

## Supporting Information for

### Palladium-catalyzed Synthesis of Fluorenones from Bis(2-bromophenyl)methanols

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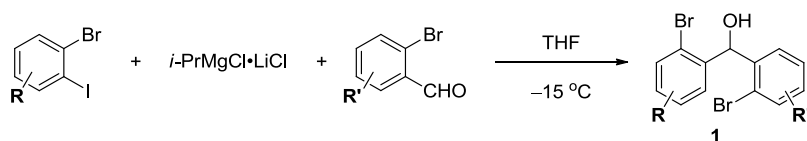
## *General*

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using standard Schlenk techniques or glovebox.

Toluene, DMSO, 1,4-dioxane, and THF were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were purchased and used as received.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Zhongke-Niujin 400 spectrometer at ambient temperature. IR spectra were recorded on a Thermo Fisher Nicolet 6700 FT-IR Analyzer. High-resolution mass spectroscopy data were obtained on an Agilent 6530 spectrometer at Suzhou Research Institute of LICP. Melting points were determined on an Electrothermal IA9000 Series Digital Melting Point Apparatus.

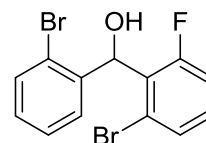
## General procedures of the synthesis of bis(2-bromophenyl)methanols 1



The preparation of **1** was adapted from literature procedures.<sup>1</sup> To a cooled (-15 °C) stirring solution of *i*-PrMgCl·LiCl (1 M in THF, 5.5 mL, 5.5 mmol) was added 2-bromoiodobenzene (5.0 mmol) in THF (20 mL). When the exchange was deemed complete for two hours, 2-bromobenzaldehyde (5.0 mmol) was added dropwisely with a syringe. The reaction was allowed to stir at -15 °C for additional 30 minutes. The reaction mixture was then diluted with ethyl acetate and quenched with 6 M HCl until the aqueous layer showed litmus red at which time an additional portion of water was added (20 mL). The phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated under attenuated pressure. The crude material was purified by flash chromatography using PE/EtOAc (25: 1) as eluent to give corresponding product. Characterization data of compounds **1a**<sup>1</sup> (CAS: 123335-02-4) and **1d**<sup>2</sup> (CAS: 2010218-53-6) are consistent with literature reported,

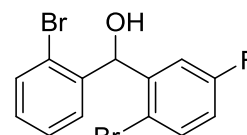
### (2-bromo-6-fluorophenyl)(2-bromophenyl)methanol (**1b**)

1.45 g, 81% yield, white solid, m.p. 92-93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.16 – 7.10 (m, 2H), 6.98 – 6.92 (m, 1H), 6.39 (d, *J* = 3.6 Hz, 1H), 3.00 (d, *J* = 2.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5 (d, *J* = 251.5 Hz), 140.2, 132.8, 130.3 (d, *J* = 9.7 Hz), 129.1, 129.0 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 3.9 Hz), 128.4 (d, *J* = 13.1 Hz), 127.0, 125.4 (d, *J* = 5.3 Hz), 122.6, 115.9 (d, *J* = 23.0 Hz), 73.4; IR (KBr, cm<sup>-1</sup>) 3269, 3064, 2926, 1569, 1453, 1242, 1015, 1067, 884, 866, 778, 721, 622; HRMS (ESI) calcd for C<sub>13</sub>H<sub>9</sub><sup>79</sup>Br<sup>81</sup>BrFNaO ([M+Na]<sup>+</sup>) 382.8881, found 382.8876.



### (2-bromo-5-fluorophenyl)(2-bromophenyl)methanol (**1c**)

0.56 g, 31% yield, m.p. 71-72 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.26 – 7.22 (m, 1H), 7.17 – 7.11 (m, 2H), 7.08 – 7.03 (m, 1H), 6.89 – 6.84 (m, 1H), 6.22 (s, 1H), 3.31 – 3.27 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.0 (d, *J* = 245.8 Hz), 143.1 (d, *J* = 6.8 Hz), 140.1, 134.0 (d, *J* = 7.7 Hz), 132.9, 129.6, 128.4, 127.7, 123.9, 117.5 (d, *J* = 3.0 Hz), 116.4 (d, *J* = 22.4 Hz), 116.0 (d, *J* = 24.1 Hz), 73.90; IR (KBr, cm<sup>-1</sup>) 3285, 2919, 2850, 1581, 1465, 1266, 1146, 1017, 749, 601; HRMS (ESI) calcd for C<sub>13</sub>H<sub>9</sub><sup>79</sup>Br<sup>81</sup>BrFNaO ([M+Na]<sup>+</sup>) 382.8881, found 382.8869.

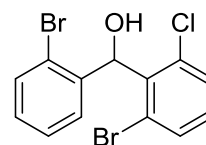


1. Wood, T. K.; Piers, W. E.; Keay, B. A.; Parvez, M. *Chem. Eur. J.* **2010**, *16*, 12199.

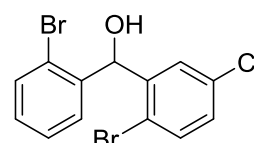
2. Vshyvenko, S.; Clapson, M. L.; Suzuki, I.; Hall, D. G. *ACS Med. Chem. Lett.*, **2016**, *7*, 1097.

**(2-bromo-6-chlorophenyl)(2-bromophenyl)methanol (1e)**

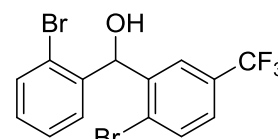
1.50 g, 87% yield, white solid, m.p. 105-106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.47 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.07 (td, *J* = 8.0, 1.6 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 3.30 (dd, *J* = 8.4, 1.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.4, 137.0, 135.3, 133.1, 132.6, 130.2, 129.8, 129.5, 129.2, 126.8, 125.7, 122.8, 74.9; IR (KBr, cm<sup>-1</sup>) 3385, 3062, 2922, 1556, 1432, 1180, 1015, 775, 749, 736; HRMS (ESI) calcd for C<sub>13</sub>H<sub>9</sub><sup>79</sup>Br<sup>81</sup>Br<sup>35</sup>ClNaO ([M+Na]<sup>+</sup>) 398.8586, found 398.8576.

**(2-bromo-5-chlorophenyl)(2-bromophenyl)methanol (1f)**

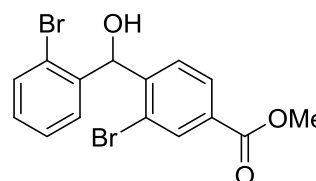
1.47 g, 79% yield, colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.57 (m, 2H), 7.35 – 7.29 (m, 4H), 7.23 – 7.18 (m, 1H), 6.36 (d, *J* = 4.0 Hz, 1H), 2.57 (d, *J* = 4.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.5, 139.8, 133.7, 133.5, 132.8, 129.4, 129.1, 128.5, 128.3, 127.5, 124.0, 121.2, 73.5; IR (KBr, cm<sup>-1</sup>) 3278, 3064, 2923, 1454, 1438, 1094, 1016, 811, 756, 740; HRMS (ESI) calcd for C<sub>13</sub>H<sub>8</sub><sup>79</sup>Br<sup>81</sup>BrCl ([M+H-H<sub>2</sub>O]<sup>+</sup>) 358.8661, found 358.8654.

**(2-bromo-5-(trifluoromethyl)phenyl)(2-bromophenyl)methanol (1g)**

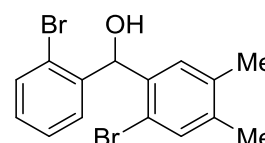
1.12 g, 70% yield, white solid, m.p. 99-100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (s, 1H), 7.66 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.58 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.27 – 7.22 (m, 1H), 7.20 – 7.14 (m, 1H), 7.09 – 7.04 (m, 1H), 6.37 (s, 1H), 2.95 – 2.89 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.1, 140.1, 133.5, 133.1, 130.1 (q, *J* = 32.9 Hz), 129.8, 128.6, 127.9, 127.2, 125.9 (q, *J* = 3.6 Hz), 125.4 (q, *J* = 3.7 Hz), 124.2, 123.8 (q, *J* = 270.8 Hz), 73.9; IR (KBr, cm<sup>-1</sup>) 3301, 2920, 1605, 1325, 1169, 1127, 1081, 1019, 826, 755; HRMS (ESI) calcd for C<sub>14</sub>H<sub>8</sub><sup>79</sup>Br<sup>81</sup>BrF<sub>3</sub> ([M+H-H<sub>2</sub>O]<sup>+</sup>) 392.8924, found 392.8916.

**methyl 3-bromo-4-((2-bromophenyl)(hydroxy)methyl)benzoate (1h)**

1.04 g, 52% yield, colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (s, 1H), 7.99 (d, *J* = 6.8 Hz, 1H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 6.0 Hz, 2H), 6.42 (s, 1H), 3.93 (s, 3H), 2.77 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.5, 145.8, 140.1, 133.6, 132.6, 130.4, 129.2, 128.3, 128.2, 128.2, 127.3, 123.8, 123.4, 73.5, 52.3; IR (KBr, cm<sup>-1</sup>) 3416, 3065, 2951, 1724, 1435, 1387, 1287, 1020, 755; HRMS (ESI) calcd for C<sub>15</sub>H<sub>13</sub><sup>79</sup>Br<sup>81</sup>BrO<sub>3</sub> ([M+H]<sup>+</sup>) 400.9211, found 400.9211.

**(2-bromo-4,5-dimethylphenyl)(2-bromophenyl)methanol (1i)**

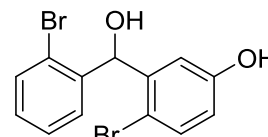
1.31 g, 71% yield, white solid, m.p. 110-111 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.11 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97 (s, 1H), 6.23 (s, 1H), 2.99 (s, 1H), 2.17 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C



NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.0, 138.1, 137.8, 136.0, 133.4, 132.7, 129.4, 129.0, 128.5, 127.3, 123.6, 120.4, 73.8, 19.4, 19.2; IR (KBr, cm<sup>-1</sup>) 3313, 3061, 2917, 1466, 1438, 1019, 755, 640; HRMS (ESI) calcd for C<sub>15</sub>H<sub>14</sub><sup>79</sup>Br<sup>81</sup>BrNaO ([M+Na]<sup>+</sup>) 392.9289, found 392.9286.

**4-bromo-3-((2-bromophenyl)(hydroxy)methyl)phenol (1j)**

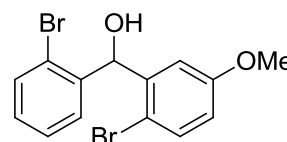
1.034 g, 58% yield, white solid, m.p. 92-93 °C. <sup>1</sup>H NMR (400 MHz, Acetone)  $\delta$  8.93 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.25 (d, *J* = 4.8 Hz, 1H), 5.25 (d, *J* = 5.2 Hz, 1H);



<sup>13</sup>C NMR (100 MHz, Acetone)  $\delta$  157.2, 143.3, 142.4, 133.3, 132.7, 129.2, 129.1, 127.5, 123.8, 116.4, 116.3, 112.2, 73.5; IR (KBr, cm<sup>-1</sup>) 3346, 2923, 2852, 1466, 1438, 1287, 1017, 752; HRMS (ESI) calcd for C<sub>13</sub>H<sub>10</sub><sup>79</sup>Br<sup>81</sup>BrNaO<sub>2</sub> ([M+Na]<sup>+</sup>) 380.8925, found 380.8923.

**(2-bromo-5-methoxyphenyl)(2-bromophenyl)methanol (1k)**

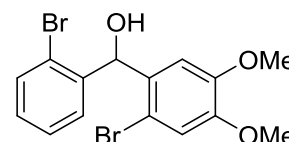
1.65 g, 88% yield, white solid, m.p. 79-80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.16 – 7.11 (m, 1H), 6.95 – 6.91 (m, 1H), 6.72 – 6.68 (m, 1H), 6.27 (s, 1H), 3.71 (d, *J* = 1.6 Hz, 3H), 2.97 (s, 1H);



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 141.8, 140.6, 133.3, 132.8, 129.3, 128.5, 127.5, 124.0, 114.6, 114.5, 113.8, 74.0, 55.3; IR (KBr, cm<sup>-1</sup>) 3373, 3064, 2934, 1572, 1467, 1294, 1235, 1012, 749; HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub><sup>79</sup>Br<sup>81</sup>BrNaO<sub>2</sub> ([M+Na]<sup>+</sup>) 392.9081, found 392.9073.

**(2-bromo-4,5-dimethoxyphenyl)(2-bromophenyl)methanol (1l)**

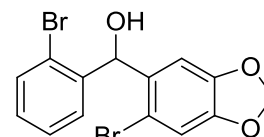
1.17 g, 58% yield, white solid, m.p. 150-151 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.04 (s, 1H), 6.89 (s, 1H), 6.34 (d, *J* = 4.0 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.56 (d, *J* = 3.8 Hz, 1H);



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 148.4, 141.1, 132.9, 132.8, 129.4, 128.5, 127.6, 123.8, 115.4, 113.7, 111.2, 74.0, 56.1, 56.0; IR (KBr, cm<sup>-1</sup>) 3357, 2920, 2849, 1501, 1437, 1261, 1155, 1026, 748; HRMS (ESI) calcd for C<sub>15</sub>H<sub>14</sub><sup>79</sup>Br<sup>81</sup>BrNaO<sub>3</sub> ([M+Na]<sup>+</sup>) 424.9187, found 424.9177.

**(6-bromobenzo[d][1,3]dioxol-5-yl)(2-bromophenyl)methanol (1m)**

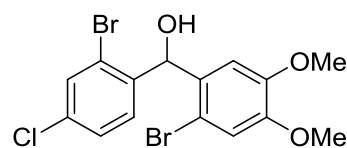
1.63 g, 84% yield, white solid, m.p. 111-112 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.48 (m, 1H), 7.46 – 7.37 (m, 1H), 7.35 – 7.28 (m, 1H), 7.20 – 7.12 (m, 1H), 7.08 – 6.89 (m, 1H), 6.81 – 6.64 (m, 1H), 6.34 – 6.22 (m, 1H), 5.97 – 5.92 (m, 2H), 2.65 – 2.57 (m, 1H);



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.9, 147.5, 141.0, 134.2, 132.9, 129.3, 128.4, 127.6, 123.5, 114.6, 112.8, 108.6, 101.8, 74.0; IR (KBr, cm<sup>-1</sup>) 3331, 2920, 1476, 1236, 1106, 1038, 933, 867, 753; HRMS (ESI) calcd for C<sub>14</sub>H<sub>10</sub><sup>79</sup>Br<sup>81</sup>BrNaO<sub>3</sub> ([M+Na]<sup>+</sup>) 408.8874, found 408.8862.

**(2-bromo-4,5-dimethoxyphenyl)(2-bromo-4-chlorophenyl)methanol (1n)**

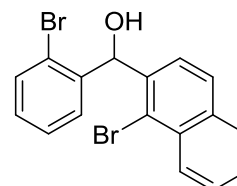
1.42 g, 65% yield, white solid, m.p. 131-132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (s, 1H), 7.32 – 7.26 (m, 2H), 7.04 (s, 1H), 6.85 (s, 1H), 6.28 (d, *J* = 3.6 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 2.53 (d, *J* = 4.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.0, 148.4, 139.8, 134.1, 132.4, 132.3, 129.2,



127.7, 124.0, 115.4, 113.6, 110.8, 73.4, 56.1, 55.9; IR (KBr, cm<sup>-1</sup>) 3439, 2930, 2839, 1502, 1463, 1381, 1262, 1156, 1025, 758, 597; HRMS (ESI) calcd for C<sub>15</sub>H<sub>13</sub><sup>79</sup>Br<sup>81</sup>BrClNaO<sub>3</sub> ([M+Na]<sup>+</sup>) 458.8797, found 458.8794.

**(1-bromonaphthalen-2-yl)(2-bromophenyl)methanol (1o)**

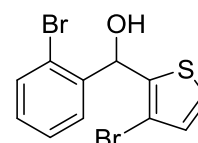
1.412 g, 72% yield, white solid, m.p. 90-91 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.49 – 7.45 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 3.04 (s, 1H); <sup>13</sup>C NMR (100



MHz, CDCl<sub>3</sub>) δ 141.0, 138.7, 134.0, 132.8, 132.2, 129.2, 128.7, 128.1, 127.8, 127.5, 127.3, 126.7, 125.2, 124.1, 123.8, 74.9; IR (KBr, cm<sup>-1</sup>) 3262, 3054, 2919, 1437, 1255, 1038, 1018, 967, 812, 749; HRMS (ESI) calcd for C<sub>17</sub>H<sub>12</sub><sup>79</sup>Br<sup>81</sup>BrNaO ([M+Na]<sup>+</sup>) 414.9132, found 414.9117.

**(2-bromophenyl)(3-bromothiophen-2-yl)methanol (1p)**

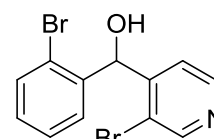
1.40 g, 81% yield, white solid, m.p. 58-59 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.14 (m, 2H), 6.98 (d, *J* = 4.0 Hz, 1H), 6.40 (s, 1H), 2.64 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.7, 140.6, 132.8, 130.1, 129.6,



127.7, 127.7, 125.9, 122.8, 110.0, 70.0; IR (KBr, cm<sup>-1</sup>) 3554, 3356, 3107, 1437, 1150, 1014, 877, 758, 715, 679; HRMS (ESI) calcd for C<sub>11</sub>H<sub>8</sub><sup>79</sup>Br<sup>81</sup>BrNaOS ([M+Na]<sup>+</sup>) 370.8540, found 370.8539.

**(2-bromophenyl)(3-bromopyridin-4-yl)methanol (1q)**

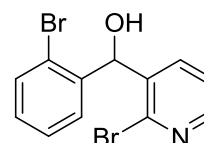
1.08 g, 63% yield, white solid, m.p. 127-128 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.64 (s, 1H), 8.51 (d, *J* = 3.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.24 – 7.18 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.34 (s, 1H), 3.36 (s, 1H); <sup>13</sup>C NMR (100 MHz,



Acetone) δ 152.4, 151.7, 149.5, 141.5, 133.7, 130.5, 129.9, 128.6, 124.7, 124.3, 122.3, 73.6; IR (KBr, cm<sup>-1</sup>) 3199, 2826, 1585, 1438, 1399, 1021, 755, 648; HRMS (ESI) calcd for C<sub>12</sub>H<sub>10</sub><sup>79</sup>Br<sup>81</sup>BrNO ([M+H]<sup>+</sup>) 343.9109, found 343.9104.

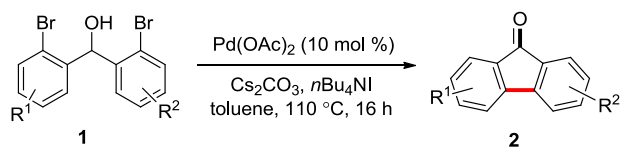
**(2-bromophenyl)(2-bromopyridin-3-yl)methanol (1r)**

0.91 g, 57% yield, white solid, m.p. 100-101 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 3.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 – 7.19 (m, 1H), 6.37 (d, *J* = 4.0 Hz, 1H), 2.97 (s, 1H); <sup>13</sup>C NMR (100 MHz, Acetone) δ 149.0, 143.4, 141.4, 139.6,



137.3, 132.9, 129.5, 128.9, 127.7, 123.5, 123.3, 72.8; IR (KBr,  $\text{cm}^{-1}$ ) 3386, 2923, 1560, 1400, 1053, 1020, 791, 756, 744, 669; HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{10}^{79}\text{Br}^{81}\text{BrNO}$  ( $[\text{M}+\text{H}]^+$ ) 343.9109, found 343.9102.

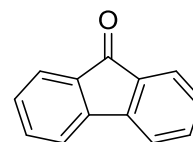
## General procedure for the synthesis of 9-Fluorenones 2



To a 25-mL flask was added Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol), bis(2-bromophenyl)methanol (0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (163 mg, 0.5 mmol), TBAI (185 mg, 0.50 mmol) and dry toluene (2.0 mL), the reaction was allowed to stirred at 110 °C for 16 hours. After cooling, the reaction mixture was diluted with ethyl acetate, passed through a pad of Celite, and concentrated under attenuated pressure. The residue was purified by column chromatography on silica gel (hexane/ ethyl acetate = 20: 1) to give corresponding fluorenone.

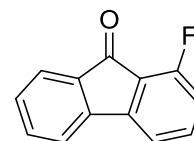
### 9H-fluoren-9-one (2a)<sup>3</sup> [CAS: 486-25-9]

24.5 mg, 70% yield, yellow solid, m.p. 80-82 °C (lit.<sup>4</sup> 80-82 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.28 – 7.23 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.8, 144.3, 134.6, 134.0, 128.9, 124.2, 120.2.



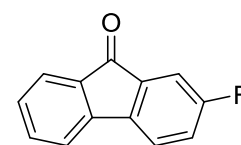
### 1-fluoro-9H-fluoren-9-one (2b)<sup>5</sup> [1514-16-5]

17.4 mg, 43% yield, yellow solid, m.p. 104-106 °C (lit.<sup>6</sup> 110-112 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.47 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 6.94 (t, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.2, 159.3 (d, *J* = 262.0 Hz), 146.3 (d, *J* = 3.3 Hz), 143.4 (d, *J* = 3.4 Hz), 137.0 (d, *J* = 8.5 Hz), 133.6, 132.9, 128.7, 123.5, 119.6, 119.9 (d, *J* = 12.8 Hz), 117.5 (d, *J* = 20.7 Hz), 116.4 (d, *J* = 2.7 Hz).



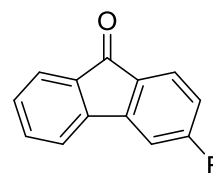
### 2-fluoro-9H-fluoren-9-one (2c)<sup>3</sup> [CAS: 343-01-1]

26.3 mg, 68%, yellow solid, m.p. 108-110 °C (lit.<sup>7</sup> 113-115 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.34 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.17 (td, *J* = 8.4, 2.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.3, 163.4 (d, *J* = 248.4 Hz), 143.7, 140.0 (d, *J* = 2.7 Hz), 136.1 (d, *J* = 7.2 Hz), 134.9, 134.1 (d, *J* = 2.2 Hz), 128.6, 124.4, 121.5 (d, *J* = 7.9 Hz), 120.7 (d, *J* = 23.1 Hz), 120.0, 111.7 (d, *J* = 23.5 Hz).



### 3-fluoro-9H-fluoren-9-one (2d)<sup>5</sup> [CAS: 1514-15-4]

16.4 mg, 41% yield, yellow solid, m.p. 115-117 °C (lit.<sup>8</sup> 121-123 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.62 (m, 2H), 7.53 – 7.48 (m, 2H), 7.34 (td, *J* = 7.2, 2.0 Hz, 1H), 7.20 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.95 (td, *J* =



3. Fukuyama, T.; Maetani, S.; Miyagawa, K.; Ryu, I. *Org. Lett.* **2014**, *16*, 3216.

4. Tilly, D.; Fu, J.-m.; Zhao, B.-p.; Alessi, M.; Castanet, A.-S.; Snieckus, V.; Mortier, J. *Org. Lett.* **2010**, *12*, 68.

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7. Zhang, X.; Ji, X.; Jiang, S.; Liu, L.; Weeks, B. L.; Zhang, Z. *Green Chem.* **2011**, *13*, 1891.

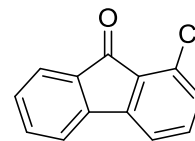
8. Thirunavukkarasu, V. S.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9462.



9.2, 2.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.0, 167.2 (d,  $J = 253.8$  Hz), 147.4 (d,  $J = 9.8$  Hz), 142.7, 134.7, 134.6, 130.1 (d,  $J = 2.5$  Hz), 129.7, 126.3 (d,  $J = 10.2$  Hz), 124.2, 120.5, 115.4 (d,  $J = 23.2$  Hz), 108.3 (d,  $J = 24.2$  Hz).

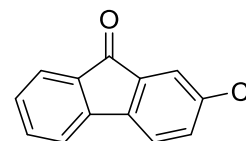
**1-chloro-9H-fluoren-9-one (2e)<sup>9</sup> [CAS: 36804-56-5]**

9.8 mg, 25% yield, yellow solid, m.p. 138-140 °C (lit.<sup>10</sup> 138-139 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 7.2$  Hz, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.38 (m, 2H), 7.35 (t,  $J = 7.2$  Hz, 1H), 7.23 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8, 146.4, 142.5, 135.2, 134.7, 133.8, 132.6, 130.9, 129.6, 129.4, 124.4, 120.4, 118.7.



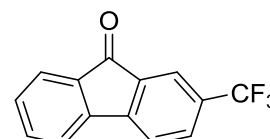
**2-chloro-9H-fluoren-9-one (2f)<sup>3</sup> [CAS: 3096-47-7]**

15.4 mg, 35% yield, yellow solid, m.p. 125-125 °C (lit.<sup>11</sup> 125-126 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 7.2$  Hz, 1H), 7.62 (s, 1H), 7.51 (d,  $J = 3.6$  Hz, 2H), 7.46 (s, 2H), 7.35 – 7.29 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.5, 143.7, 142.6, 135.6, 135.0, 134.2, 133.9, 129.3, 124.7, 124.6, 121.4, 120.4.



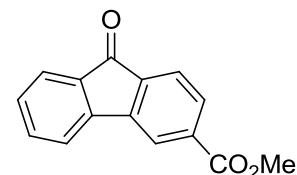
**2-(trifluoromethyl)-9H-fluoren-9-one (2g)<sup>3</sup> [CAS: 22052-25-1]**

25.8 mg, 52% yield, yellow solid, m.p. 120-122 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.72 (d,  $J = 8.0$  Hz, 1H), 7.67 (d,  $J = 7.2$  Hz, 1H), 7.59 – 7.50 (m, 3H), 7.38 – 7.33 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.0, 147.3, 143.0, 135.1, 134.4, 134.2, 131.5 (q,  $J = 3.6$  Hz), 131.3 (q,  $J = 32.7$  Hz), 130.2, , 124.7, 123.6 (d,  $J = 270.7$  Hz), 121.1 (d,  $J = 3.6$  Hz), 121.1, 120.4.



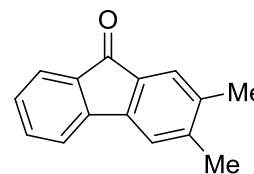
**methyl 9-oxo-9H-fluorene-3-carboxylate (2h) [CAS: 19063-40-2]**

11.9 mg, 25%, yellow solid, m.p. 125-127 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (s, 1H), 8.00 (d,  $J = 7.6$  Hz, 1H), 7.71 (t,  $J = 7.6$  Hz, 2H), 7.62 (d,  $J = 7.6$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 1H), 3.98 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.9, 166.1, 144.3, 143.7, 137.3, 135.5, 135.1, 134.0, 130.7, 129.5, 124.5, 123.9, 121.1, 120.7, 52.5; IR (KBr,  $\text{cm}^{-1}$ ) 3401, 1723, 1710, 1431, 1280, 1250, 1106, 748, 730, 668; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{11}\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ) 239.0708, found 239.0705.



**2,3-dimethyl-9H-fluoren-9-one (2i)<sup>12</sup> [CAS: 4627-17-2]**

17.7 mg, 42% yield, yellow solid, m.p. 107-109 °C (lit.<sup>13</sup> 109-110 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 7.2$  Hz, 1H), 7.46 – 7.41 (m, 3H), 7.28 (s, 1H), 7.23 (dd,  $J = 7.6, 4.0$  Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.1, 144.6, 144.2, 142.5, 137.6, 134.6, 134.4, 132.3, 128.5, 125.5, 124.0, 121.8, 119.8, 20.7, 19.9.



9. Thirunavukkarasu, V. S.; Cheng, C. H. *Chem. Eur. J.* **2011**, *17*, 14723.

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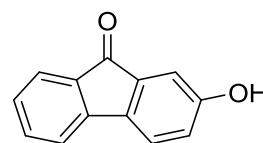
11. Beaven, G. H.; Mare, P. B. D. D. I.; Johnson, E. A.; Klassen, N. V. *J. Chem. Soc.* **1961**, 988.

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**2-hydroxy-9H-fluoren-9-one (2j) [CAS: 6949-73-1]**

17.3 mg, 42%, yellow solid, m.p. 197-199 °C. <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.10 (s, 1H), 7.63 – 7.57 (m, 2H), 7.55 – 7.50 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.98 – 6.92 (m, 2H); <sup>13</sup>C NMR (100 MHz, Acetone) δ 193.9, 159.8, 146.0, 136.8, 136.6, 135.9, 134.9, 128.6,

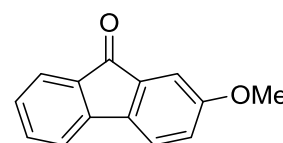


124.5, 122.9, 121.7, 120.6, 111.8; IR (KBr, cm<sup>-1</sup>) 3220, 2921, 1681, 1597, 1449, 1385, 1288, 849, 817, 760, 735; HRMS (ESI) calcd for C<sub>13</sub>H<sub>9</sub>NaO<sub>2</sub> ([M+Na]<sup>+</sup>) 219.0422, found 219.0430.

**2-methoxy-9H-fluoren-9-one (2k) <sup>3</sup> [CAS: 3133-07-1]**

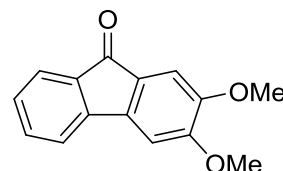
26.9 mg, 64% yield, yellow solid, m.p. 71-73 °C (lit.<sup>14</sup> 72-74 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.22 – 7.17 (m, 2H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.85 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.8, 160.7, 144.8, 136.9, 135.8, 134.8, 134.2, 127.8, 124.2, 121.3, 120.2, 119.5, 109.3, 55.6;

**2,3-dimethoxy-9H-fluoren-9-one (2l)<sup>15</sup> [CAS: 2041-27-2]**

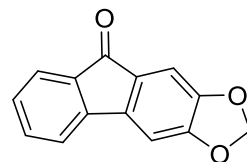
35.9 mg, 74% yield, orange solid, m.p. 157-159 °C (lit.<sup>16</sup> 160-161 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.24 – 7.15 (m, 2H), 7.00 (s, 1H), 4.02 (s, 3H), 3.93 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.0, 154.4, 149.5, 143.8, 139.3, 134.6, 134.1, 128.0, 126.6, 123.5, 119.0, 106.9, 103.2, 56.2, 56.1.

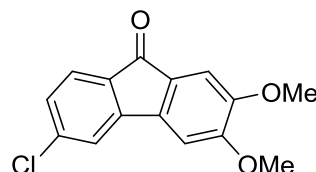
**9H-fluoreno[2,3-d][1,3]dioxol-9-one (2m)<sup>4</sup> [CAS: 66396-08-5]**

29.7 mg, 65% yield, orange solid, m.p. 150-152 °C (lit.<sup>5</sup> 145-147 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.07 (s, 1H), 6.93 (s, 1H), 6.05 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.3, 153.3, 148.4, 143.6, 141.7, 134.7, 134.3, 128.6, 128.3, 123.7, 119.2, 105.1, 102.2, 101.7.

**6-chloro-2,3-dimethoxy-9H-fluoren-9-one (2n)**

18.9 mg, 35% yield, orange solid, m.p. 160-162 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.21 (s, 1H), 7.18 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.99 (s, 1H), 4.03 (s, 3H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.6, 154.5, 150.1, 145.6, 140.4, 138.0, 132.9, 127.8, 127.1,



124.6, 119.8, 107.0, 103.4, 56.4, 56.2; IR (KBr, cm<sup>-1</sup>) 3398, 3077, 2961, 2928, 1709, 1592, 1499, 1414, 1289, 1215, 1057, 1026, 898, 862, 777, 637; HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>ClO<sub>3</sub> ([M+H]<sup>+</sup>) 275.0475, found 275.0470.

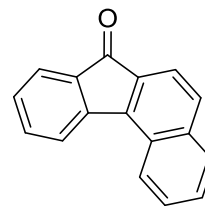
14. Dickinson, J. D.; Eaborn, C. *J. Chem. Soc.* **1959**, 2337.

15. Liu, T. P.; Liao, Y. X.; Xing, C. H.; Hu, Q. S. *Org. Lett.*, **2011**, *13*, 2452.

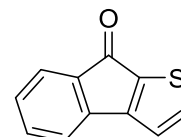
16. Koelsch, C. F.; Flesch, R. N. *J. Org. Chem.* **1955**, *20*, 1270.

**7H-benzo[*c*]fluoren-7-one (2o) [CAS: 6051-98-5]**

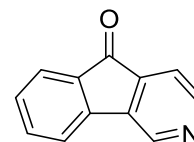
24.7 mg, 54% yield, yellow solid, m.p. 118-120 °C (lit.<sup>17</sup> 110-112 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.62 (m, 3H), 7.61 – 7.53 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 194.3, 144.8, 142.7, 137.8, 134.3, 131.6, 129.8, 129.5, 128.63, 128.56, 128.1, 127.6, 124.7, 123.9, 123.2, 119.7.

**8H-indeno[2,1-*b*]thiophen-8-one (2p)<sup>18</sup> [CAS: 13132-12-2]**

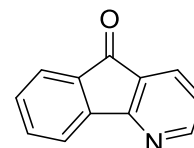
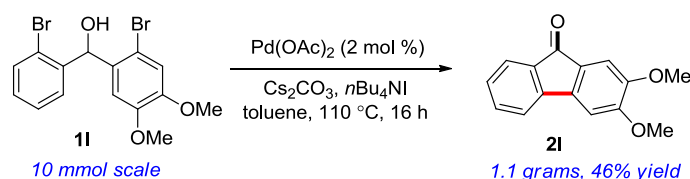
24.5 mg, 64% yield, yellow solid, m.p. 103-105 °C (lit.<sup>19</sup> 107-109 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 4.8 Hz, 1H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.19 – 7.11 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 185.5, 158.7, 139.5, 139.1, 137.7, 136.9, 133.6, 128.0, 123.9, 120.1, 119.5.

**5H-indeno[1,2-*c*]pyridin-5-one (2q)<sup>20</sup> [CAS: 18631-22-6]**

20.7 mg, 55% yield, yellow solid, m.p. 113-115 °C (lit.<sup>21</sup> 118-119 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.90 (s, 1H), 8.71 (d, *J* = 4.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.0, 151.7, 143.1, 142.1, 140.1, 137.4, 135.5, 133.3, 129.8, 125.2, 121.2, 117.2.

**5H-indeno[1,2-*b*]pyridin-5-one (2r)<sup>22</sup> [CAS: 3882-46-0]**

15.0 mg, 42% yield, yellow solid, m.p. 130-132 °C (lit.<sup>23</sup> 139 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 – 8.55 (m, 1H), 7.89 (ddd, *J* = 5.6, 4.0, 1.6 Hz, 1H), 7.85 (dd, *J* = 7.2, 4.0 Hz, 1H), 7.73 (dd, *J* = 7.2, 3.6 Hz, 1H), 7.61 (td, *J* = 7.6, 2.8 Hz, 1H), 7.44 (td, *J* = 7.6, 2.8 Hz, 1H), 7.22 (ddd, *J* = 7.6, 4.8, 3.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.8, 165.1, 154.0, 143.5, 135.4, 134.7, 131.4, 131.0, 128.3, 124.2, 123.3, 120.9.

**Gram-scale synthesis of fluorenone 2l**

To a 100-mL flask was added Pd(OAc)<sub>2</sub> (44.9 mg, 0.2 mmol), diarylmethanol **11** (4.02 g, 10 mmol), Cs<sub>2</sub>CO<sub>3</sub> (8.15 g, 25 mmol), TBAI (9.25 g, 25 mmol) and dry toluene (20.0 mL), the reaction was allowed to stirred at 110 °C for 16 hours. After cooling, the reaction mixture

17. Waldo, J. P.; Zhang, X.; Shi, F.; Larock, R. C. *J. Org. Chem.* **2008**, *73*, 6679.

18. Campo, M. A.; Larock, R. C. *J. Org. Chem.*, **2002**, *67*, 5617.

19. Arcus, C. L.; Barrett, G. C. *J. Chem. Soc.* **1960**, 2098.

20. Laha, J. K.; Jethava, K. P.; Patel, S.; Patel, K. V. *J. Org. Chem.*, **2017**, *82*, 76.

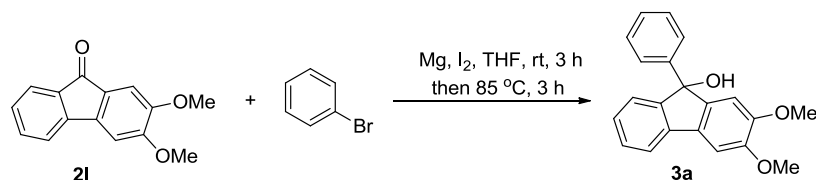
21. Tilly, D.; Castanet, A.-S.; Mortier, J. *Tetrahedron Lett.* **2006**, *47*, 1121.

22. Laha, J. K.; Jethava, K. P.; Patel, S. *Org. Lett.*, **2015**, *17*, 5890.

23. Davis, P. J.; Harris, L.; Karim, A.; Thompson, A. L.; Gilpin, M.; Moloney, M. G.; Pound, M. J.; Thompson, C. *Tetrahedron Lett.* **2011**, *52*, 1553.

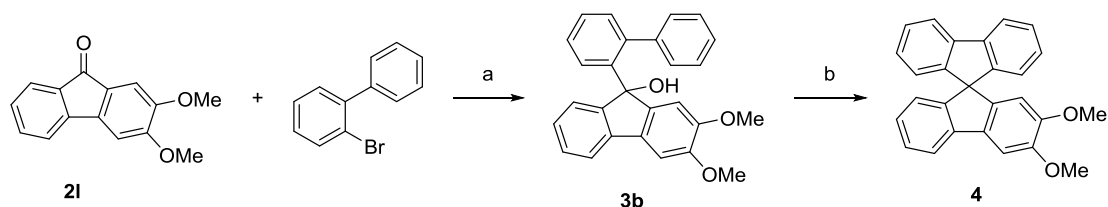
was diluted with ethyl acetate, passed through a pad of Celite, and concentrated in vacuum. The residue was purified by column chromatography on silica gel (hexane/ ethyl acetate = 20: 1) to give corresponding fluorenone **2l** as orange solid (1.10 g, 46% yield). The characterization data is consistent with that is obtained with small scale.

#### Preparation of 2,3-dimethoxy-9-phenyl-9H-fluoren-9-ol (**3a**)



The preparation of **3a** was adapted from literature procedures.<sup>24</sup> To a two neck round bottom flask under nitrogen gas atmosphere bromobenzene (628 mg, 4.0 mmol), magnesium turnings (96 mg, 4.0 mmol) in THF (4 mL) and a catalytic amount of iodine were added. The contents were stirred for 3 h. After complete generation of the Grignard reagent, the solution of 2,3-dimethoxy-9H-fluoren-9-one (480 mg, 2.0 mmol) in THF (5 mL) was added into it drop-wise. The contents were further refluxed for 3 hours. Then, the reaction mixture was cooled to room temperature and quenched with aqueous sat.  $\text{NH}_4\text{Cl}$  (5 mL). The organic portion was extracted with ethyl acetate ( $2 \times 10$  mL), then the organic layer was washed with water (10 mL), followed by brine solution (20 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the solvent was evaporated to dryness at the rotary evaporator. The crude residue thus obtained was purified by silica gel column chromatography using PE/ethyl acetate (19: 1) as eluent to afford **3a** (520 mg, 80% yield) as white solid (m.p. 170-172 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.9$  Hz, 1H), 7.38 (d,  $J = 6.8$  Hz, 2H), 7.33 – 7.22 (m, 5H), 7.18 – 7.12 (m, 2H), 6.83 (s, 1H), 3.96 (s, 3H), 3.80 (s, 3H), 2.47 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.1, 149.7, 143.2, 142.8, 139.7, 132.1, 128.9, 128.2, 127.1, 125.3, 124.3, 119.0, 107.6, 103.0, 83.6, 56.1, 56.1; IR (KBr,  $\text{cm}^{-1}$ ) 3477, 2932, 1459, 1269, 1138, 1037, 756, 744, 699; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{18}\text{NaO}_3$  ( $[\text{M}+\text{Na}]^+$ ) 341.1154, found 341.1150.

#### Preparation of 2,3-dimethoxy-9,9'-spirobi[fluorene] (**4**)<sup>25</sup> [CAS: 1859903-53-9]



a) Mg,  $\text{I}_2$ , THF, 80 °C, 5 h, 85 °C, 12 h, 82%. b) HCl,  $\text{CH}_3\text{COOH}$ , 125 °C, reflux, 2 h, 94%.

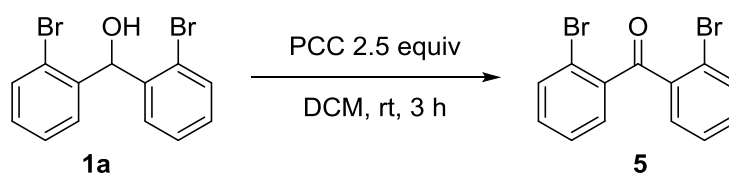
24. Jagarapu, R.; Parthasarathy, V. *Chem. Asian J.* **2017**, *12*, 181.

25. Taylor, R. G. D.; Bezzu, C. G.; Carta, M.; Msayib, K. J.; Walker, J.; Short, R.; Kariuki, B. M.; McKeown, N. B. *Chem. - Eur. J.* **2016**, *22*, 2466.

The preparation of **3b** was adapted from literature procedures.<sup>11</sup> To a two neck round bottom flask under nitrogen gas atmosphere 2-bromobiphenyl (559 mg, 2.4 mmol), magnesium turnings (63.4 mg, 2.64 mmol) in THF (5 mL) and a catalytic amount of iodine were added. The contents were refluxed for 6 h. After complete generation of the Grignard reagent, the solution of 2,3-dimethoxy-9*H*-fluoren-9-one (582 mg, 2.4 mmol) in THF (5 mL) was added into it drop-wise. The contents were further refluxed for 12 h. Then, the reaction mixture was cooled to room temperature and quenched with NH<sub>4</sub>Cl (5 mL). The organic portion was extracted into ethyl acetate (2 × 10 mL), then the organic layer was washed with water (10 mL), followed by brine solution (15 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was evaporated to dryness at the rotary evaporator. The crude residue thus obtained was purified by silica gel column chromatography using PE/ethyl acetate (19: 1) as eluent to afford **3b** (775 mg, 82% yield) as white solid (m.p. 179-181 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.10 – 7.06 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.72 – 6.59 (m, 4H), 6.09 (d, *J* = 6.0 Hz, 1H), 5.97 (d, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.26 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.9, 149.9, 149.6, 142.9, 140.9, 140.5, 140.4, 139.6, 133.0, 131.3, 128.7, 128.6, 127.1, 126.8, 126.7, 126.3, 126.1, 126.0, 125.1, 124.0, 119.0, 107.4, 103.4, 82.4, 56.2; IR (KBr, cm<sup>-1</sup>) 3448, 2927, 1499, 1437, 1270, 1205, 1129, 1015, 759, 747, 699, 655; HRMS (ESI) calcd for C<sub>27</sub>H<sub>22</sub>NaO<sub>3</sub> ([M+Na]<sup>+</sup>) 417.1467, found 417.1459.

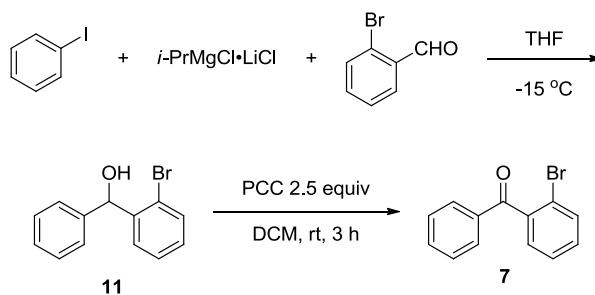
The preparation of **4** was adapted from literature procedures.<sup>11</sup> To a 25 mL flask containing **3b** (39.4 mg, 0.1 mmol) in acetic acid (0.6 mL), 10 μL of concentrated hydrochloric acid (12 N) was added dropwisely and the reaction mixture was allowed to reflux for 3 h. After this time, the reaction contents were cooled to room temperature. Upon cooling, the reaction mixture was solidified. The solids were filtered off, and purified by silica gel column chromatography using PE/ethyl acetate (19: 1) as eluent to afford a colorless solid **4** (36.5 mg, 94% yield) as white solid (m.p. 181-183 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.29 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 1H), 6.23 (s, 1H), 4.02 (s, 3H), 3.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.5, 149.4, 149.0, 148.8, 141.9, 141.7, 140.7, 134.4, 127.8, 127.6, 127.5, 126.5, 124.0, 123.6, 119.9, 118.8, 106.8, 102.9, 65.8, 56.1, 56.0.

**Preparation of bis(2-bromophenyl)methanone (**5**)<sup>26</sup> [CAS: 25187-01-3]**



To a 25-mL round-bottom flask containing **1a** (684 mg, 2.0 mmol) in DCM (5.0 mL), pyridinium chlorochromate complex (PCC) (646.6 mg, 3.0 mmol) was added and the reaction mixture was stirred at rt for 3 h. The reaction mixture was diluted with ethyl acetate, passed through a pad of Celite, and concentrated in vacuum. The crude material was purified by flash chromatography (hexane: ethyl acetate) to give a colorless solid **5** (508 mg, 75% yield) of desired product (m.p. 81-82 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.61 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.34 (m, 4H).

**Preparation of (2-bromophenyl)(phenyl)methanone (**7**)<sup>27</sup> [CAS: 13047-06-8]**



To a cooled (-15 °C) stirring solution of *i*-PrMgCl·LiCl (1M THF, 5.2 mL, 5.2 mmol) was added iodobenzene (1.02 g, 5.0 mmol). When the exchange was deemed complete for two hours, 2-bromobenzaldehyde (925 mg, 5.0 mmol) was added dropwise with a syringe. the reaction was allowed to stir at -15 °C for 30 minutes. The reaction mixture was diluted with ethyl acetate and quenched with 6 M HCl until the aqueous layer showed litmus red at which time an additional portion of water was added (10 mL). The phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (30 mL), dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The crude material was purified by flash chromatography using PE/EtOAc as eluent to give **11** (933.6 mg, 71% yield) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.55 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 3H), 7.29 – 7.25 (m, 1H), 7.16 – 7.11 (m, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 2.48 (d, *J* = 3.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.4, 142.0, 132.6, 128.9, 128.3, 127.5, 126.9, 122.6, 74.5.

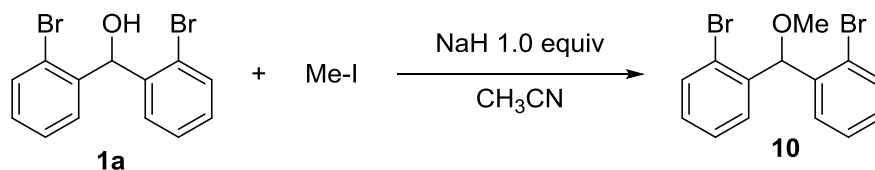
To a 25-mL round-bottom flask containing **11** (263 mg, 1.0 mmol) in DCM (3.0 mL), pyridinium chlorochromate complex (PCC) (323.3 mg, 1.5 mmol) was added and the reaction mixture was stirred at rt for 3 h. The reaction mixture was diluted with ethyl acetate, passed through a pad of Celite, and concentrated in vacuum. The crude material was purified by flash chromatography using PE/EtOAc (20: 1) as eluent to give **7** (203.6 mg, 78% yield) as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.76 (m, 2H), 7.68 – 7.58 (m, 2H), 7.50 – 7.32 (m,

26. Kobayashi, K.; Nishimura, Y.; Gao, F.; Gotoh, K.; Nishihara, Y.; Takagi, K. *J. Org. Chem.* **2011**, *76*, 1949.

27. Wojcik, P.; Mart, M.; Ulukanli, S.; Trzeciak, A. M. *RSC Adv.* **2016**, *6*, 36491.

5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 140.5, 135.9, 133.6, 133.0, 131.0, 130.0, 128.8, 128.5, 127.1, 119.3.

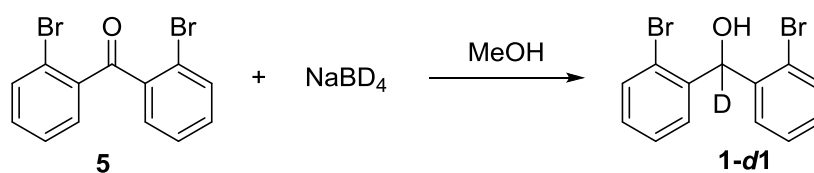
**Preparation of 2,2'-(methoxymethylene)bis(bromobenzene) (**10**)<sup>28</sup> [CAS: 343-01-1]**



To a 25-mL round-bottom flask containing **1a** (342 mg, 1.0 mmol) in  $\text{CH}_3\text{CN}$  (3.0 mL), NaH (40 mg, 1.0 mmol) was added. When the reaction mixture was stirred at rt for 30 minutes, MeI (142 mg, 1.0 mmol) was added dropwisely with a syringe. The reaction was allowed to stir at rt for 30 minutes. The reaction mixture was diluted with ethyl acetate, passed through a pad of Celite, and concentrated in vacuum. The crude material was purified by flash chromatography (hexane / ethyl acetate) to give a colorless solid **10** (237 mg, 67% yield) of desired product (m.p. 61-62 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 8.0$  Hz, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 5.89 (s, 1H), 3.51 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 133.0, 129.3, 128.9, 127.4, 124.9, 82.9, 58.1.

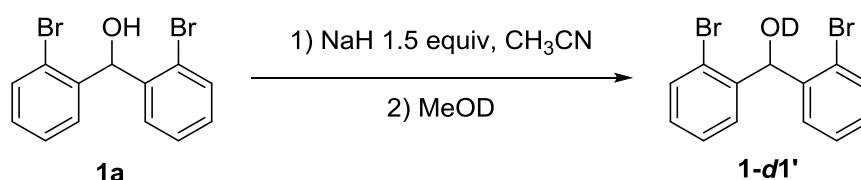
28. Perron, Q.; Praz, J.; Alexakis, A. *Tetrahedron: Asymmetry* **2009**, *20*, 1004.

**Preparation of bis(2-bromophenyl)methan-*d*-ol (1-*d*1)**



To a 25 mL round-bottom flask containing **5** (340 mg, 1.0 mmol) in MeOH (2.0 mL), NaBD<sub>4</sub> (50.4 mg, 1.2 mmol) was added. The reaction mixture was stirred at rt for 10 minutes. The reaction mixture was diluted with ethyl acetate, passed through a pad of Celite, and concentrated in vacuo. The crude material was purified by flash chromatography using PE/EtOAc as eluent to give **1-*d*1** (329 mg, 96% yield, 95% **D**) as white solid (m.p. 79-80 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.28 (m, 4H), 7.21 – 7.16 (m, 2H), 2.60 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.8, 132.9, 129.3, 128.6, 127.5, 123.8, 73.8 (t, *J* = 22.4 Hz). IR (KBr, cm<sup>-1</sup>) 3423, 2923, 1638, 1465, 1436, 1400, 1065, 1018, 748; HRMS (ESI) calcd for C<sub>13</sub>H<sub>9</sub>D<sup>79</sup>Br<sup>81</sup>BrNaO ([M+Na]<sup>+</sup>) 365.9038, found 365.9032.

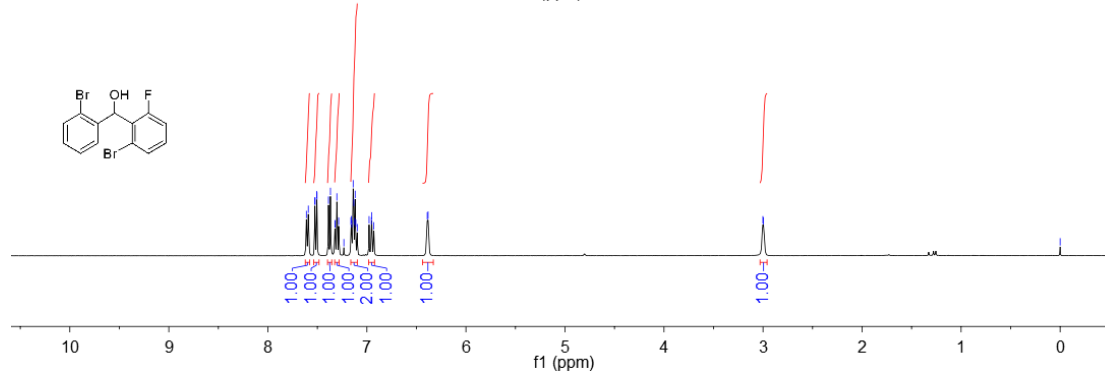
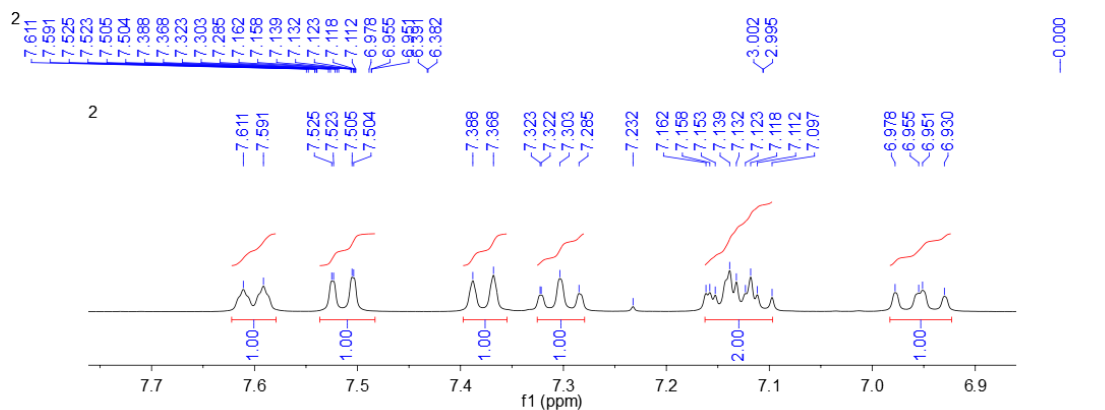
**Preparation of bis(2-bromophenyl)methanol-*d* (1-*d*1')**



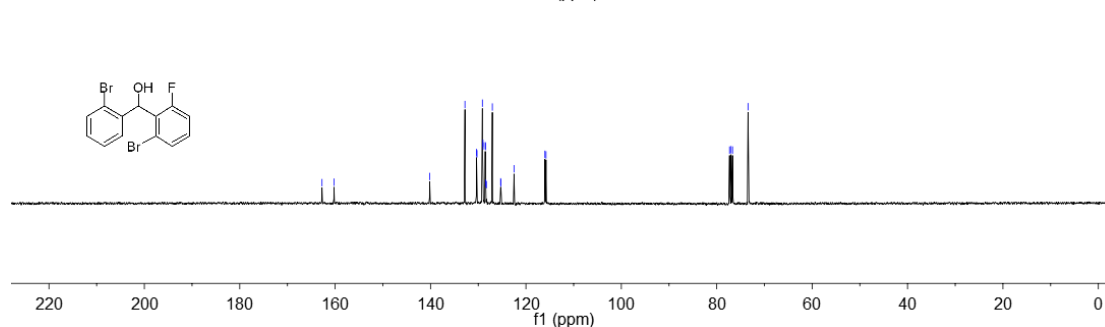
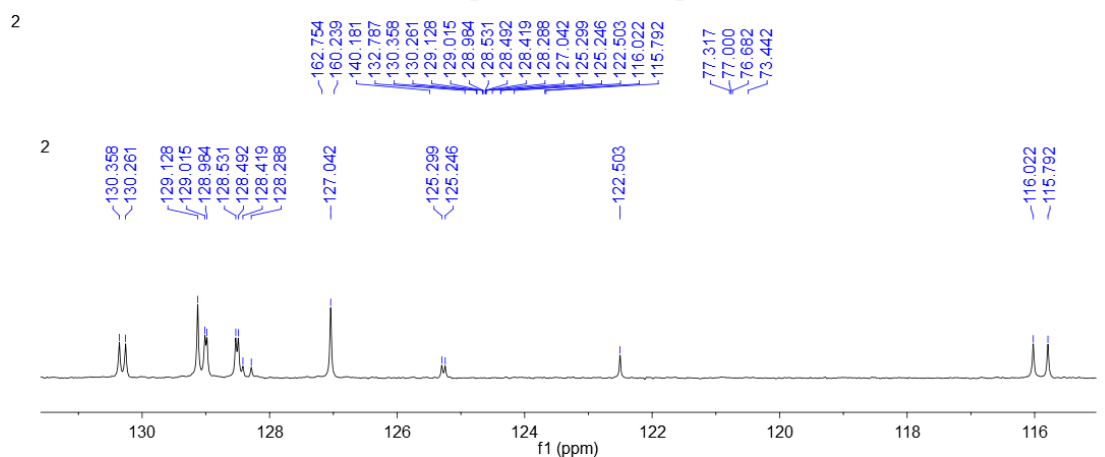
To a 25 mL round-bottom flask containing **1a** (342 mg, 1.0 mmol) in CH<sub>3</sub>CN (3.0 mL), NaH 100% (28.8 mg, 1.2 mmol) was added. When the reaction mixture was stirred at rt for 10 minutes, MeOD (39.6 mg, 1.2 mmol) was added dropwise with a syringe. The reaction was allowed to stir at rt for 30 minutes. The reaction mixture was concentrated in vacuum and washed with *n*-hexane for 3 times to afford product **1-*d*1'** (>95% **D**). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.53 (m, 2H), 7.35 – 7.29 (m, 4H), 7.21 – 7.17 (m, 2H), 6.41 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.9, 132.9, 129.4, 128.6, 127.6, 123.8, 74.1.



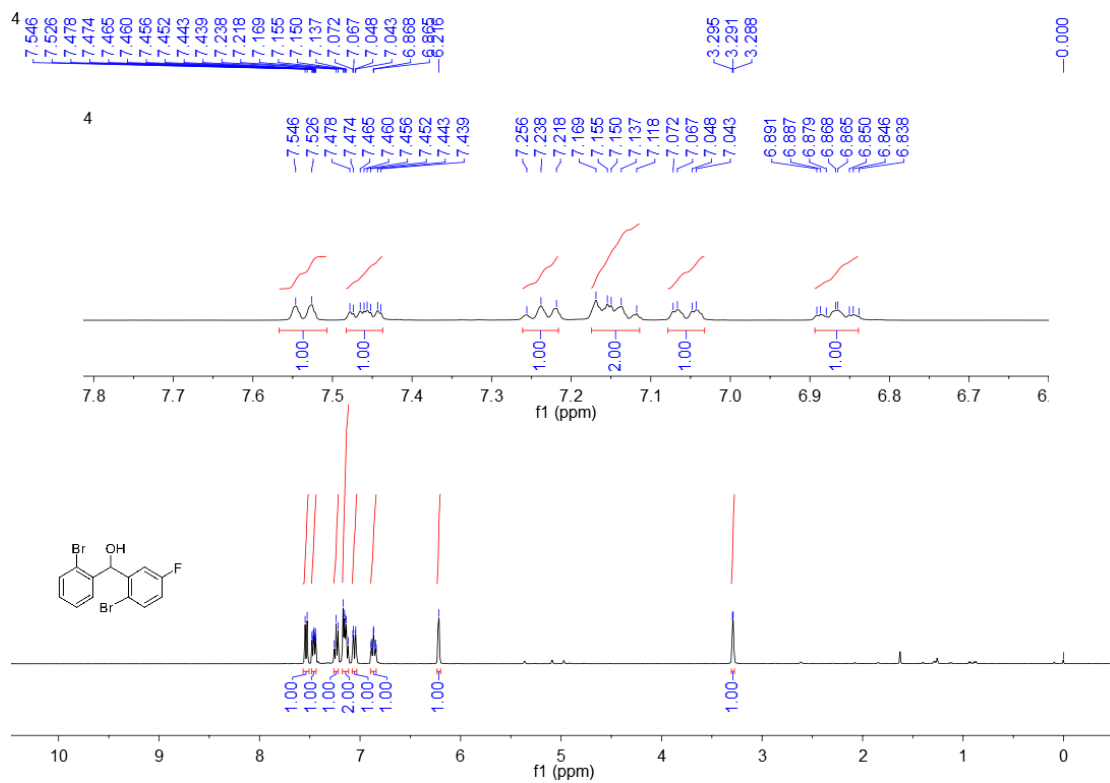
## NMR data of all compounds



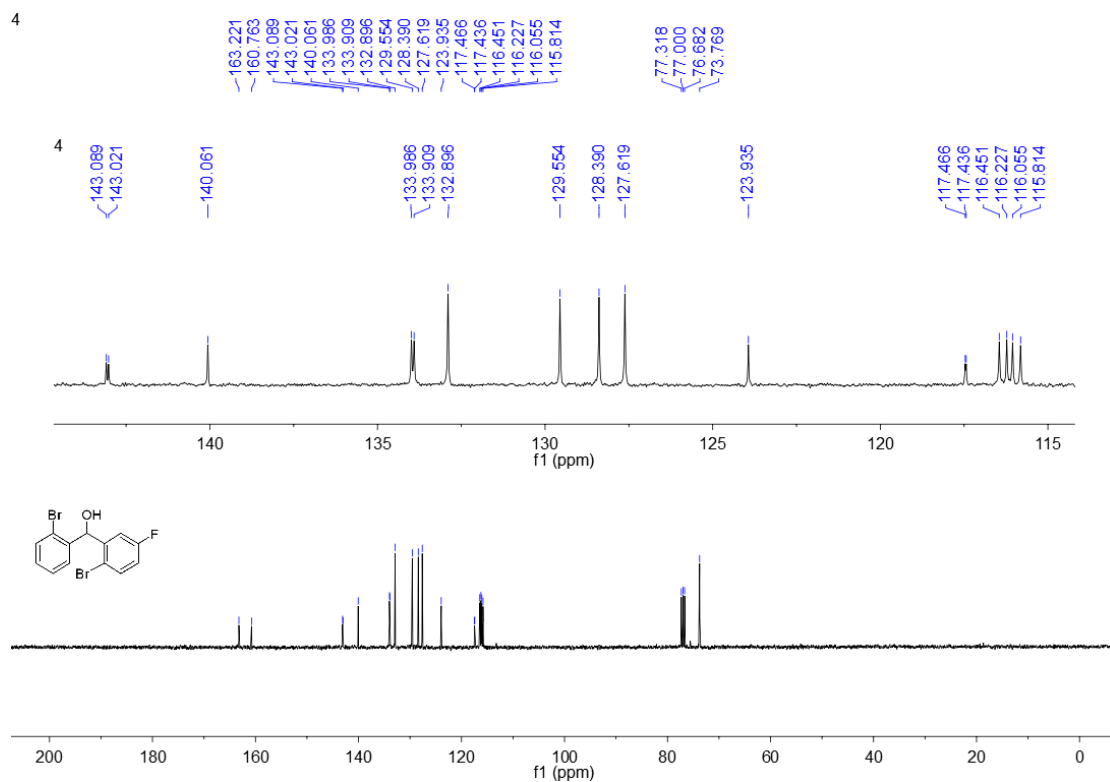
<sup>1</sup>H NMR Spectrum of Compound 1b



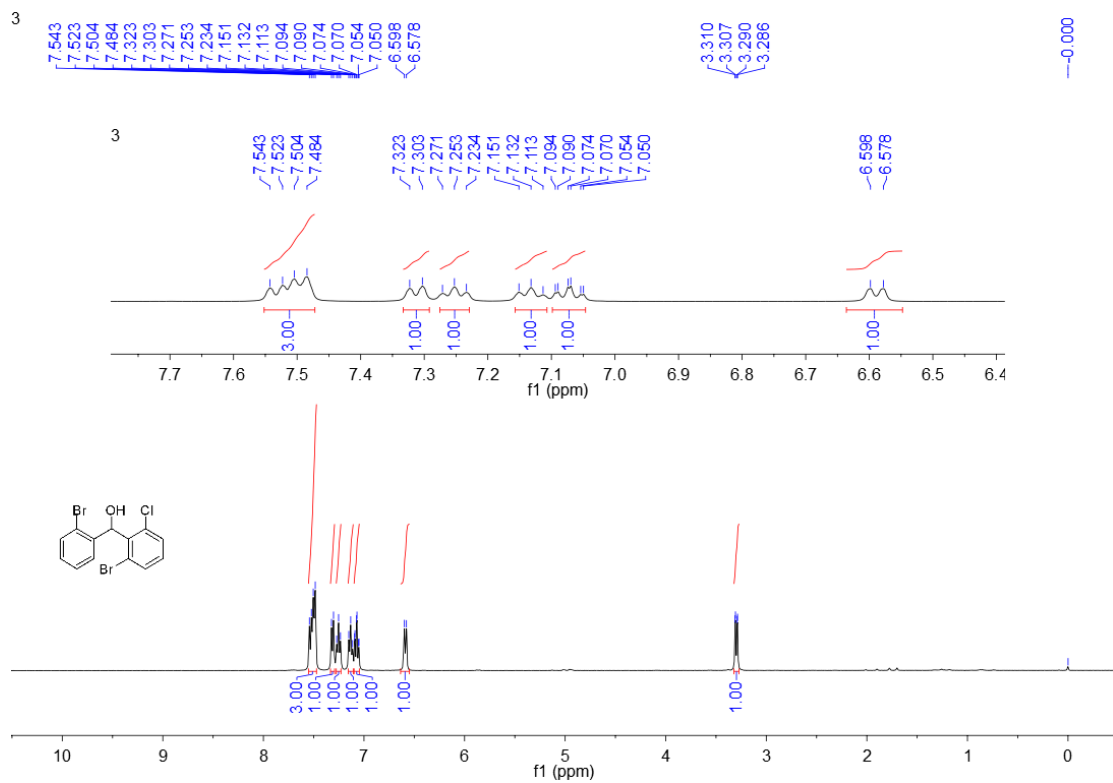
<sup>13</sup>C NMR Spectrum of Compound 1b



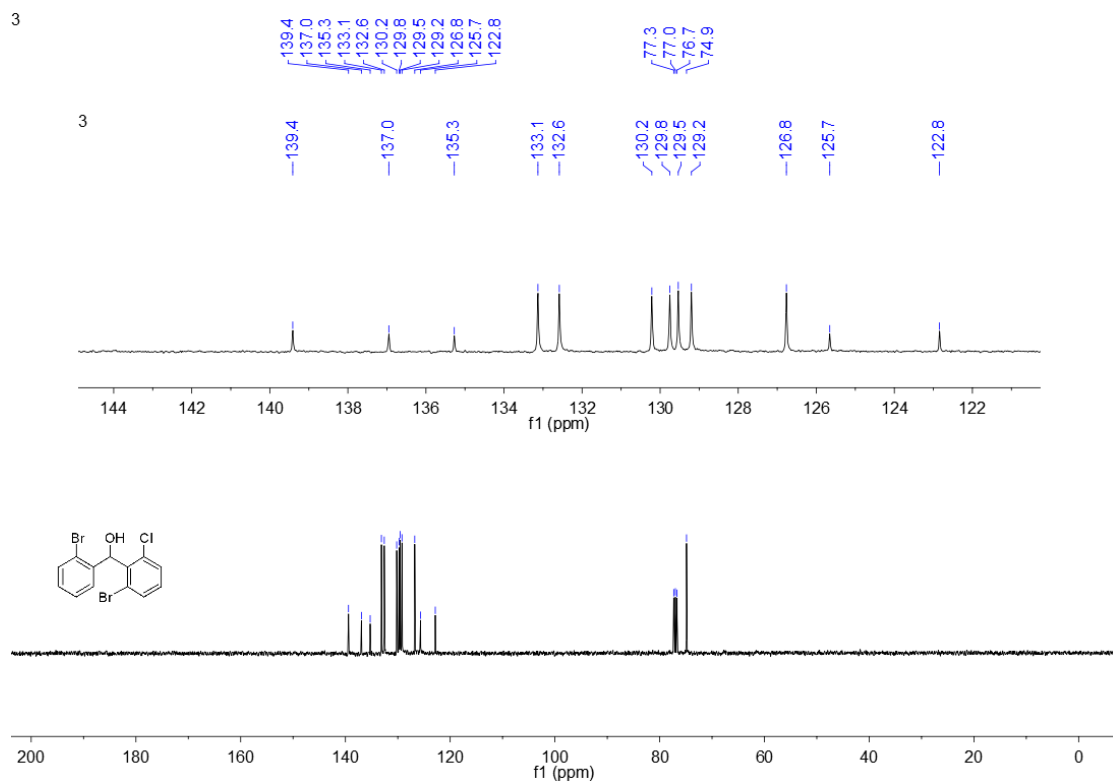
**<sup>1</sup>H NMR Spectrum of Compound 1c**



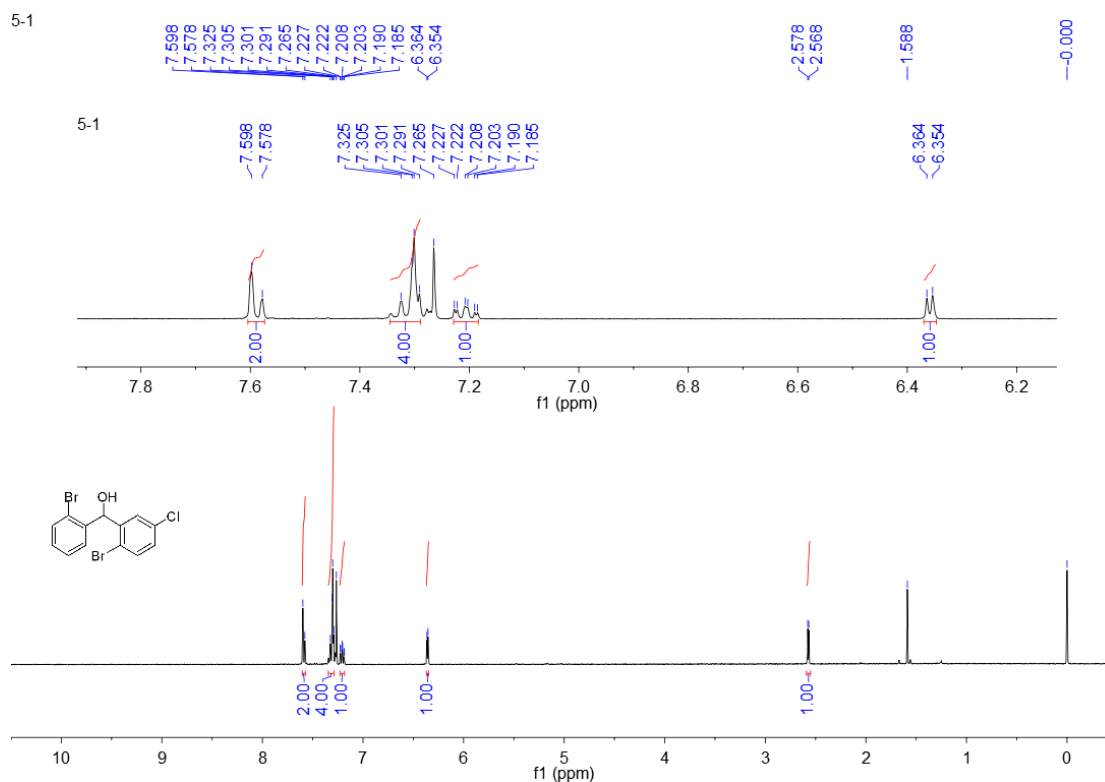
**<sup>13</sup>C NMR Spectrum of Compound 1c**



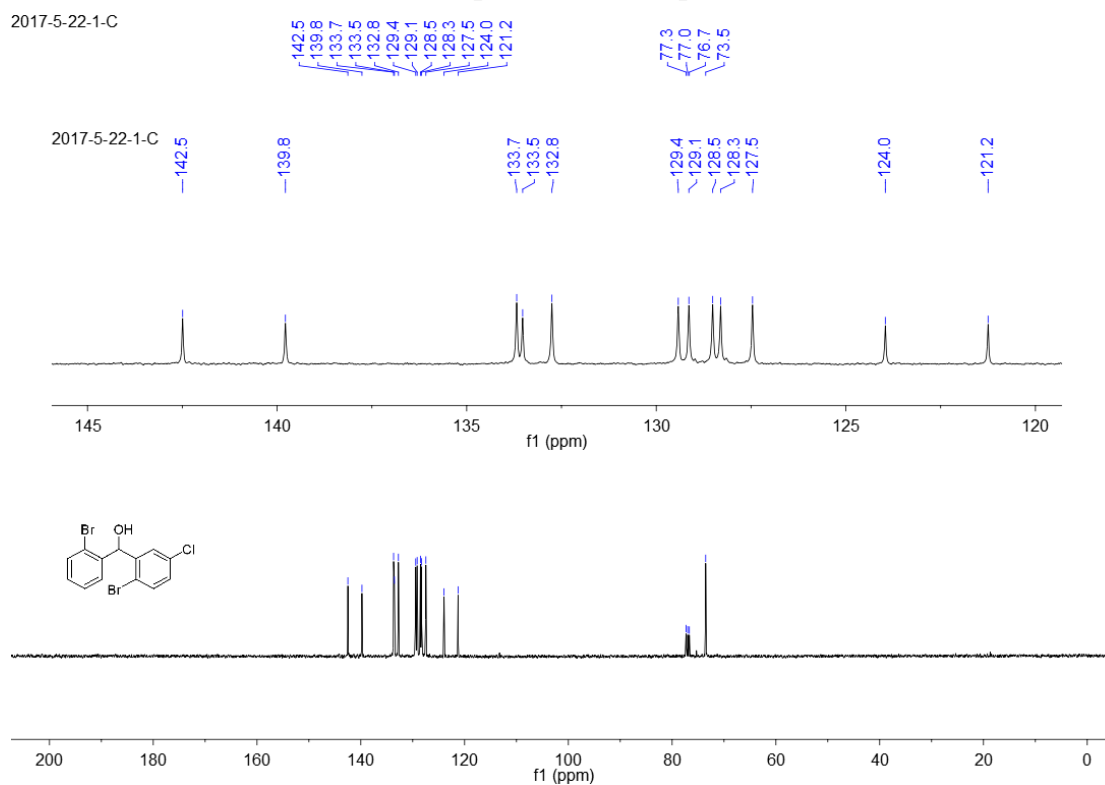
<sup>1</sup>H NMR Spectrum of Compound 1e



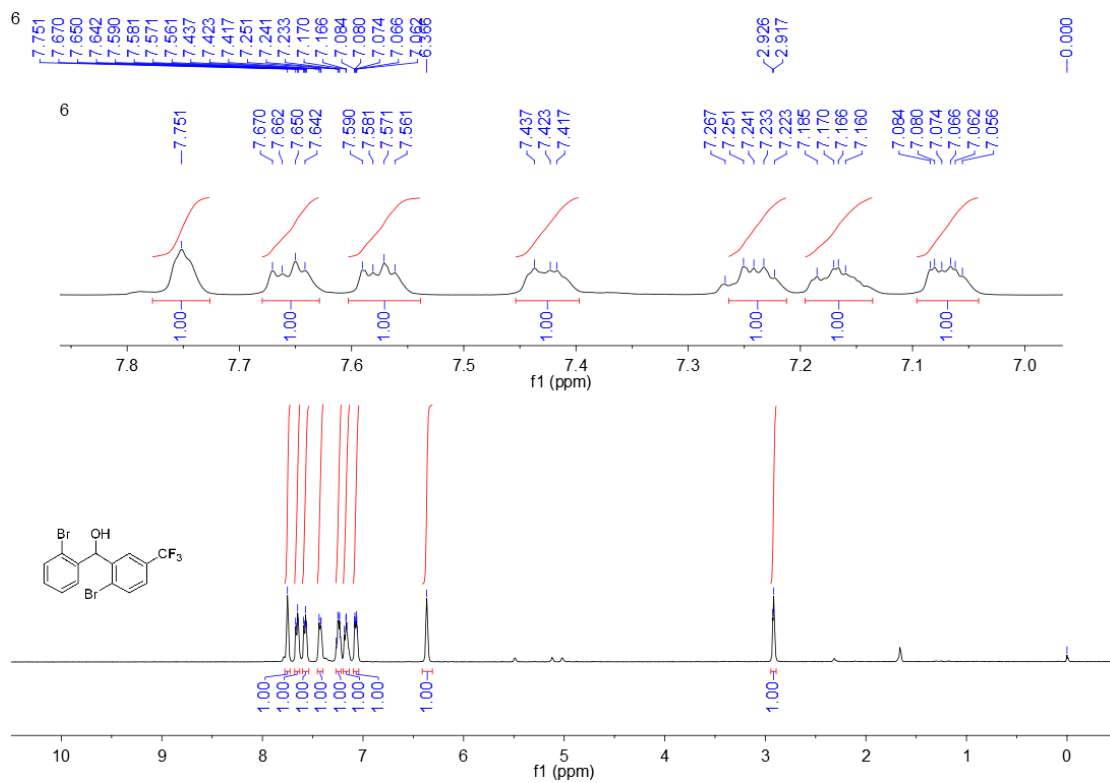
<sup>13</sup>C NMR Spectrum of Compound 1e



**<sup>1</sup>H NMR Spectrum of Compound 1f**

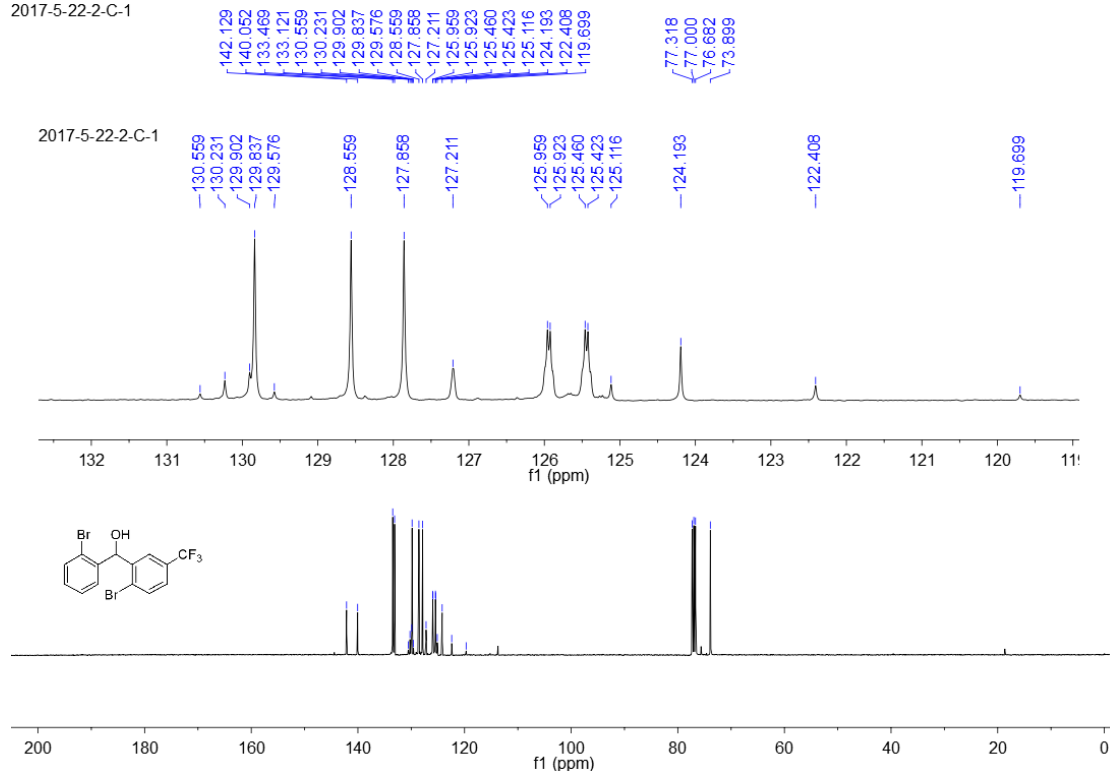


**<sup>13</sup>C NMR Spectrum of Compound 1f**

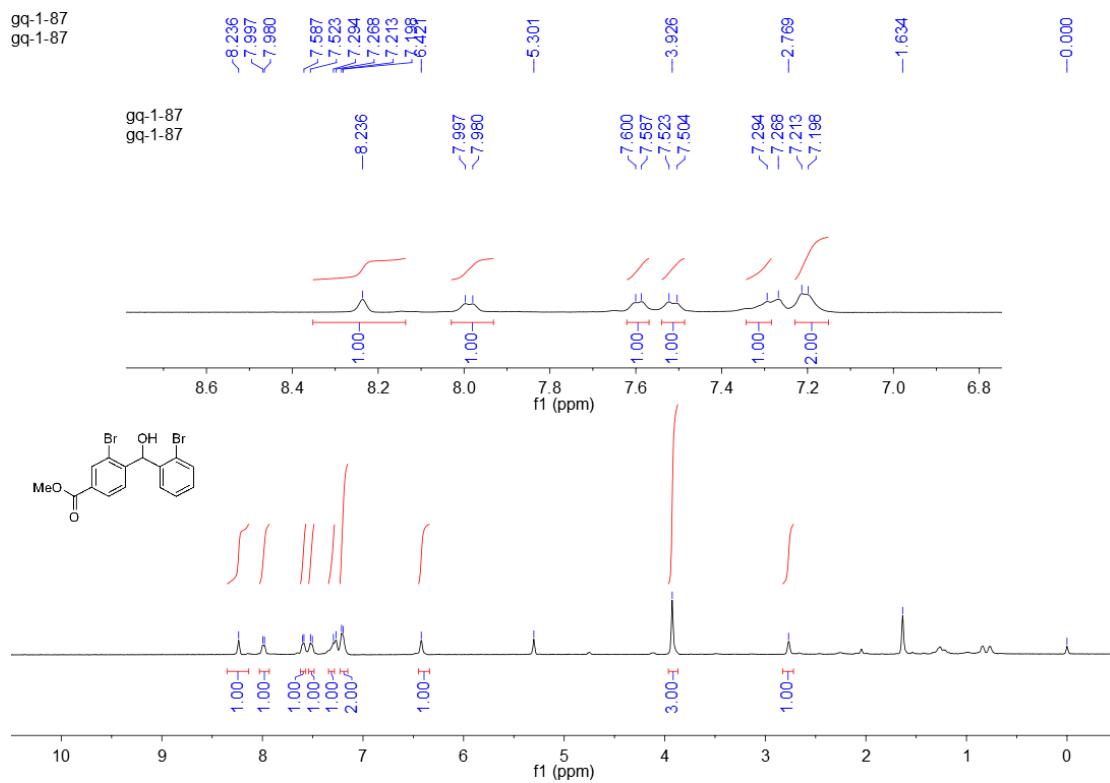


<sup>1</sup>H NMR Spectrum of Compound 1g

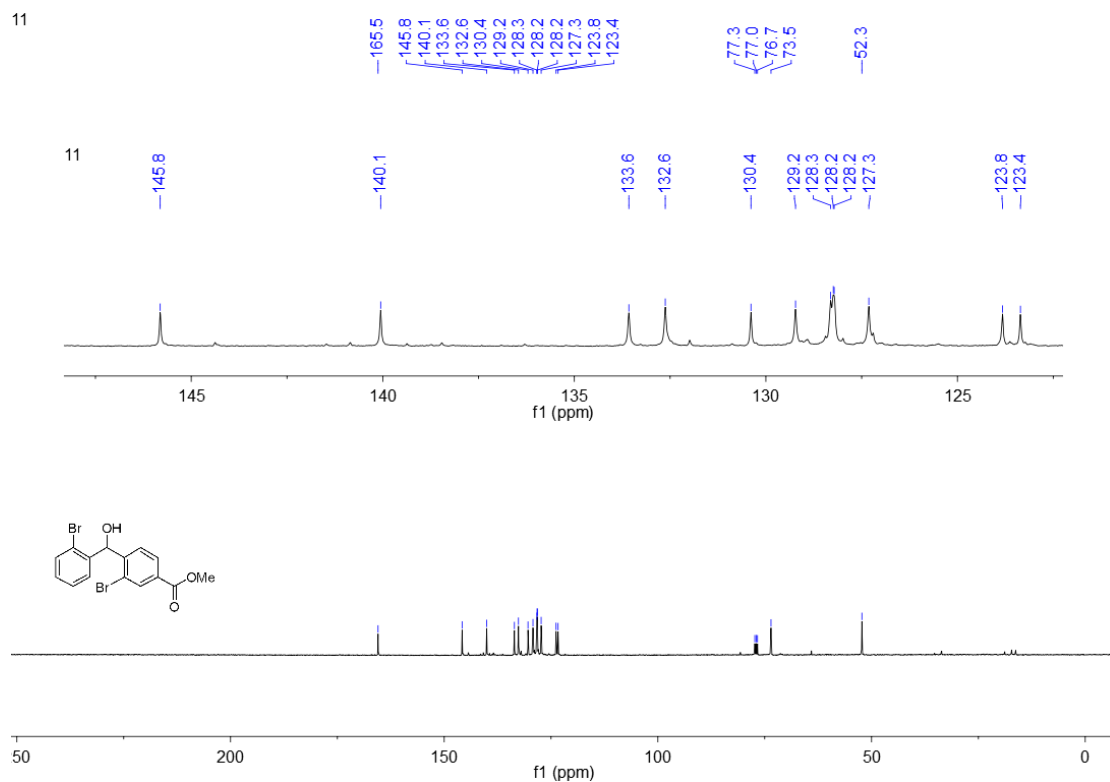
2017-5-22-2-C-1



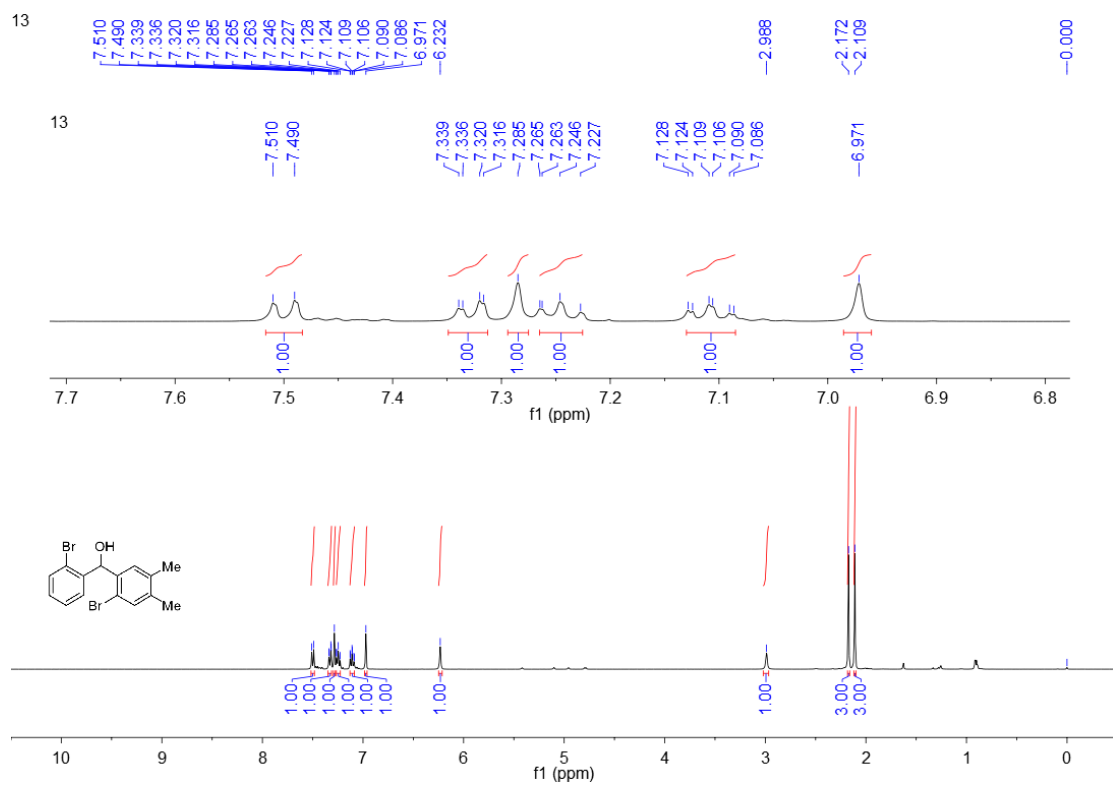
<sup>13</sup>C NMR Spectrum of Compound 1g



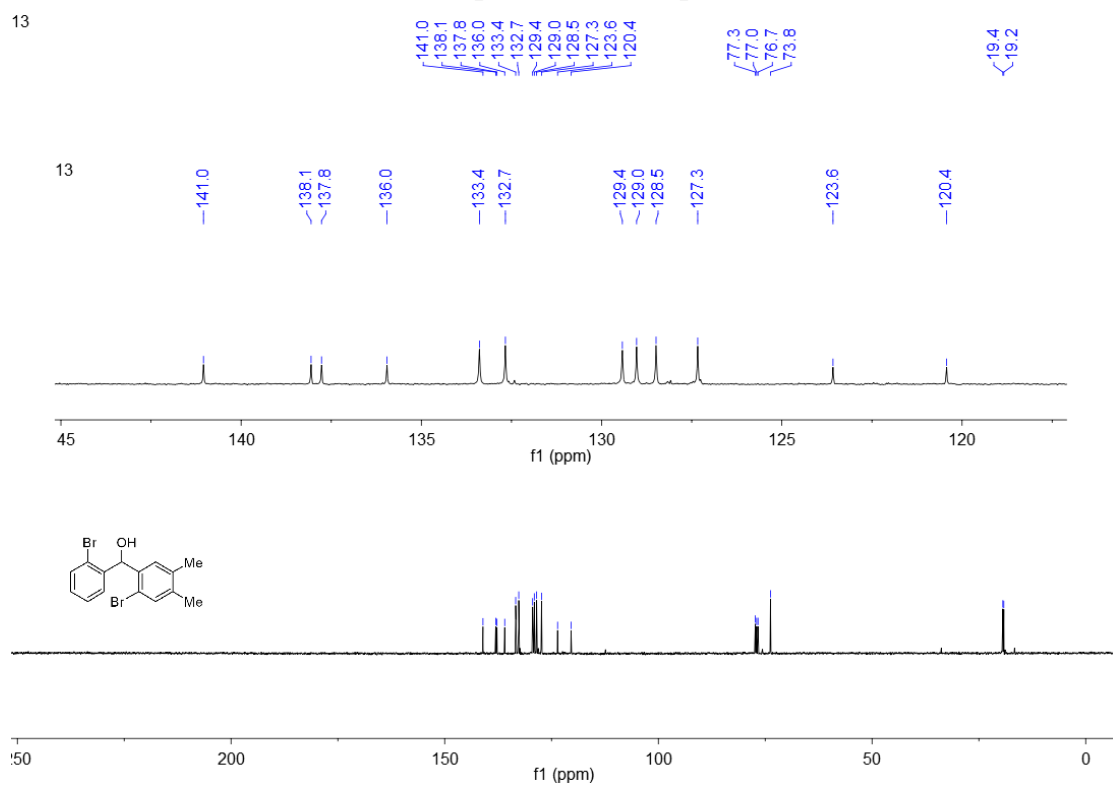
**<sup>1</sup>H NMR Spectrum of Compound 1h**



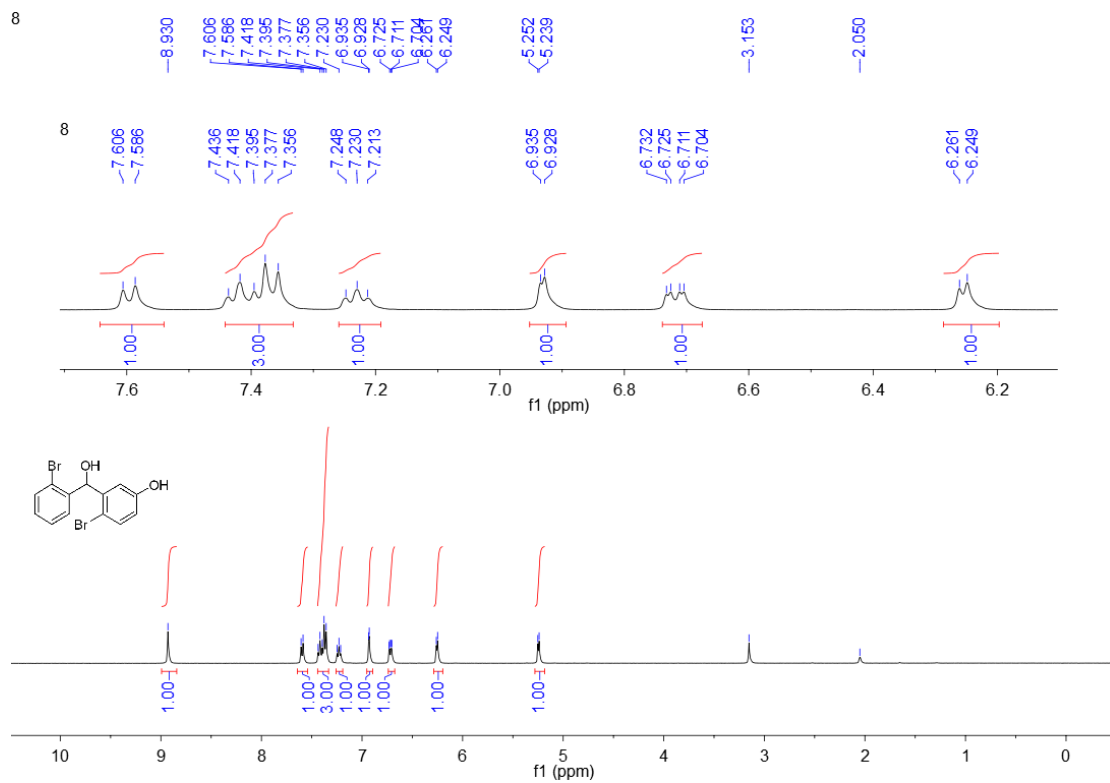
**<sup>13</sup>C NMR Spectrum of Compound 1h**



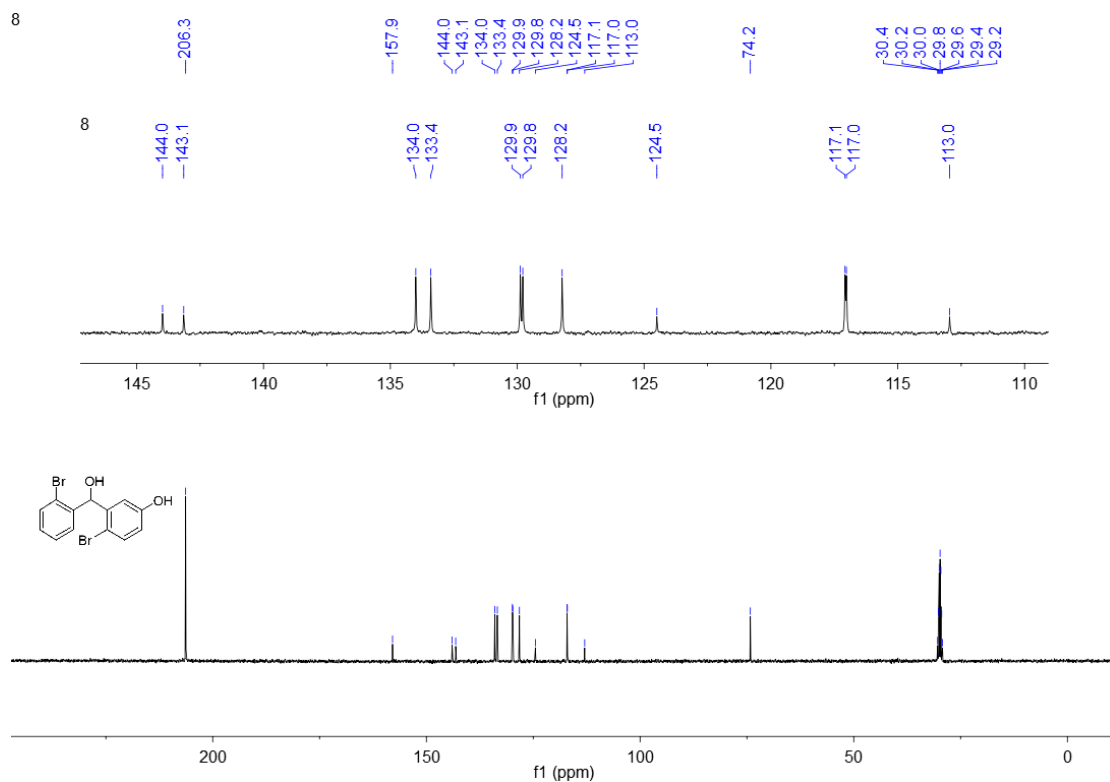
**<sup>1</sup>H NMR Spectrum of Compound 1i**



**<sup>13</sup>C NMR Spectrum of Compound 1i**

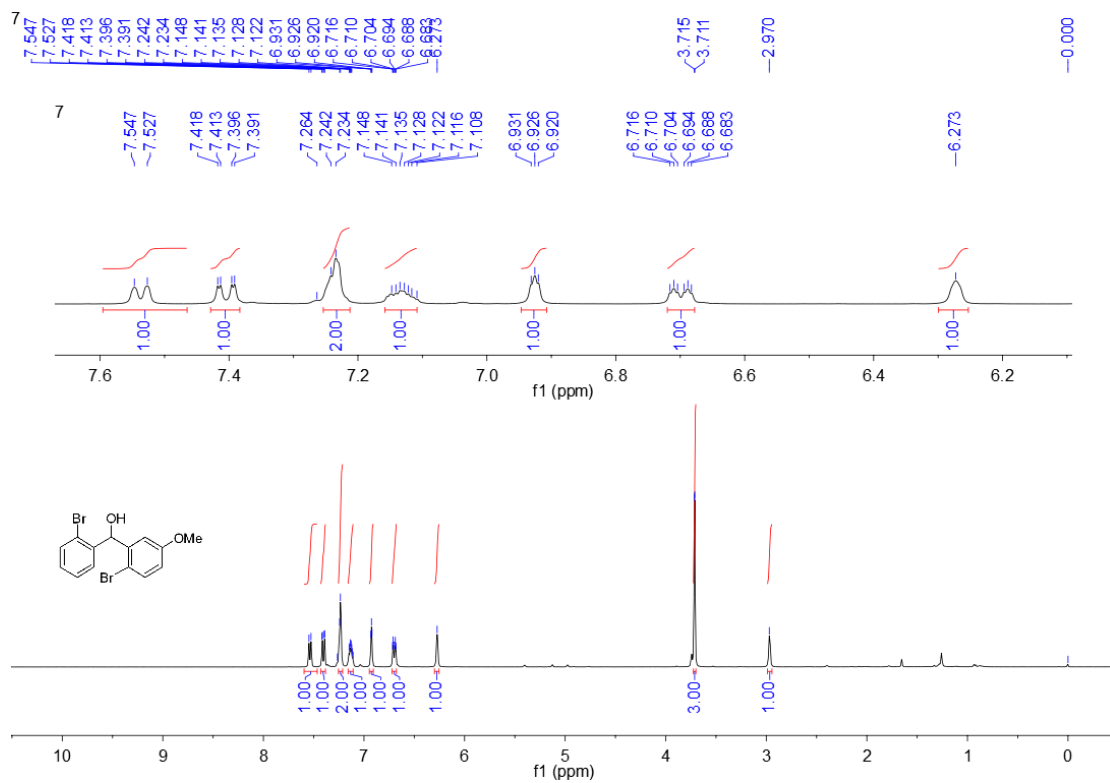


<sup>1</sup>H NMR Spectrum of Compound 1j

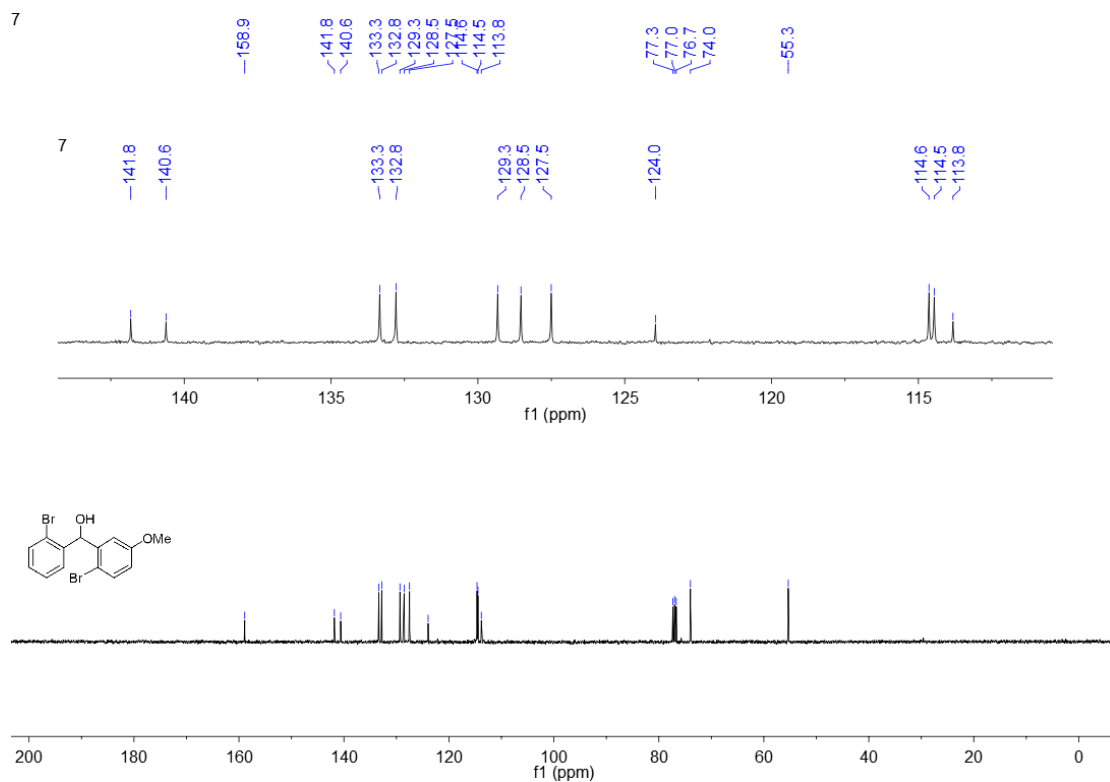


<sup>13</sup>C NMR Spectrum of Compound 1j

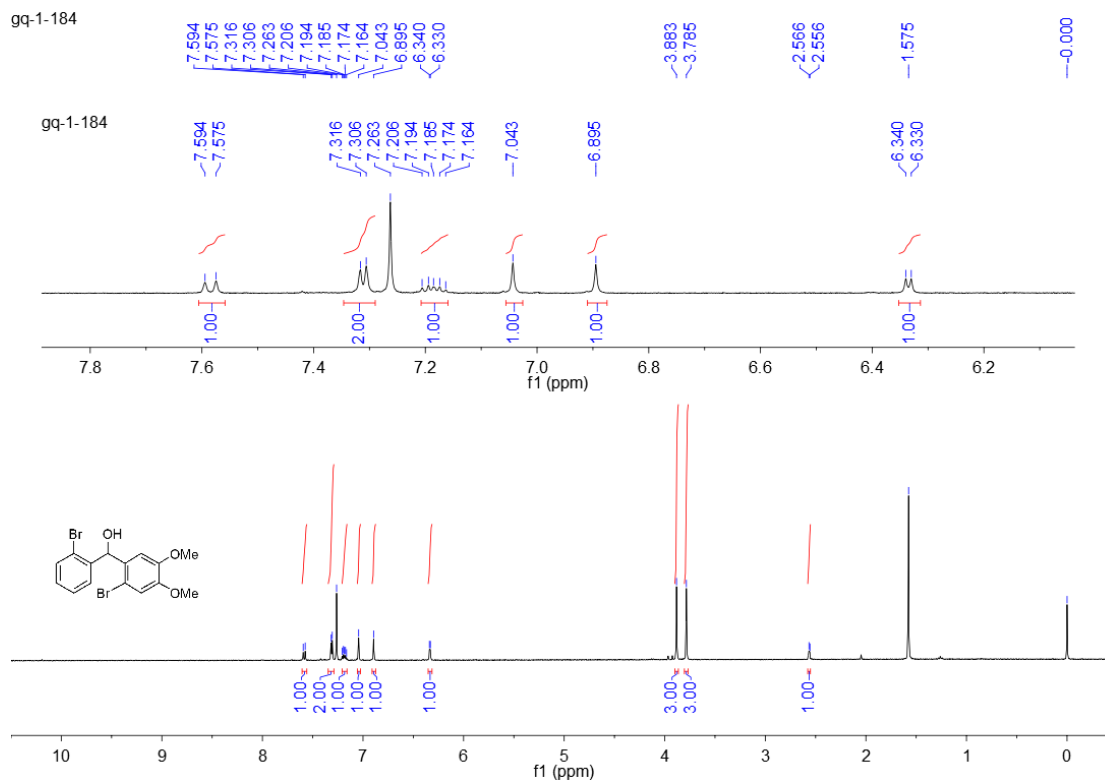




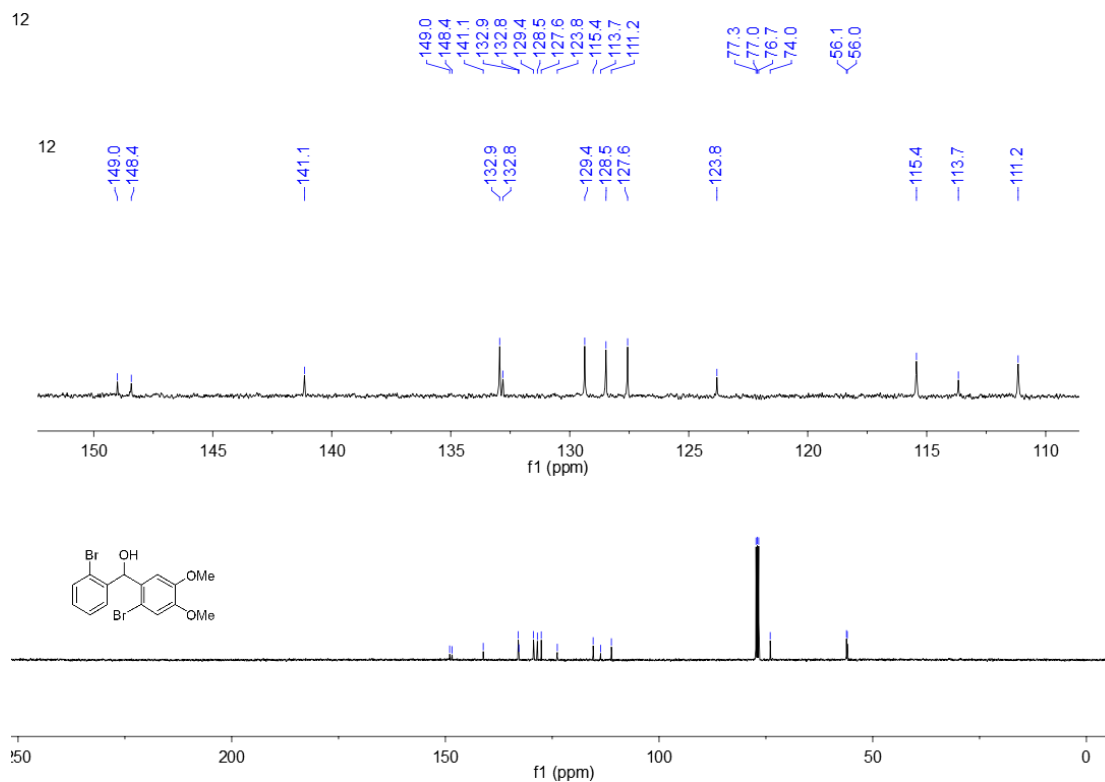
**<sup>1</sup>H NMR Spectrum of Compound 1k**



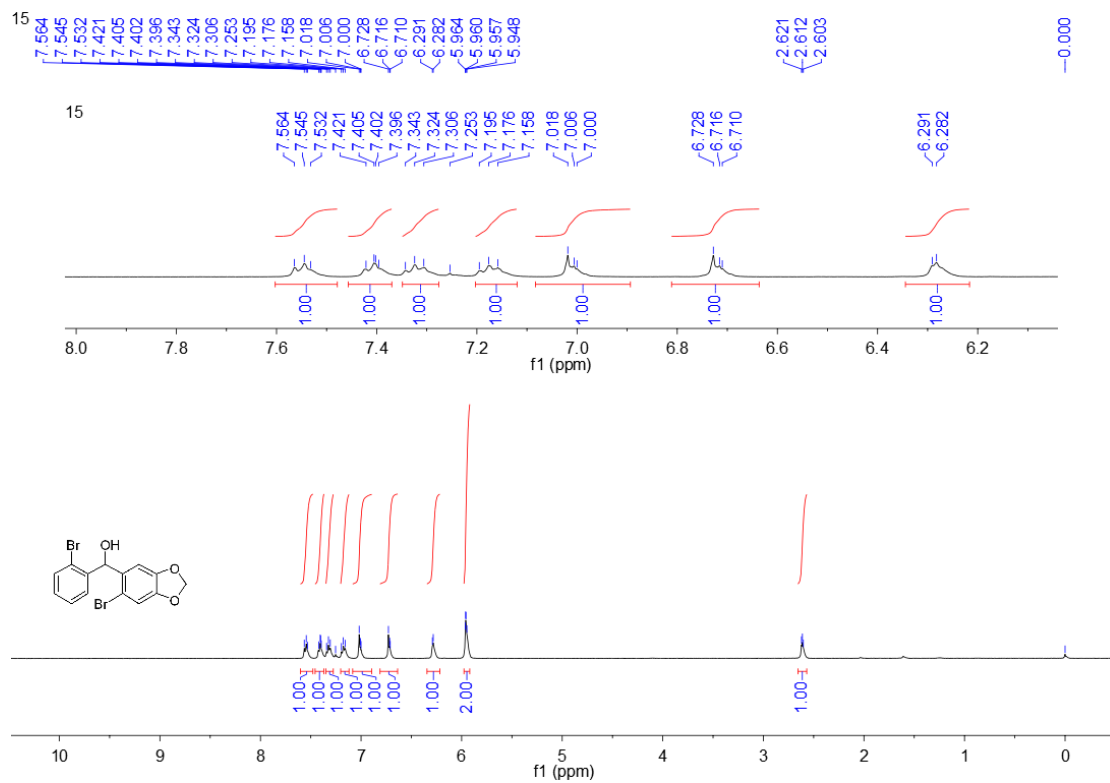
**<sup>13</sup>C NMR Spectrum of Compound 1k**



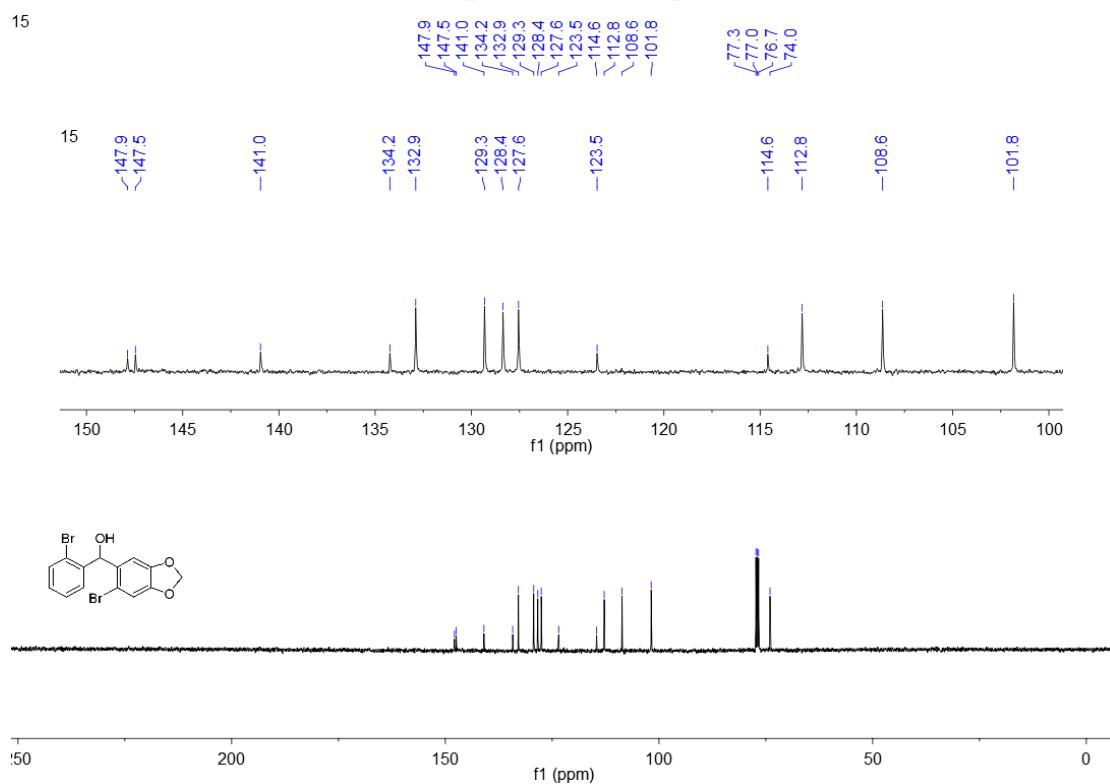
**<sup>1</sup>H NMR Spectrum of Compound 11**



**<sup>13</sup>C NMR Spectrum of Compound 11**

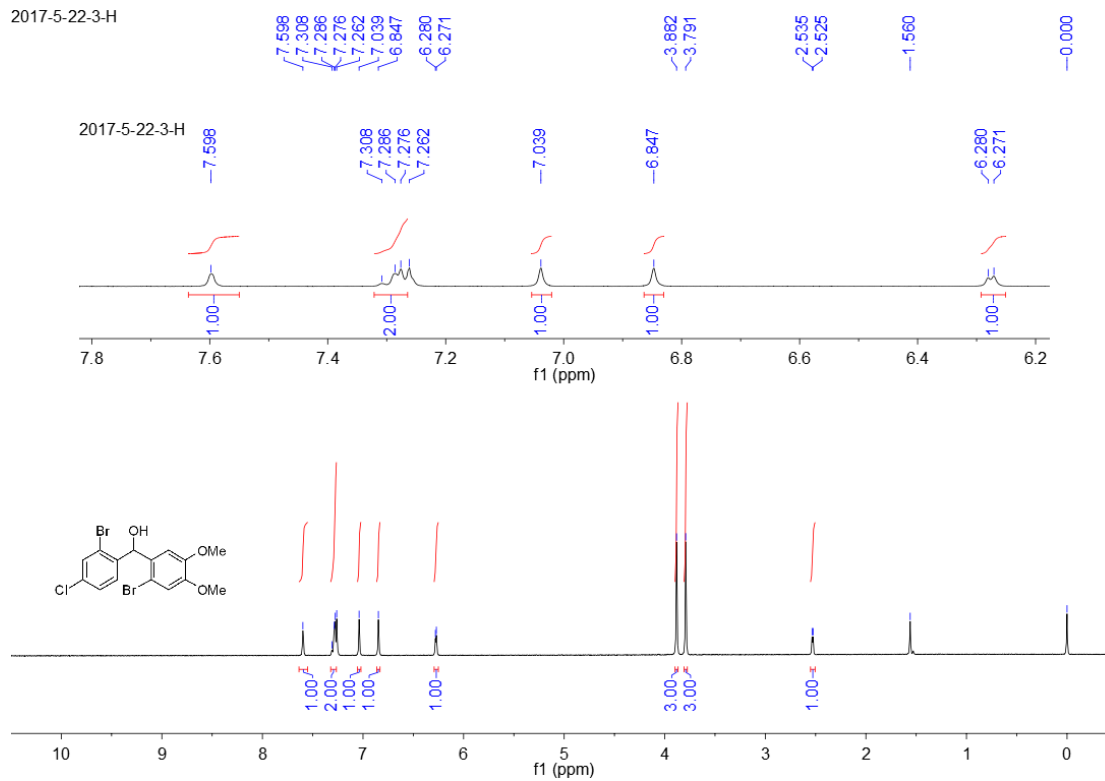


**<sup>1</sup>H NMR Spectrum of Compound 1m**



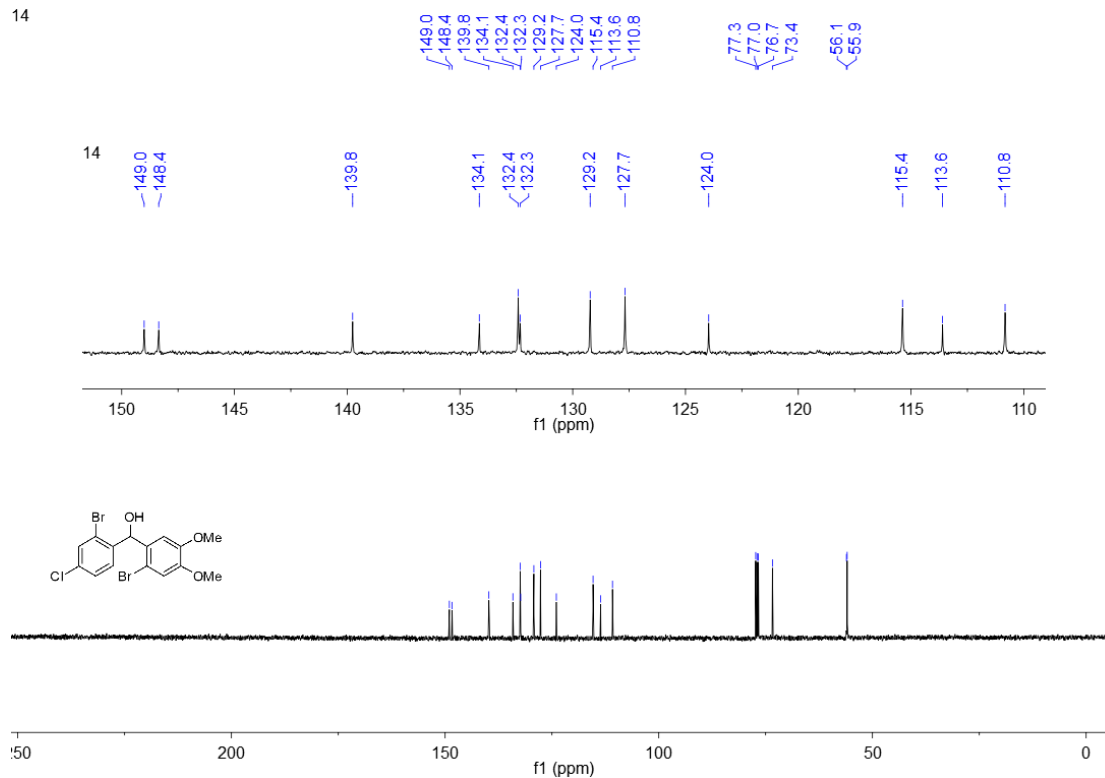
**<sup>13</sup>C NMR Spectrum of Compound 1m**

2017-5-22-3-H

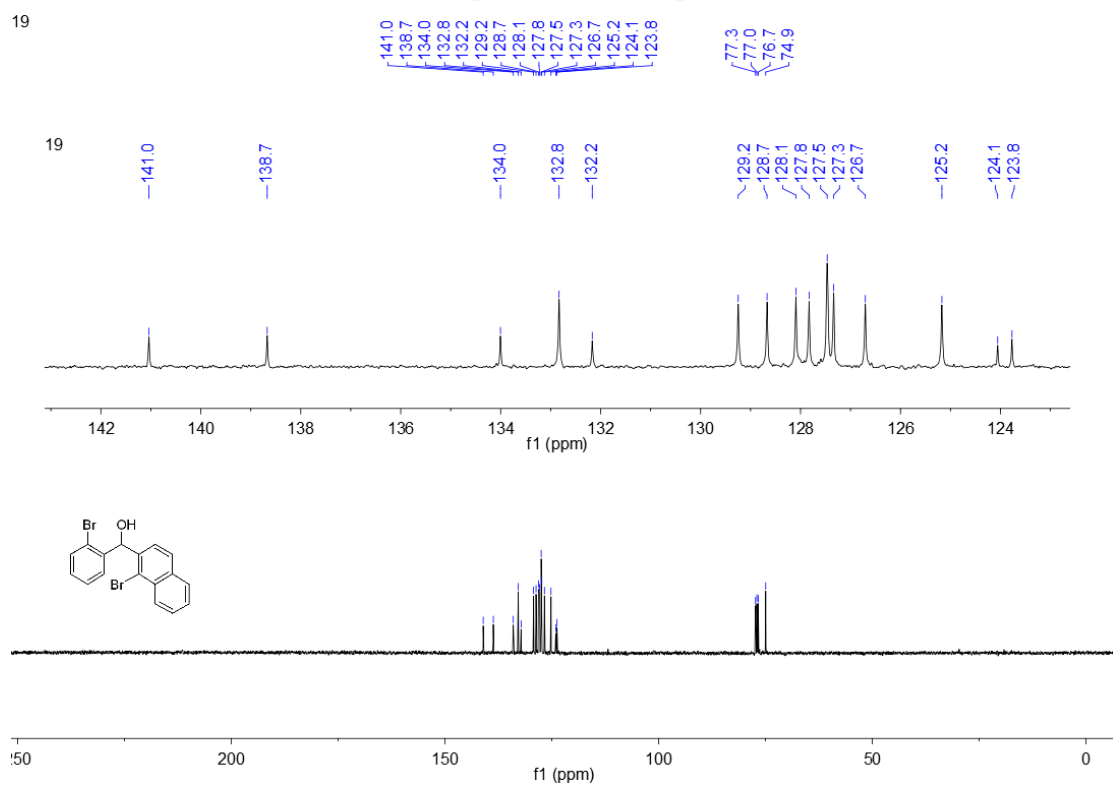
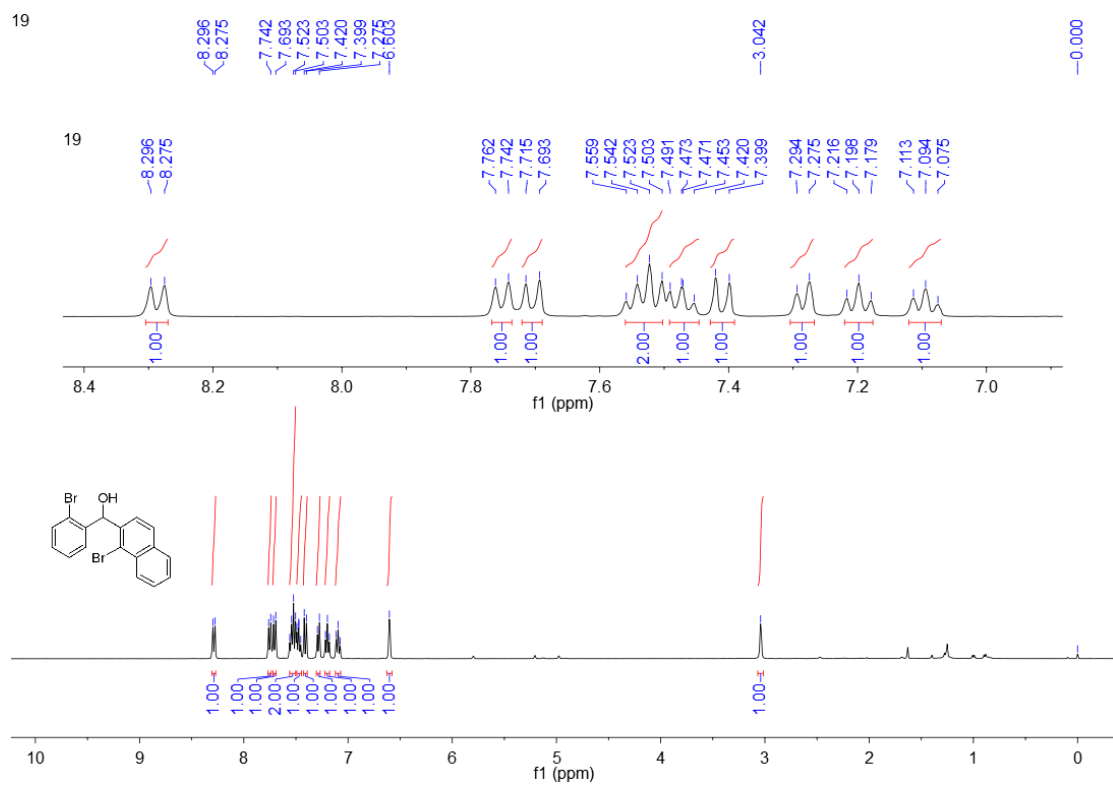


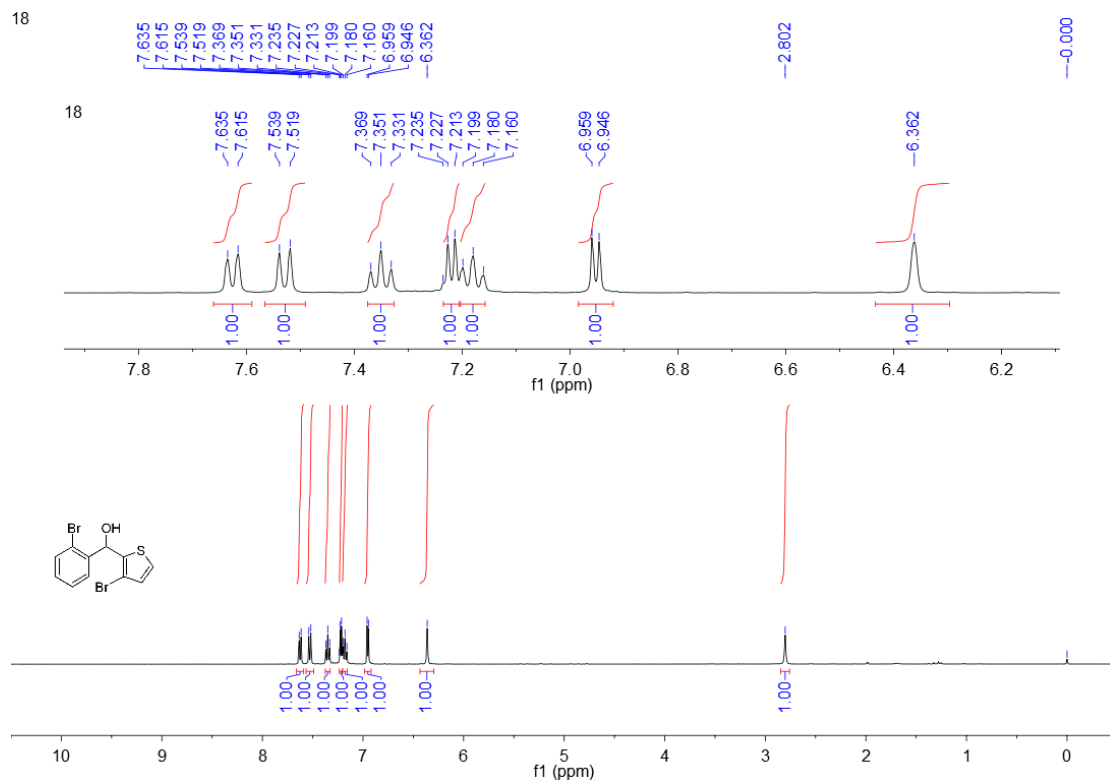
### <sup>1</sup>H NMR Spectrum of Compound 1n

14

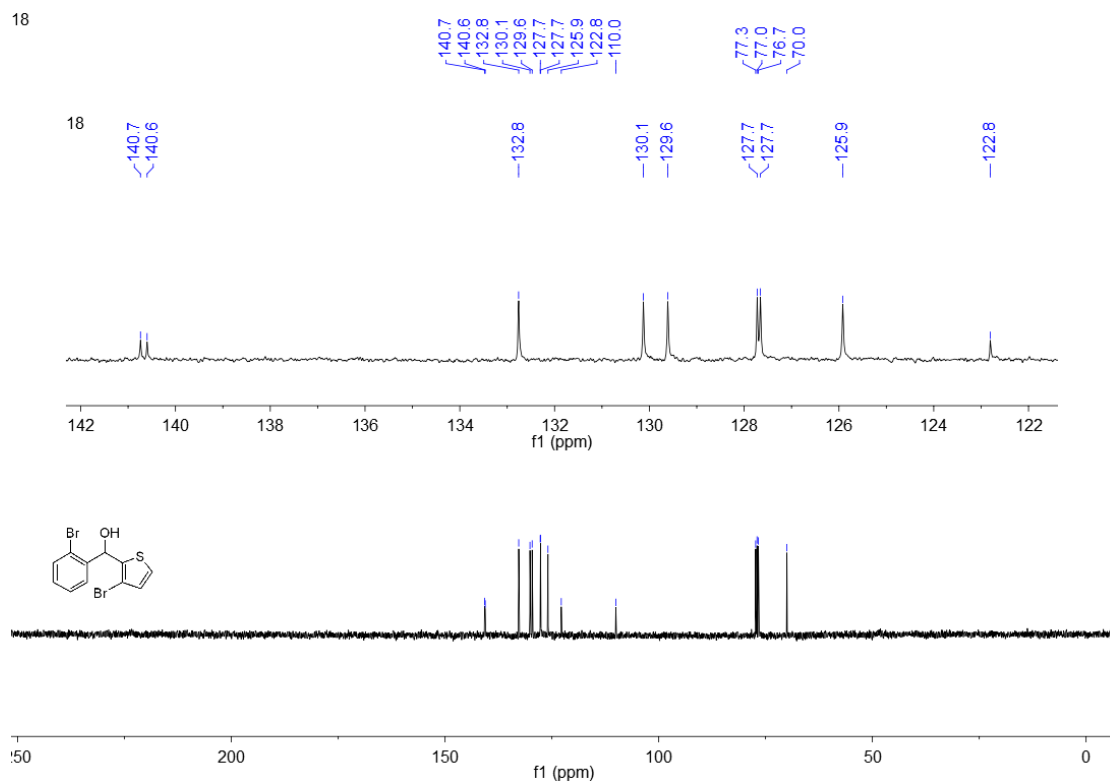


### <sup>13</sup>C NMR Spectrum of Compound 1n

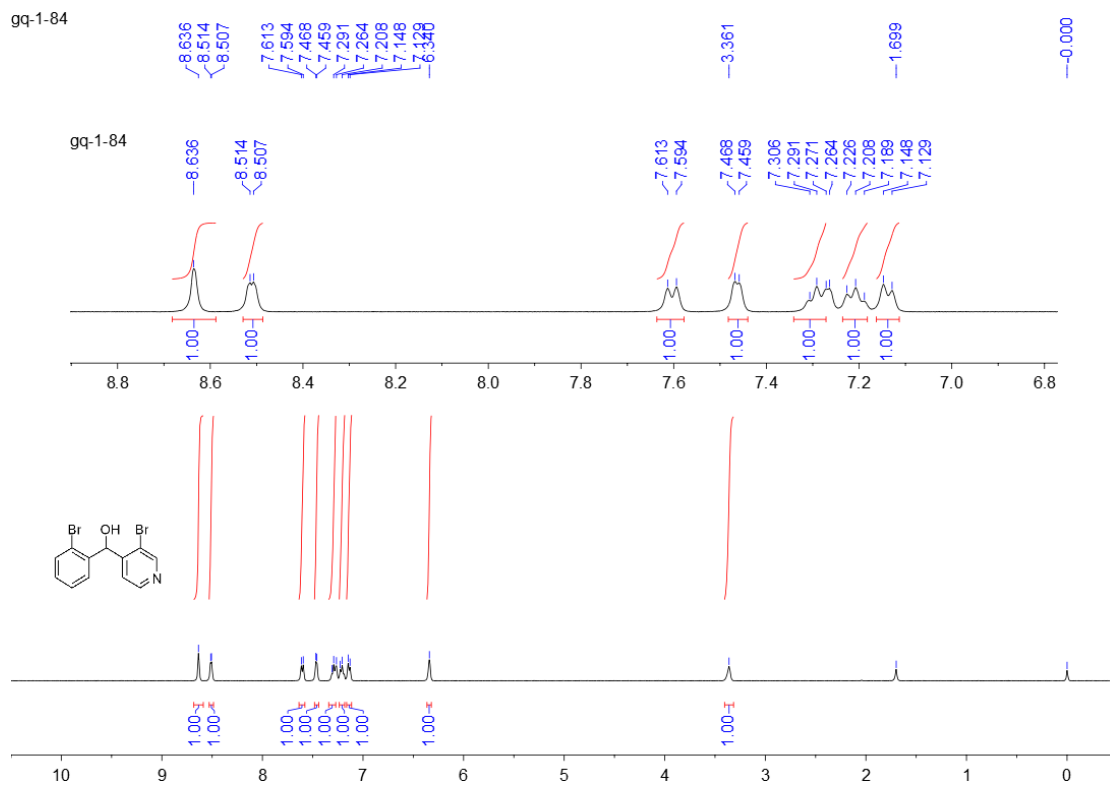




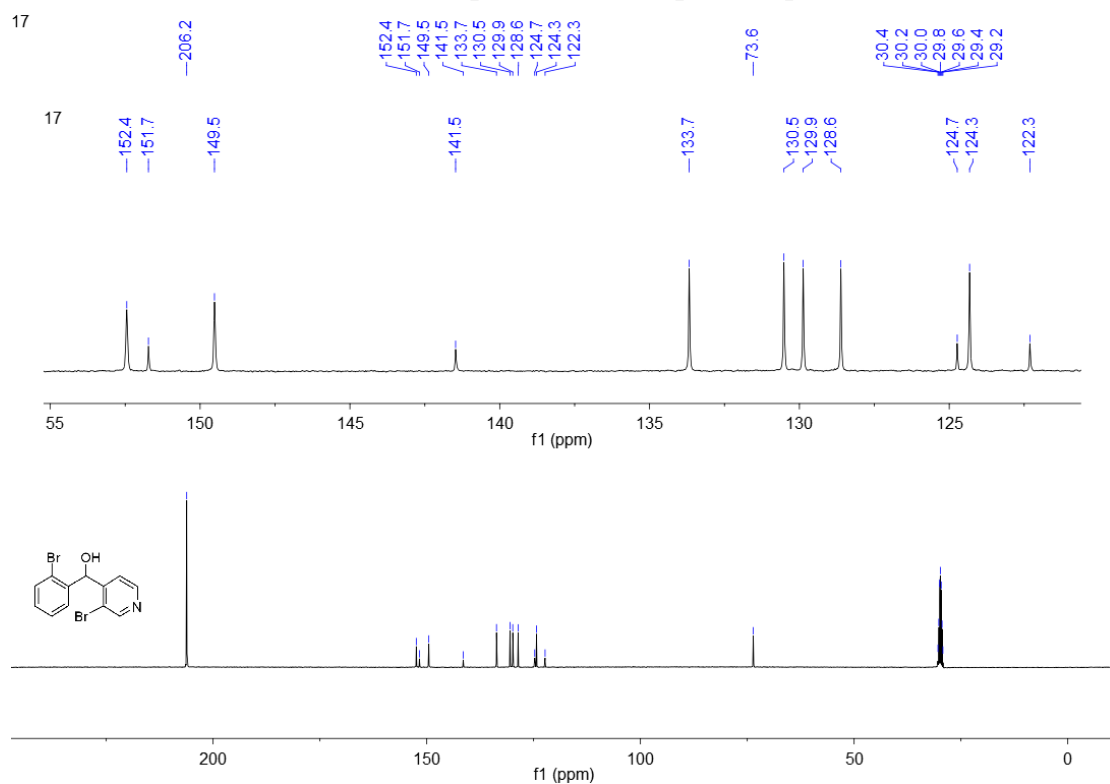
**<sup>1</sup>H NMR Spectrum of Compound 1p**



**<sup>13</sup>C NMR Spectrum of Compound 1p**

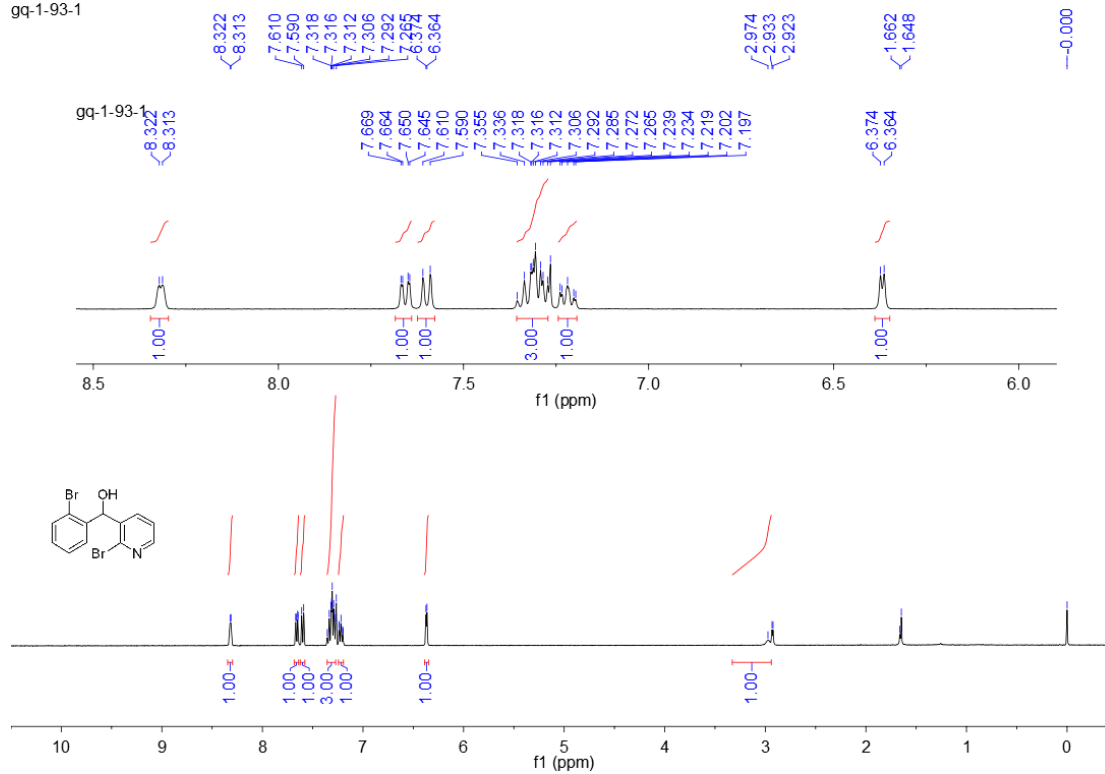


<sup>1</sup>H NMR Spectrum of Compound 1q

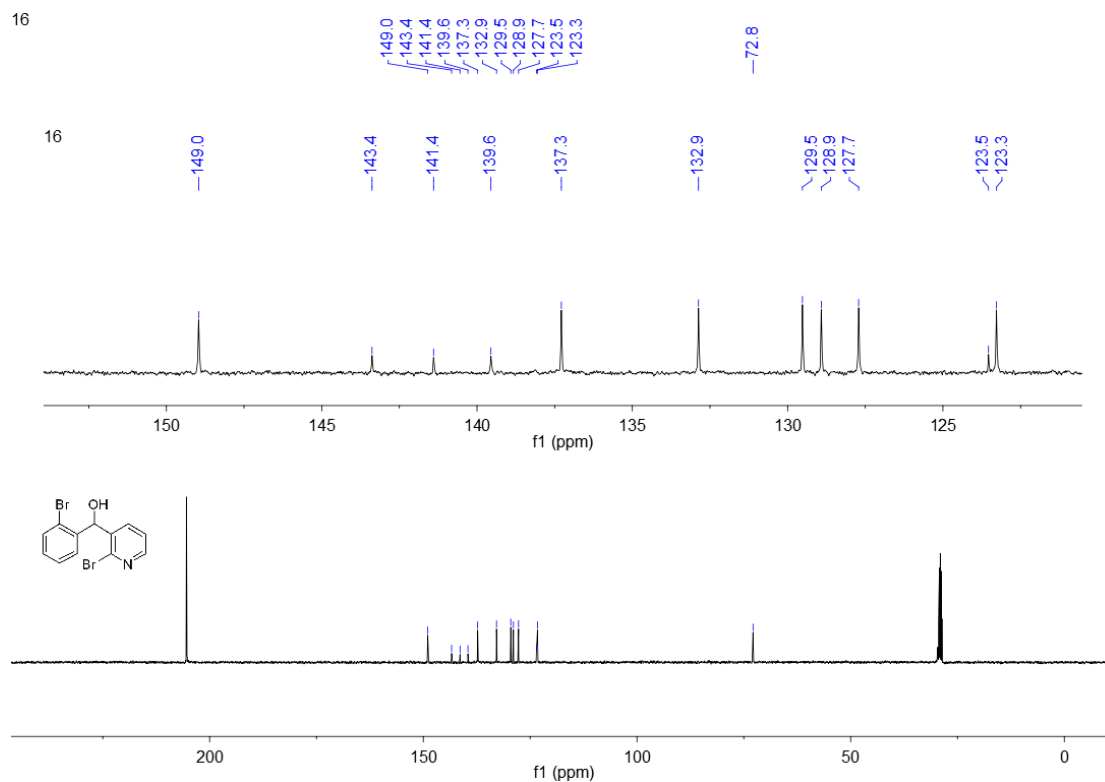


<sup>13</sup>C NMR Spectrum of Compound 1q

gq-1-93-1



**<sup>1</sup>H NMR Spectrum of Compound 1r**



**<sup>13</sup>C NMR Spectrum of Compound 1r**

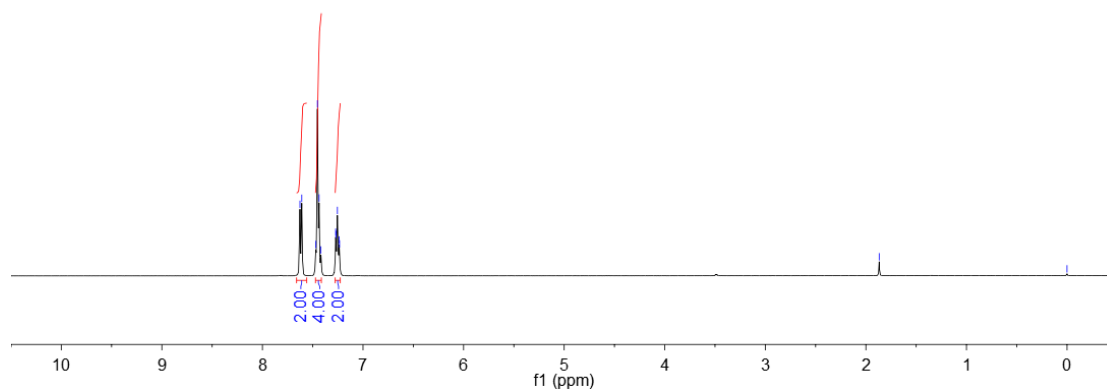
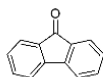


biaozhun-H

7.627  
7.609  
7.489  
7.453  
7.437  
7.418  
7.272  
7.268  
7.255  
7.237  
7.233

-1.868

-0.000



<sup>1</sup>H NMR Spectrum of Compound 2a

biaozhun-C

-193.8

-144.3

134.6

134.0

128.9

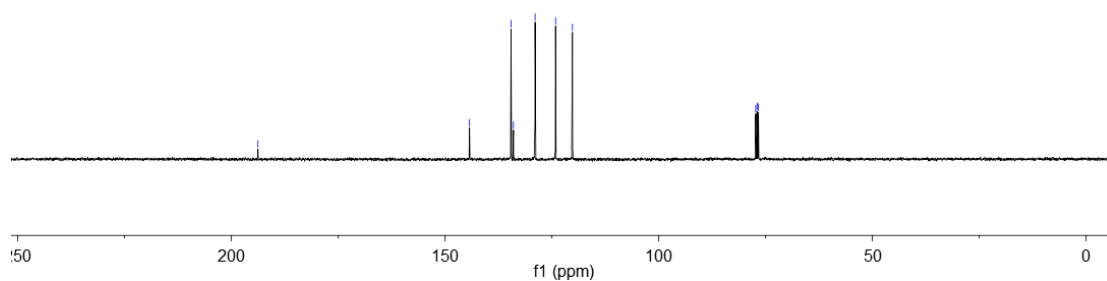
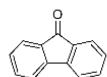
124.2

120.2

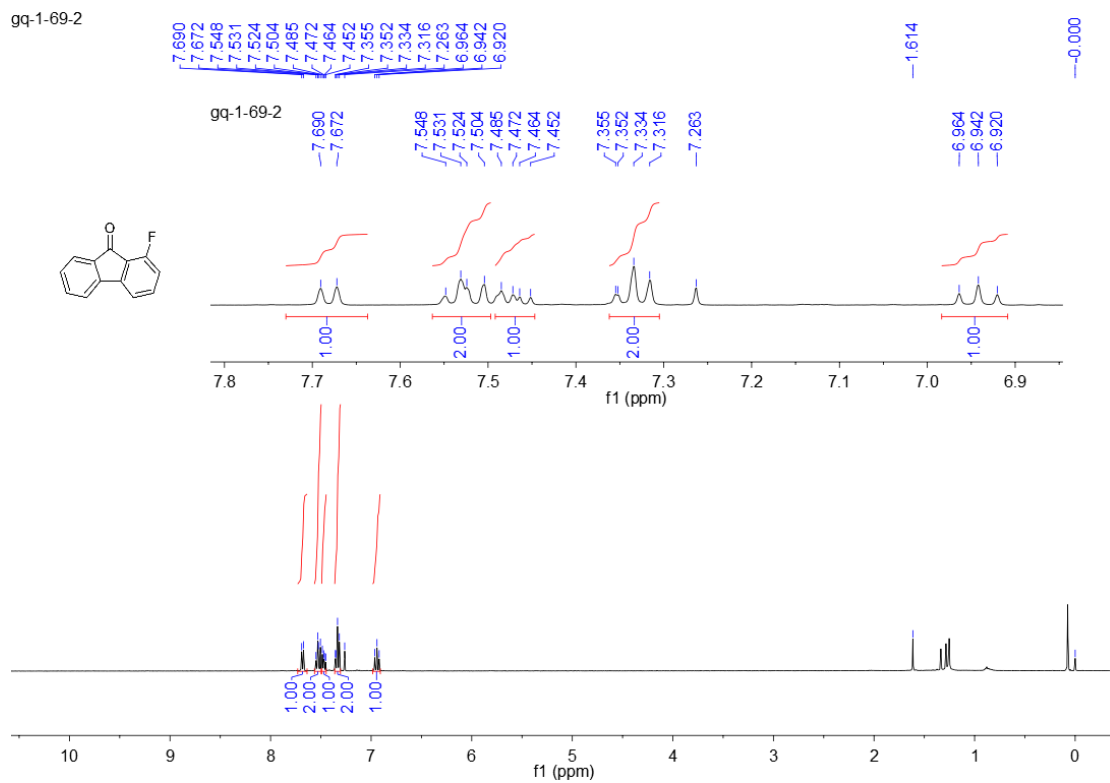
77.3

77.0

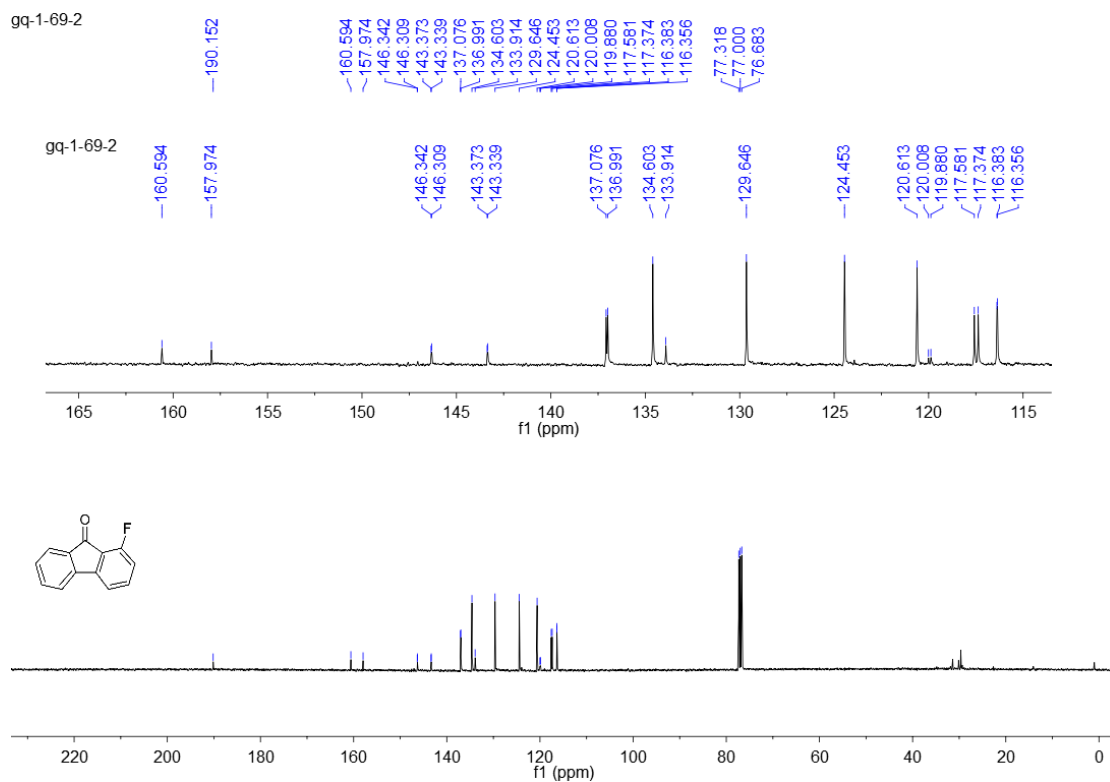
76.7



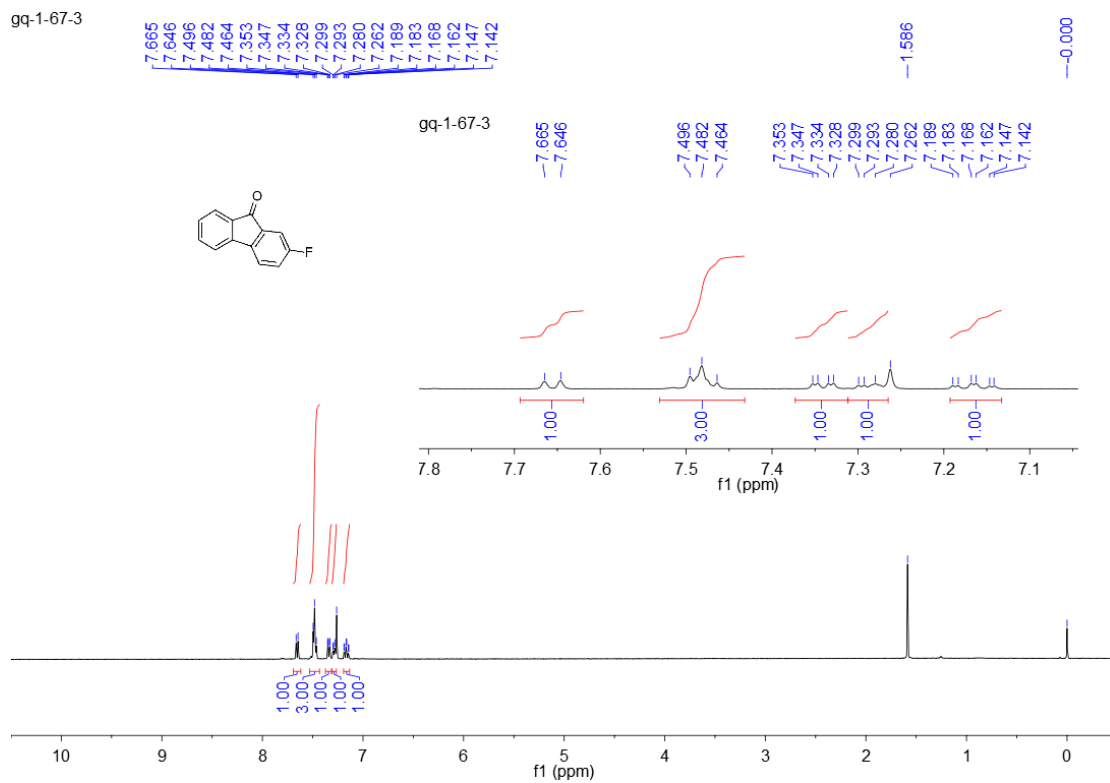
<sup>13</sup>C NMR Spectrum of Compound 2a



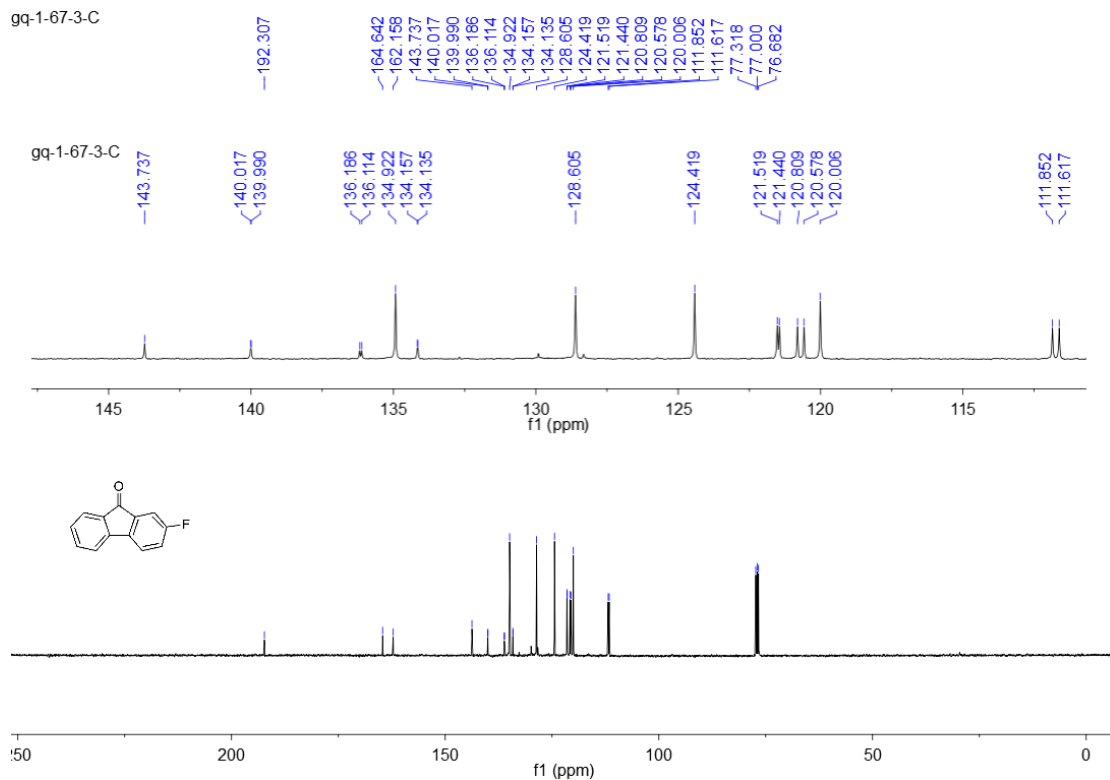
### <sup>1</sup>H NMR Spectrum of Compound 2b



### <sup>13</sup>C NMR Spectrum of Compound 2b

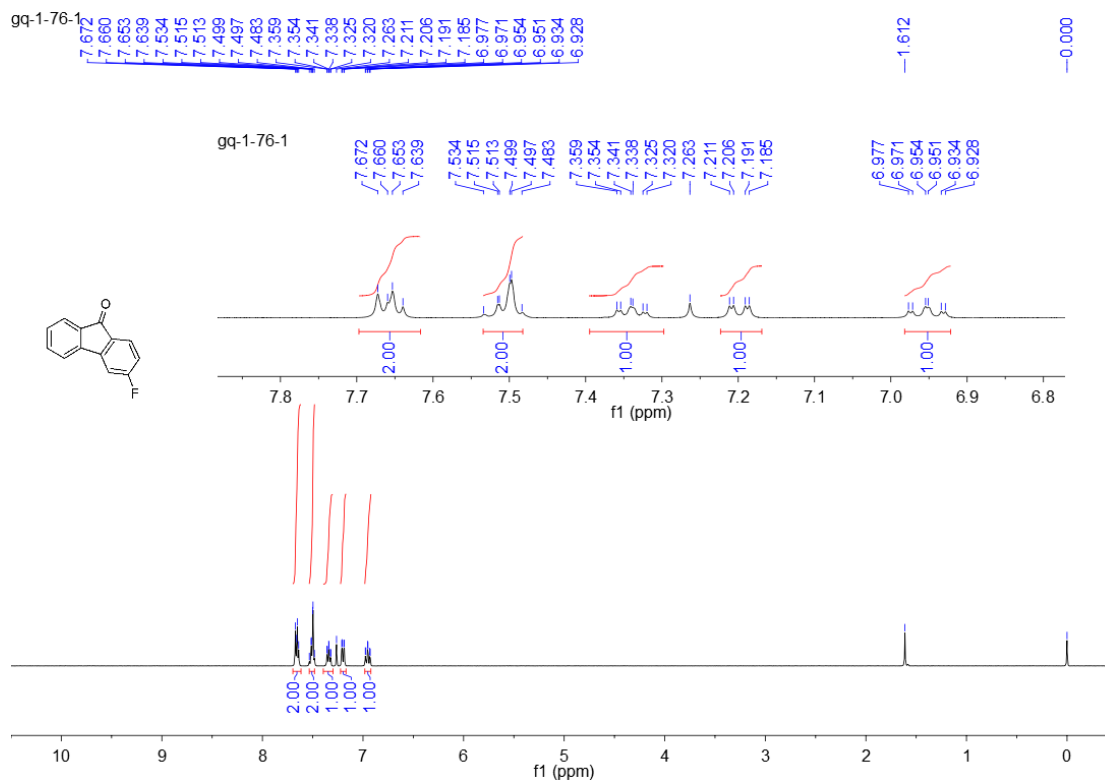


**<sup>1</sup>H NMR Spectrum of Compound 2c**

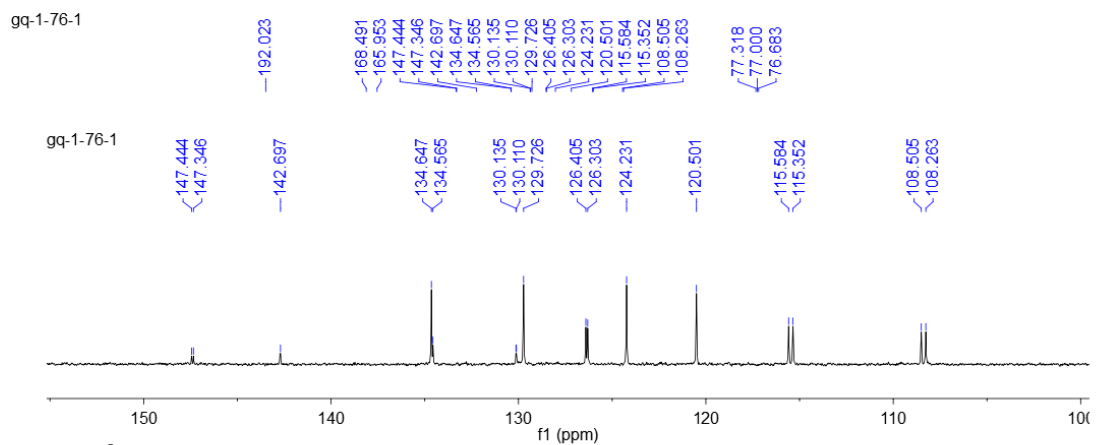


**<sup>13</sup>C NMR Spectrum of Compound 2c**

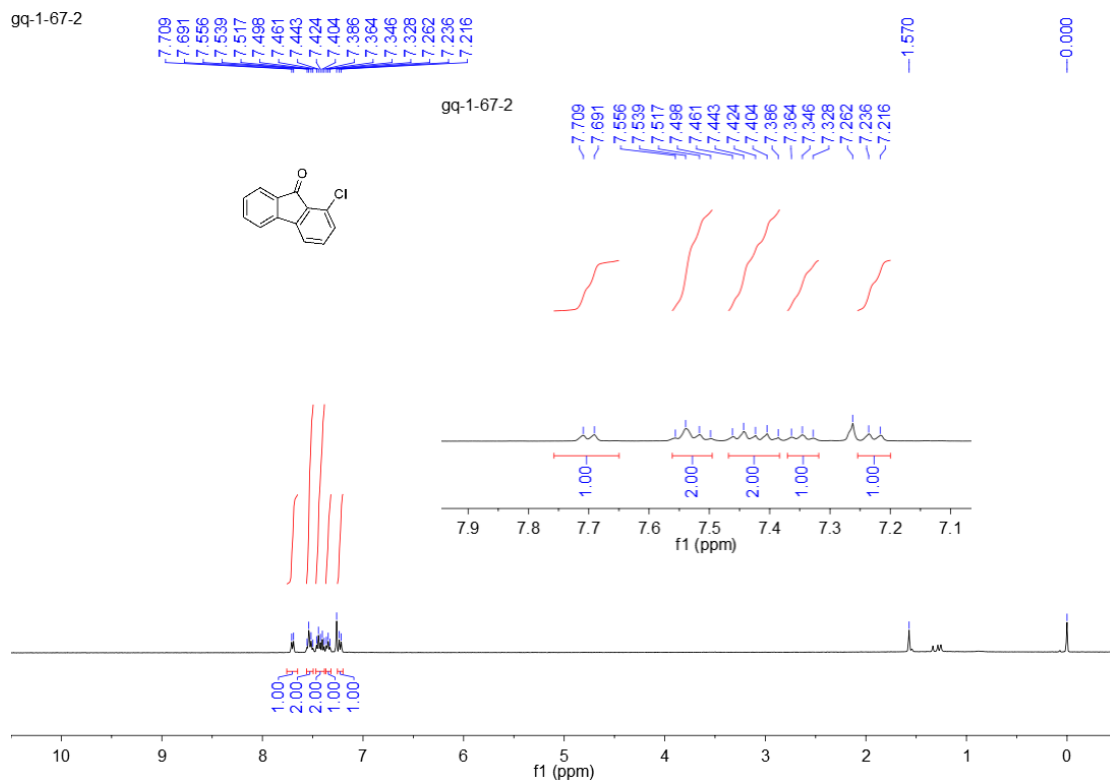




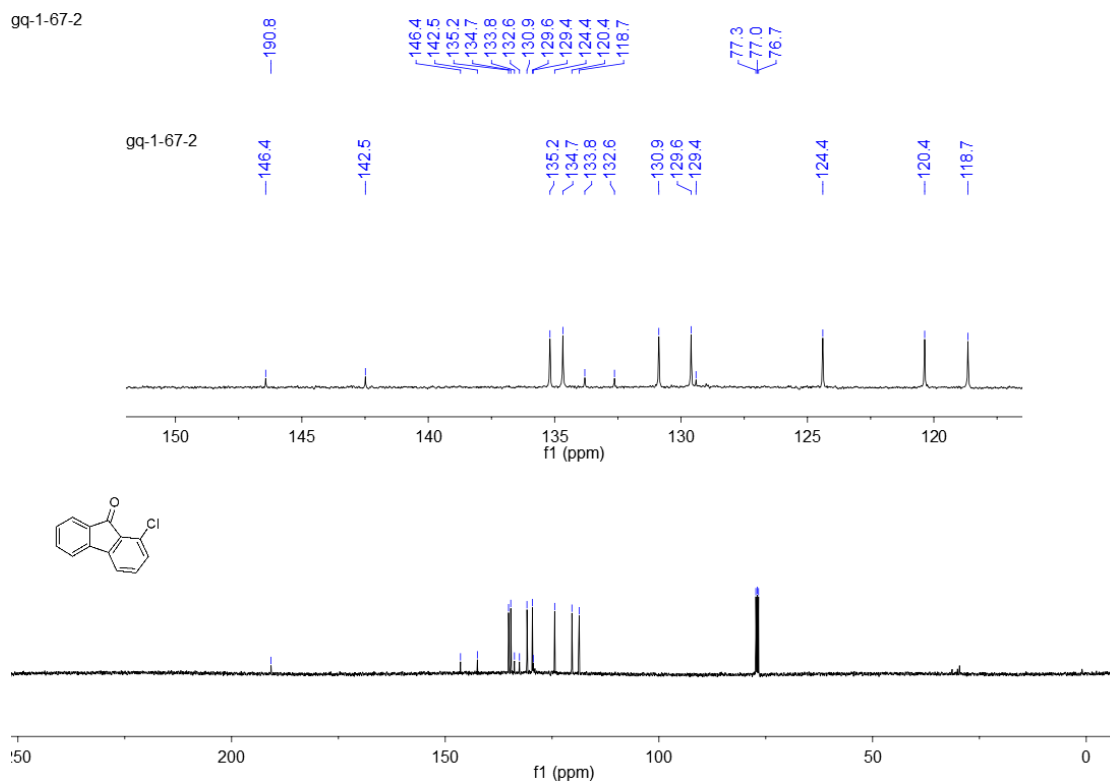
### <sup>1</sup>H NMR Spectrum of Compound 2d



### <sup>13</sup>C NMR Spectrum of Compound 2d



**<sup>1</sup>H NMR Spectrum of Compound 2e**



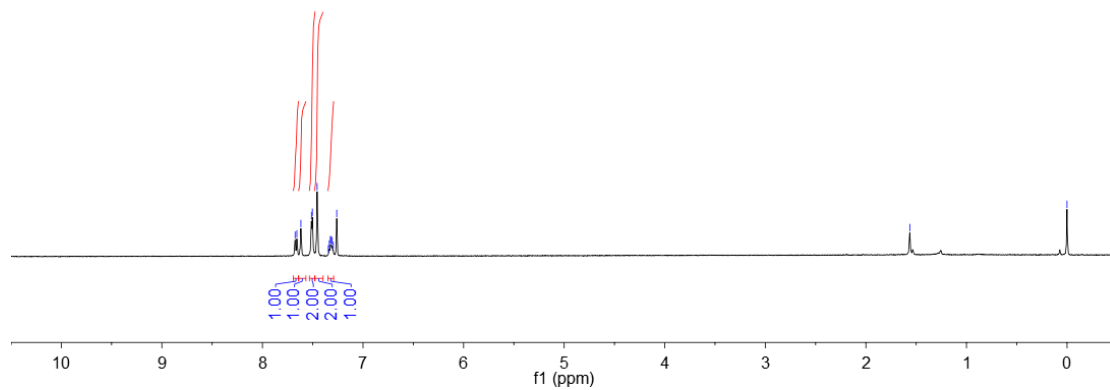
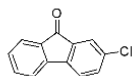
**<sup>13</sup>C NMR Spectrum of Compound 2e**

gq-1-80-1-H

7.675  
7.657  
7.618  
7.513  
7.504  
7.466  
7.345  
7.335  
7.325  
7.316  
7.306  
7.295  
7.261

-1.564

-0.000



<sup>1</sup>H NMR Spectrum of Compound 2f

gq-1-80-1

-192.5

143.7  
142.6  
135.6  
135.0  
134.2  
133.9  
129.3  
124.7  
124.6  
121.4  
120.4

-129.3

77.3  
77.0  
76.7

-0.0

gq-1-80-1

-143.7

-142.6

135.6

135.0

134.2

133.9

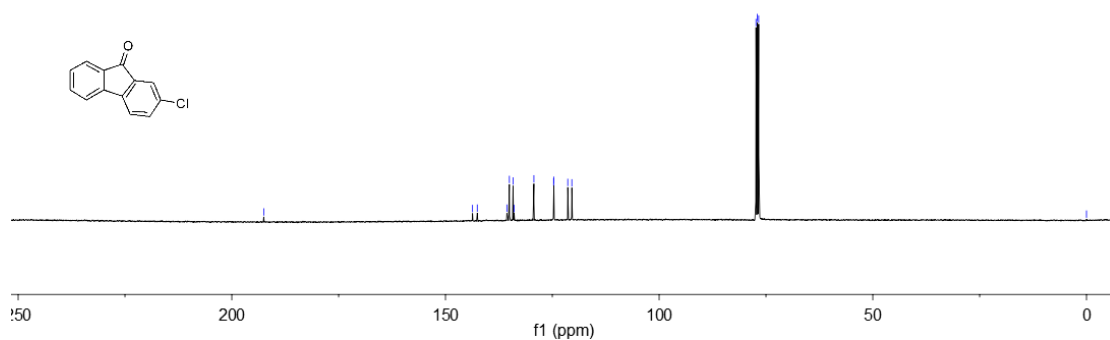
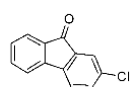
-129.3

124.7

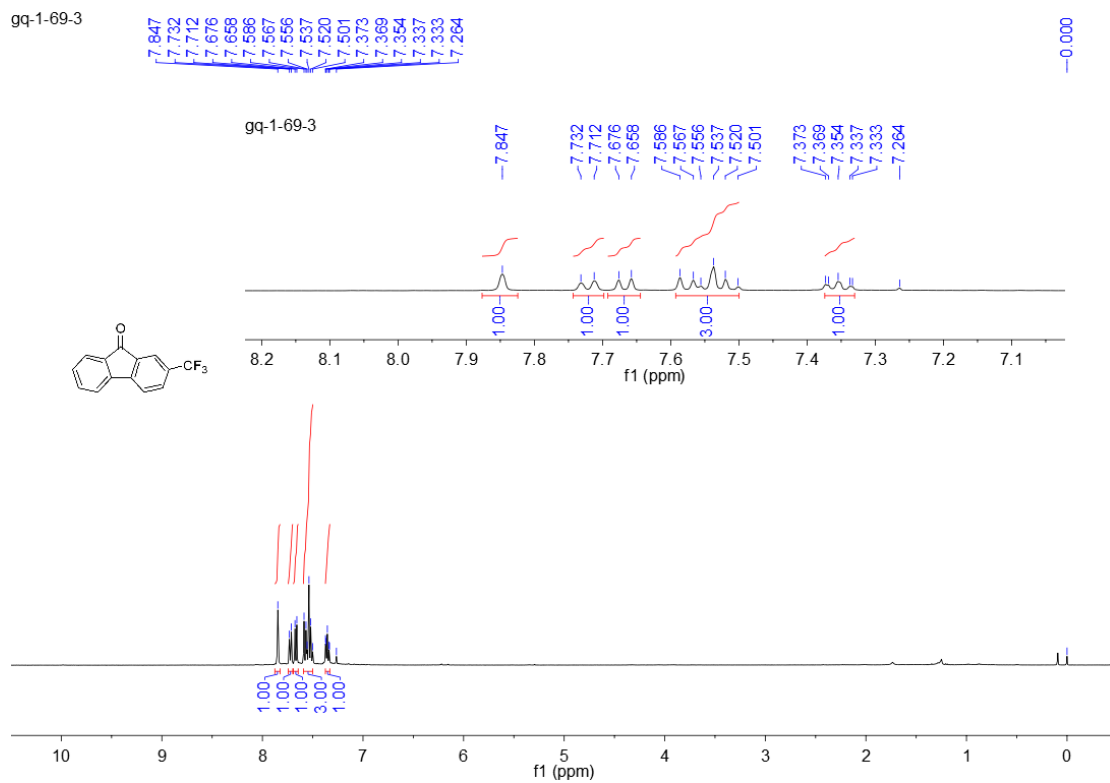
124.6

-121.4

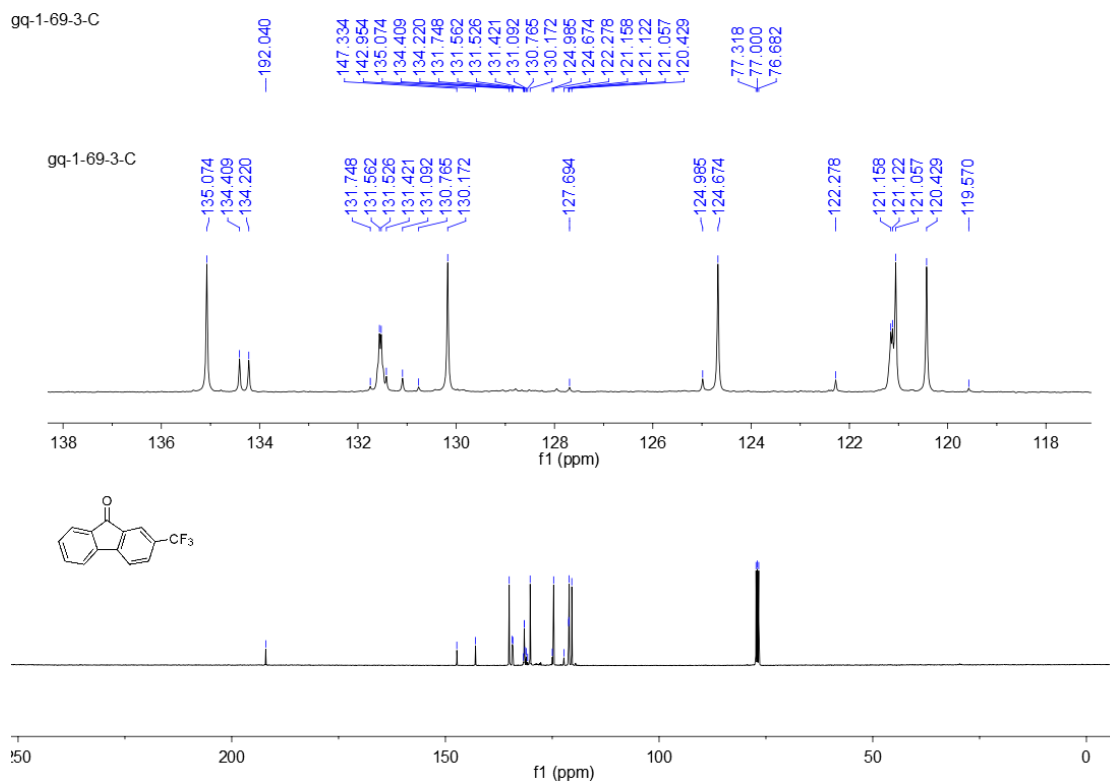
-120.4



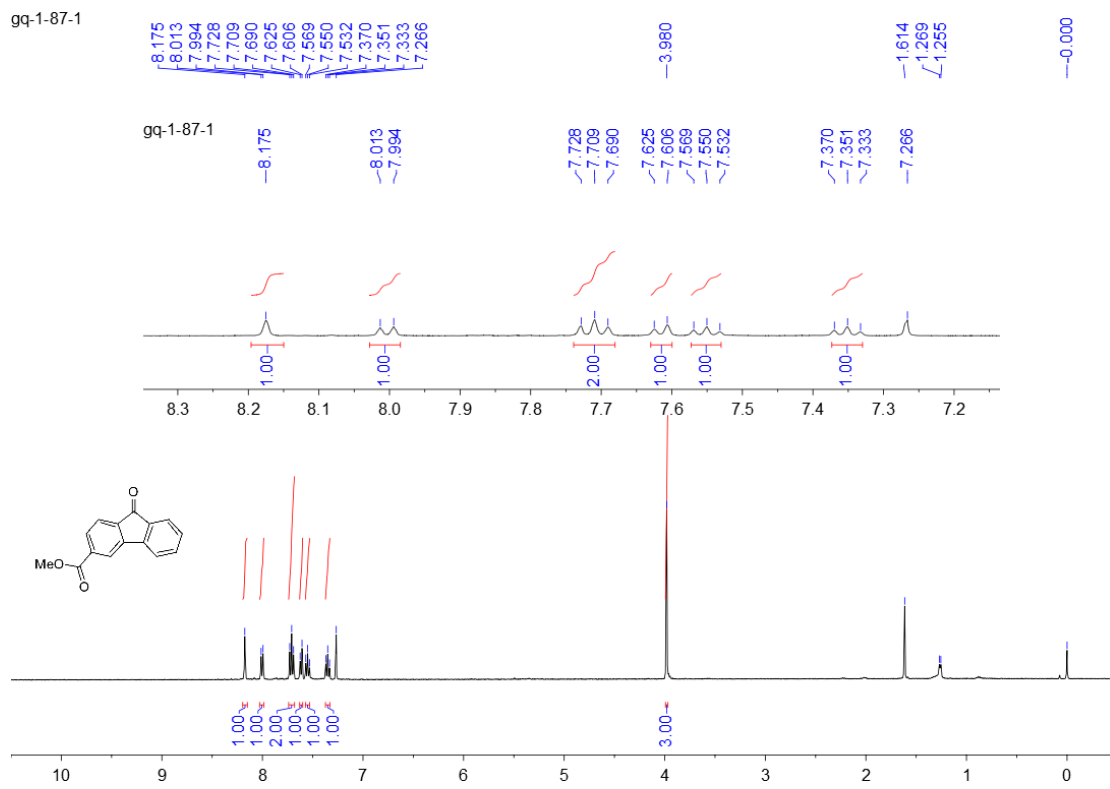
<sup>13</sup>C NMR Spectrum of Compound 2f



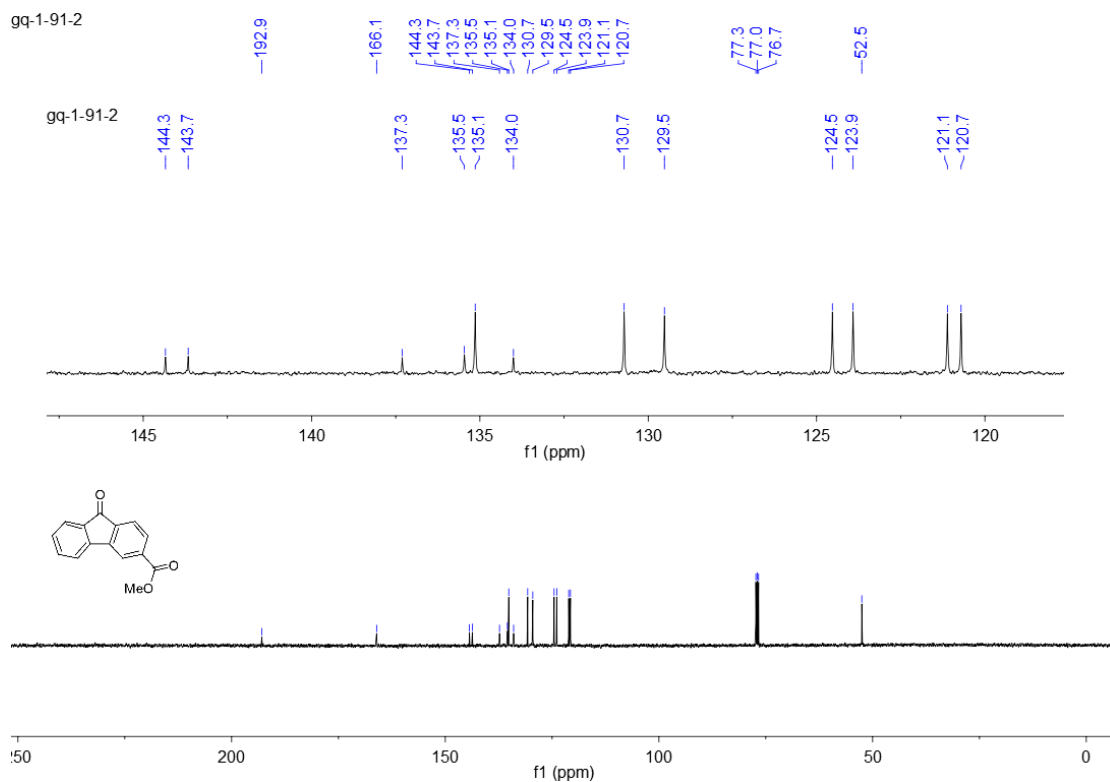
### <sup>1</sup>H NMR Spectrum of Compound 2g



### <sup>13</sup>C NMR Spectrum of Compound 2g



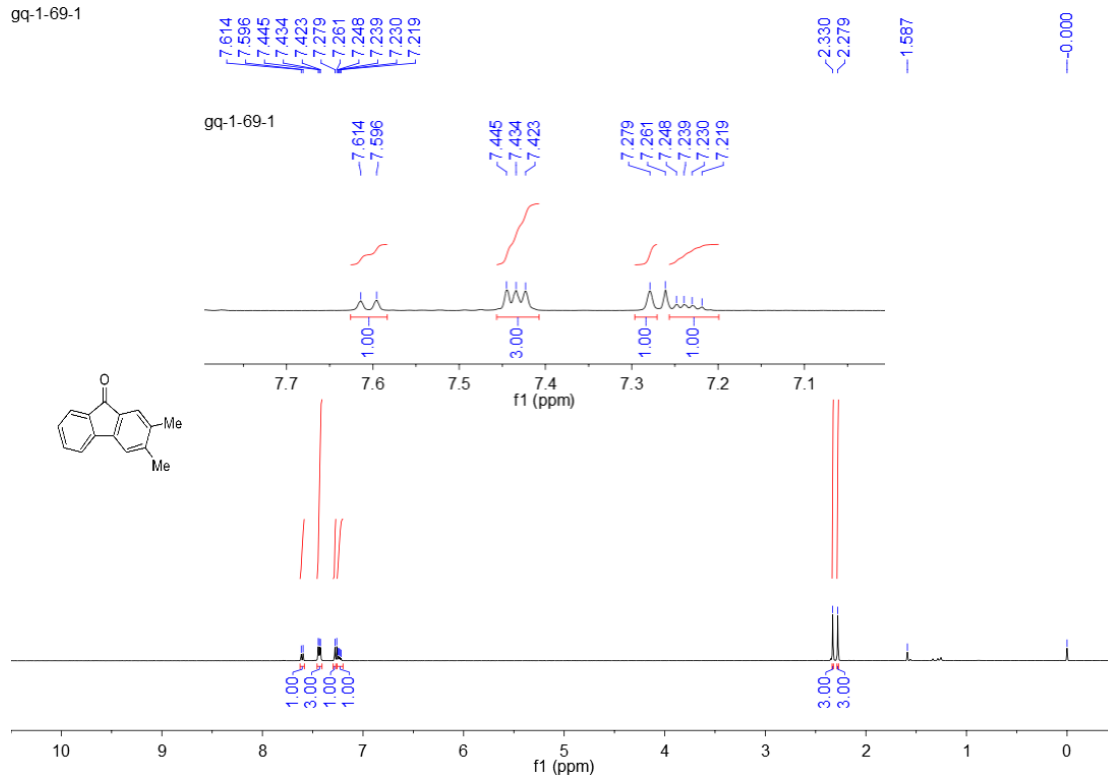
**<sup>1</sup>H NMR Spectrum of Compound 2h**



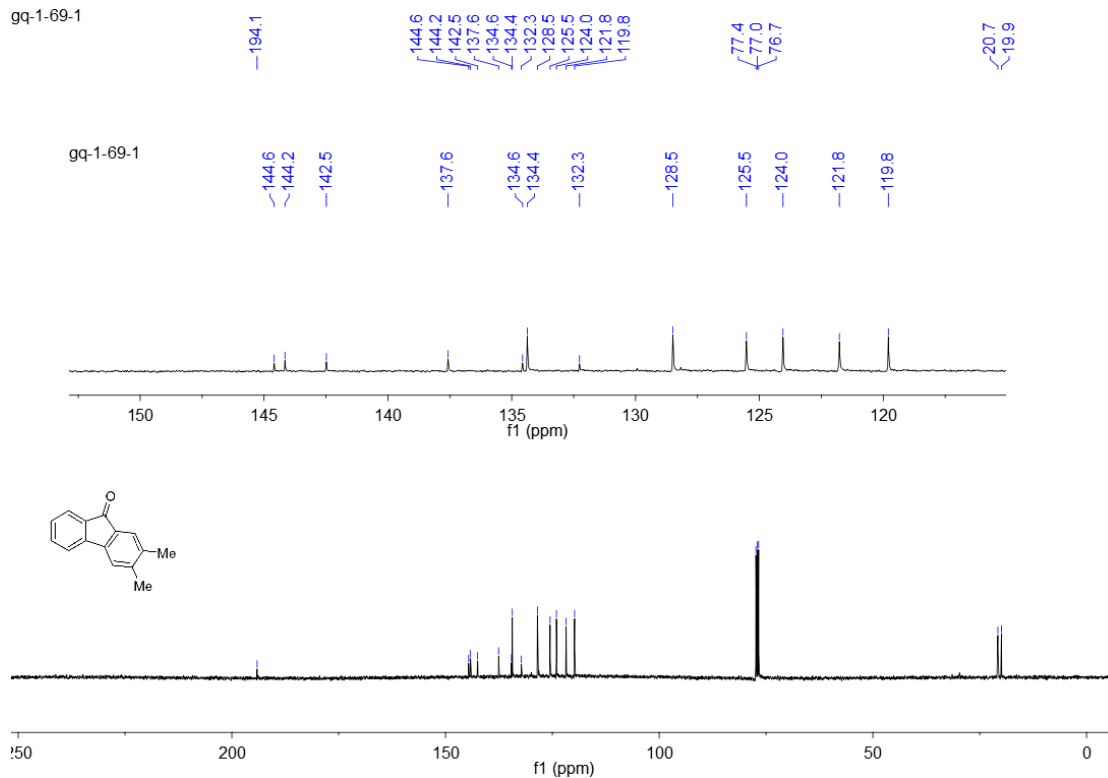
**<sup>13</sup>C NMR Spectrum of Compound 2h**

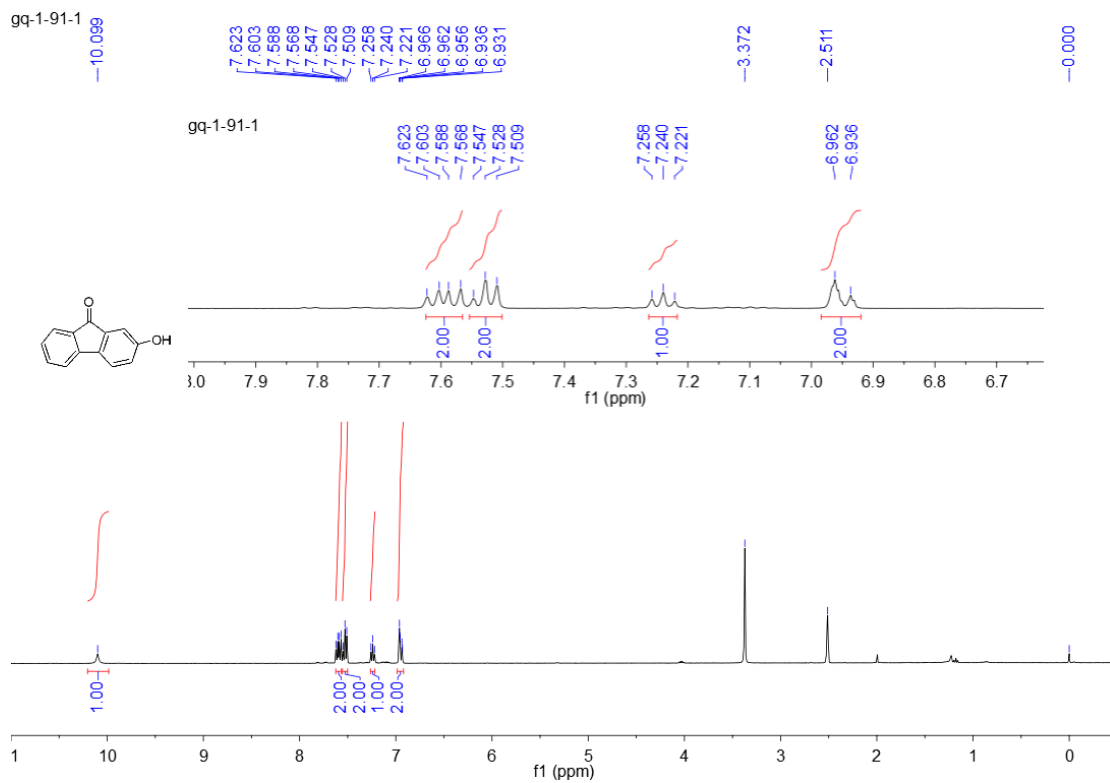


gq-1-69-1

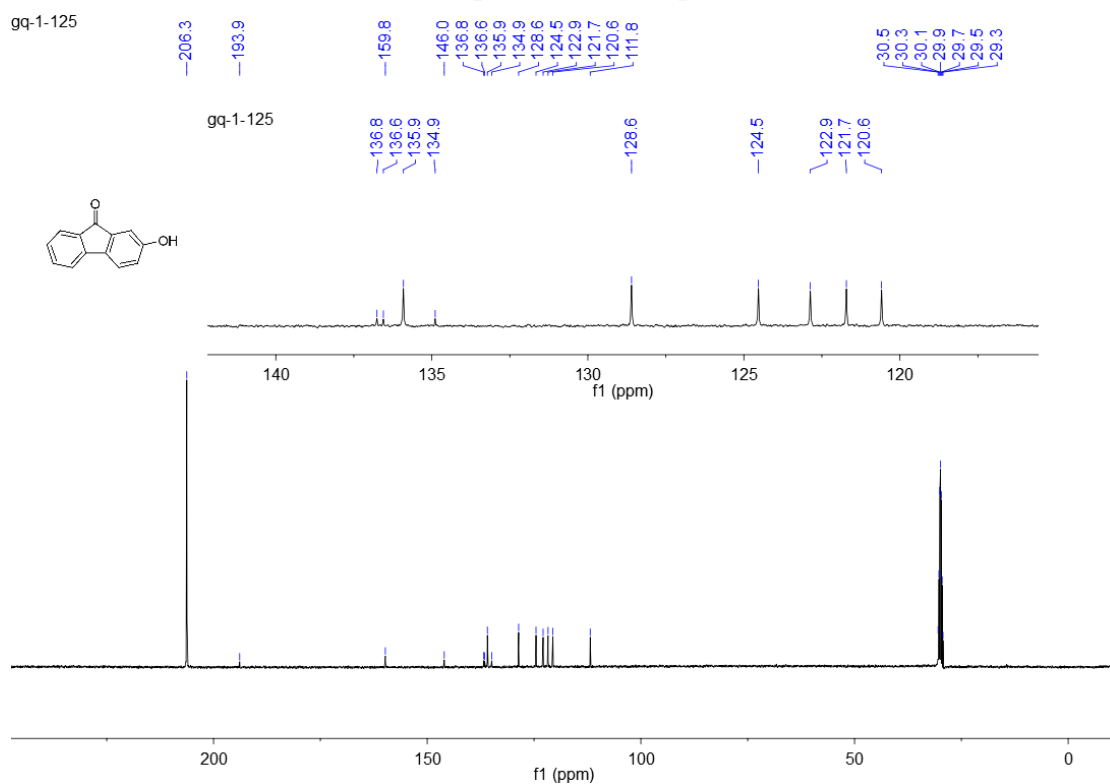


gq-1-69-1

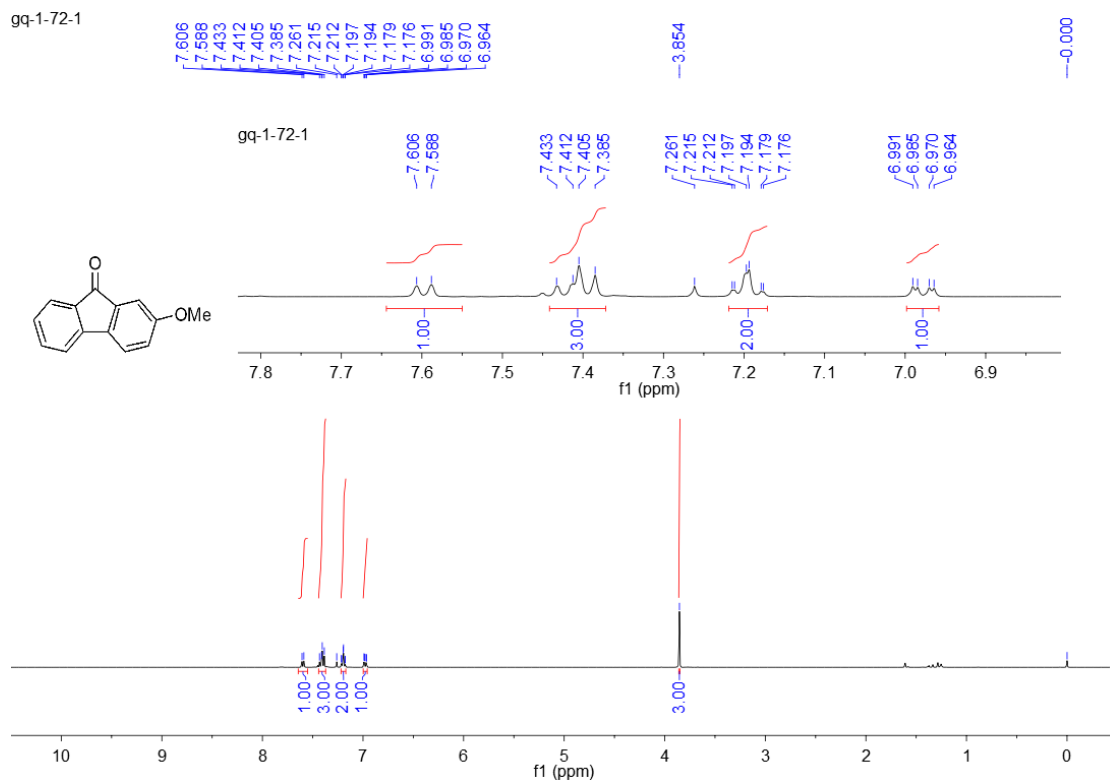




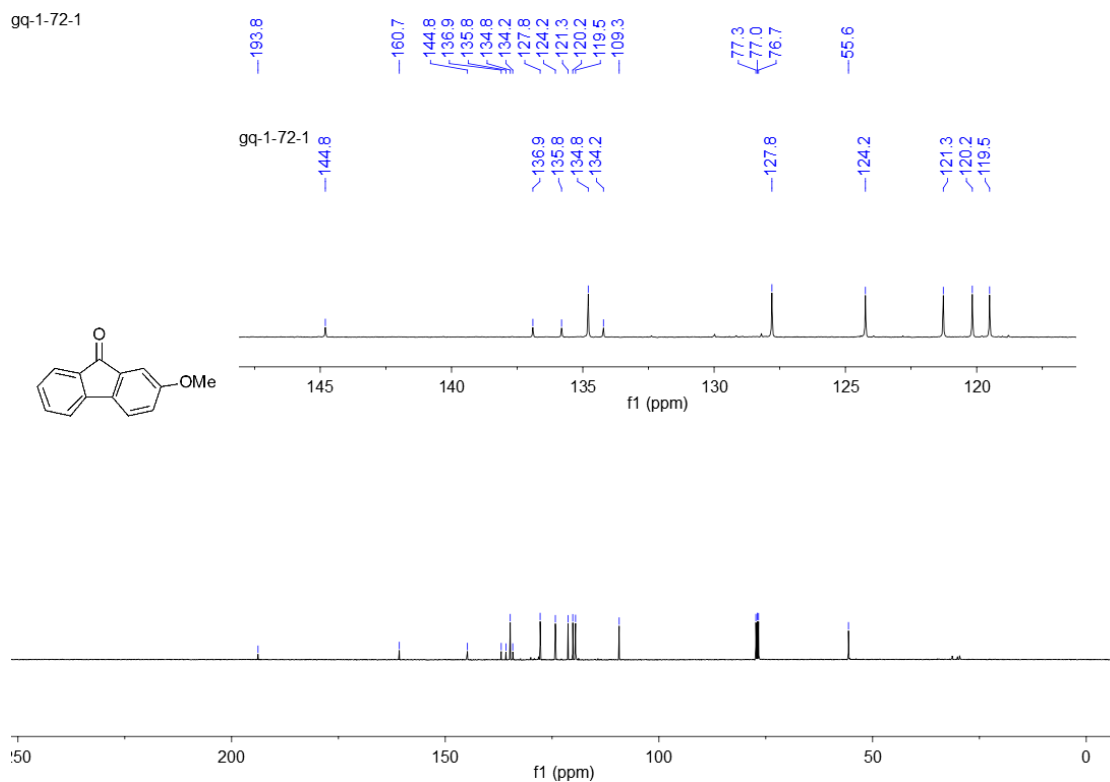
<sup>1</sup>H NMR Spectrum of Compound 2j



<sup>13</sup>C NMR Spectrum of Compound 2j



### <sup>1</sup>H NMR Spectrum of Compound 2k

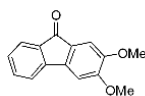
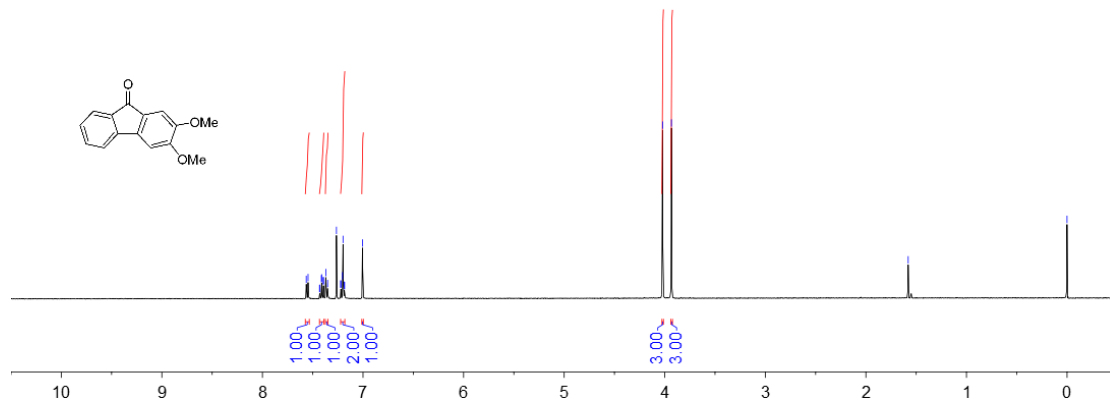
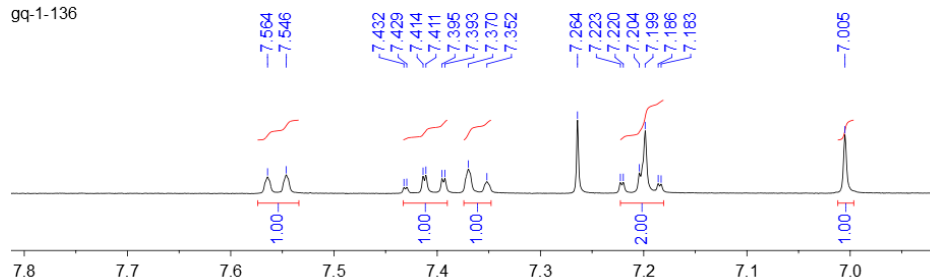


### <sup>13</sup>C NMR Spectrum of Compound 2k

gq-1-136



gq-1-136

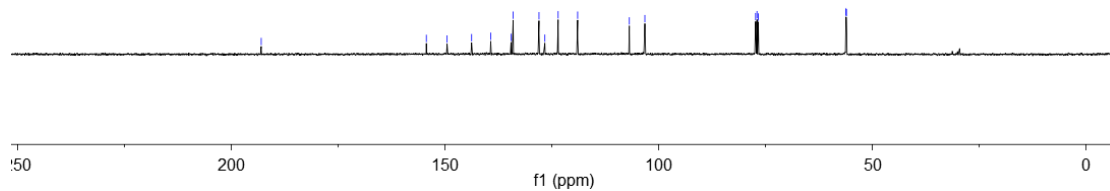
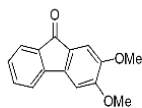
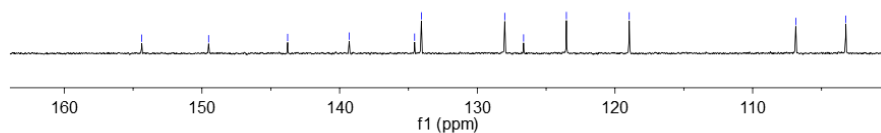


<sup>1</sup>H NMR Spectrum of Compound 21

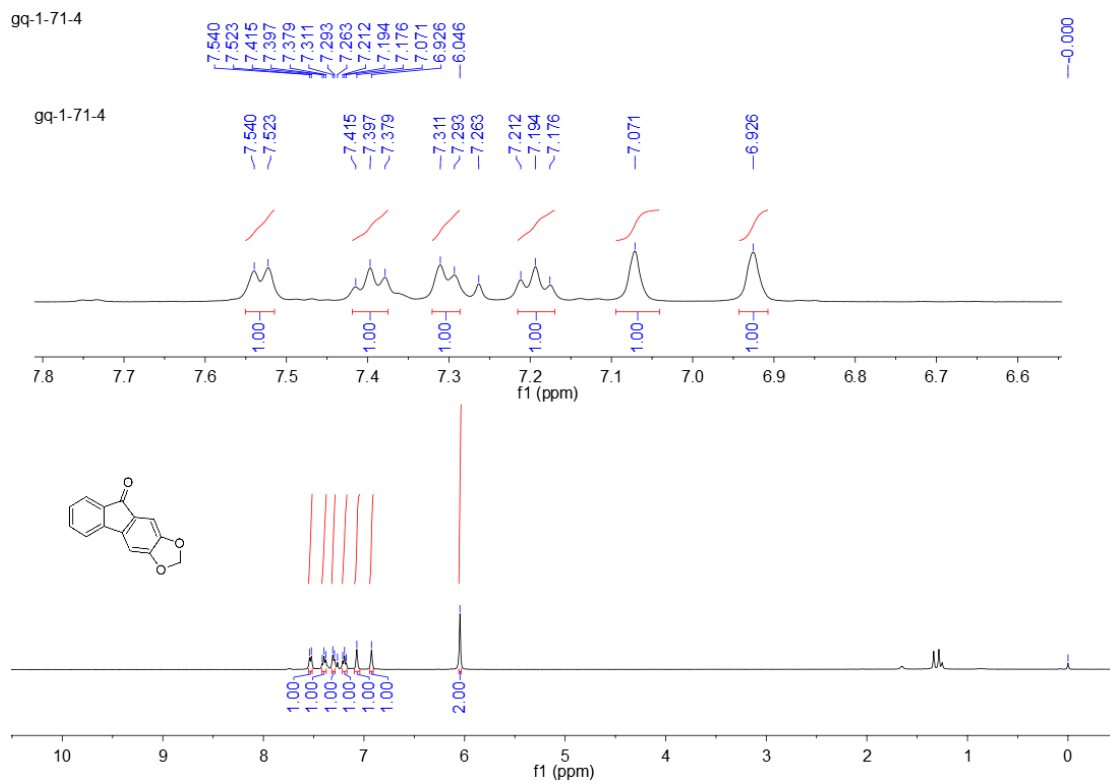
gq-1-67-4



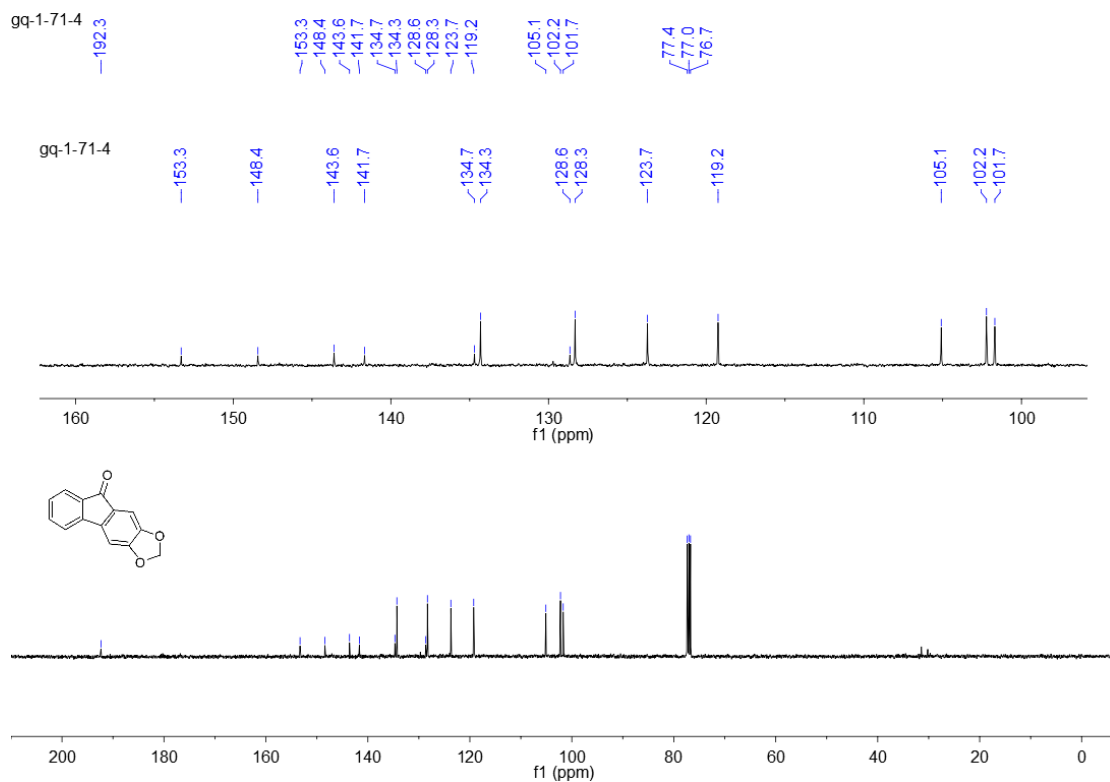
gq-1-67-4



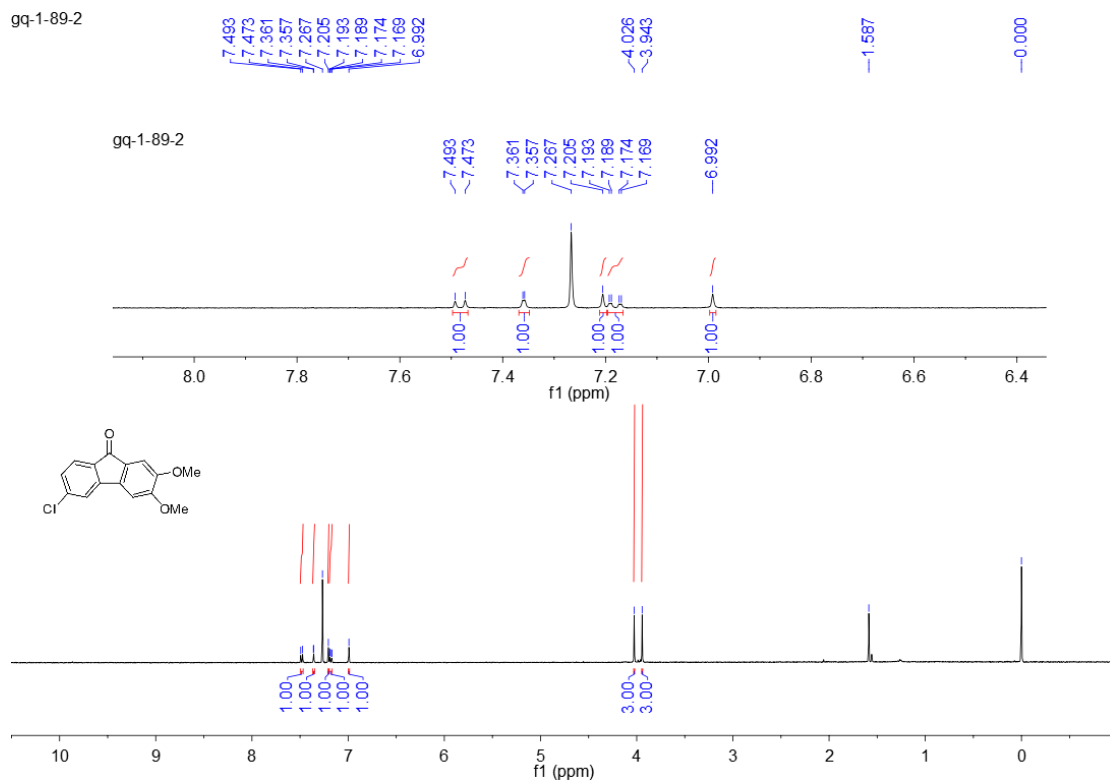
<sup>13</sup>C NMR Spectrum of Compound 21



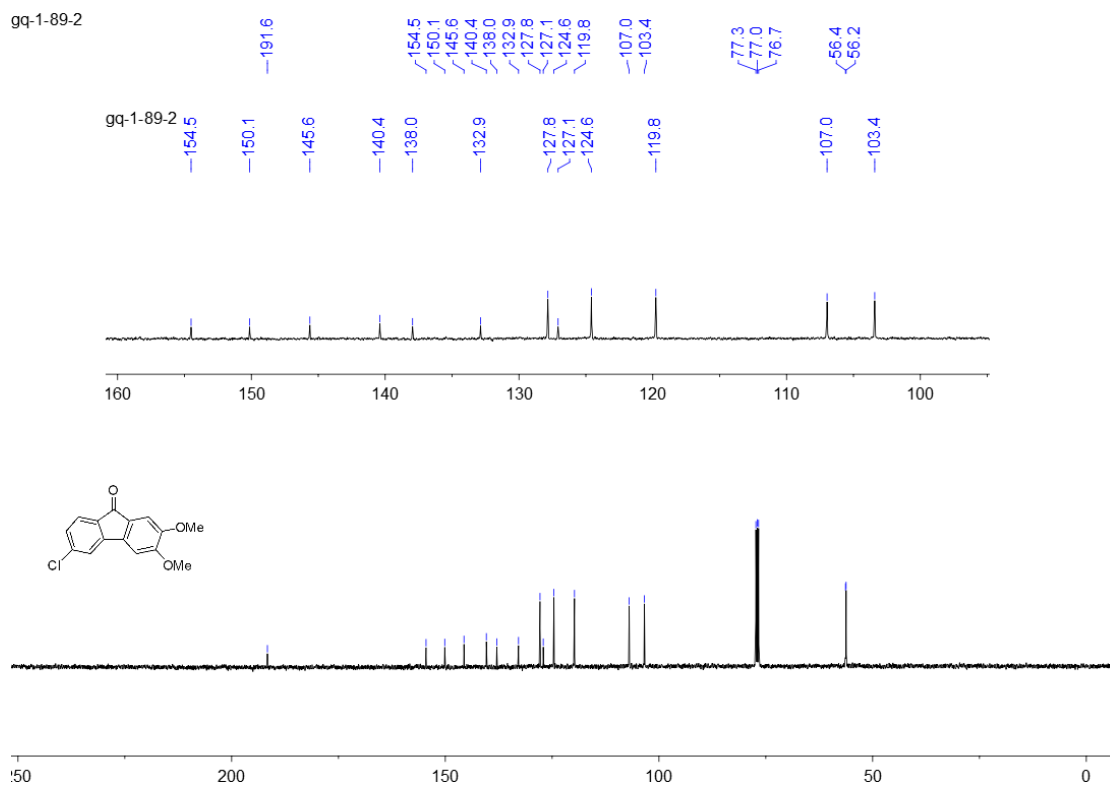
**<sup>1</sup>H NMR Spectrum of Compound 2m**



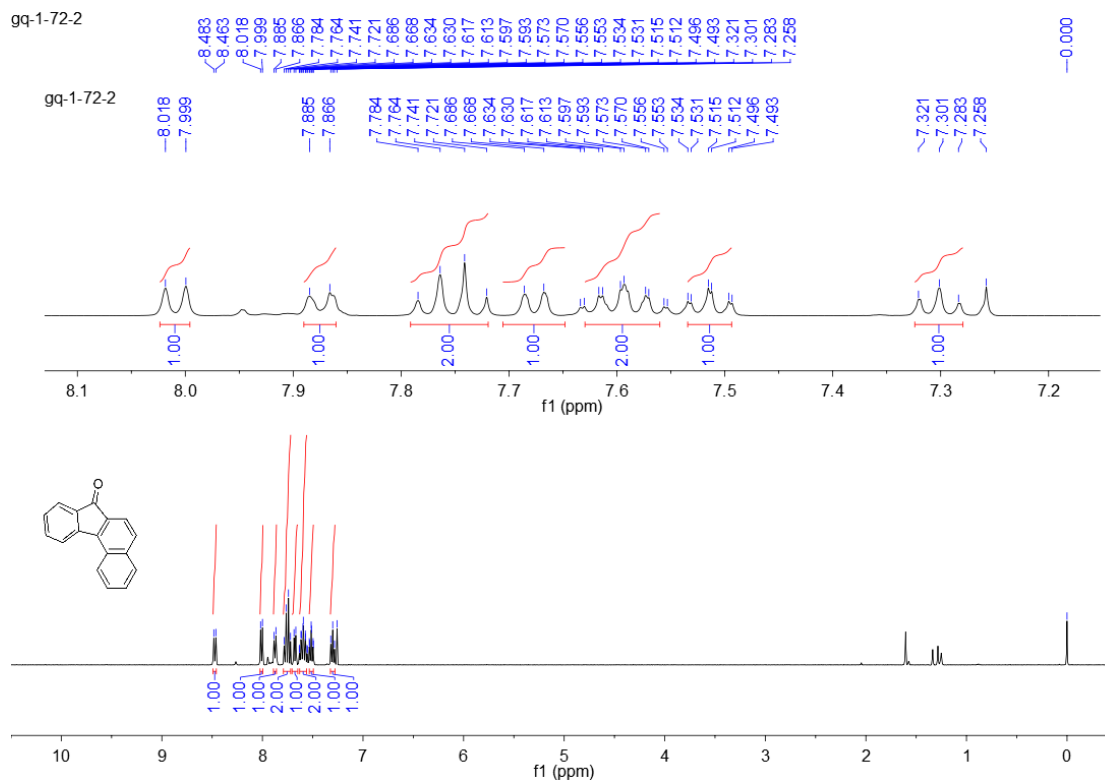
**<sup>13</sup>C NMR Spectrum of Compound 2m**



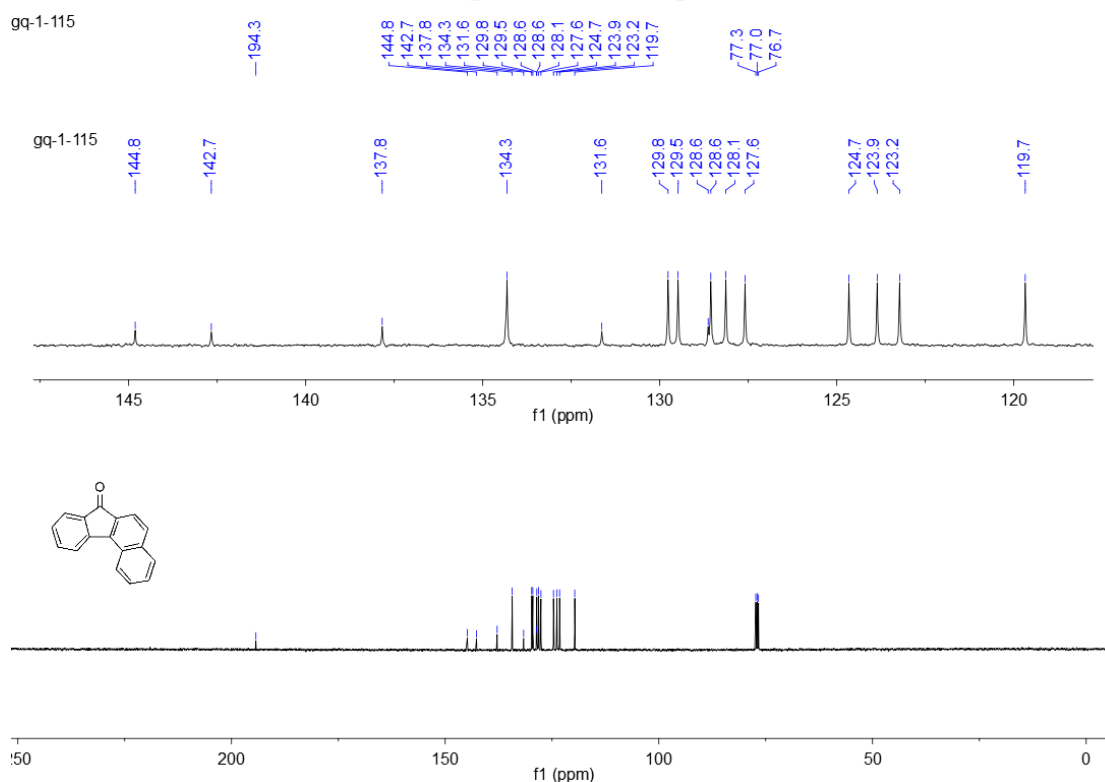
### <sup>1</sup>H NMR Spectrum of Compound 2n



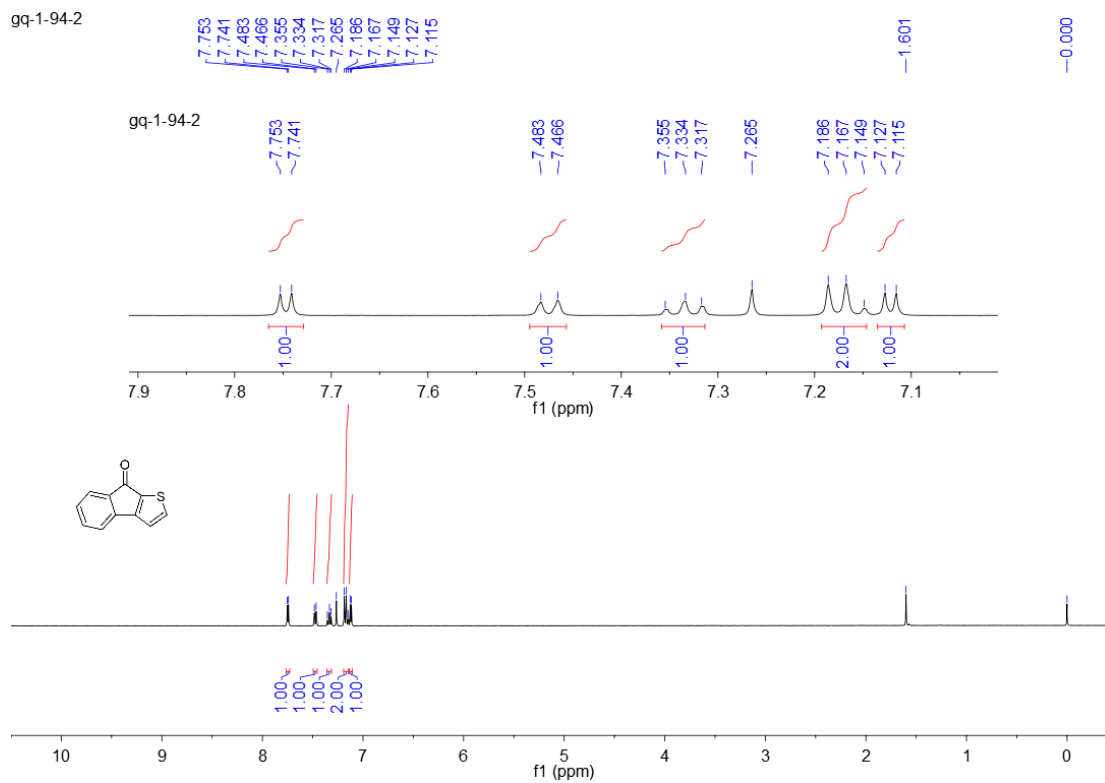
### <sup>13</sup>C NMR Spectrum of Compound 2n



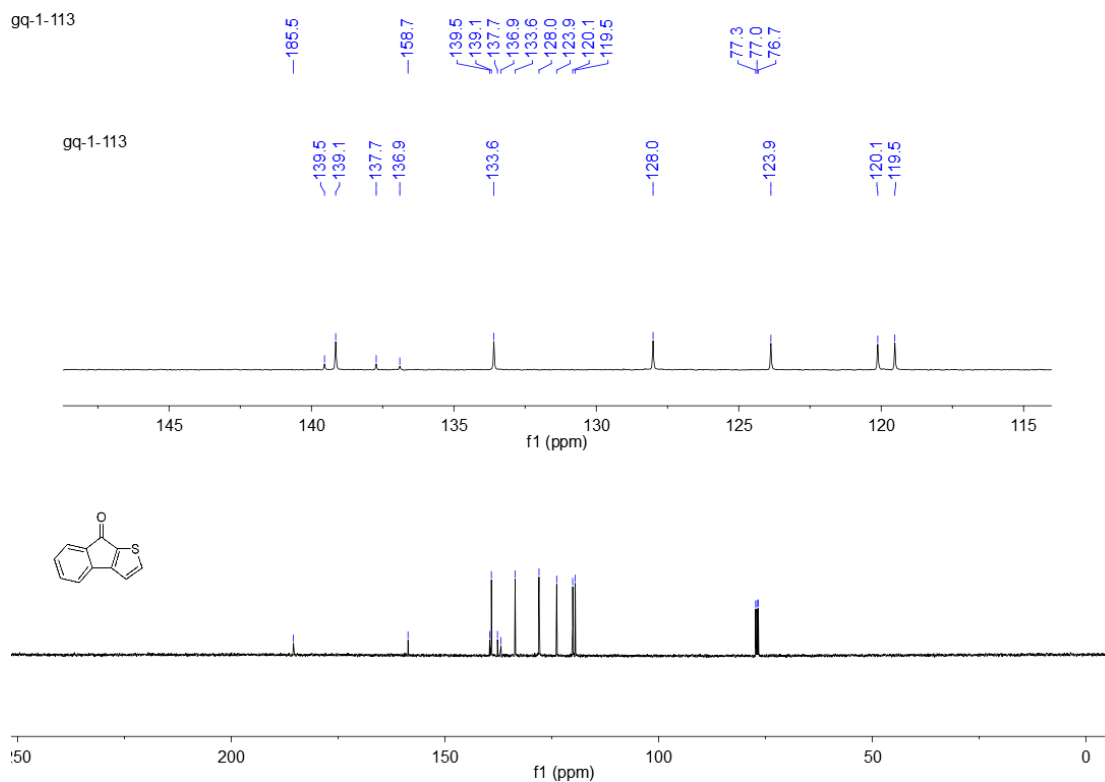
### <sup>1</sup>H NMR Spectrum of Compound 2o



### <sup>13</sup>C NMR Spectrum of Compound 2o



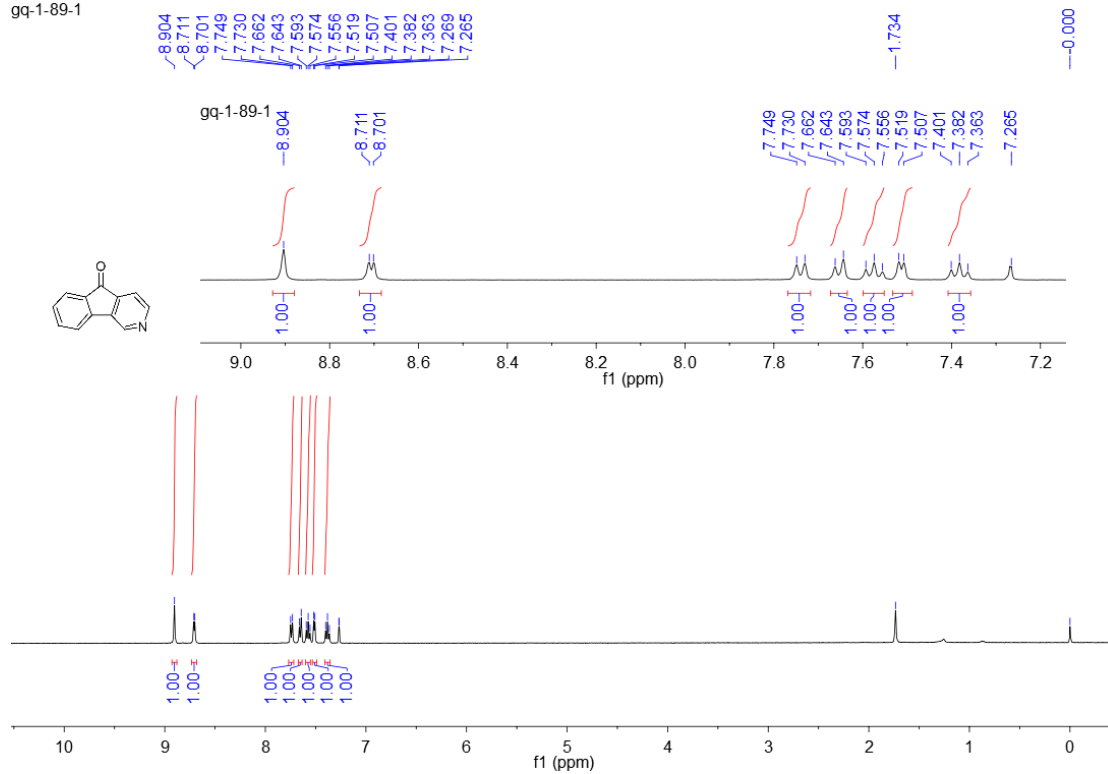
### <sup>1</sup>H NMR Spectrum of Compound 2p



### <sup>13</sup>C NMR Spectrum of Compound 2p

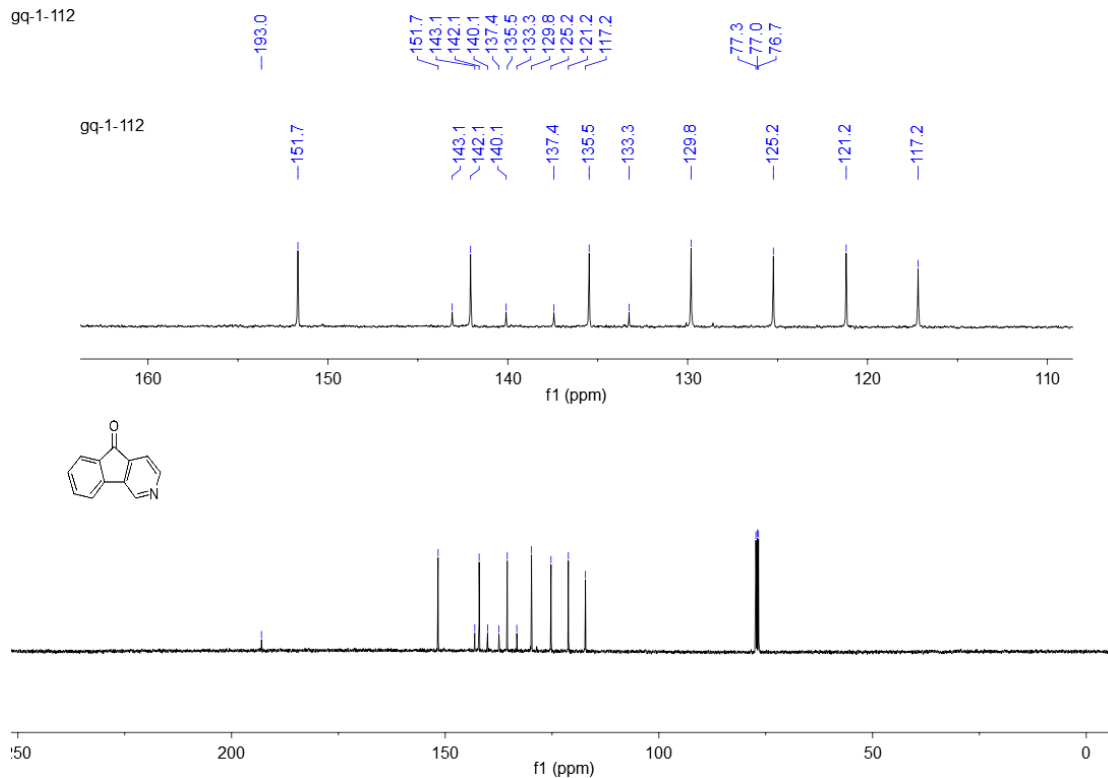


gq-1-89-1

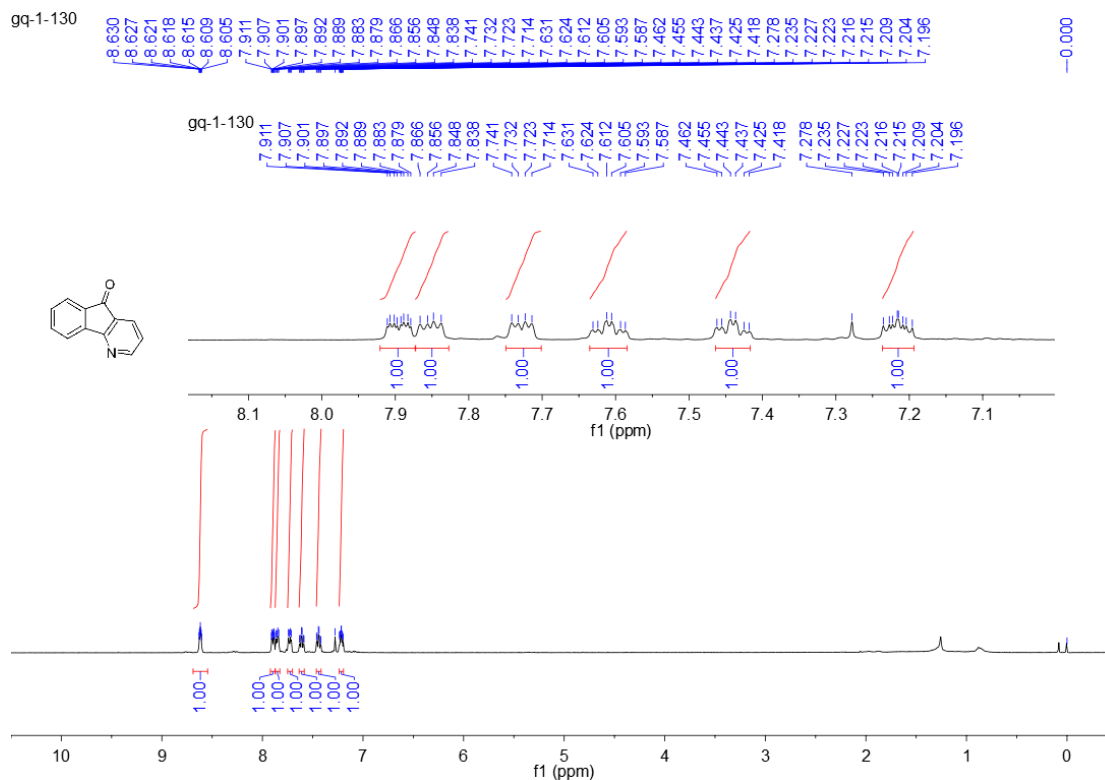


### <sup>1</sup>H NMR Spectrum of Compound 2q

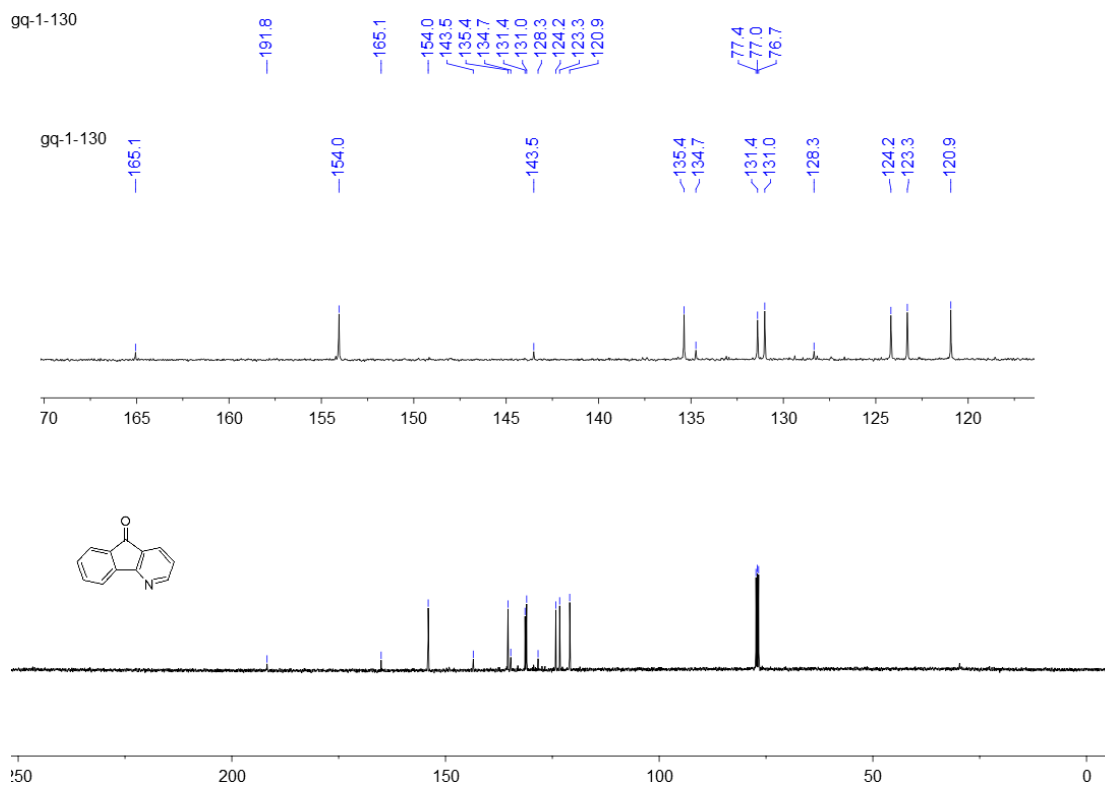
gq-1-112



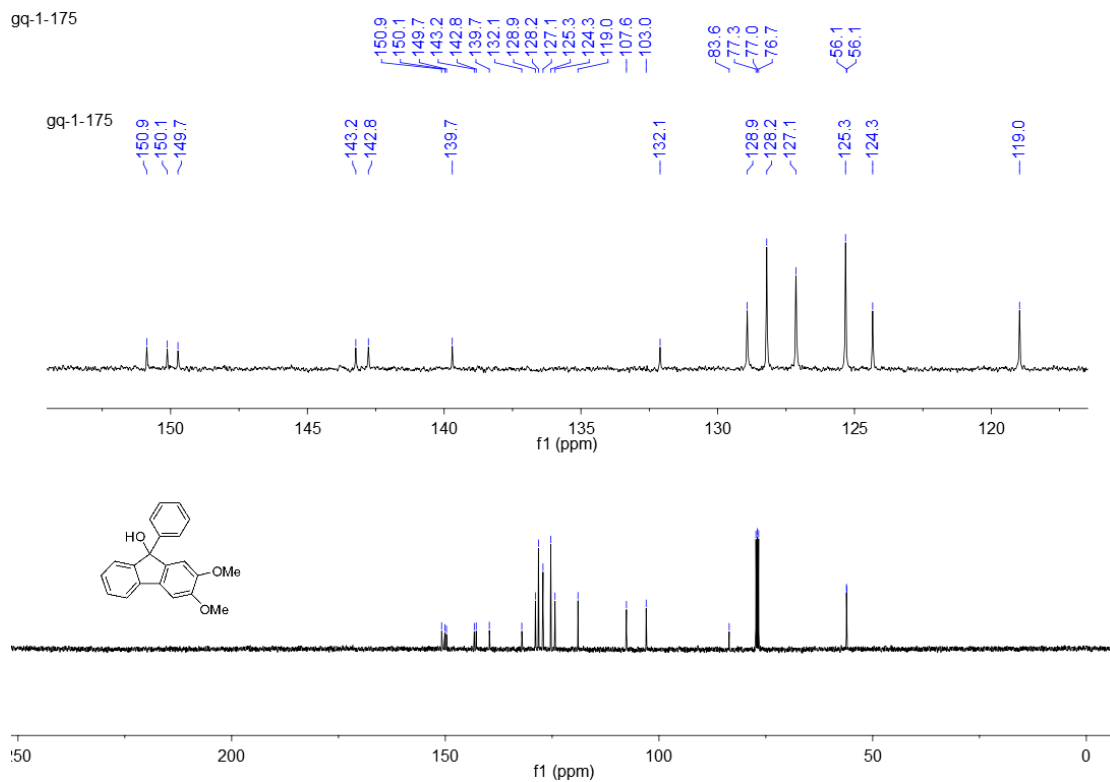
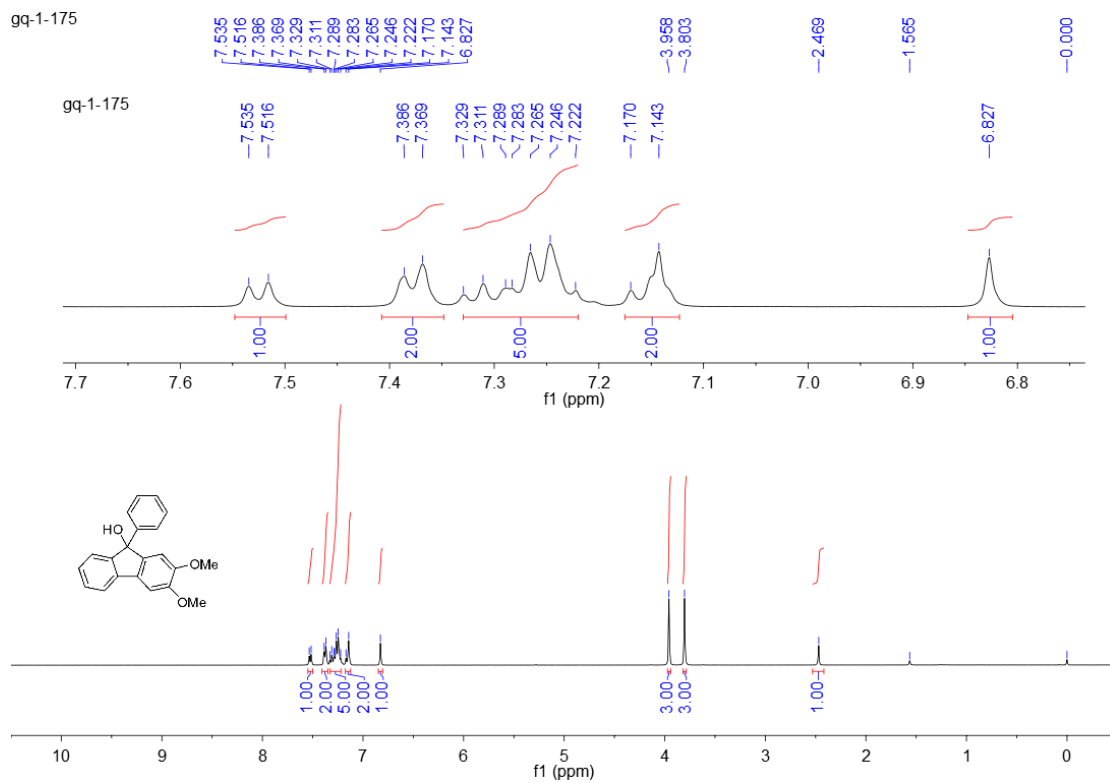
### <sup>13</sup>C NMR Spectrum of Compound 2q

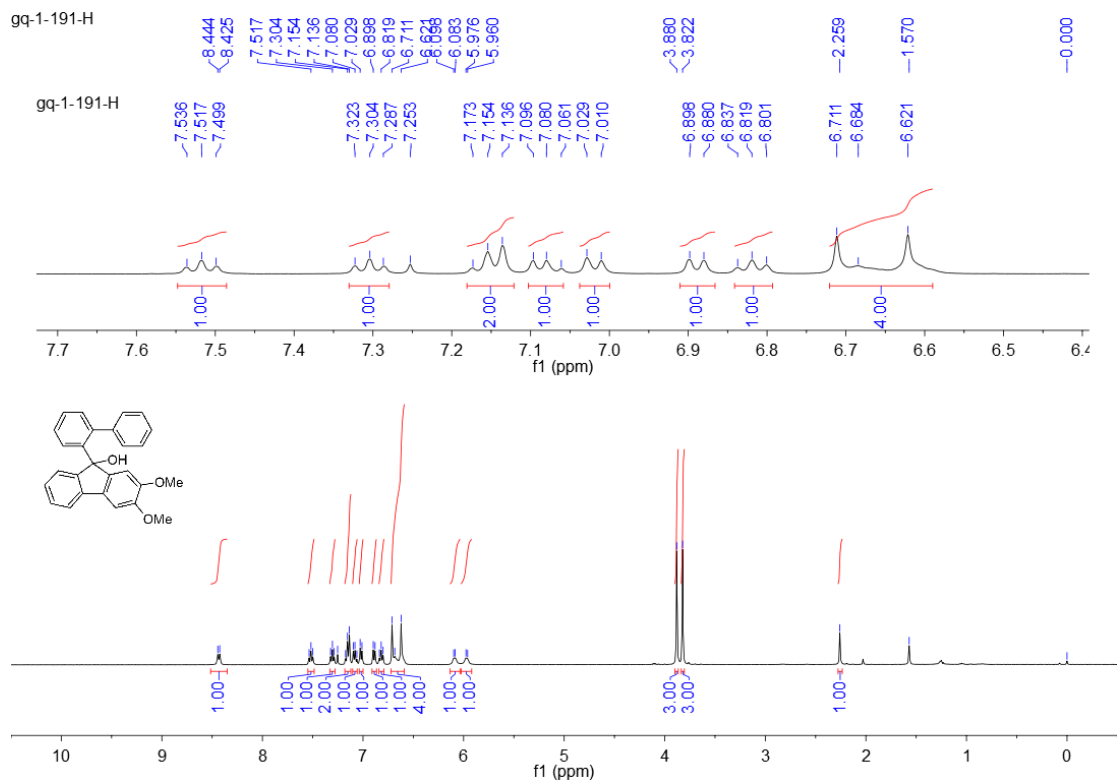


<sup>1</sup>H NMR Spectrum of Compound 2r

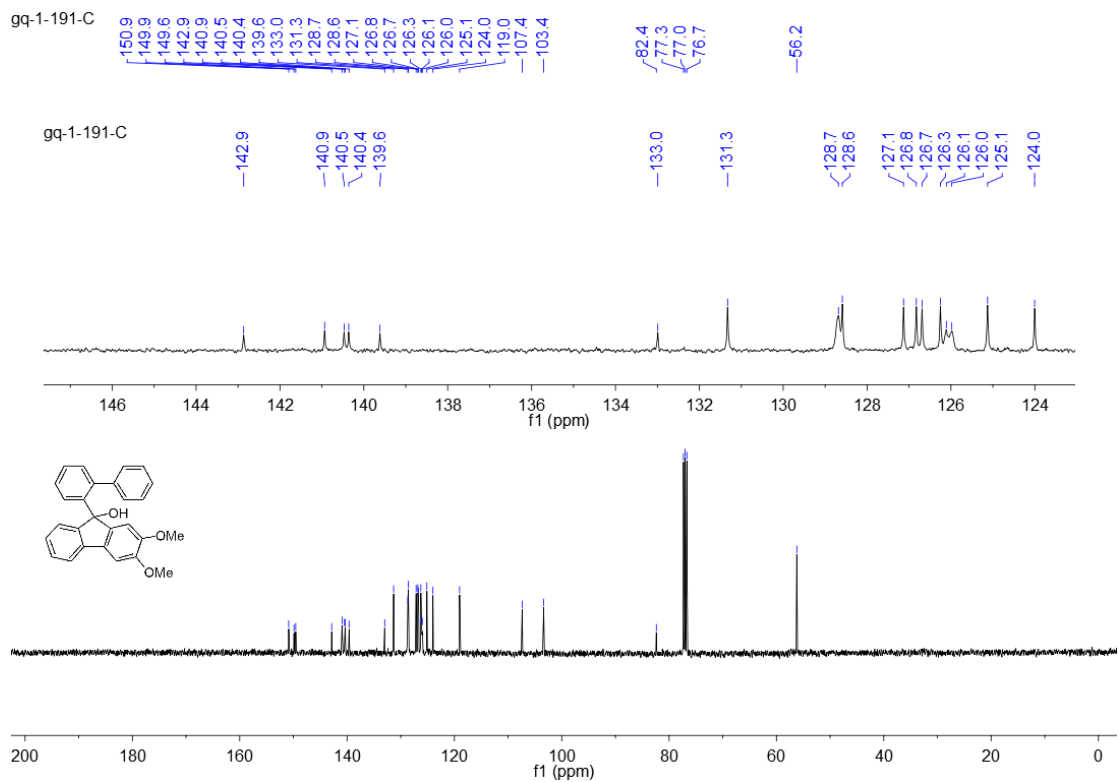


<sup>13</sup>C NMR Spectrum of Compound 2r

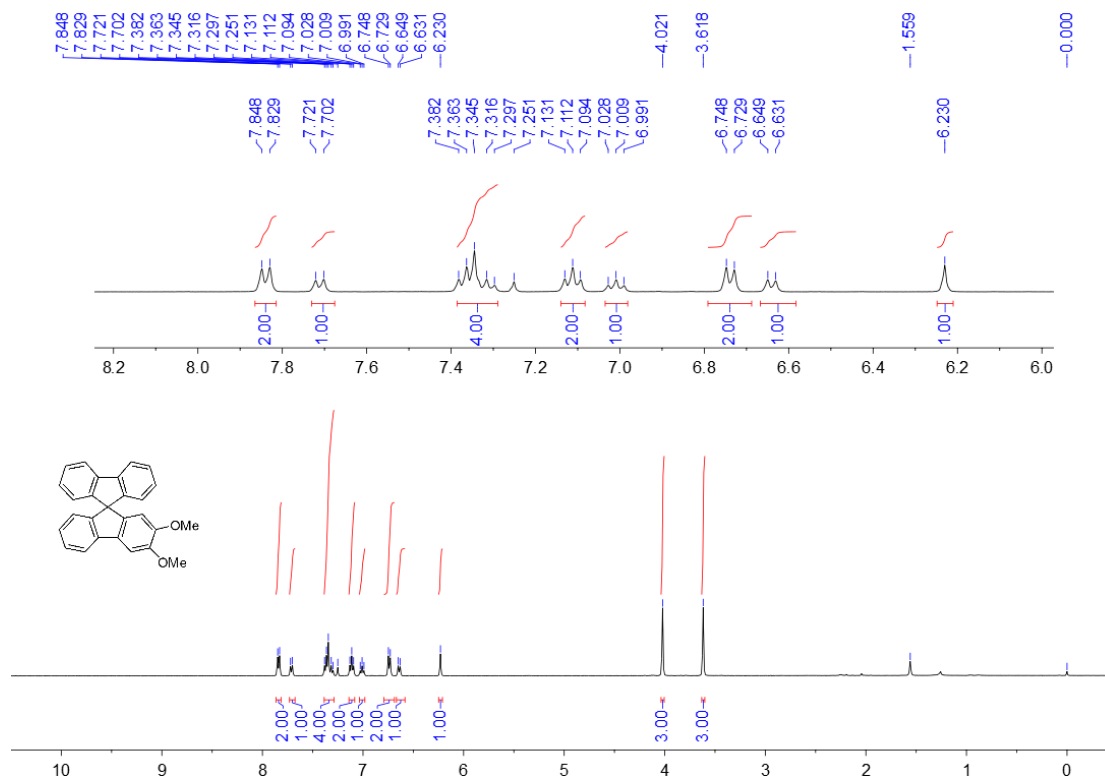




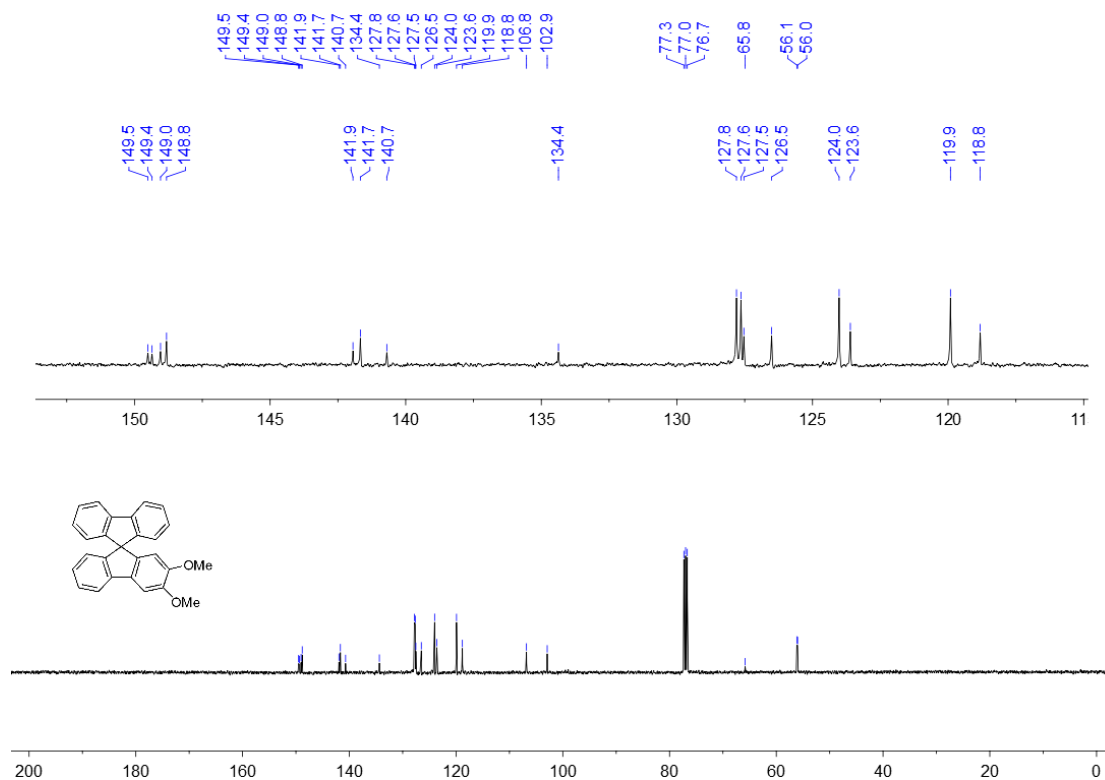
**<sup>1</sup>H NMR Spectrum of Compound 3b**



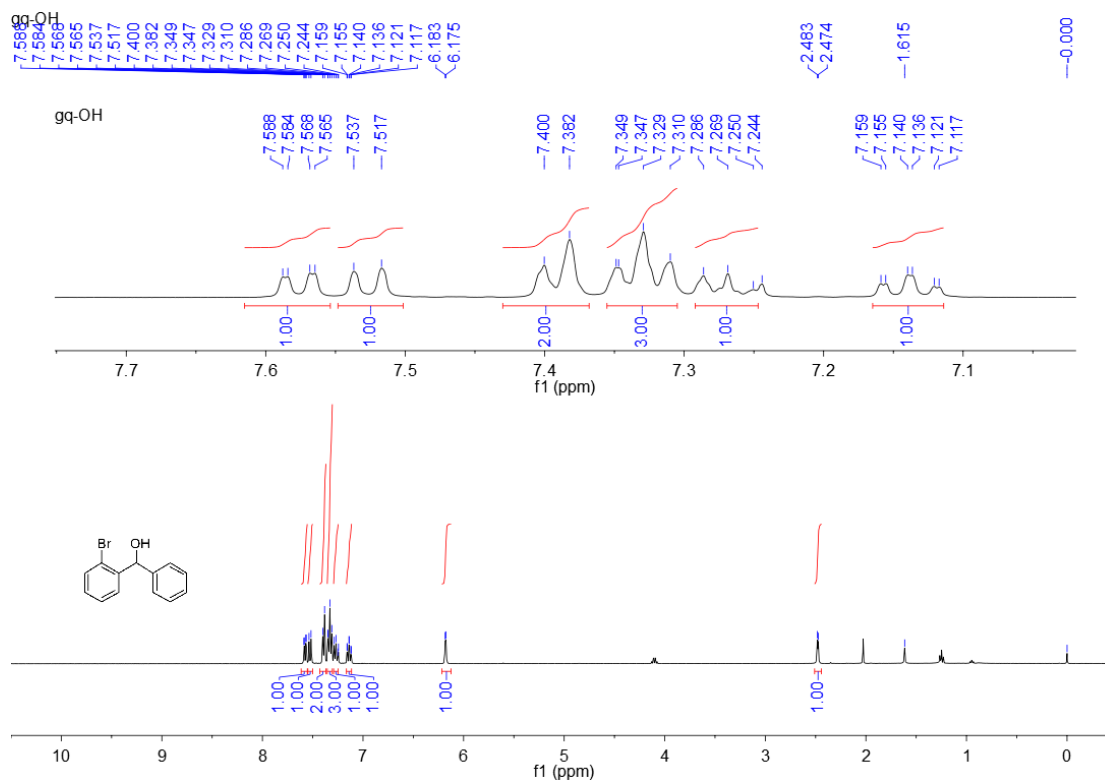
**<sup>13</sup>C NMR Spectrum of Compound 3b**



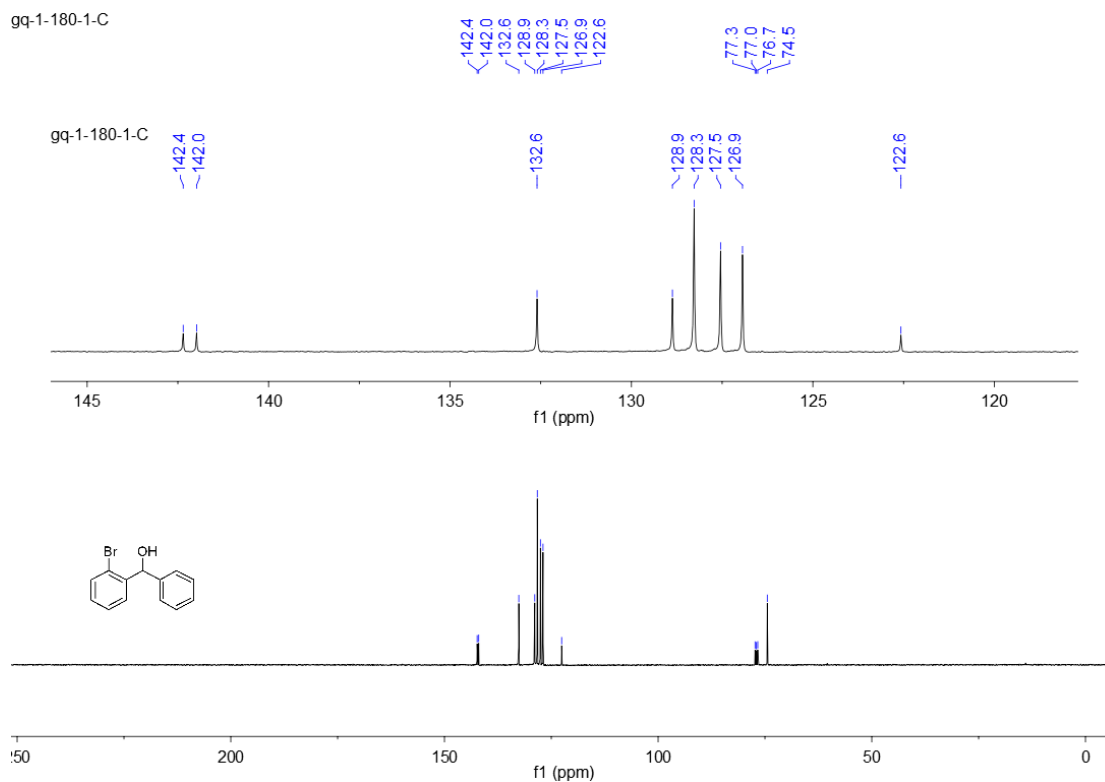
**<sup>1</sup>H NMR Spectrum of Compound 4**



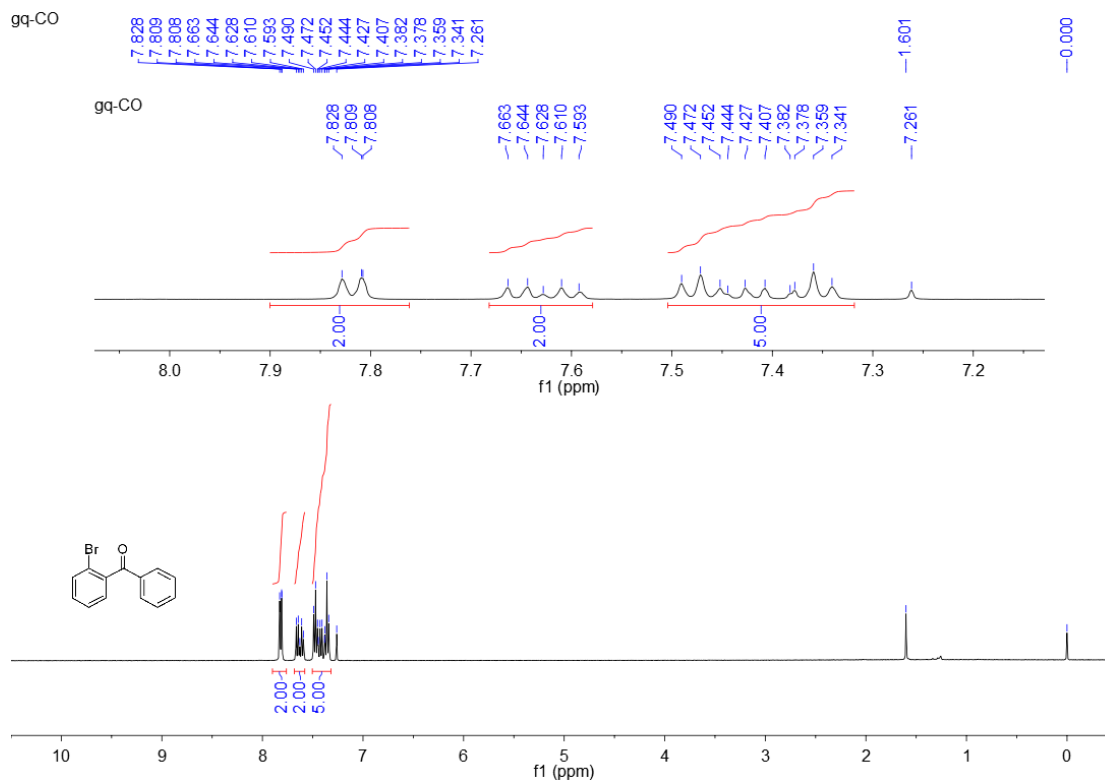
**<sup>13</sup>C NMR Spectrum of Compound 4**



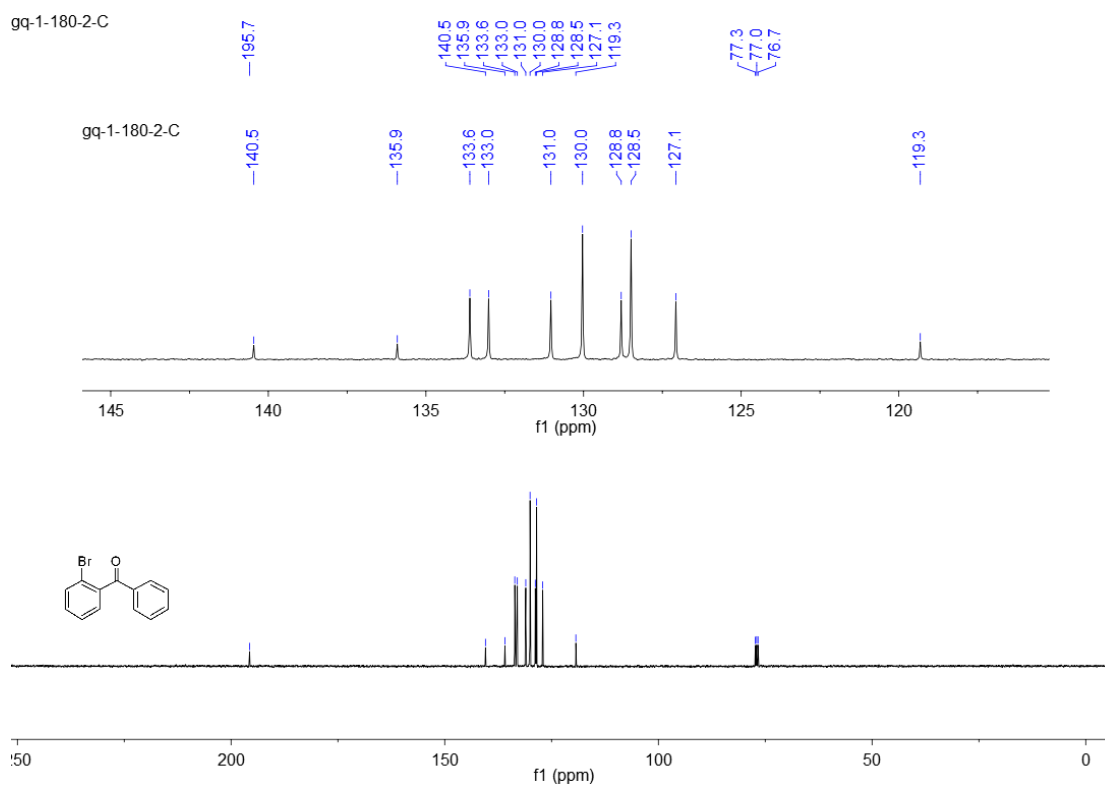
### <sup>1</sup>H NMR Spectrum of Compound S1



### <sup>13</sup>C NMR Spectrum of Compound S1

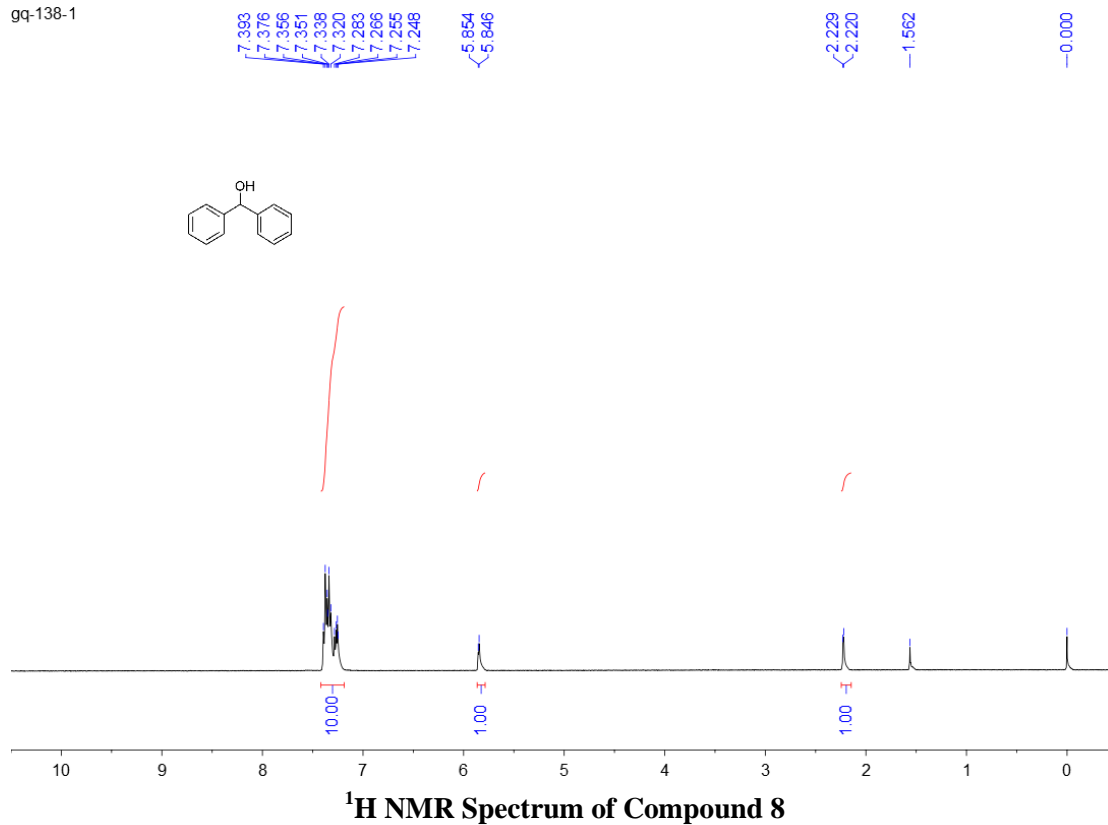


**<sup>1</sup>H NMR Spectrum of Compound 7**

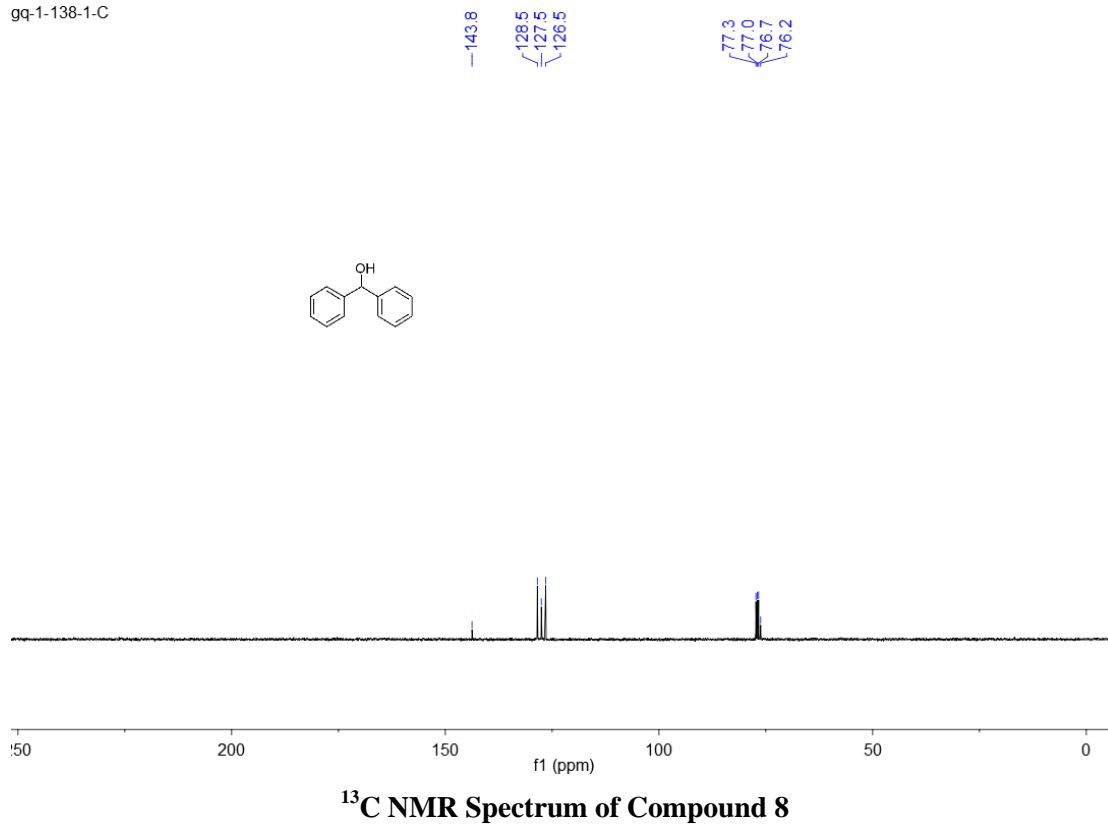


**<sup>13</sup>C NMR Spectrum of Compound 7**

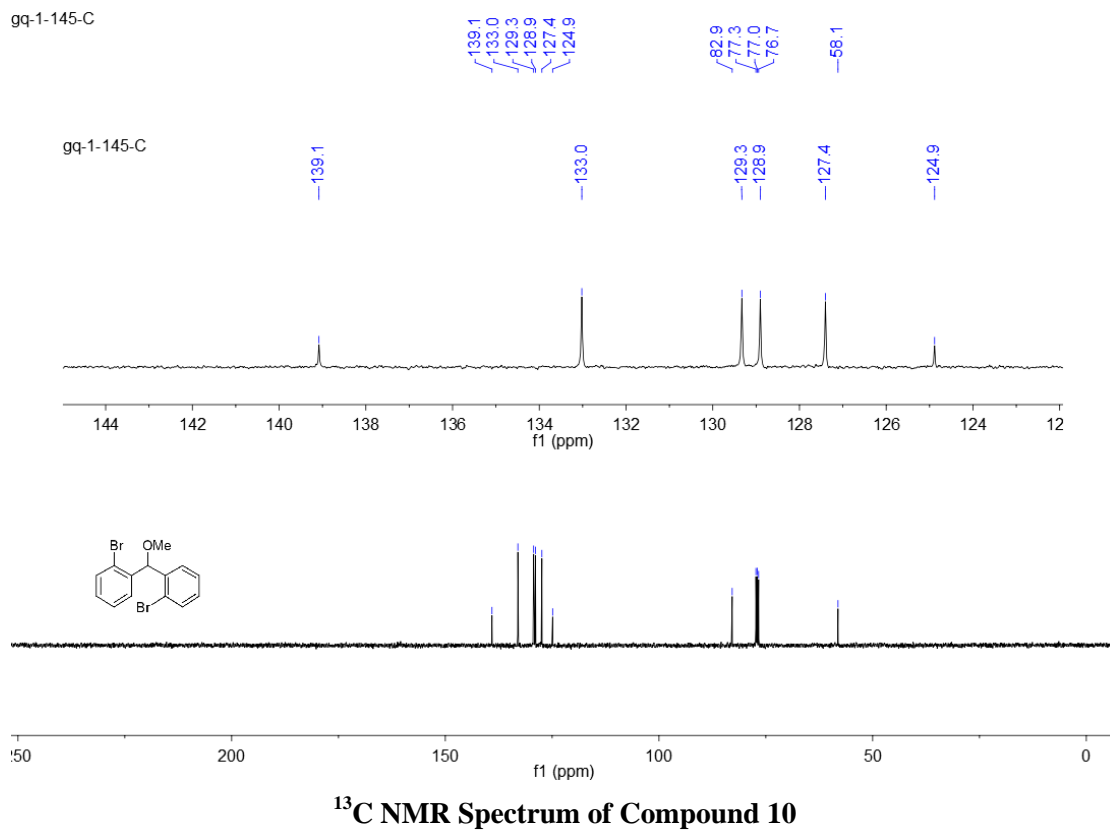
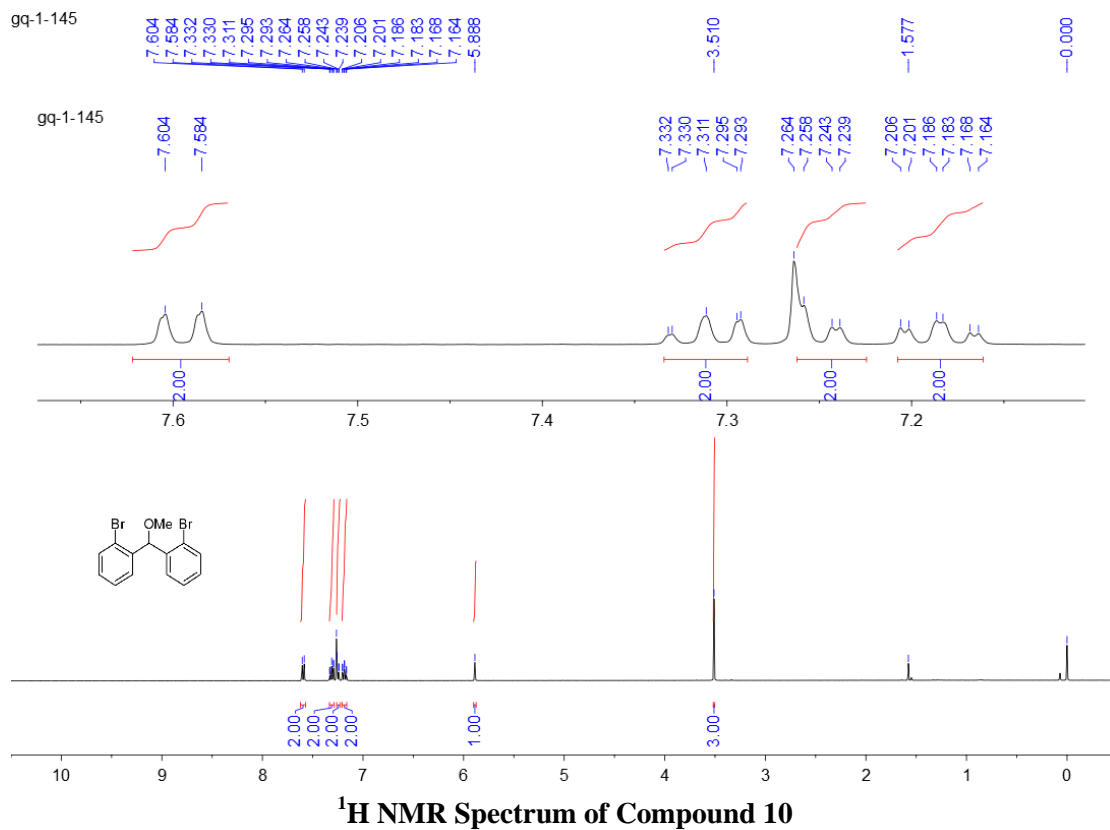
gq-138-1

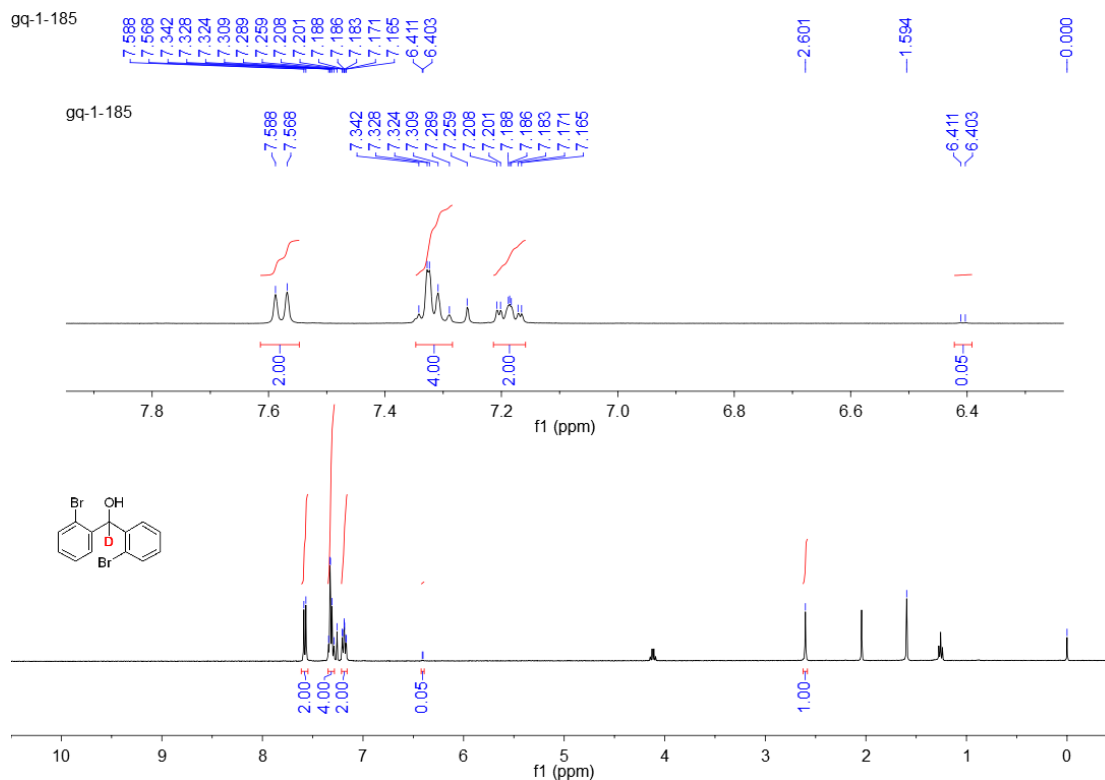


gq-1-138-1-C

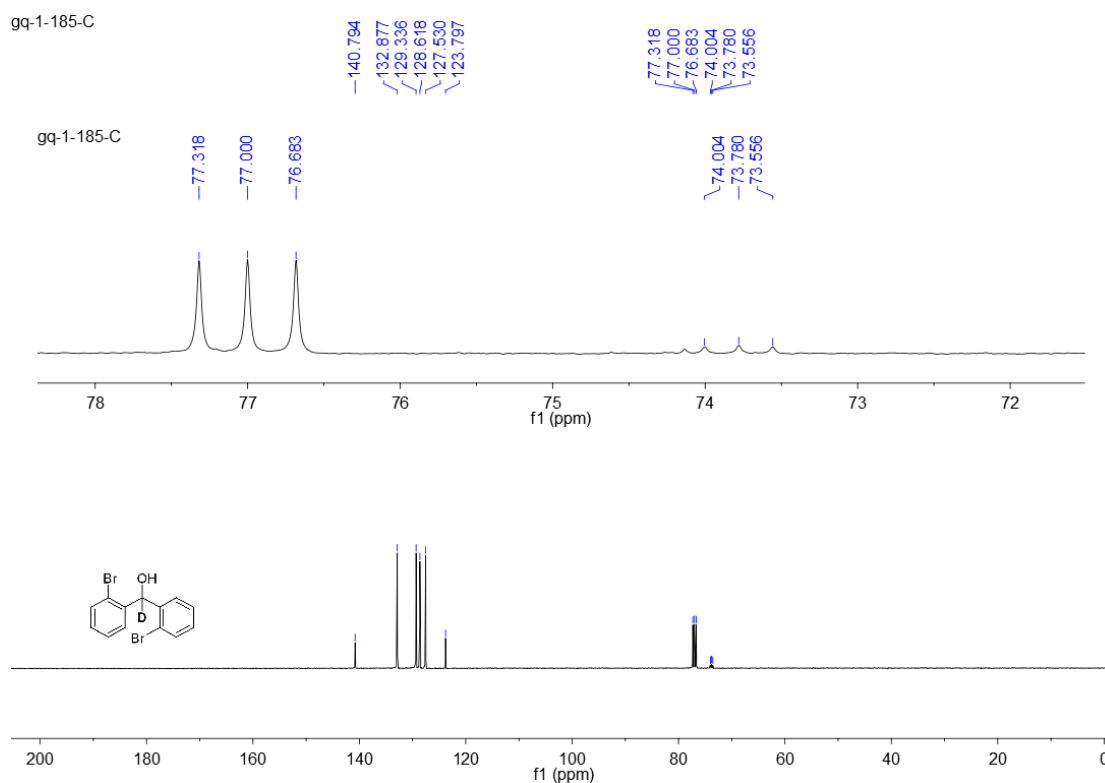




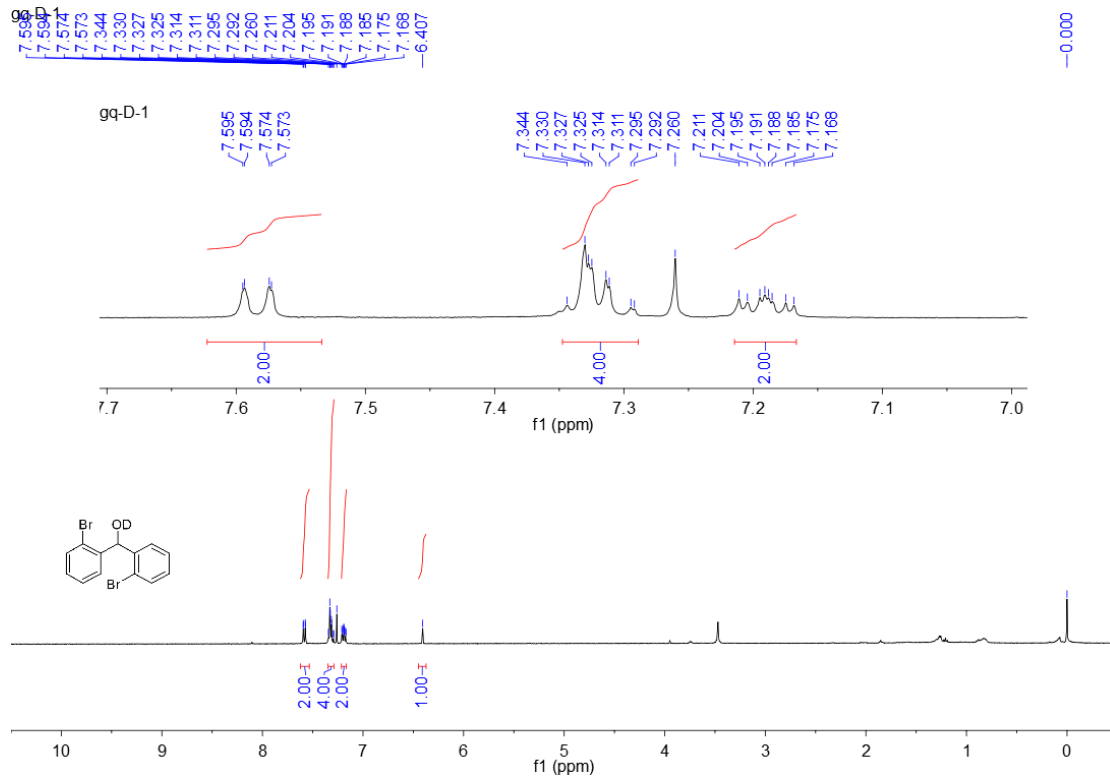




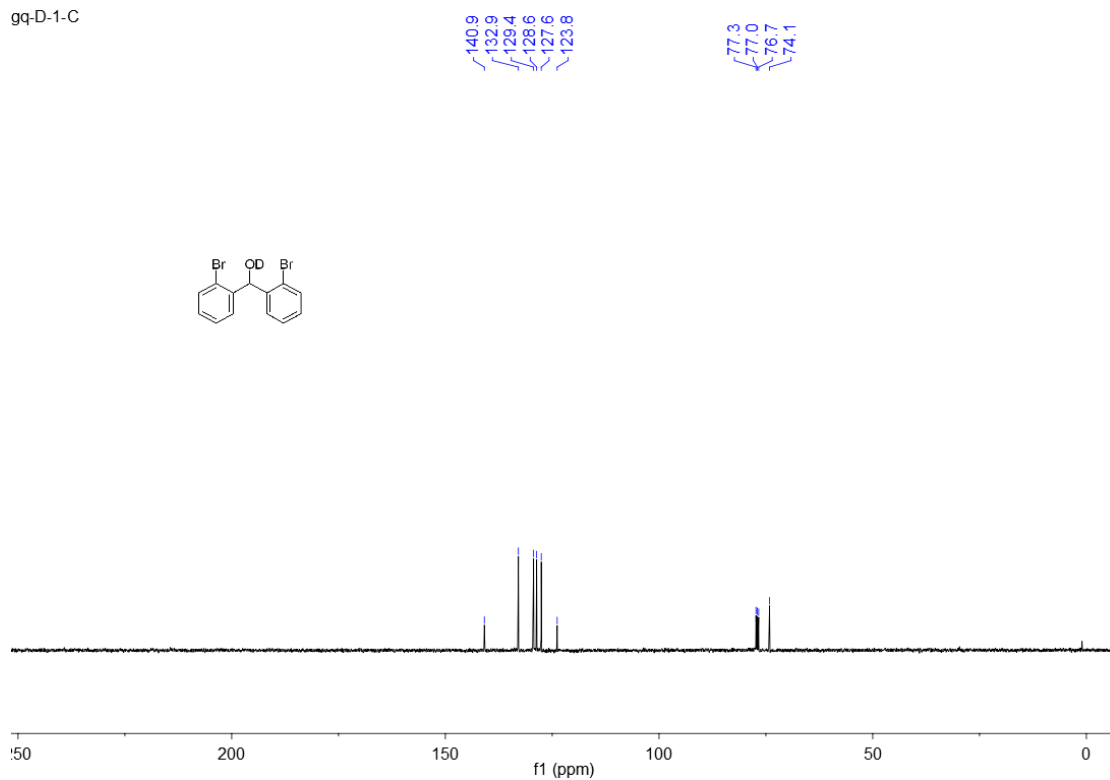
**<sup>1</sup>H NMR Spectrum of Compound 1-*d*1**



**<sup>13</sup>C NMR Spectrum of Compound 1-*d*1**



**<sup>1</sup>H NMR Spectrum of Compound 1-d1'**



**<sup>13</sup>C NMR Spectrum of Compound 1-d1'**