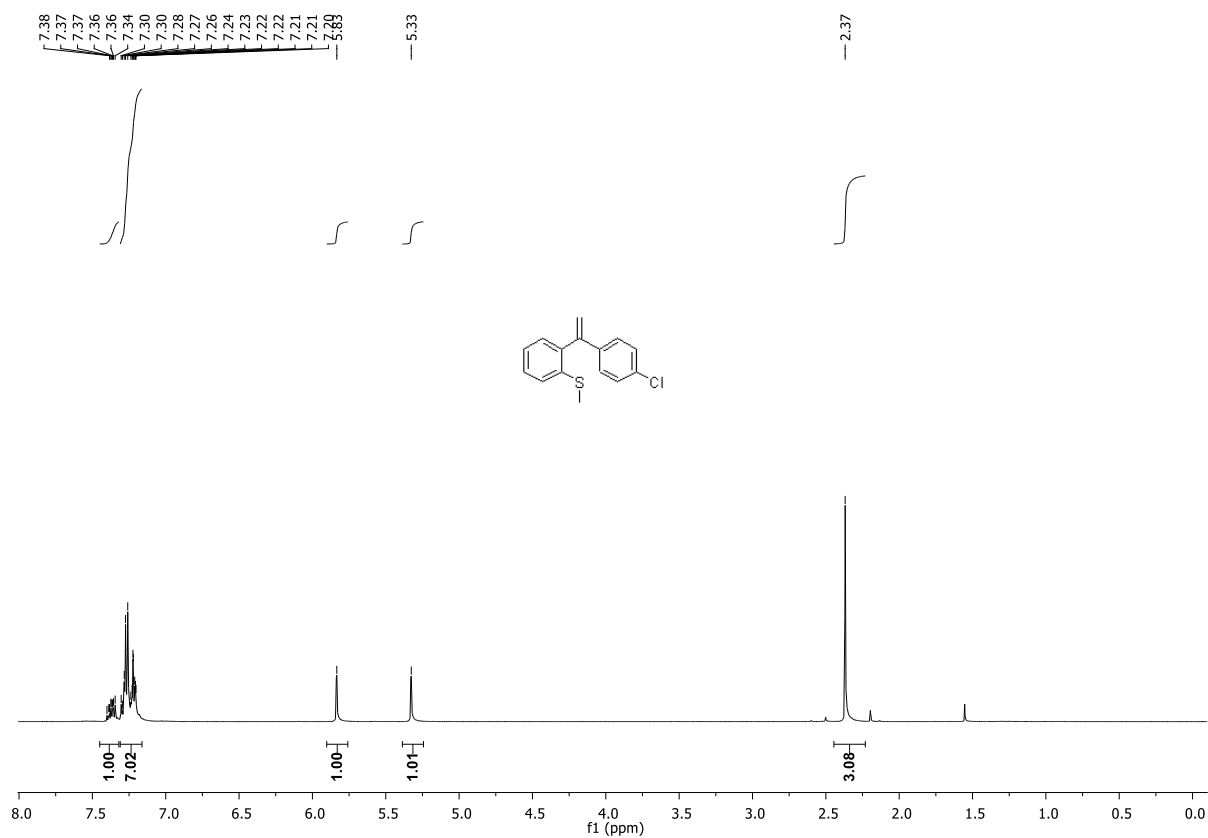
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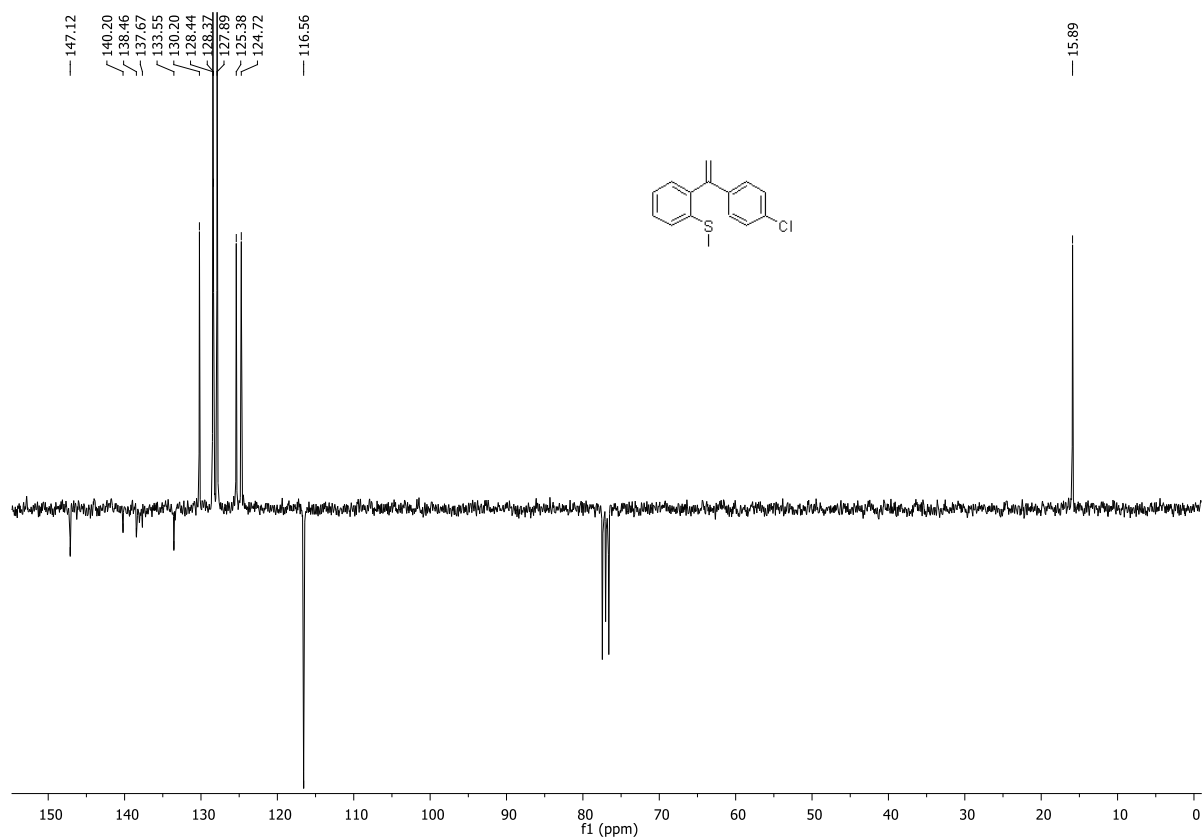
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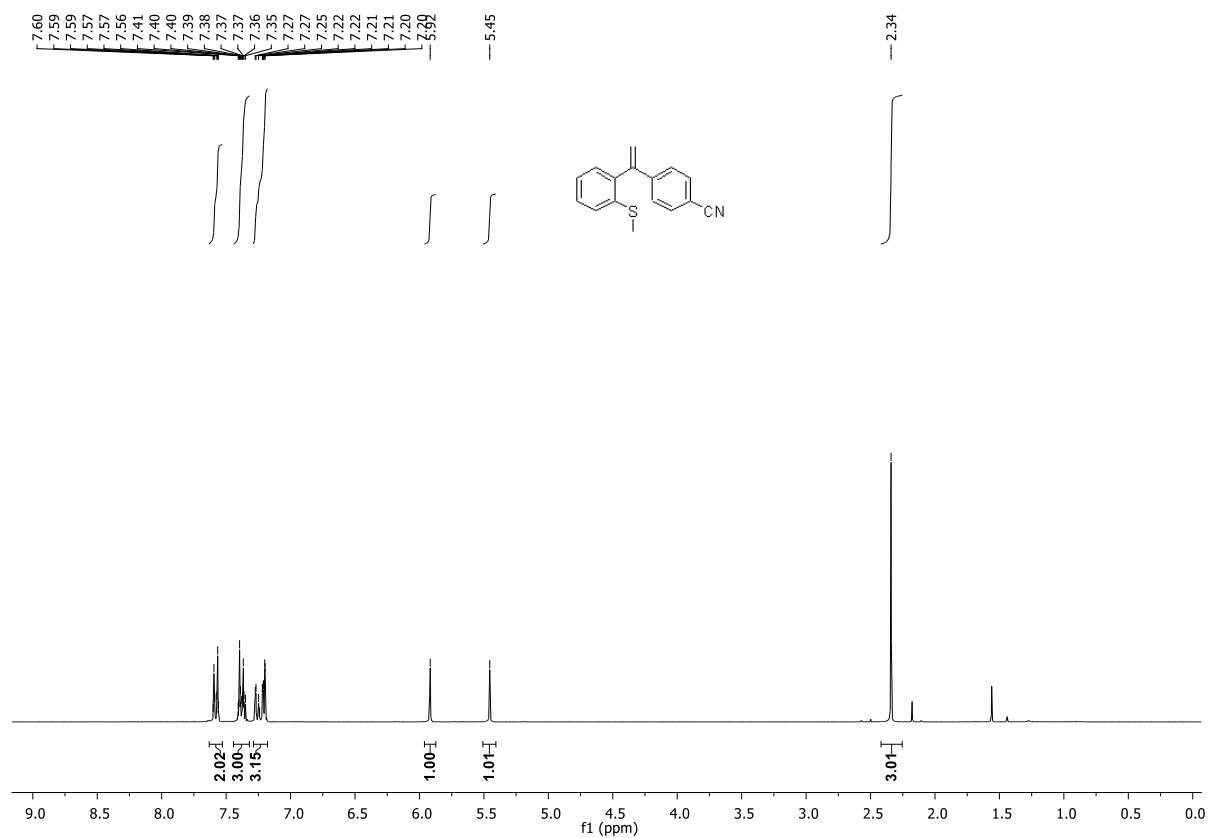
¹H NMR (300 MHz, CDCl₃) of **3i**



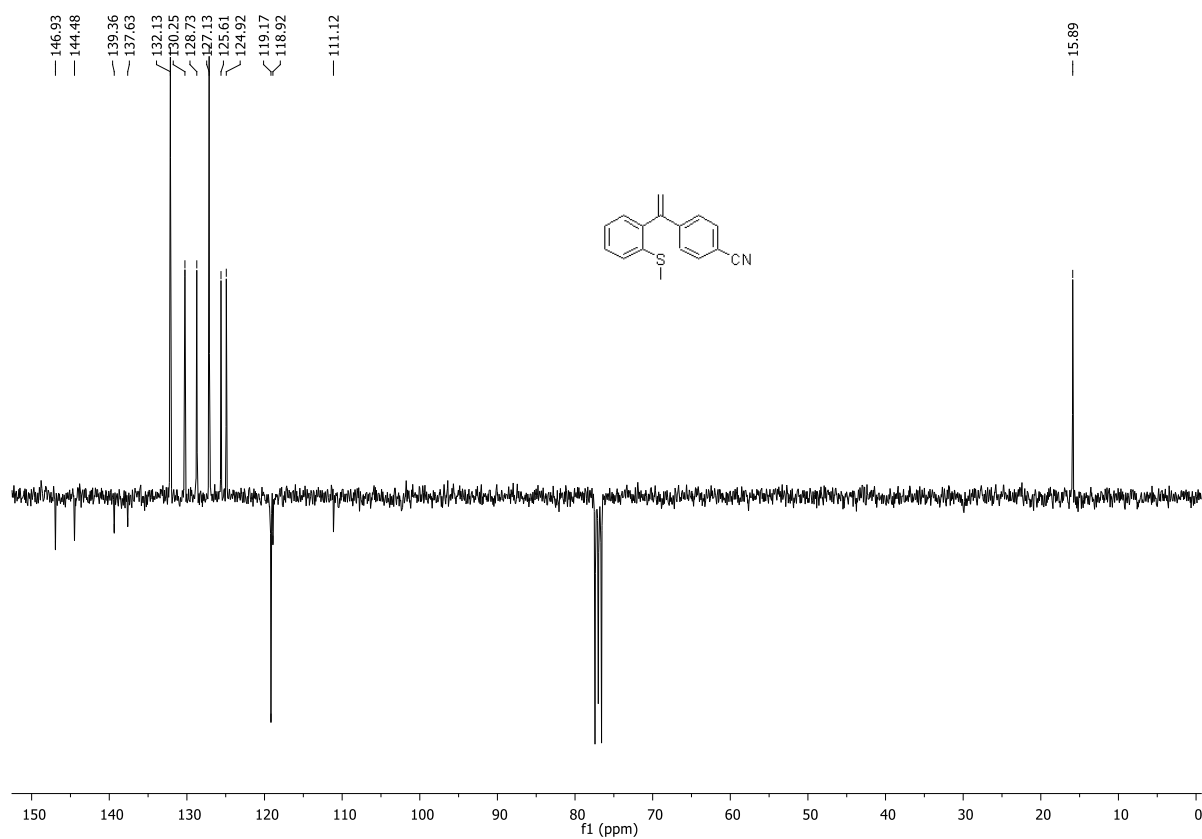
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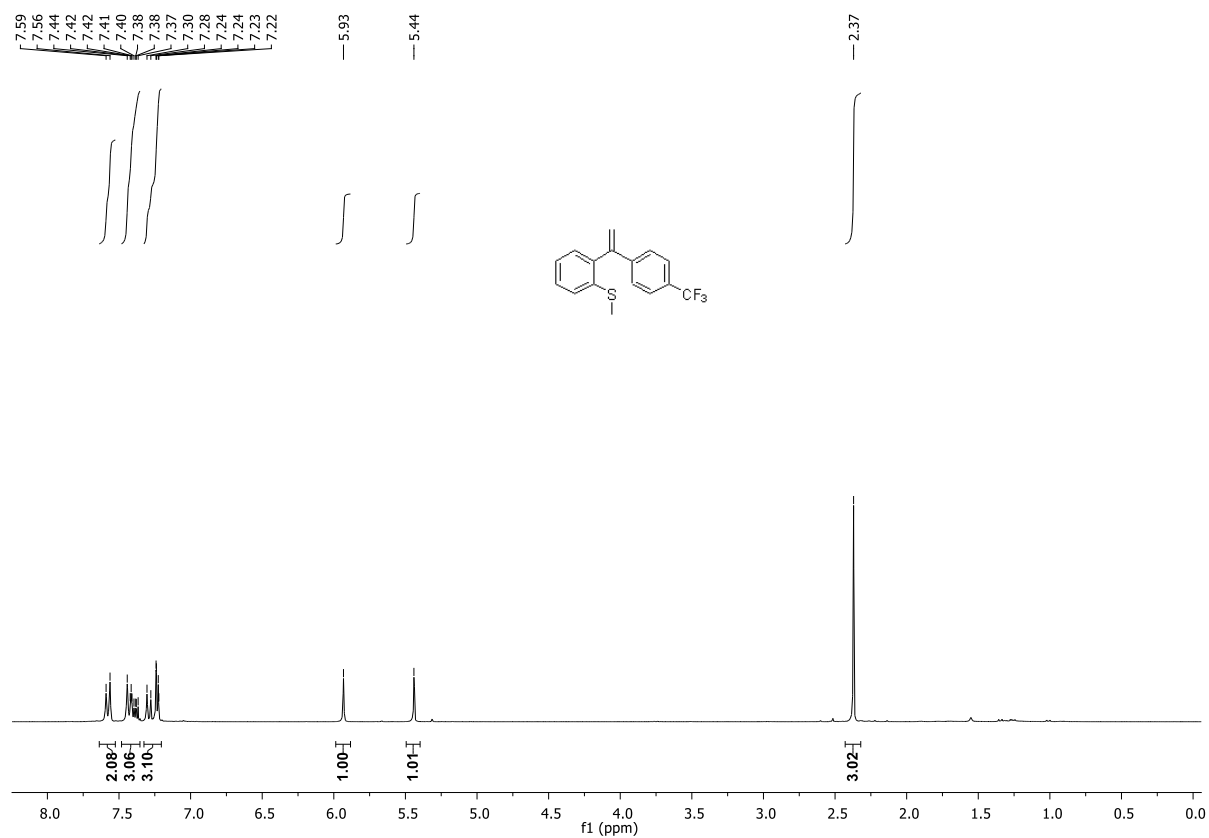
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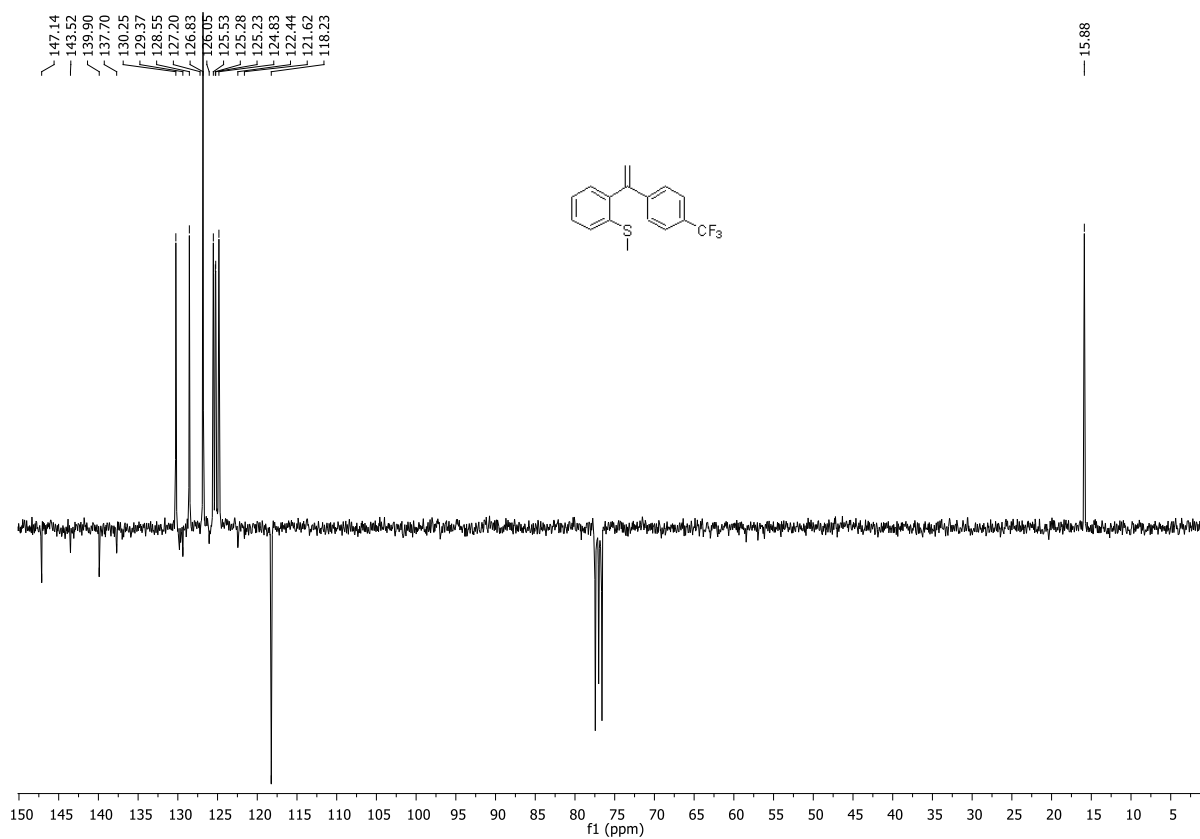
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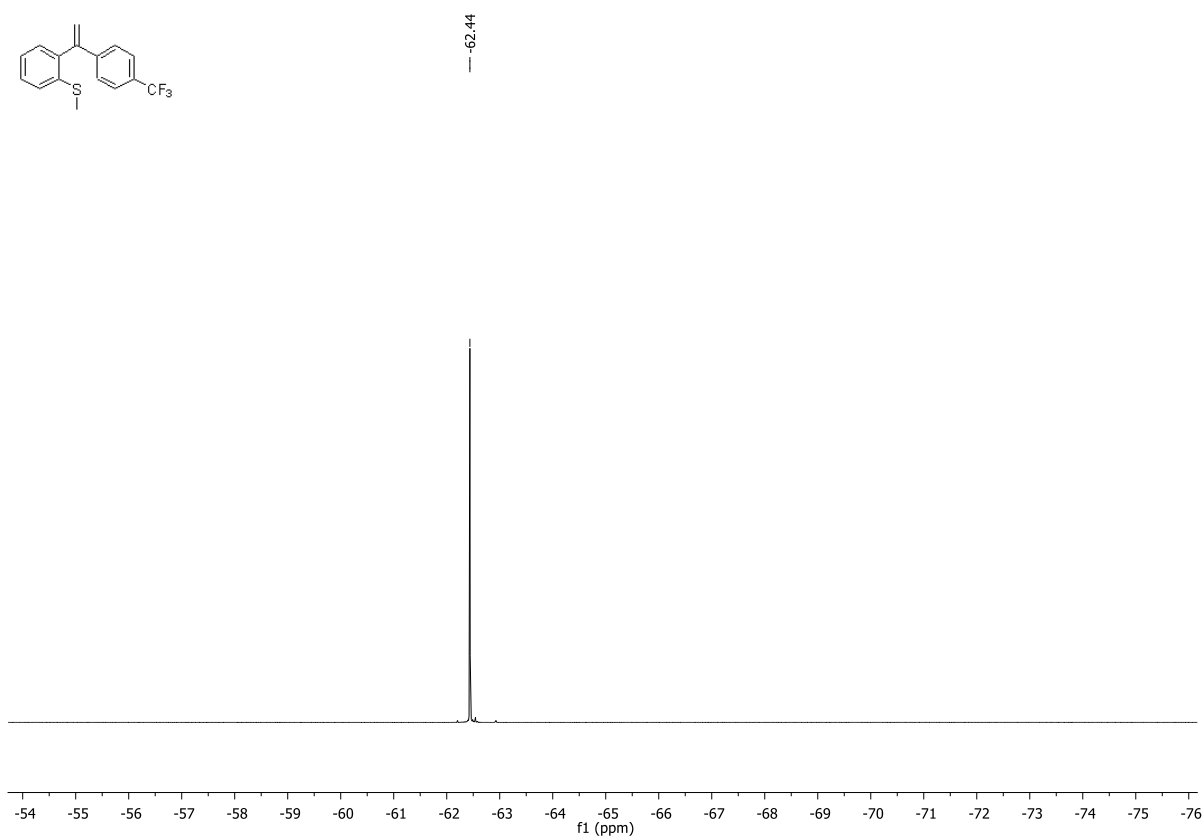
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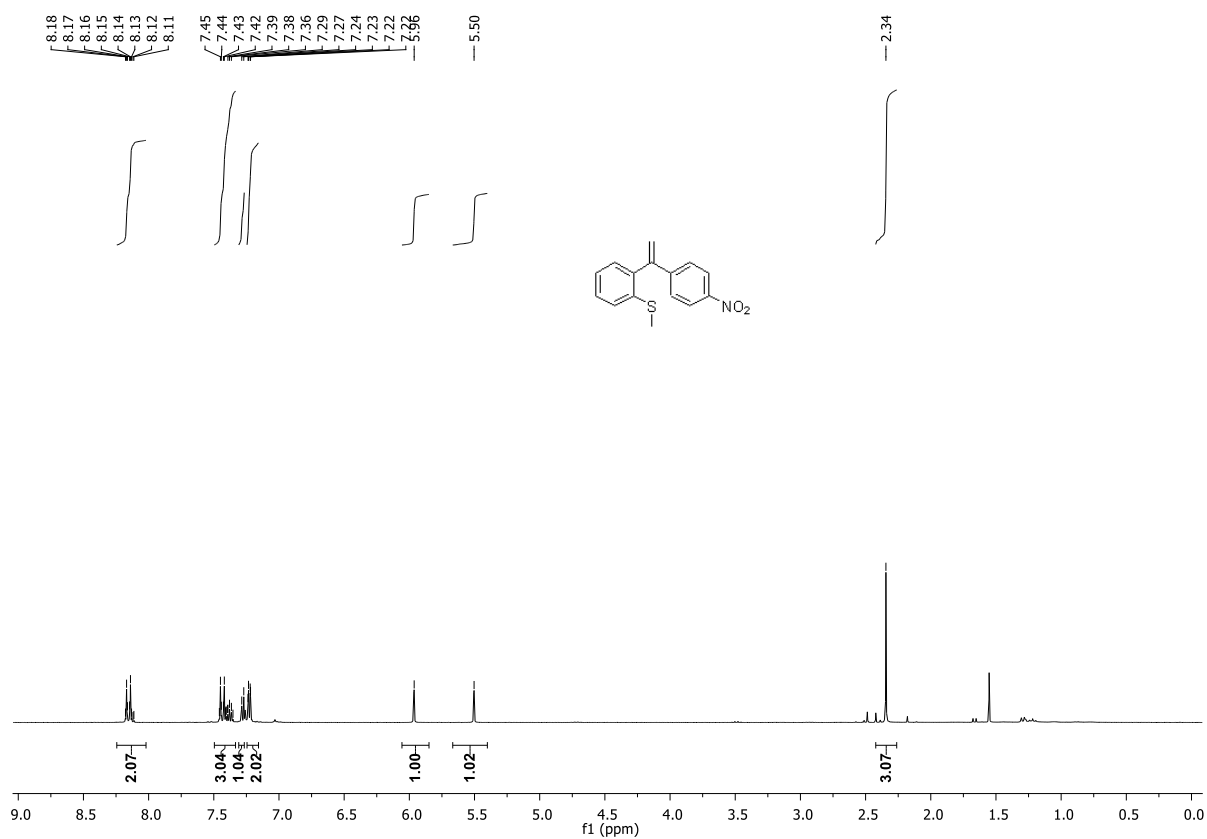
^{13}C NMR (75 MHz, CDCl_3) of **3k**



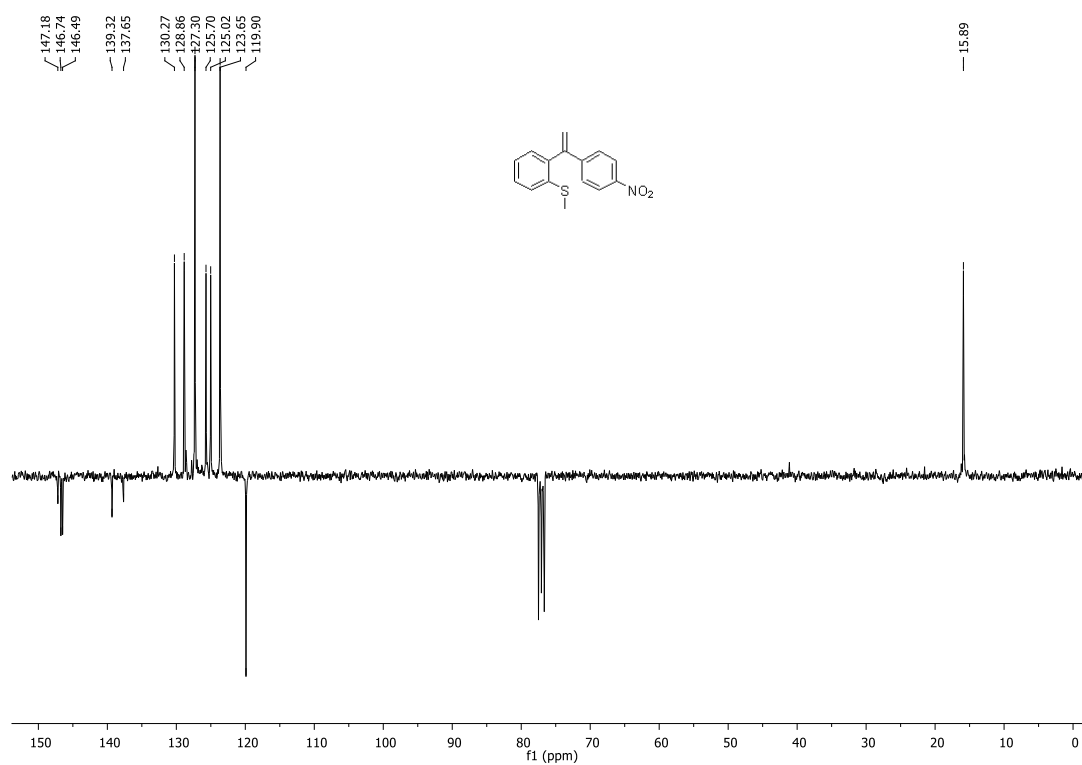
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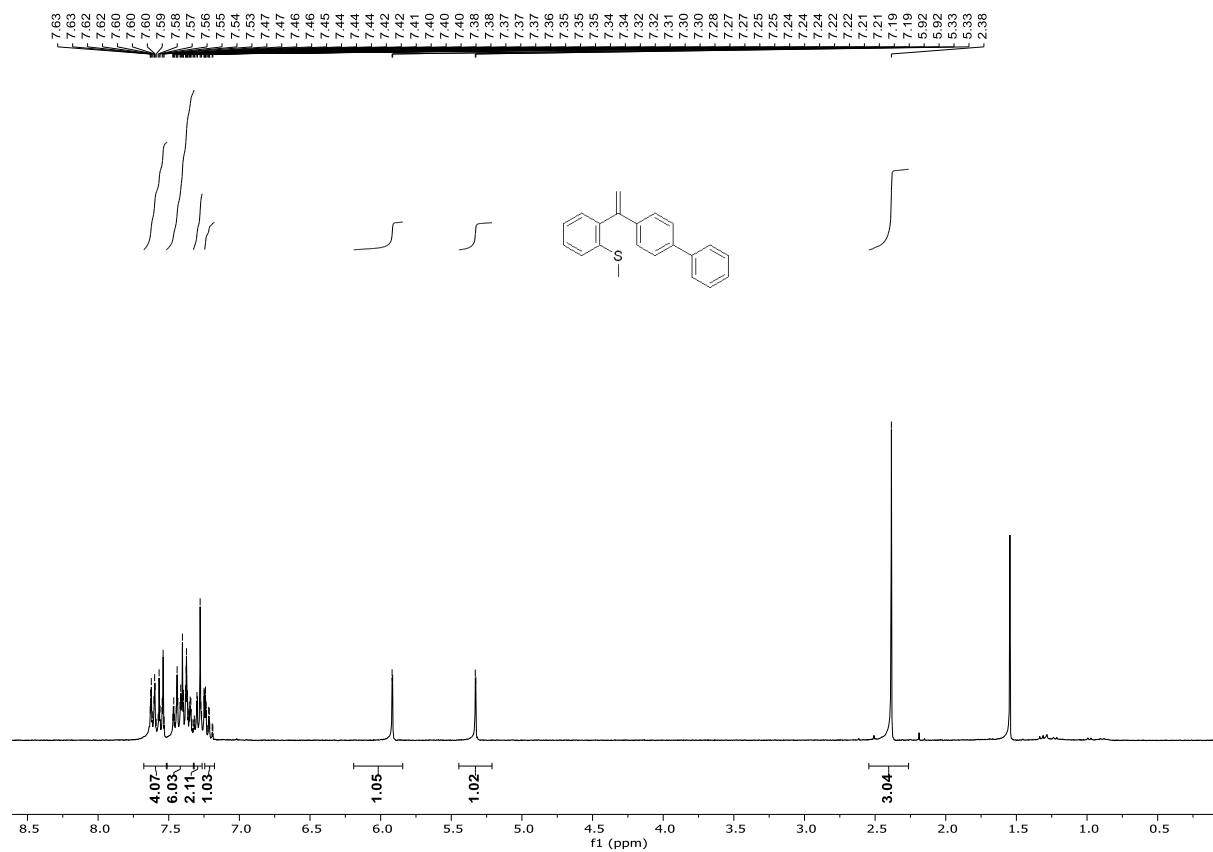
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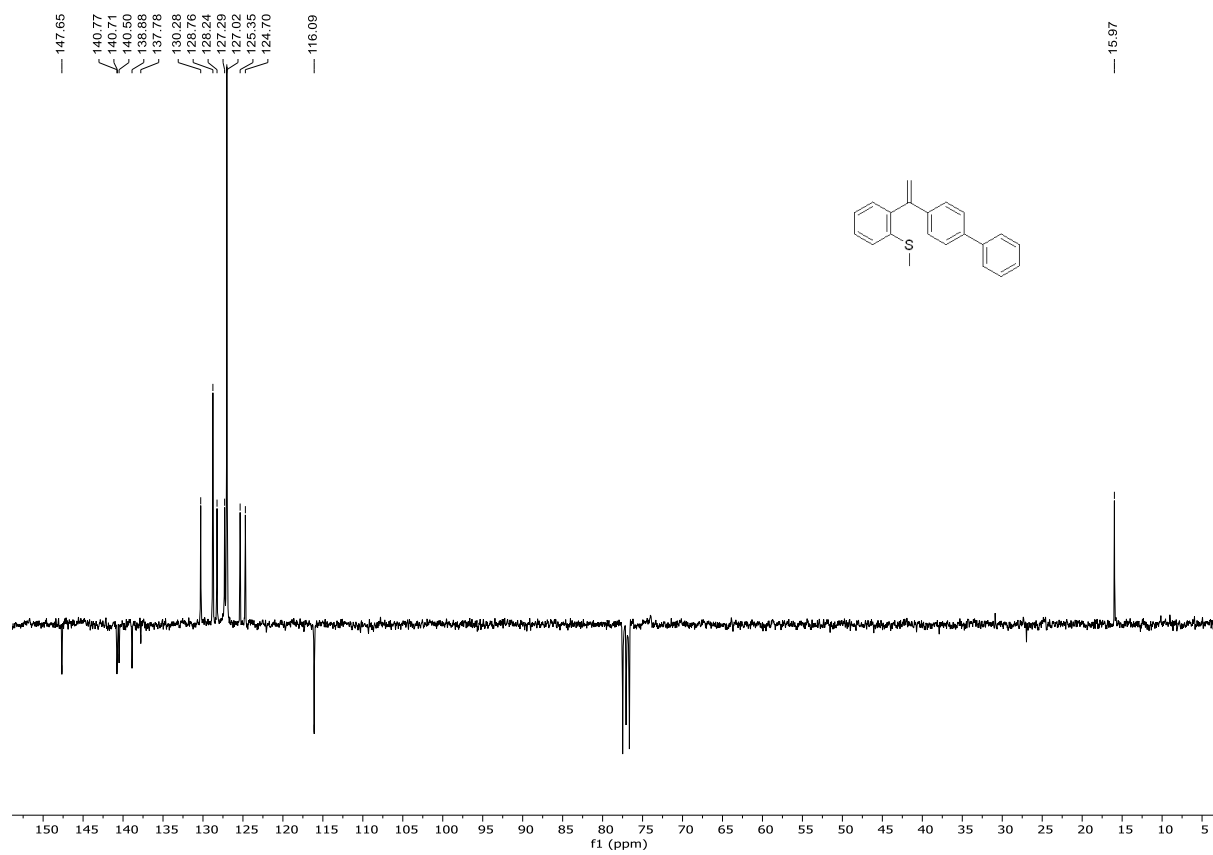
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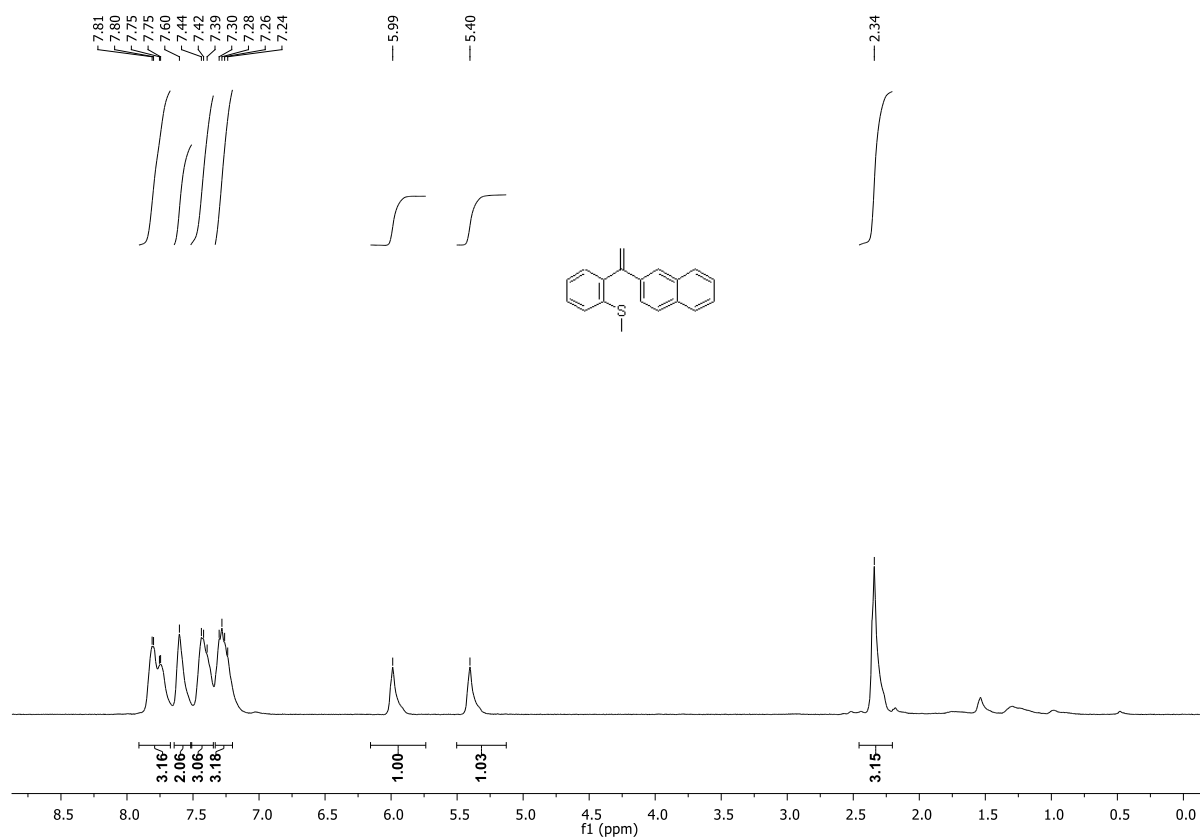
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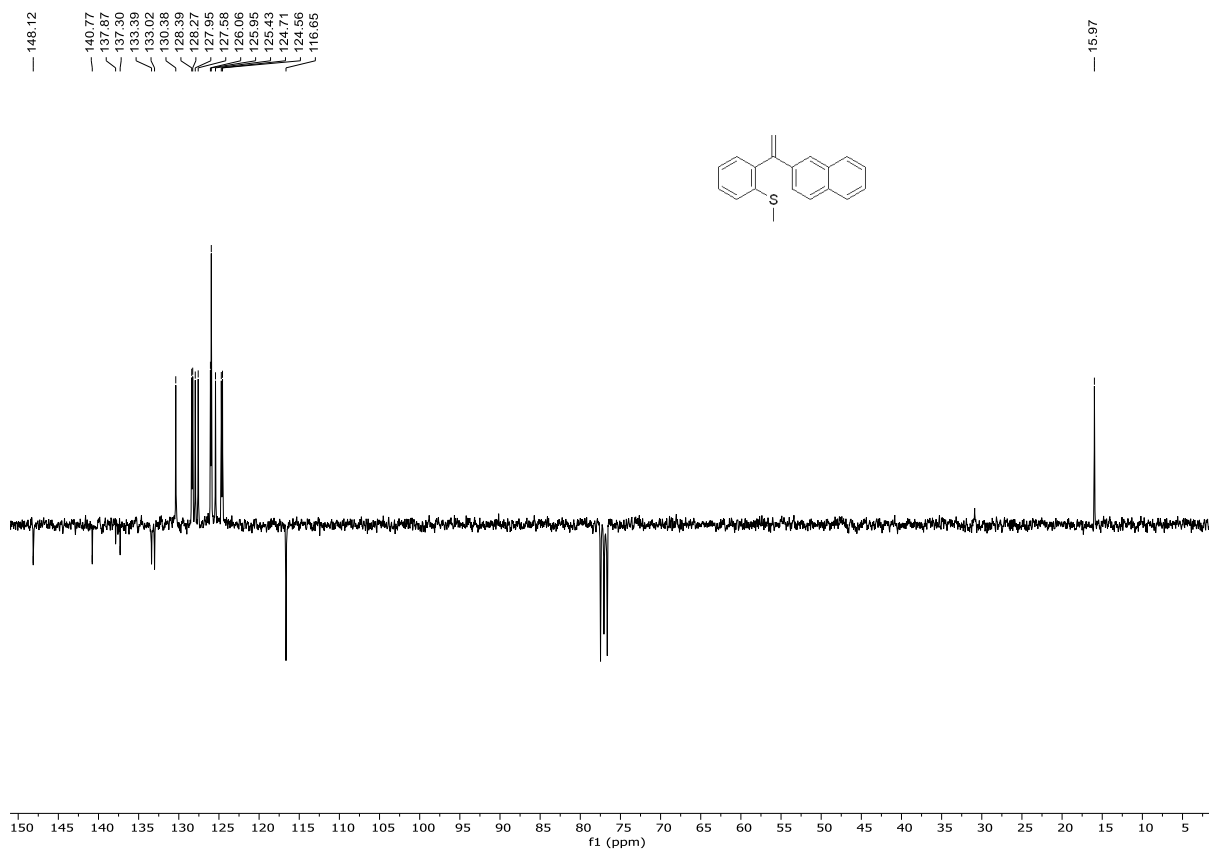
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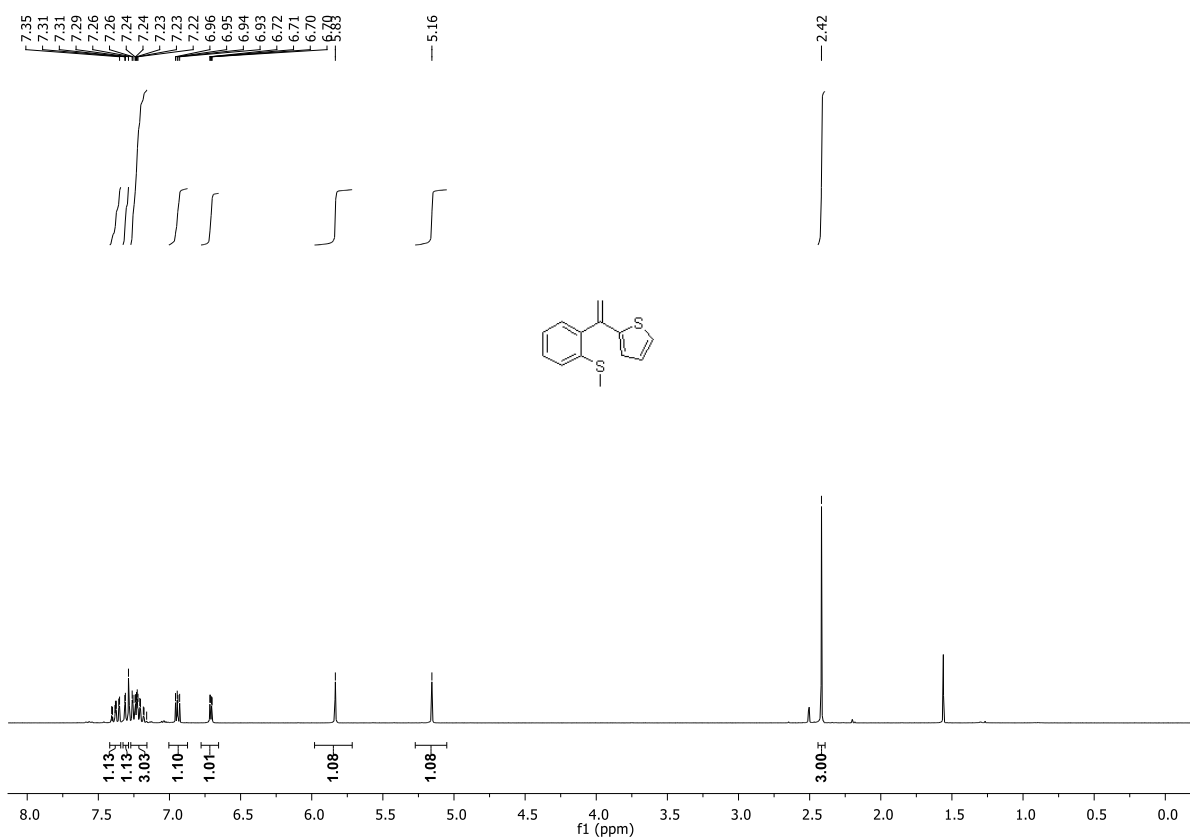
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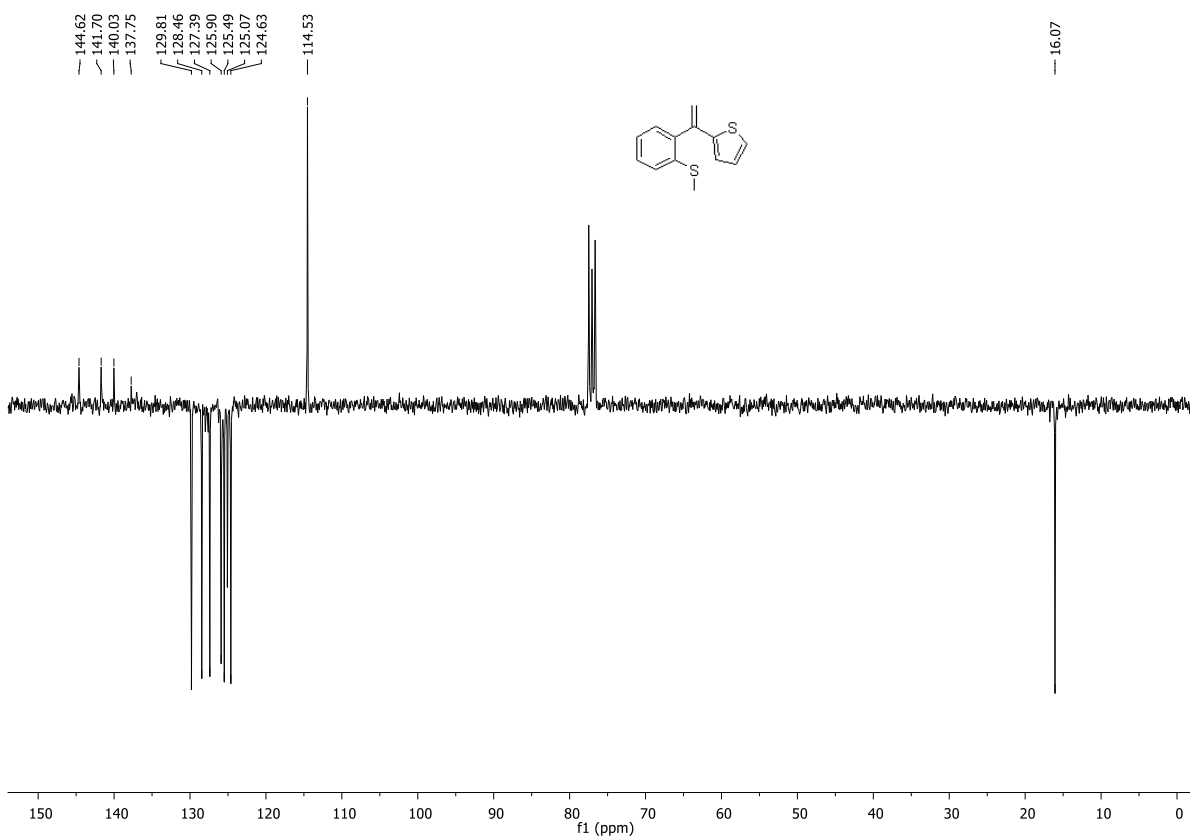
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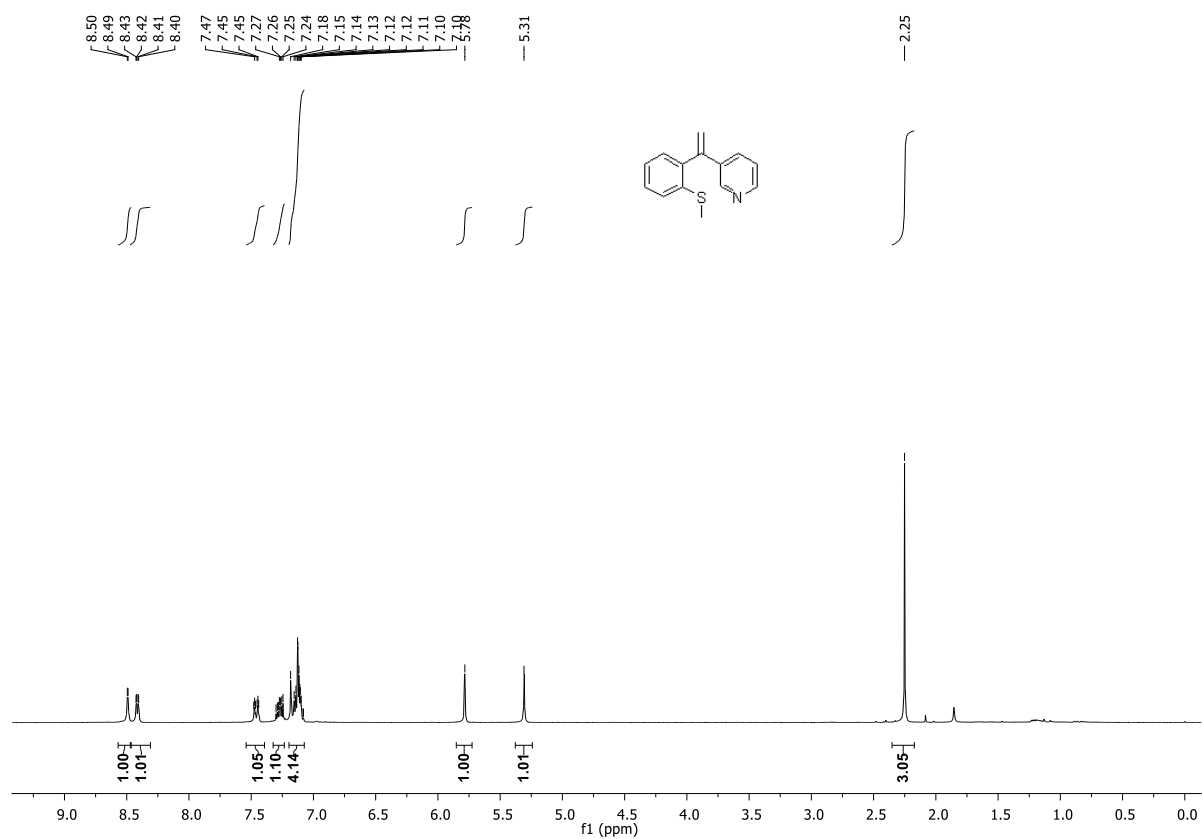
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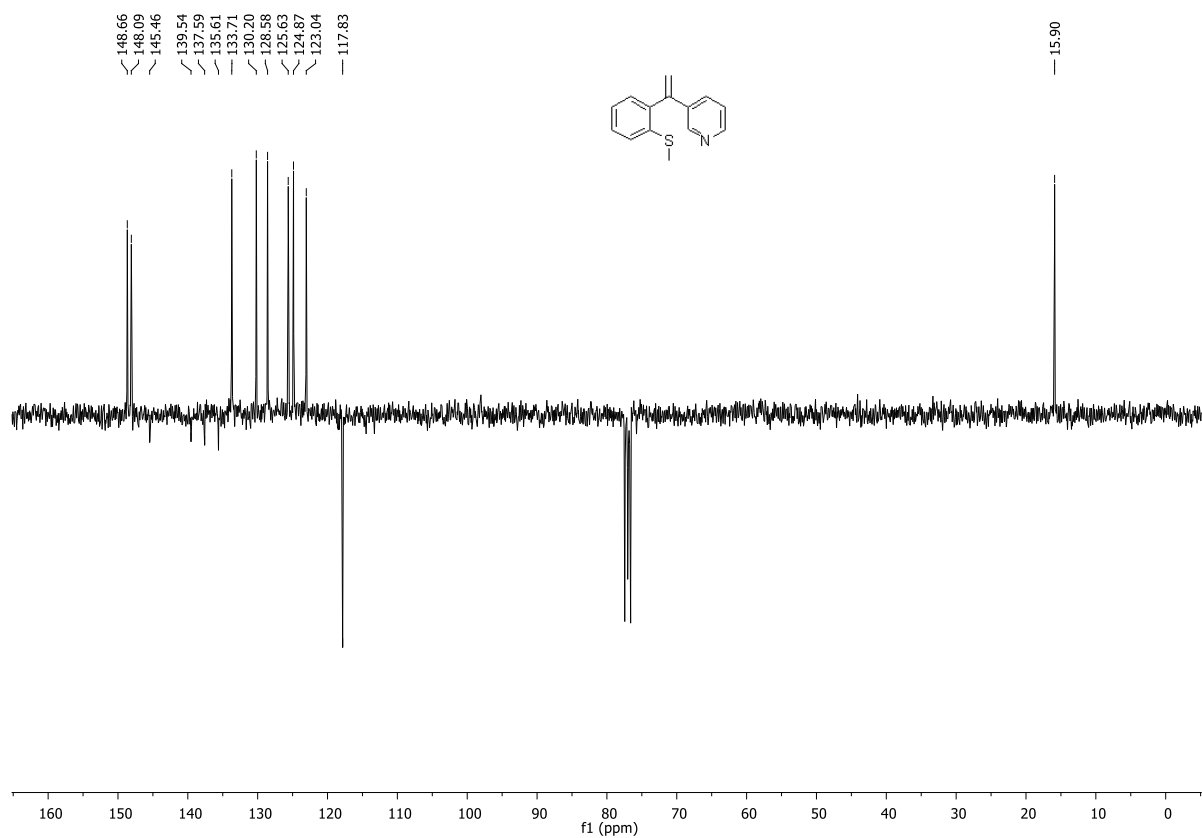
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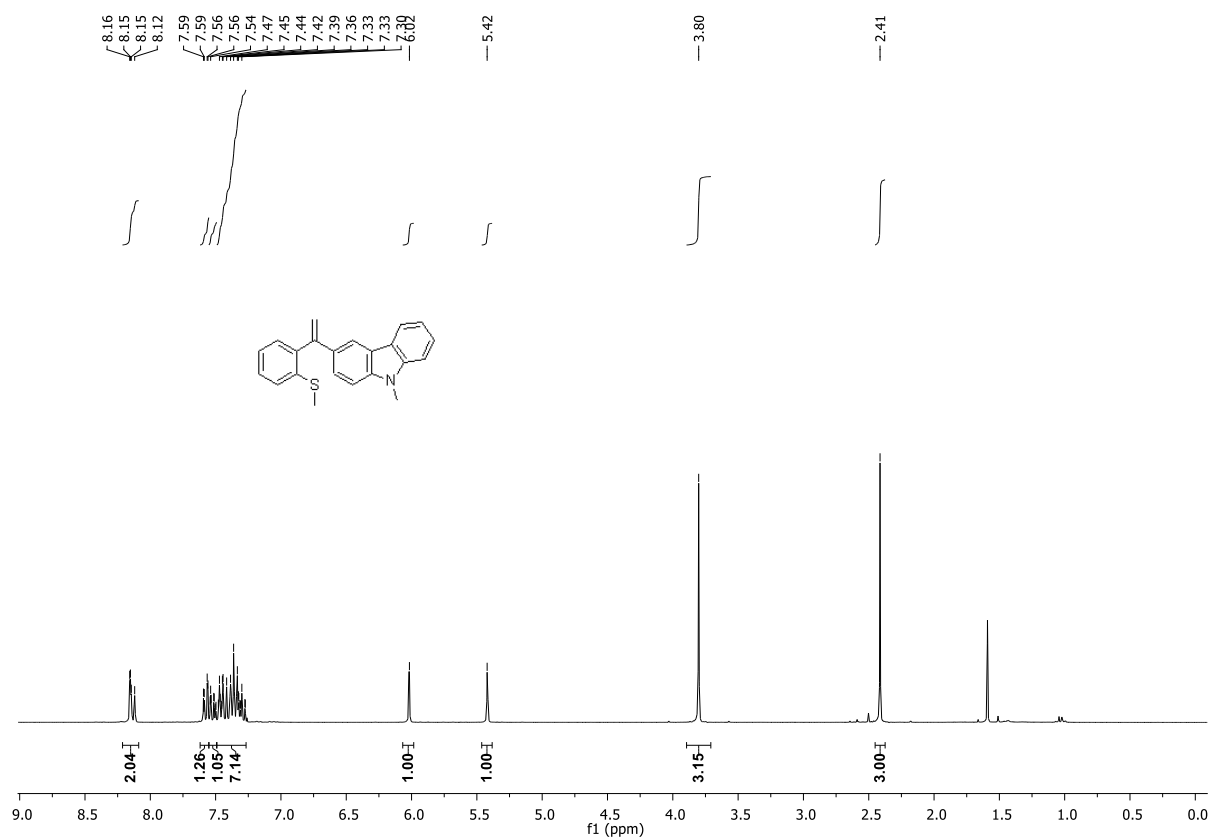
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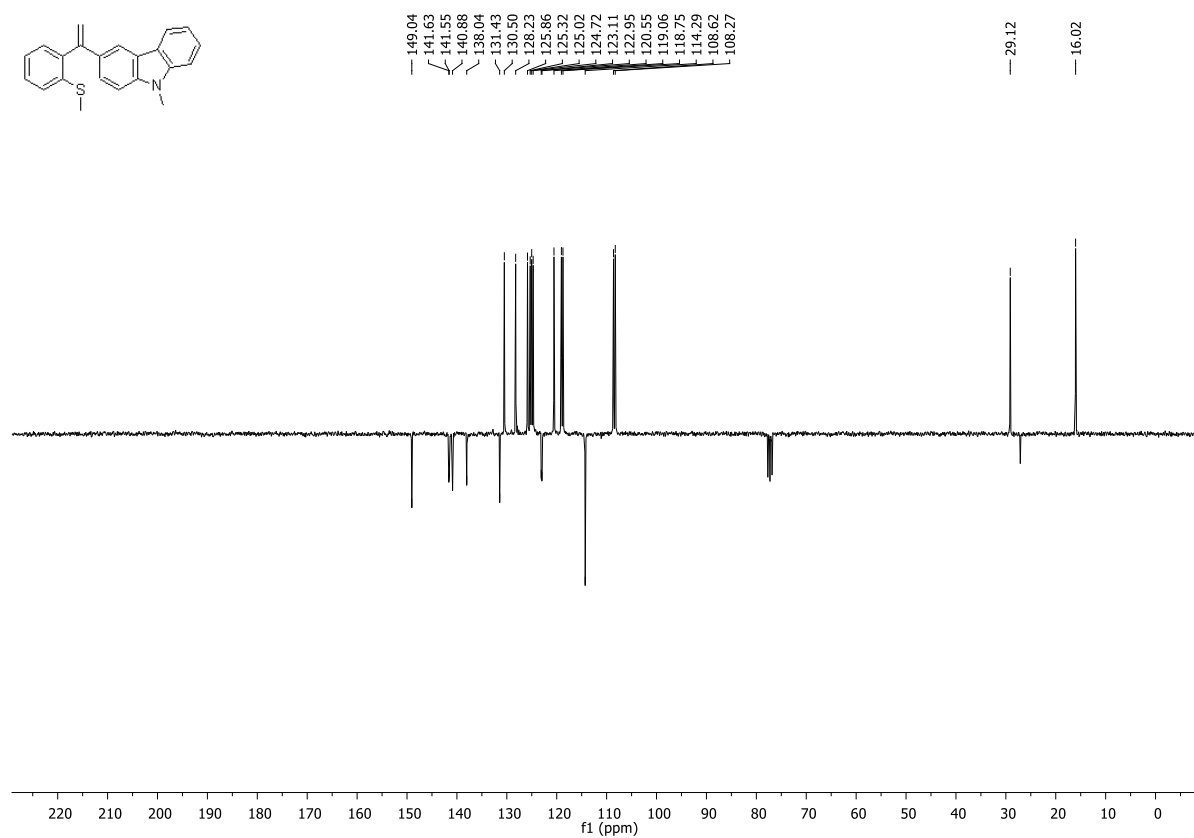
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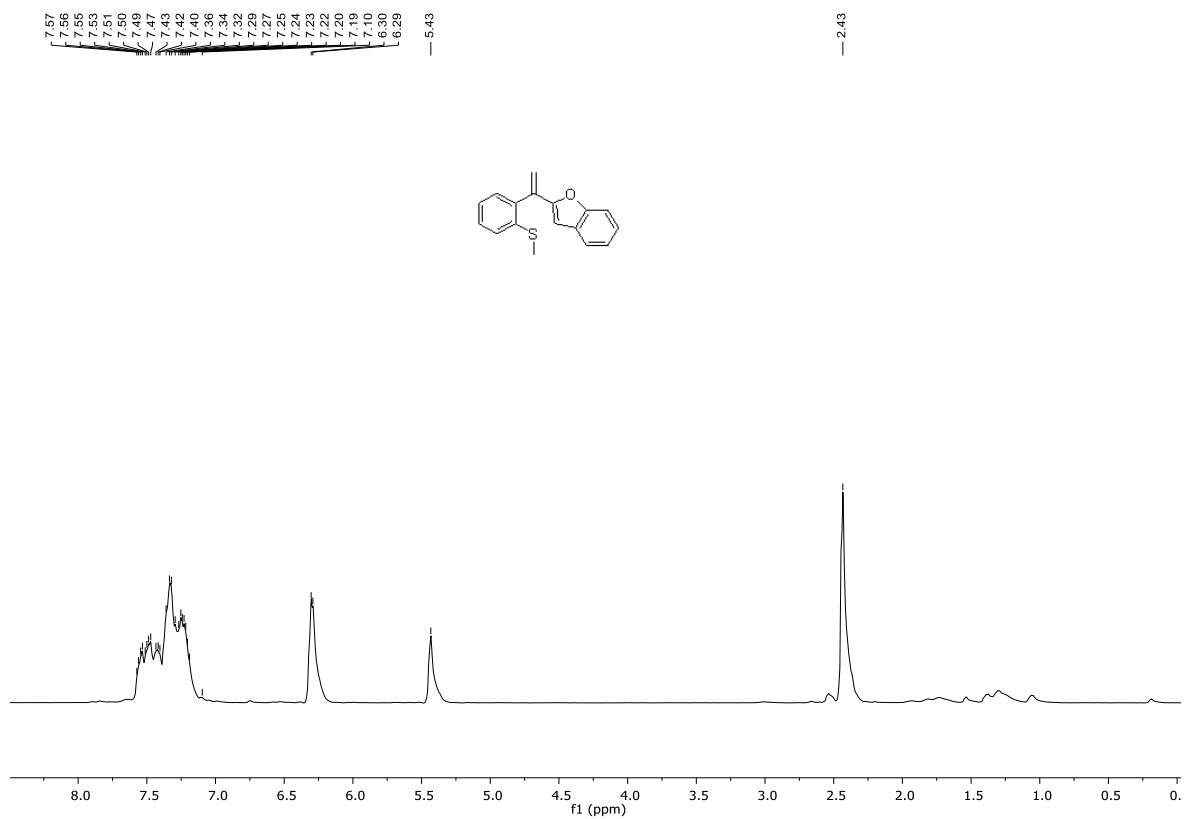
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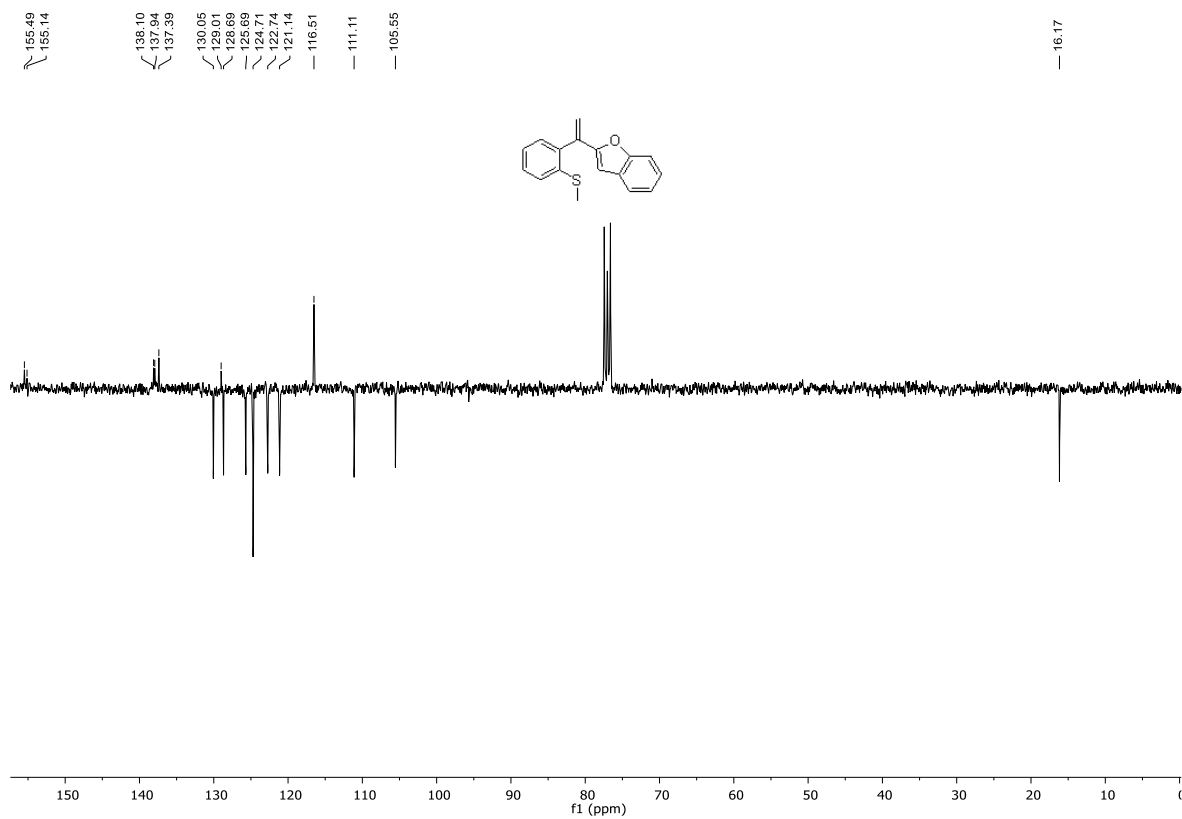
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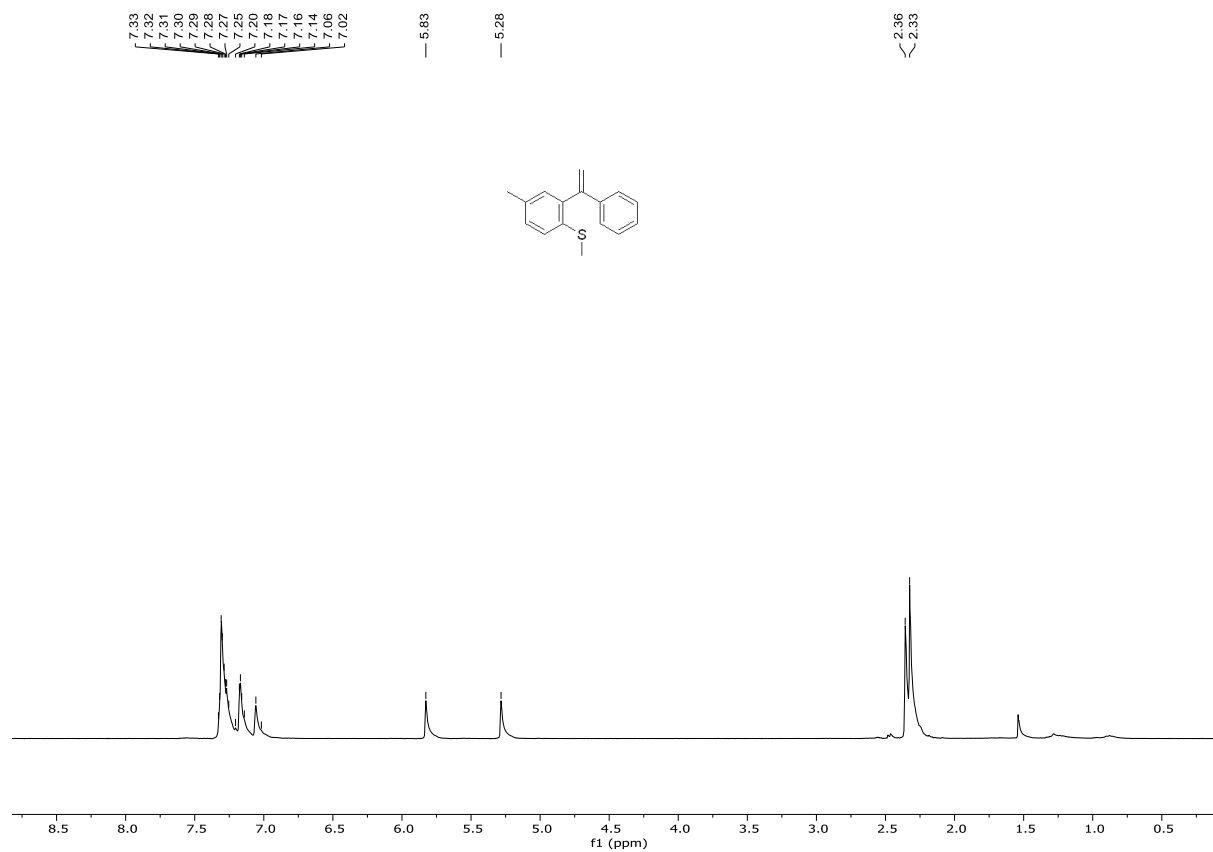
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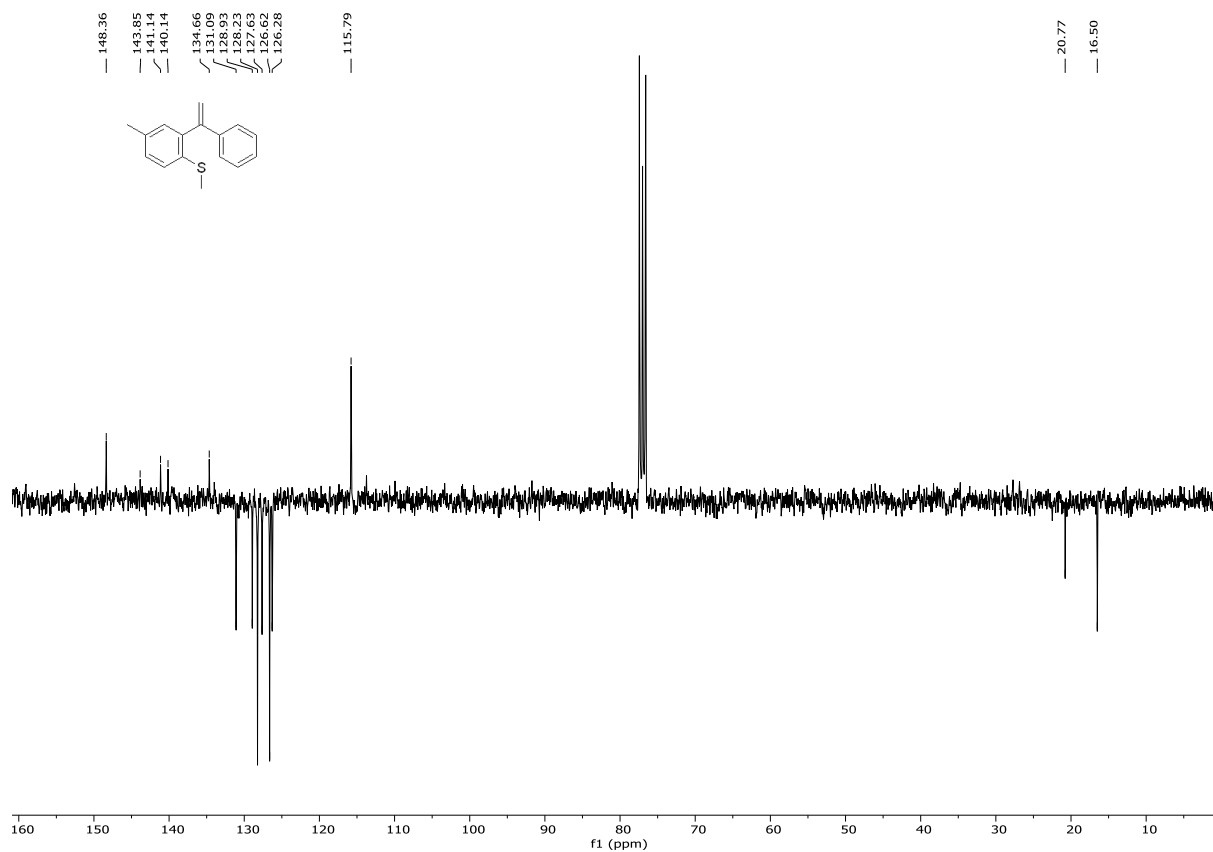
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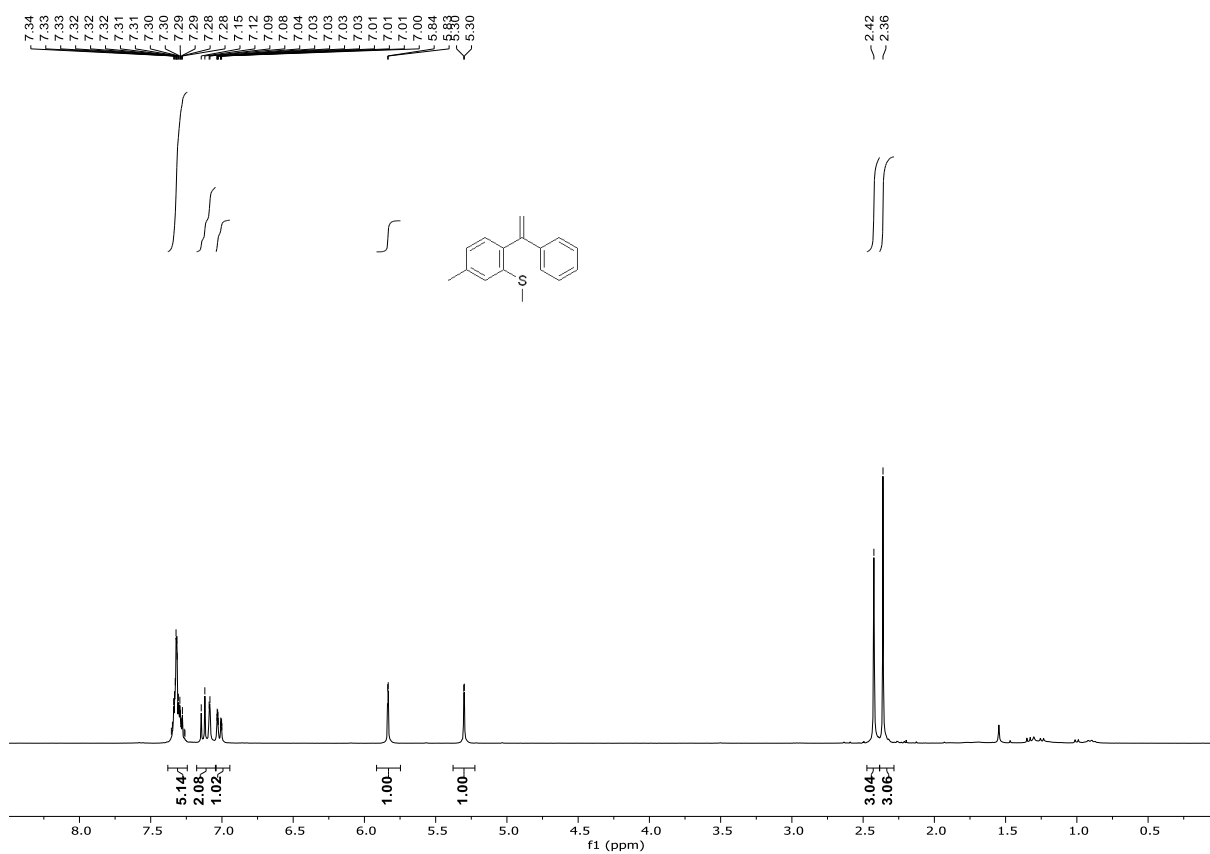
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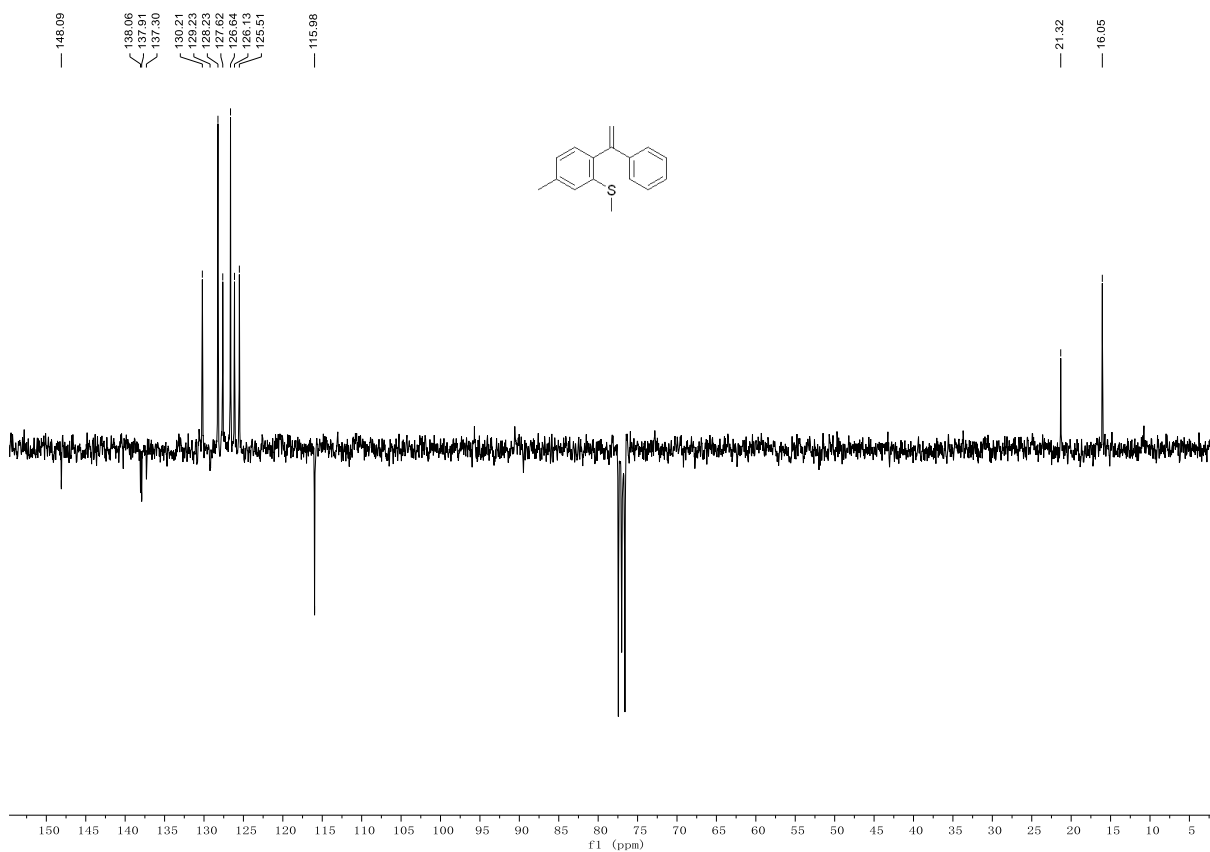
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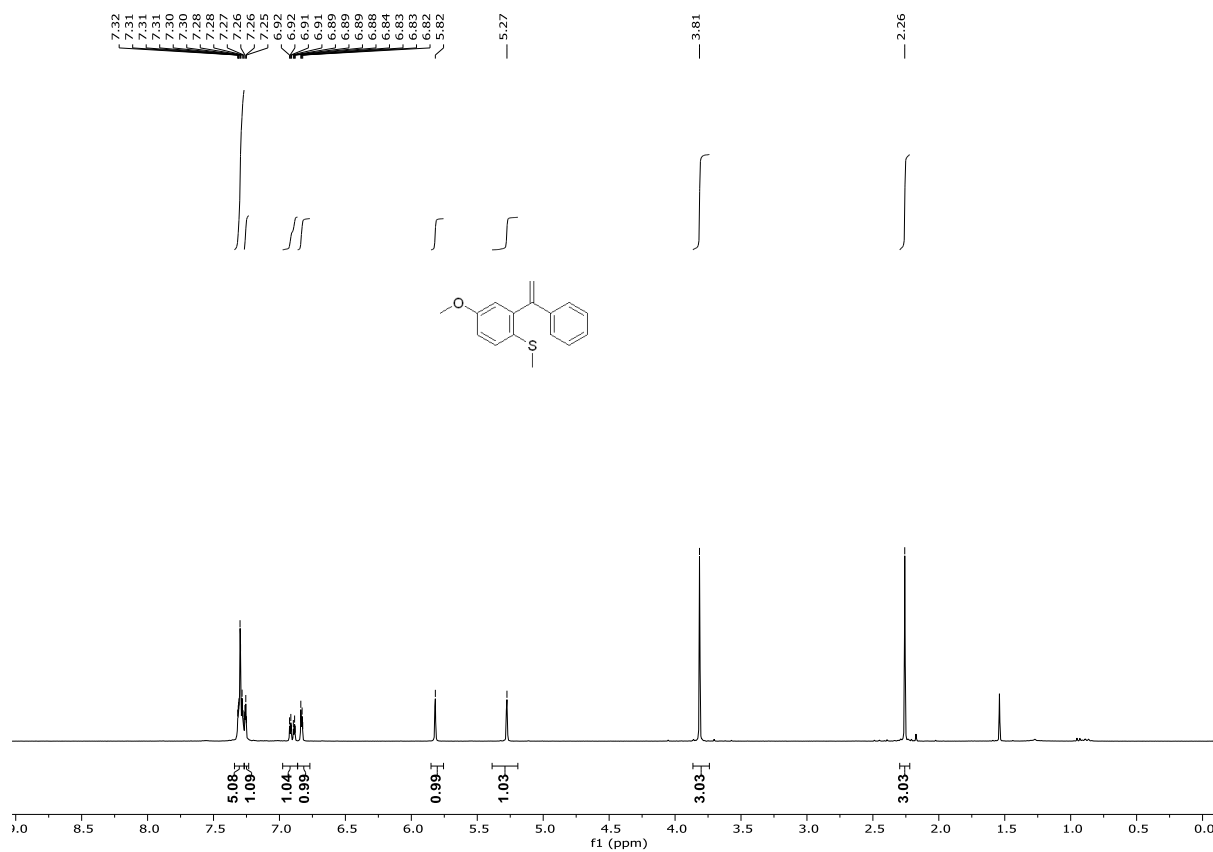
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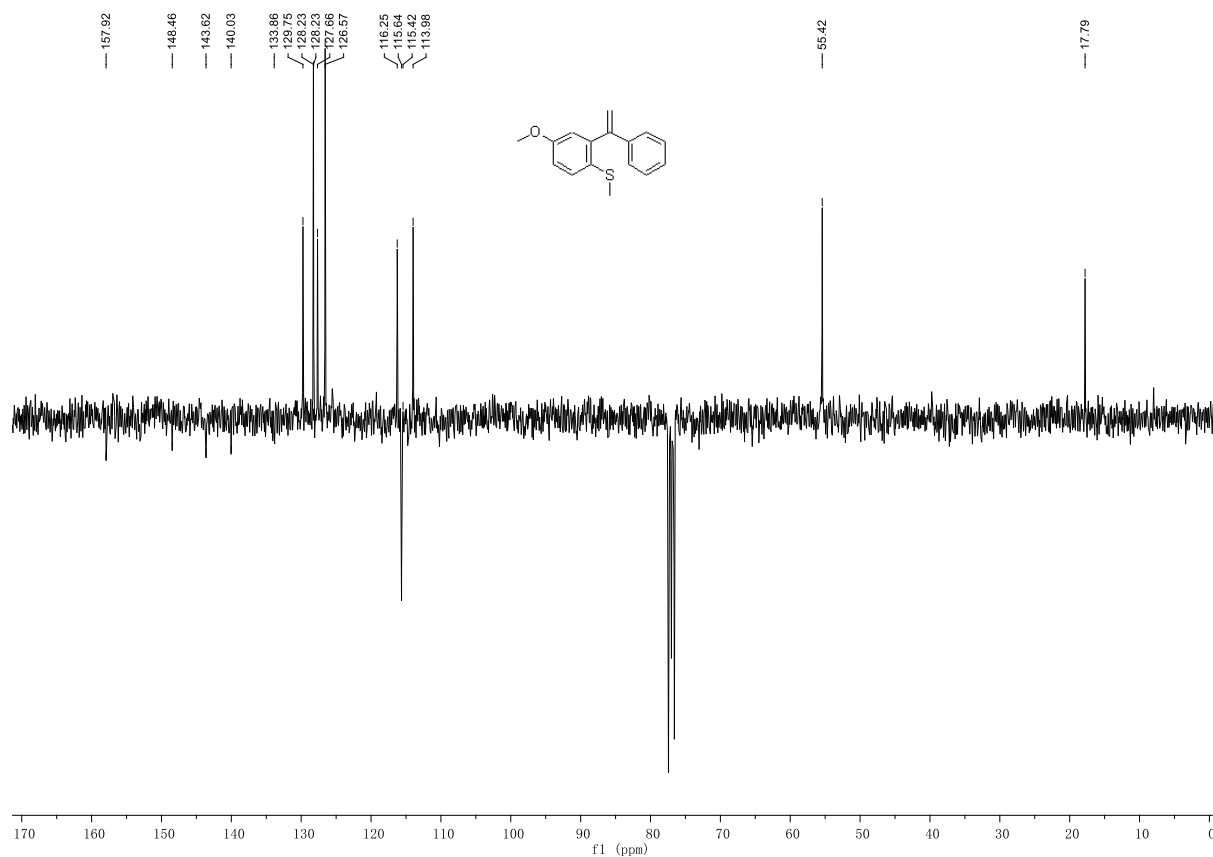
¹³C NMR (75 MHz, CDCl₃) of **3t**



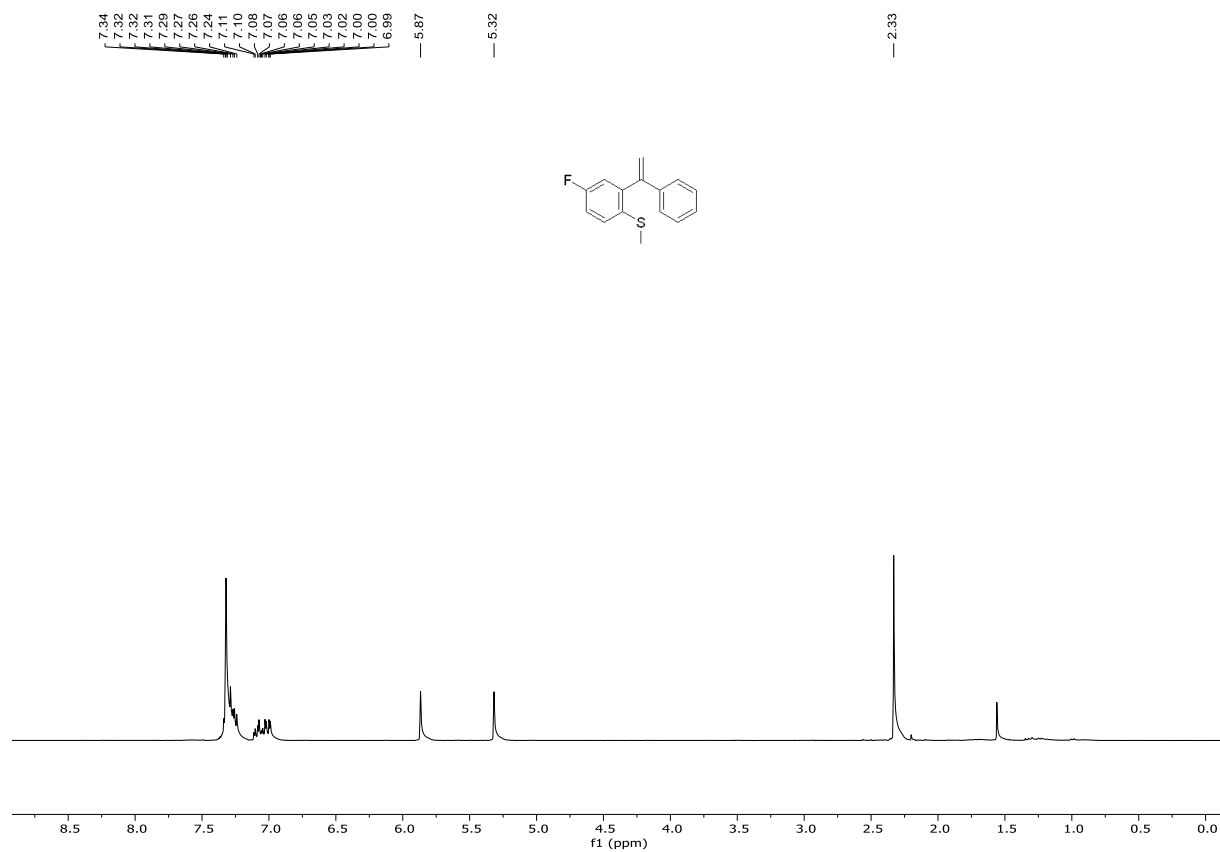
¹H NMR (300 MHz, CDCl₃) of **3u**



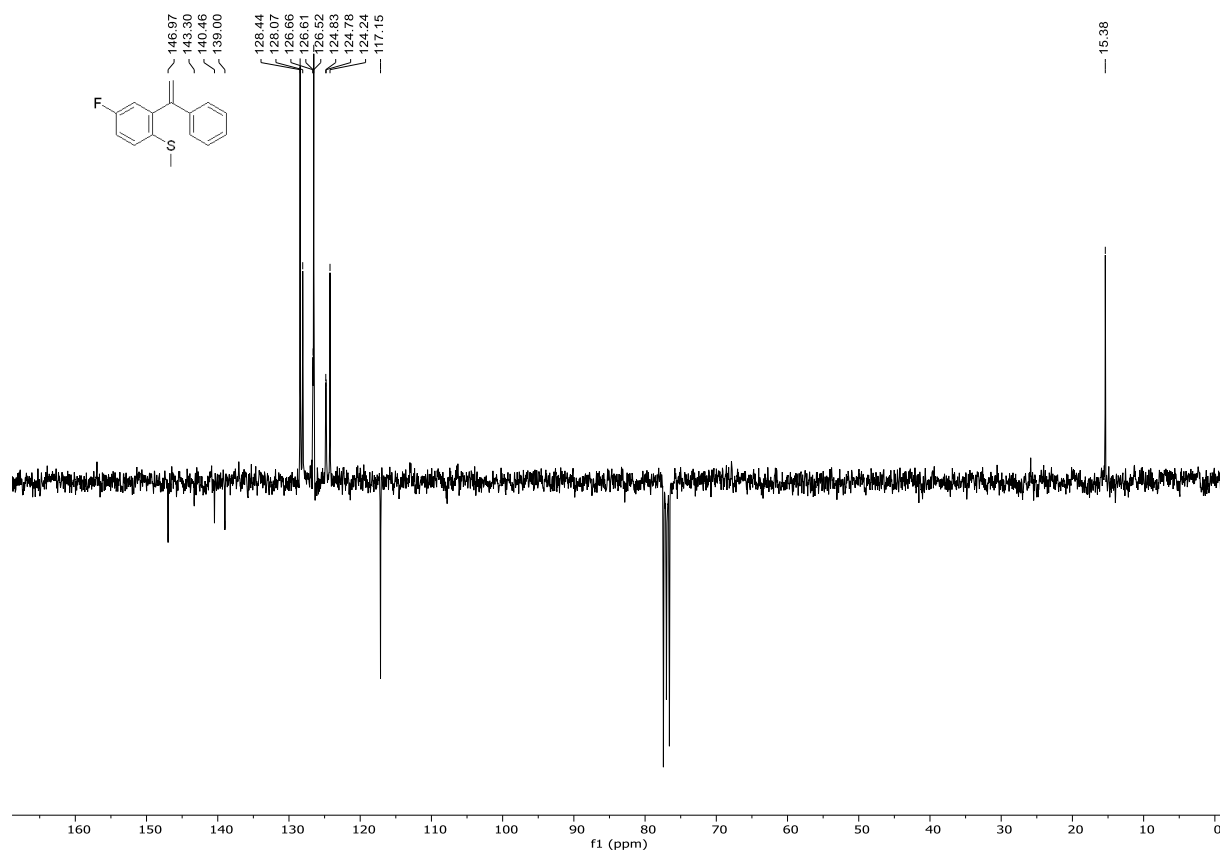
¹³C NMR (75 MHz, CDCl₃) of **3u**



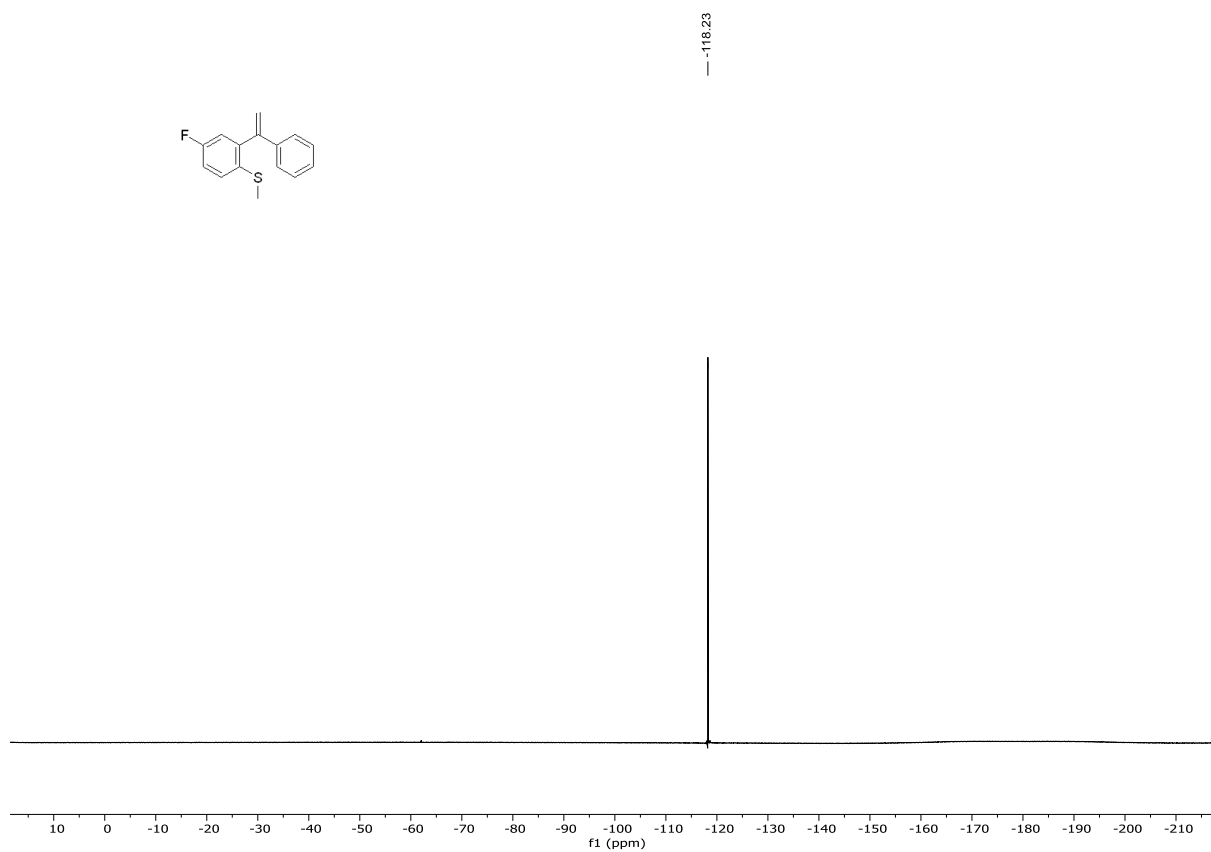
¹H NMR (300 MHz, CDCl₃) of **3v**



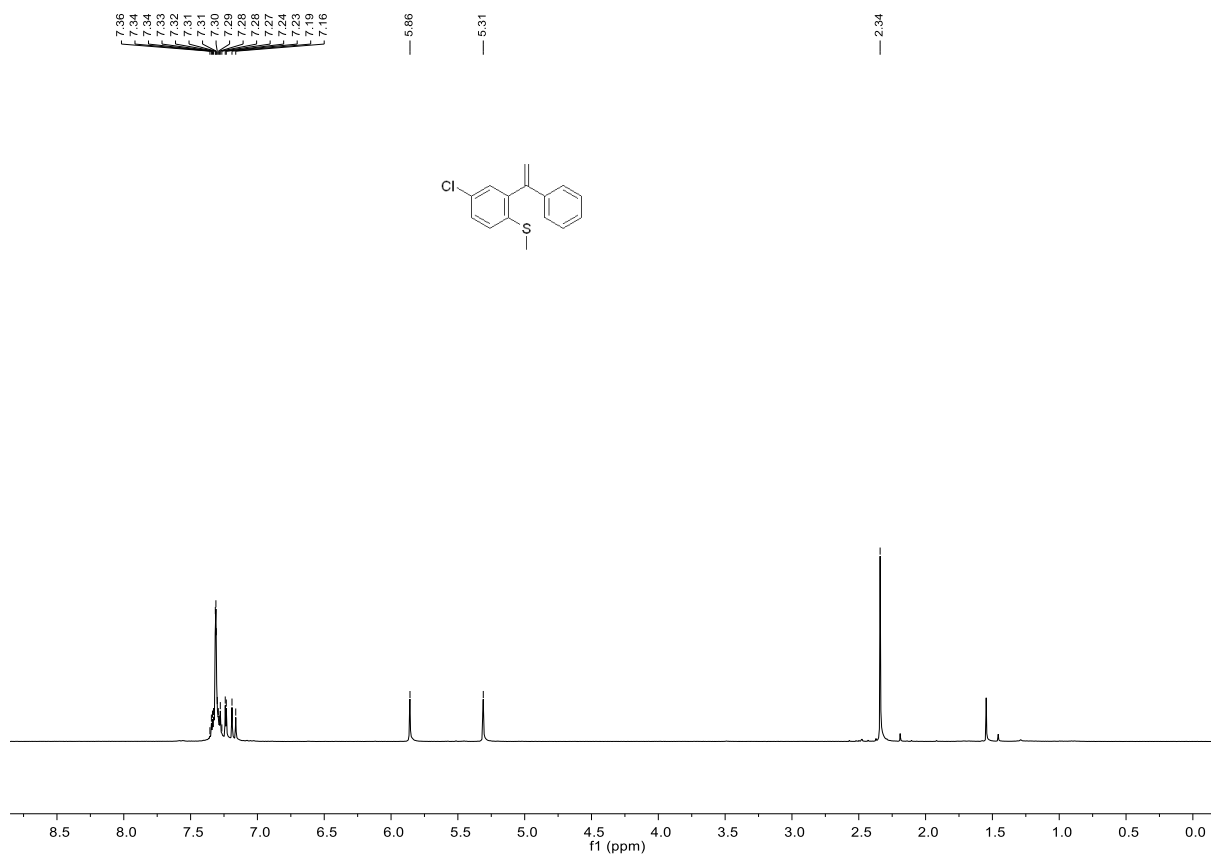
¹³C NMR (75 MHz, CDCl₃) of **3v**



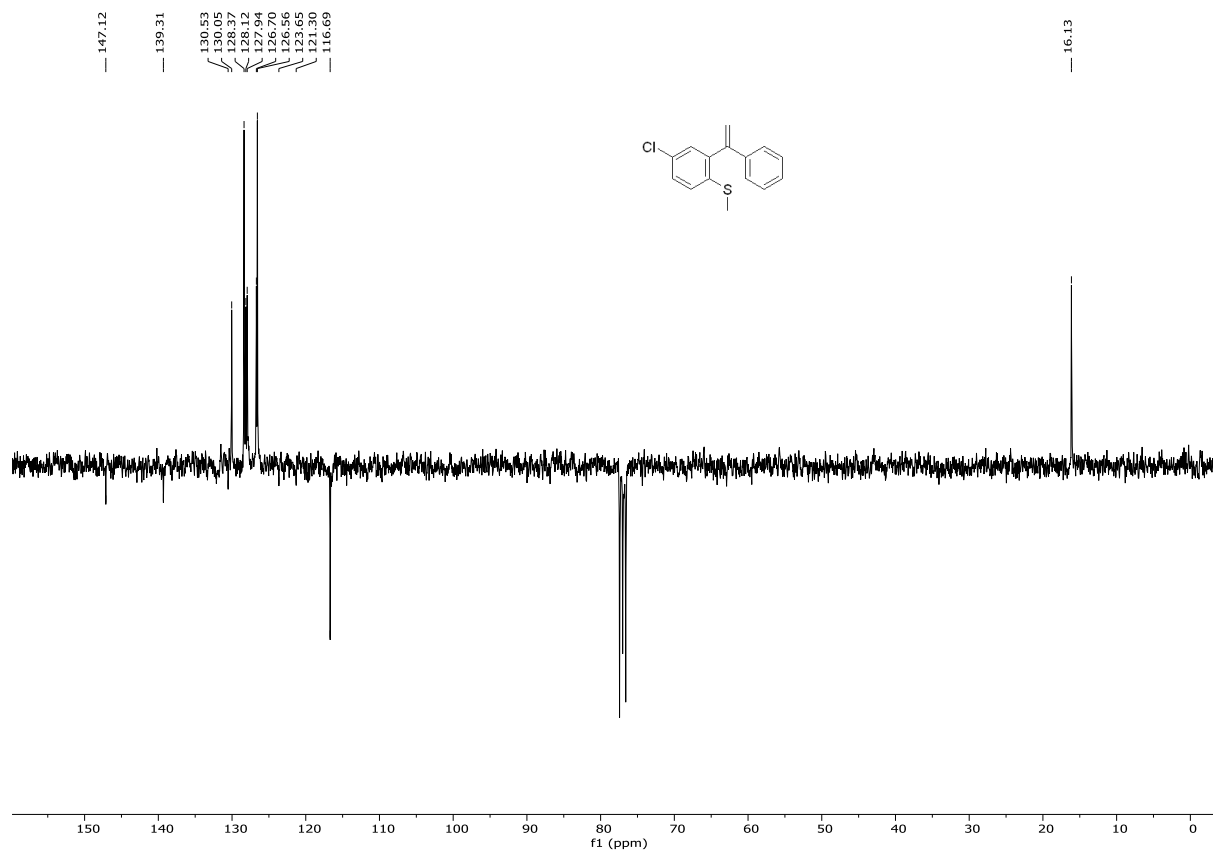
^{19}F NMR (377 MHz, CDCl_3) of **3v**



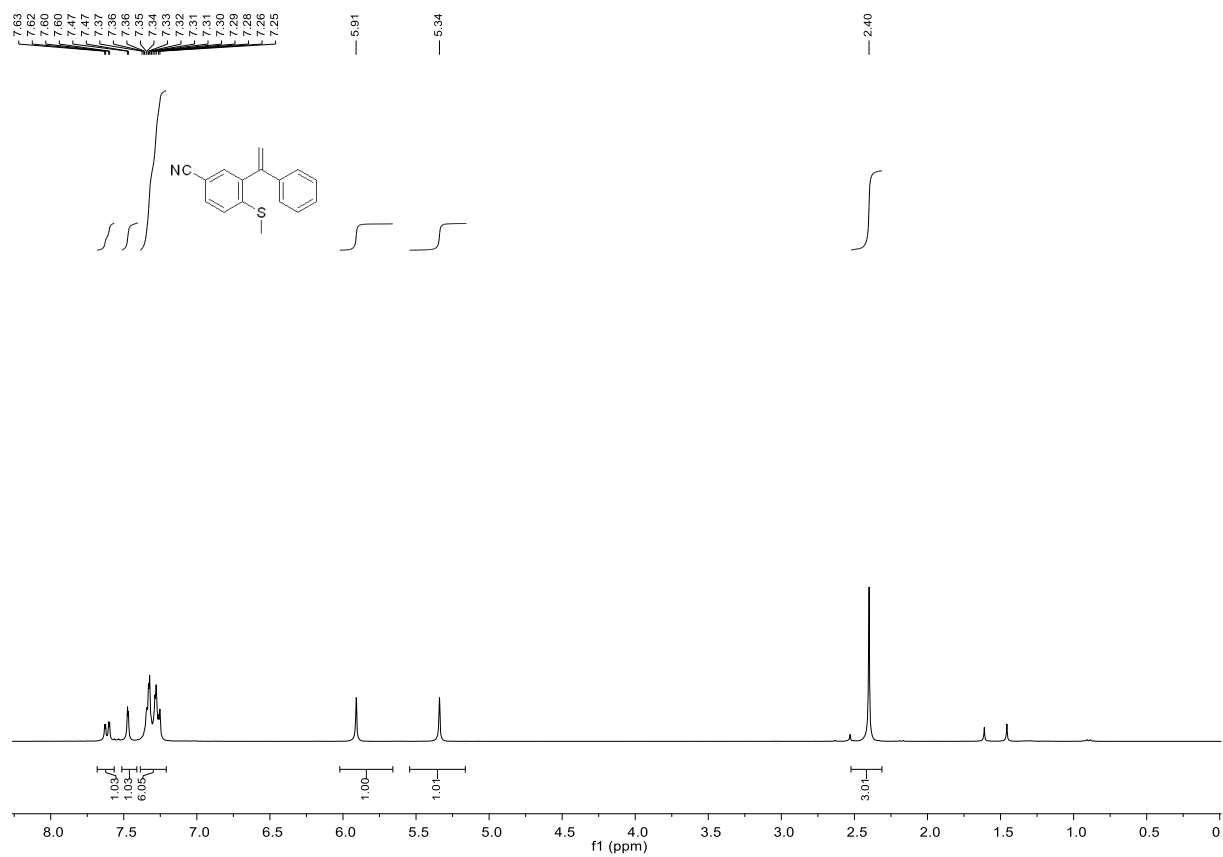
^1H NMR (300 MHz, CDCl_3) of **3w**



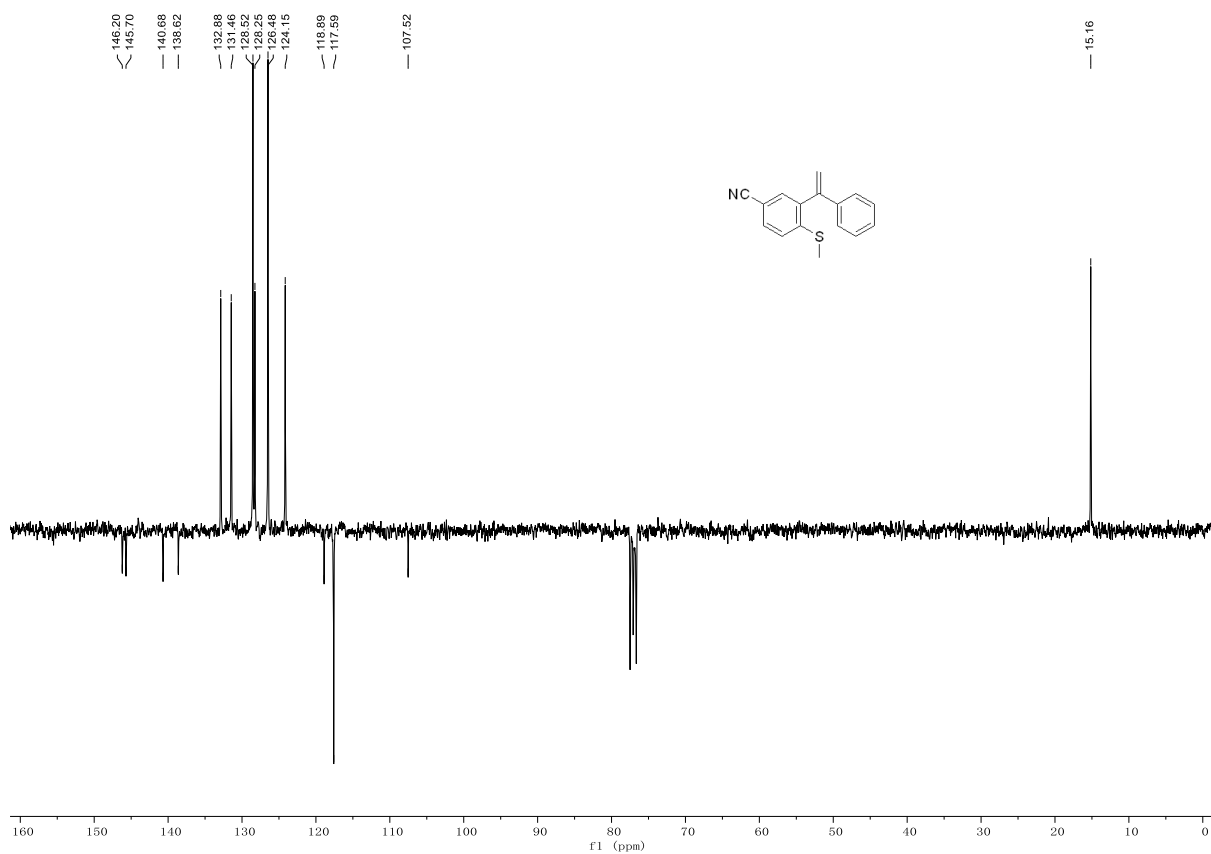
^{13}C NMR (75 MHz, CDCl_3) of **3w**



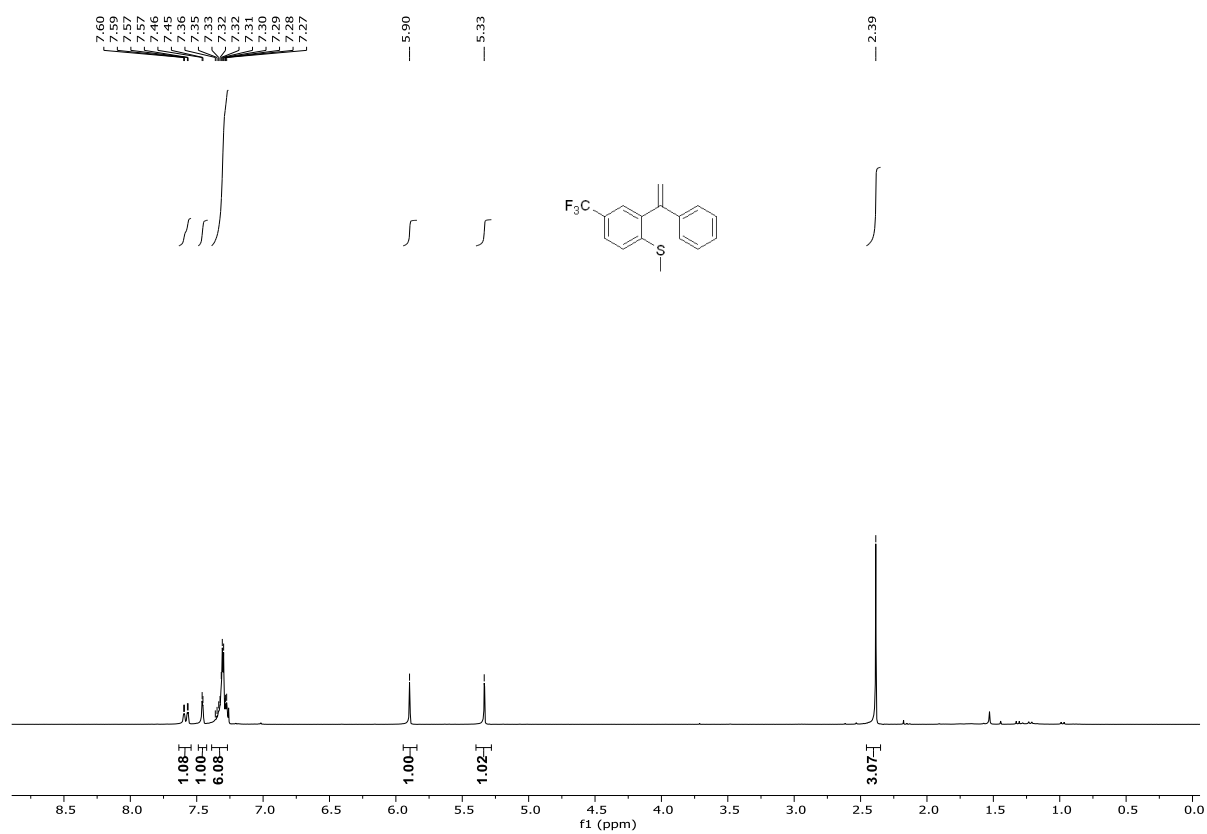
^1H NMR (300 MHz, CDCl_3) of **3x**



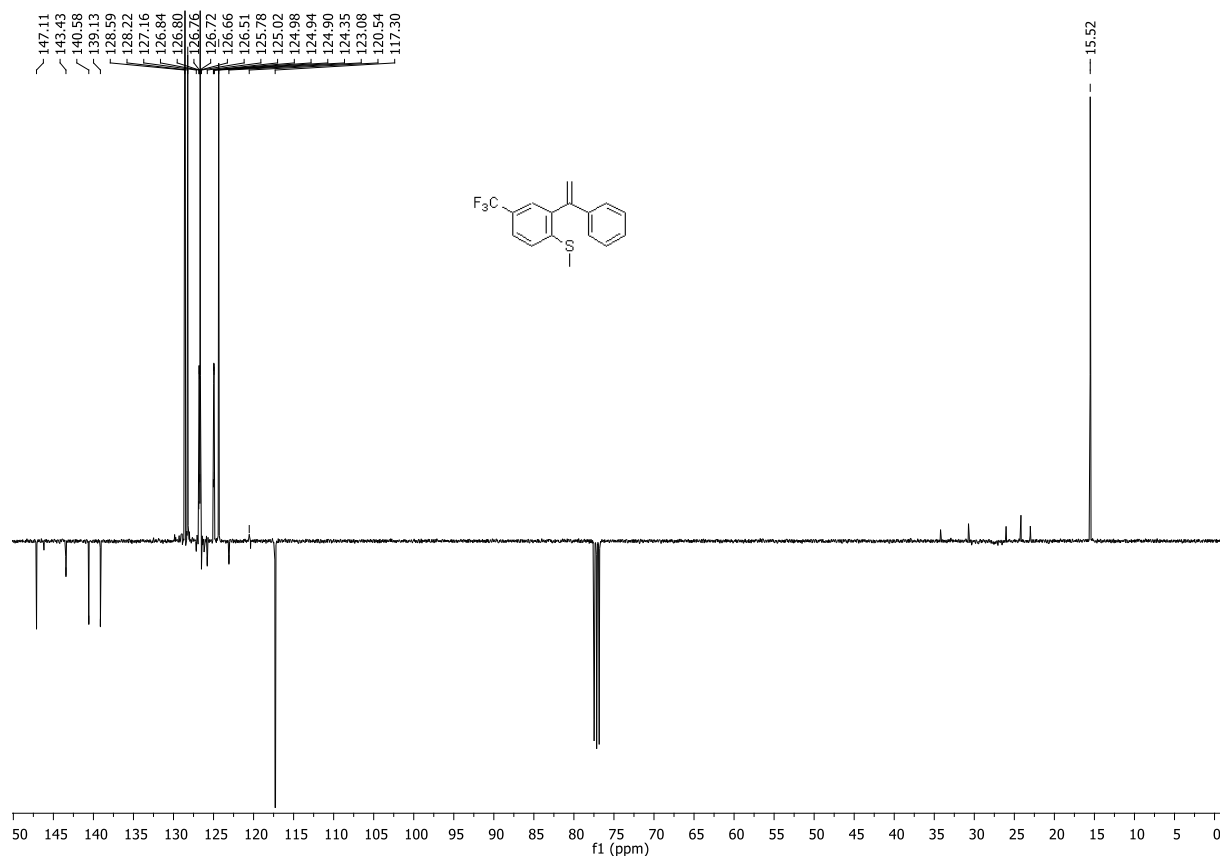
^{13}C NMR (75 MHz, CDCl_3) of **3x**



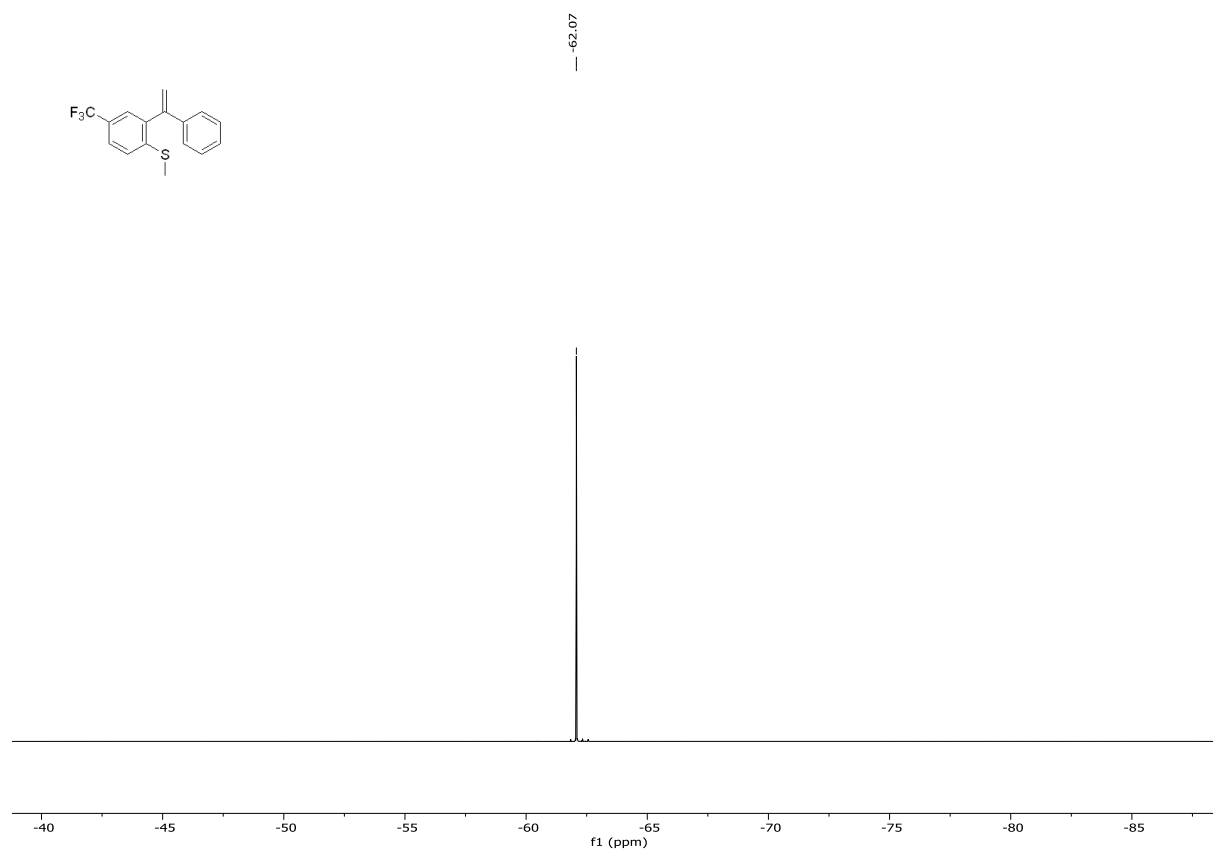
^1H NMR (300 MHz, CDCl_3) of **3y**



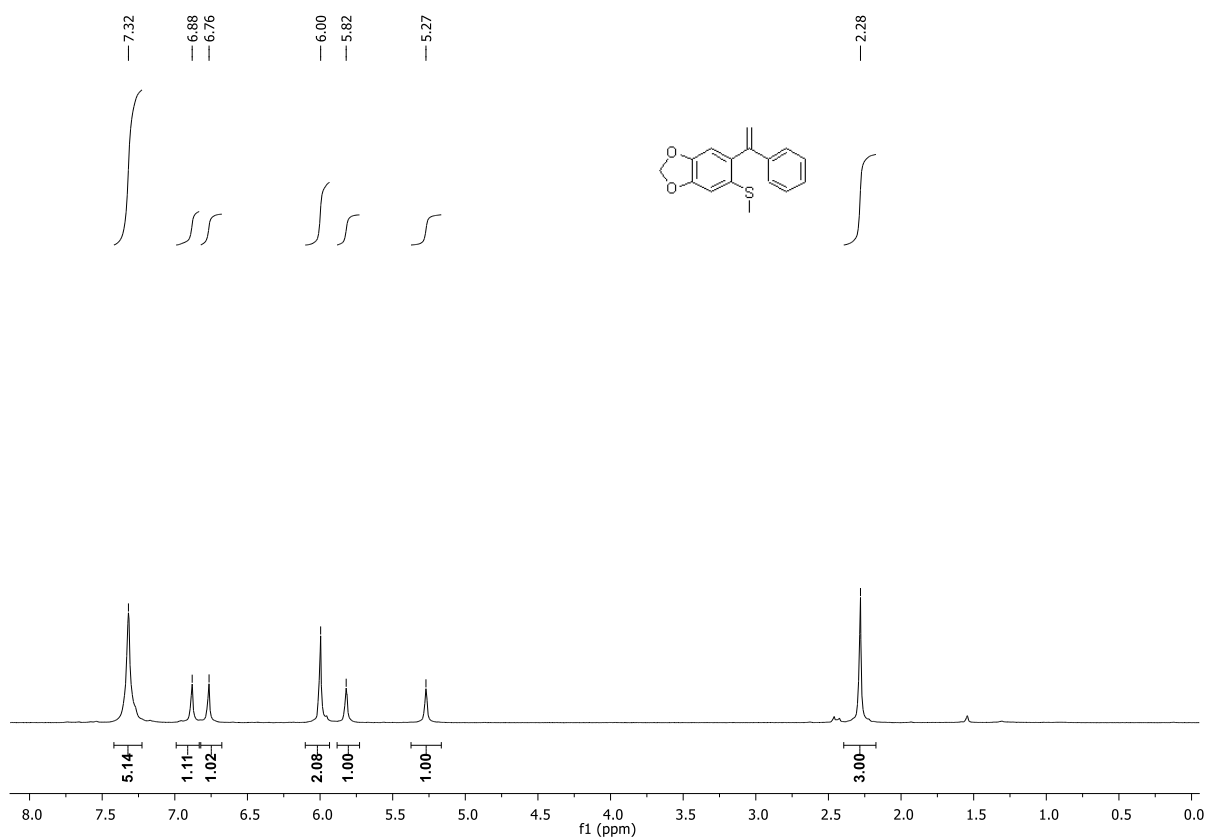
¹³C NMR (101 MHz, CDCl₃) of **3y**



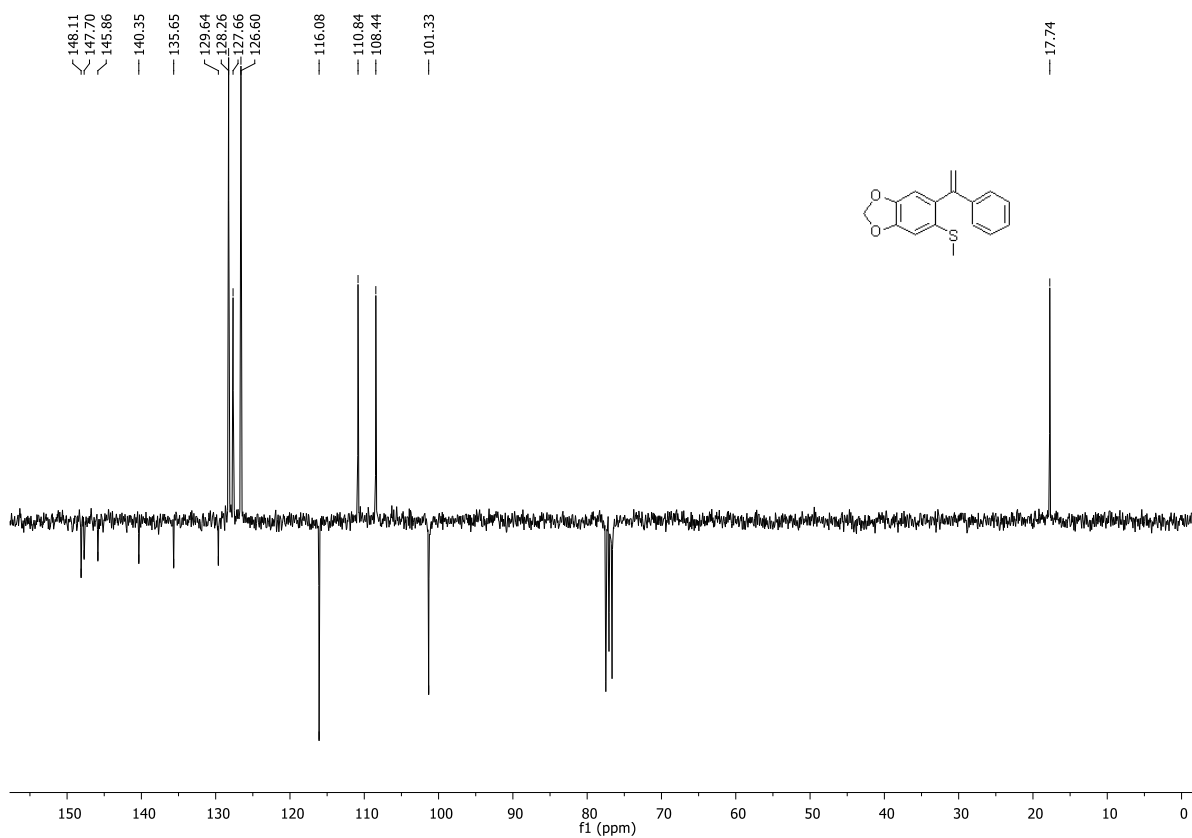
¹⁹F NMR (377 MHz, CDCl₃) of **3y**



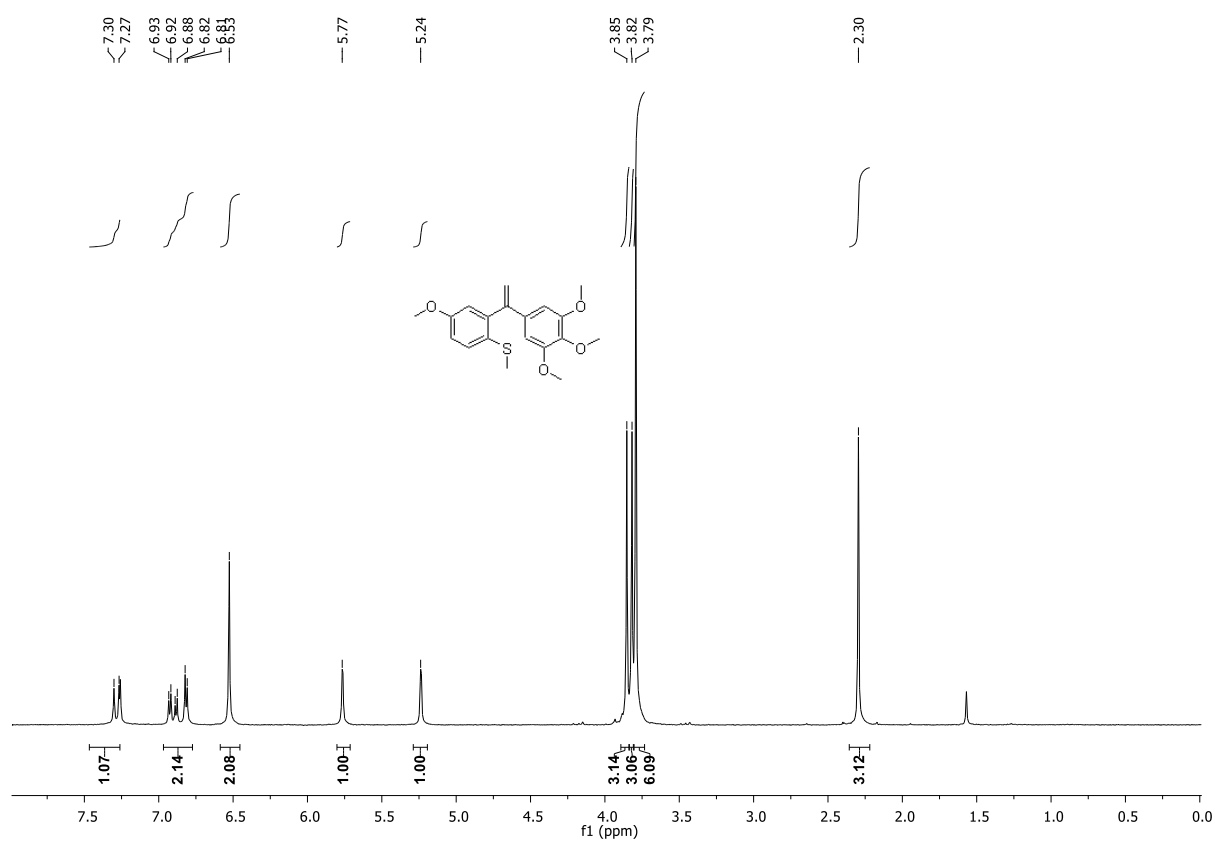
¹H NMR (200 MHz, CDCl₃) of **3z**



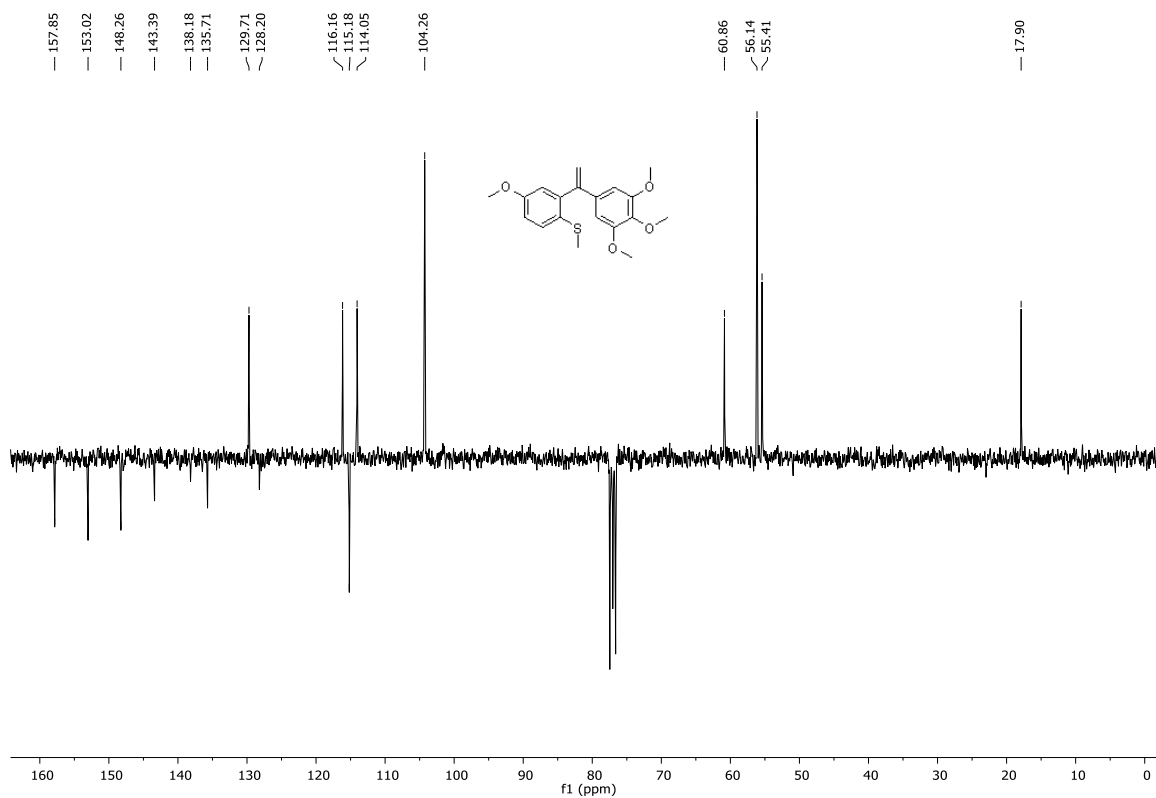
¹³C NMR (75 MHz, CDCl₃) of **3z**



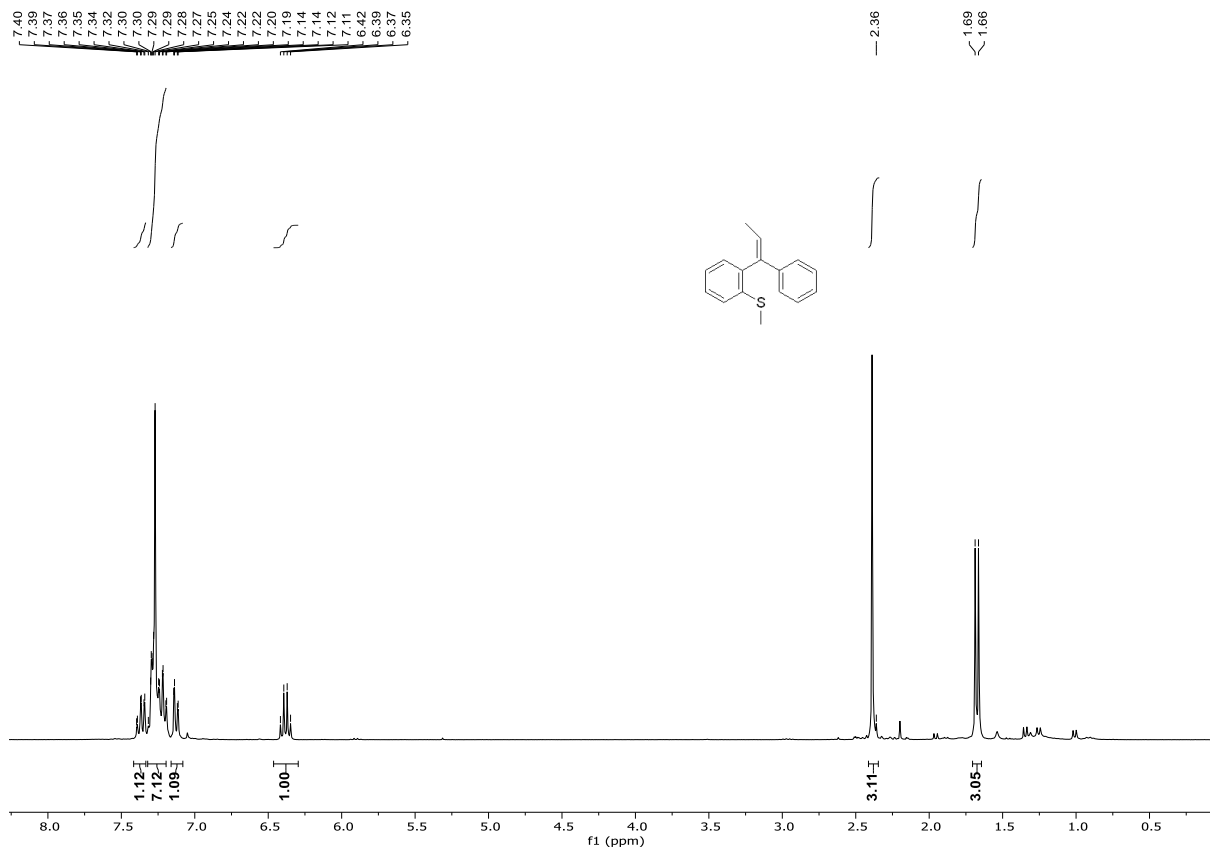
¹H NMR (200 MHz, CDCl₃) of **3aa**



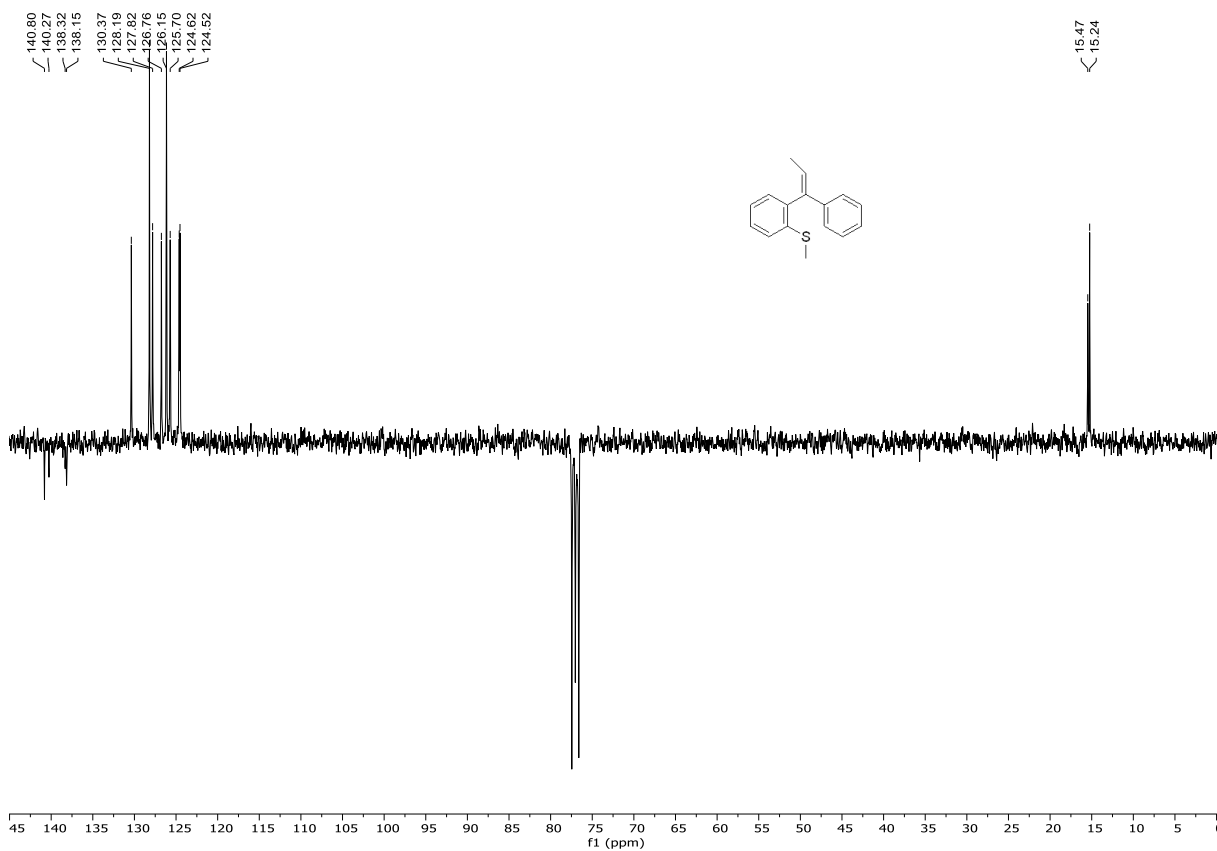
¹³C NMR (75 MHz, CDCl₃) of **3aa**



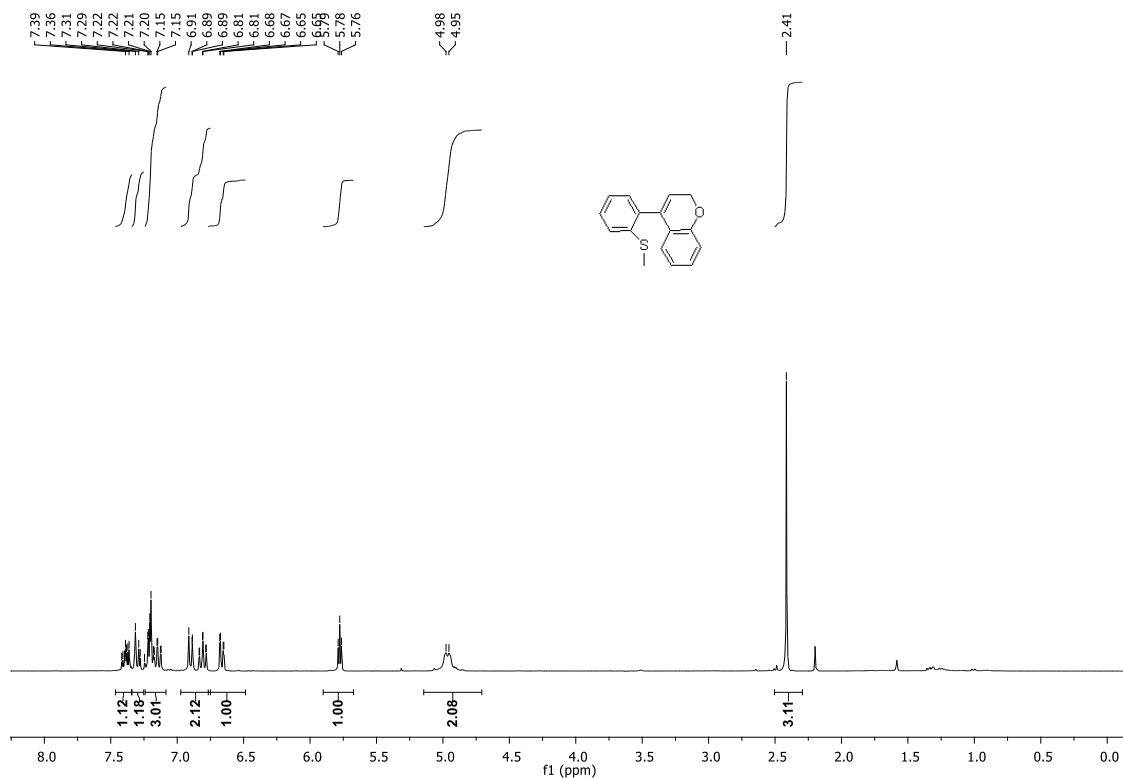
¹H NMR (300 MHz, CDCl₃) of **3ab**



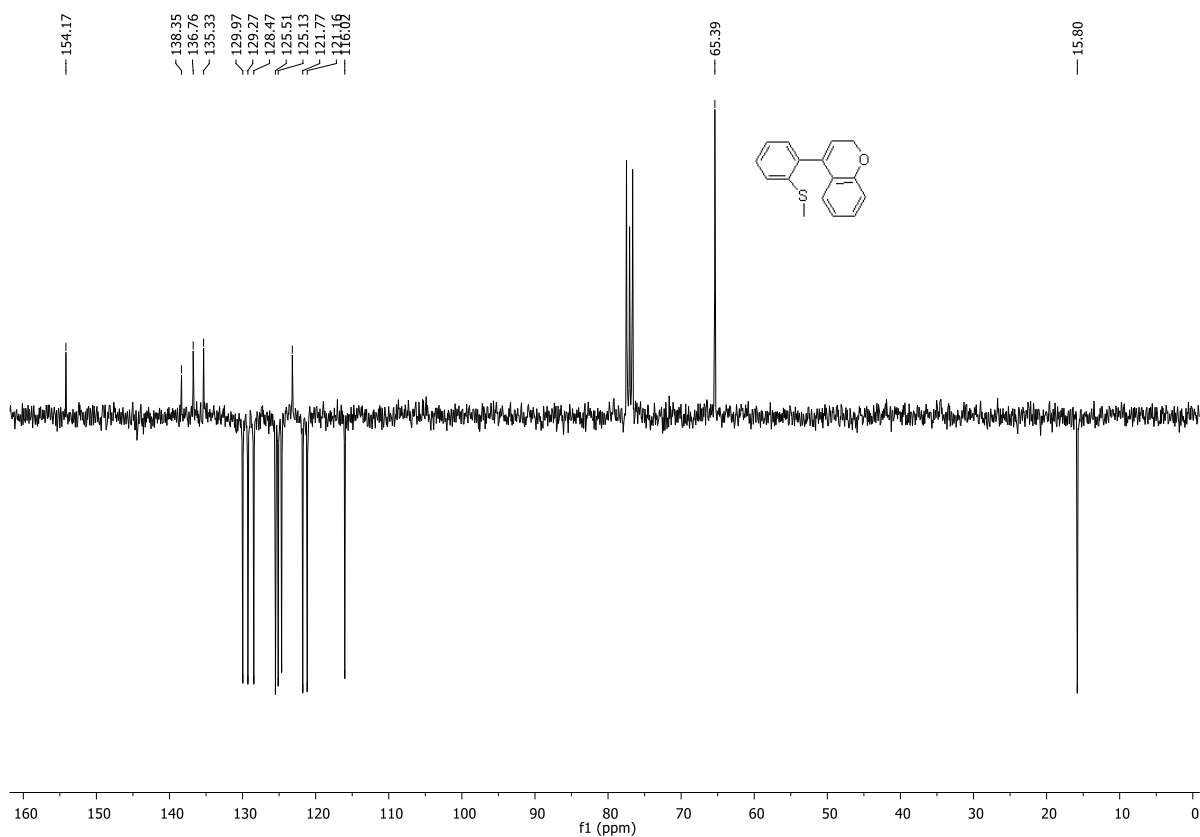
^{13}C NMR (75 MHz, CDCl_3) of 3ab



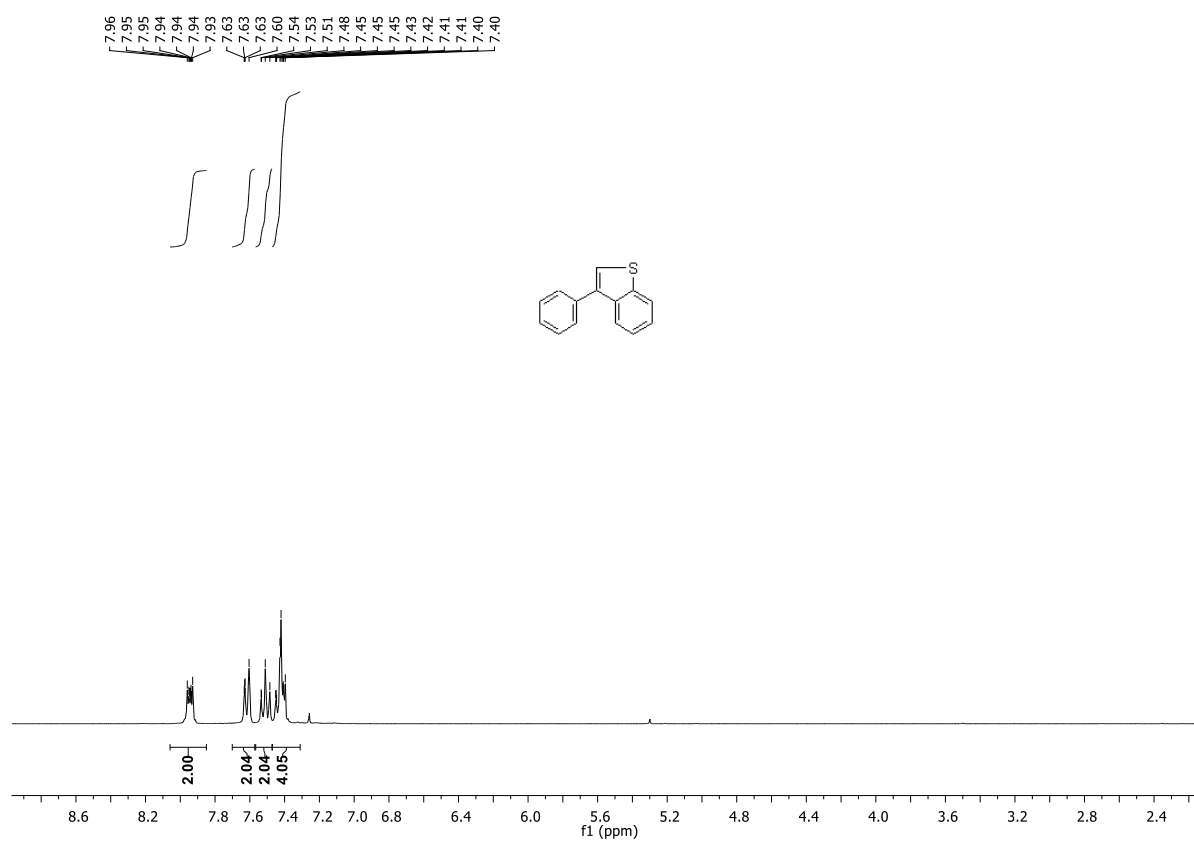
¹H NMR (300 MHz, CDCl₃) of **3ac**



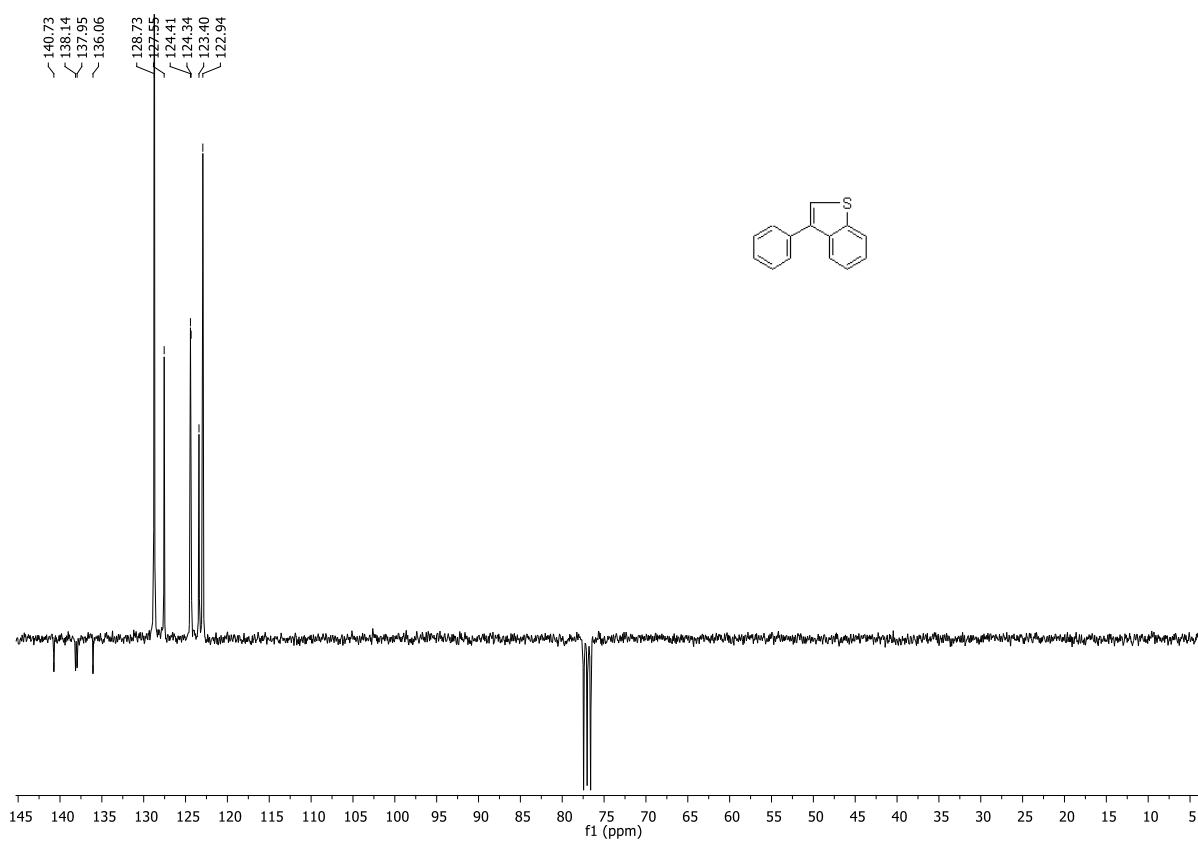
¹³C NMR (75 MHz, CDCl₃) of **3ac**



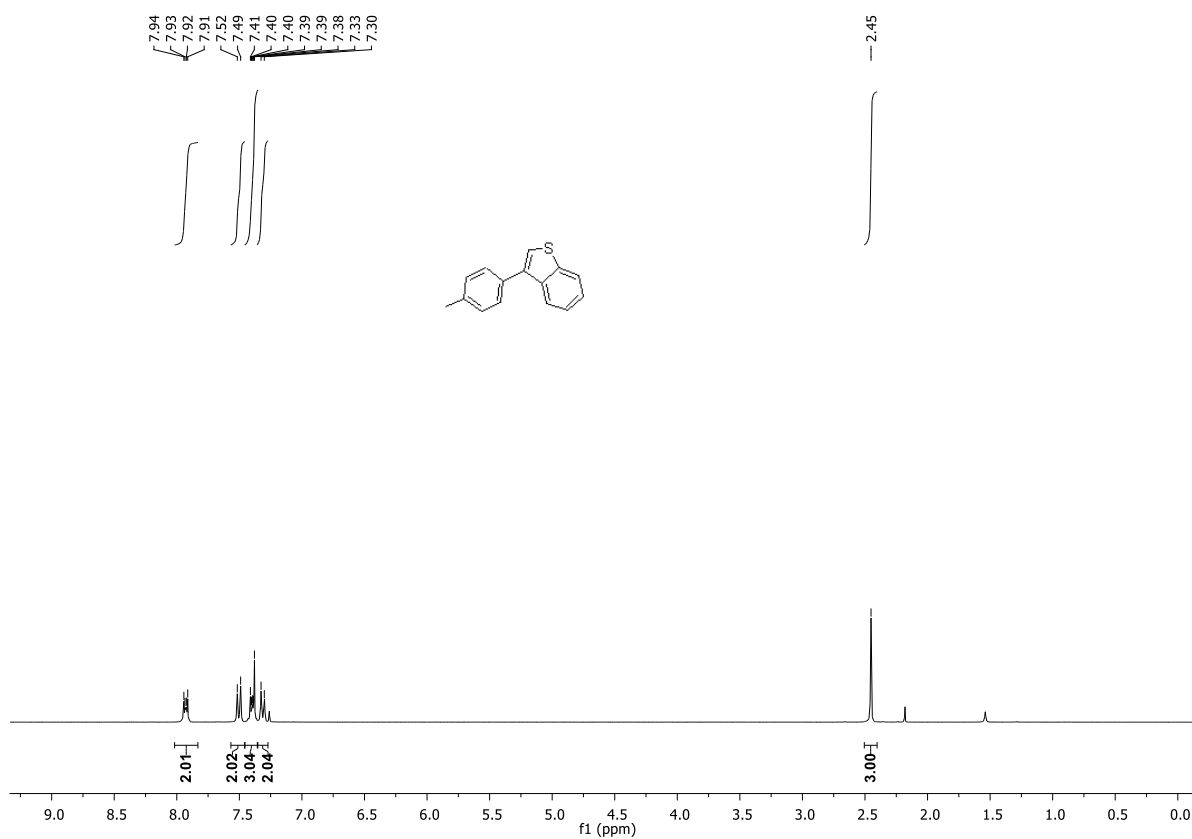
¹H NMR (300 MHz, CDCl₃) of **4a**



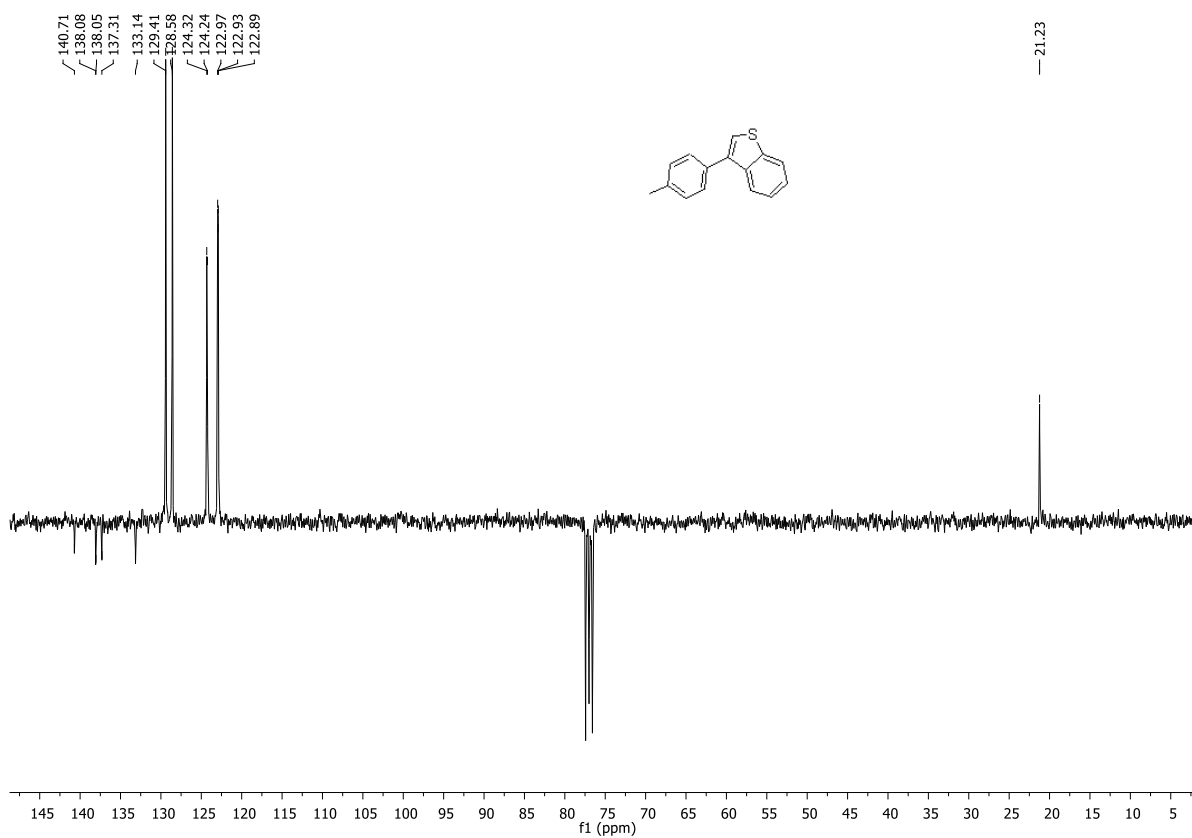
¹³C NMR (75 MHz, CDCl₃) of **4a**



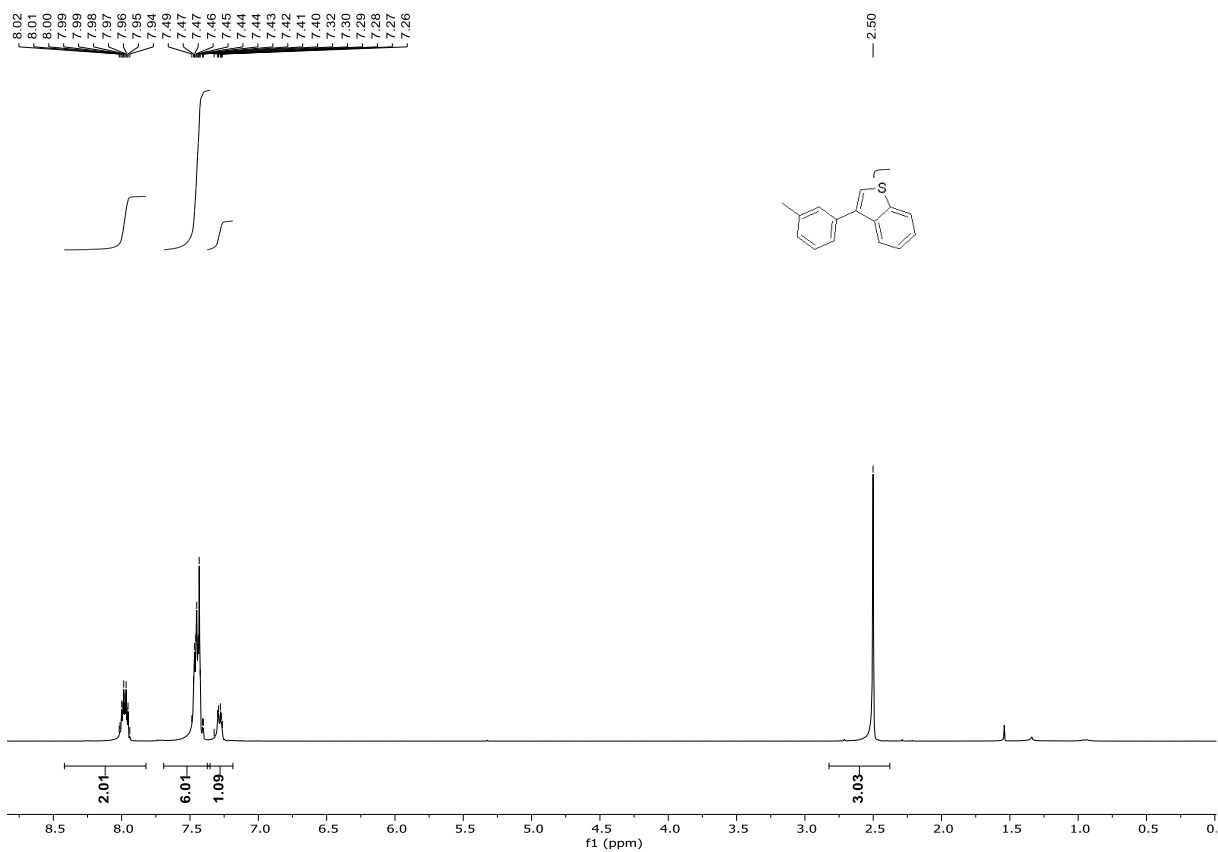
¹H NMR (300 MHz, CDCl₃) of **4b**



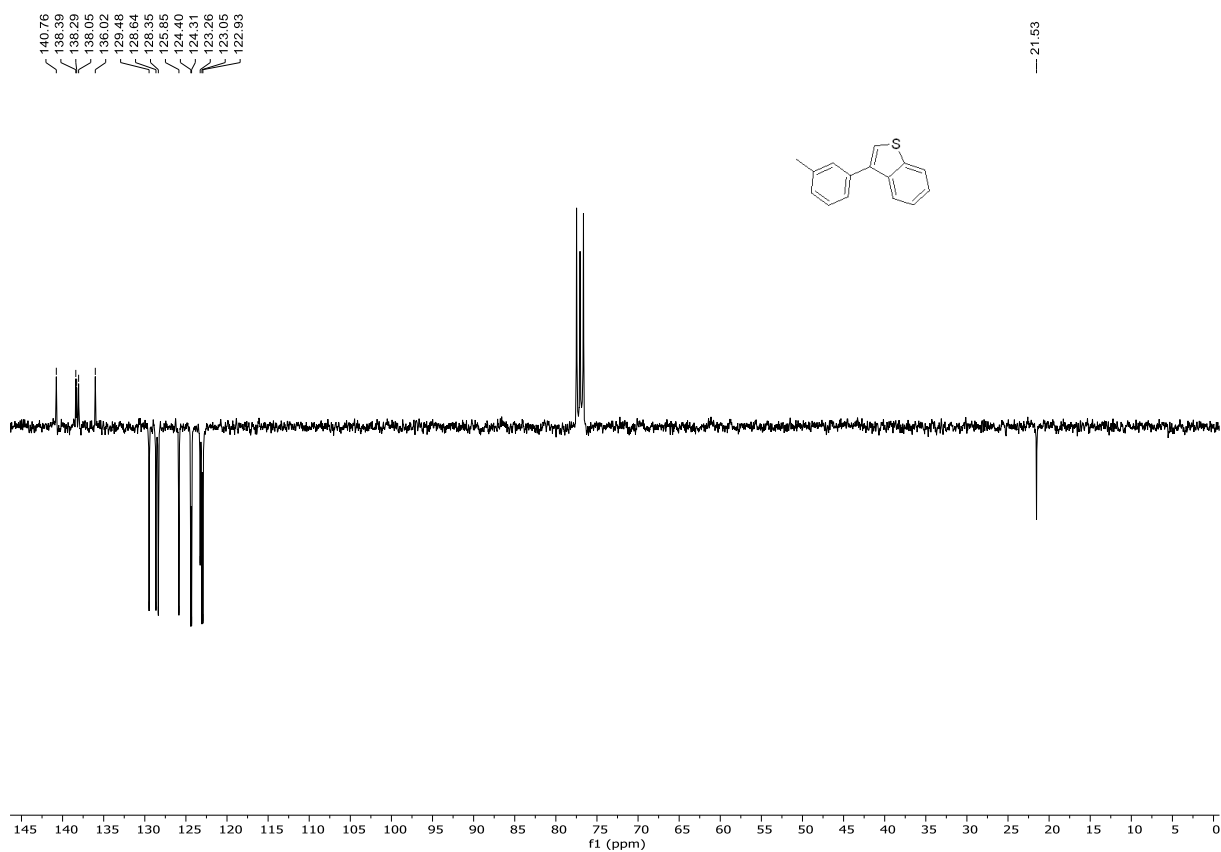
¹³C NMR (75 MHz, CDCl₃) of **4b**



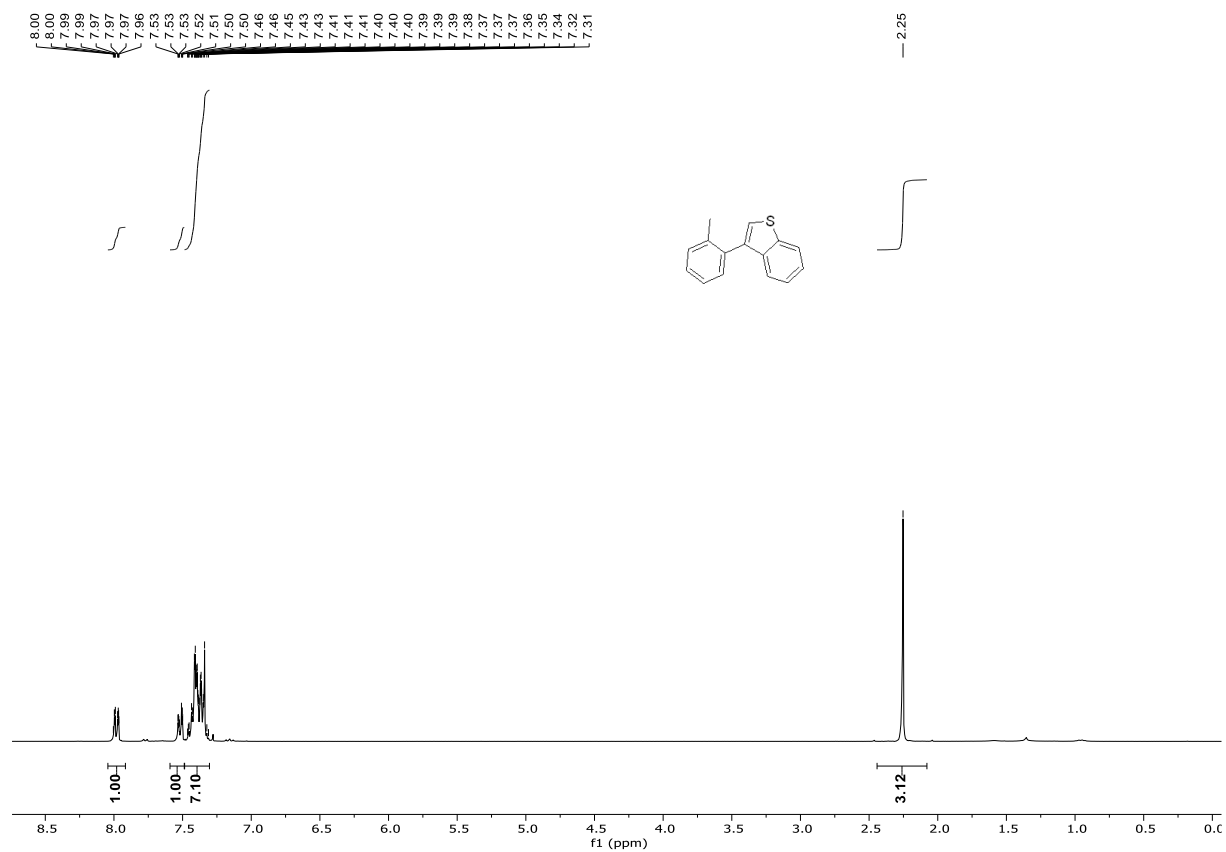
^1H NMR (300 MHz, CDCl_3) of **4c**



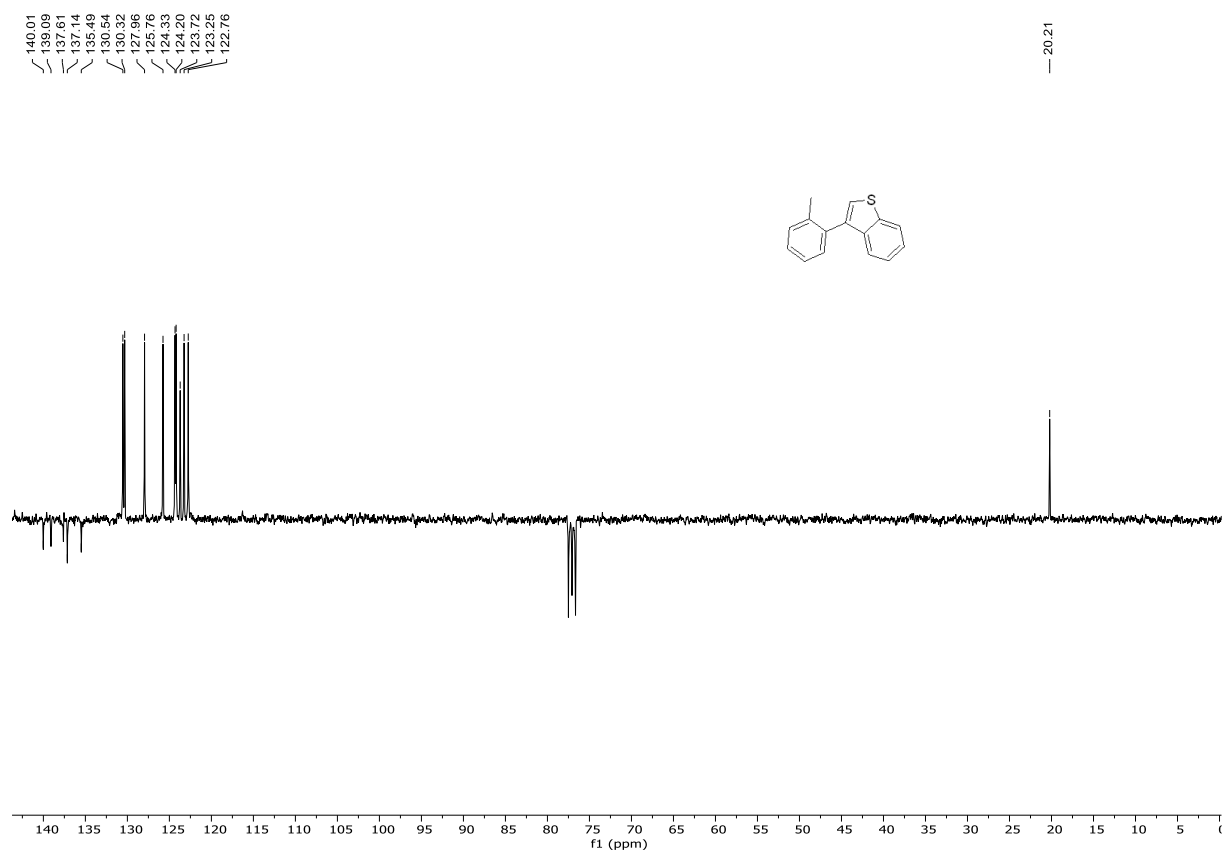
^{13}C NMR (75 MHz, CDCl_3) of **4c**



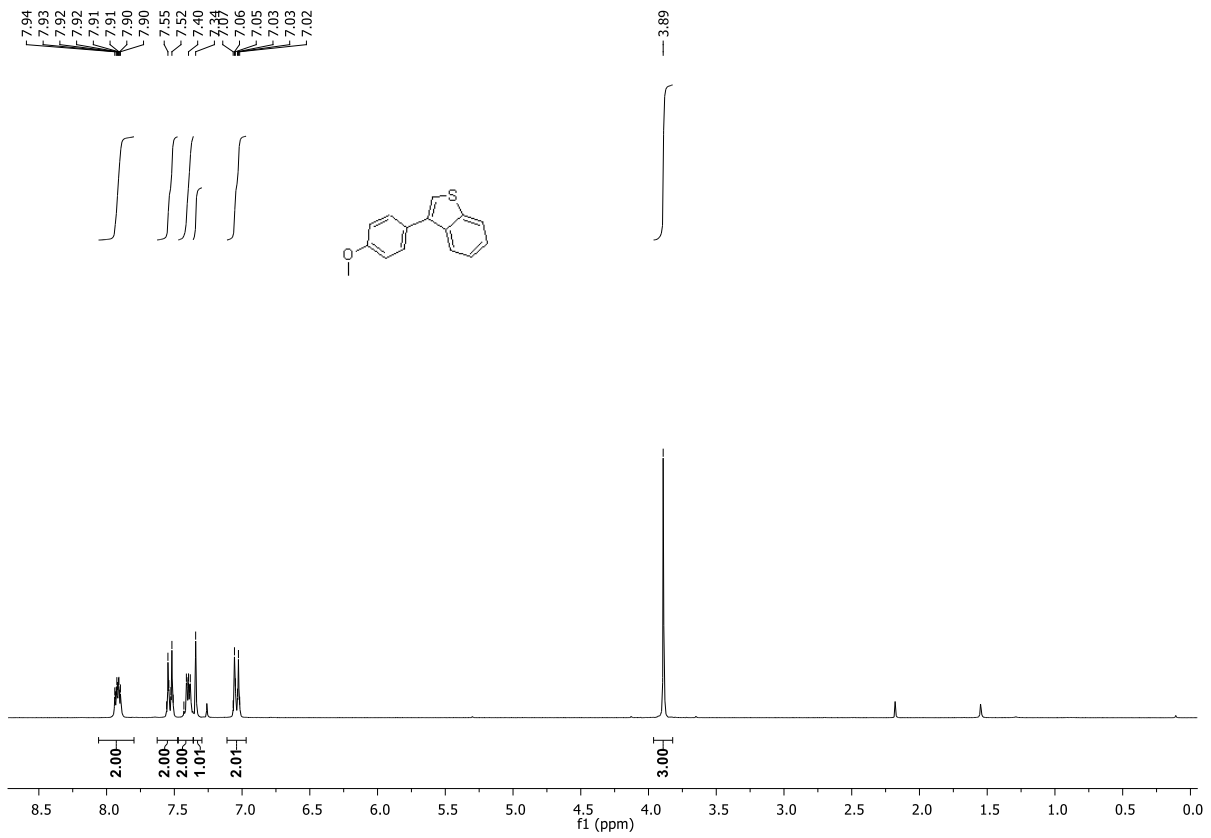
¹H NMR (300 MHz, CDCl₃) of **4d**



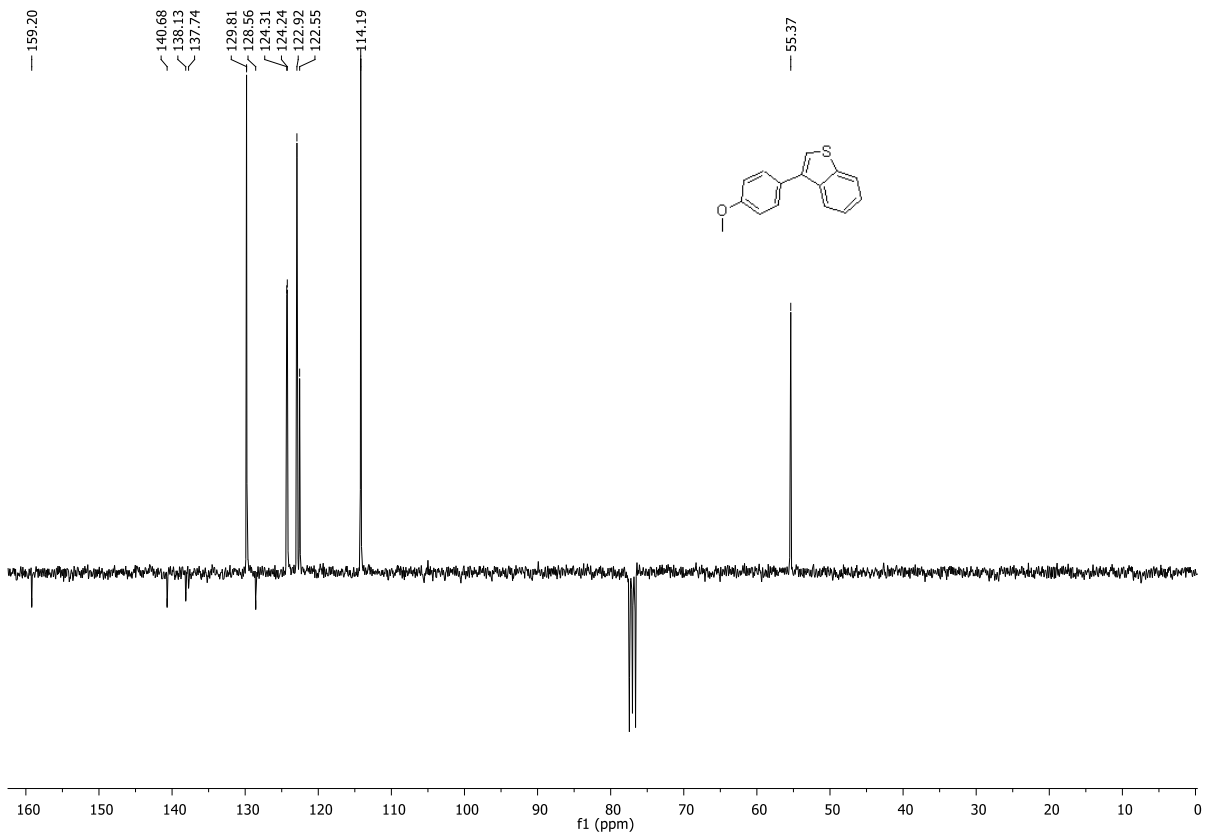
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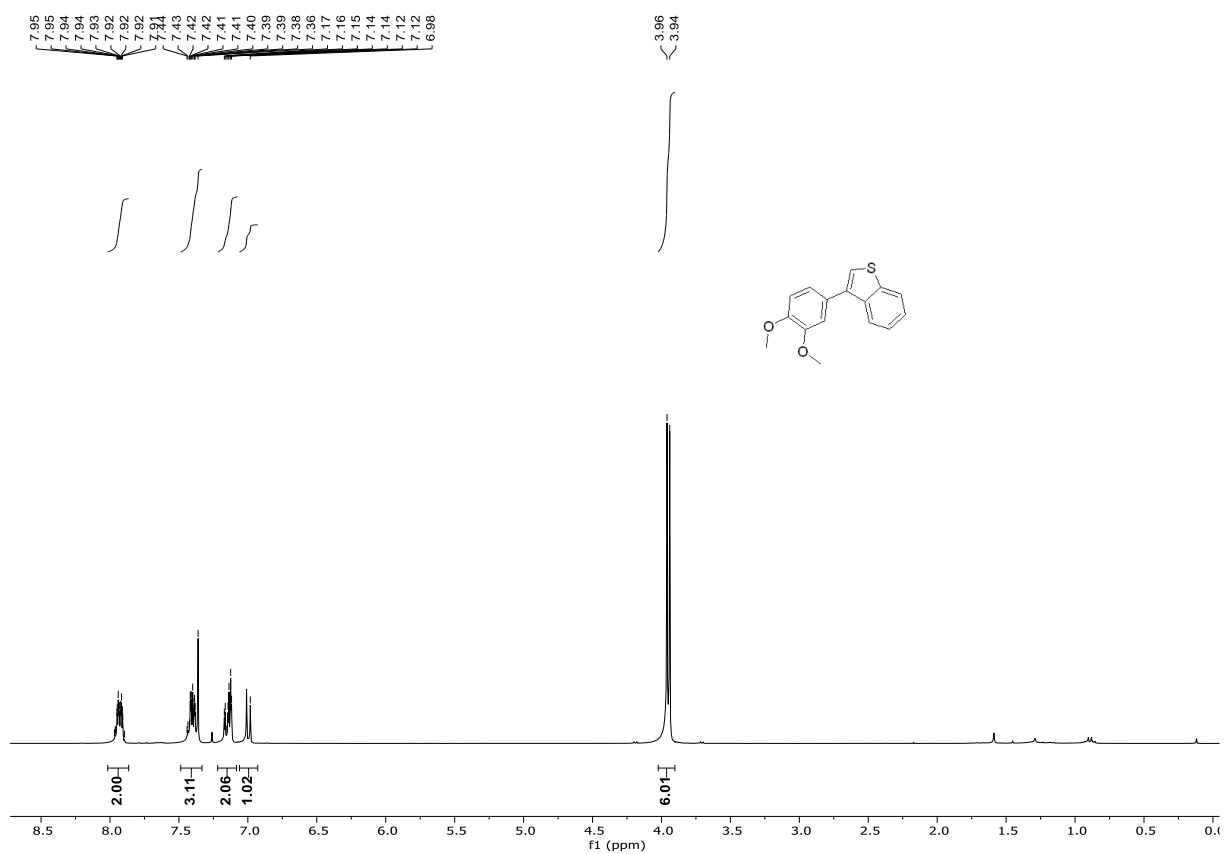
¹H NMR (300 MHz, CDCl₃) of 4e



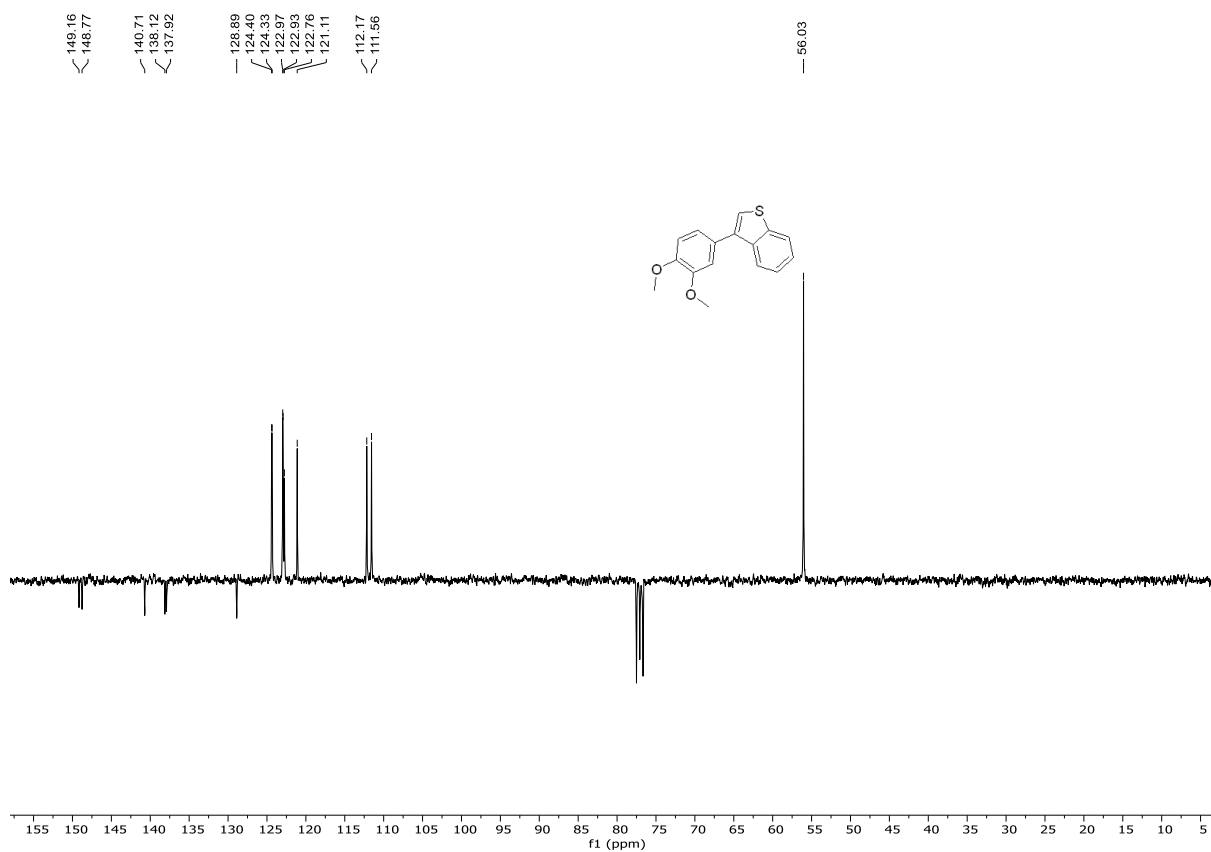
¹³C NMR (75 MHz, CDCl₃) of 4e



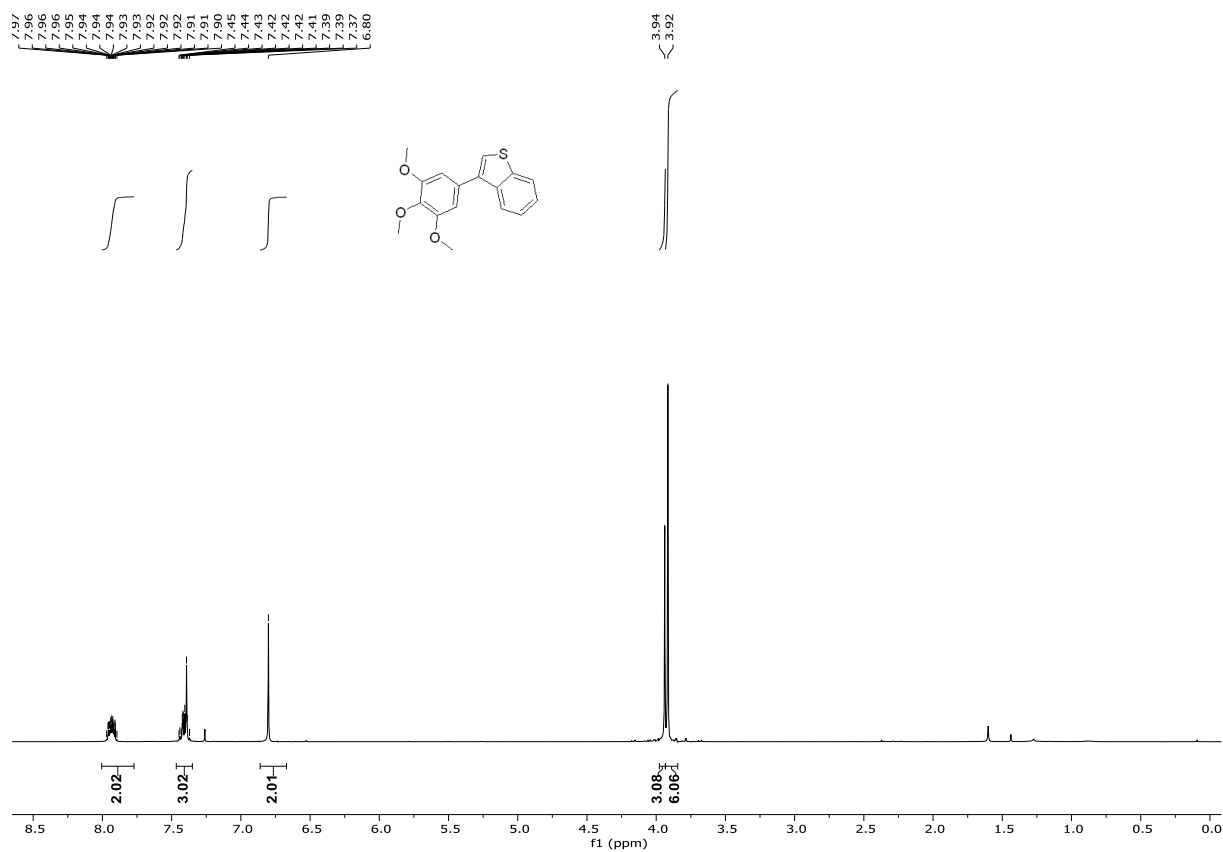
¹H NMR (300 MHz, CDCl₃) of **4f**



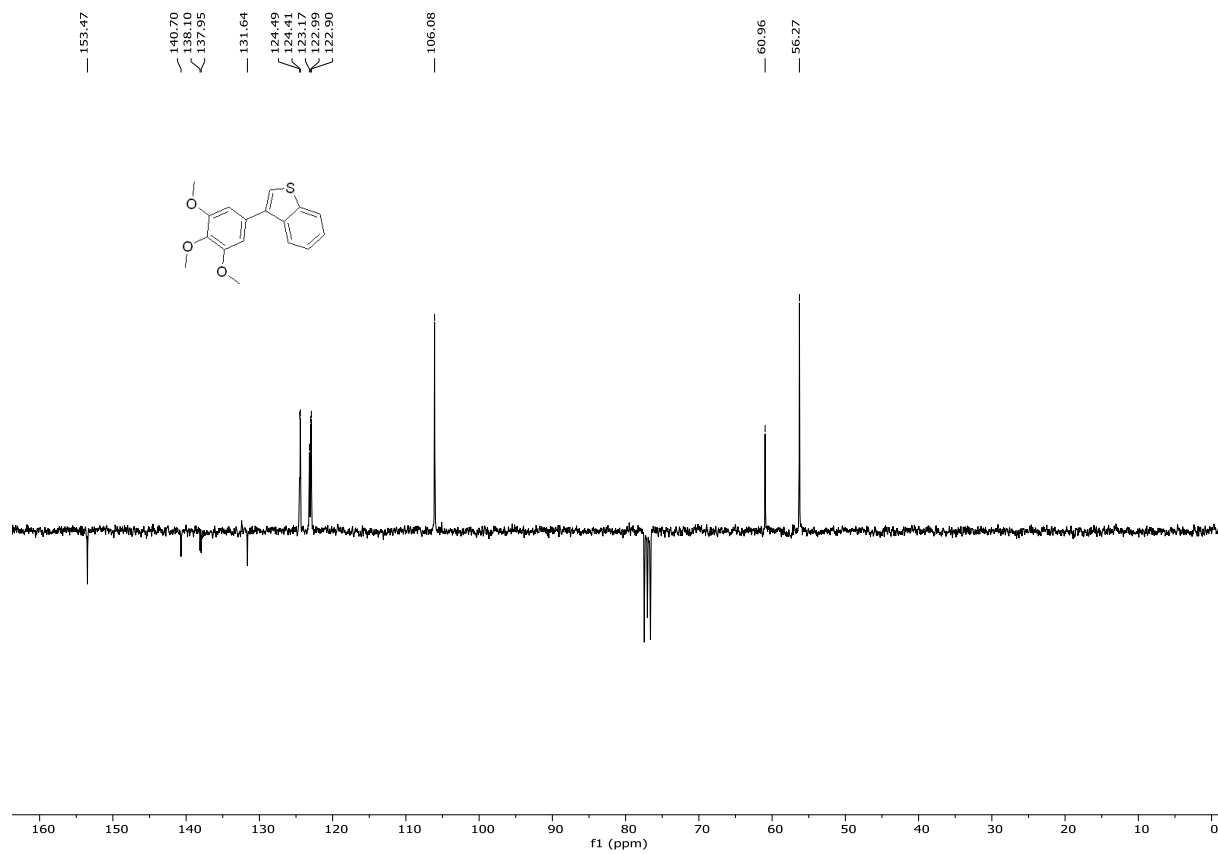
¹³C NMR (75 MHz, CDCl₃) of **4f**



¹H NMR (300 MHz, CDCl₃) of **4g**

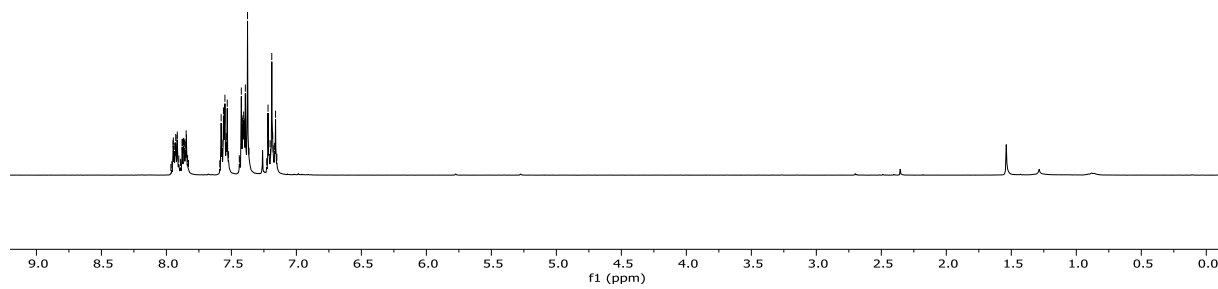
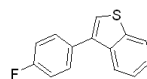


¹³C NMR (75 MHz, CDCl₃) of **4g**

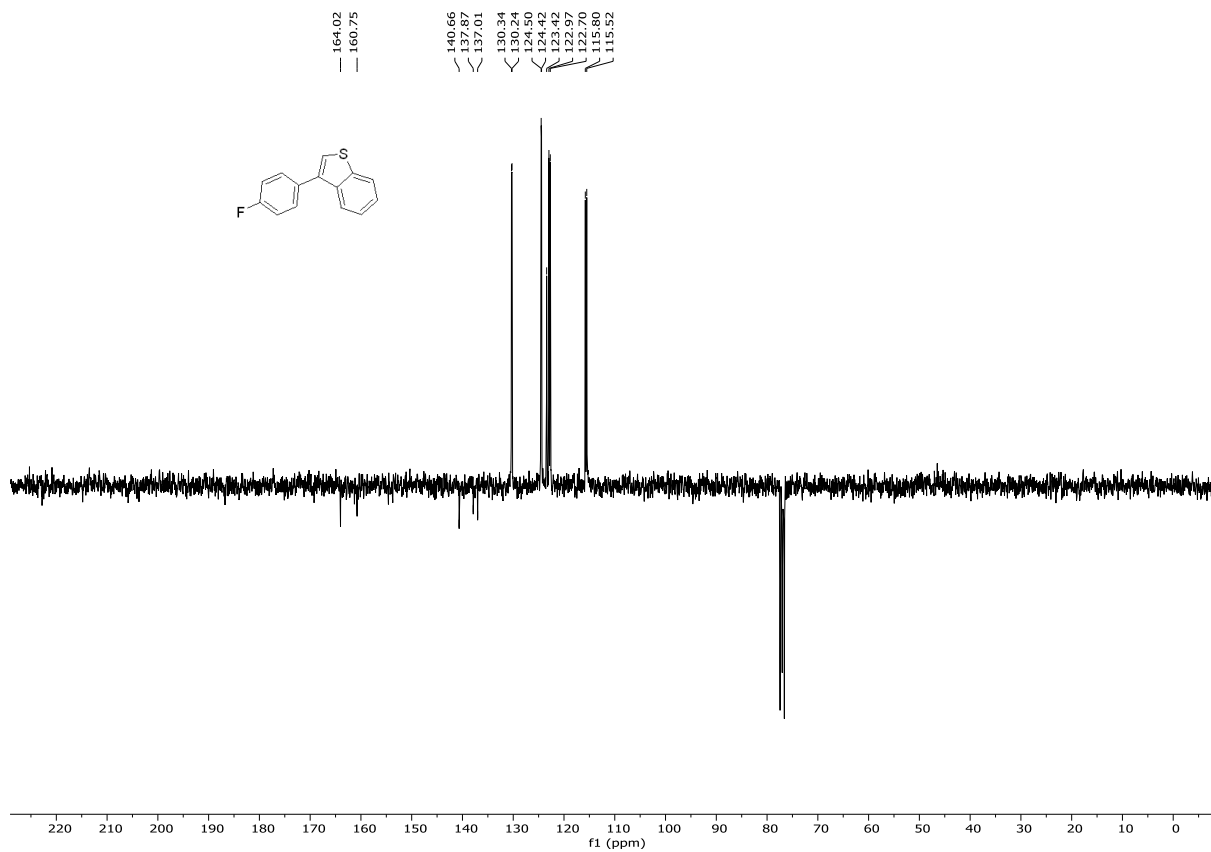


¹H NMR (300 MHz, CDCl₃) of **4h**

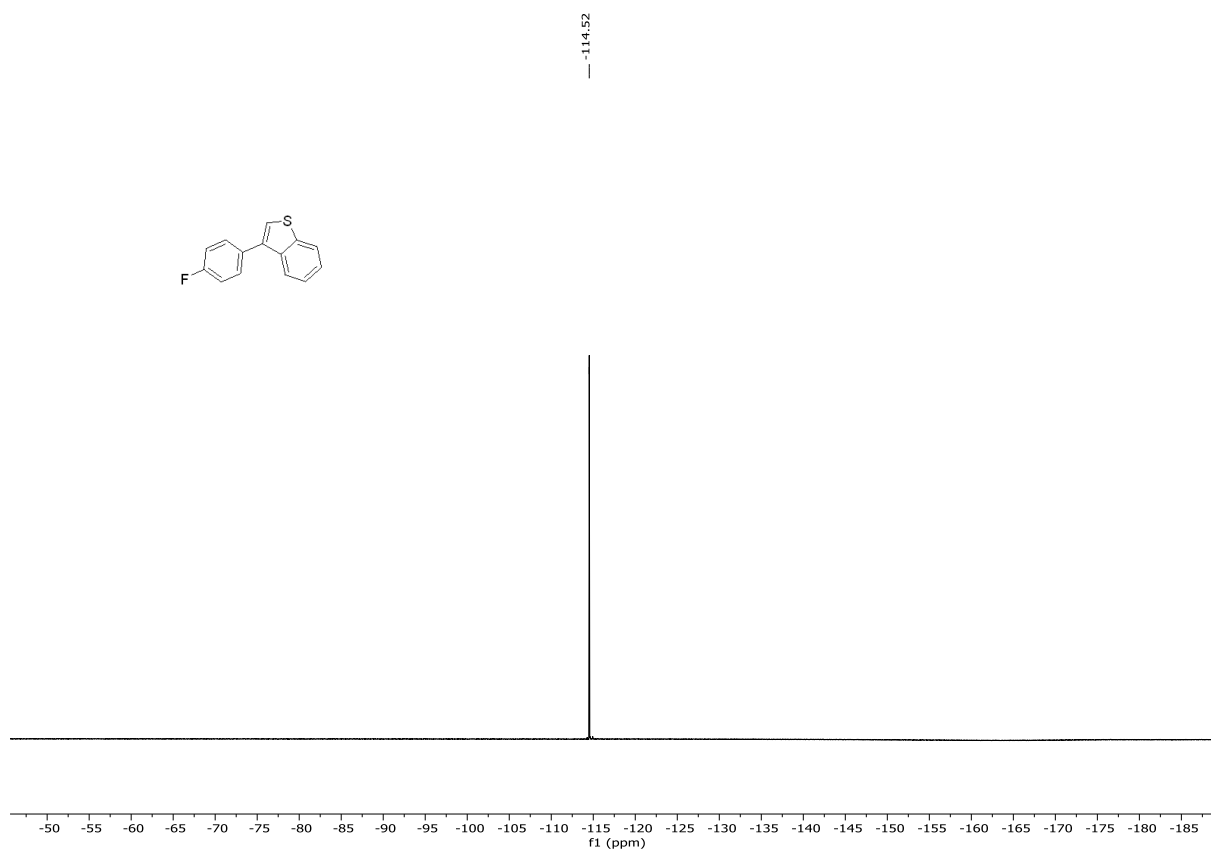
7.95
7.93
7.93
7.92
7.88
7.88
7.87
7.86
7.85
7.85
7.59
7.59
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7.56
7.56
7.55
7.54
7.53
7.52
7.52
7.43
7.42
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7.41
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7.38
7.36
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.15



¹³C NMR (75 MHz, CDCl₃) of **4h**

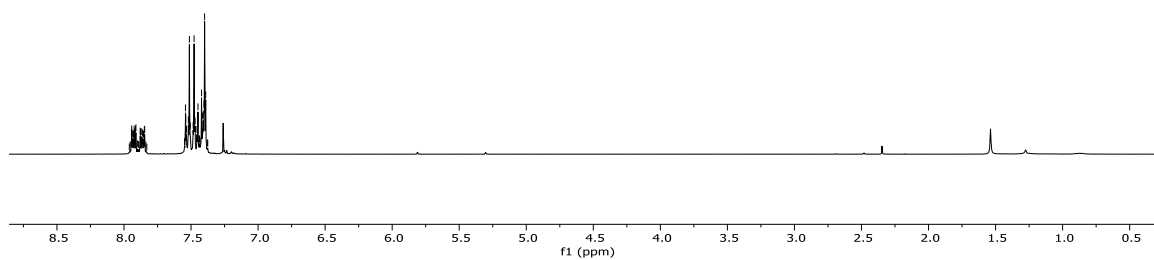
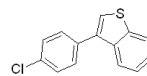


¹⁹F NMR (377 MHz, CDCl₃) of **4h**

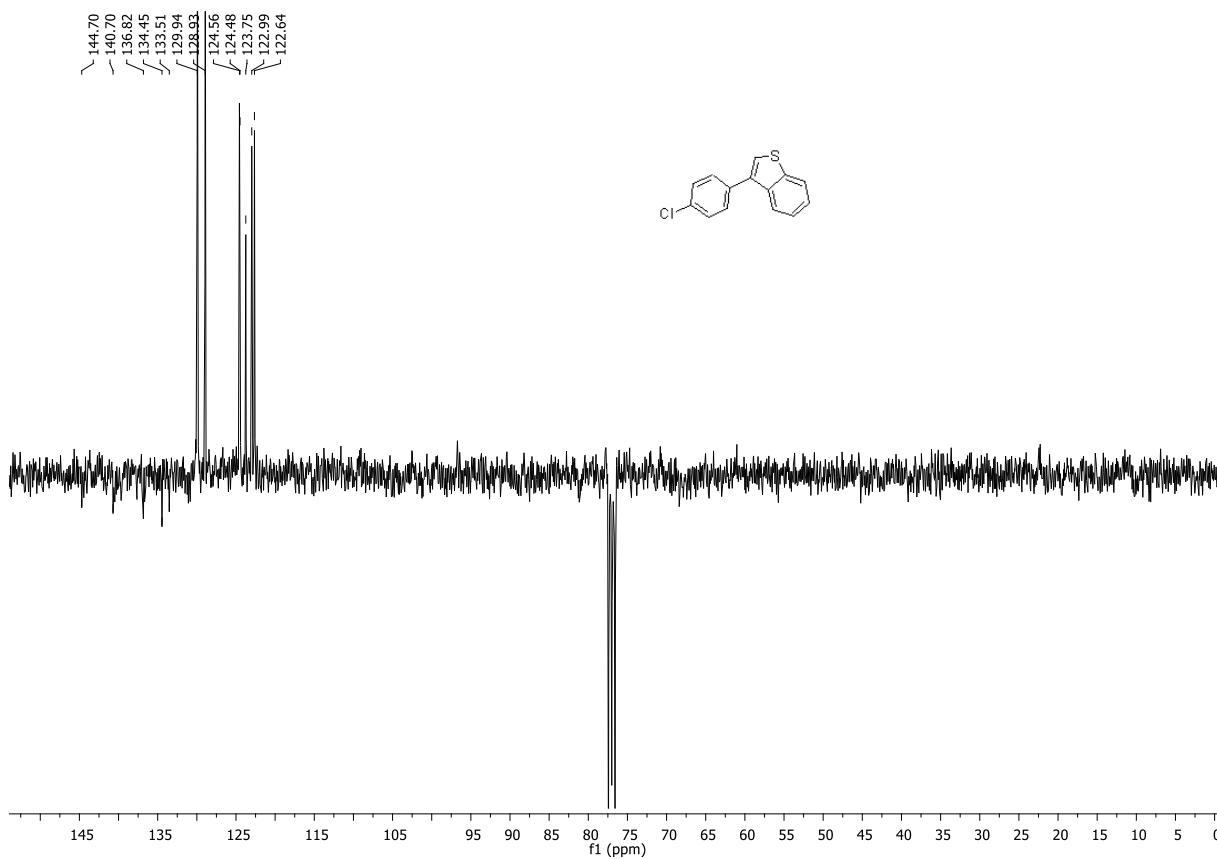


¹H NMR (300 MHz, CDCl₃) of **4i**

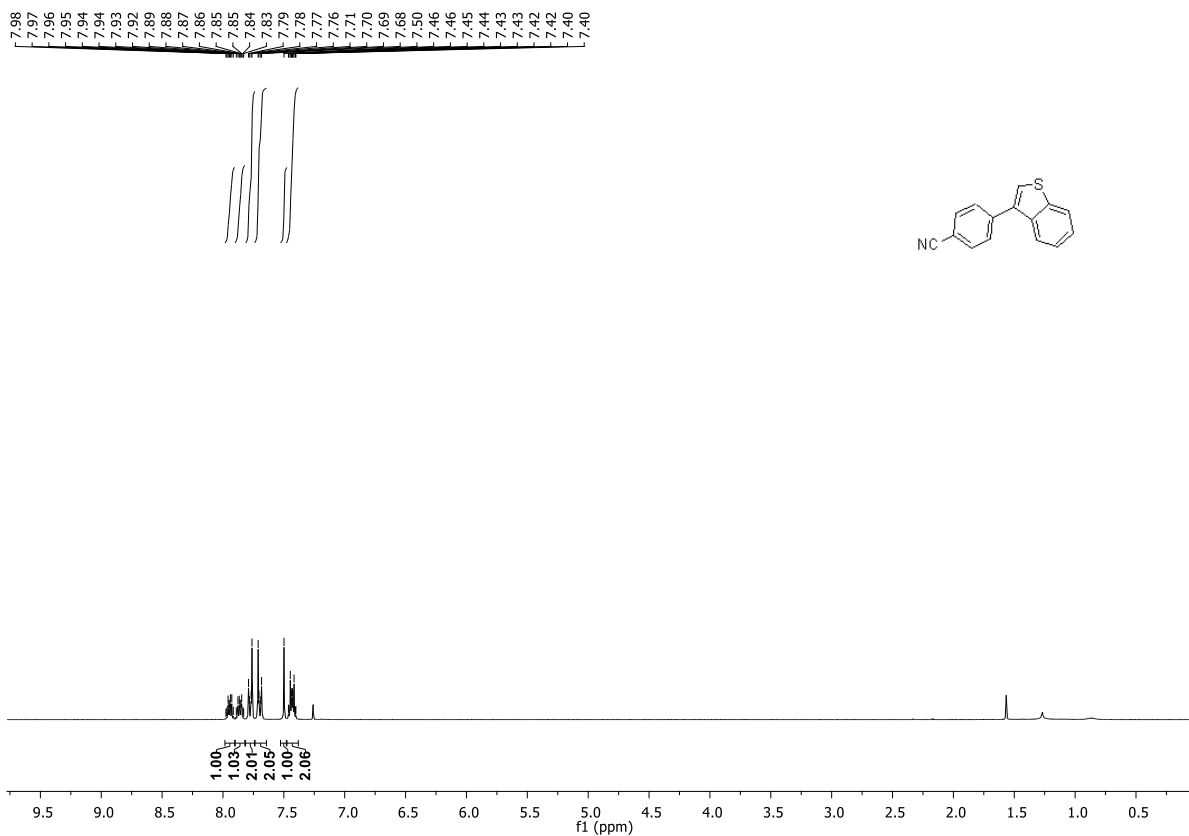
7.95
7.94
7.94
7.94
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7.92
7.91
7.90
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7.87
7.86
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7.84
7.83
7.83
7.82
7.81
7.81
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7.79
7.78
7.78
7.77
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7.71
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7.70
7.69
7.68
7.68



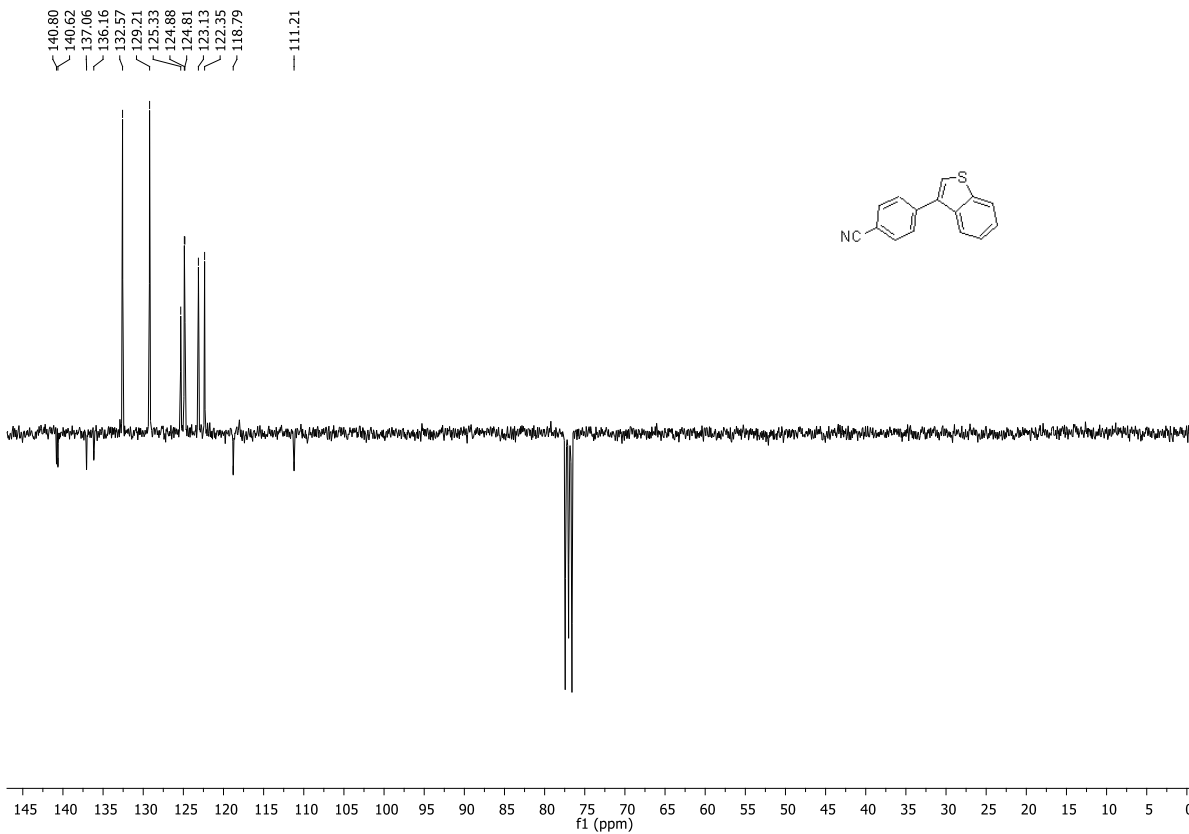
¹³C NMR (75 MHz, CDCl₃) of 4i



¹H NMR (300 MHz, CDCl₃) of 4j



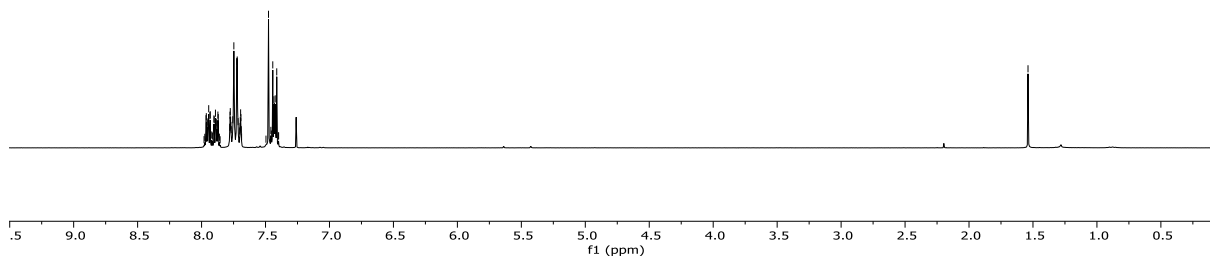
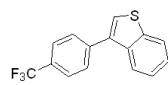
¹³C NMR (75 MHz, CDCl₃) of **4j**



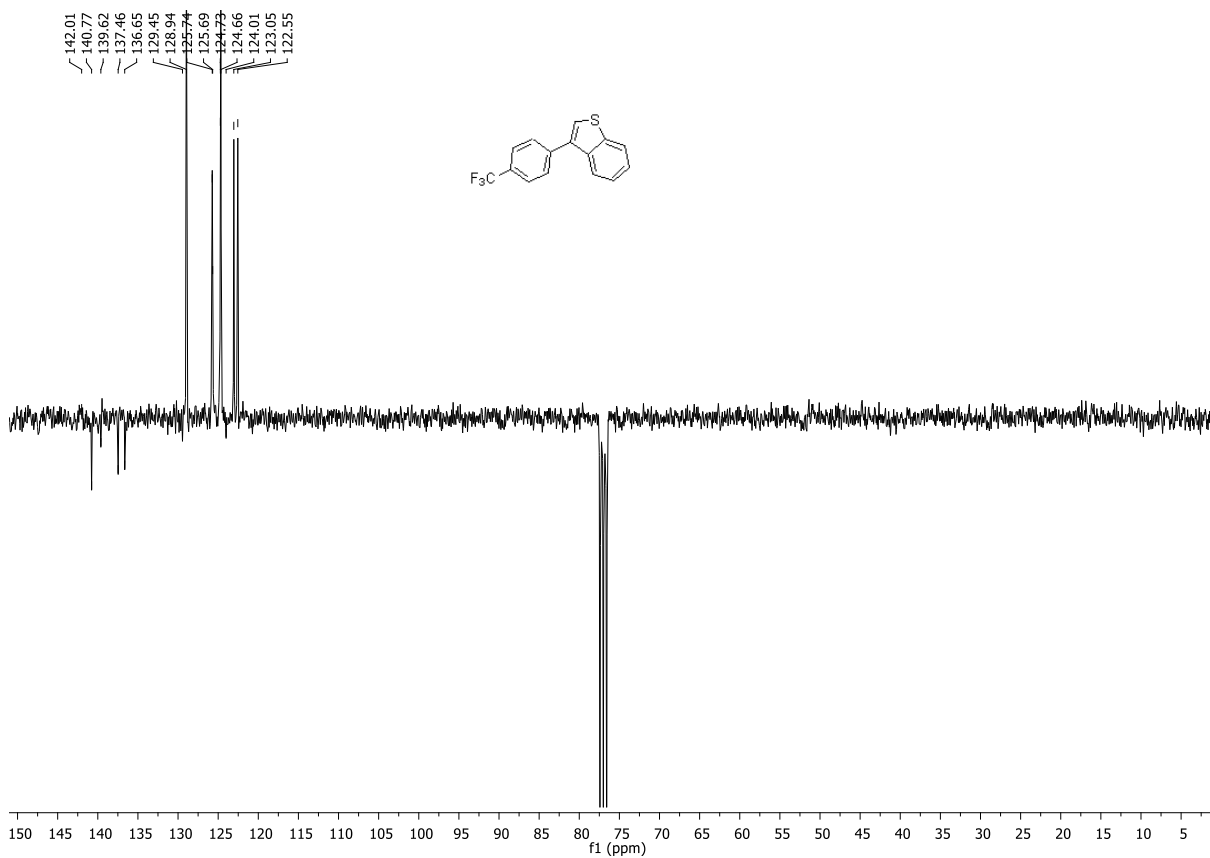
¹H NMR (300 MHz, CDCl₃) of **4k**

7.98
7.97
7.96
7.95
7.94
7.93
7.92
7.90
7.89
7.88
7.87
7.86
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7.82
7.81
7.80
7.79
7.78
7.77
7.76
7.75
7.72
7.71
7.70
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7.40

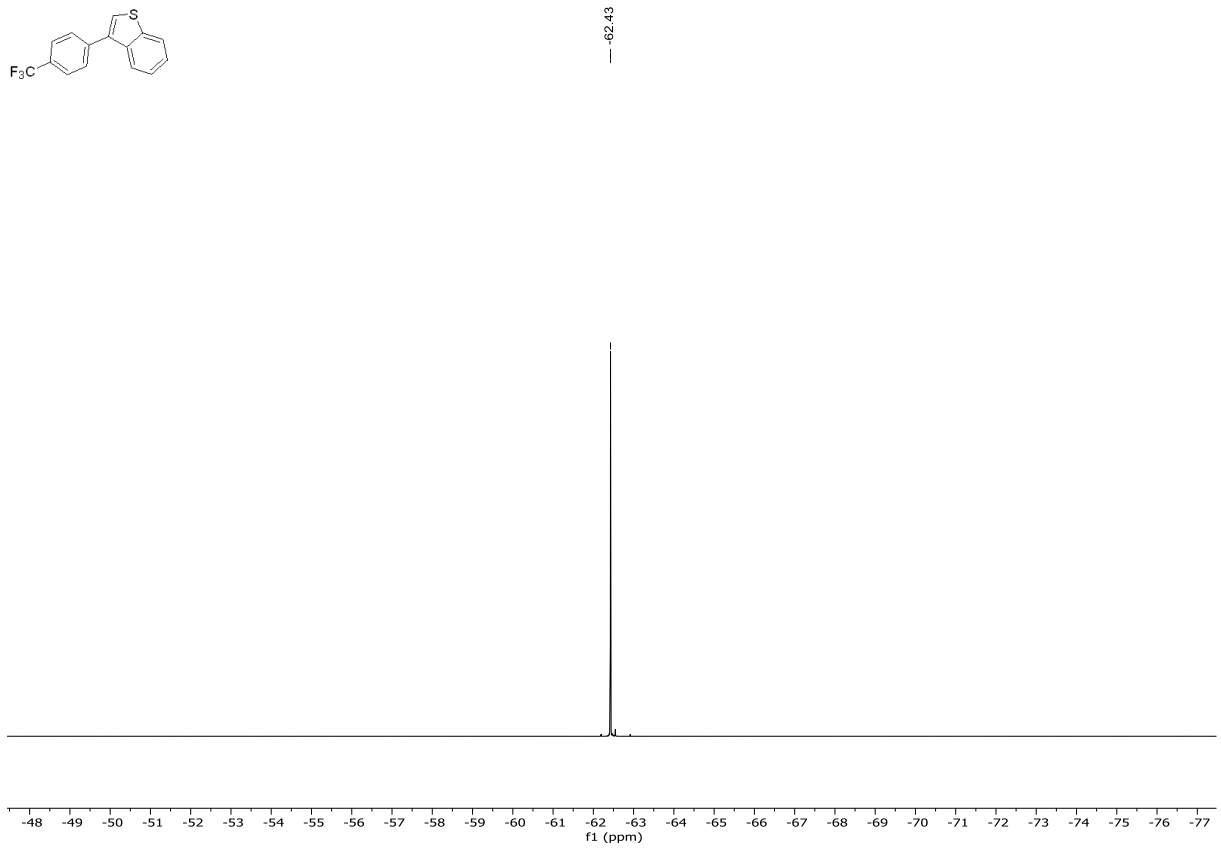
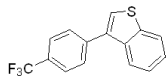
— 1.54



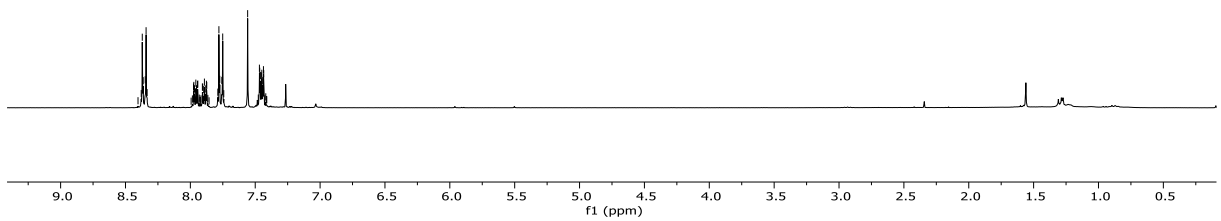
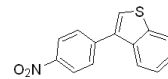
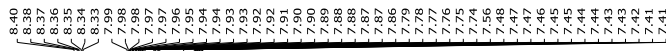
¹³C NMR (75 MHz, CDCl₃) of **4k**



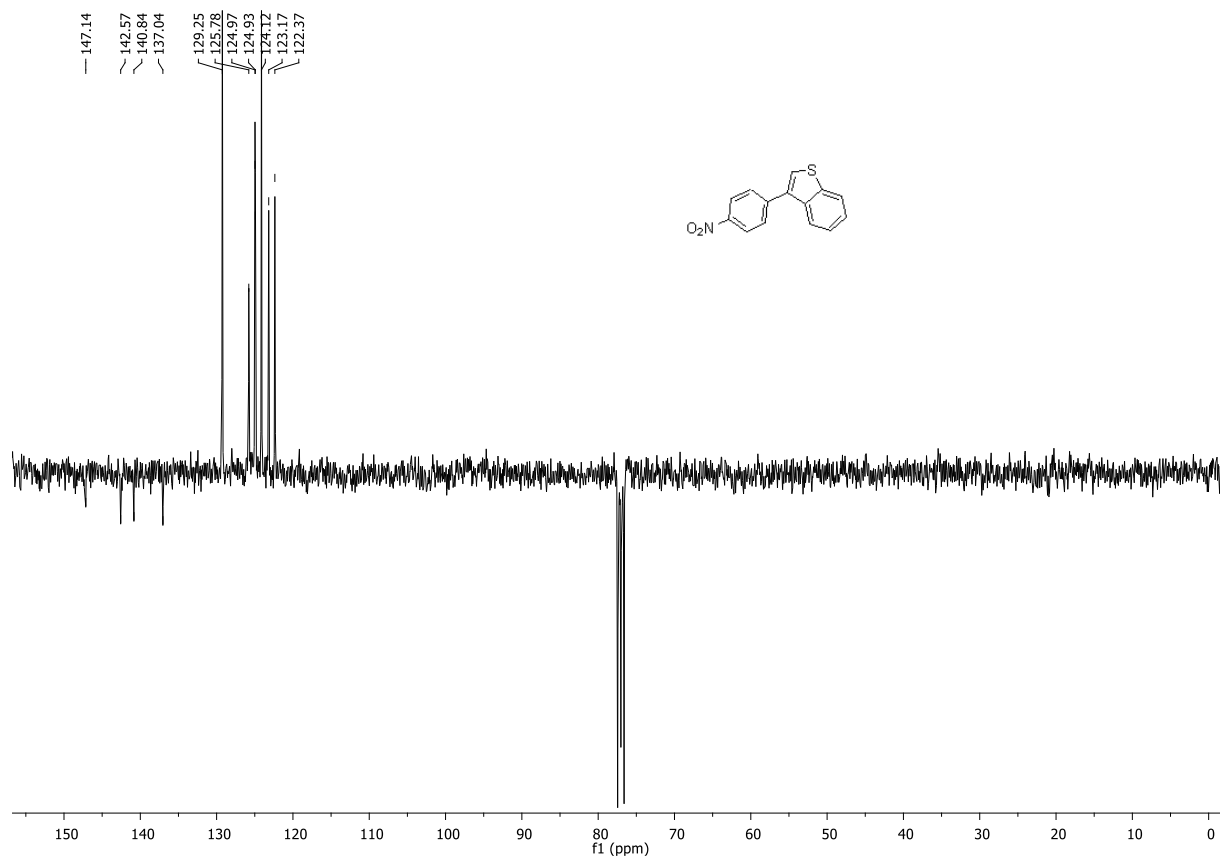
¹⁹F NMR (377 MHz, CDCl₃) of **4k**



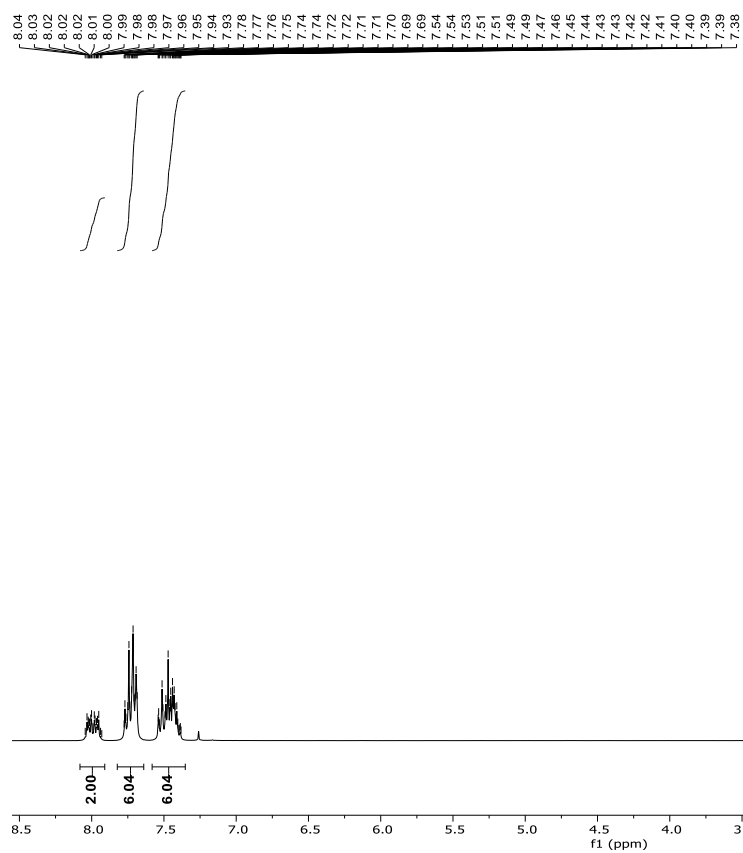
1H NMR (300 MHz, CDCl₃) of **4I**



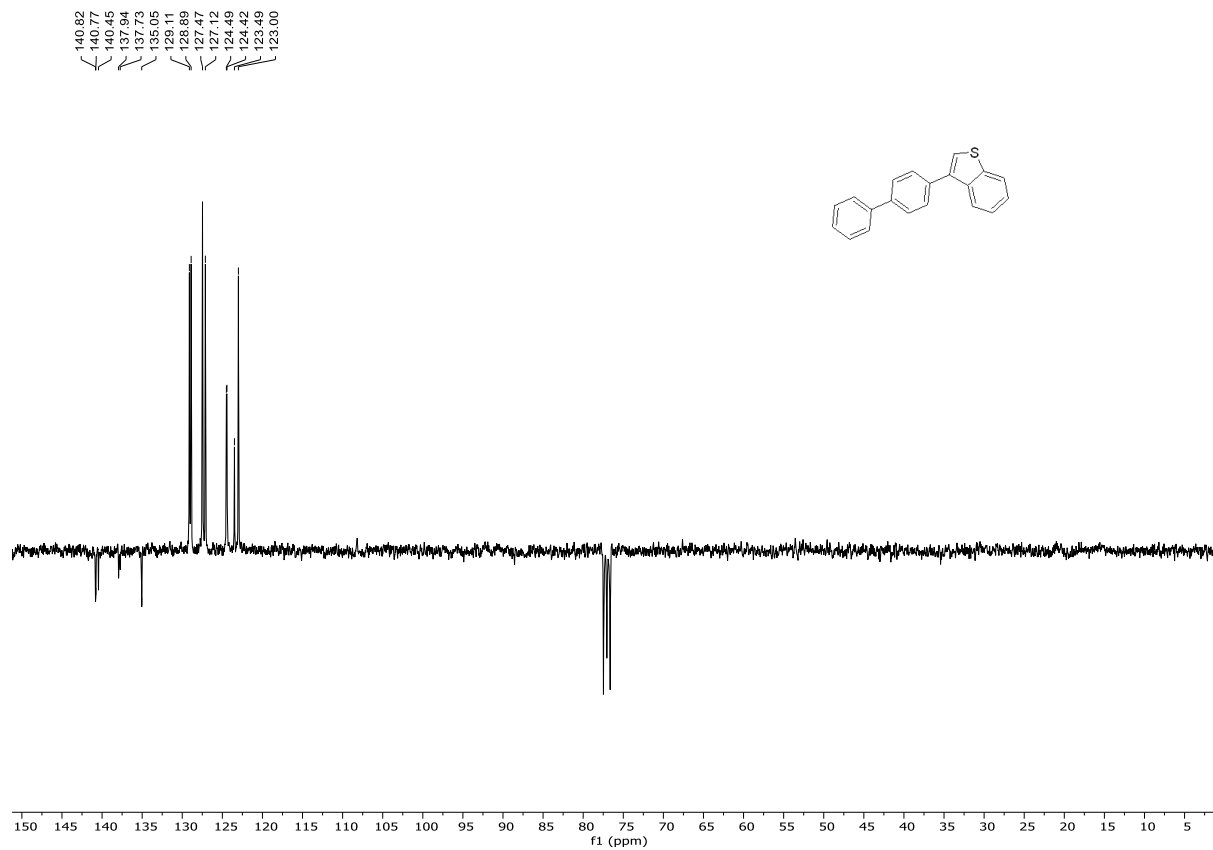
13C NMR (75 MHz, CDCl₃) of **4I**



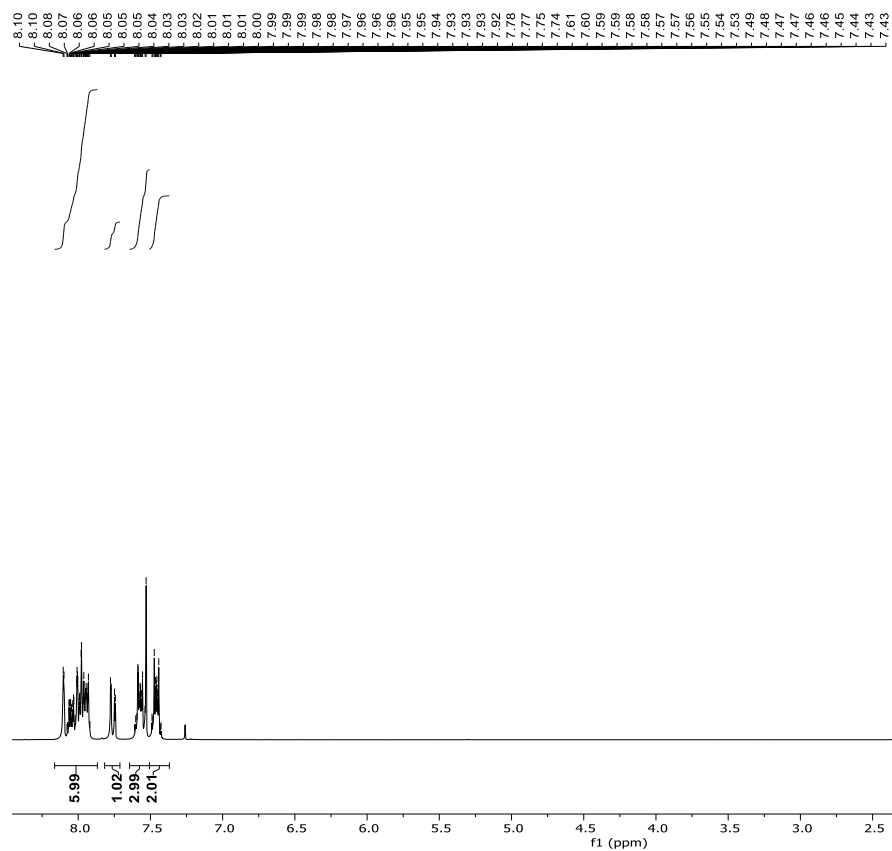
¹³C NMR (300 MHz, CDCl₃) of **4m**



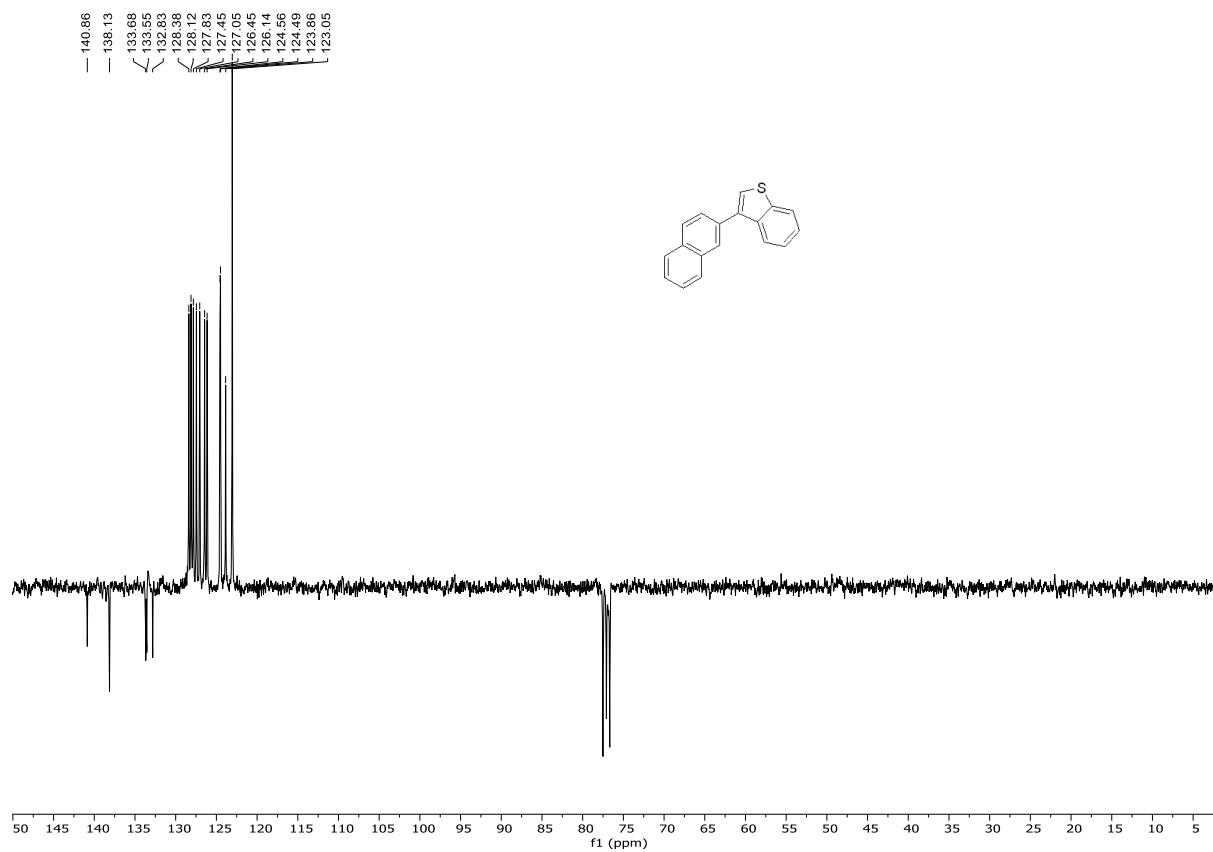
¹H NMR (75 MHz, CDCl₃) of **4m**



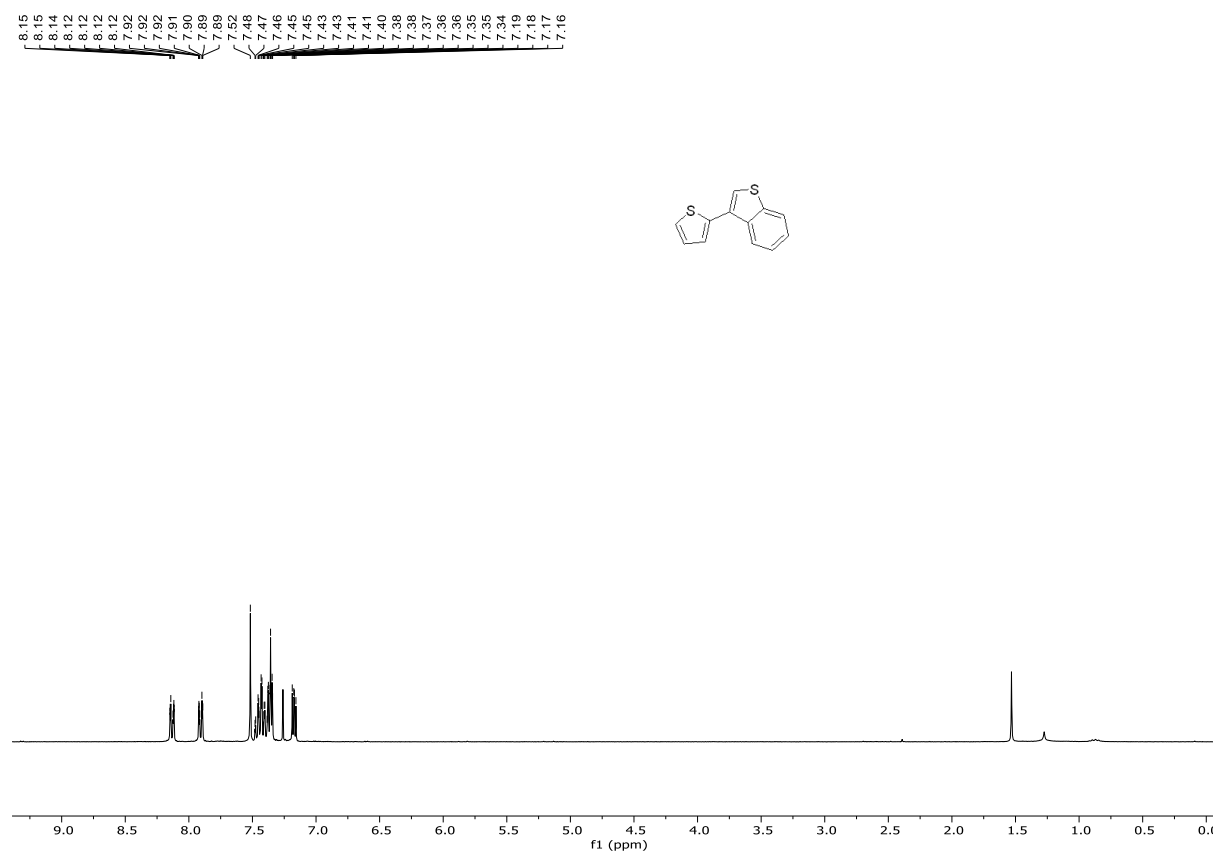
^1H NMR (300 MHz, CDCl_3) of **4n**



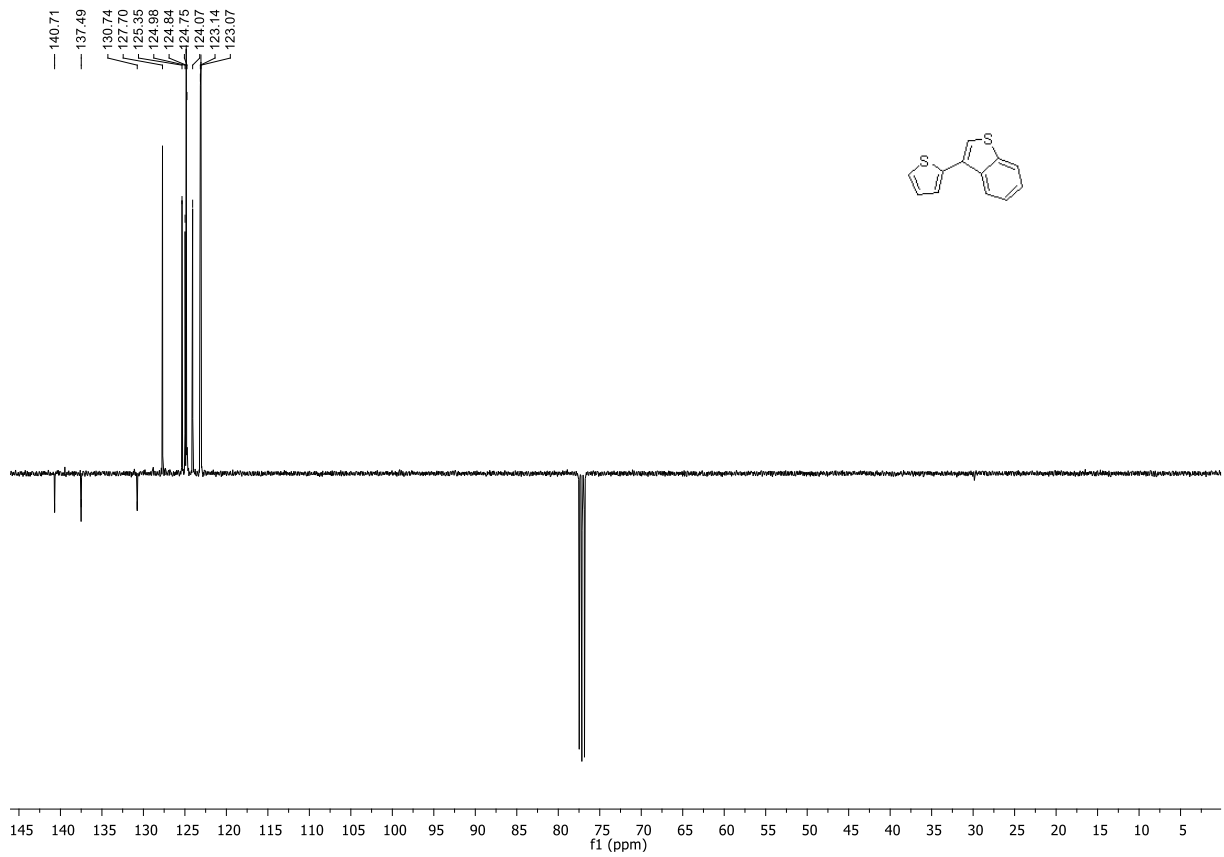
^{13}C NMR (75 MHz, CDCl_3) of **4n**



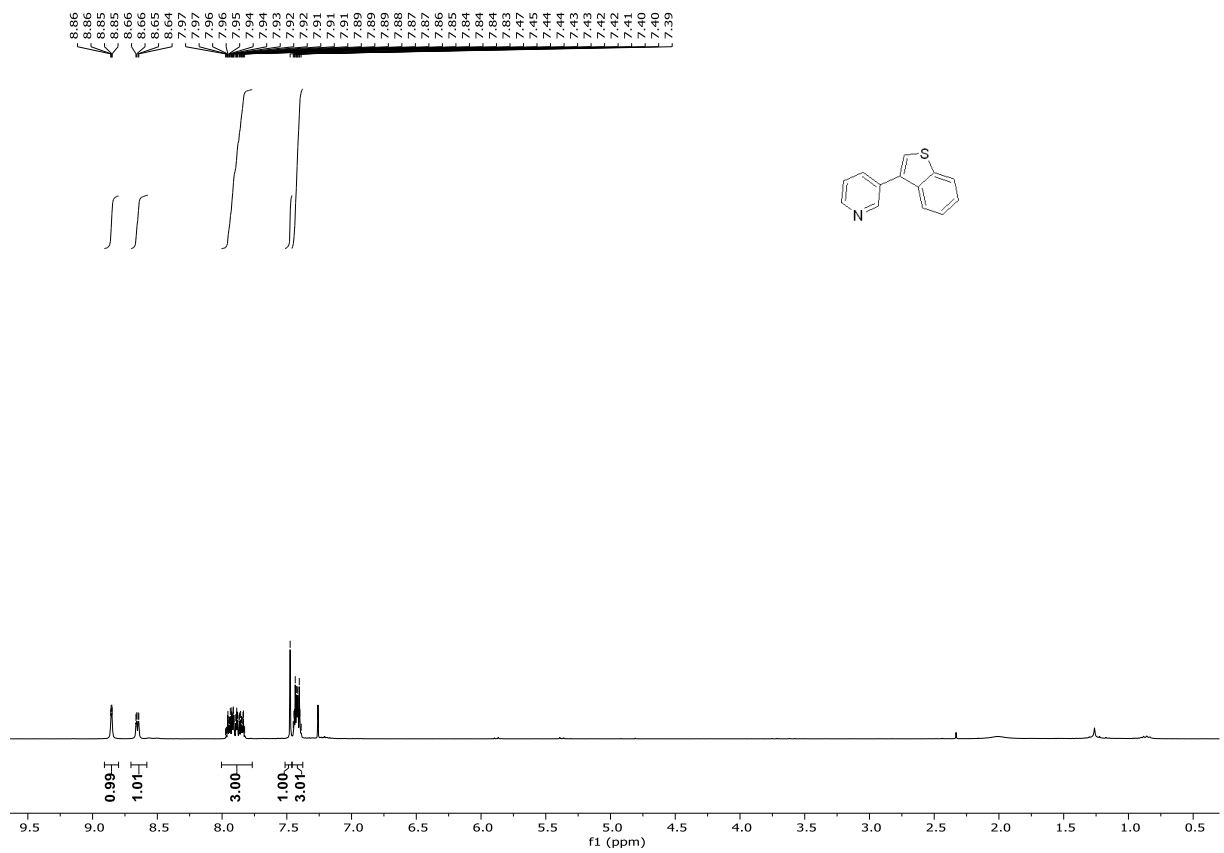
^1H NMR (300 MHz, CDCl_3) of **4o**



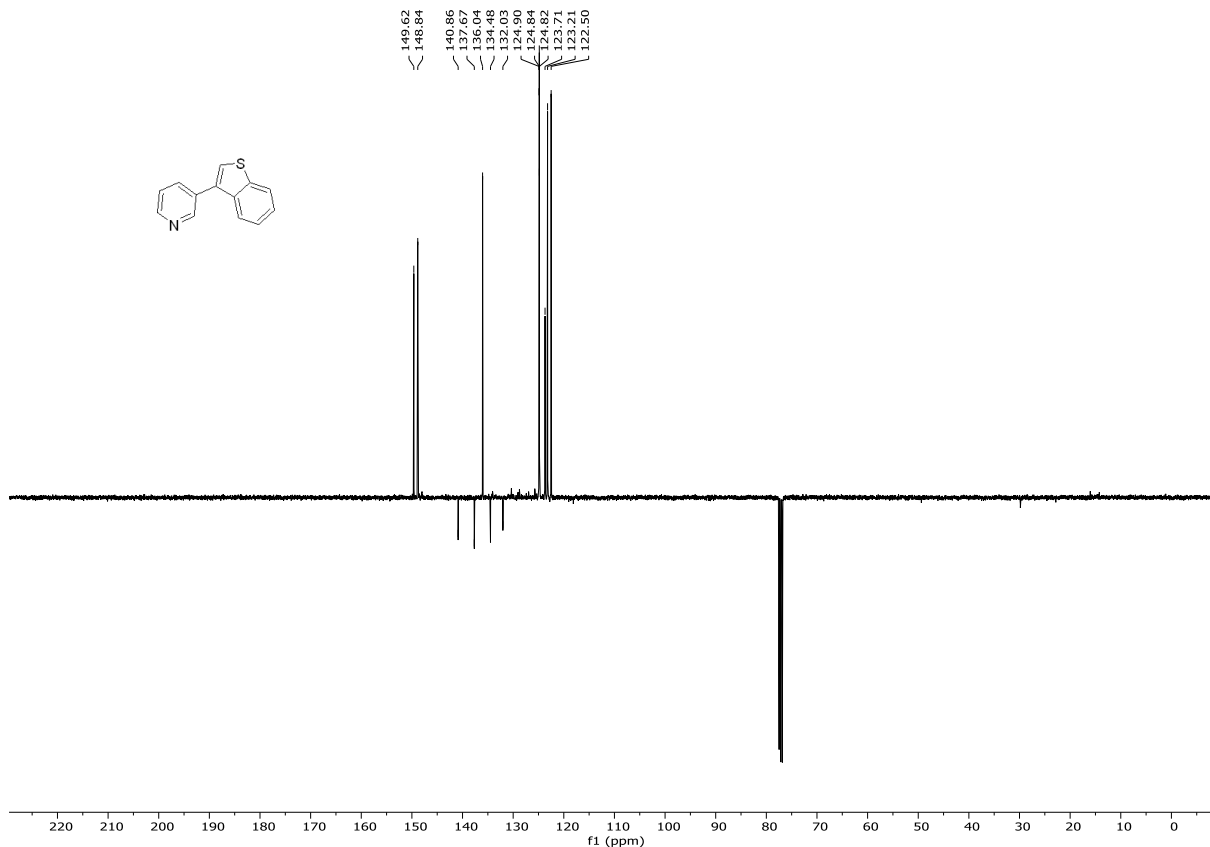
^{13}C NMR (101 MHz, CDCl_3) of **4o**



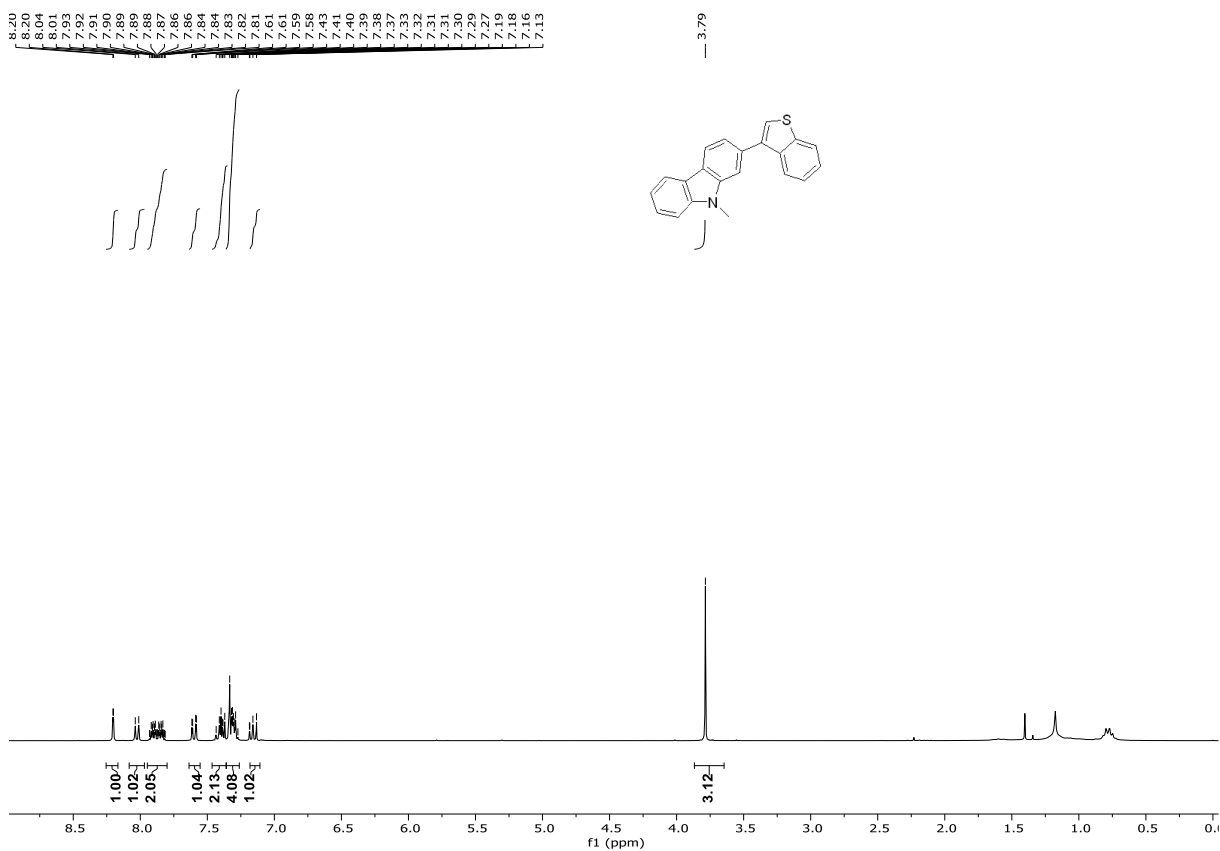
^1H NMR (300 MHz, CDCl_3) of 4p



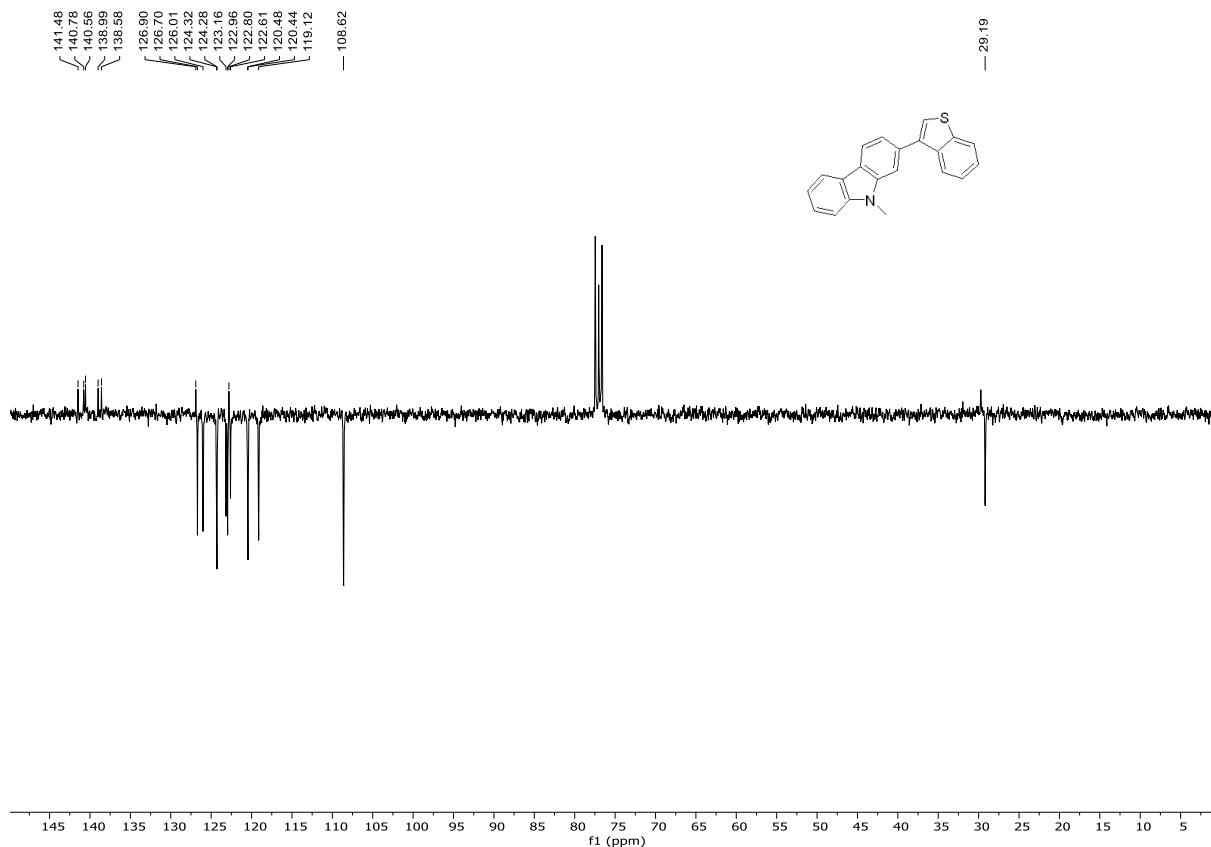
^{13}C NMR (75 MHz, CDCl_3) of 4p



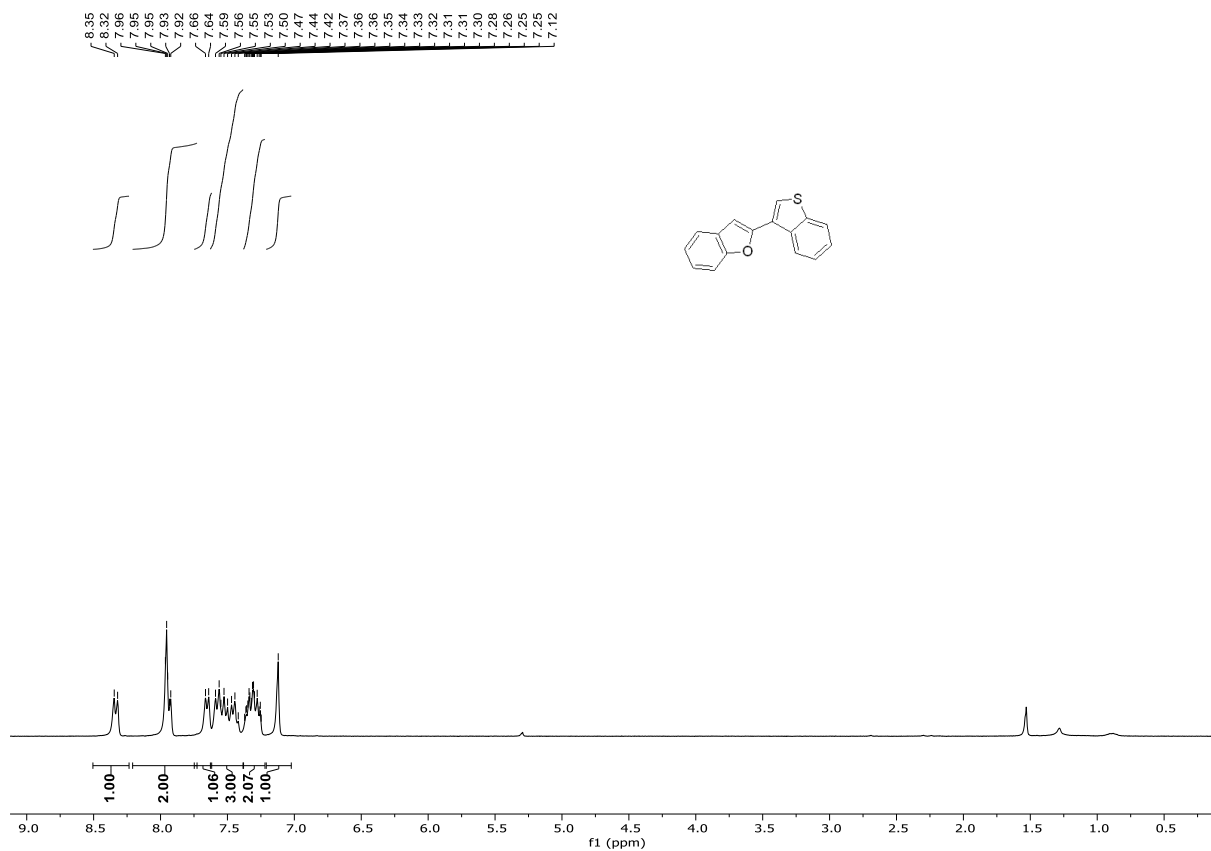
¹H NMR (300 MHz, CDCl₃) of **4q**



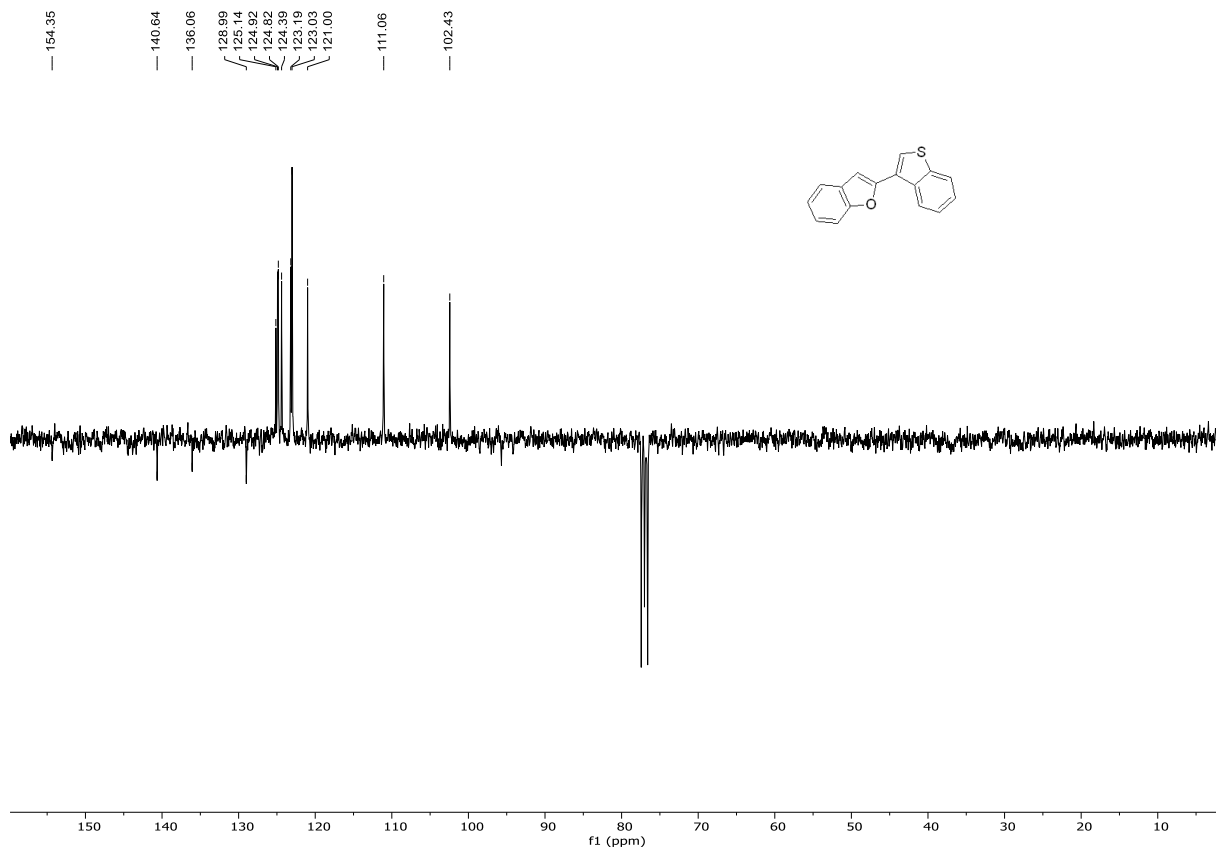
¹³C NMR (75 MHz, CDCl₃) of **4q**



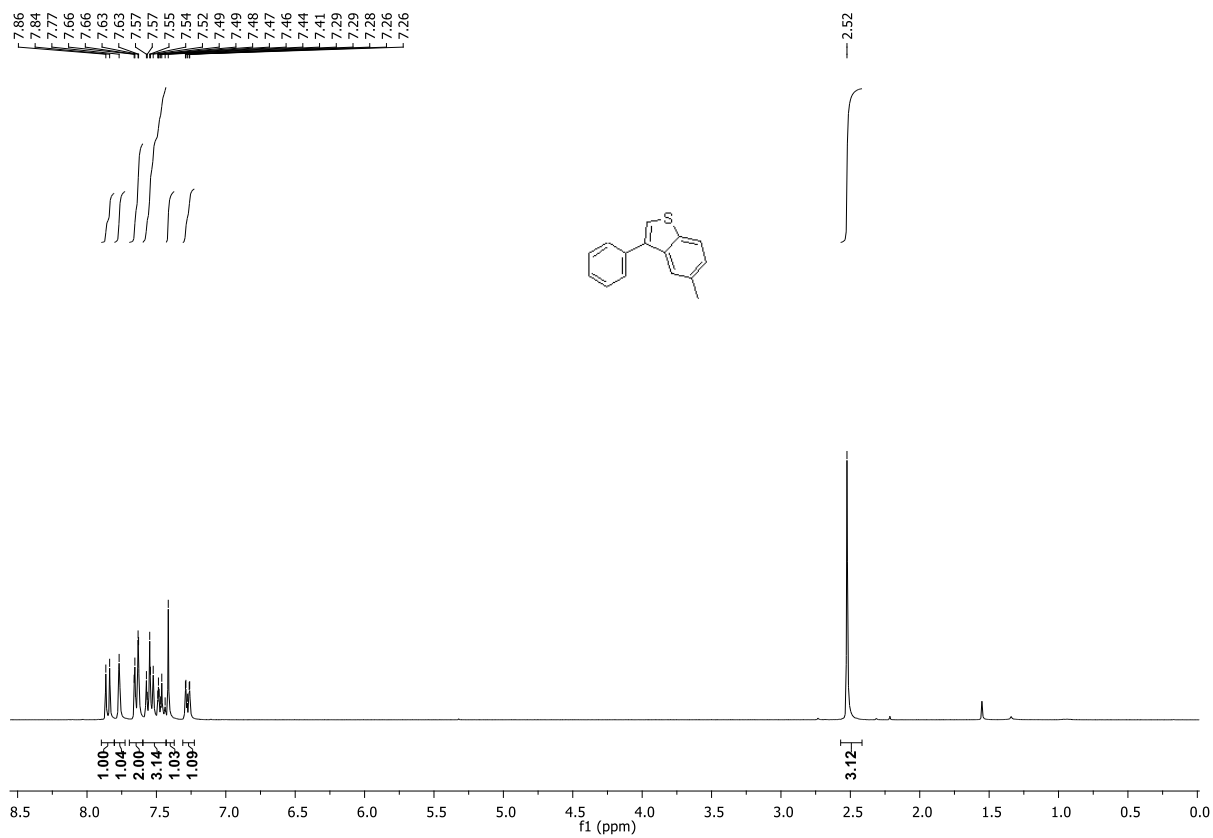
^1H NMR (300 MHz, CDCl_3) of **4r**



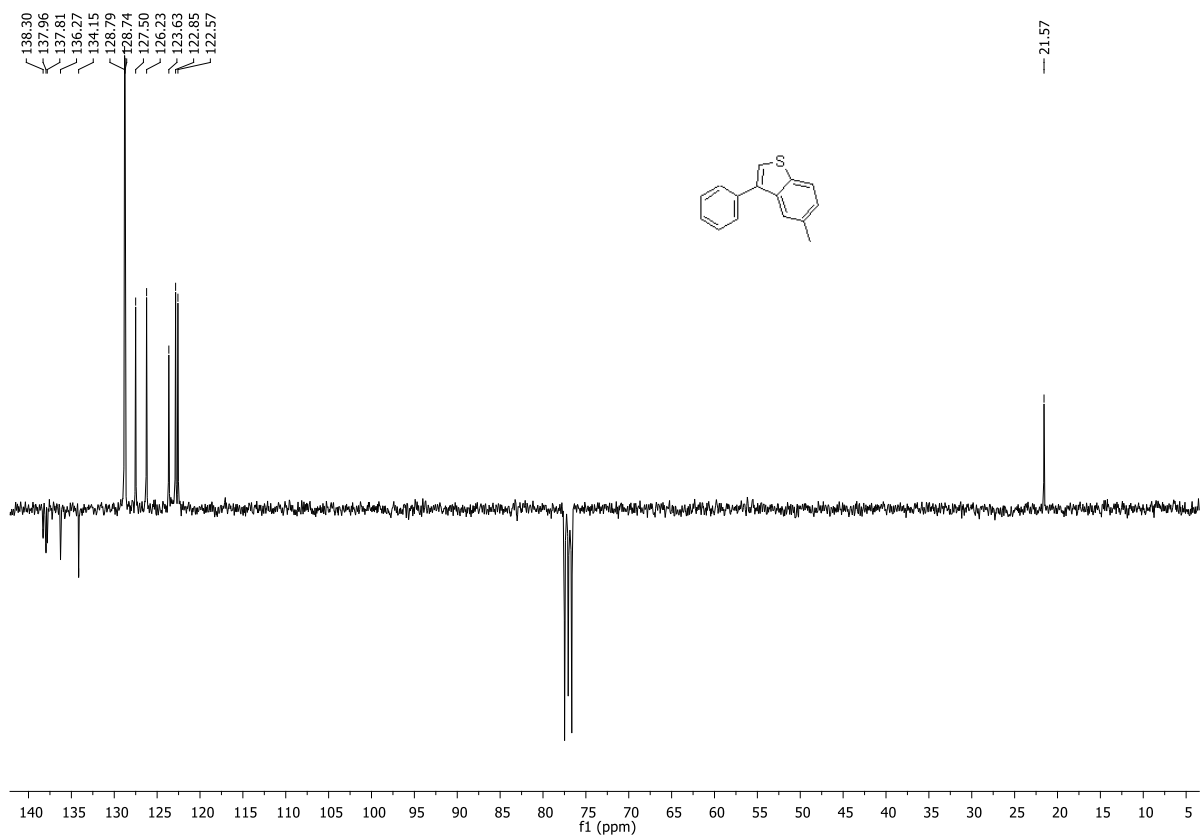
^{13}C NMR (75 MHz, CDCl_3) of **4r**



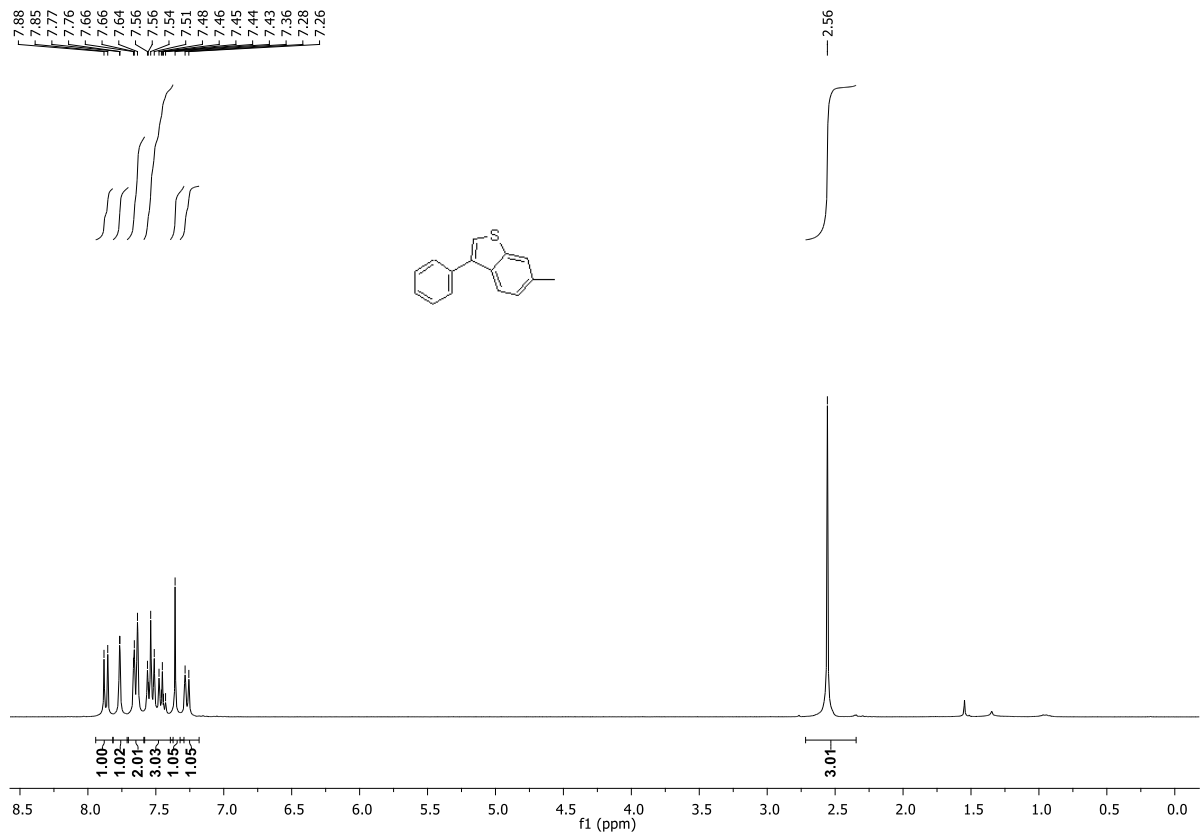
¹H NMR (300 MHz, CDCl₃) of **4s**



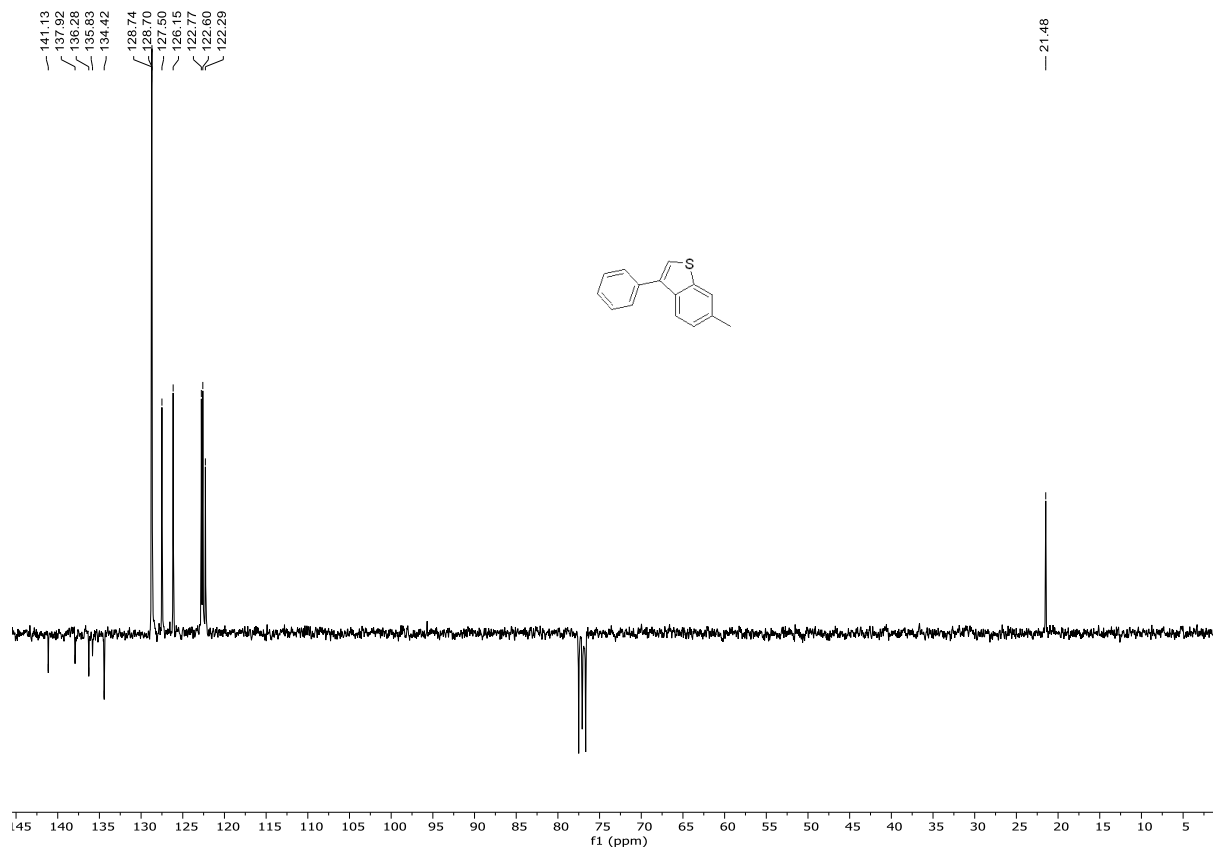
¹³C NMR (75 MHz, CDCl₃) of **4s**



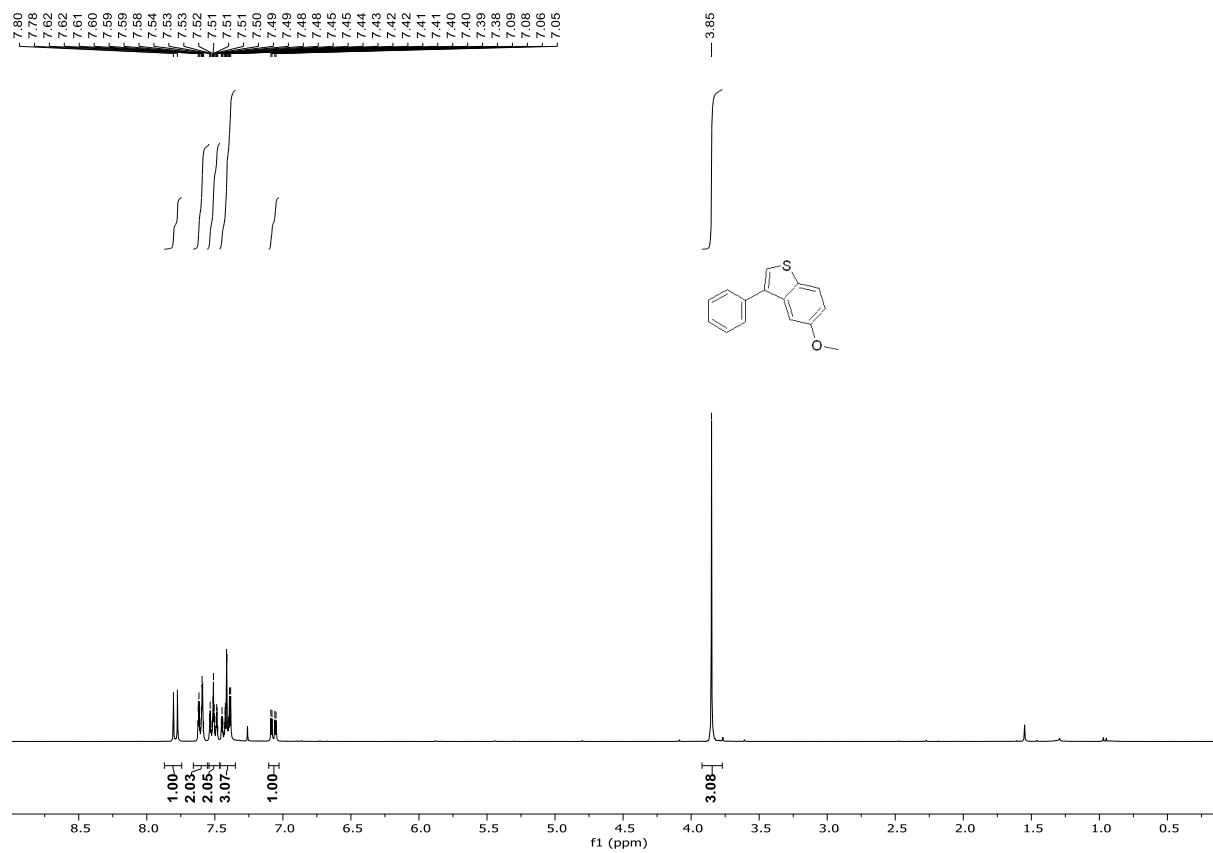
¹H NMR (300 MHz, CDCl₃) of **4t**



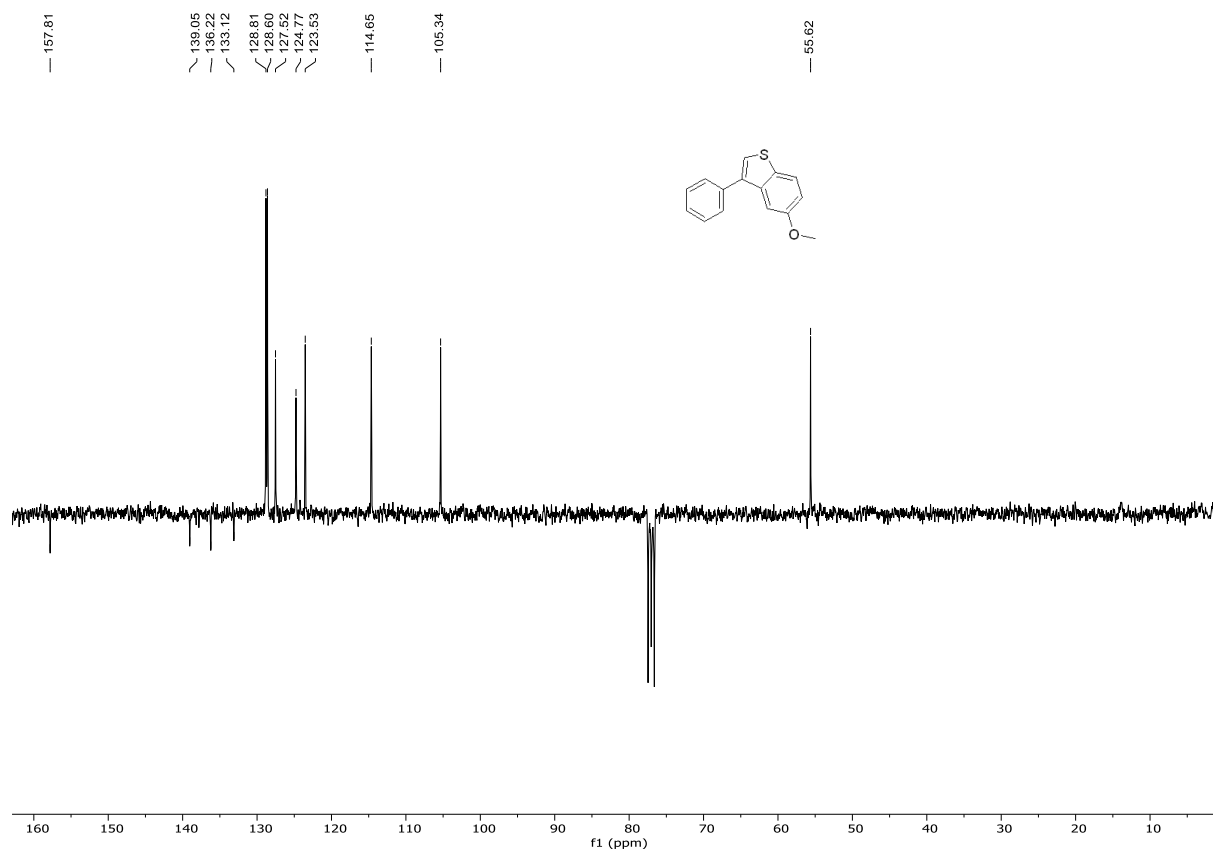
¹³C NMR (75 MHz, CDCl₃) of **4t**



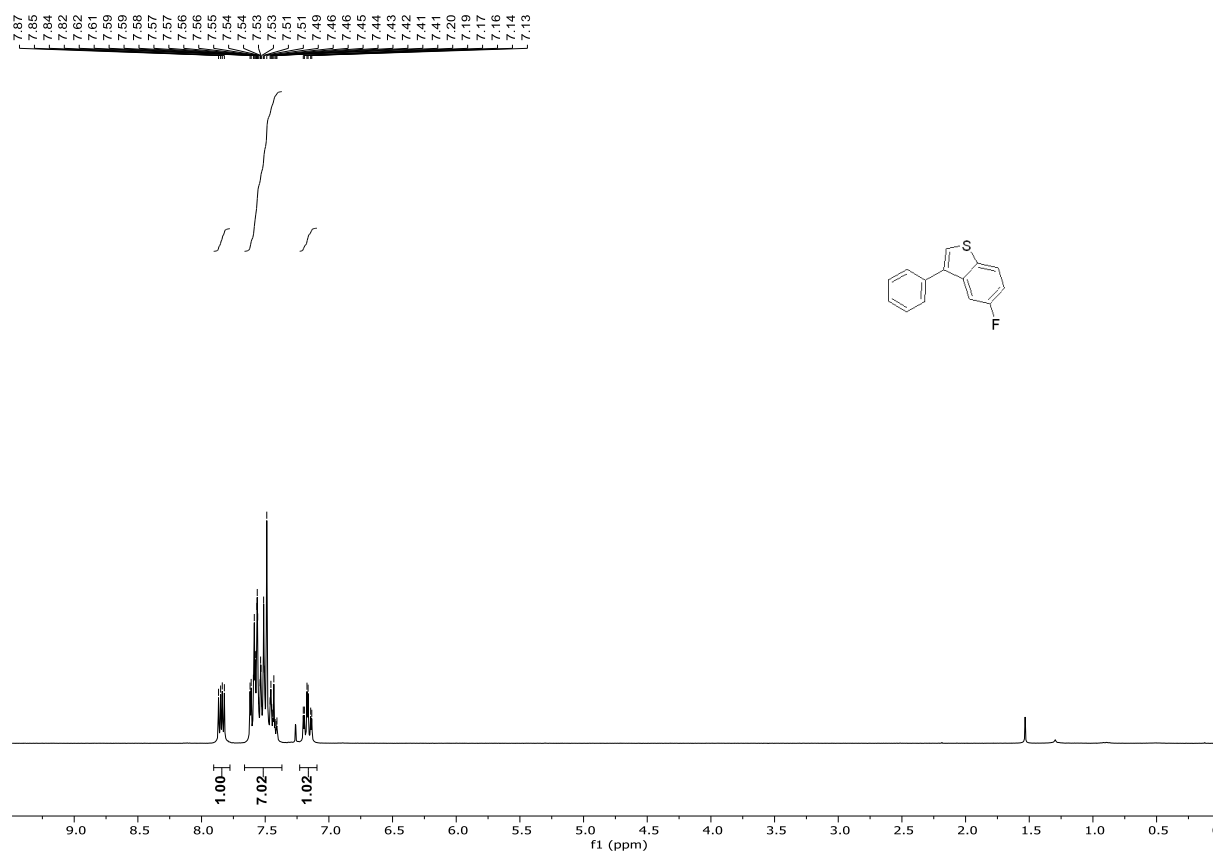
^1H NMR (300 MHz, CDCl_3) of 4u



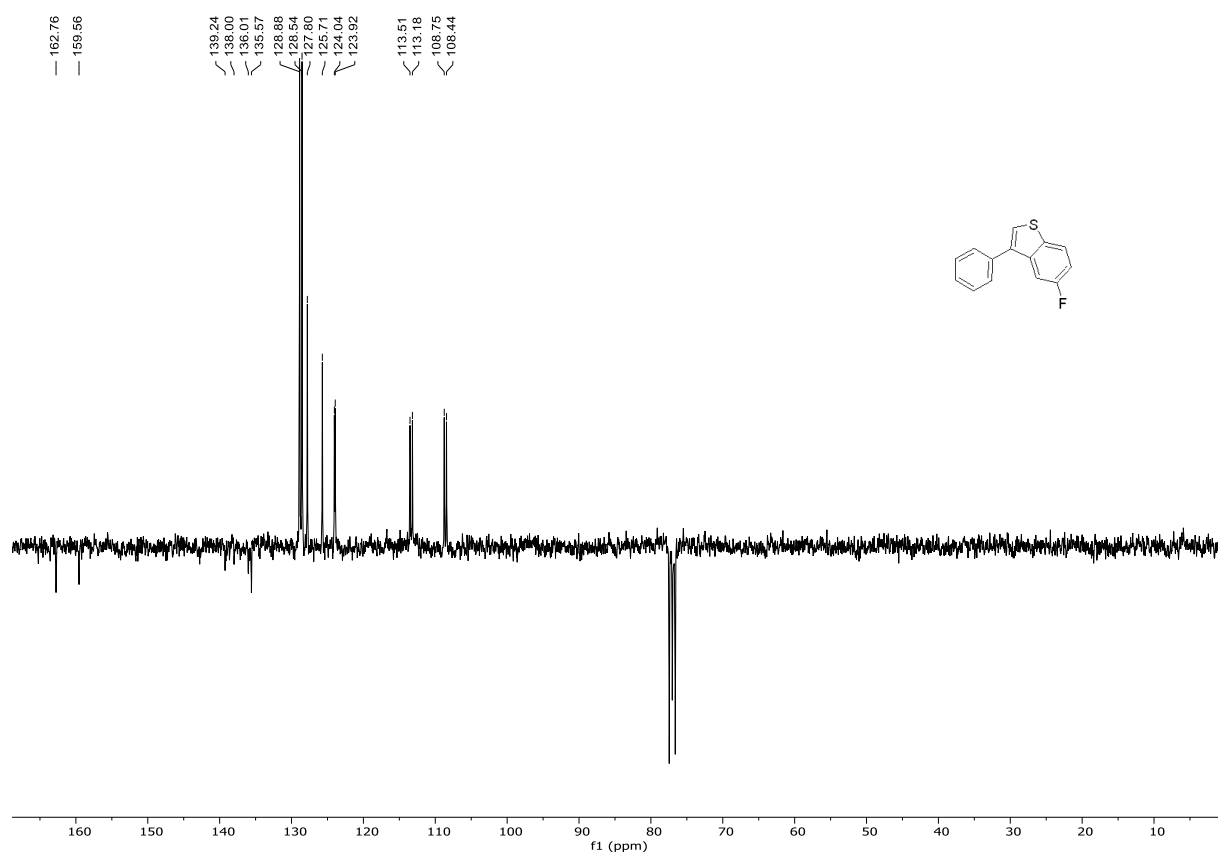
^{13}C NMR (75 MHz, CDCl_3) of 4u



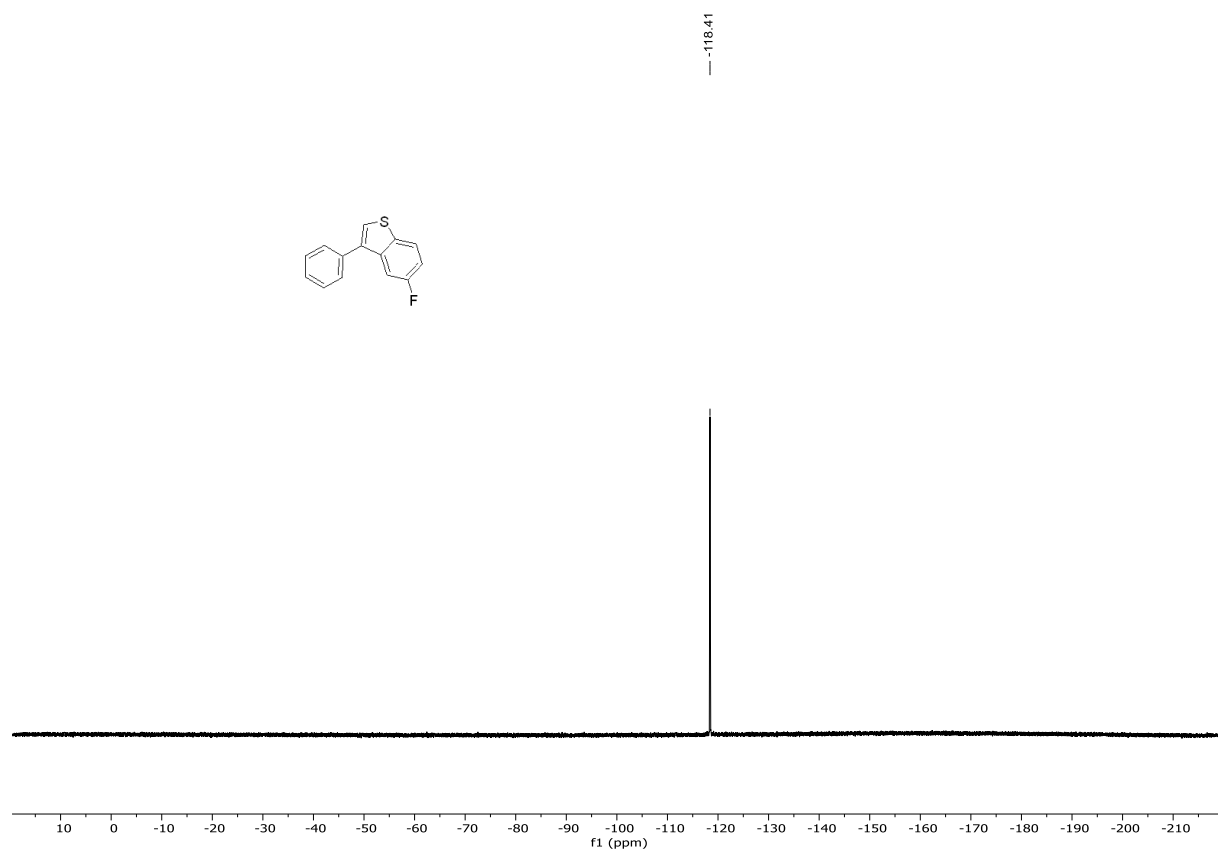
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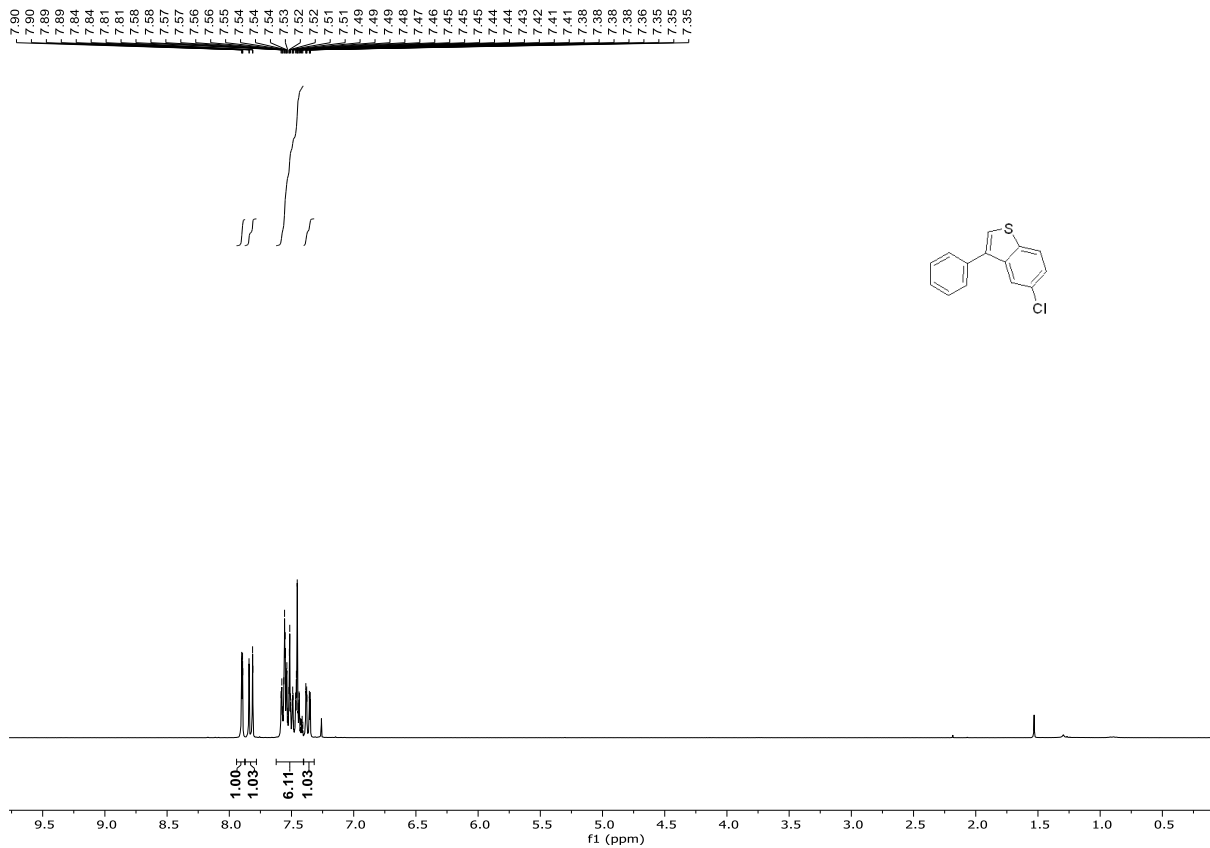
^{13}C NMR (75 MHz, CDCl_3) of **4v**



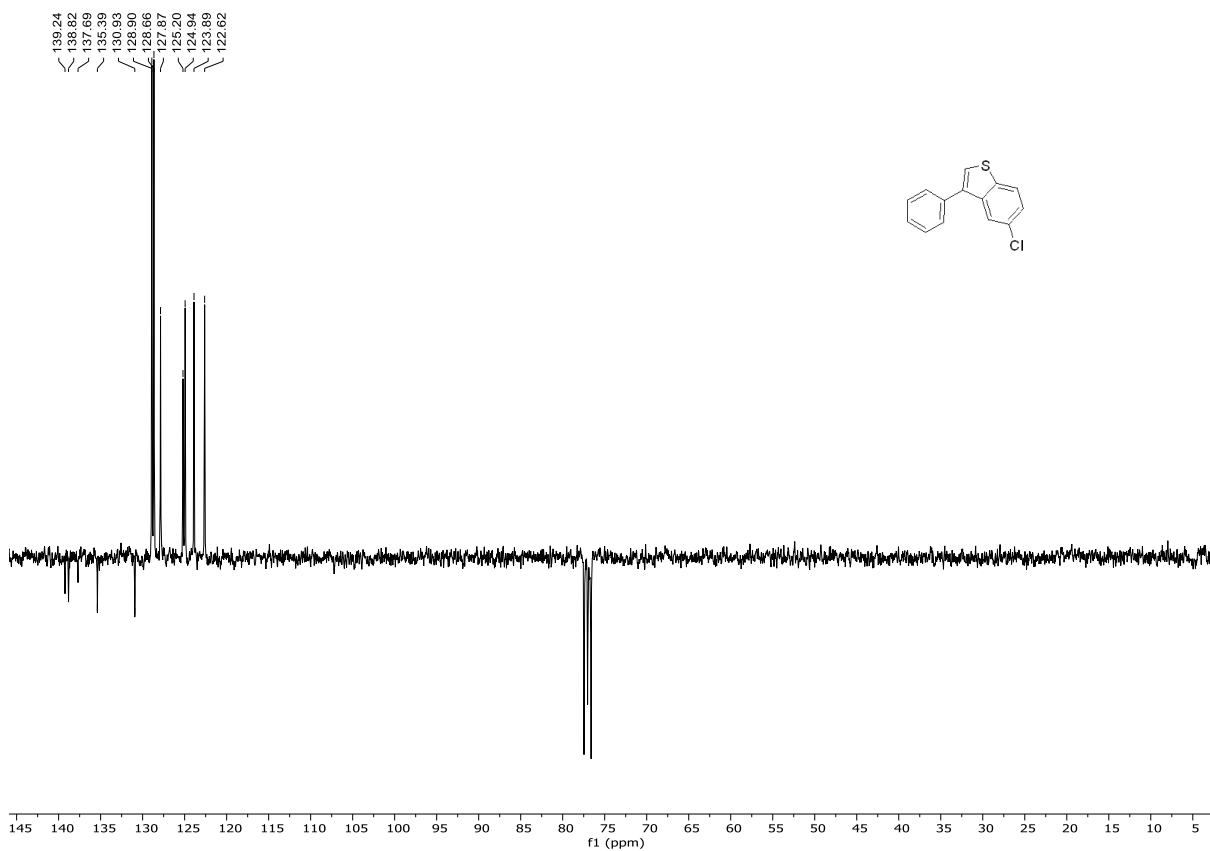
¹⁹F NMR (188 MHz, CDCl₃) of **4v**



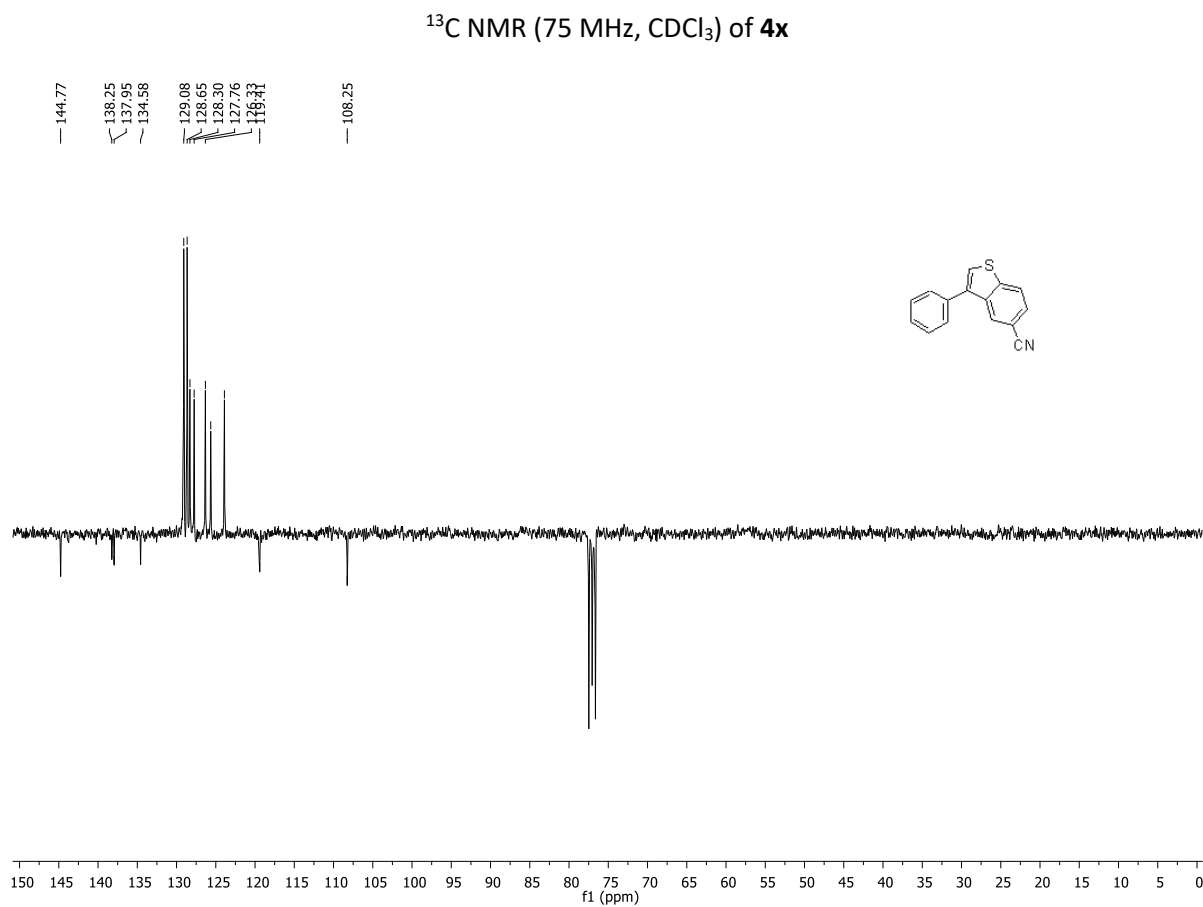
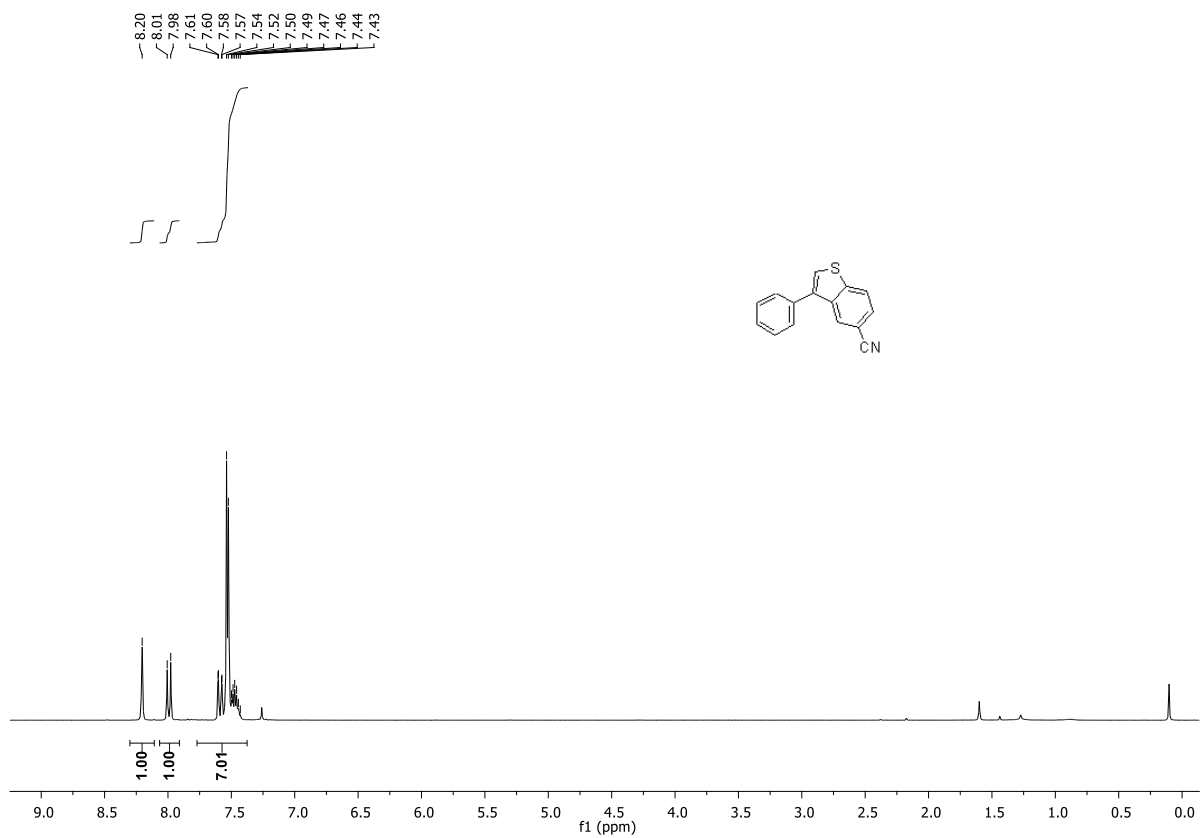
¹H NMR (300 MHz, CDCl₃) of **4w**



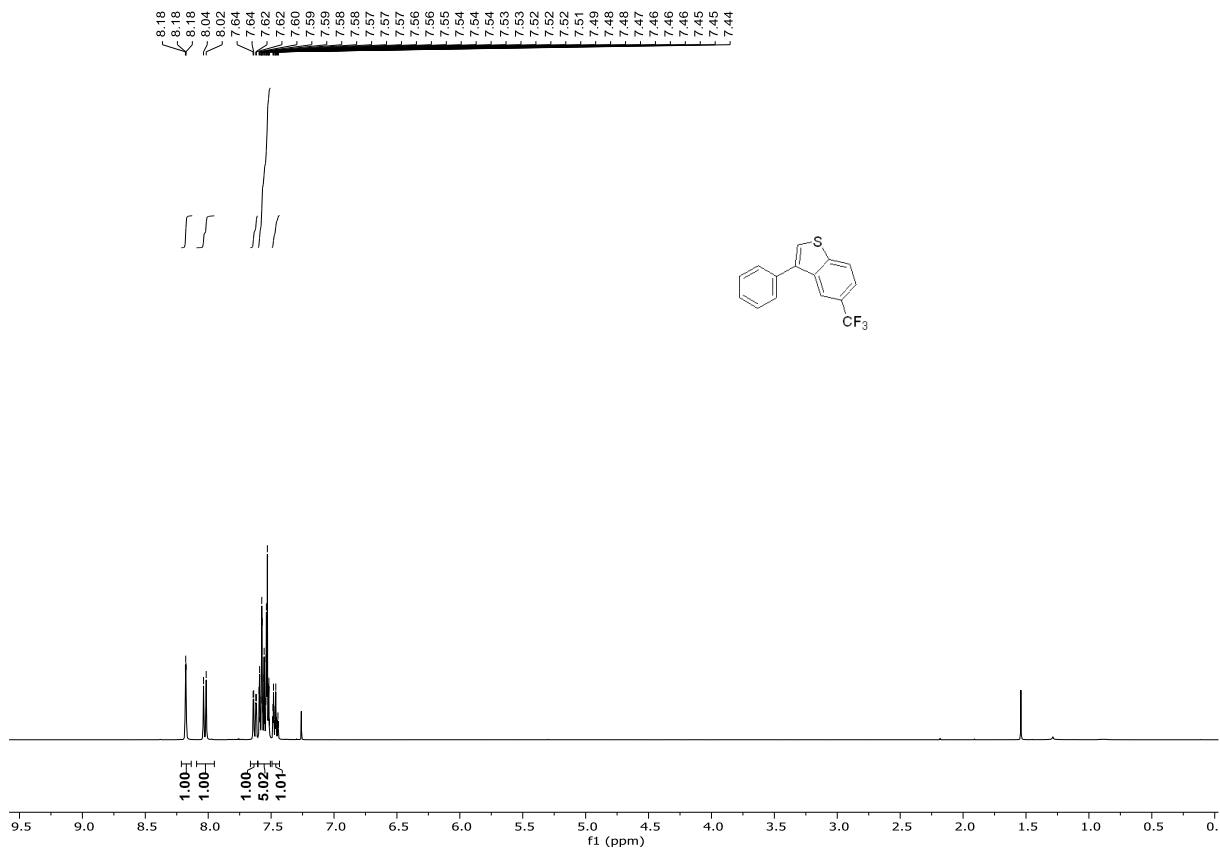
¹³C NMR (75 MHz, CDCl₃) of **4w**



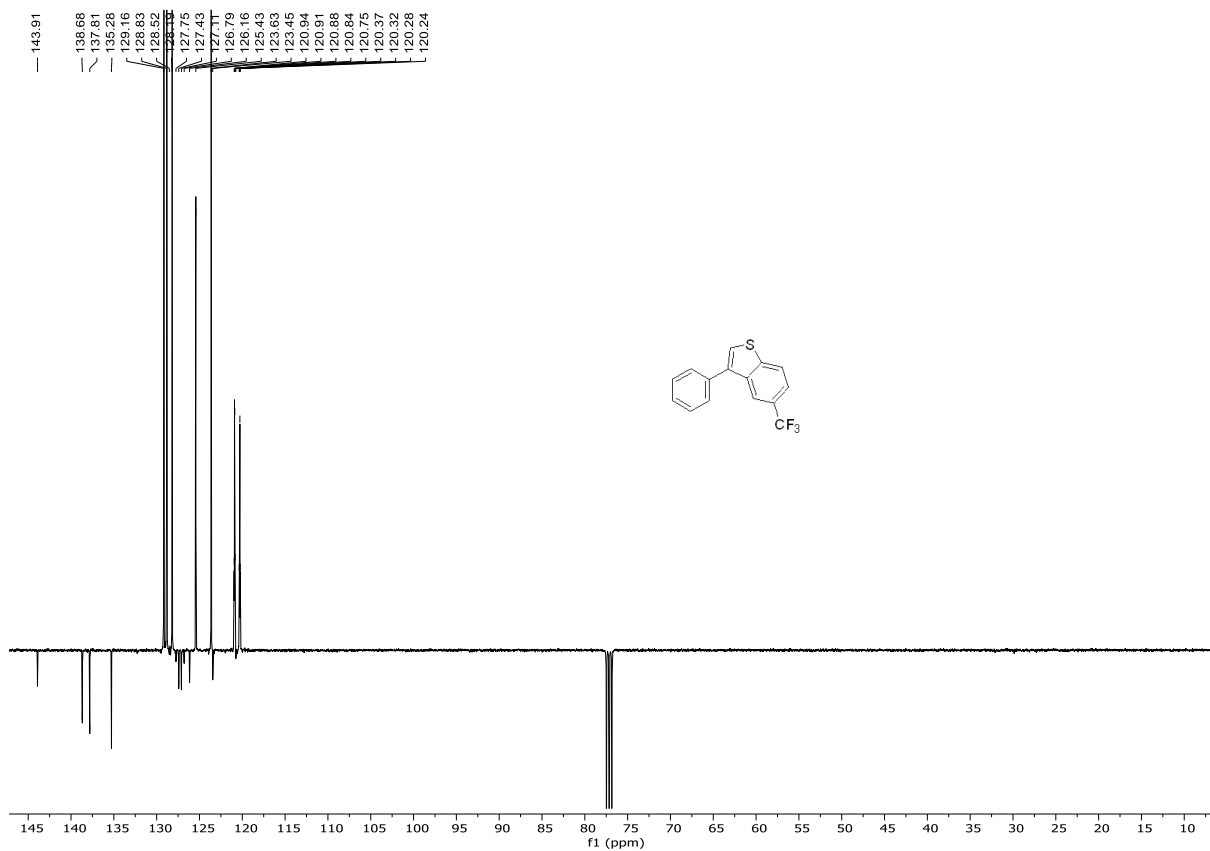
¹H NMR (300 MHz, CDCl₃) of **4x**



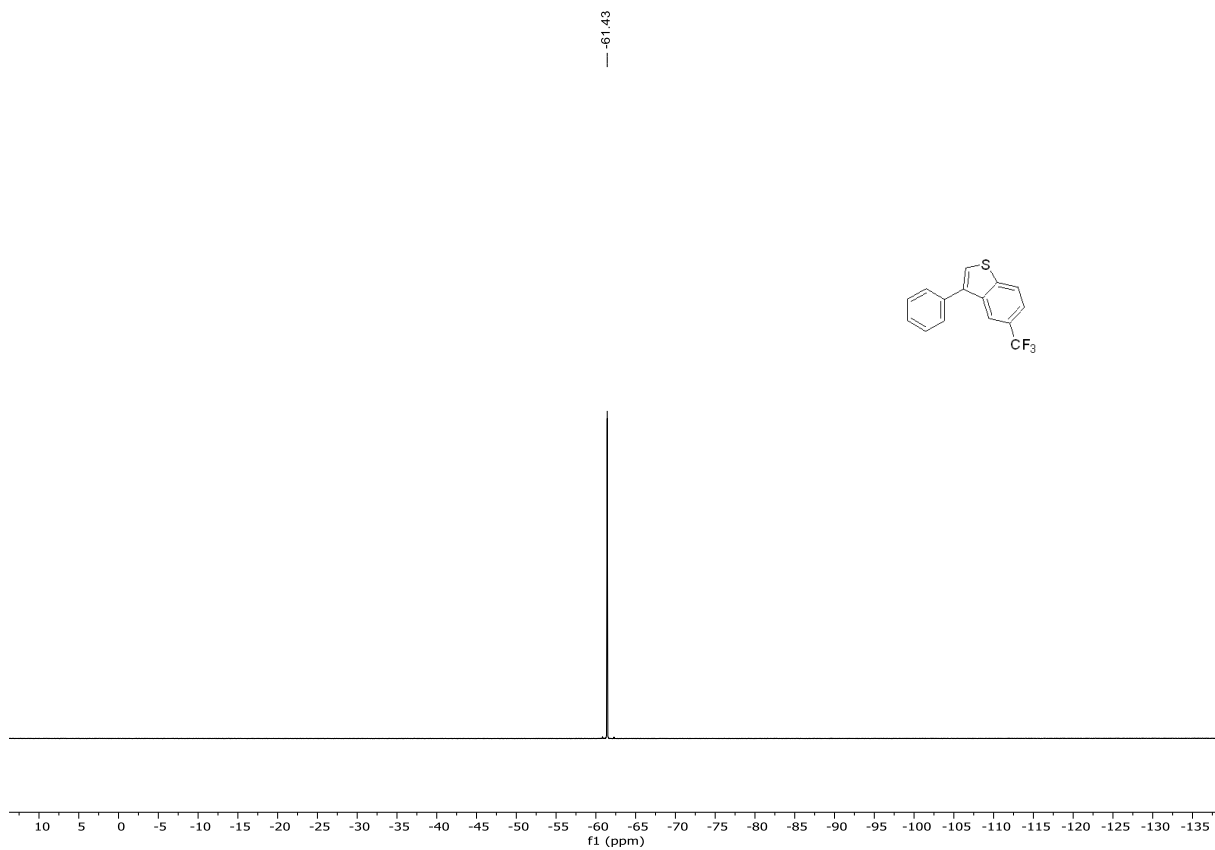
¹H NMR (400 MHz, CDCl₃) of 4y



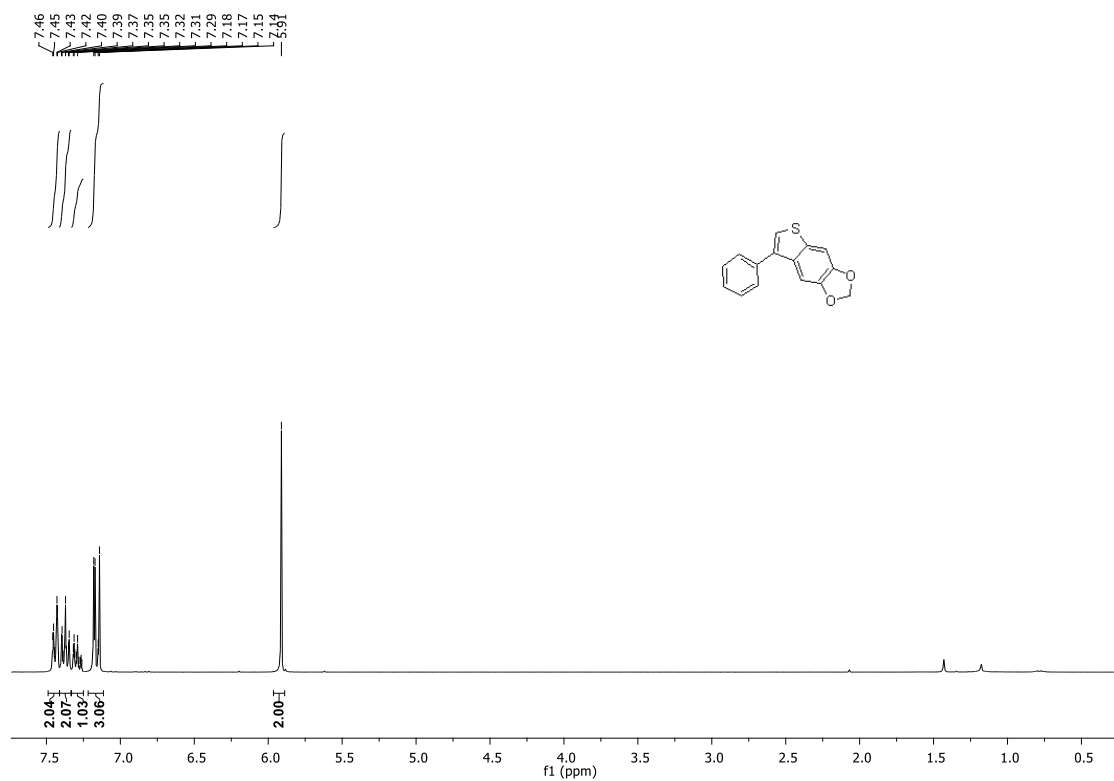
¹³C NMR (101 MHz, CDCl₃) of **4y**



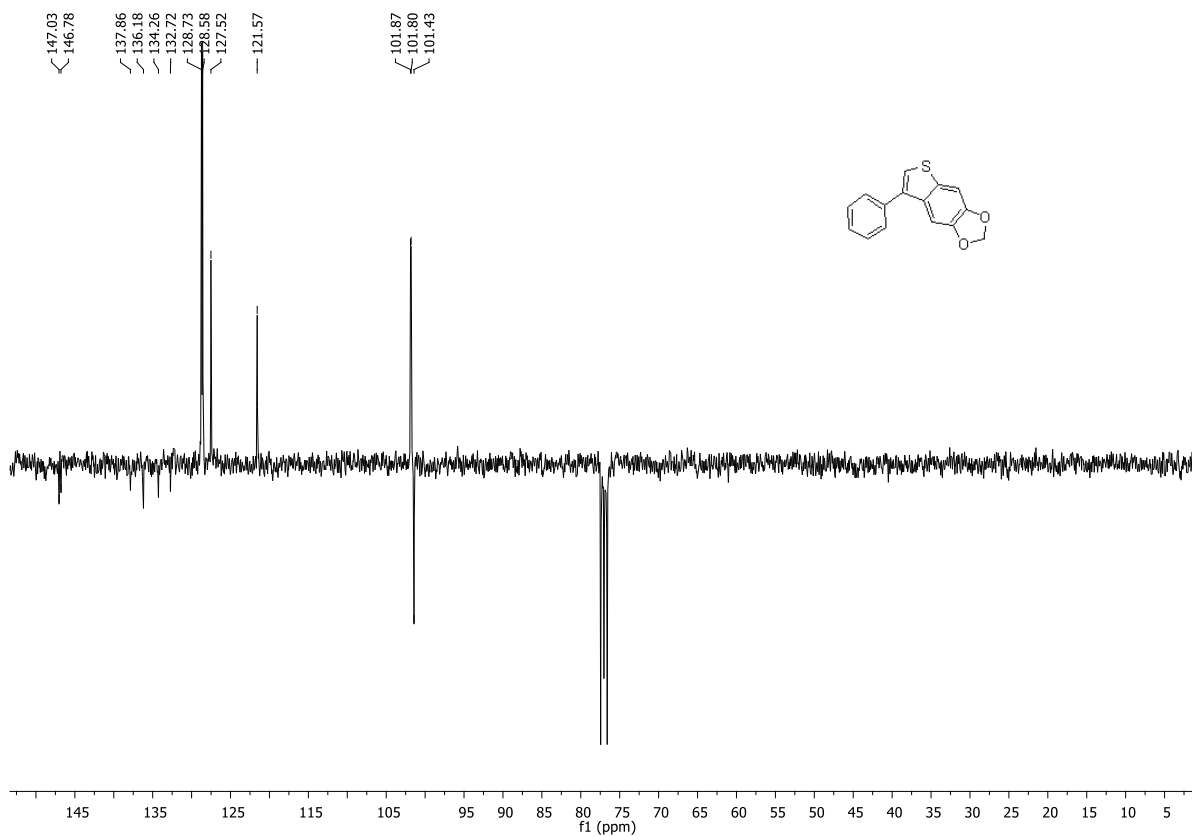
¹⁹F NMR (188 MHz, CDCl₃) of **4y**



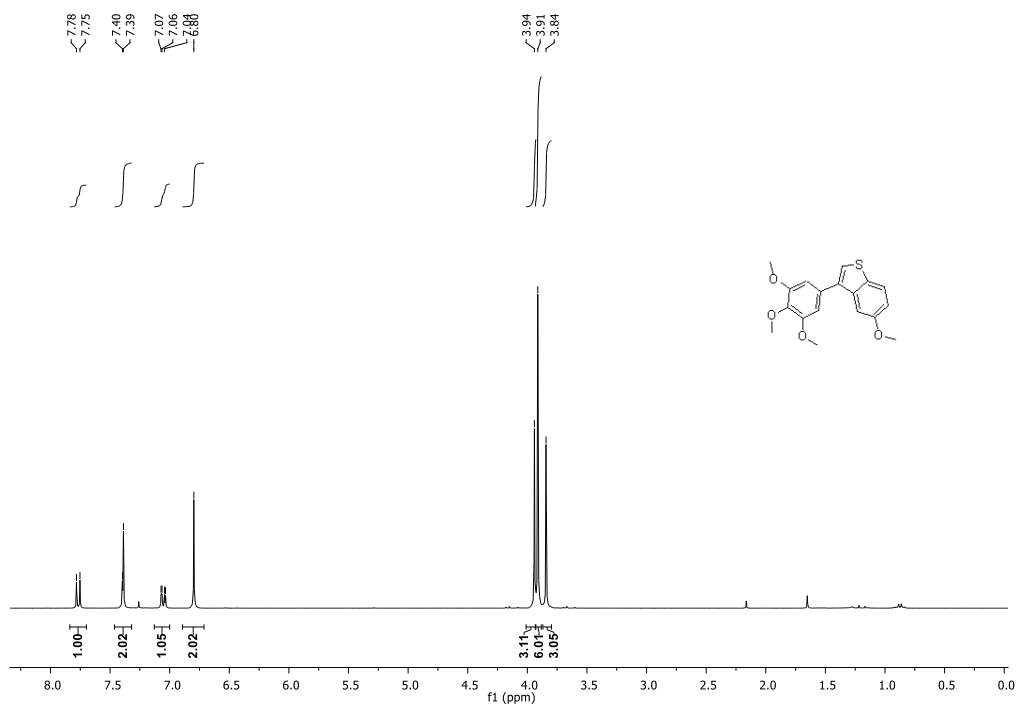
¹H NMR (300 MHz, CDCl₃) of **4z**



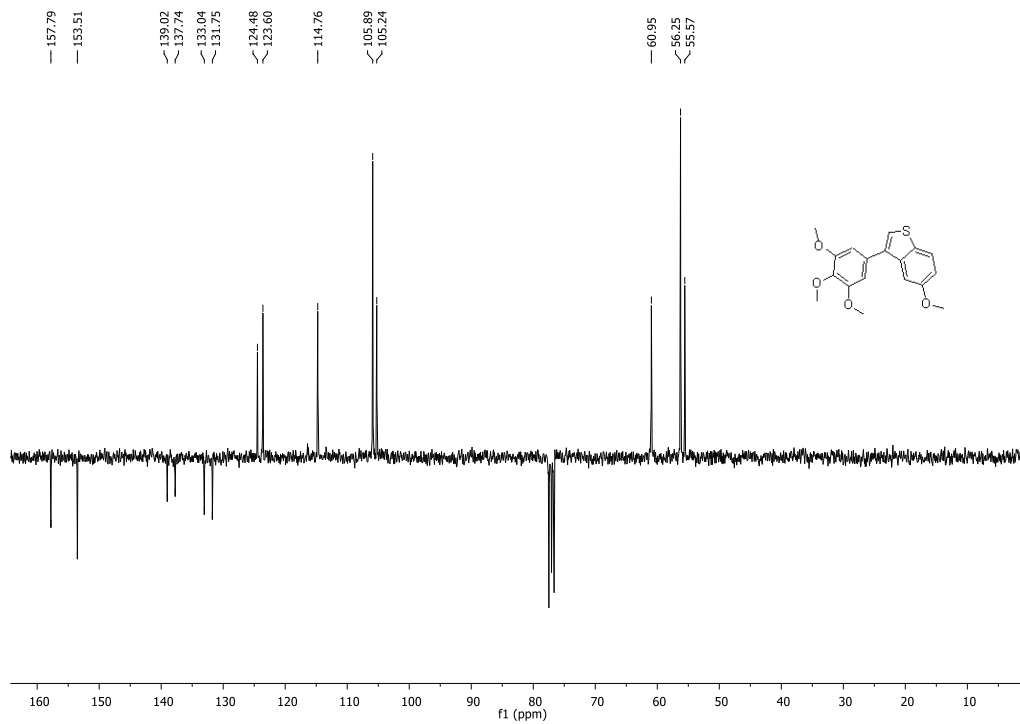
¹³C NMR (75 MHz, CDCl₃) of **4z**



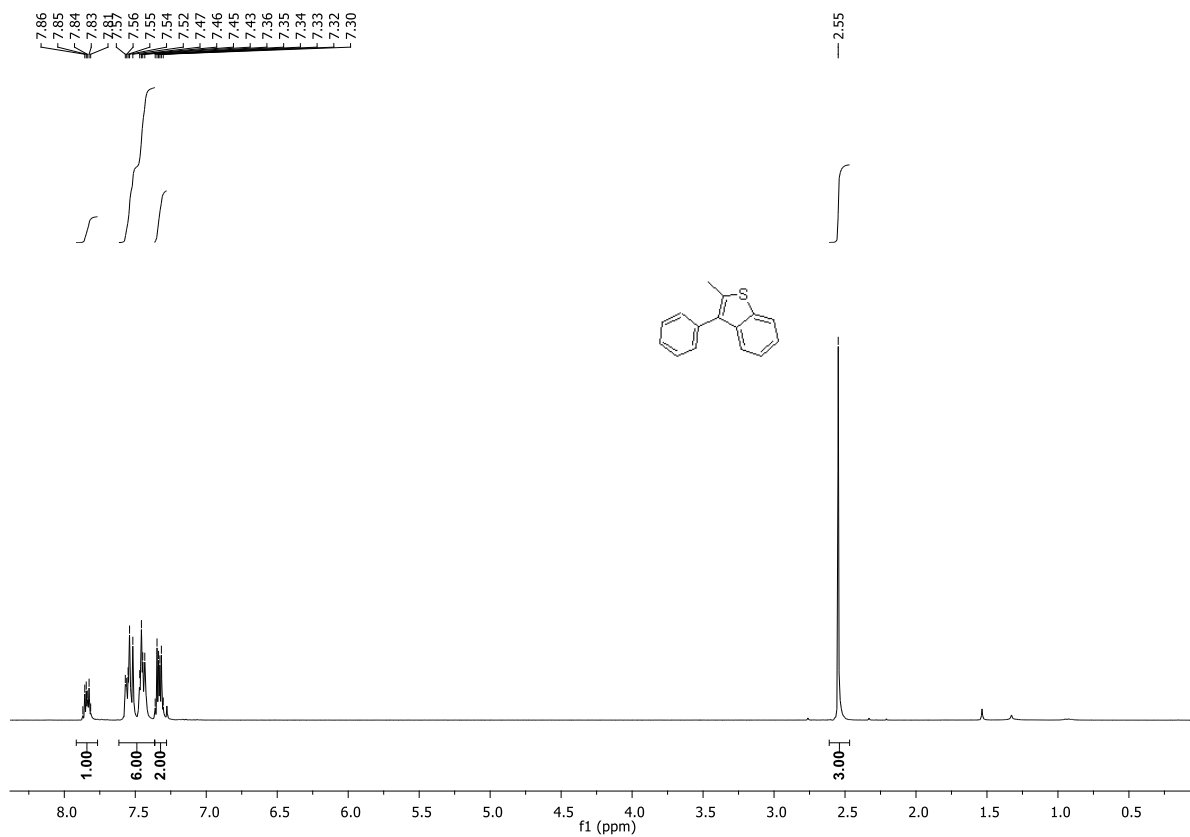
^1H NMR (300 MHz, CDCl_3) of 4aa



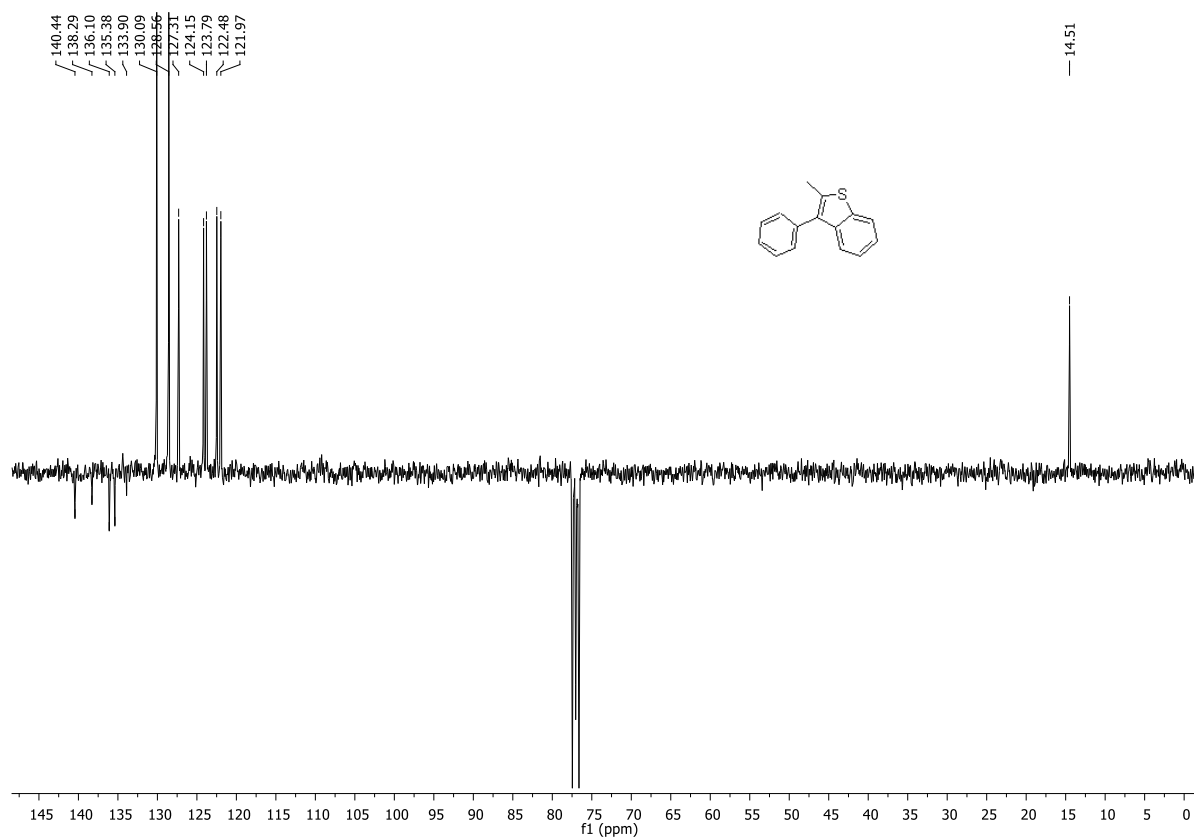
^{13}C NMR (75 MHz, CDCl_3) of 4aa



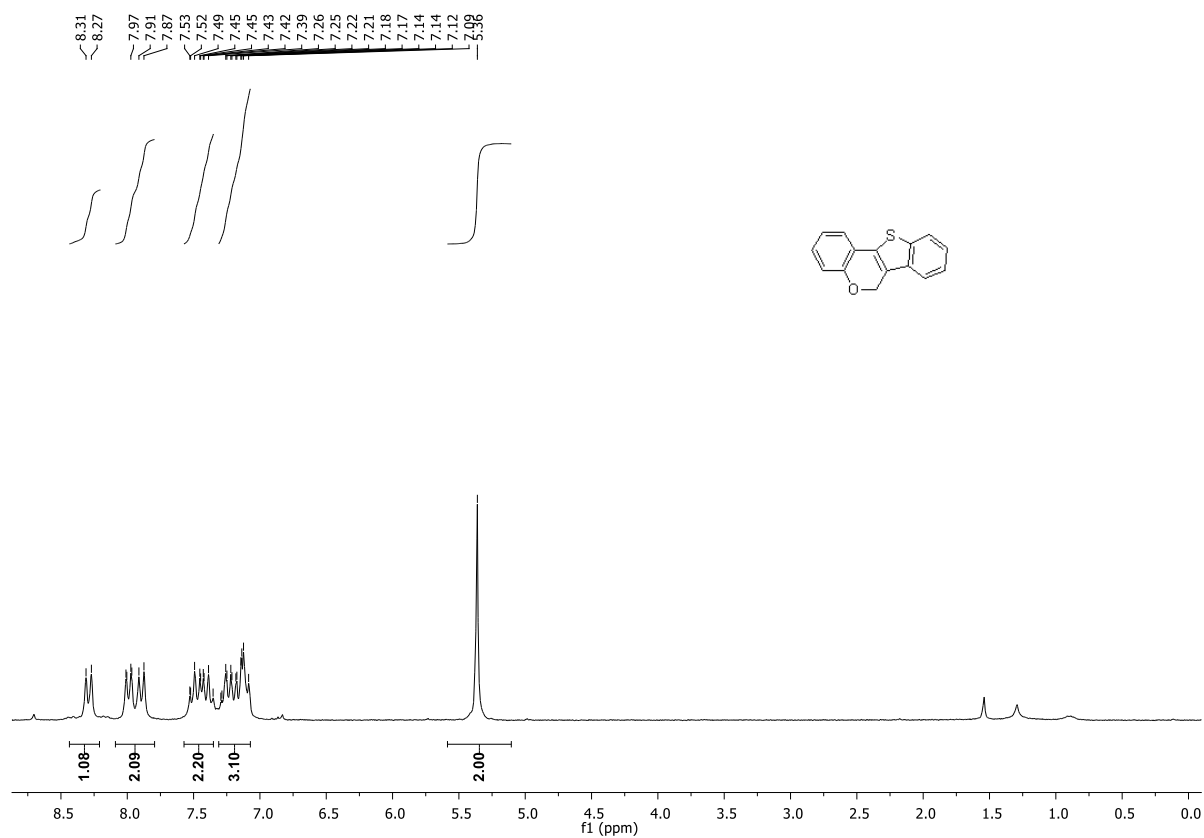
¹H NMR (300 MHz, CDCl₃) of **4ab**



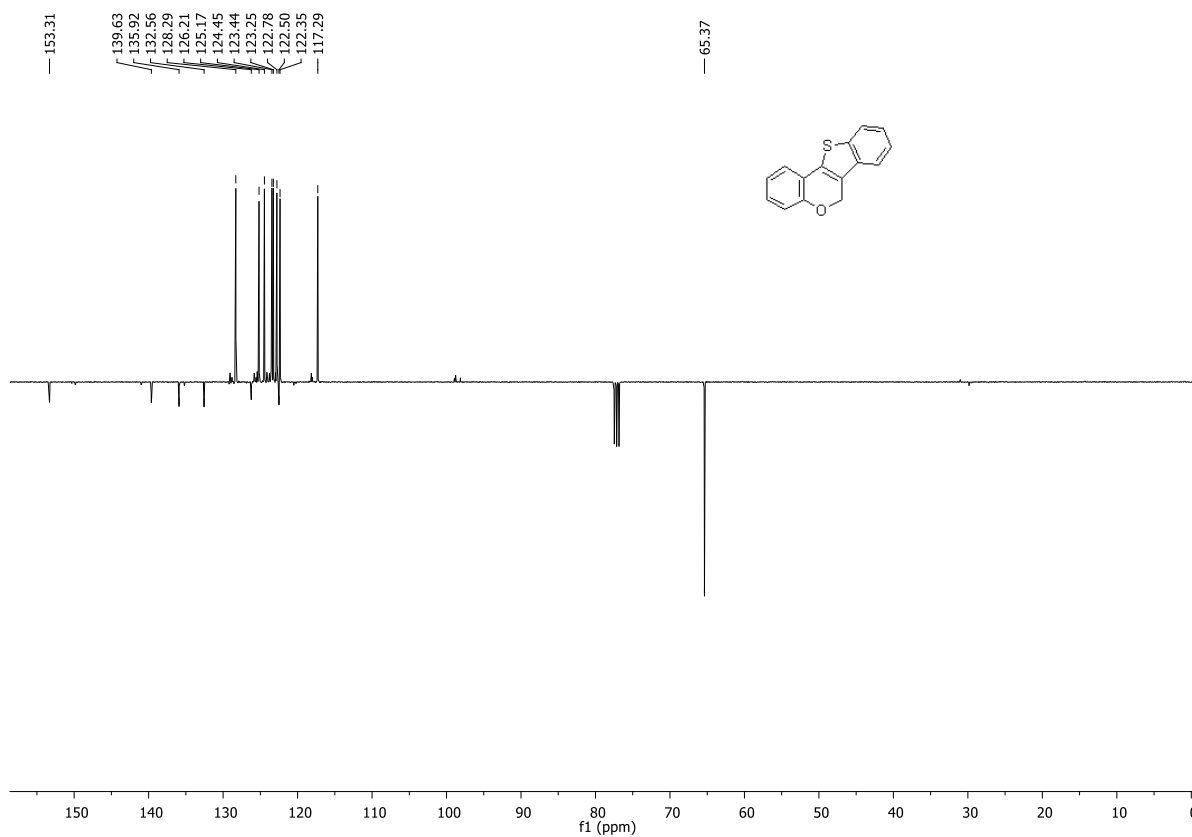
¹³C NMR (75 MHz, CDCl₃) of **4ab**



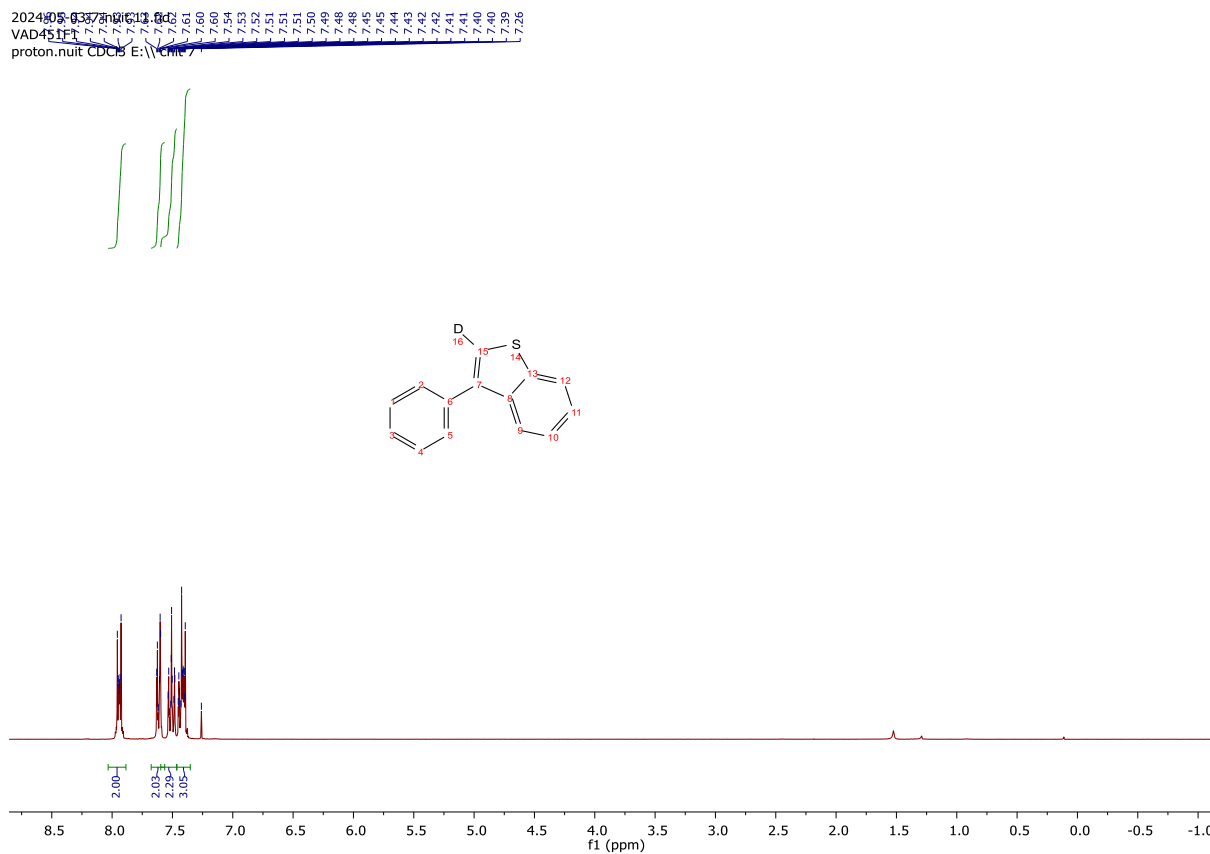
¹H NMR (200 MHz, CDCl₃) of **4ac**



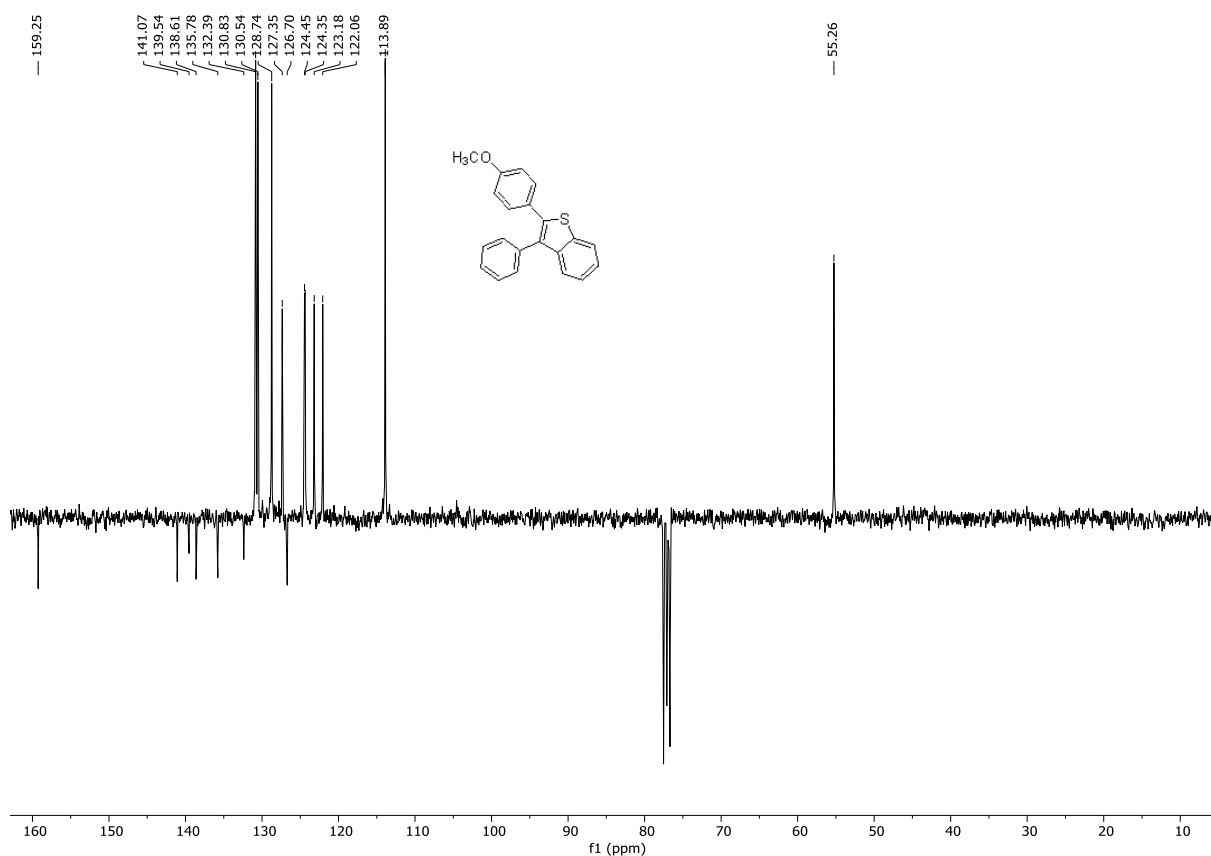
¹³C NMR (101 MHz, CDCl₃) of 4ac



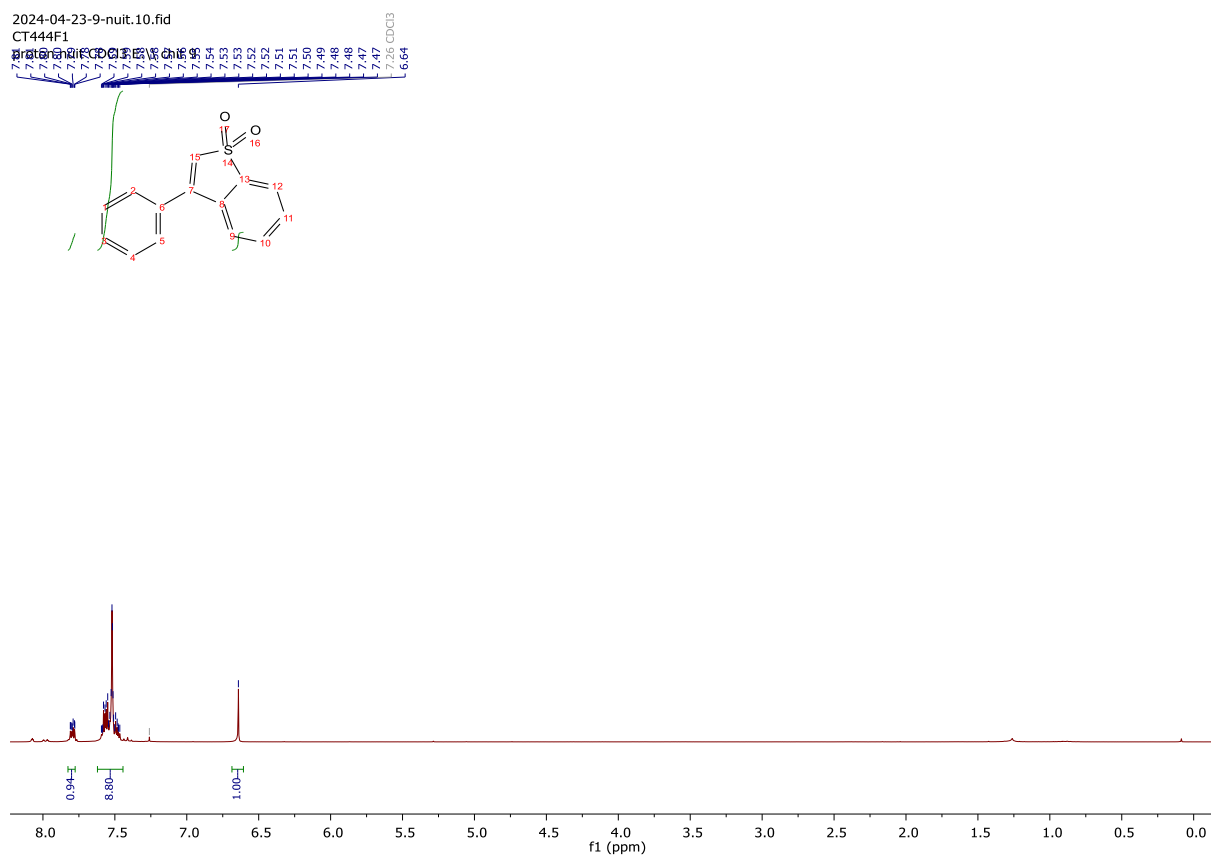
¹H NMR (300 MHz, CDCl₃) of 4a-D



^{13}C NMR (101 MHz, CDCl_3) of 5a



^1H NMR (300 MHz, CDCl_3) of 6a

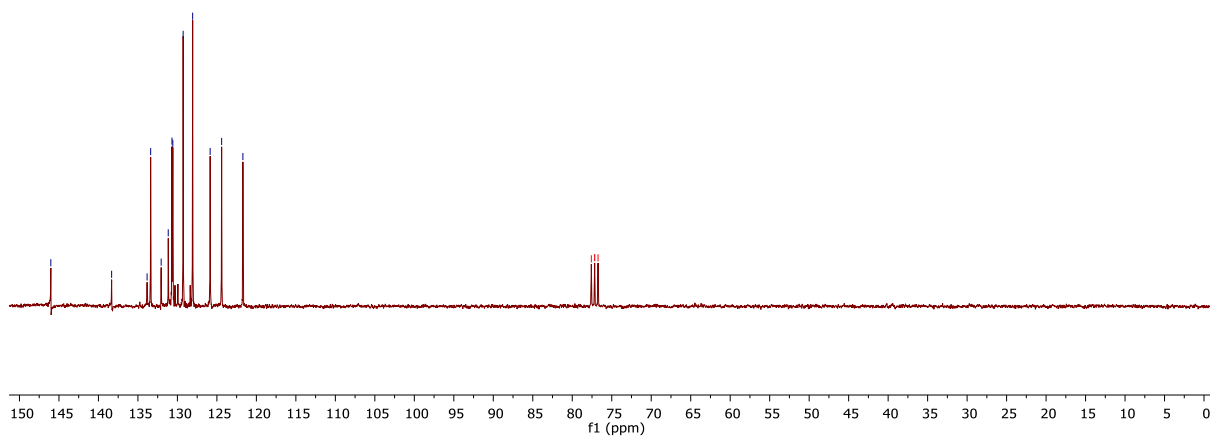
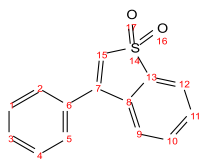


^{13}C NMR (75 MHz, CDCl_3) of 6a

2024-04-23-9-nuit.11.fid
CT444F1
udeft CDCl_3 E:

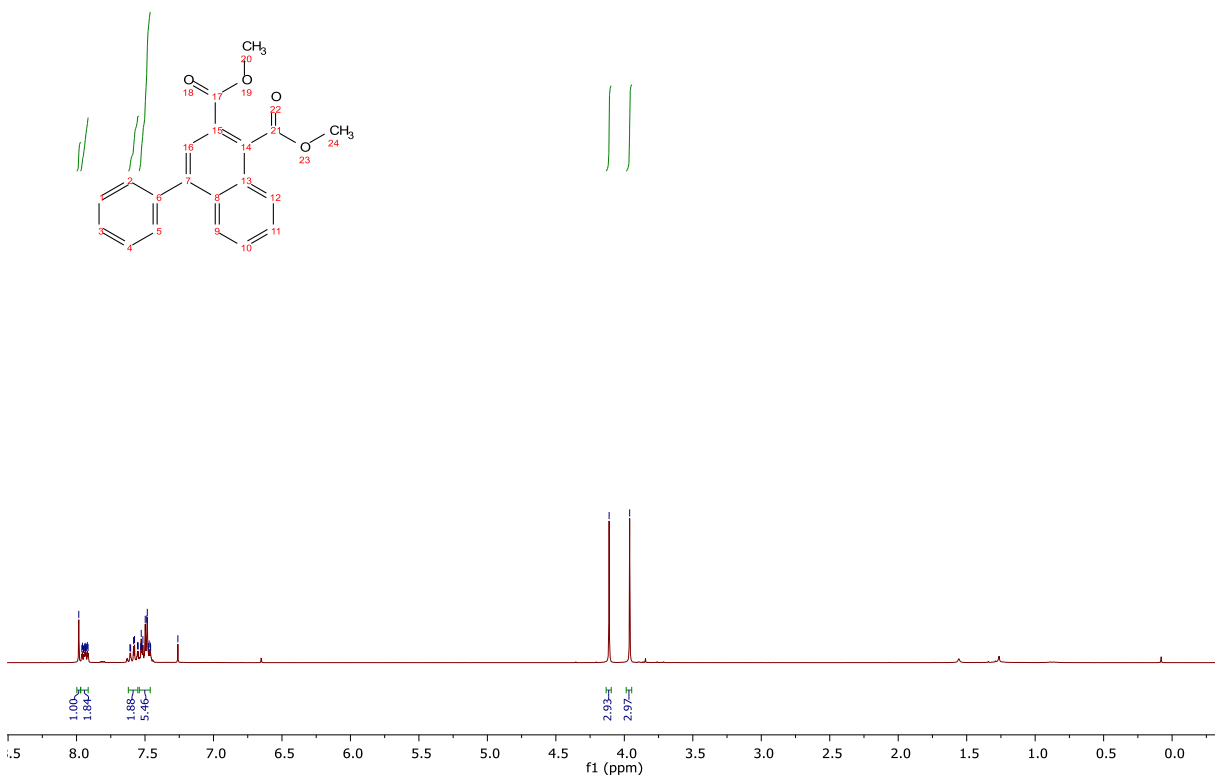
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132.86
131.16
130.69
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121.71

77.58 CDCl_3
77.16 CDCl_3
76.74 CDCl_3



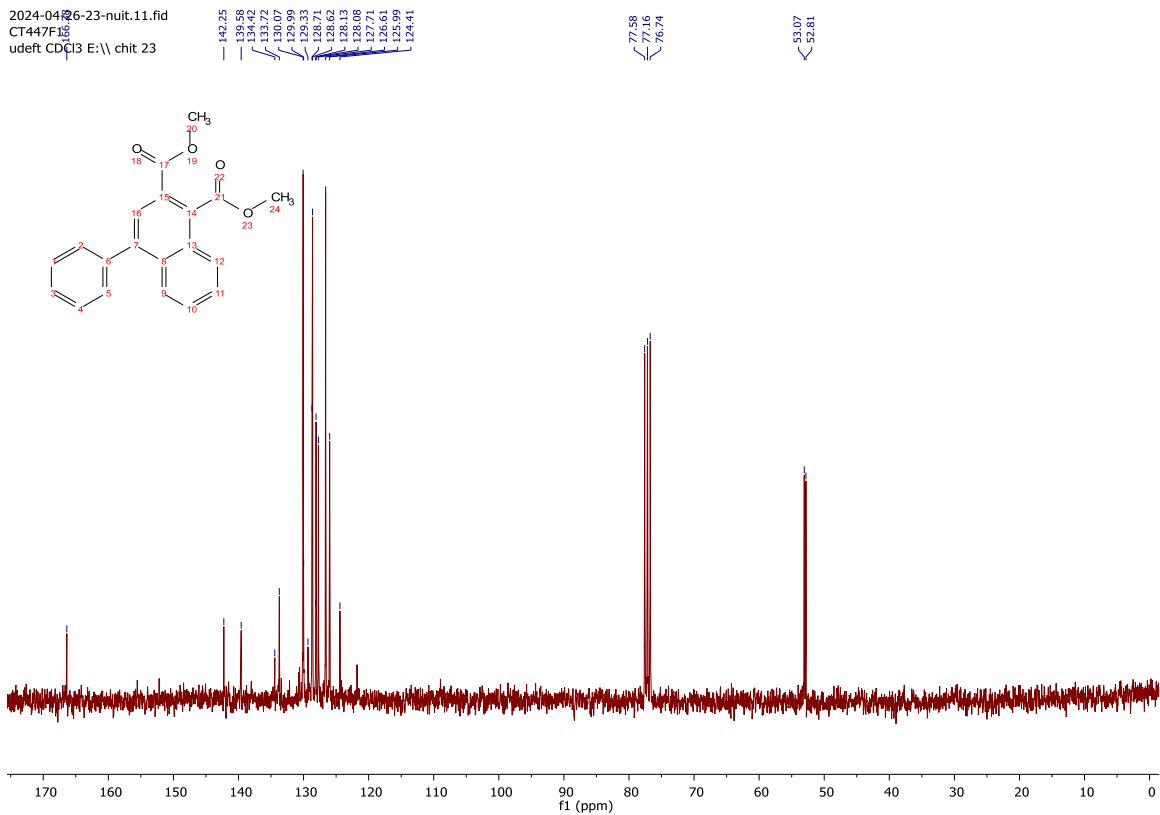
^1H NMR (300 MHz, CDCl_3) of 7a

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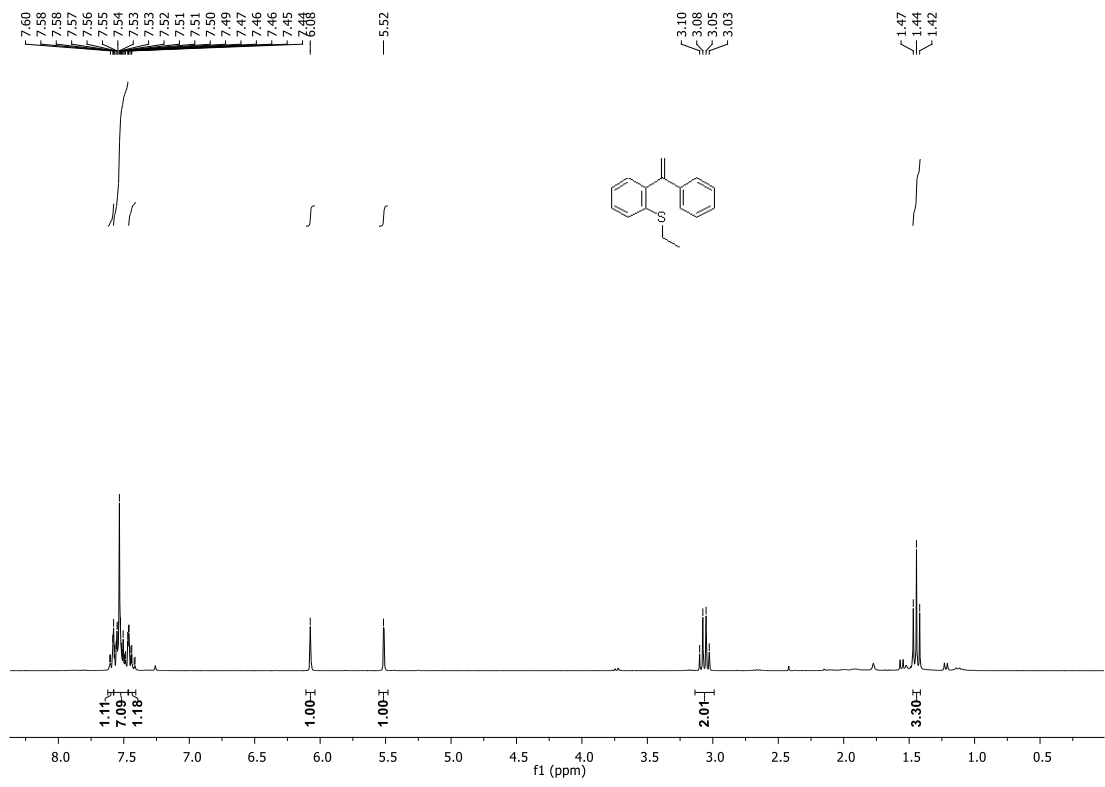


¹³C NMR (75 MHz, CDCl₃) of 7a

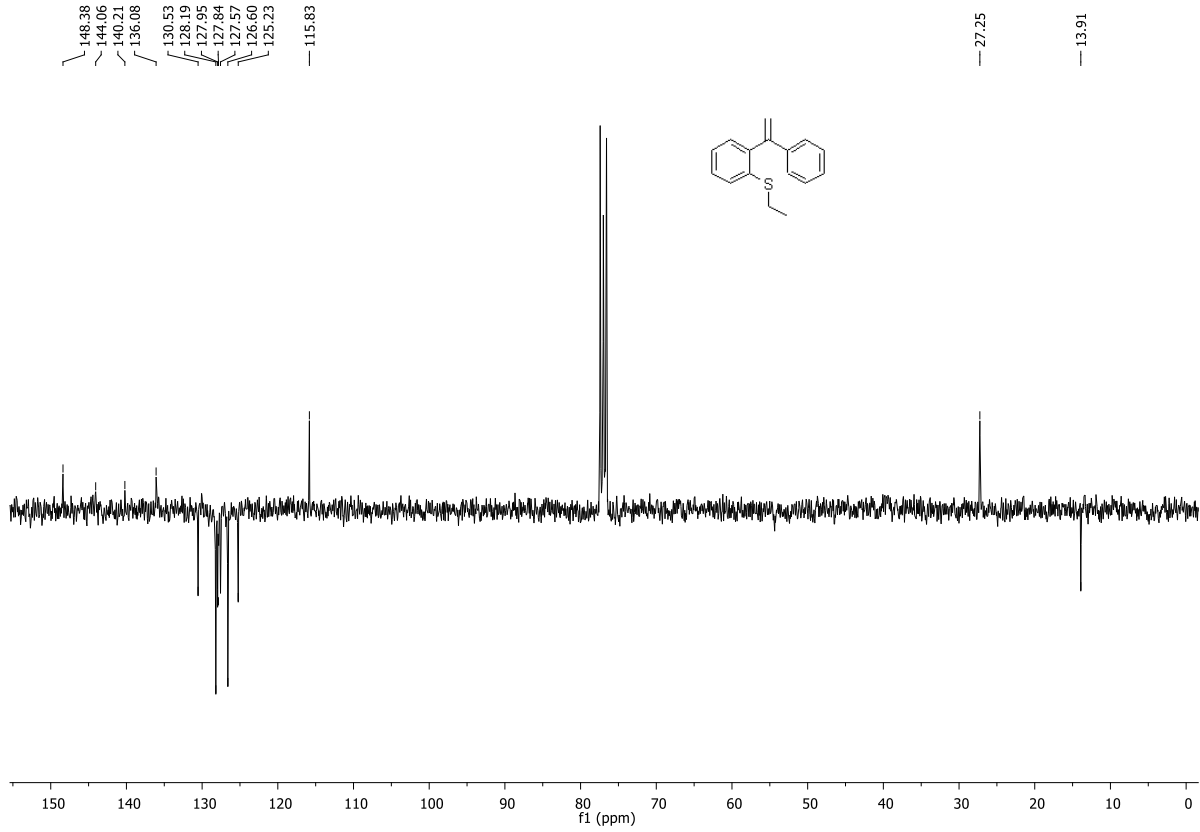
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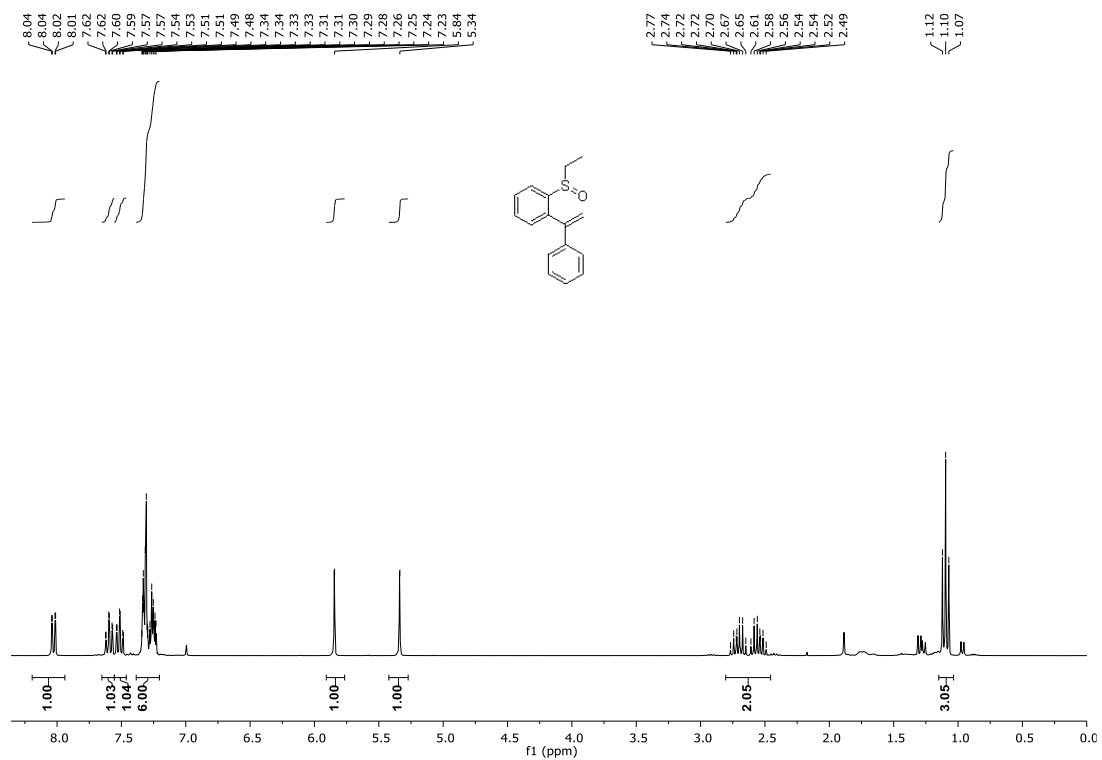
¹H NMR (300 MHz, CDCl₃) of 8a



¹³C NMR (75 MHz, CDCl₃) of 8a



¹H NMR (300 MHz, CDCl₃) of 9a



¹³C NMR (75 MHz, CDCl₃) of 9a

