Supplementary Information for

Application of thiopyrylium trifluoromethanesulfonates as Lewis acids in organocatalytic reactions

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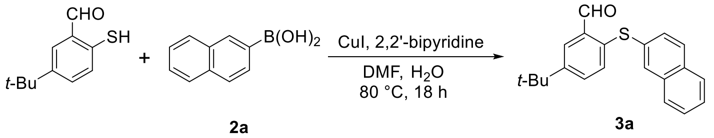
Experimental Details

General. All solvents were purified by standard methods. Preparative thin-layer chromatography (PTLC) was performed on Merck silica gel 60 PF254. Column chromatography was performed on silica gel 60N (Kanto Chemical) under an ambient atmosphere. ^{1}H (400 MHz) and ^{13}C NMR (101 Hz) spectra were recorded in $CDCl_3$ on a Bruker Avance spectrometer using the residual resonances of $CHCl_3$ (δ_H = 7.26) and $CDCl_3$ (δ_C = 77.0) as well as of CD_3CN (δ_H = 1.94; δ_C = 1.32) as the internal standards to reference the ^{1}H and ^{13}C NMR spectra. ^{19}F NMR (376 MHz) spectra were recorded on a Bruker Avance spectrometer using $CFCl_3$ (δ_F = 0.00) as the external standard. The assignment of the signals was typically accomplished on the basis of 1D (homodecoupling and DEPT) and 2D (COSY, HMQC, and HMBC) NMR techniques. Unless otherwise stated, all ^{13}C and ^{19}F NMR experiments were performed using broad-band ^{1}H decoupling. EI and ESI-TOF mass spectral data were obtained on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively. Elemental analyses were carried out on a JM11 CHN analyzer by J-Science Lab. All melting points were determined on a Yanaco micro-melting point apparatus or a Mettler Toledo MP90 melting point system, and are uncorrected.

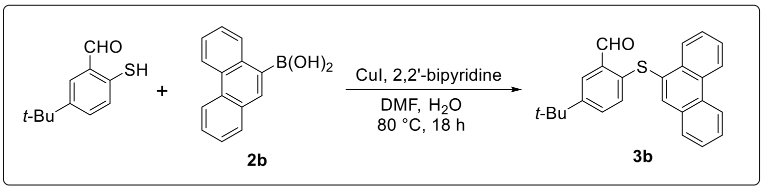
Materials. Unless stated otherwise, all materials were purchased from common commercial chemical suppliers and used without further purification unless stated otherwise. All reactions were carried out under an inert atmosphere of argon or nitrogen. 5-(*tert*-Butyl)-2-sunfanylbenzaldehyde was prepared by the procedures in the literature.[1]



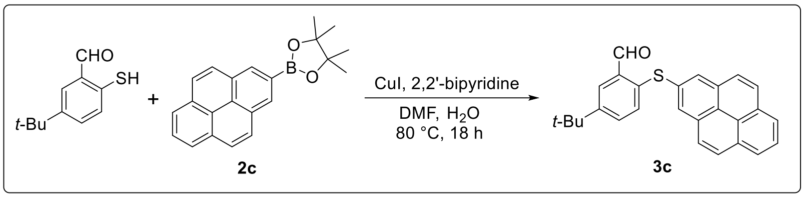
2a

3a

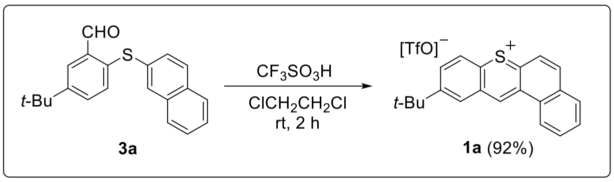
Synthesis of Thioether 3a. 5-(*tert*-Butyl)-2-sunfanylbenzaldehyde (0.323 g, 1.66 mmol), 2-naphthaleneboronic acid (0.287 g, 1.67 mmol), copper(I) iodide (0.157 g, 1.97 mmol), and 2,2´-bipyridine (0.128 g, 0.820 mmol) were dissolved in DMF (26 mL) and deionized water (5 mL). After being stirred at 80 °C for 18 h, the reaction mixture was allowed to cool to room temperature. After organic layer was extracted with ethyl acetate, the organic layer was dried over anhydrous sodium sulfate. All volatile materials were removed under reduced pressure. Purification of the crude product by column chromatography on silica gel (eluent: dichloromethane/hexane = 1/1, v/v) afforded thioether **3a** (0.232 g, 0.724 mmol, 44%) as yellow oil. Spectroscopic data for **3a** are exhibited in the previously reported literature.[1]



Synthesis of Thioether 3b. 5-(*tert*-Butyl)-2-sunfanylbenzaldehyde (0.328 g, 1.69 mmol), 9-phenanthreneboronic acid (0.374 g, 1.68 mmol), copper(I) iodide (0.115 g, 0.814 mmol), and 2,2´-bipyridine (0.136 g, 0.871 mmol) were dissolved in DMF (32 mL) and deionized water (5 mL). After being stirred at 80 °C for 18 h, the reaction mixture was allowed to cool to room temperature. After organic layer was extracted with ethyl acetate, the organic layer was dried over anhydrous sodium sulfate. All volatile materials were removed under reduced pressure. Purification of the crude product by column chromatography on silica gel (eluent: dichloromethane) afforded thioether **3b** (0.302 g, 0.815 mmol, 48%) as yellow solids. **3b**: mp 58.0–59.0 °C; ^{1}H NMR ($CDCl_3$) δ 10.45 (s, 1H, CHO), 8.71 (d, J = 8.2 Hz, 1H, ArH), 8.67 (d, J = 8.3 Hz, 1H, ArH), 8.40 (dd, J = 1.0, 8.2 Hz, 1H, ArH), 8.04 (s, 1H, ArH), 7.90 (d, J = 2.3 Hz, 1H, ArH), 7.79 (dd, J = 1.0, 7.9 Hz, 1H, ArH), 7.70–7.65 (m, 2H, ArH), 7.60–7.55 (m, 2H, ArH), 7.20 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 6.75 (d, J = 8.4 Hz, 1H, ArH), 1.26 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.75 (CH), 148.86 (C), 138.53 (C), 135.56 (CH), 132.65 (C), 134.45 (C), 131.63 (C), 131.61 (C), 131.47 (CH), 131.05 (C), 130.91 (C), 129.46 (CH), 128.90 (CH), 128.63 (CH), 128.30 (C), 127.80 (CH), 127.38 (CH), 127.25 (CH), 127.04 (CH), 126.45 (CH), 123.06 (CH), 122.64 (CH), 34.36 (C), 30.98 (CH_3); MS (ESI, positive mode) *m/z* 393 ([M+Na; $C_{25}H_{22}OSNa$)]$^+$), Anal. calcd for $C_{25}H_{22}OS$: C, 81.04; H, 5.99%; found: C, 80.82; H, 6.32%.

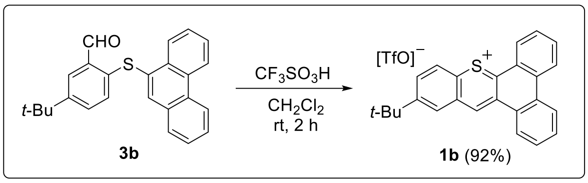


Synthesis of Thioether 3c. 5-(*tert*-Butyl)-2-sunfanylbenzaldehyde (0.750 g, 3.86 mmol), 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (1.290 g, 3.930 mmol), copper(I) iodide (0.375 g, 1.97 mmol), and 2,2´-bipyridine (0.313 g, 2.00 mmol) were dissolved in DMF (25 mL) and deionized water (7.5 mL). After being stirred at 80 °C for 18 h, the reaction mixture was allowed to cool to room temperature. After organic layer was extracted with ethyl acetate, the organic layer was dried over anhydrous sodium sulfate. All volatile materials were removed under reduced pressure. Purification of the crude product by column chromatography on silica gel (eluent: dichloromethane) afforded thioether **3c** (0.467 g, 1.18 mmol, 30%) as yellow solids. **3c**: mp 140.5–141.5 °C; ^{1}H NMR ($CDCl_3$) δ 10.53 (s, 1H, CHO), 8.20 (d, *J* = 6.8 Hz, 4H, ArH), 8.09 (d, *J* = 8.9 Hz, 2H, ArH), 8.03 (d, *J* = 7.3 Hz, 1H, ArH), 8.00 (d, *J* = 5.0 Hz, H, ArH), 7.97 (t, *J* = 2.2 Hz, 2H, ArH), 7.42 (dd, *J* = 2.3, 8.4 Hz, 1H, ArH), 7.09 (d, *J* = 8.3 Hz, 1H, ArH), 1.33 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.94 (CH), 150.23 (C), 138.15 (C), 133.81 (C), 132.20 (C), 131.75 (CH), 131.46 (C), 131.23 (C), 131.11 (CH), 128.43 (CH), 128.37 (CH), 128.26 (CH), 126.76 (CH), 126.34 (CH), 125.57 (CH), 124.32 (C), 124.11 (C), 34.63 (C), 31.07 (CH_3); MS (ESI, positive mode) *m/z* 417 ([M+Na; $C_{27}H_{22}OSNa)]^{+}$), Anal. calcd for $C_{27}H_{22}OS$: C, 82.20; H, 5.62%; found: C, 81.92; H, 5.77%.

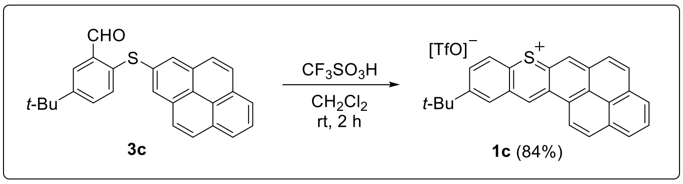


Synthesis of Thiopyrylium Triflate 1a. Trifluoromethanesulfonic acid (0.142 g, 0.946 mmol) was added to a solution of thioether **3a** (0.150 g, 0.460 mmol) in dichloromethane (10 mL) at 0 °C. After stirring at room temperature for 2 h, the solution was added dropwise to a cooled Et_2O (50 mL). Purification of the resulting suspension using a centrifugal separator afforded thiopyrylium trifluoromethanesulfonate **1a** (0.191 g, 0.423 mmol, 92%) as orange powder. Spectroscopic data for **1a** are exhibited in the previously reported literature.[1]

Synthesis of Thiopyrylium Triflate 1b. Trifluoromethanesulfonic acid (0.284 g, 1.89 mmol) was added to a solution of thioether **3b** (0.699 g, 1.89 mmol) in dichloromethane (12 mL) at 0 °C. After stirring at room temperature for 2 h, the solution was added dropwise to a cooled Et_2O (200 mL). Purification of the resulting suspension using a centrifugal separator afforded thiopyrylium trifluoromethanesulfonate **1b** (0.876 g, 1.84 mmol, 92%) as red-orange powder. **1b**: mp 221.5–222.3 °C; ^{1}H NMR (CD_3CN) δ 10.45 (s, 1H, CH), 8.86–8.83 (m, 2H, ArH), 8.82 (br, 1H, ArH), 8.72–8.66 (m, 2H, ArH), 8.65 (d, *J* = 9.0 Hz, 1H, ArH), 8.53 (dd, *J* = 2.0, 8.9 Hz, 1H, ArH), 8.06 (dd, *J* = 8.0, 8.0 Hz, 1H, ArH), 7.90–7.83 (m, 3H, ArH), 1.58 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (CD_3CN) δ 157.53 (CH), 157.32 (CH), 151.30 (C), 141.24 (CH), 137.54 (C), 136.99 (C), 133.41 (CH), 132.12 (C), 132.07 (C), 131.45 (CH), 130.71 (CH), 129.95 (CH), 129.84 (CH), 128.14 (C), 127.89 (C), 126.71 (C), 126.62 (C), 125.49 (C), 125.12 (C), 124.97 (C), 36.72 (C), 31.02 (CH_3); ^{19}F NMR (CD_3CN) δ –79.2; MS (ESI-TOF, positive mode) *m/z* 353 ([M–OTf; $C_{25}H_{21}S$]$^+$); Anal. Calcd for $C_{26}H_{21}F_3O_3S_2$: C, 62.14; H, 4.21%. Found: C, 62.50; H, 4.51%.

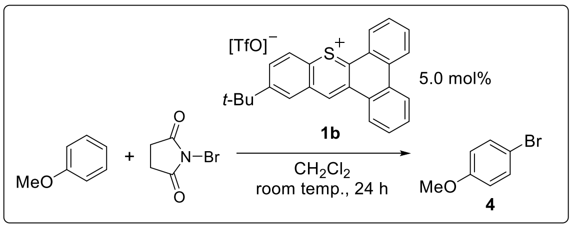


Synthesis of Thiopyrylium Triflate 1c. Trifluoromethanesulfonic acid (0.142 g, 0.946 mmol) was added to a solution of thioether **3c** (0.172 g, 0.426 mmol) in dichloromethane (5 mL) at 0 °C. After stirring at room temperature for 2 h, the solution was added dropwise to a cooled Et_2O (50 mL). Purification of the resulting suspension using a centrifugal separator afforded thiopyrylium trifluoromethanesulfonate **1c** (0.192 g, 0.365 mmol, 84%) as dark green powder. **1c**: mp 248.5 °C (decomp.); ^{1}H NMR (CD_3CN) δ 10.18 (s, 1H, CH), 8.90 (d, *J* = 9.1 Hz,1H, ArH), 8.69 (d, *J* = 1.9 Hz, 1H), 8.56 (1H, d, *J* = 8.9 Hz, 1H, ArH), 8.42 (dd, *J* = 2.1, 8.8 Hz, 1H, ArH), 8.30 (d, *J* = 3.6 Hz, 1H, ArH), 8.28 (d, *J* = 3.8 Hz, 1H, ArH), 8.22 (d, *J* = 7.7 Hz, 1H, ArH), 8.11 (d, *J* = 7.5 Hz, 1H, ArH), 7.95 (d, *J* = 9.0 Hz, 1H, ArH), 7.79 (dd, *J* = 7.6, 7.6 Hz, 1H, ArH), 1.63 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (CD_3CN) δ 154.88 (C), 150.57 (CH), 143.60 (C), 141.81 (C), 138.88 (C), 137.94 (CH), 137.44 (CH), 133.86 (CH), 133.26 (C), 133.14

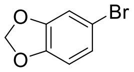


(CH), 131.69 (CH), 130.78 (CH), 130.54 (C), 129.81 (C), 129.46 (CH), 128.45 (C), 127.36 (CH), 126.88 (CH), 123.68 (C), 122.62 (C), 122.47 (CH), 122.25 (C), 121.89 (CH), 36.45 (C), 31.17 (CH_3); ^{19}F NMR (CD_3CN) δ –79.3; MS (ESI-TOF, positive mode) *m/z* 377 ([M–OTf; $C_{27}H_{21}S]^+$); Anal. Calcd for $C_{28}H_{21}F_3O_3S_2$: C, 63.87; H, 4.02%. Found: C, 64.09; H, 4.30%.

General Procedure of Bromination; Bromination of Anisole with *N*-Bromosuccinimide in the Presence of Thiopyrylium Trifluoromethanesulfonate 1b.

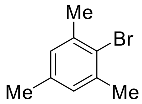


NBS (0.0765 g, 0.430 mmol) was added to a solution of anisole (0.0512 g, 0.473 mmol) and thiopyrylium triflate **1b** (10.8 mg, 21.5 μmol) in dichloromethane (6.5 mL) at room temperature under dark conditions. After stirring at room temperature for 24 h, the reaction mixture was purified by column chromatography on silica gel (eluent: dichloromethane) to afford 4-bromoanisole (0.0466 g, 0.249 mmol, 58%) as colorless oil. 4-bromoanisole (**4**): ^{1}H NMR ($CDCl_3$) δ 7.29 (d, J = 8.9 Hz, 2H, ArH), 6.70 (d, J = 8.9 Hz, 2H, ArH), 3.69 (s, 3H, CH_3).



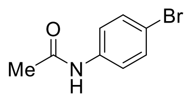
5

Bromobenzodioxole (**5**): ^{1}H NMR ($CDCl_3$) δ 6.95–6.93 (m, 2H, ArH), 6.68 (d, J = 8.6 Hz, 1H, ArH), 5.96 (s, 2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.57 (C), 146.98 (C), 124.29 (CH), 113.02 (C), 112.28 (CH), 109.55 (CH_2), 101.57 (CH); MS (ESI, positive mode) *m/z* 223 ([M+Na]$^+$).



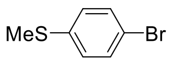
6

Bromomesitylene (**6**): ^{1}H NMR ($CDCl_3$) δ 6.88 (s, 2H, ArH), 2.36 (s, 6H, CH_3), 2.23 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.86 (C), 136.23 (C), 128.99 (CH), 124.16 (C), 23.56 (CH_3), 20.62 (CH_3); MS (ESI, positive mode) *m/z* 221 ([M+Na]$^+$).



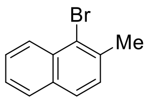
7

N-(4-bromophenyl)acetamide (**7**): ^{1}H NMR ($CDCl_3$) δ 7.42 (d, *J* = 9.2 Hz, 2H, ArH), 7.40 (d, *J* = 9.2 Hz, 2H, ArH), 2.17 (s, 3H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 168.23 (C), 136.93 (C), 131.96 (CH), 121.36 (CH), 116.87 (C), 24.58 (CH_3); MS (ESI, positive mode) *m/z* 236 ($[M+Na]^+$).



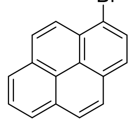
8

4-Bromothioanisole (**8**): ^{1}H NMR ($CDCl_3$) δ 8.41 (d, *J* = 8.8 Hz, 2H, ArH), 8.13 (d, *J* = 8.8 Hz, 2H, ArH), 2.48 (s, 3H, SCH_3); MS (ESI, positive mode) *m/z* 225 ($[M+Na]^+$).



9

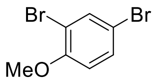
1-Bromo-2-methylnaphthalene (**9**): ^{1}H NMR ($CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 1H, ArH), 7.74 (d, *J* = 8.1 Hz, 1H, ArH), 7.64 (d, *J* = 8.3 Hz, 1H, ArH), 7.52 (dd, *J* = 7.7, 7.7 Hz, 1H, ArH), 7.42 (dd, *J* = 7.5, 7.5 Hz, 1H, ArH), 7.28 (d, *J* = 8.3 Hz, 1H, ArH), 2.58 (s, 3H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 135.94 (C), 132.98 (C), 132.50 (C), 128.64 (CH), 127.97 (CH), 127.23 (CH), 127.22 (CH), 126.89 (CH), 125.60 (CH), 123.99 (C), 24.11 (CH_3); MS (ESI, positive mode) *m/z* 243 ($[M+Na]^+$).



10

1-Bromopyrene (**10**): ^{1}H NMR ($CDCl_3$) δ 8.43 (d, *J* = 9.2 Hz, 1H, ArH), 8.22 (dd, *J* = 2.4, 8.0 Hz, 3H, ArH), 8.16 (d, *J* = 9.3 Hz, 1H, ArH), 8.07 (dd, *J* = 8.7, 8.7 Hz, 1H, ArH), 8.03–7.99

(m, 3H, ArH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 131.04 (C), 130.98 (C), 130.78 (C), 130.41 (C), 129.83 (CH), 129.43 (C), 128.77 (CH), 127.51 (CH), 126.90 (CH), 126.31 (CH), 125.74 (CH), 125.56 (CH), 125.37 (CH), 125.31 (CH), 123.81 (C); MS (ESI, positive mode) *m/z* 303 ($[M+Na]^+$).



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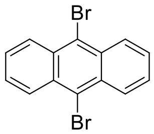
2,4-Dibromoanisole (**11**): ^1H NMR ($CDCl_3$) δ 7.65 (d, J = 2.3 Hz, 1H, ArH), 7.36 (dd, J = 2.4, 8.7 Hz, 1H, ArH), 6.75 (d, J = 8.8 Hz, 1H, ArH), 3.86 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.17 (C), 135.39 (CH), 131.17 (CH), 113.07 (CH), 112.82 (C), 112.50 (C), 56.34 (CH_3); MS (ESI, positive mode) *m/z* 287 ($[M+Na]^+$).



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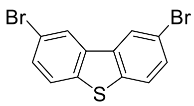
9,10-Dibromoanthracene (**12**): ^1H NMR ($CDCl_3$) δ 8.60–8.57 (m, 4H, ArH), 7.64–7.62 (m, 4H, ArH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 131.01 (C), 128.24 (CH), 127.41 (CH), 123.50 (CH); MS (ESI, positive mode) *m/z* 336 ($[M]^+$).



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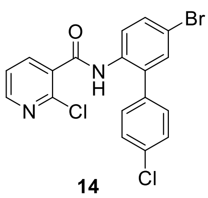
2,8-Dibromodibenzothiophene (**13**): ^1H NMR ($CDCl_3$) δ 8.23 (d, J = 2.0 Hz, 2H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.57 (dd, J = 1.6, 8.4 Hz, 2H, ArH); MS (ESI, positive mode) *m/z* 365 ($[M+Na]^+$).



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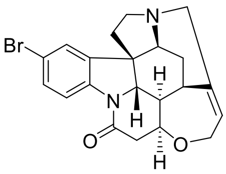
N-(5-Bromo-4'-chloro-[1,1'-biphenyl]-2-yl)-2-chloronicotinamide (**14**): ^{1}H NMR ($CDCl_3$) δ 8.46 (dd, *J* = 2.0, 4.8 Hz, 1H, ArH), 8.37 (d, *J* = 8.8 Hz, 1H, ArH), 8.17 (d, *J* = 1.6, 7.6 Hz, 1H, ArH), 8.17 (s, 1H, NH), 7.57 (dd, *J* = 2.4, 8.8 Hz, 1H, ArH), 7.46 (d, *J* = 8.4 Hz, 2H, ArH), 7.41 (d, *J* = 2.4 Hz, 1H, ArH), 7.36 (dd, *J* = 4.4, 7.8 Hz,1H, ArH), 7.32 (d, *J* = 8.8 Hz, 2H, ArH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 162.31 (C), 151.51 (CH), 146.59 (C), 140.39 (CH), 135.08 (CH), 134.81 (C), 133.86 (C), 133.63 (C), 132.84 (CH), 131.76 (CH), 130.66 (CH), 129.52 (CH), 123.39 (CH), 122.95 (CH), 117.98 (C); MS (ESI, positive mode) *m/z* 445 ([M+Na]$^{+}$).



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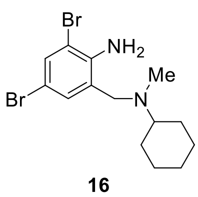
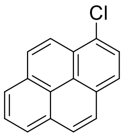
2-Bromostrychnine (**15**): ^{1}H NMR ($CDCl_3$) δ 7.97 (d, 1H, *J* = 8.6 Hz), 7.36 (dd, 1H, *J* = 2.0, 8.6 Hz), 7.27 (d, 1H, *J* = 2.1 Hz), 5.96 (t, 1H, *J* = 5.8 Hz), 4.29 (dt, 1H, *J* = 2.8, 5.8 Hz), 4.19–4.13 (m, 1H), 4.09–4.02 (m, 1H), 3.97–3.84 (m, 2H), 3.75 (dd, 1H, *J* = 1.2, 14.6 Hz), 3.32–3.09 (m, 4H), 2.94–2.83 (m, 1H), 2.79 (d, 1H, *J* = 14.6 Hz), 2.65 (dd, 1H, *J* = 3.3, 17.5 Hz), 2.38 (dt, 1H, *J* = 4.9, 9.4 Hz), 1.95–1.88 (m, 2H), 1.49 (d, 1H, *J* = 14.6 Hz), 1.27 (dt, 1H, *J* = 3.7, 6.8 Hz).



16

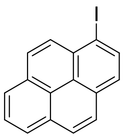
2,4-Dibromo-6-((cyclohexyl(methyl)amino)methyl)aniline (**16**): ^{1}H NMR ($CDCl_3$) δ 7.46 (d, *J* = 2.0 Hz, 1H, ArH), 7.04 (d, *J* = 2.0 Hz, 1H, ArH), 5.48 (br s, 2H, NH_2), 3.59 (s, 2H, CH_2), 2.41 (dd, *J* = 10.8, 10.8 Hz, 1H, C_6H_{11}), 2.11 (s, 3H, CH_3), 1.80 (d, *J* = 10.8 Hz, 4H, C_6H_{11}), 1.63 (d, *J* = 12.8 Hz, 1H, C_6H_{11}), 1.35–1.08 (m, 5H, C_6H_{11}); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.10

(C), 132.98 (CH), 131.69 (CH), 126.04 (C), 110.05 (C), 108.04 (C), 133.86 (C), 61.94 (CH), 57.74 (CH_2), 36.35 (CH_3), 28.19 (CH_2), 26.24 (CH_2), 25.87 (CH_2); MS (ESI, positive mode) *m/z* 377 ($[M+H]^+$).



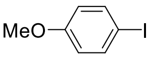
17

1-Chloropyrene (**17**): ^{1}H NMR ($CDCl_3$) δ 8.46 (d, *J* = 9.2 Hz, 2H, ArH), 8.22–8.20 (m, 3H, ArH), 8.17 (d, *J* = 9.2 Hz, 2H, ArH), 8.08–7.98 (m, 3H, ArH); MS (ESI, positive mode) *m/z* 259 ($[M+Na]^+$).



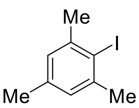
18

1-Iodopyrene (**18**): ^{1}H NMR ($CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H, ArH), 8.30 (d, *J* = 9.2 Hz, 1H, ArH), 8.23–8.17 (m, 2H, ArH), 8.13 (d, *J* = 9.2 Hz, 1H, ArH), 8.11–8.00 (m, 3H, ArH), 7.86 (d, *J* = 8.0 Hz, 1H, ArH); MS (ESI, positive mode) *m/z* 351 ($[M+Na]^+$).



19

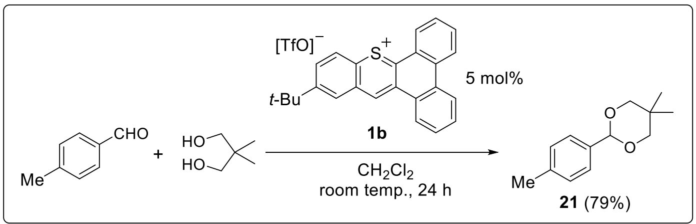
4-Iodoanisole (**19**): ^{1}H NMR ($CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H, ArH), 6.68 (d, *J* = 8.8 Hz, 2H, ArH), 3.77 (s, 3H, OCH_3); MS (ESI, positive mode) *m/z* 257 ($[M+Na]^+$).



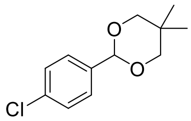
20

Iodomesitylene (**20**): ^{1}H NMR ($CDCl_3$) δ 6.88 (d, 2H, ArH), 2.42 (s, 6H, CH_3), 2.23 (s, 3H, CH_3); MS (ESI, positive mode) *m/z* 269 ($[M+Na]^+$).

Procedure for Catalyst Recycling Experiment. NBS (0.0718 g, 0.403 mmol) was added to a solution of pyrene (0.0815 g, 0.403 mmol) and thiopyrylium triflate **1b** (10.2 mg, 20.3 μmol) in dichloromethane (6.5 mL) at room temperature under dark conditions. After stirring at room temperature for 24 h, the reaction mixture was added dropwise to cooled hexane. The orange solid precipitated and was isolated by centrifugation. Purification of the resulting supernatant using column chromatography on silica gel (eluent: dichloromethane) to afford 1-bromopyrene (0.1031 g, 0.367 mmol, 91%). The obtained orange solid was repeatedly used as a catalyst to a next bromination reaction of pyrene. The product yield from the second to the fifth experiments was 100%, 86%, 86%, and 82%.

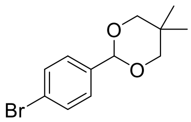


General Procedure of Acetalization; Reaction of *p*-Tolualdehyde with 2,2-Dimethylpropane-1,3-diol in the Presence of Thiopyrylium Trifluoromethanesulfonate 1b. 2,2-Dimethylpropane-1,3-diol (0.121 g, 1.16 mmol) was added to a solution of *p*-tolualdehyde (0.065 g, 0.54 mmol) and thiopyrylium triflate **1b** (13.6 mg, 0.0270 mmol) in dichloromethane (1.0 mL) at room temperature under dark conditions. After stirring at room temperature for 24 h, the reaction mixture was purified by column chromatography on silica gel (eluent: dichloromethane) to afford 5,5-dimethyl-2-(*p*-tolyl)-1,3-dioxane (0.088 g, 0.43 mmol, 79%) as colorless oil. 5,5-Dimethyl-2-(*p*-tolyl)-1,3-dioxane (**21**): ^{1}H NMR ($CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H, ArH), 7.16 (d, *J* = 8.0 Hz, 2H, ArH), 5.35 (s, 1H, CH), 3.74 (d, *J* = 10.8 Hz, 2H, C**H**H), 3.62 (d, *J* = 10.8 Hz, 2H, CH**H**), 2.33 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 0.77 (s, 3H, CH_3); MS (ESI, positive mode) *m/z* 229 ($[M+Na]^+$).



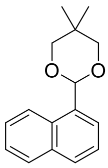
22

2-(4-Chlorophenyl)-5,5-dimethyl-1,3-dioxane (**22**): [1]H NMR ($CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H, ArH), 7.34 (d, J = 8.0 Hz, 2H, ArH), 5.36 (s, 1H, CH), 3.77 (d, J = 12.0 Hz, 2H, C**H**H), 3.64 (d, J = 12.0 Hz, 2H, CH**H**), 1.28 (s, 3H, CH_3), 0.80 (s, 3H, CH_3).



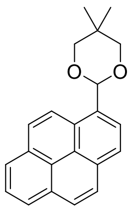
23

2-(4-Bromophenyl)-5,5-dimethyl-1,3-dioxane (**23**): [1]H NMR ($CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H, ArH), 7.38 (d, J = 8.4 Hz, 2H, ArH), 5.35 (s, 1H, CH), 3.76 (d, J = 12.0 Hz, 2H, C**H**H), 3.63 (d, J = 12.0 Hz, 2H, CH**H**), 1.27 (s, 3H, CH_3), 0.80 (s, 3H, CH_3).



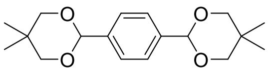
24

5,5-Dimethyl-2-(naphthalen-1-yl)-1,3-dioxane (**24**): [1]H NMR ($CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H, ArH), 7.83–7.79 (m, 3H, ArH), 7.51–7.79 (m, 3H, ArH), 5.94 (s, 1H, CH), 3.82 (d, J = 10.8 Hz, 2H, C**H**H), 3.73 (d, J = 10.8 Hz, 2H, CH**H**), 1.34 (s, 3H, CH_3), 0.78 (s, 3H, CH_3).



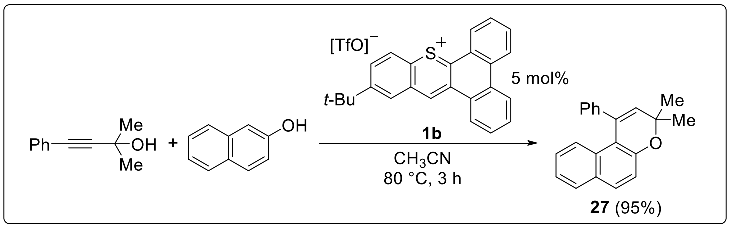
25

5,5-Dimethyl-2-(pyren-1-yl)-1,3-dioxane (**25**): pale yellow solids; mp 120.1–121.0 °C; [1]H NMR ($CDCl_3$) δ 8.44 (d, J = 9.2 Hz, 1H, ArH), 8.37 (d, J = 8.0 Hz, 1H, ArH), 8.21-8.18 (m, 3H, ArH), 8.14 (d, J = 9.2 Hz, 1H, ArH), 8.08 (d, J = 8.8 Hz, 1H, ArH), 8.05 (d, J = 9.2 Hz, 1H, ArH), 8.00 (dd, J = 8.0, 8.0 Hz, 1H, ArH), 6.30 (s, 1H, CH), 3.95 (d, J = 10.8 Hz, 2H, C**H**H), 3.91 (d, J = 10.8 Hz, 2H, CH**H**), 1.45 (s, 3H, CH_3), 0.91 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 131.71 (C), 131.21 (C), 131.15 (C), 130.59 (C), 128.25 (C), 127.73 (CH), 127.63 (CH), 127.39 (CH), 127.59 (CH), 125.28 (CH), 125.18 (CH), 124.77 (C), 124.70 (CH), 123.90 (CH), 123.08 (CH), 100.50 (CH), 78.13 (CH_2), 30.35 (C), 23.37 (CH_3), 21.96 (CH_3). A signal for the quaternary carbons of **25** might be overlapped; MS (ESI, positive mode) *m/z* 339 ($[M+Na]^+$).

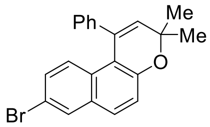


26

1,4-Bis(5,5-dimethyl-1,3-dioxan-2-yl)benzene (**26**): colorless powder; mp 58.0–59.0 °C; ^1H NMR ($CDCl_3$) δ 7.50 (s, 4H, ArH), 5.39 (s, 1H, CH), 3.76 (d, J = 12.0 Hz, 2H, C**H**H), 3.64 (d, J = 12.0 Hz, 2H, CH**H**), 1.27 (s, 3H, CH_3), 0.79 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 139.05 (C), 126.04 (CH), 101.40 (CH), 77.58 (CH_2), 33.02 (C), 23.03 (CH_3), 21.90 (CH_3); MS (ESI, positive mode) *m/z* 329 ($[M+Na]^+$).

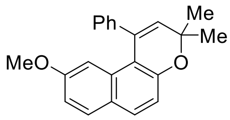


General Procedure of Cascade Reaction; Reaction of Naphthalen-2-ol with 2-Methyl-4-phenyl-3-butyn-2-ol in the Presence of Thiopyrylium Trifluoromethanesulfonate 1b. Naphthalen-2-ol (0.088 g, 0.61 mmol) was added to a solution of 2-methyl-4-phenyl-3-butyn-2-ol (0.080 g, 0.50 mmol) and thiopyrylium triflate **1b** (12.6 mg, 0.0250 mmol) in acetonitrile (3.0 mL) at room temperature under dark conditions. After stirring at 80 °C for 3 h, the reaction mixture was purified by column chromatography on silica gel (eluent: dichloromethane) to afford 3,3-dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (0.136 g, 0.475 mmol, 95%) as colorless solids. 3,3-Dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (**27**): ^1H NMR ($CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H, ArH), 7.33–7.29 (m, 3H, ArH), 7.22–7.18 (m, 4H, ArH), 8.14 (d, J = 9.2 Hz, 1H, ArH), 7.09 (d, J = 8.4 Hz, 1H, ArH), 7.02 (ddd, J = 1.2, 6.8, 9.2 Hz, 1H, ArH), 5.71 (s, 1H, CH), 1.51 (s, 6H, CH_3); MS (ESI, positive mode) *m/z* 341 ($[M+MeOH+Na]^+$).



28

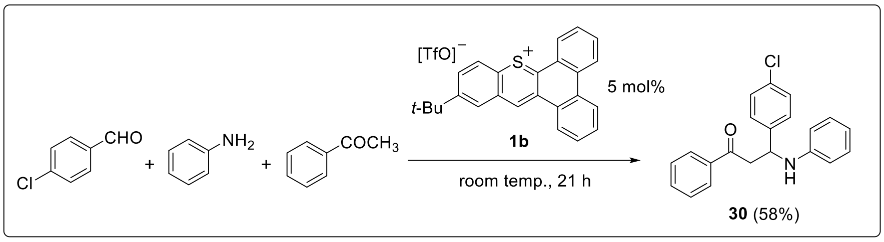
8-Bromo-3,3-dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (**28**): colorless solids; ^{1}H NMR ($CDCl_3$) δ 7.86 (d, *J* = 2.0 Hz, 1H, ArH), 7.62 (d, *J* = 8.8 Hz, 1H, ArH), 7.32–7.30 (m, 3H, ArH), 7.20 (d, *J* = 8.8 Hz, 1H, ArH), 7.18–7.15 (m, 2H, ArH), 7.08 (dd, *J* = 2.4, 9.2 Hz, 1H, ArH), 6.94 (d, *J* = 9.2 Hz,1H, ArH), 5.71 (s, 1H, CH), 1.50 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 153.27 (C), 141.20 (C), 135.01 (C), 131.34 (C), 130.80 (CH), 130.17 (CH), 129.82 (CH), 128.50 (CH), 128.37 (C), 128.15 (CH), 127.99 (CH), 127.75 (C), 127.47 (CH), 119.87 (CH), 116.70 (C), 116.25 (C), 75.52 (C), 26.35 (CH_3); MS (ESI, positive mode) *m/z* 365 ($[M+H]^+$).



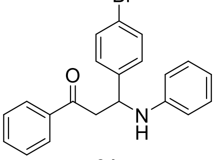
29

9-Methoxy-3,3-dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (**29**): colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 1H, ArH), 7.08 (d, *J* = 8.8 Hz, 1H, ArH), 7.35–7.26 (m, 3H, ArH), 7.24–7.22 (m, 2H, ArH), 7.04 (d, *J* = 8.8 Hz, 1H, ArH), 6.83 (dd, *J* = 2.4, 9.2 Hz, 1H, ArH), 6.43 (d, *J* = 2.4 Hz,1H, ArH), 5.68 (s, 1H, CH), 1.51 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.74 (C), 153.55 (C), 141.86 (C), 135.52 (C), 131.03 (C), 130.07 (CH), 130.03 (CH), 129.68 (CH), 128.43 (CH), 128.08 (CH), 127.11 (CH), 125.36 (C), 116.24 (CH), 115.70 (CH), 115.20 (C), 105.58 (CH), 75.26 (C), 54.16 (CH_3), 26.39 (CH_3); MS (ESI, positive mode) *m/z* 339 ($[M+Na]^+$).

General Procedure of Mannich Reaction; Reaction of *p*-Chlorobenzaldehyde and Aniline with Acetophenone in the Presence of Thiopyrylium Trifluoromethanesulfonate 1b.



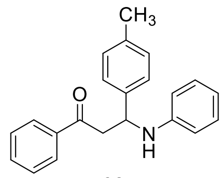
Acetophenone (0.085 g, 0.71 mmol) was added to a solution of *p*-chlorobenzaldehyde (0.101 g, 0.719 mmol), aniline (0.072 g, 0.77 mmol), and thiopyrylium triflate **1b** (17.8 mg, 0.0355 mmol) at room temperature under dark conditions. After stirring at room temperature for 21 h, the reaction mixture was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane = 10/1; v/v) to afford 3-(4-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (0.139 g, 0.413 mmol, 58%) as pale yellow solids. 3-(4-Chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (**30**): colorless solids; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H, ArH), 7.57 (dd, *J* = 7.4, 7.4 Hz, 1H, ArH), 7.45 (dd, *J* = 7.7, 7.7 Hz, 2H, ArH), 7.38 (d, *J* = 8.5 Hz, 2H, ArH), 7.28 (d, *J* = 8.6 Hz, 2H, ArH), 7.10 (dd, *J* = 8.0, 8.0 Hz, 2H, ArH), 6.68 (dd, *J* = 7.3, 7.3 Hz, 1H, ArH), 6.53 (d, *J* = 7.6 Hz, 2H, ArH), 4.97 (dd, *J* = 5.6, 5.6 Hz, 1H, CH), 4.55 (br s, 1H, NH), 3.48 (dd, *J* = 5.6, 16.3 Hz, 1H, C**H**H), 3.41 (dd, 1H, *J* = 5.6, 16.3 Hz, CH**H**); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 197.83 (C), 146.65 (C), 141.47 (C), 136.51 (C), 133.49 (CH), 132.88 (C), 129.10 (CH), 128.88 (CH), 128.68 (CH), 128.10 (CH), 127.78 (CH), 118.00 (CH), 113.81 (CH), 54.09 (CH), 46.02 (CH_2); MS (ESI, positive mode) *m/z* 360 ([M+Na]$^+$).



31

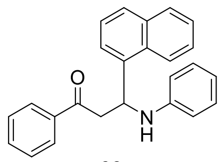
3-(4-Bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one (**31**): colorless solids; ^{1}H NMR ($CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H, ArH), 7.57 (dd, *J* = 7.4, 7.4 Hz, 1H, ArH), 7.45 (dd, *J* = 8.2, 8.2 Hz, 4H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 7.09 (dd, *J* = 7.6, 7.6 Hz, 2H, ArH), 6.68 (dd, *J* = 7.3, 7.3 Hz, 1H, ArH), 6.53 (d, *J* = 7.7 Hz, 2H, ArH), 4.96 (dd, *J* = 5.5, 5.5 Hz, 1H, CH), 4.55 (br s, 1H, NH), 3.47 (dd, *J* = 5.5, 16.3 Hz, 1H, CH), 3.41 (dd, *J* = 5.5, 16.3 Hz, 1H, CH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 197.82 (C), 146.66 (C), 142.05 (C), 136.53 (C), 133.53

(CH), 131.87 (C), 129.13 (CH), 128.72 (CH), 128.18 (CH), 128.13 (CH), 121.02 (C), 118.05 (CH), 113.83 (CH), 54.19 (CH), 46.02 (CH); MS (ESI, positive mode) *m/z* 404 ($[M+Na]^+$).



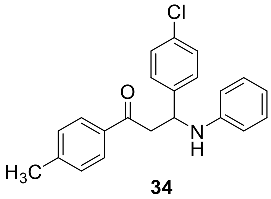
32

1-Phenyl-3-(phenylamino)-3-(*p*-tolyl)propan-1-one (**32**): colorless solids; ^{1}H NMR ($CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H, ArH), 7.56 (dd, *J* = 7.2, 7.2 Hz, 1H, ArH), 7.44 (dd, *J* = 8.0, 8.0 Hz, 2H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.12 (d, *J* = 7.6 Hz, 2H, ArH), 7.08 (dd, *J* = 8.0, 8.0 Hz, 2H, ArH), 6.65 (dd, *J* = 7.2, 7.2 Hz, 1H, ArH), 6.56 (d, *J* = 8.0 Hz, 2H, ArH), 4.97 (dd, *J* = 5.6, 7.2 Hz, 1H, CH), 4.50 (br s, 1H, NH), 3.50 (dd, *J* = 5.6, 16.4 Hz, 1H, C**H**H), 3.40 (dd, *J* = 7.2, 16.4 Hz, 1H, CH**H**), 2.31 (s, 3H, CH_3); MS (ESI, positive mode) *m/z* 338 ($[M+Na]^+$).



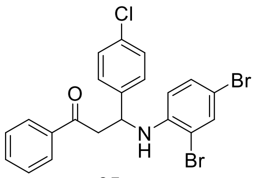
33

3-(Naphthalen-2-yl)-1-phenyl-3-(phenylamino)propan-1-one (**33**): colorless powder; mp 144.5–145.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H, ArH), 7.93–7.87 (m, 3H, ArH), 7.75 (d, *J* = 8.0 Hz, 1H, ArH), 7.69 (d, *J* = 7.2 Hz, 1H, ArH), 7.61–7.51 (m, 3H, ArH), 7.44–7.36 (m, 3H, ArH), 7.06 (dd, *J* = 8.0, 8.0 Hz, 2H, ArH), 6.64 (dd, *J* = 7.6, 7.6 Hz, 1H, ArH), 6.53 (d, *J* = 8.0 Hz, 1H, ArH), 5.82 (br, CH), 4.63 (br s, 1H, NH), 3.63 (dd, *J* = 16.8, 2.0 Hz, 1H, C**H**H), 3.52 (dd, *J* = 16.8, 8.0 Hz, 1H, CH**H**); ^{13}C NMR ($CDCl_3$) δ 198.28 (C), 146.96 (C), 137.70 (C), 136.78 (C), 134.21 (CH), 133.43 (C), 130.48 (C), 129.30 (CH), 129.09 (CH), 128.67 (CH), 128.17 (CH), 127.88 (CH), 126.47 (CH), 125.76 (CH), 125.61 (CH), 123.47 (CH), 122.30 (CH), 117.76 (CH), 113.74 (CH), 50.68 (CH), 45.00 (CH_2); MS (ESI, positive mode) *m/z* 374 [($M+Na^+$)] .



34

3-(4-Chlorophenyl)-3-(phenylamino)-1-(*p*-tolyl)propan-1-one (**34**): pale yellow solids; mp 114.8–115.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H, ArH), 7.37 (d, J = 8.4 Hz, 2H, ArH), 7.28-7.23 (m, 4H, ArH), 7.08 (dd, J = 8.0, 8.0 Hz, 2H, ArH), 6.67 (dd, J = 7.6, 7.6 Hz, 1H, ArH), 6.52 (d, J = 8.4 Hz, 2H, ArH), 4.95 (dd, J = 6.0, 6.4 Hz, 1H, CH), 4.57 (br s, 1H, NH), 3.43 (dd, J = 6.0, 16.4 Hz, 1H, C**H**H), 3.37 (dd, J = 6.4, 16.4 Hz, 1H, CH**H**), 2.34 (s, 3H, CH_3), ^{13}C{^{1}H} NMR ($CDCl_3$) δ 197.46 (C), 146.72 (C), 144.41 (C), 141.60 (C), 134.10 (C), 132.82 (C), 129.35 (CH), 129.07 (CH), 128.85 (CH), 128.24 (CH), 127.77 (CH), 117.92 (CH), 113.79 (CH), 54.19 (CH), 45.91 (CH_2), 21.58 (CH_3); MS (ESI, positive mode) *m/z* 372 ([M+Na]$^+$).



35

3-(4-Chlorophenyl)-3-((2,4-dibromophenyl)amino)-1-phenylpropan-1-one (**35**): pale yellow oil; ^{1}H NMR ($CDCl_3$) δ7.90 (d, J = 7.6 Hz, 2H, ArH), 7.58 (dd, J = 7.6, 7.6 Hz, 1H, ArH), 7.53 (d, J = 2.4 Hz, 1H, ArH), 7.45 (dd, J = 7.6, 7.6 Hz, 2H, ArH), 7.33 (d, J = 8.8 Hz, 2H, ArH), 7.29 (d, J = 8.8 Hz, 2H, ArH), 7.11 (dd, J = 2.4, 8.8 Hz, 1H, ArH), 6.30 (d, J = 8.8 Hz, 1H, ArH), 5.23 (br s, 1H, NH), 5.01 (dd, J = 6.0, 12.8 Hz, 1H, CH), 3.52 (dd, J = 6.0, 16.4 Hz, 1H, C**H**H), 3.42 (dd, J = 6.0, 16.4 Hz, 1H, CH**H**); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 197.22 (C), 140.69 (C), 140.25 (C), 136.48 (C), 134.29 (CH), 133.61 (CH), 133.29 (C), 131.02 (CH), 129.06 (CH), 128.72 (CH), 128.10 (CH), 127.67 (CH), 113.72 (CH), 110.50 (C), 108.95 (C), 54.09 (CH), 45.92 (CH_2); MS (ESI, positive mode) *m/z* 516 ([M+Na]$^+$).

NMR experiments. Thiopyrylium triflate **1b** (12.6 mg, 0.0250 mmol) and NBS (4.45 mg, 0.0250 mmol) were dissolved in a mixture of $CDCl_3$ (800 μL) and CD_3CN (200 μL) at room temperature. After the resulting solution was transferred into an NMR tube, ^1H and ^{13}C NMR spectra of the solution were recorded.

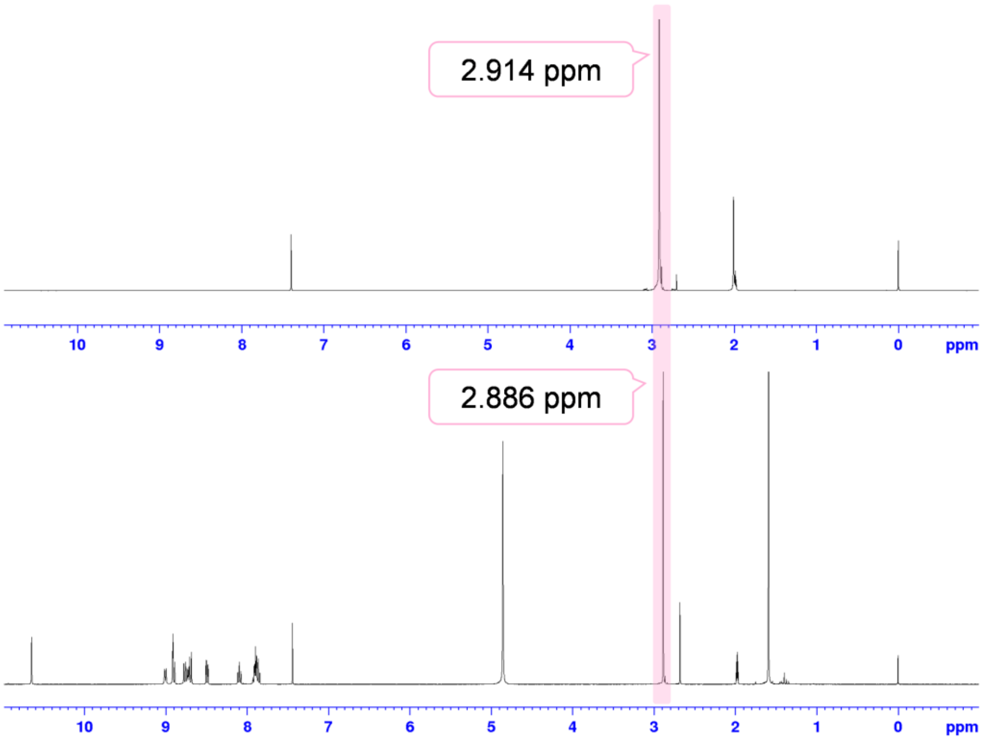


Figure S1. ^1H NMR spectra of (top) NBS and (bottom) NBS + thiopyrylium trifrate **1b** in $CDCl_3/CD_3CN$ = 4/1 (V/V) at room temperature.

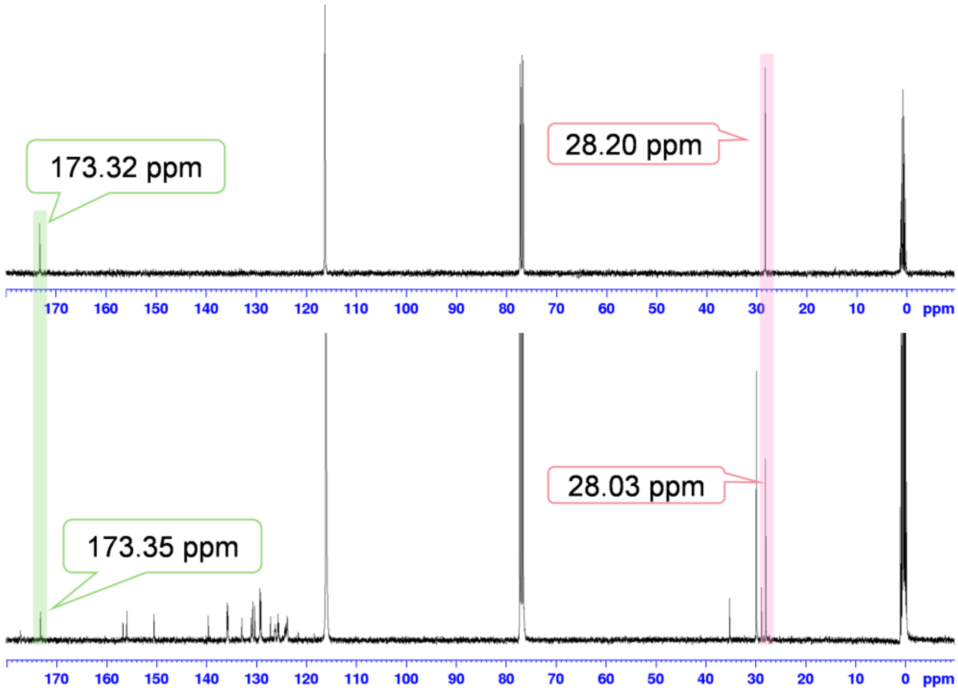


Figure S2. ^{13}C NMR spectra of (top) NBS and (bottom) NBS + thiopyrylium trifrate **1b** in $CDCl_3/CD_3CN$ = 4/1 (V/V) at room temperature.

Theoretical Calculations. All theoretical calculations were performed utilizing the Gaussian 16 package.[2] Density functional theory (DFT) calculations were carried out with M06-2X hybrid meta functionals.[3,4] The geometries of thiopyrylium cations **1a´**–**1c´**, where the counter anions were omitted, were optimized by the 6-31G(d) basis sets. Harmonic vibrational frequency calculations were carried out for the stationary points to confirm each structure being either a minimum, with no imaginary frequency.

(a) (b)

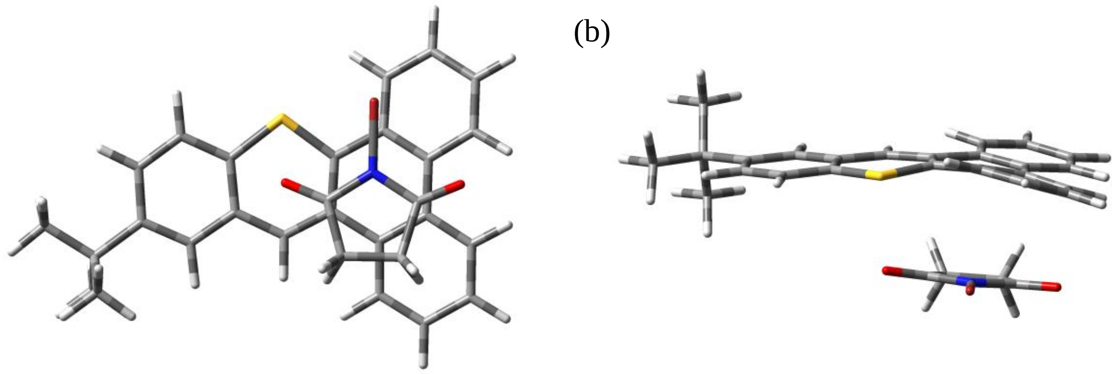


Figure S3. (a) Top- and (b) side-views of the optimized structure of **1b´**·NBS complex at M06-2X level of theory (color code: carbon = gray; hydrogen = white; nitrogen = blue; oxygen = red; sulfur = yellow; bromine = brown).

Table S1. Theoretically optimized cartesian coordinates of thiopyrylium cation **1b´** at M06-2x/6-31G(d) level of theory.

atom	x	y	z
C	-1.402929	-1.346292	-0.005112
C	-1.543876	0.059989	0.0002
C	-0.416854	0.90524	0.001806
C	0.925229	0.537099	-0.001544
C	1.295328	-0.835918	-0.003197
S	0.139497	-2.102319	-0.00695
C	1.981505	1.563423	-0.001964
C	3.337723	1.170155	0.001399
C	3.691016	-0.250519	0.003457
C	2.68052	-1.245642	-0.000608
C	-2.53975	-2.165925	-0.007861
C	-3.791804	-1.585665	-0.005038
C	-3.982414	-0.179905	0.000616
C	-2.85074	0.610289	0.003151
C	1.673109	2.936894	-0.006584
C	2.664917	3.896427	-0.006334
C	4.007419	3.508222	-0.001934
C	4.331593	2.167416	0.001469
C	-5.371794	0.462373	0.003774
C	-6.489584	-0.585755	0.001145
C	-5.518051	1.332726	1.2644
C	-5.519888	1.340997	-1.250881
C	5.032742	-0.677207	0.008599
C	5.366833	-2.01545	0.008696
C	4.365189	-2.997827	0.003686
C	3.046206	-2.614229	-0.00062
H	-0.651148	1.963174	0.006629
H	-2.435571	-3.24656	-0.011955
H	-4.655399	-2.240786	-0.007147

Zero-point correction=	0.390131 (Hartree/Particle)
Thermal correction to Energy=	0.411373
Thermal correction to Enthalpy=	0.412317
Thermal correction to Gibbs Free Energy=	0.338365
Sum of electronic and zero-point Energies=	-1362.476173
Sum of electronic and thermal Energies=	-1362.454932
Sum of electronic and thermal Enthalpies=	-1362.453988
Sum of electronic and thermal Free Energies=	-1362.527940

Table S2. Theoretically optimized cartesian coordinates of NBS at M06-2x/6-31G(d) level of theory.

atom	x	y	z
C	2.365839	-0.767076	0.003129
C	2.365836	0.767078	-0.003307
C	0.901418	1.184441	0.000367
N	0.154799	0.000000	0.000586
C	0.901419	-1.184441	0.000361
O	0.442994	-2.292369	-0.001714
O	0.442989	2.292370	0.001038
Br	-1.678692	-0.000001	-0.000033
H	2.840273	-1.197546	0.888040
H	2.847581	-1.206229	-0.873400
H	2.839820	1.197551	-0.888457
H	2.848022	1.206231	0.872978
C	2.365839	-0.767076	0.003129
C	2.365836	0.767078	-0.003307
C	0.901418	1.184441	0.000367
N	0.154799	0.000000	0.000586
C	0.901419	-1.184441	0.000361
O	0.442994	-2.292369	-0.001714
O	0.442989	2.292370	0.001038
Br	-1.678692	-0.000001	-0.000033
H	2.840273	-1.197546	0.888040
H	2.847581	-1.206229	-0.873400
H	2.839820	1.197551	-0.888457
H	2.848022	1.206231	0.872978
C	2.365839	-0.767076	0.003129
C	2.365836	0.767078	-0.003307
C	0.901418	1.184441	0.000367
N	0.154799	0.000000	0.000586
C	0.901419	-1.184441	0.000361
O	0.442994	-2.292369	-0.001714
O	0.442989	2.292370	0.001038

Zero-point correction=	0.082753 (Hartree/Particle)
Thermal correction to Energy=	0.090085

Thermal correction to Enthalpy=	0.091029
Thermal correction to Gibbs Free Energy=	0.049056
Sum of electronic and zero-point Energies=	-2931.575850
Sum of electronic and thermal Energies=	-2931.568517
Sum of electronic and thermal Enthalpies=	-2931.567573
Sum of electronic and thermal Free Energies=	-2931.609547

Table S3. Theoretically optimized cartesian coordinates of **1b´**·NBS complex at M06-2x/6-31G(d) level of theory.

atom	x	y	z
C	4.508679	-1.613096	-0.233601
C	4.757767	-0.218066	-0.168103
C	3.68501	0.62541	-0.373078
C	2.381714	0.139171	-0.644087
C	2.181494	-1.259376	-0.707212
C	3.257518	-2.131791	-0.494074
C	6.147102	0.356315	0.119696
C	7.1936	-0.744368	0.323306
C	6.582348	1.233107	-1.067531
C	6.080861	1.211755	1.397031
S	0.637472	-1.943373	-1.007448
C	-0.416959	-0.627923	-1.26986
C	-0.016411	0.723068	-1.092171
C	-1.043743	1.77741	-1.151506
C	-2.407472	1.41394	-1.206309
C	-2.787417	0.007584	-1.360383
C	-1.789935	-0.979154	-1.545893
C	-4.130491	-0.408313	-1.349332
C	-4.474867	-1.721633	-1.601552
C	-3.487753	-2.672568	-1.900837
C	-2.162892	-2.305417	-1.862646
C	-0.702963	3.143394	-1.1156
C	-1.675944	4.124155	-1.09387
C	-3.028118	3.763264	-1.109253
C	-3.381974	2.429823	-1.169828
C	1.308602	1.036036	-0.809874
H	5.324565	-2.308636	-0.07438
H	3.819957	1.70313	-0.3299

H	3.106386	-3.206011	-0.53432
H	8.164583	-0.283851	0.525115
H	6.950723	-1.386067	1.176928

Zero-point correction=	0.474202 (Hartree/Particle)
Thermal correction to Energy=	0.504082
Thermal correction to Enthalpy=	0.505026
Thermal correction to Gibbs Free Energy=	0.413168
Sum of electronic and zero-point Energies=	-4294.079607
Sum of electronic and thermal Energies=	-4294.049726
Sum of electronic and thermal Enthalpies=	-4294.048782
Sum of electronic and thermal Free Energies=	-4294.140640

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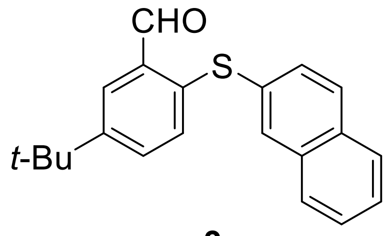
^{1}H and ^{13}C NMR Spectra

[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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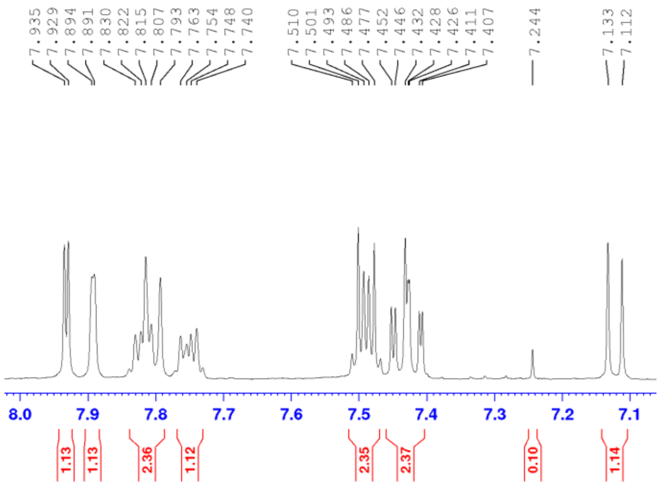
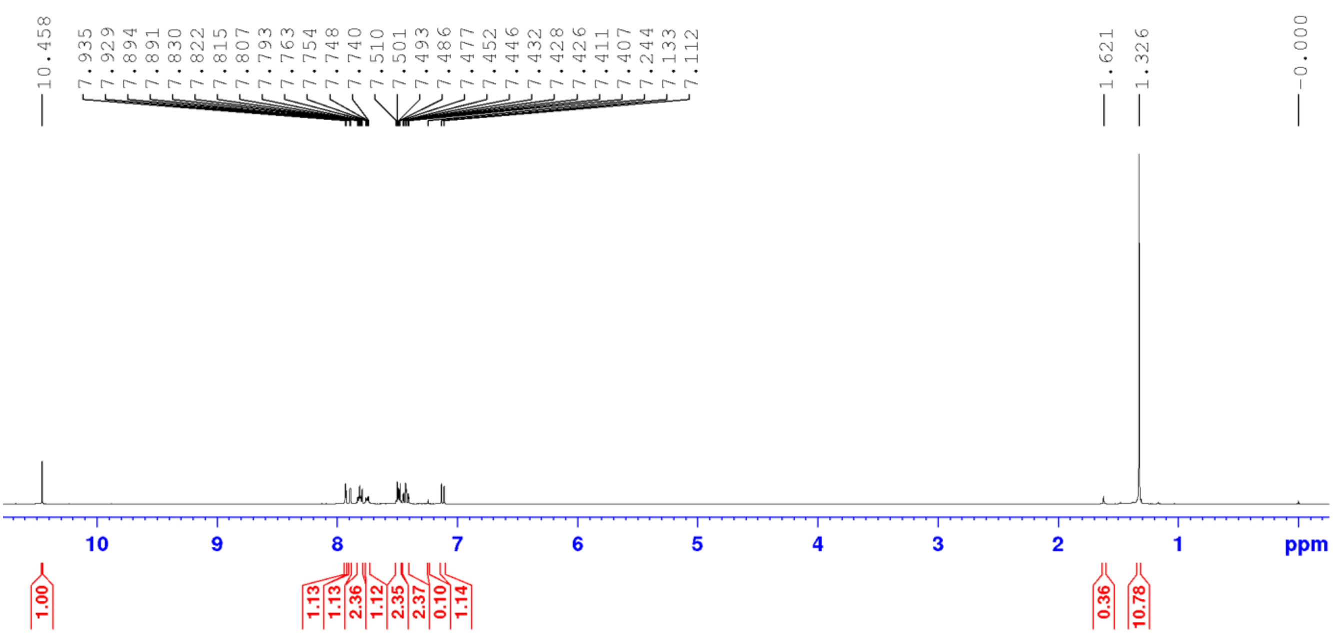
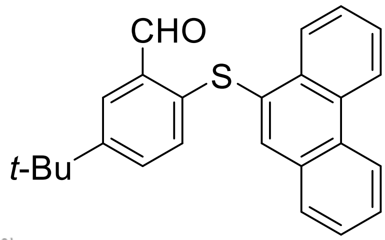




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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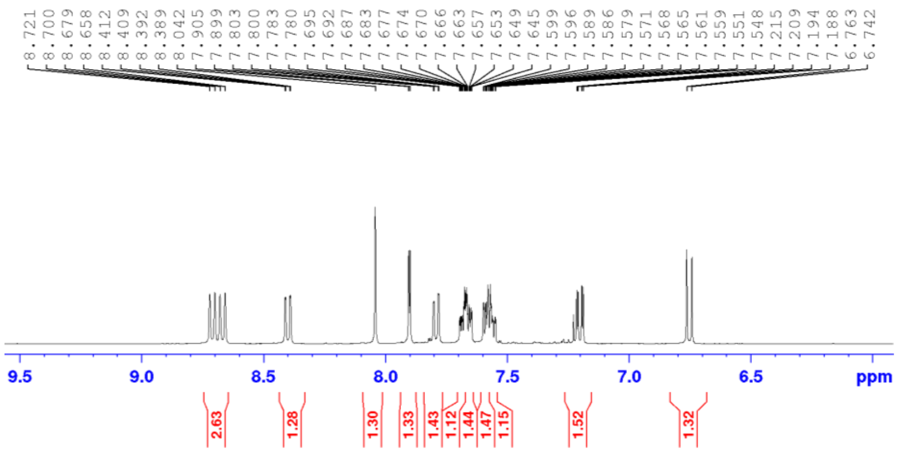
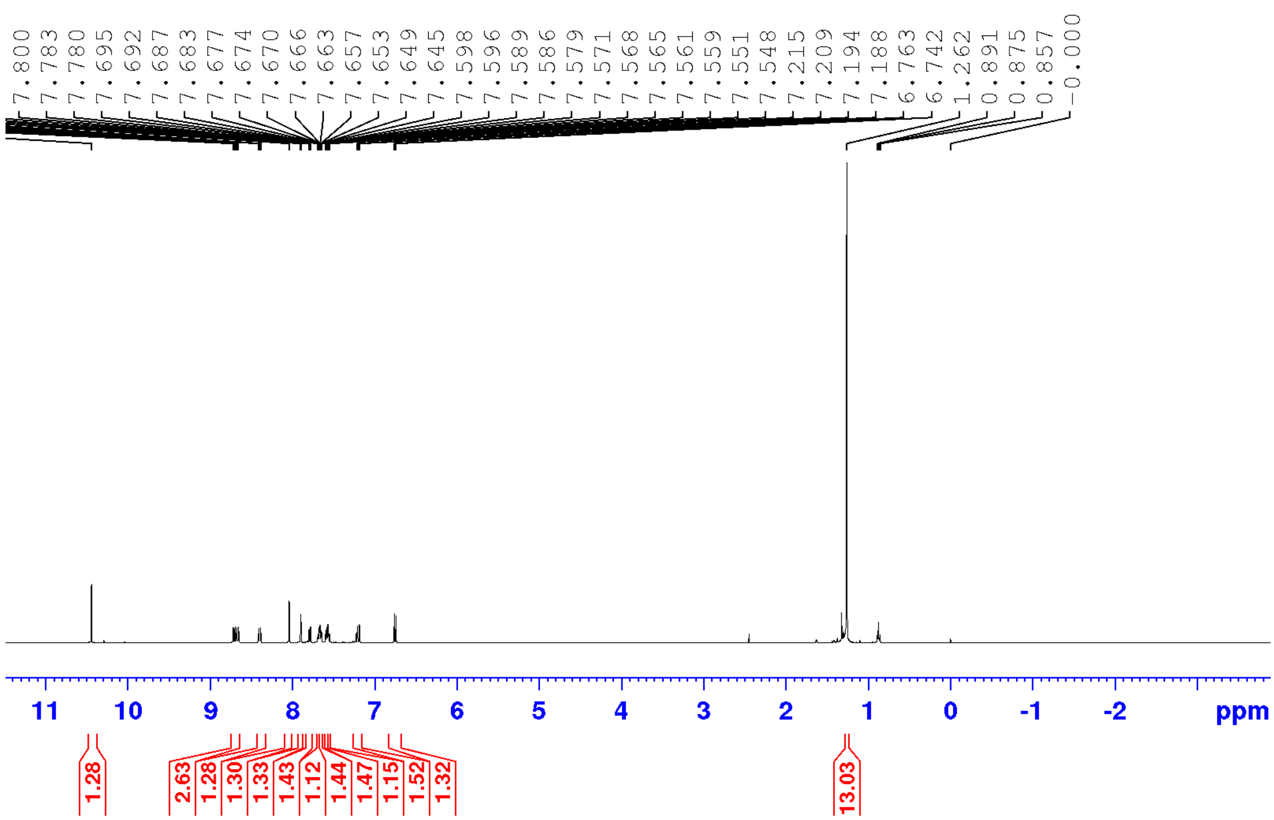
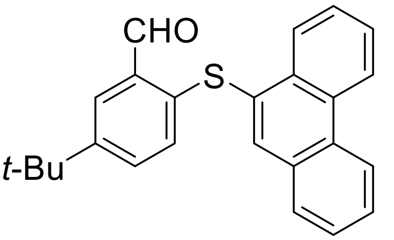




$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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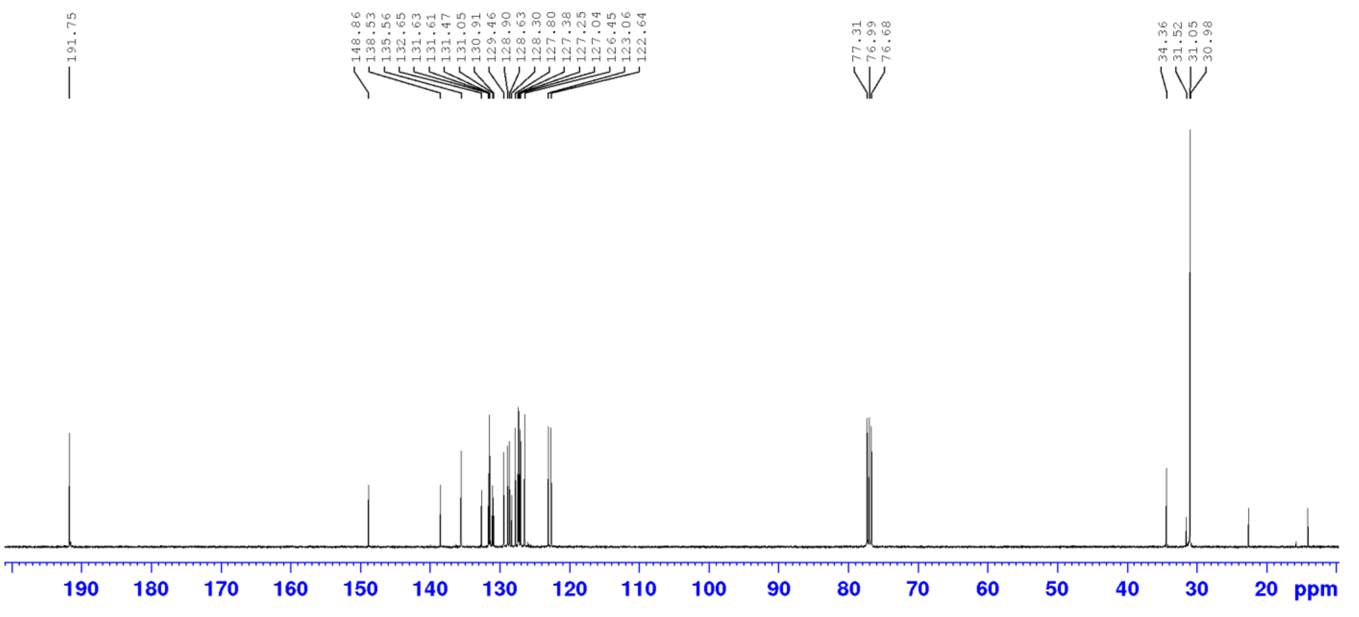
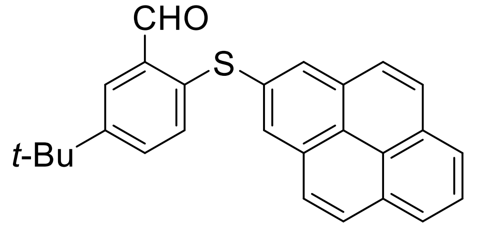


^1H NMR (400 MHz, $CDCl_3$, 298 K)



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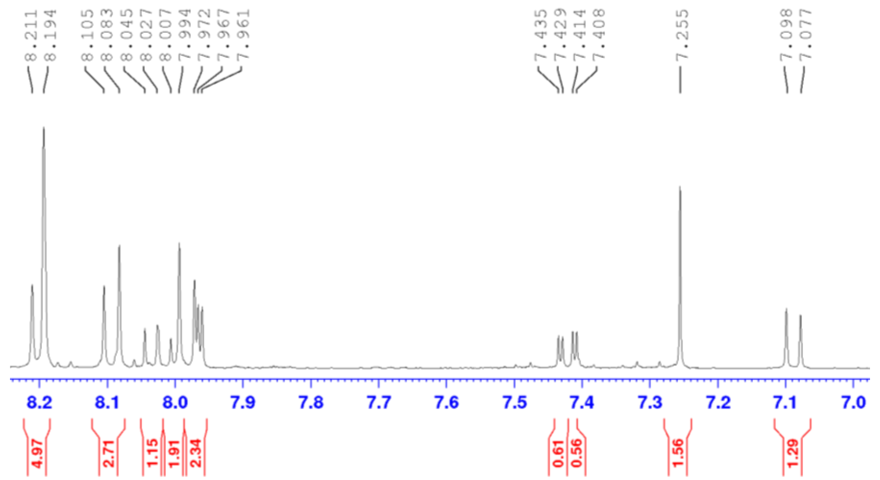
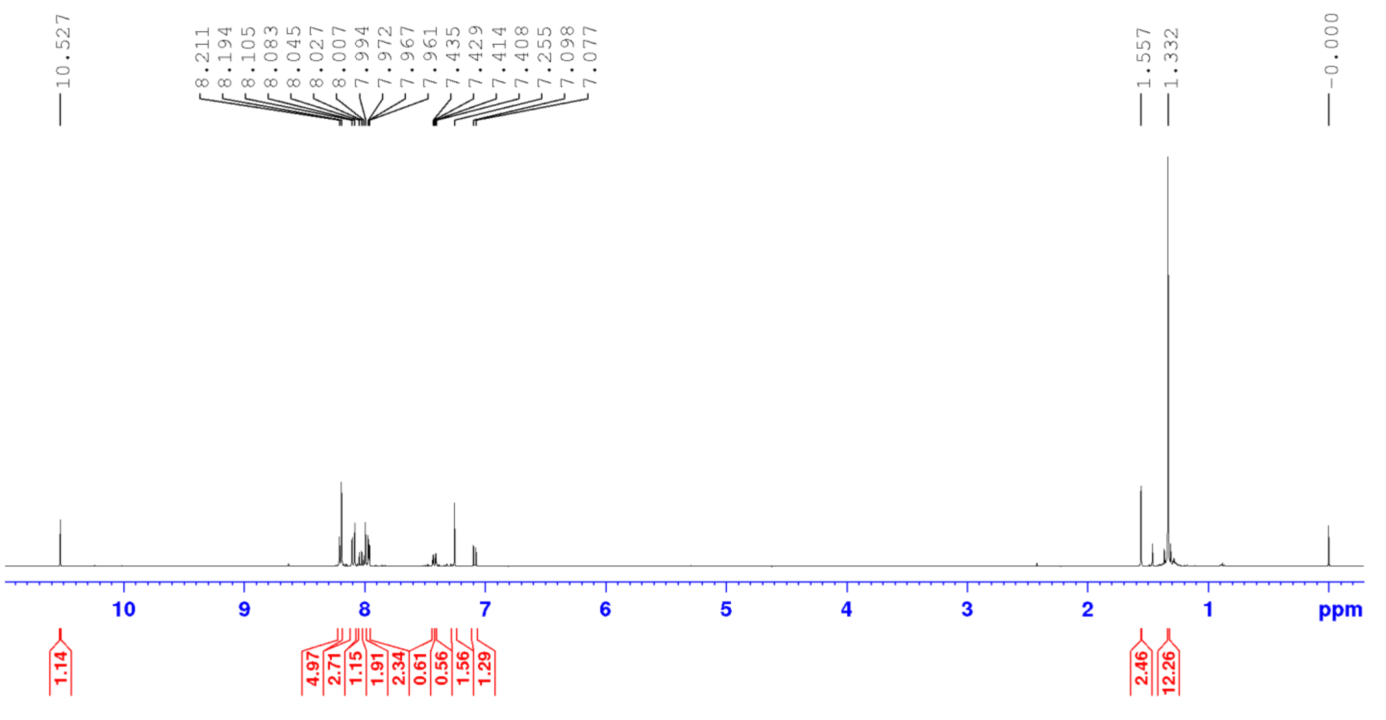
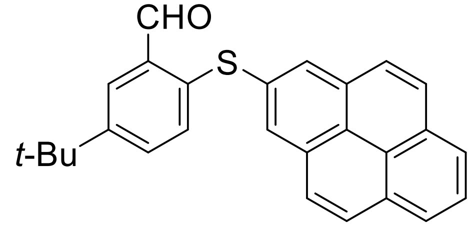




$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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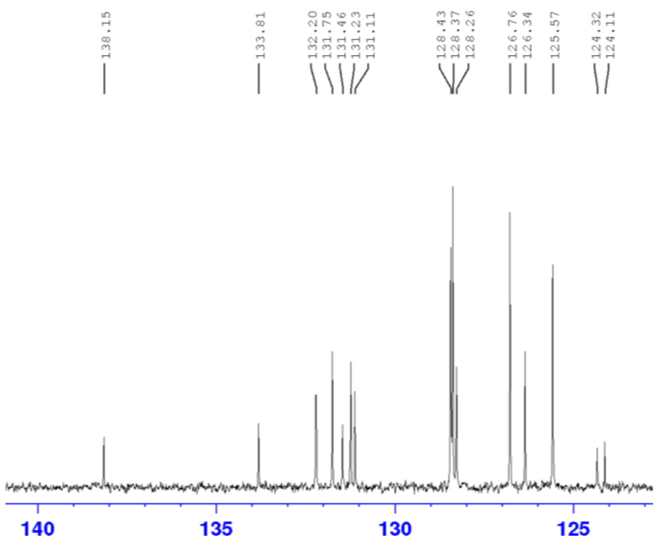
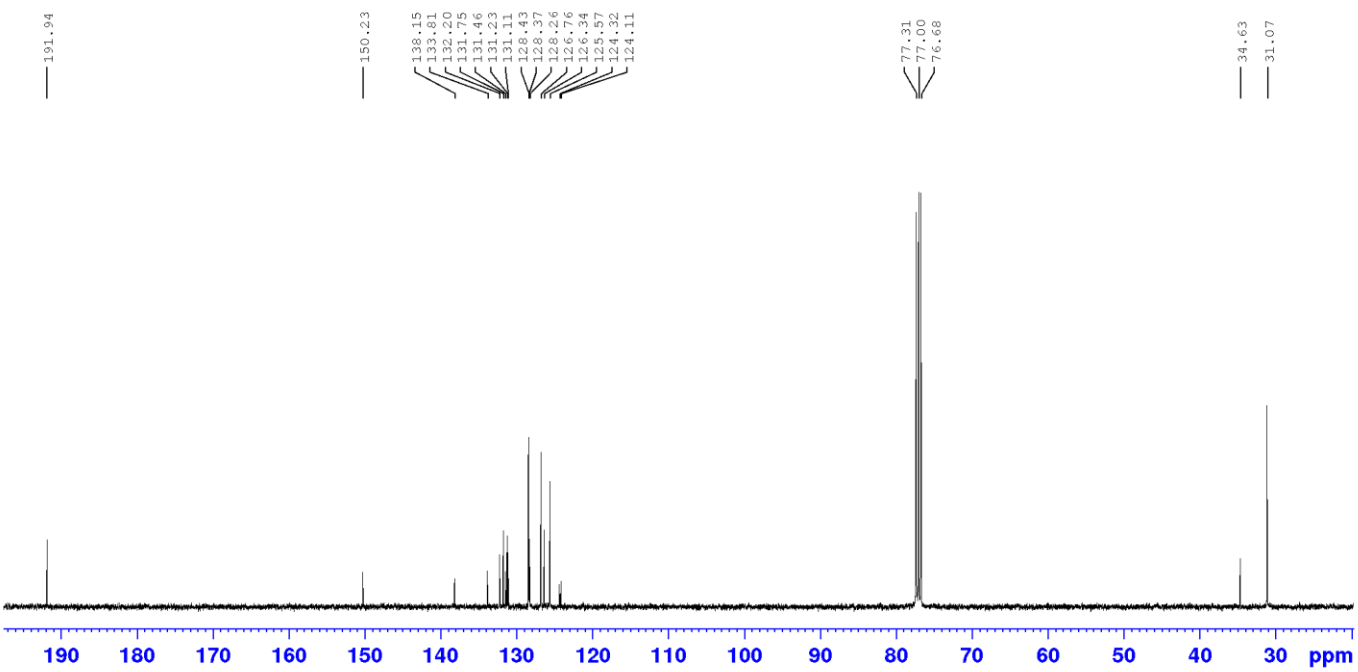
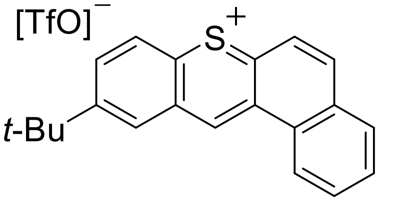




^{1}H NMR (400 MHz, CD_3CN, 298 K)



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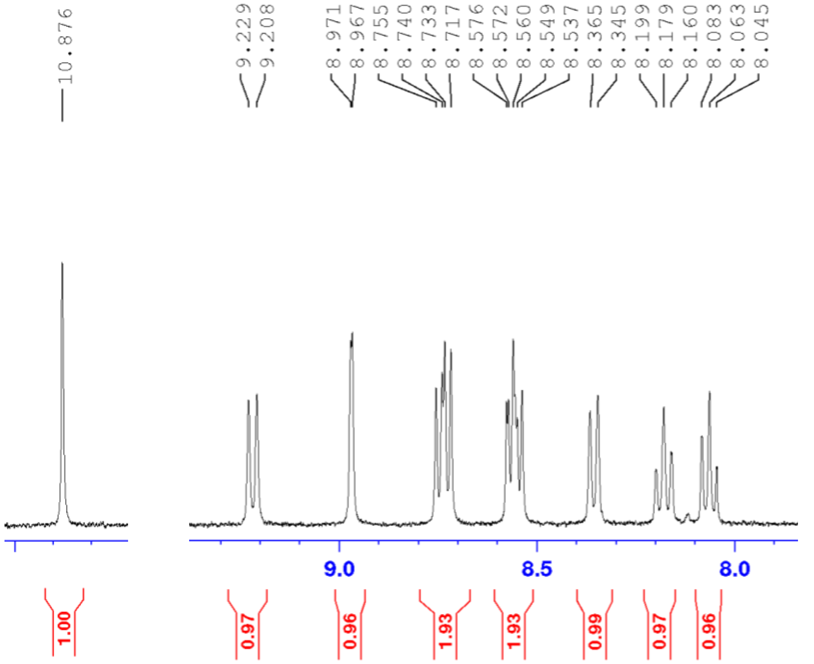
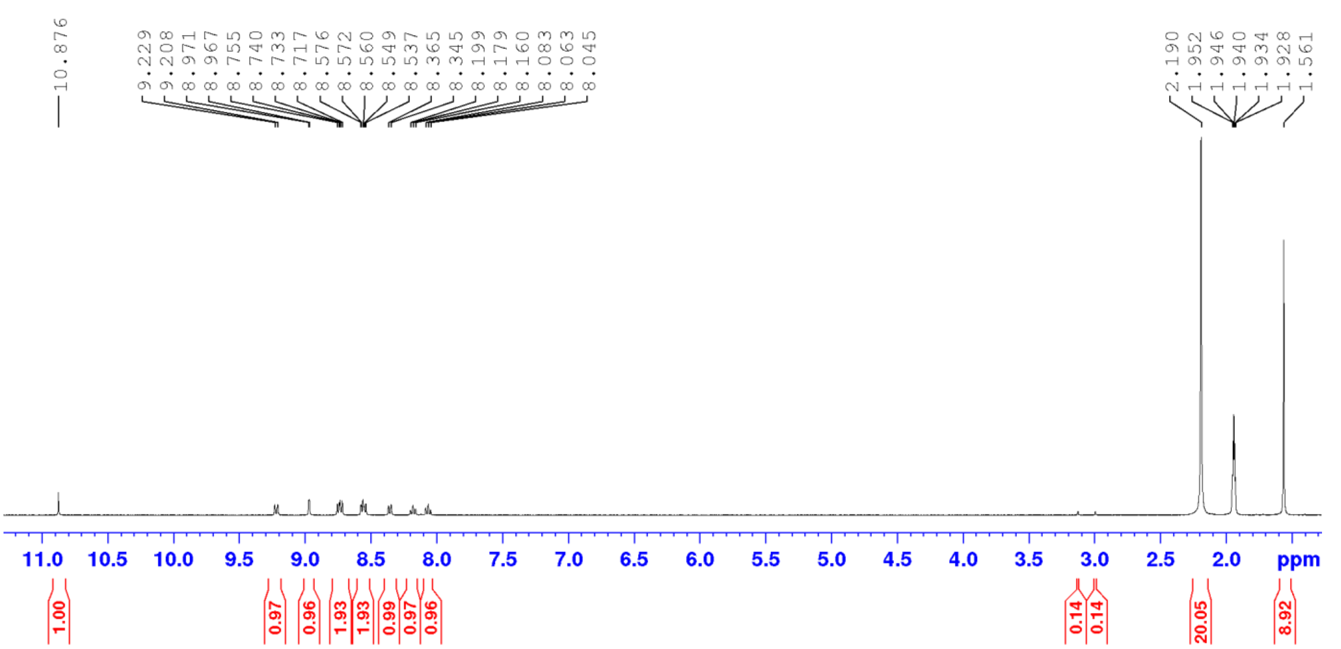
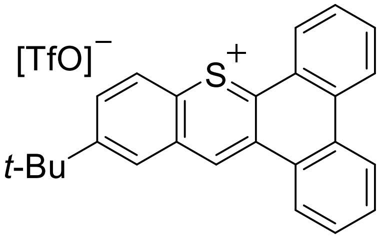




^{1}H NMR (400 MHz, CD_3CN, 298 K)



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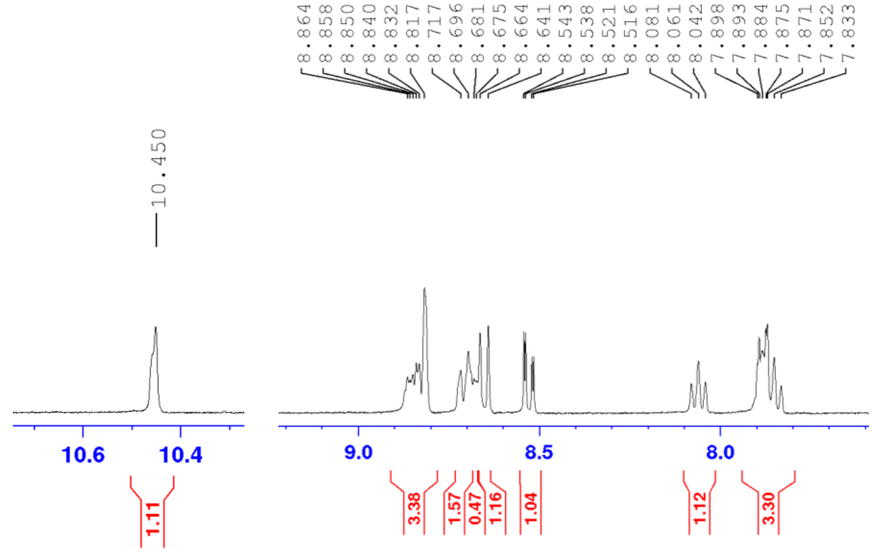
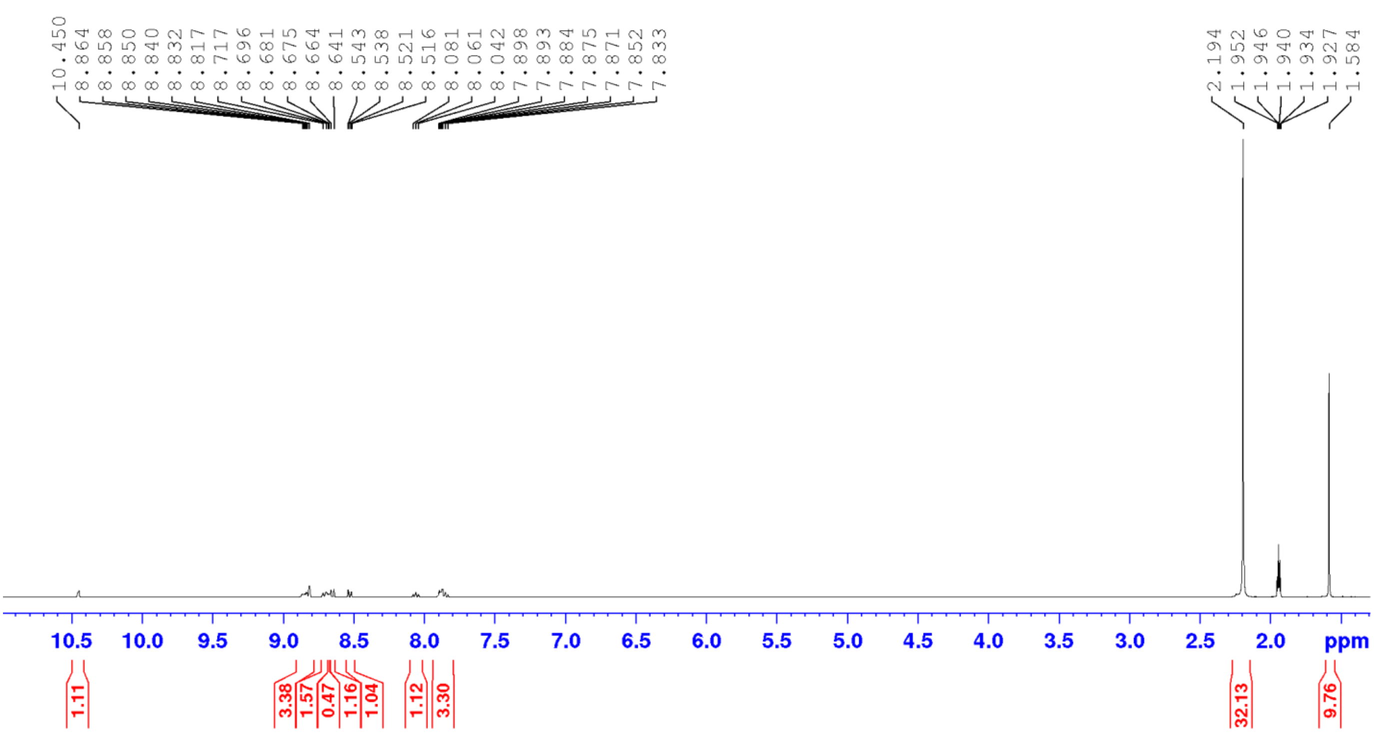
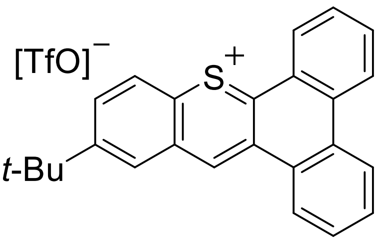




$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN, 298 K)



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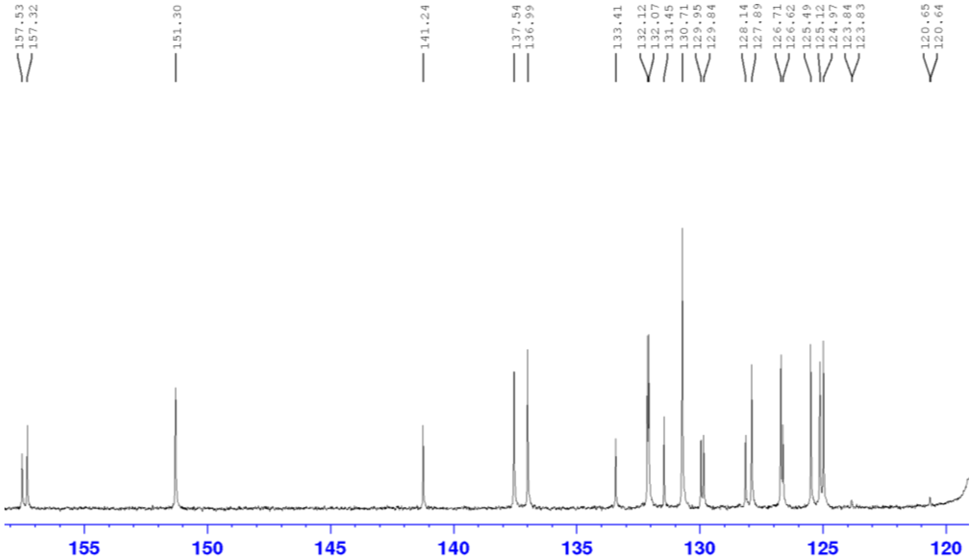
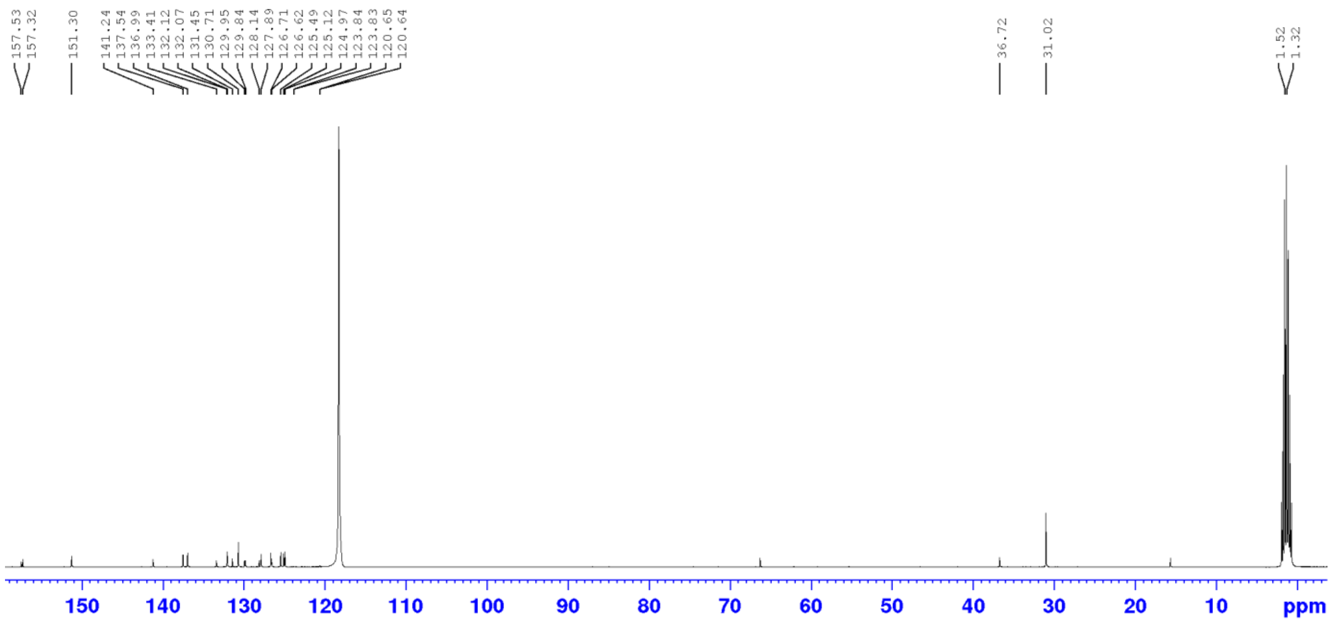
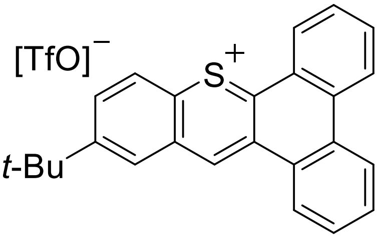




$^{19}F\{^1H\}$ NMR (376 MHz, CD_3CN, 298 K)



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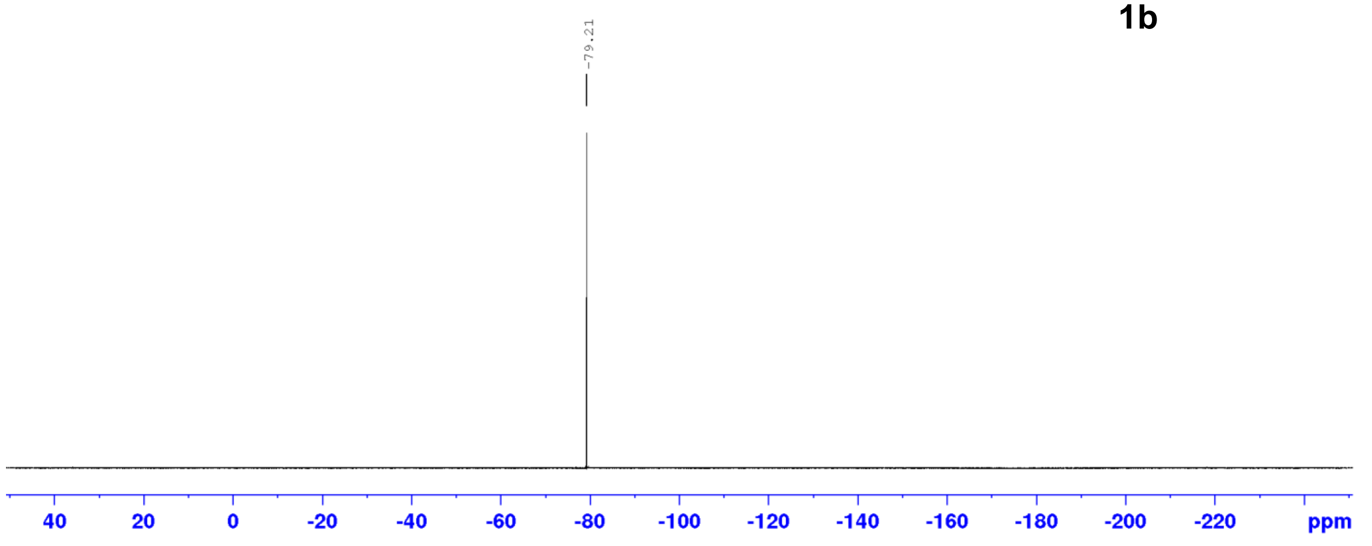
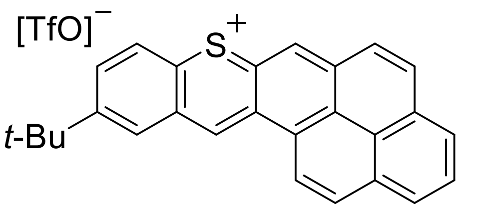


^{1}H NMR (400 MHz, CD_3CN, 298 K)



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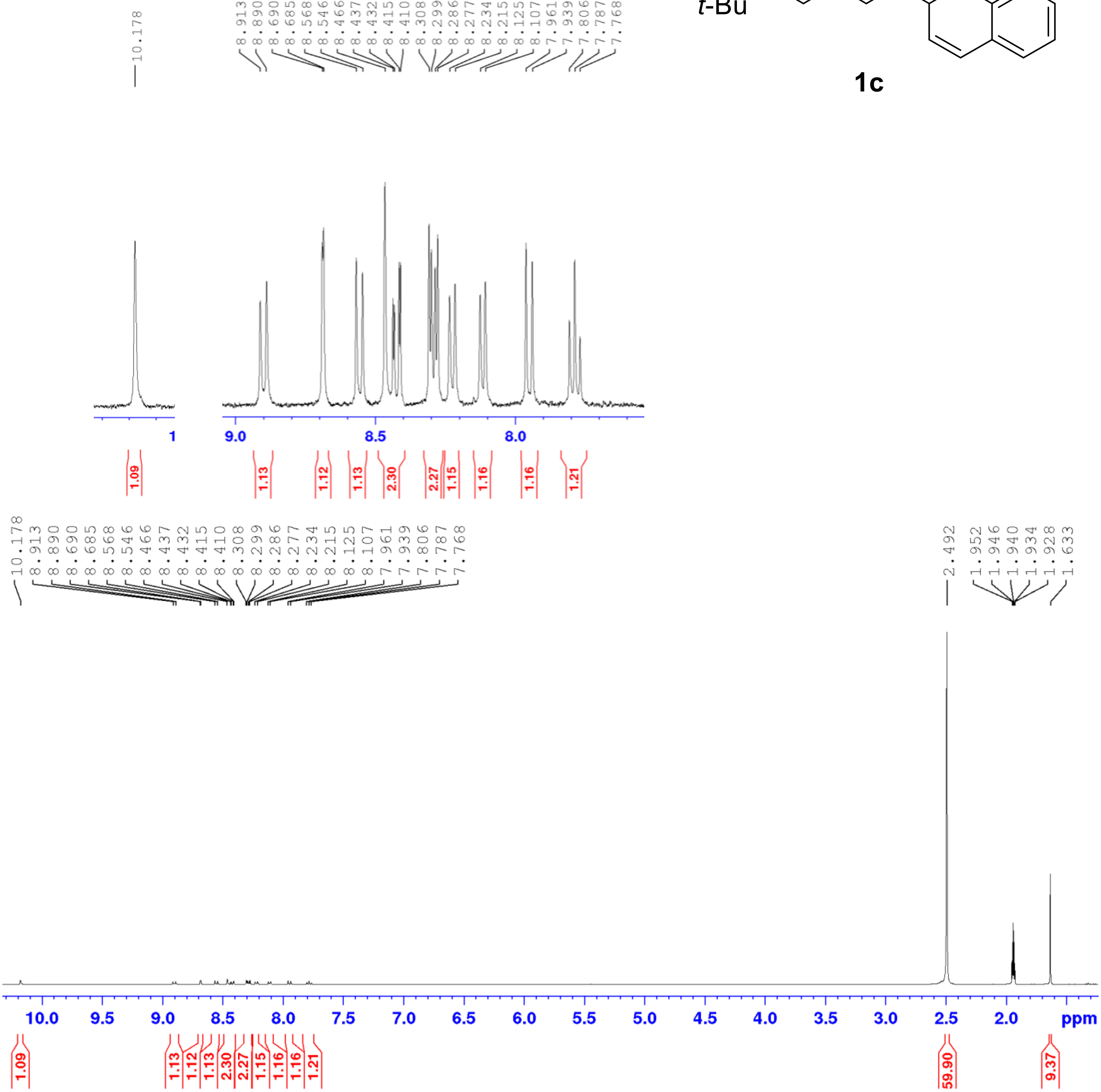
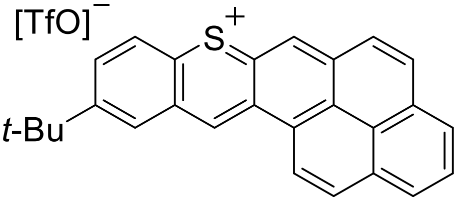


$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN, 298 K)



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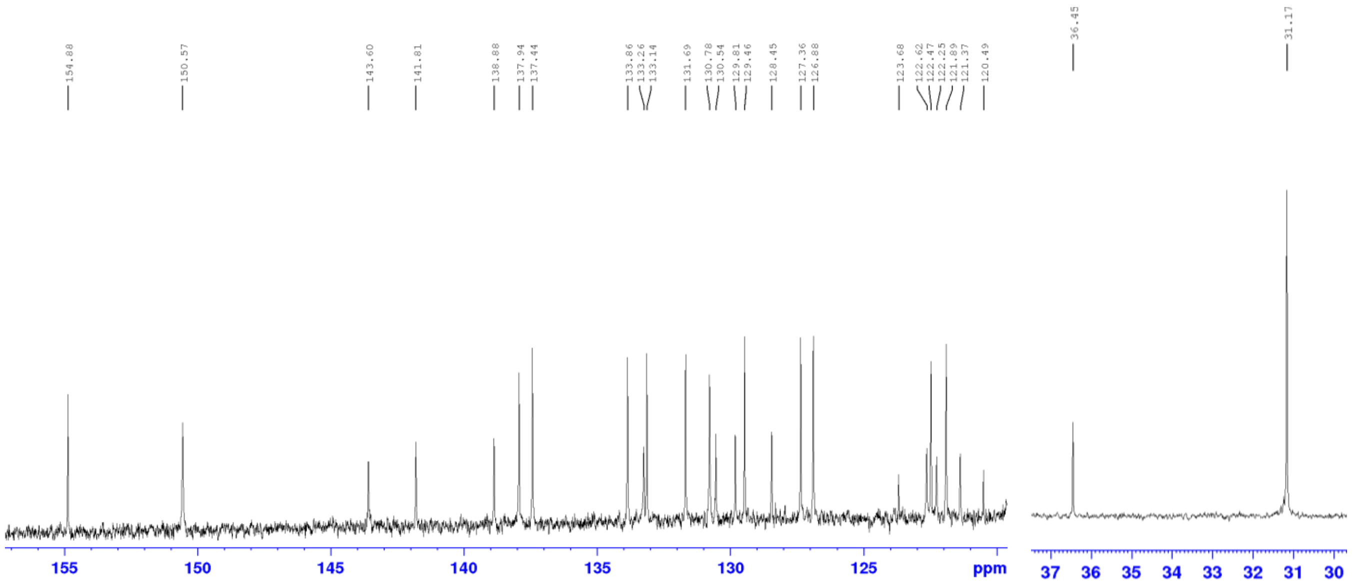
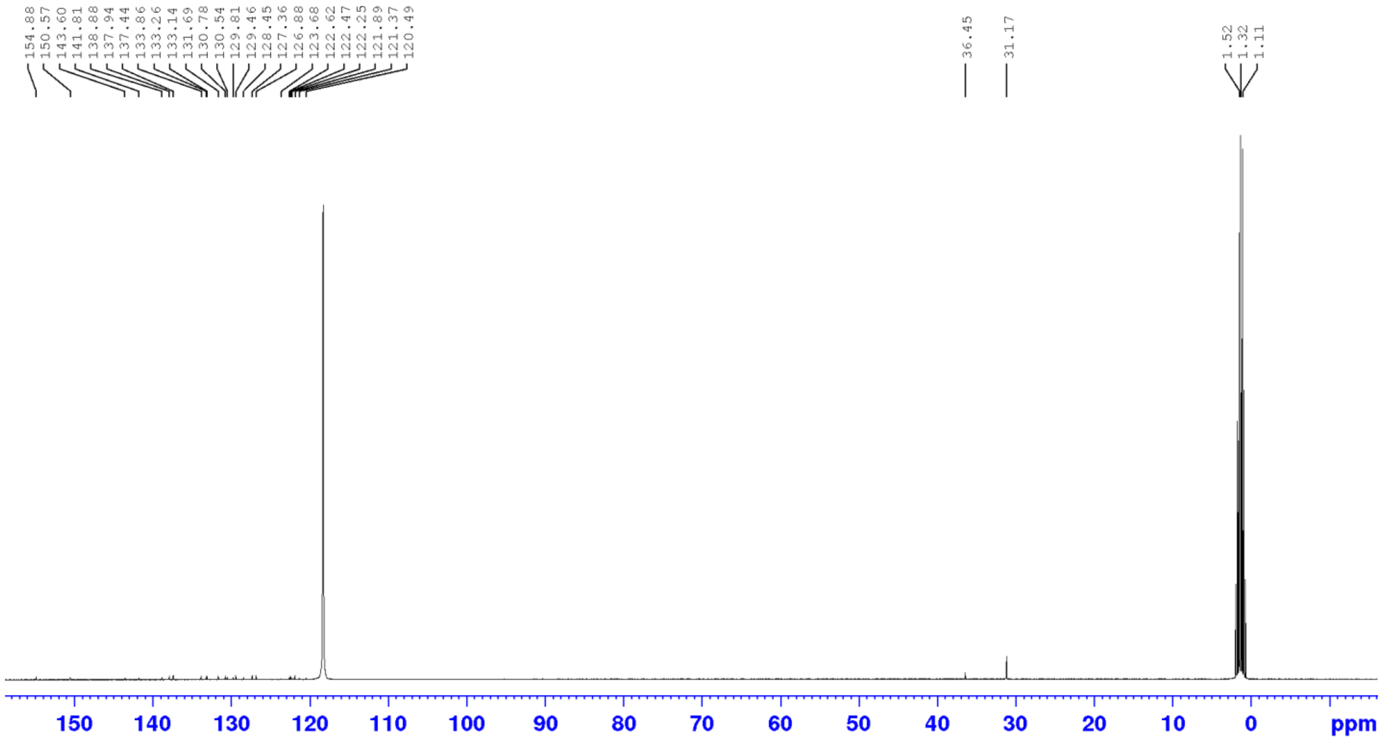
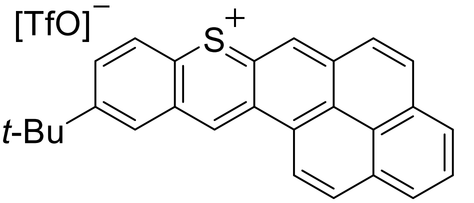




$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN, 298 K)



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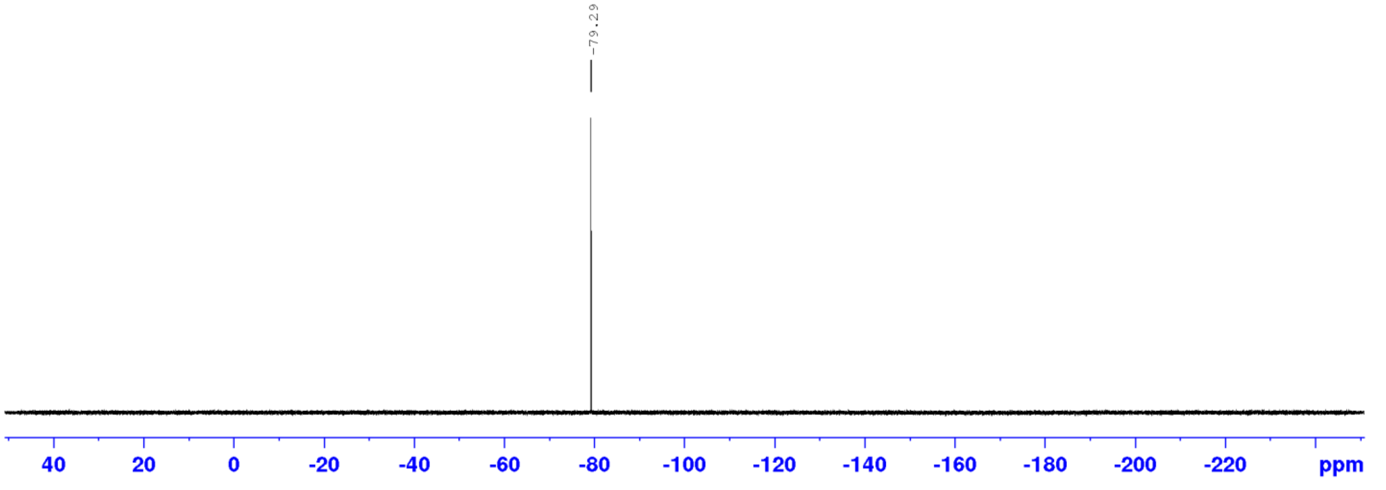
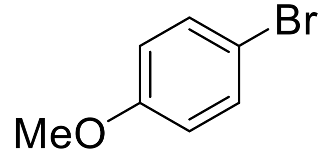


[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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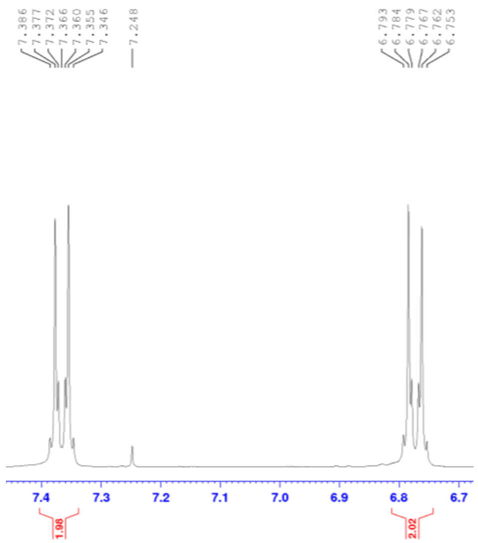
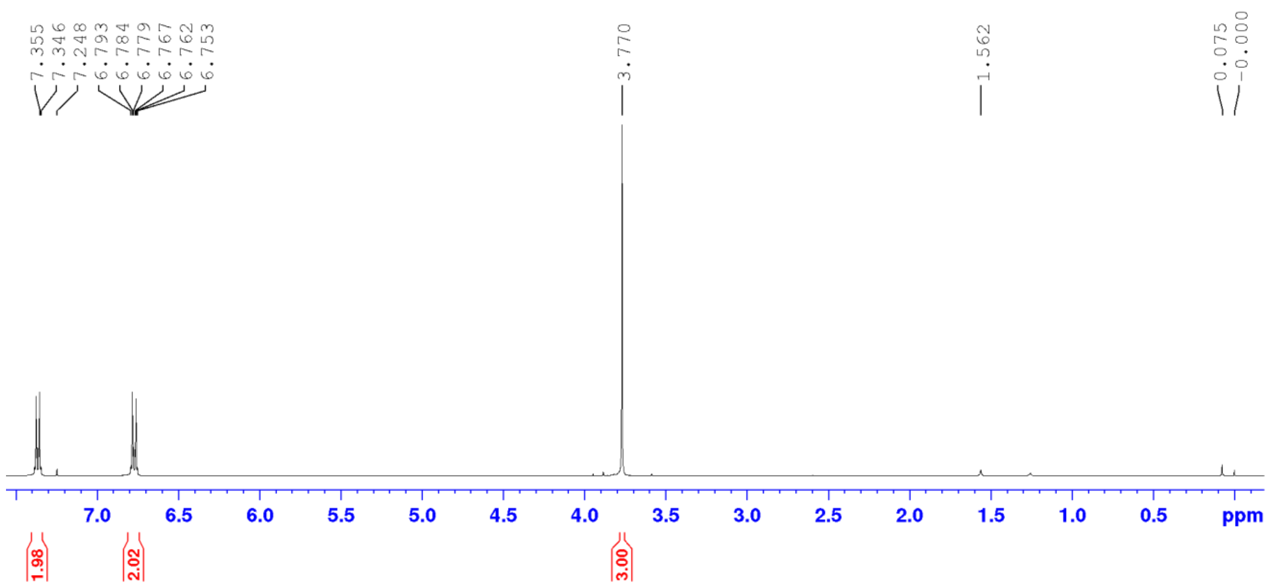
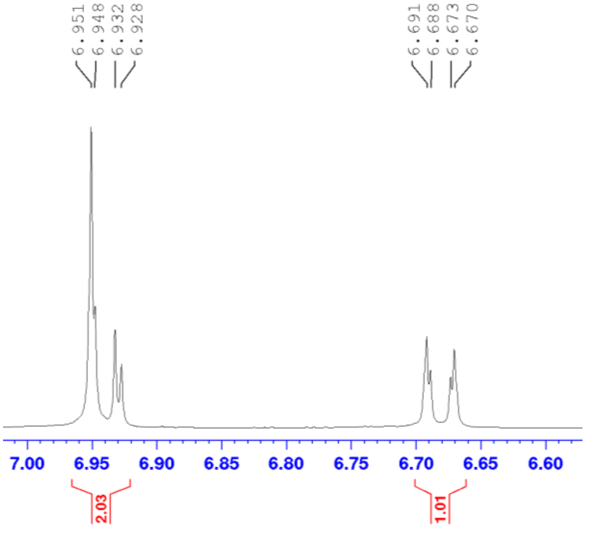
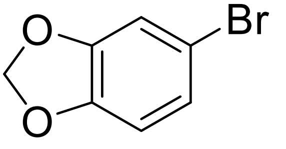




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)





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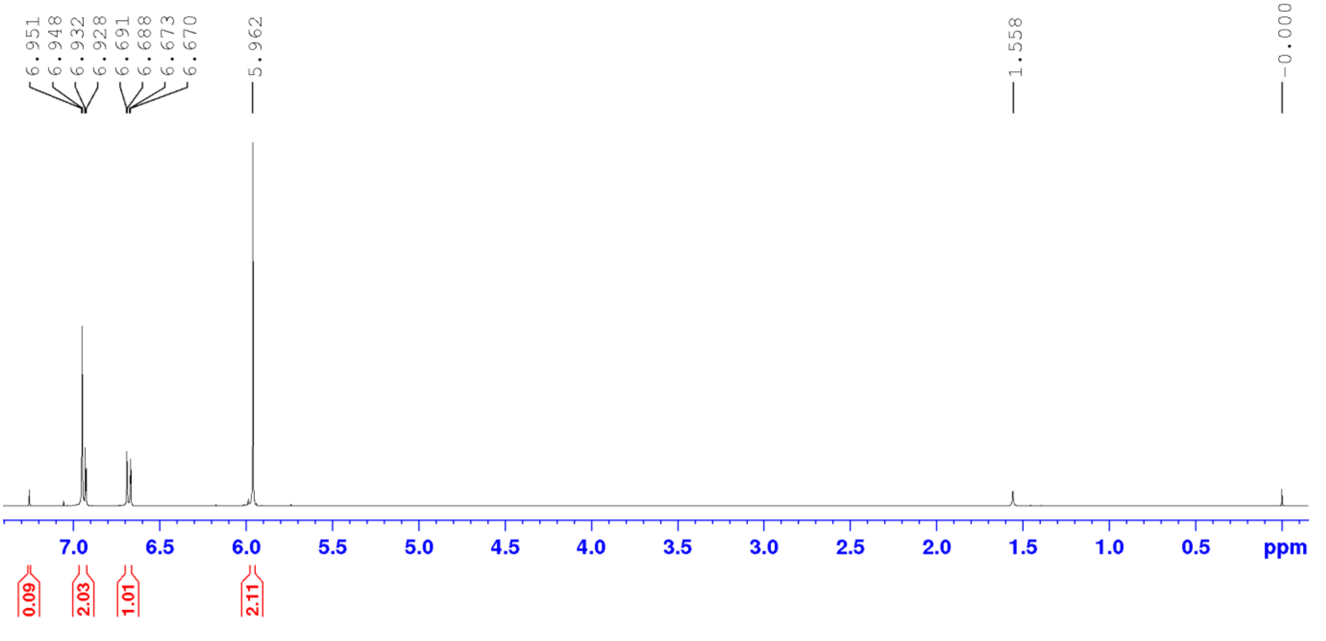
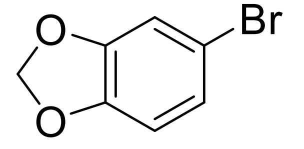


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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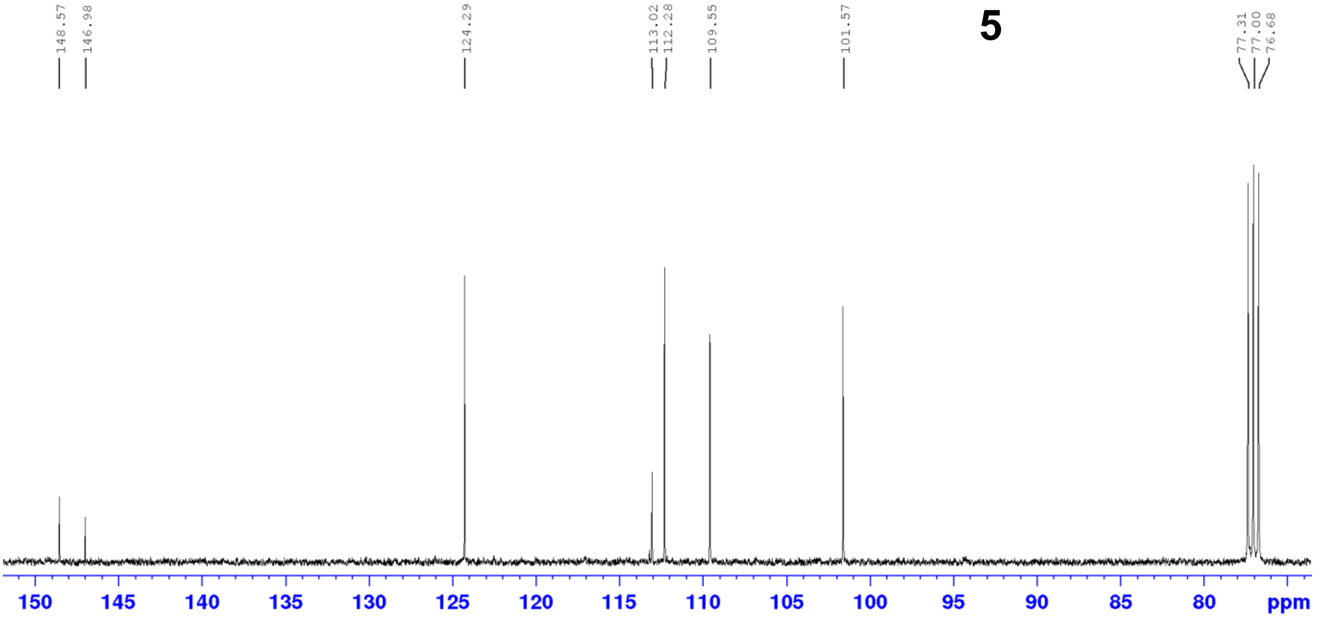
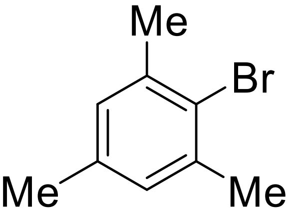


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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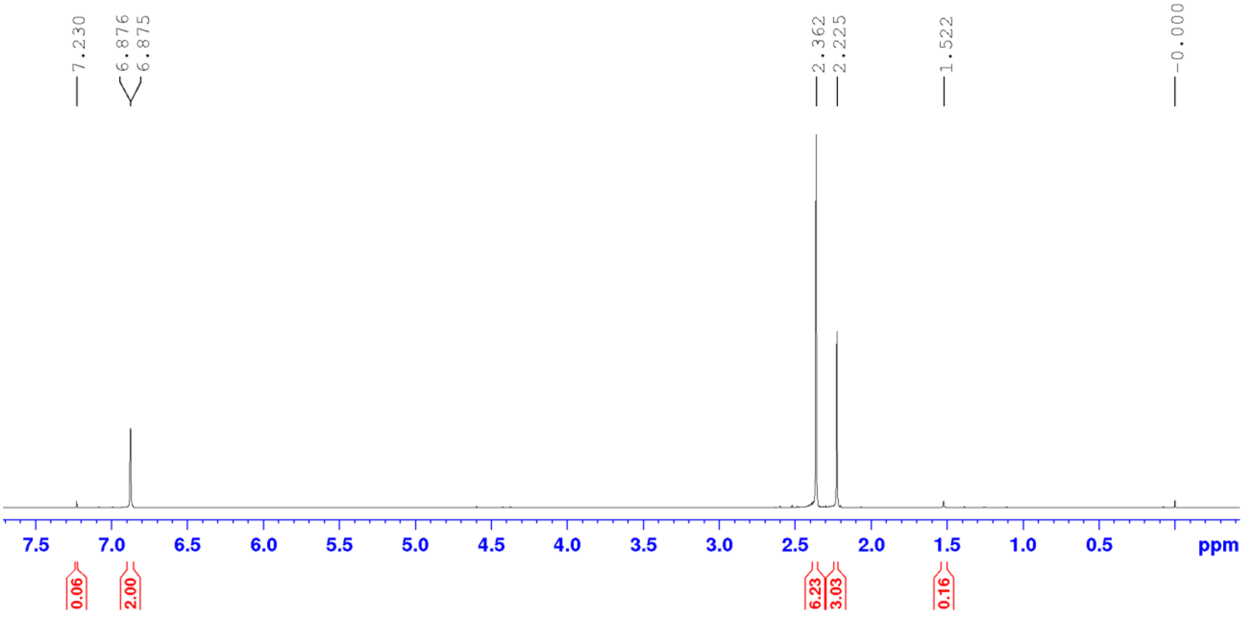
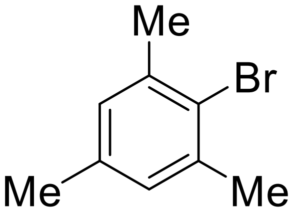


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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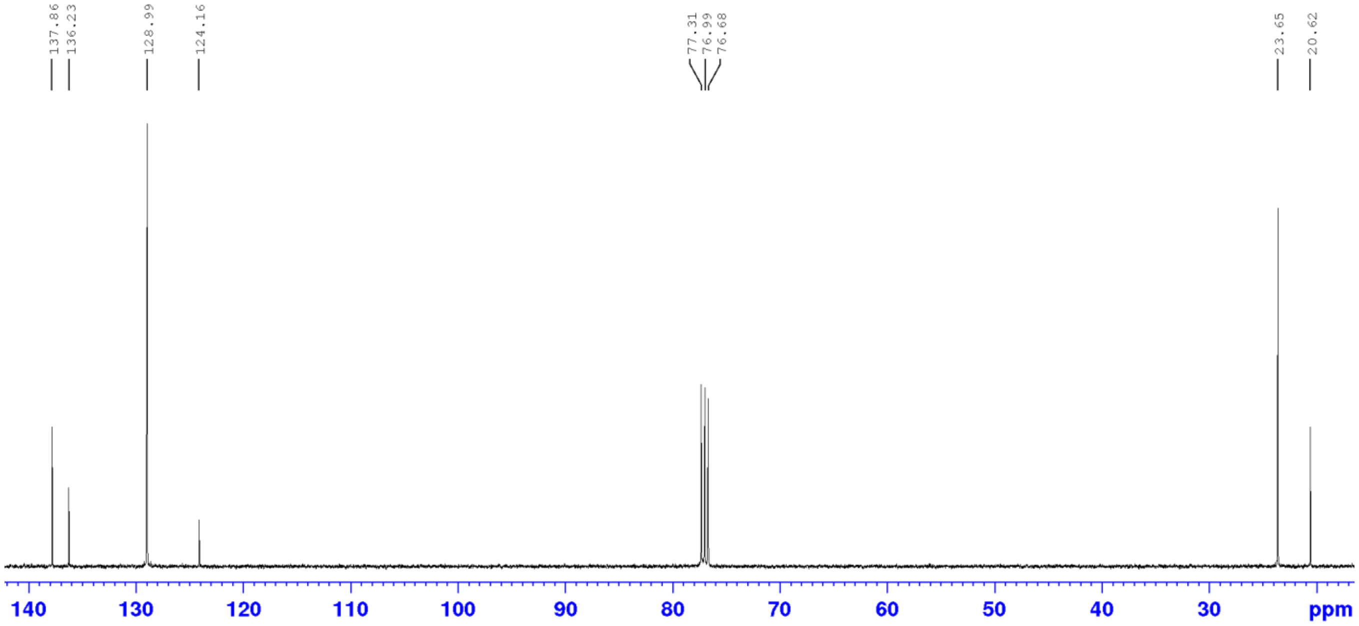
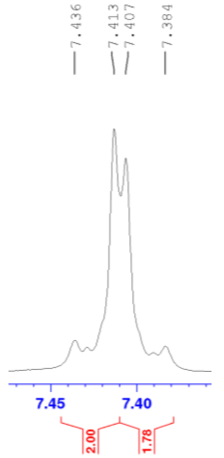
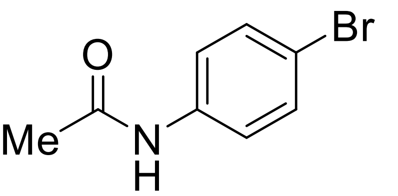


^1H NMR (400 MHz, $CDCl_3$, 298 K)





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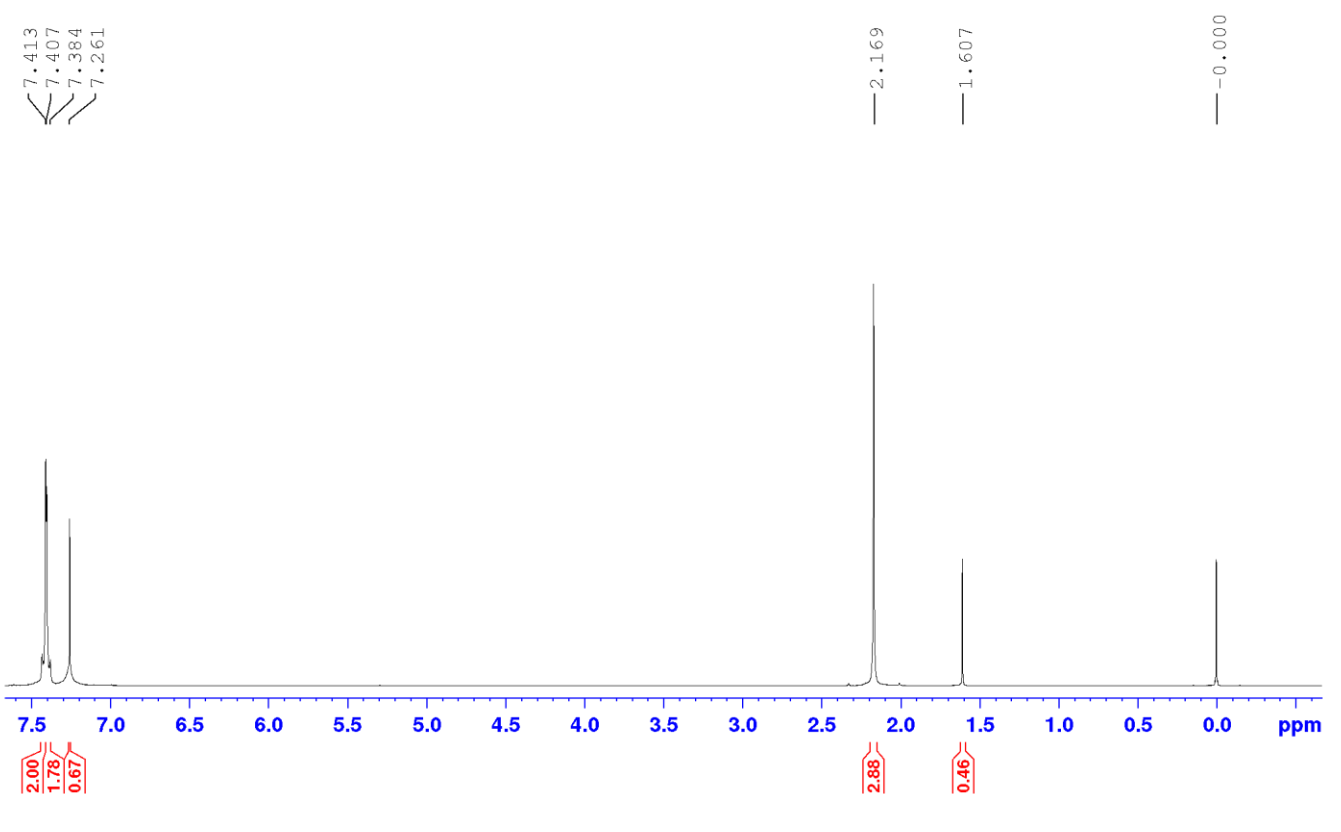
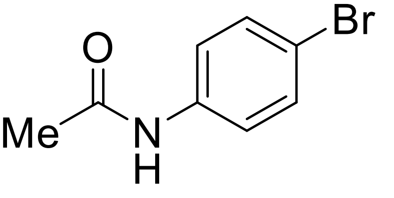


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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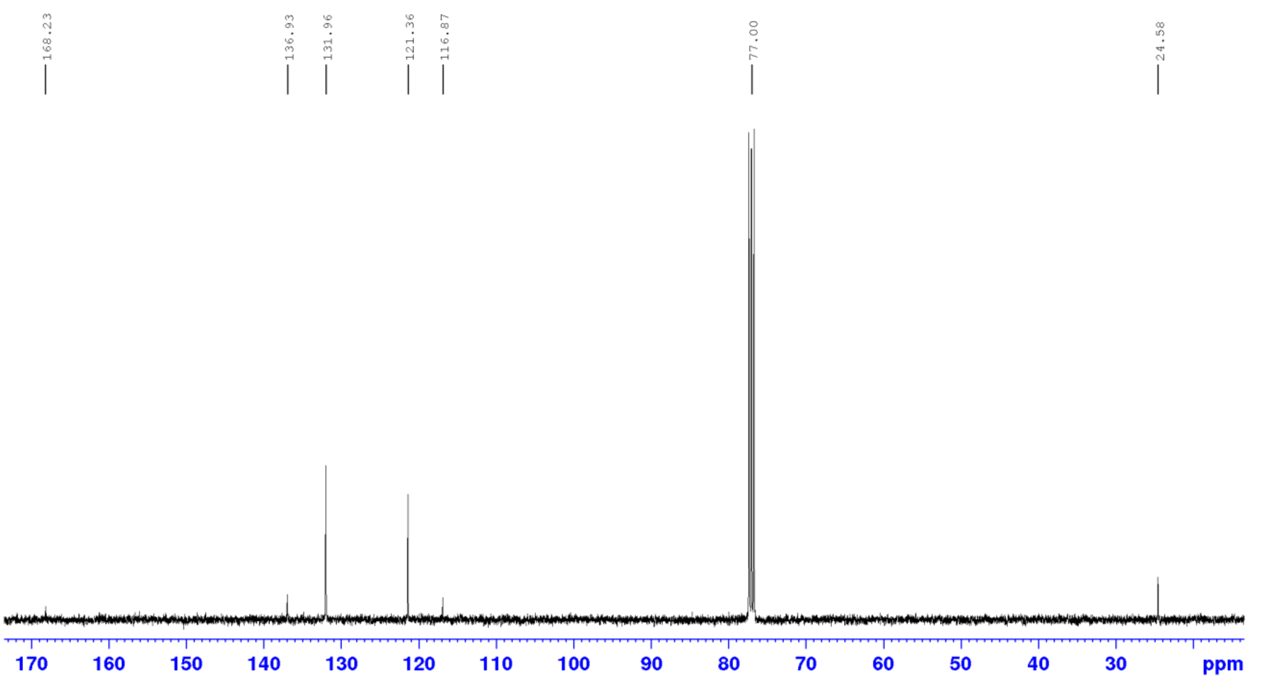
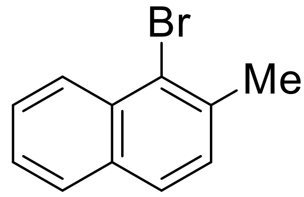


[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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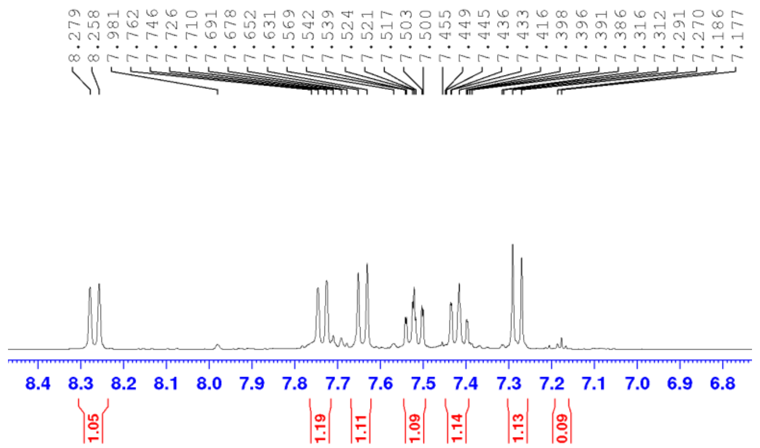
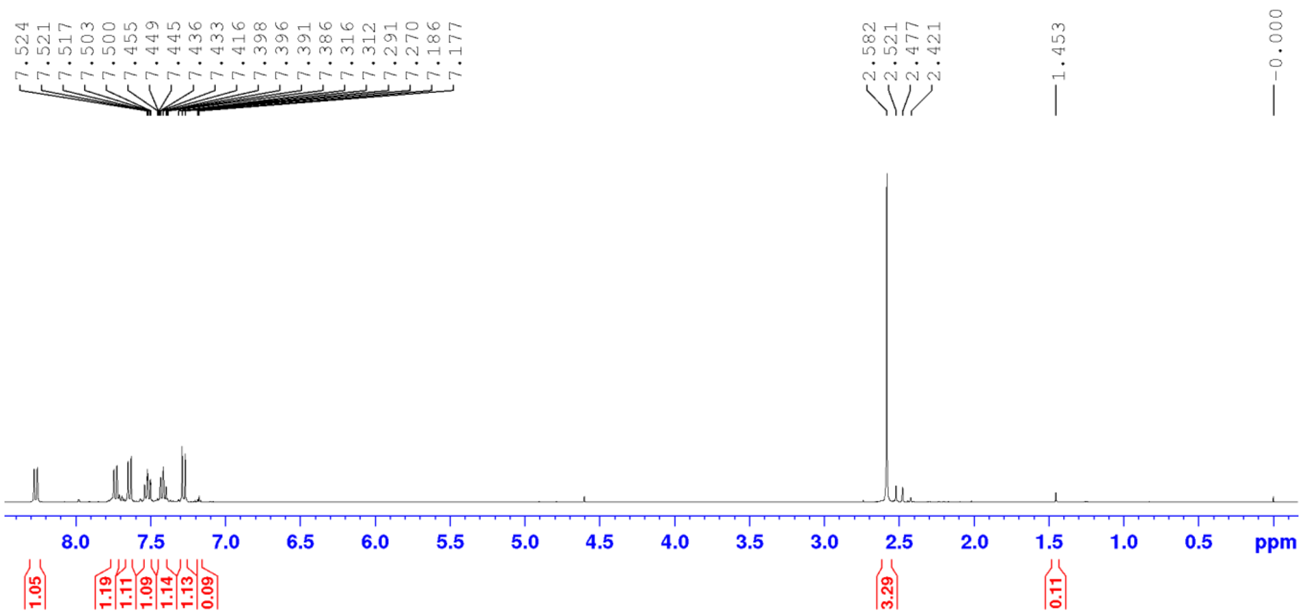
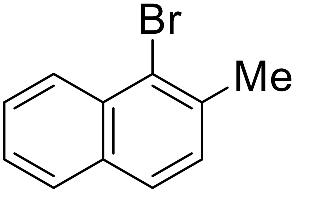




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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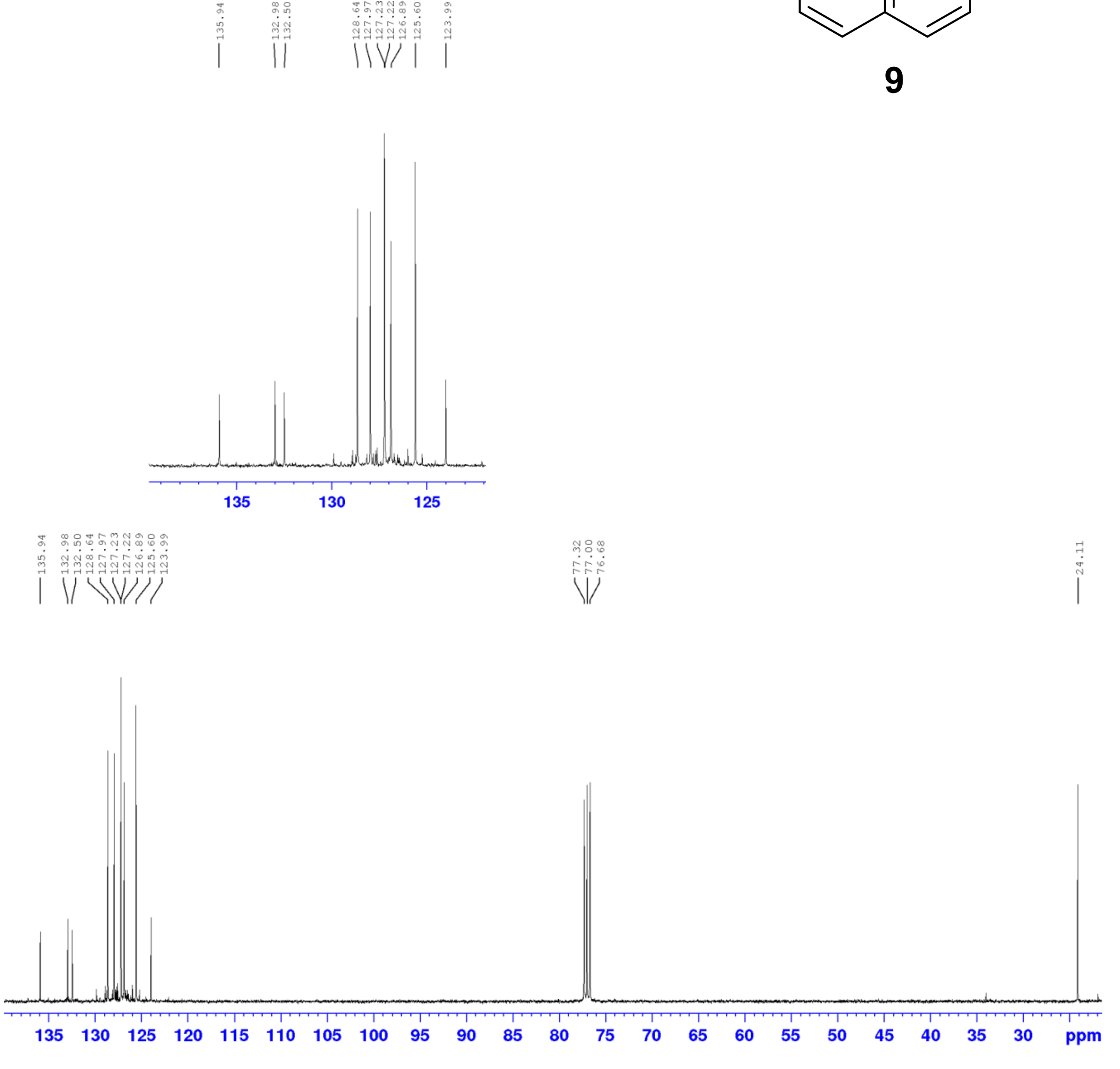
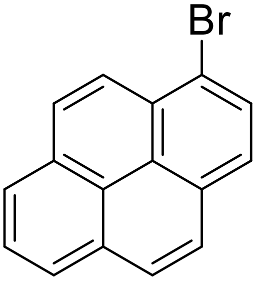


[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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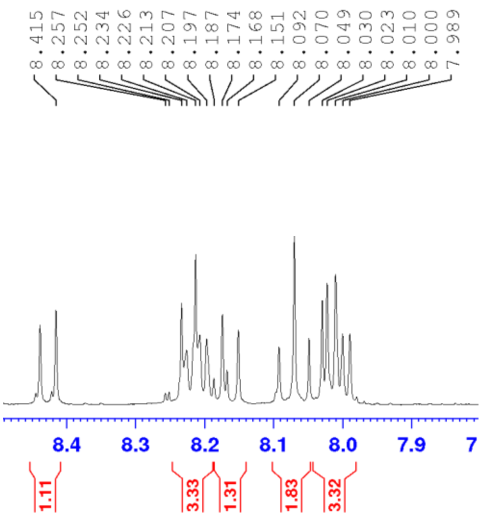
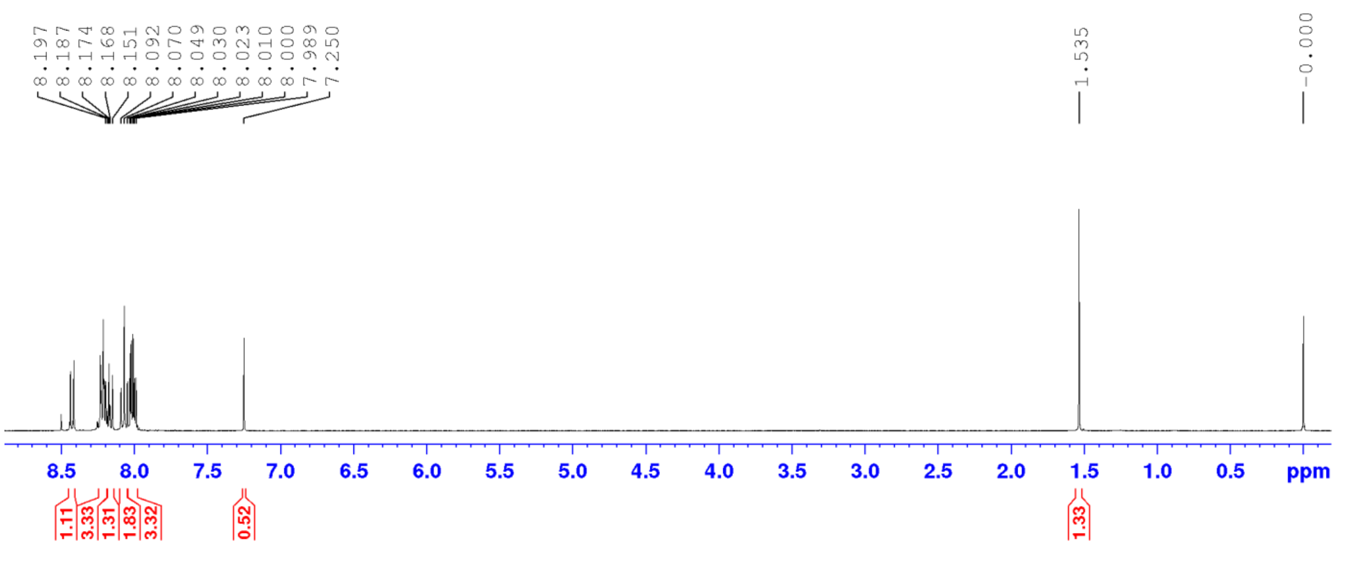
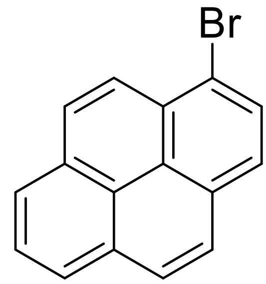




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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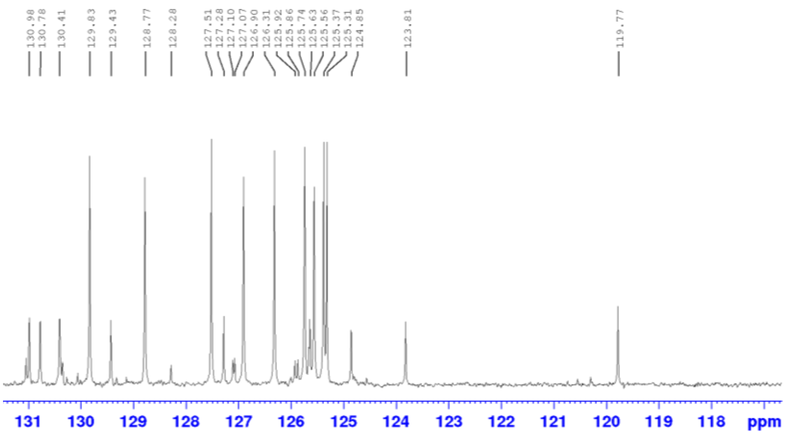
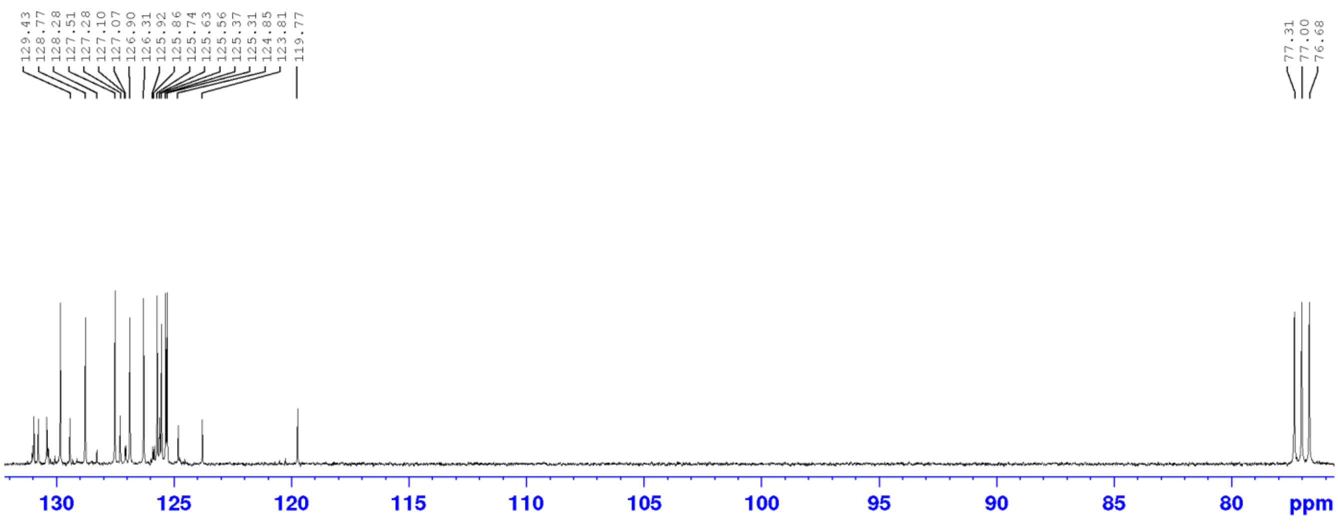
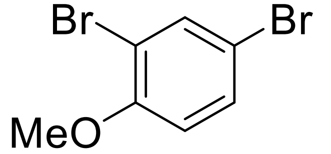




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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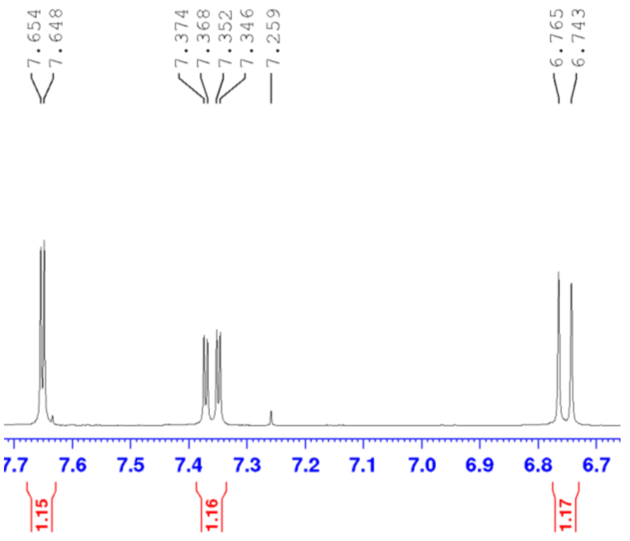
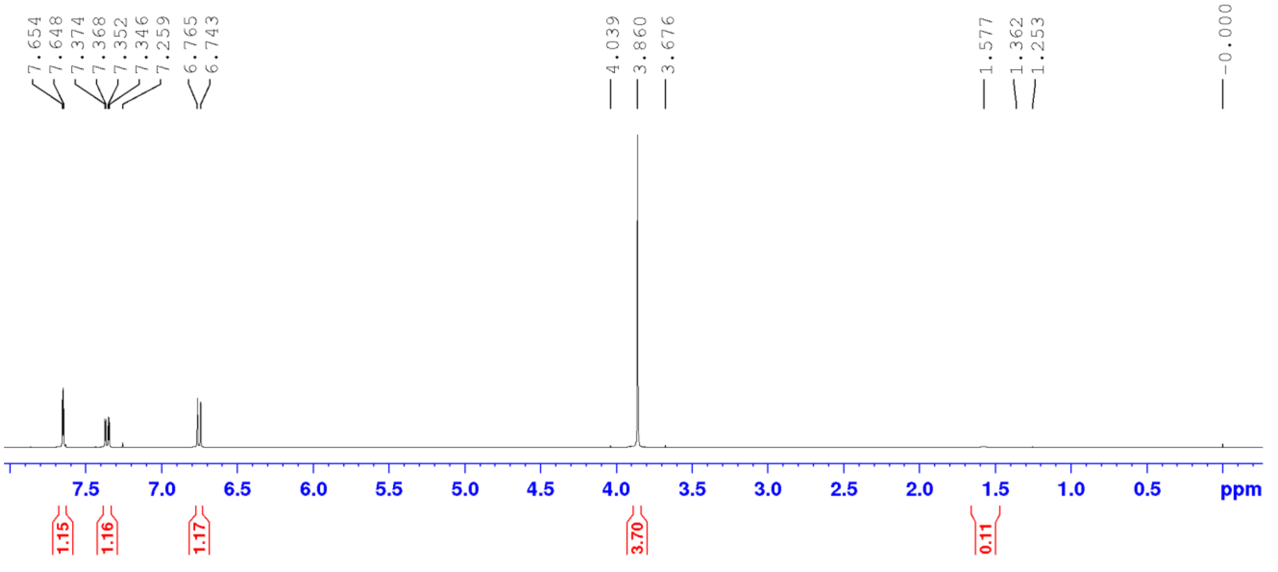
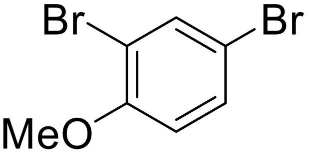




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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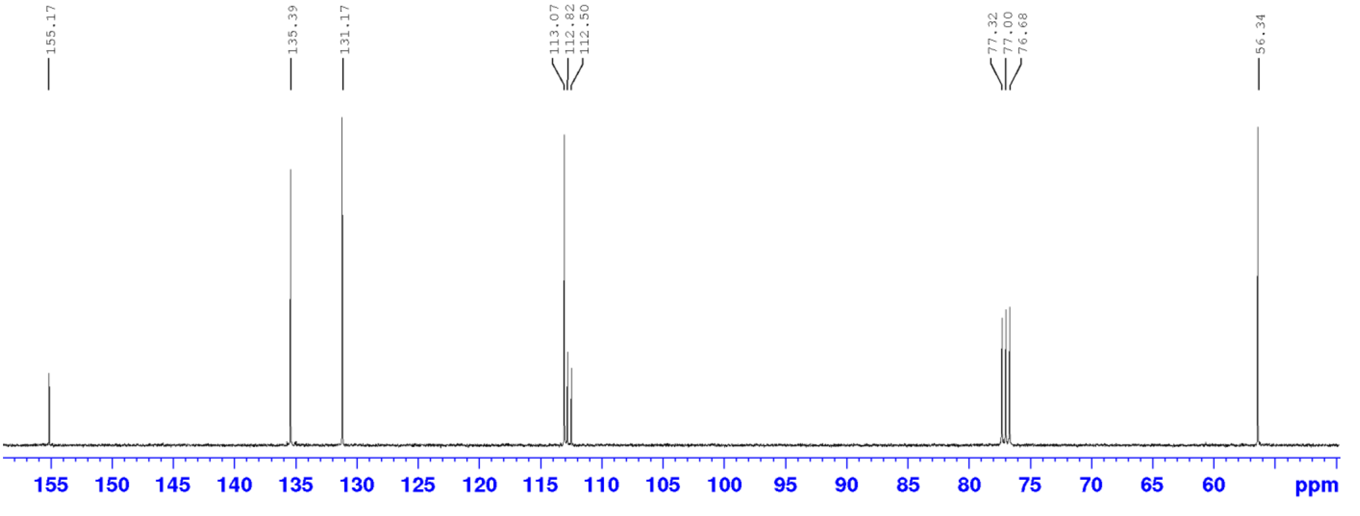
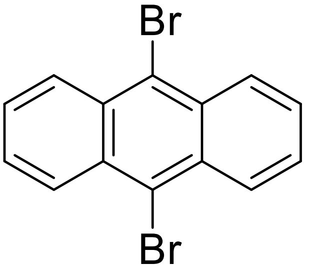


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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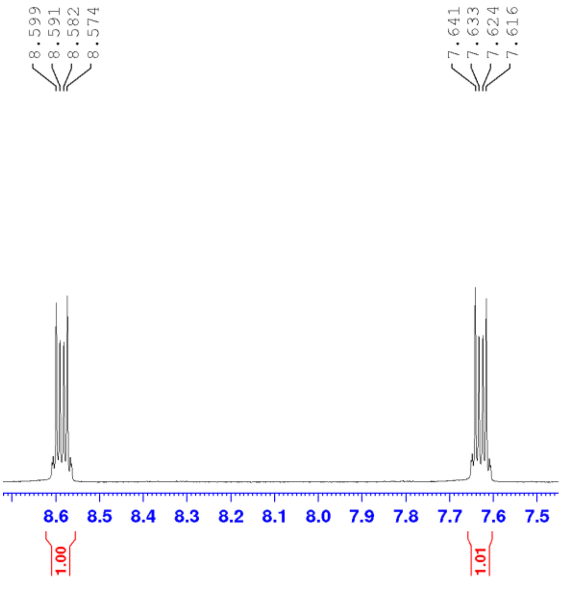
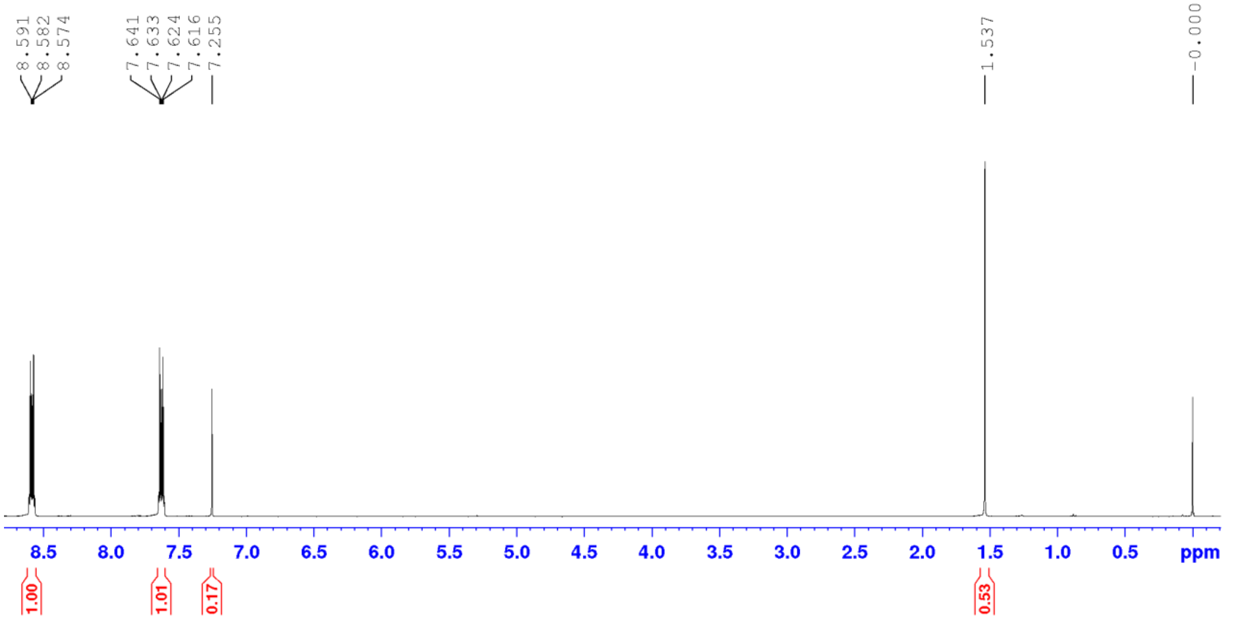
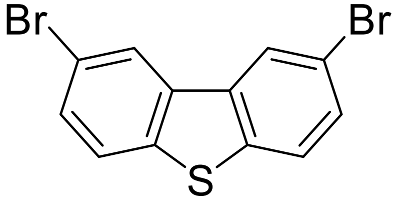




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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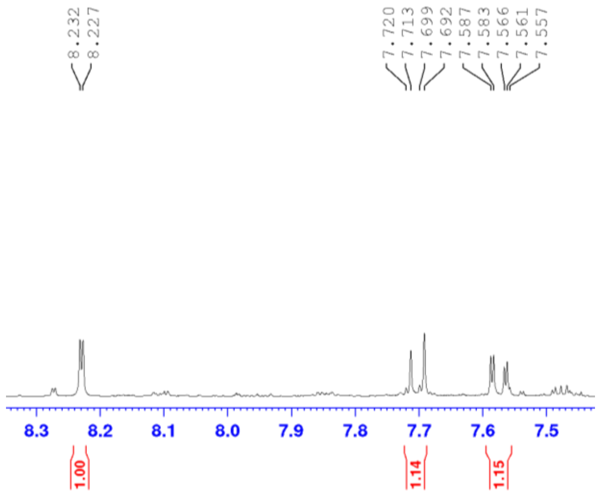
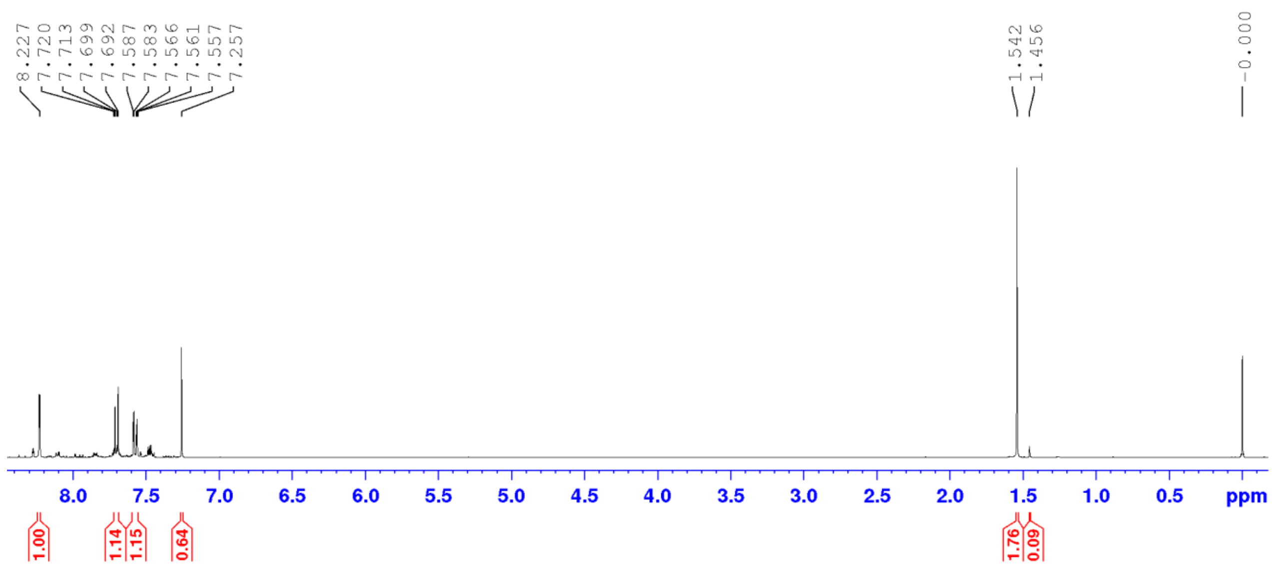
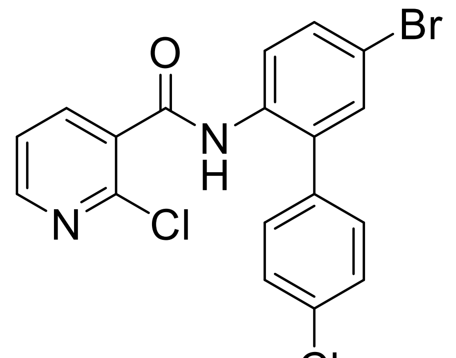




[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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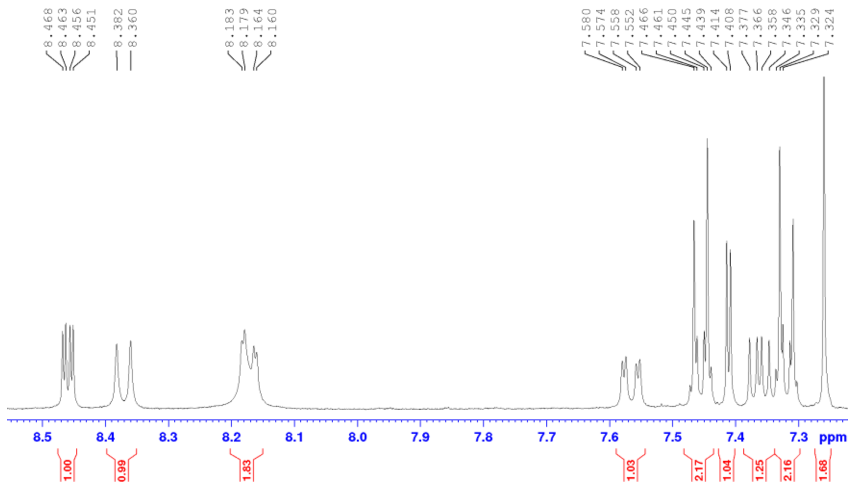
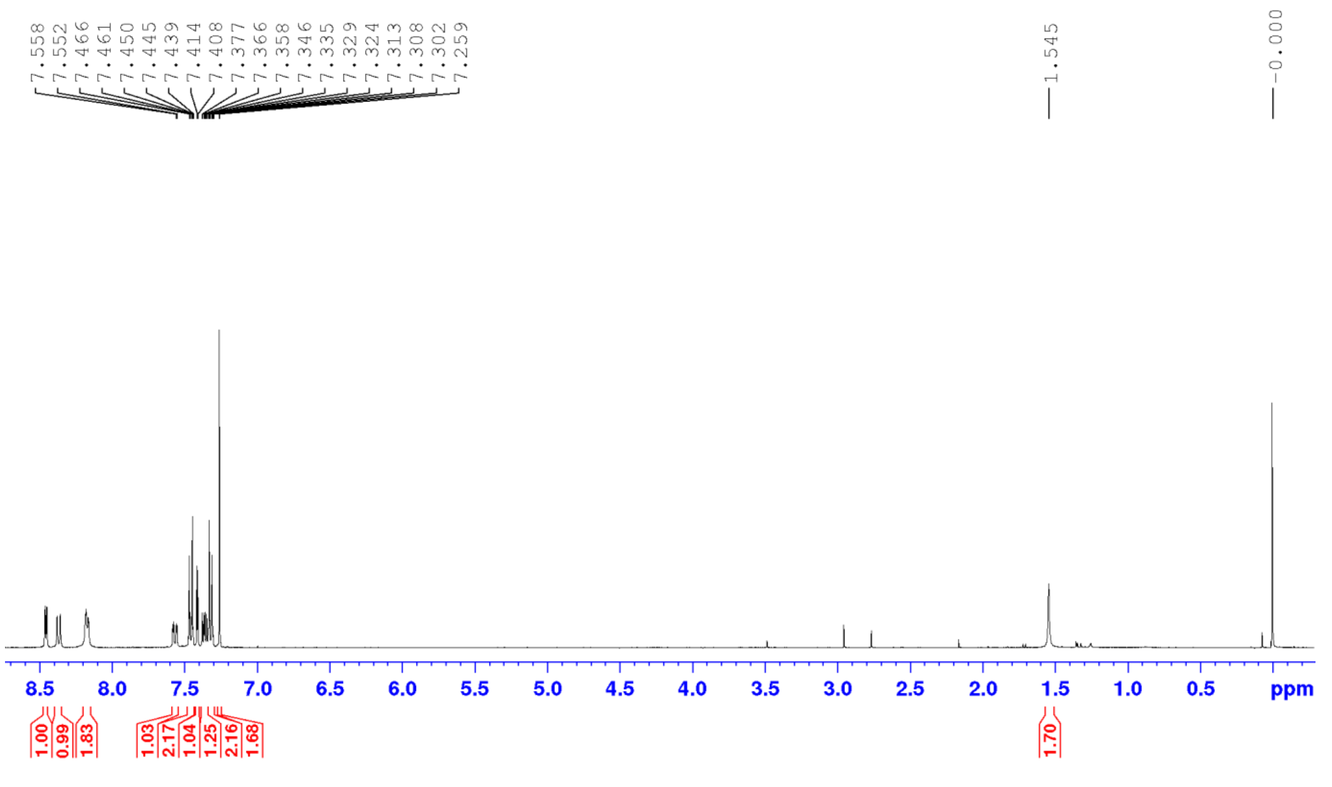
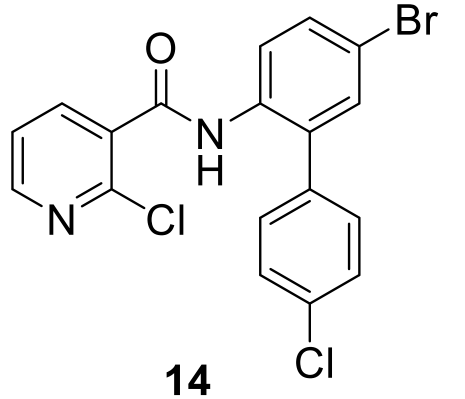




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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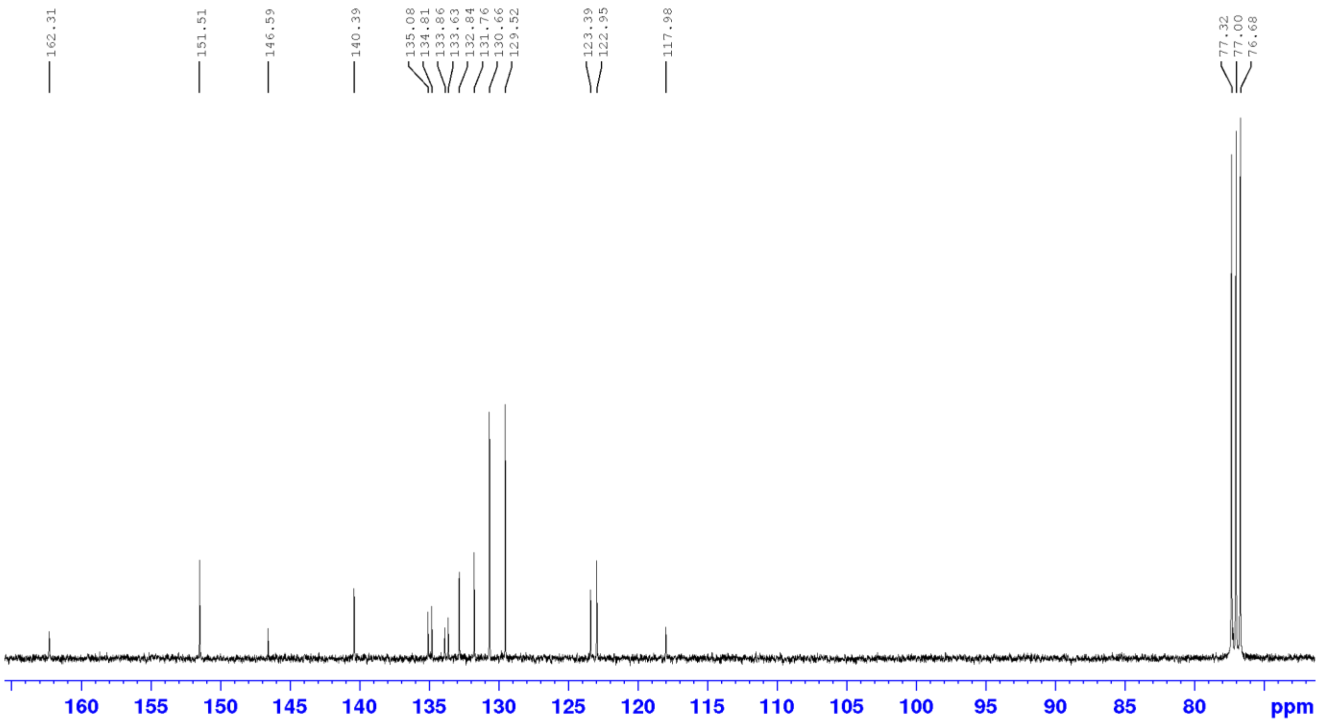

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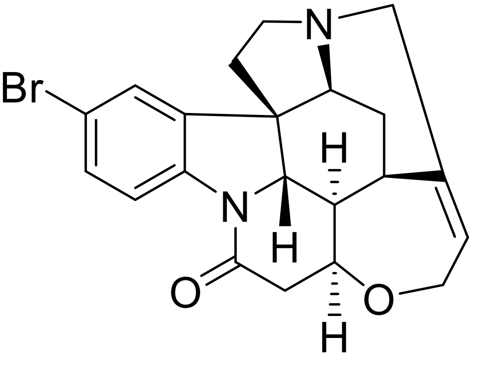

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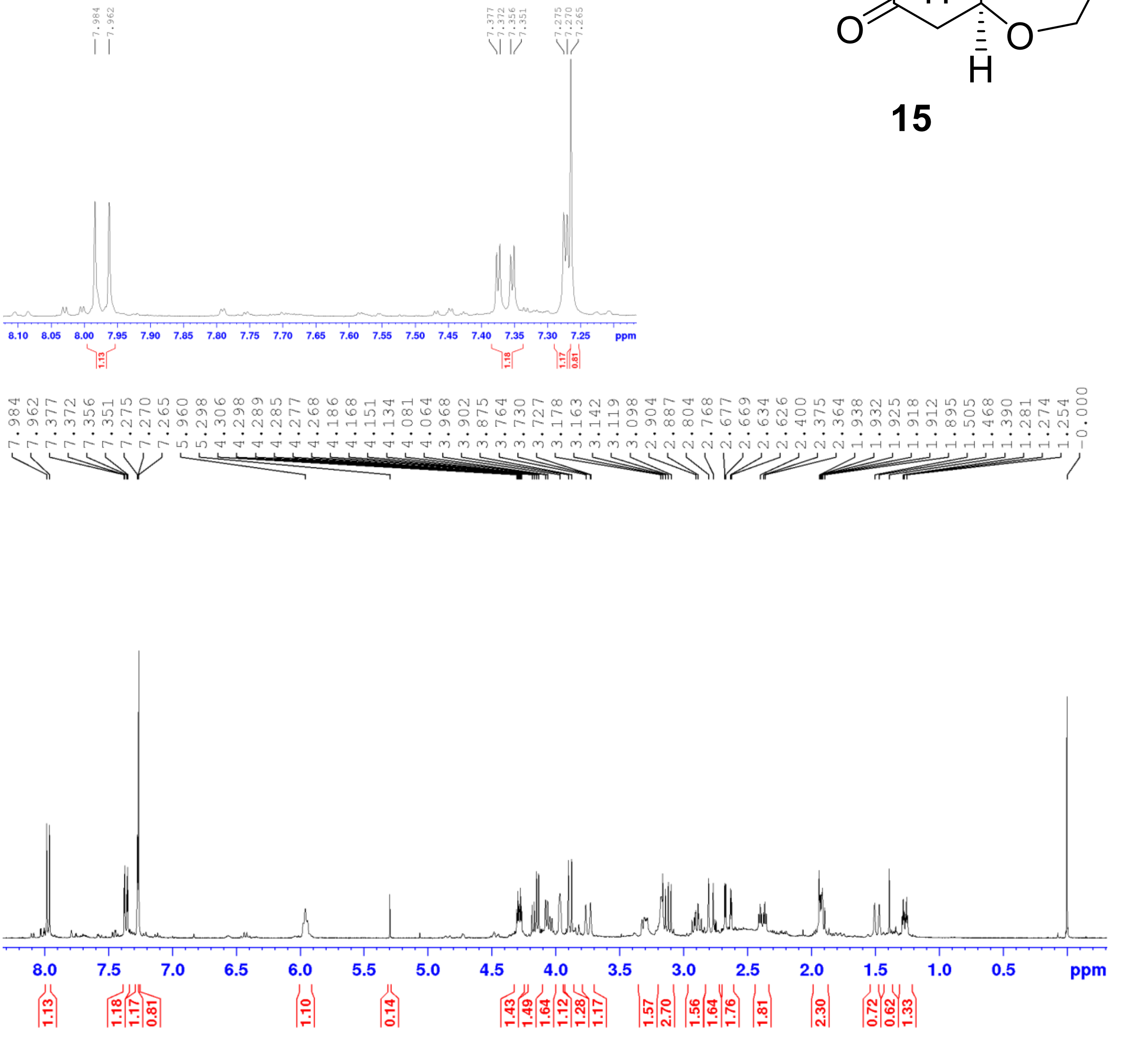
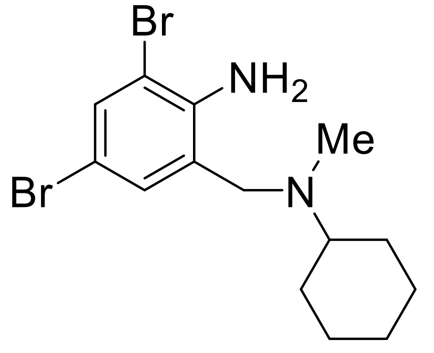


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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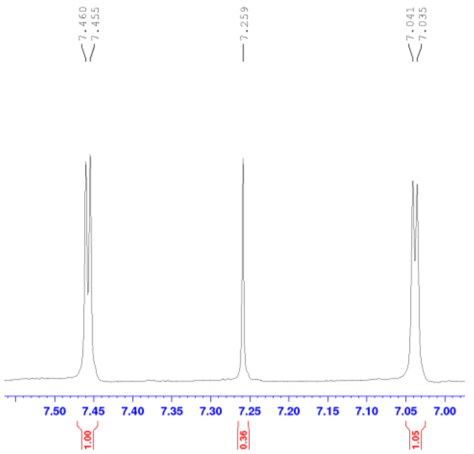
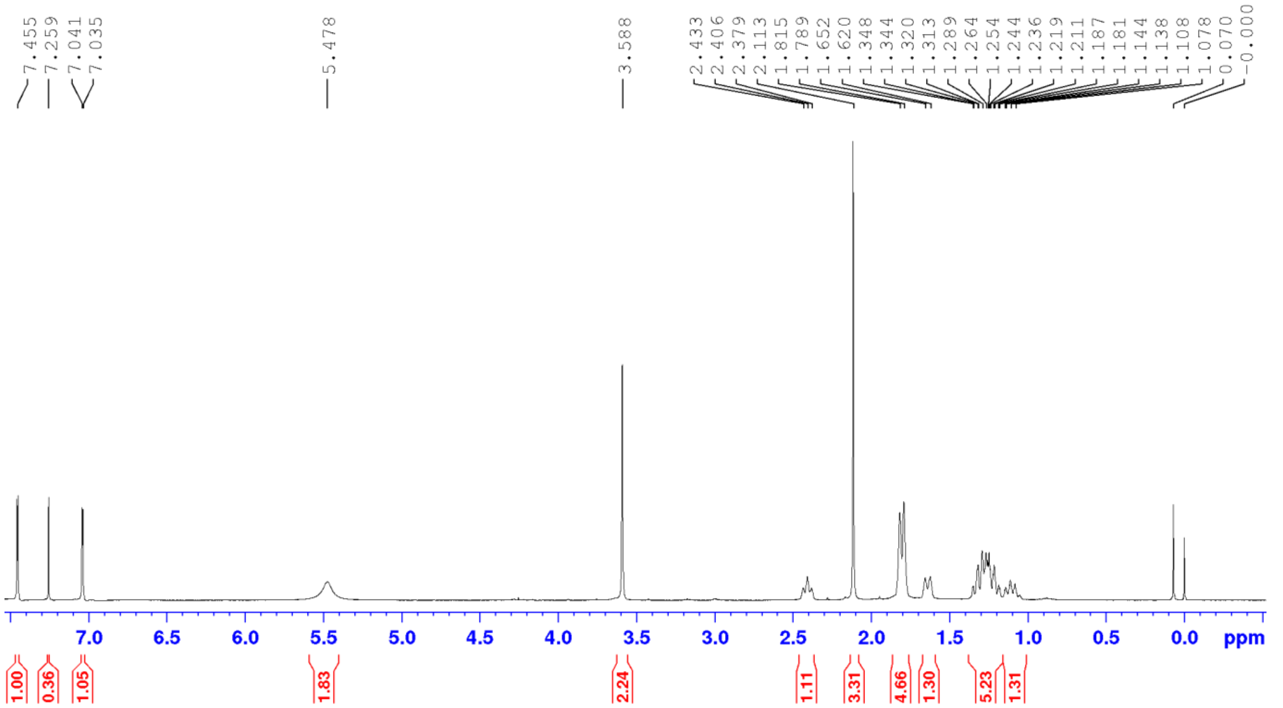
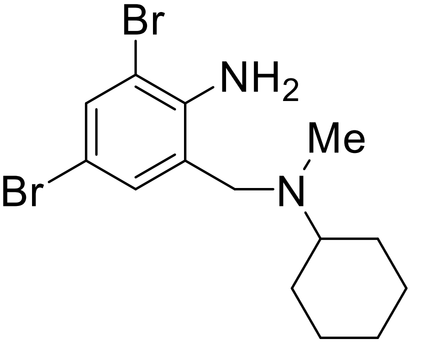




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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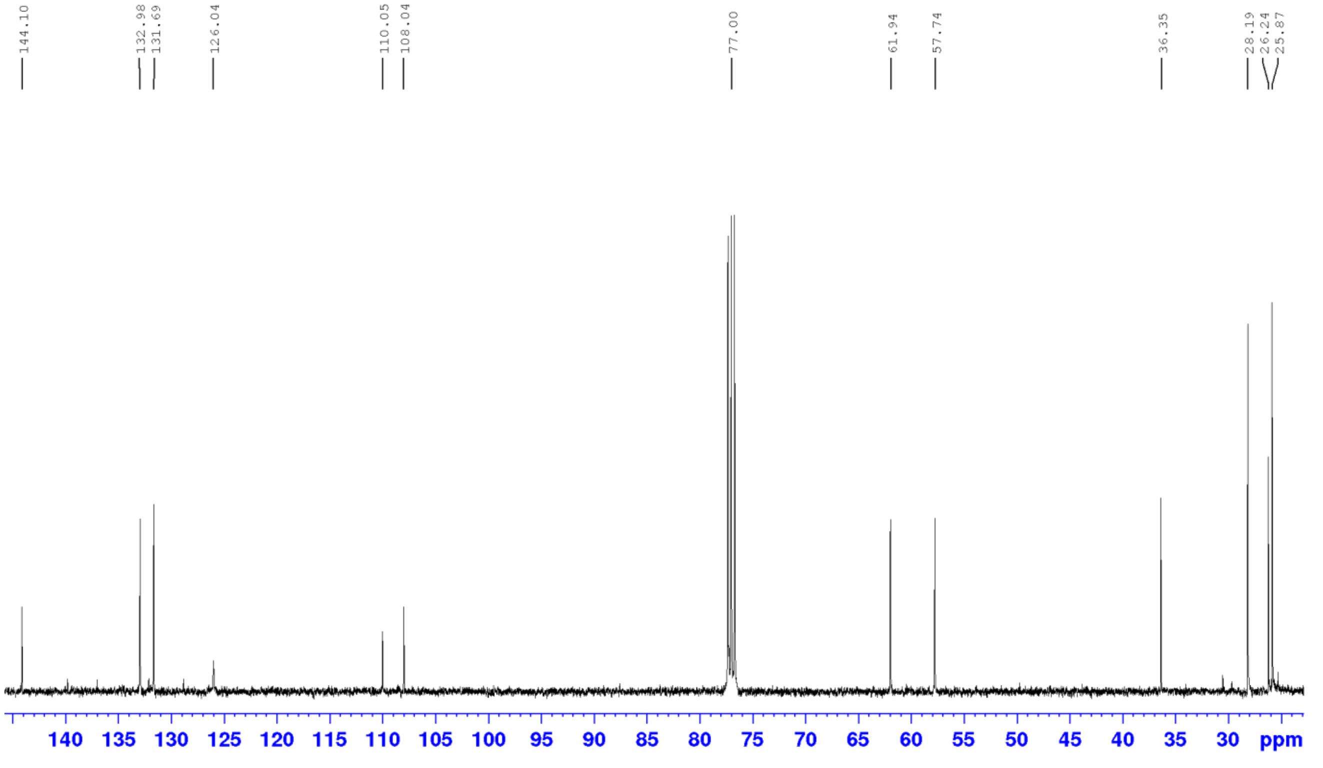
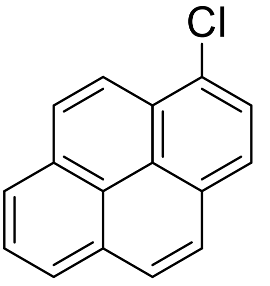


^1H NMR (400 MHz, $CDCl_3$, 298 K)



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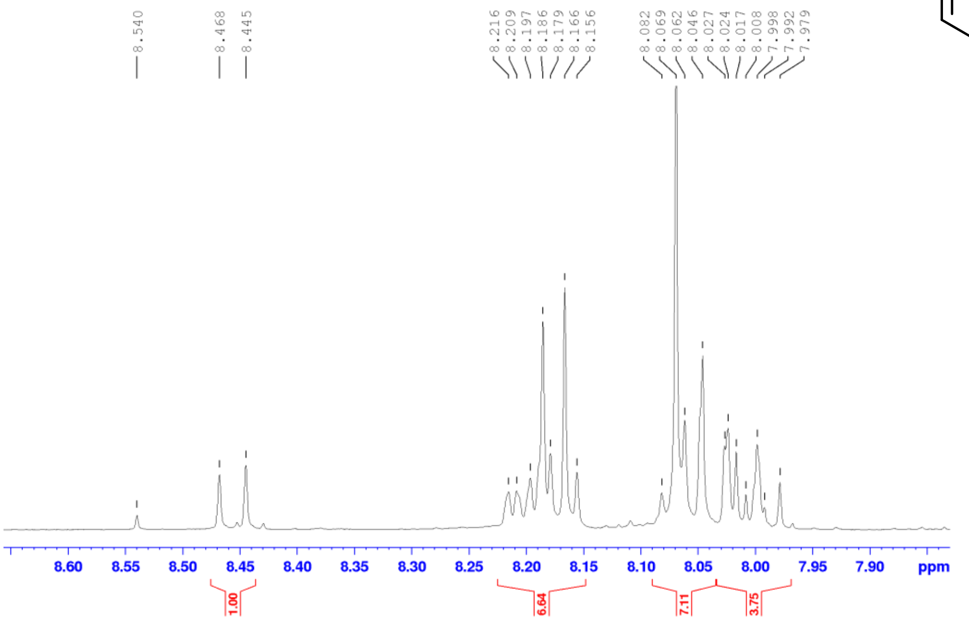
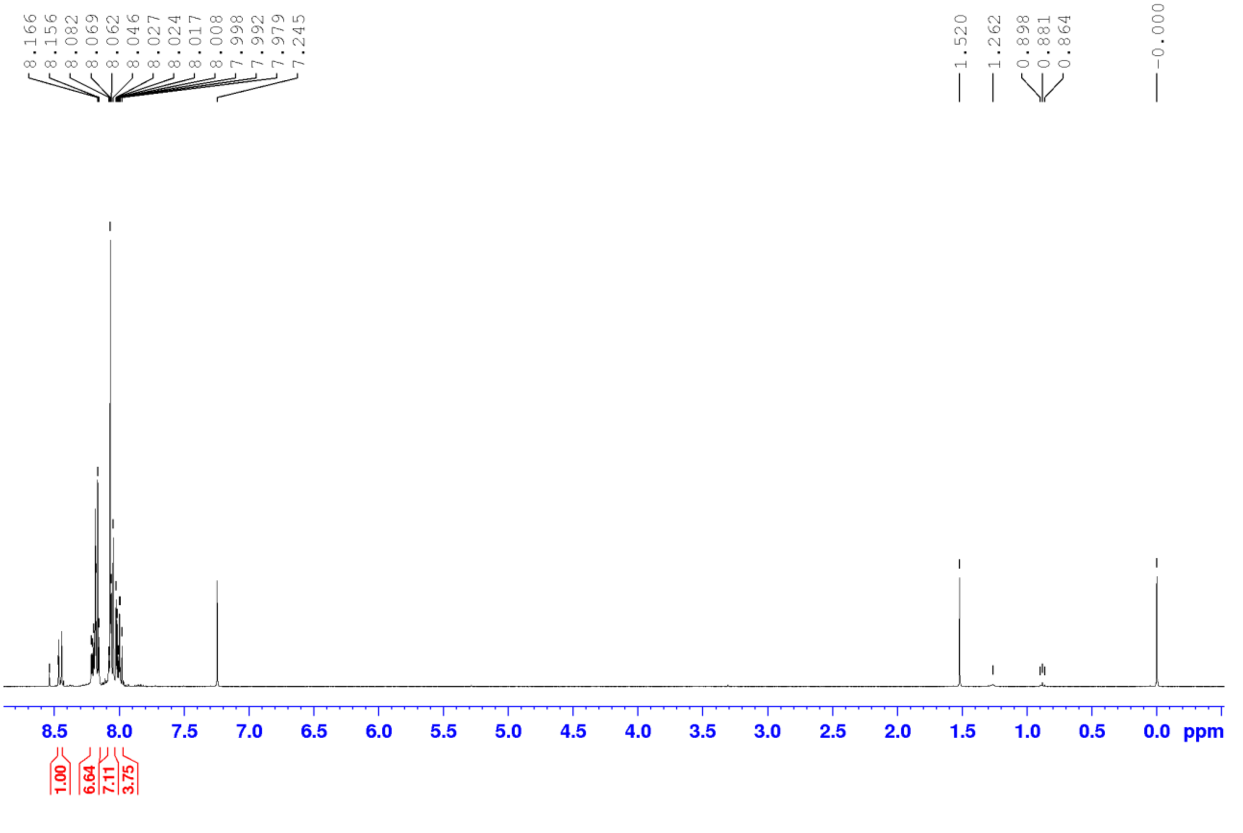
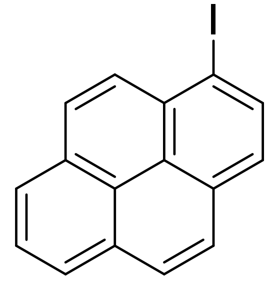




[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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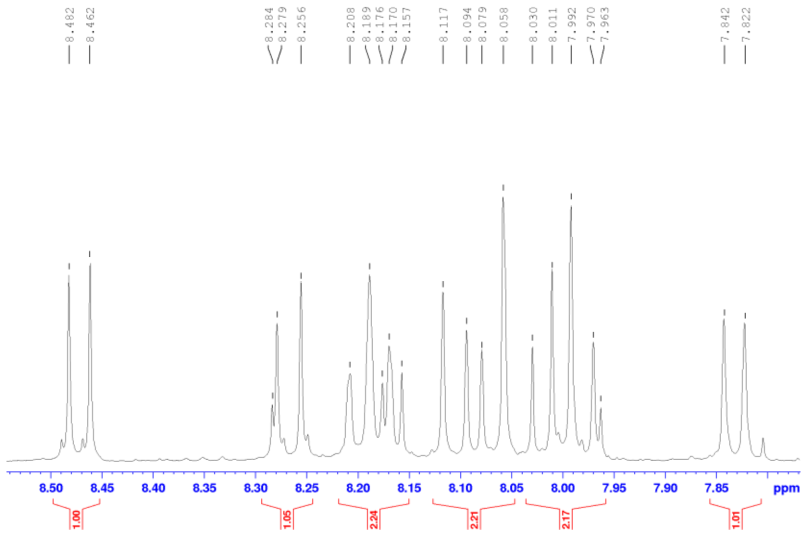
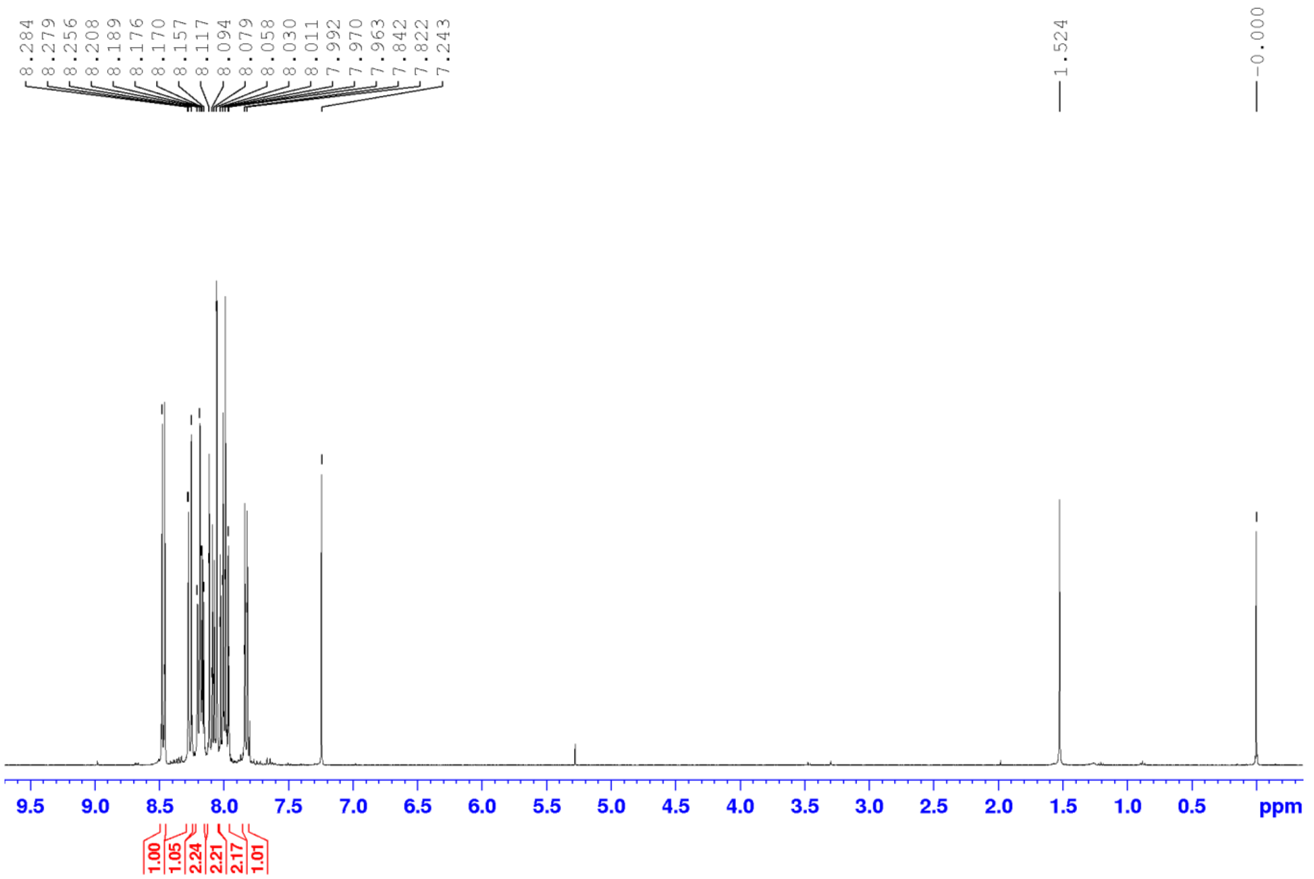
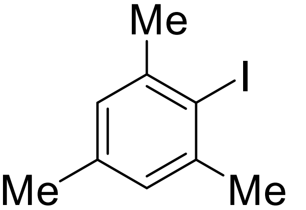




^1H NMR (400 MHz, $CDCl_3$, 298 K)



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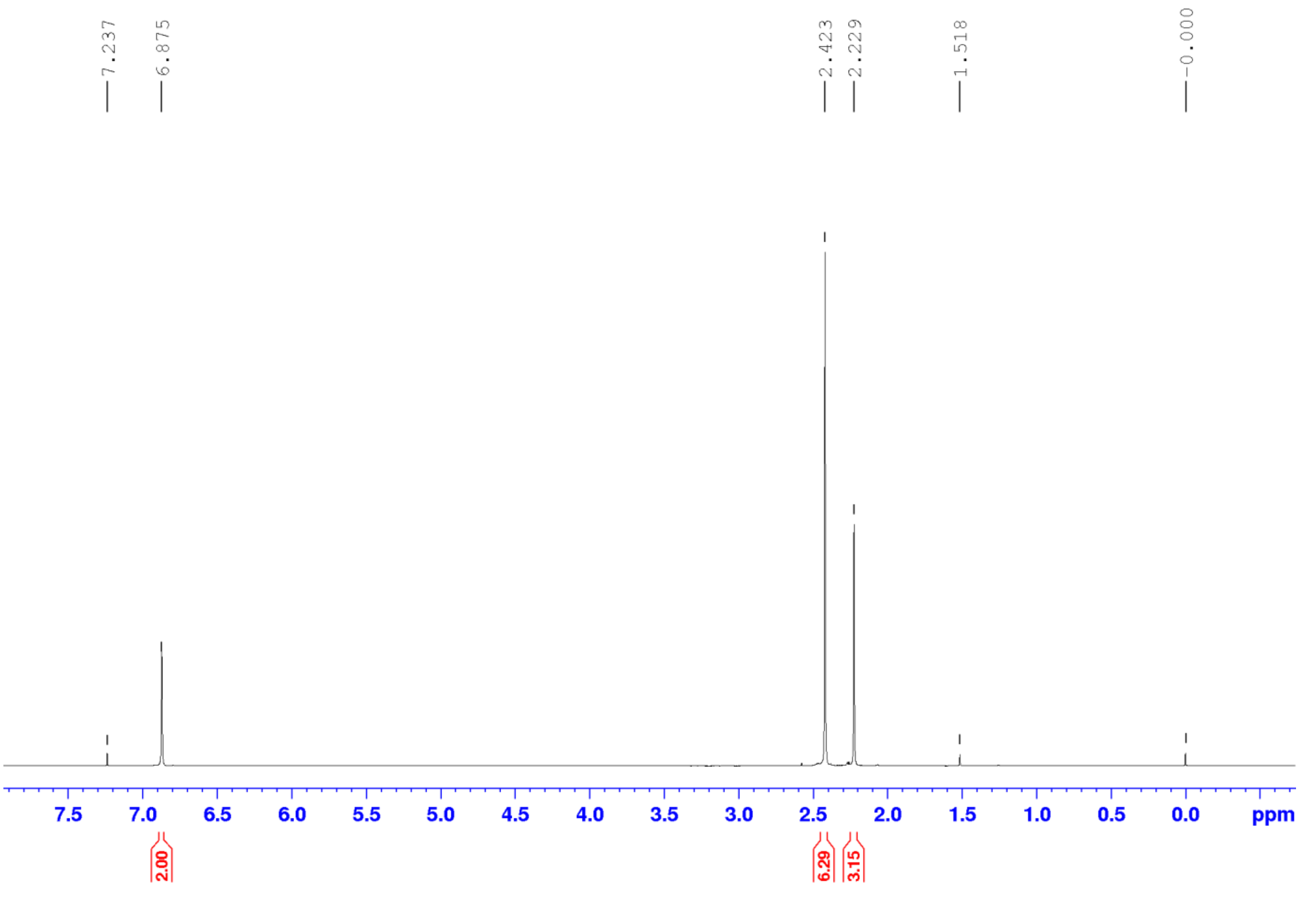
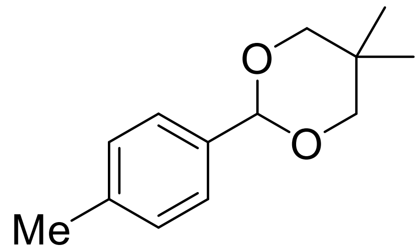


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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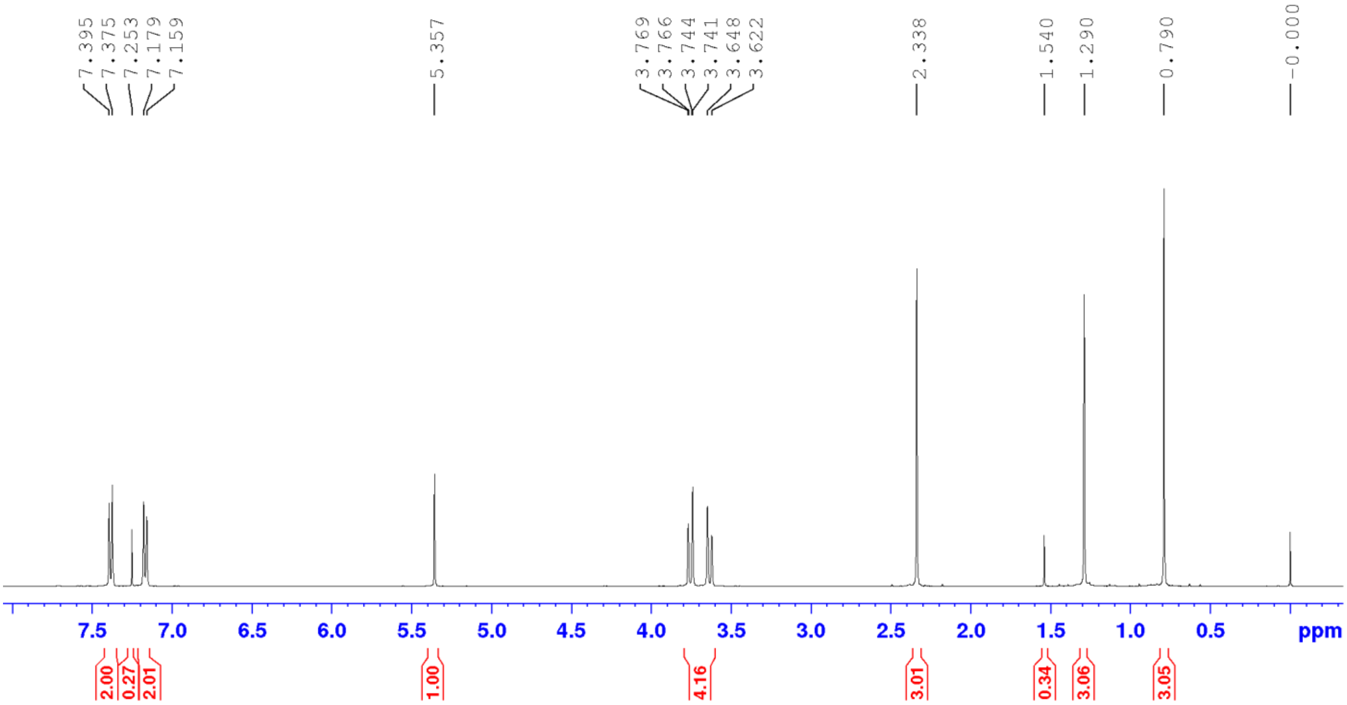
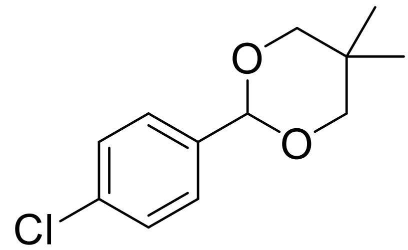


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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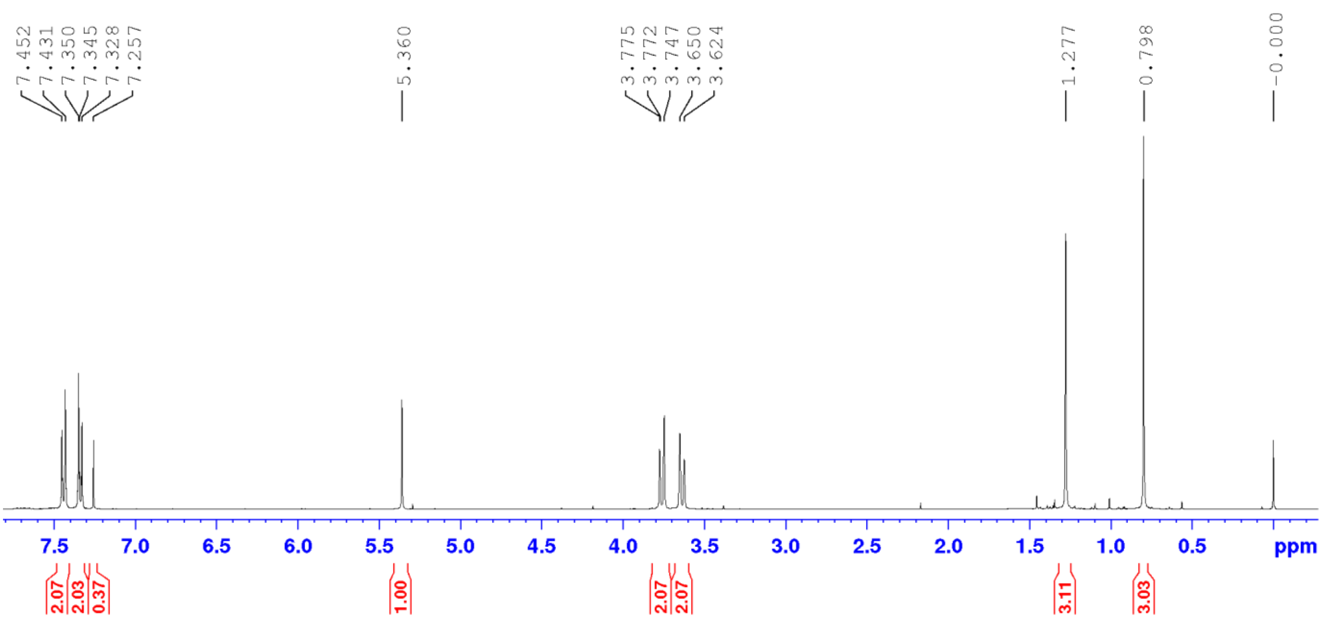
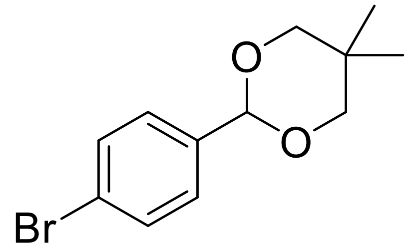


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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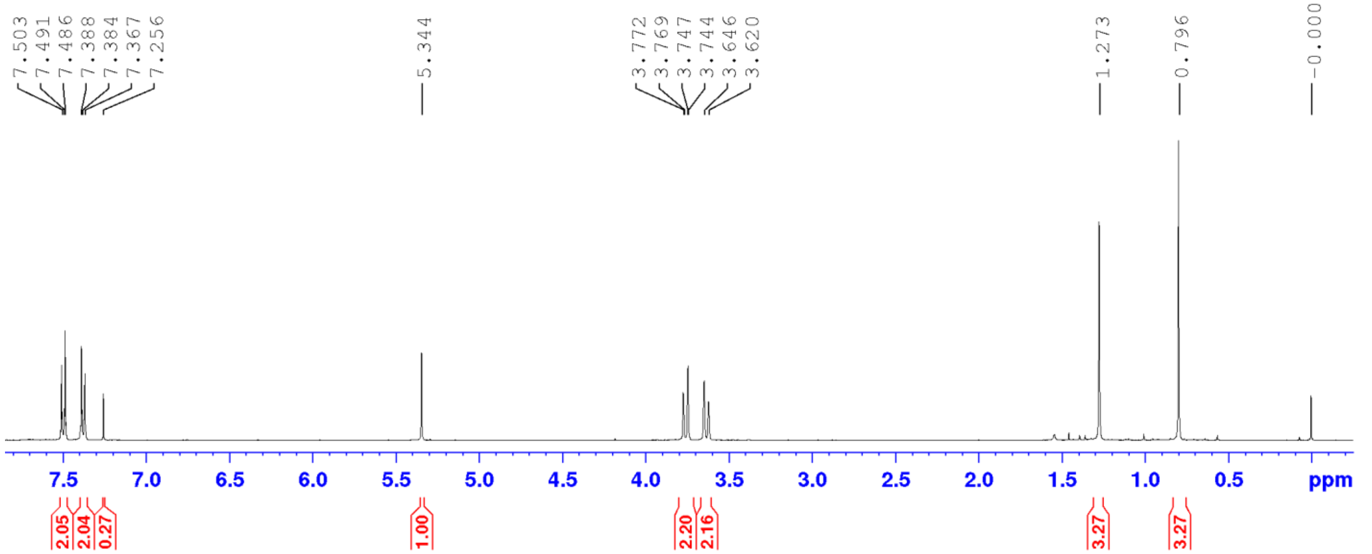
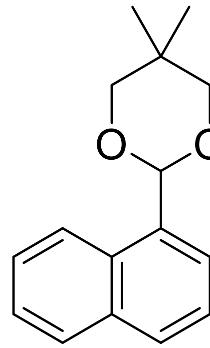


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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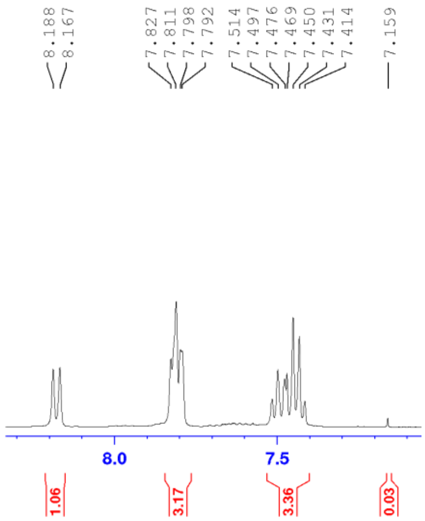
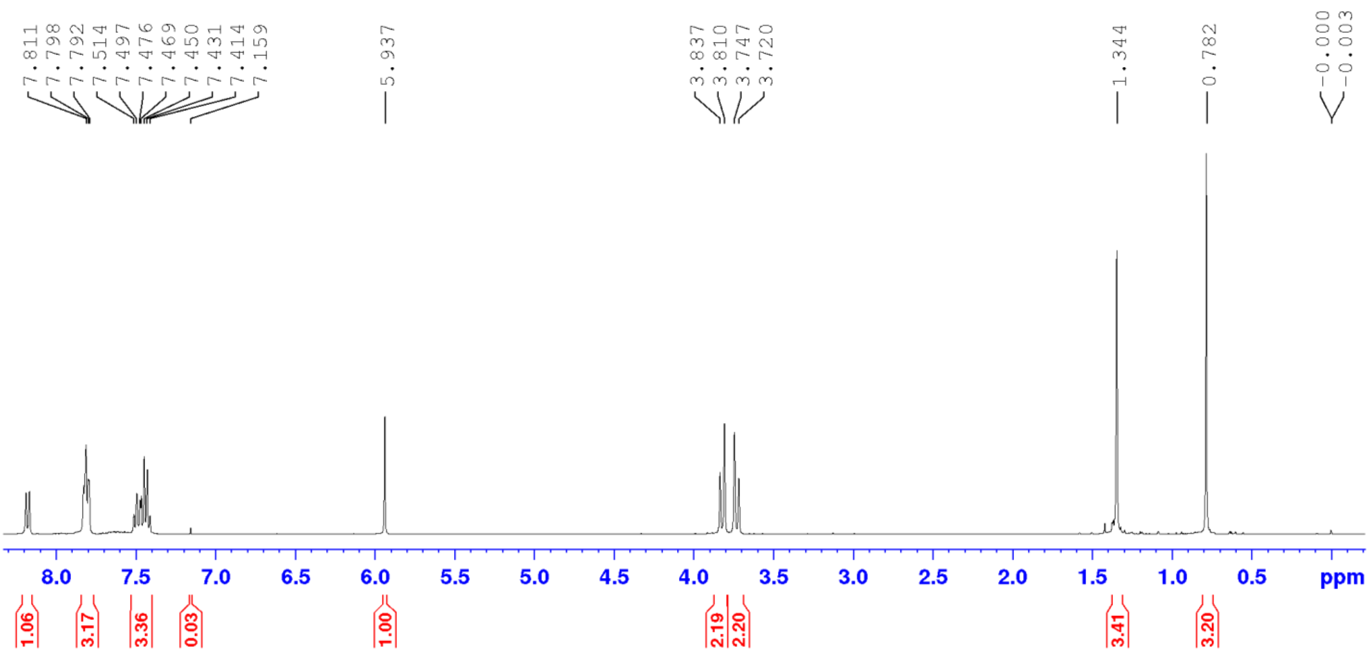
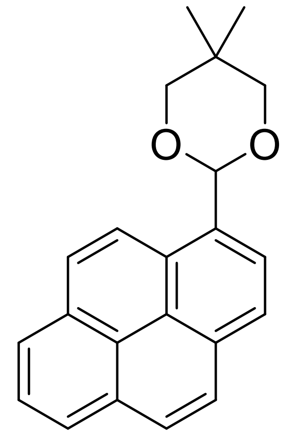




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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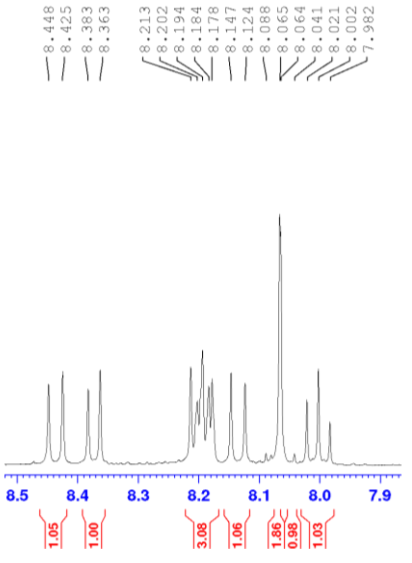
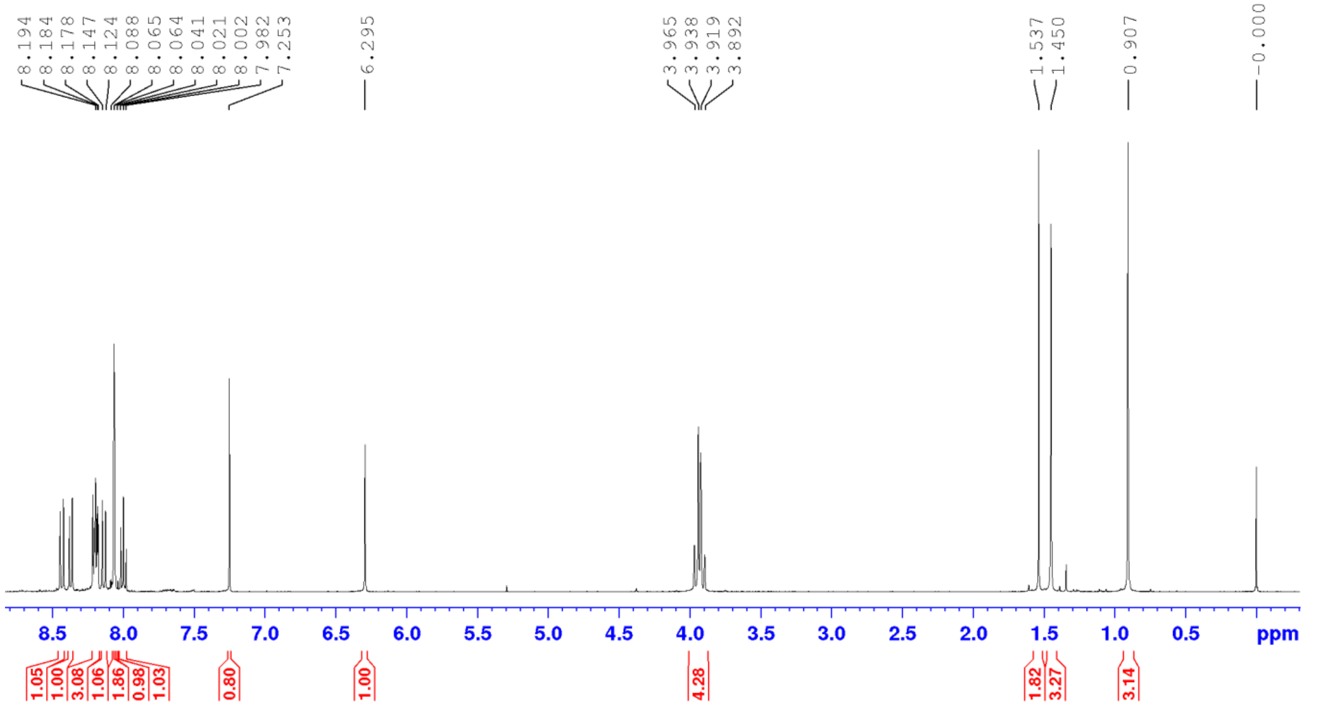
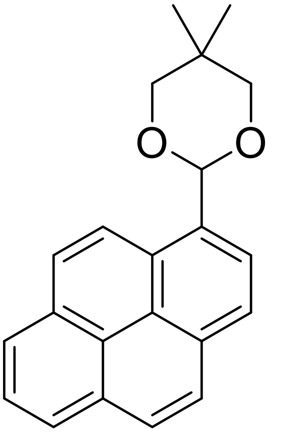




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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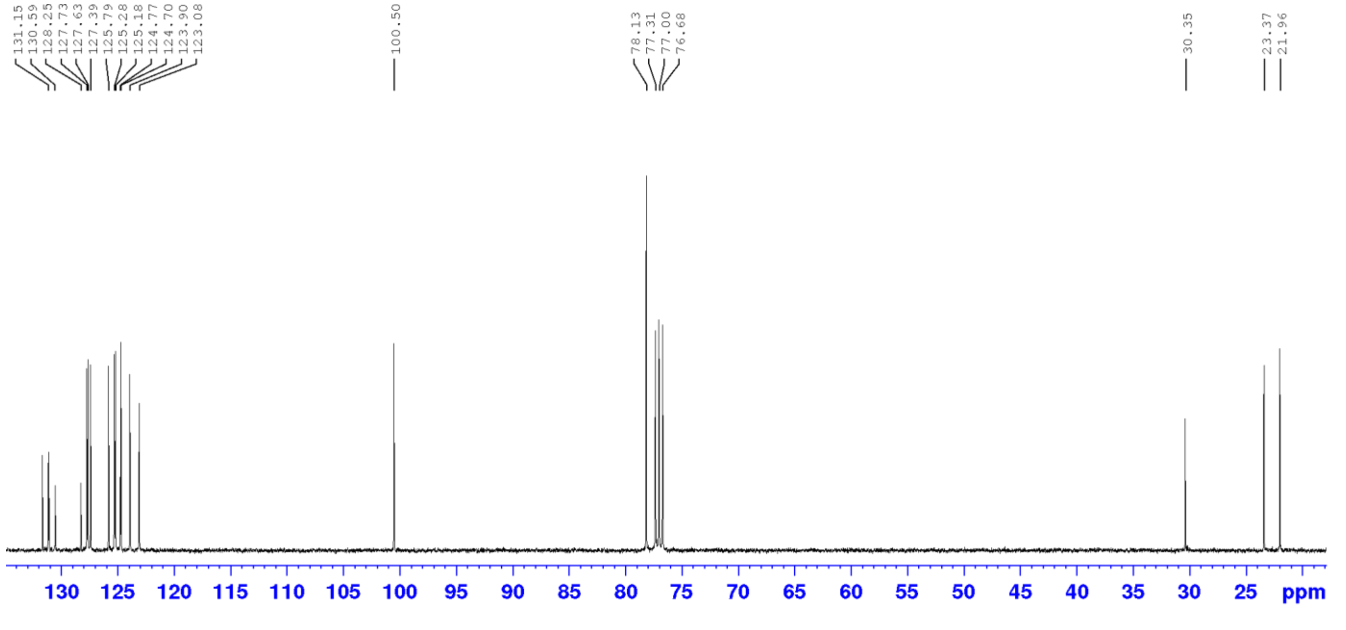
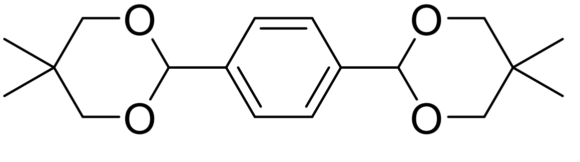


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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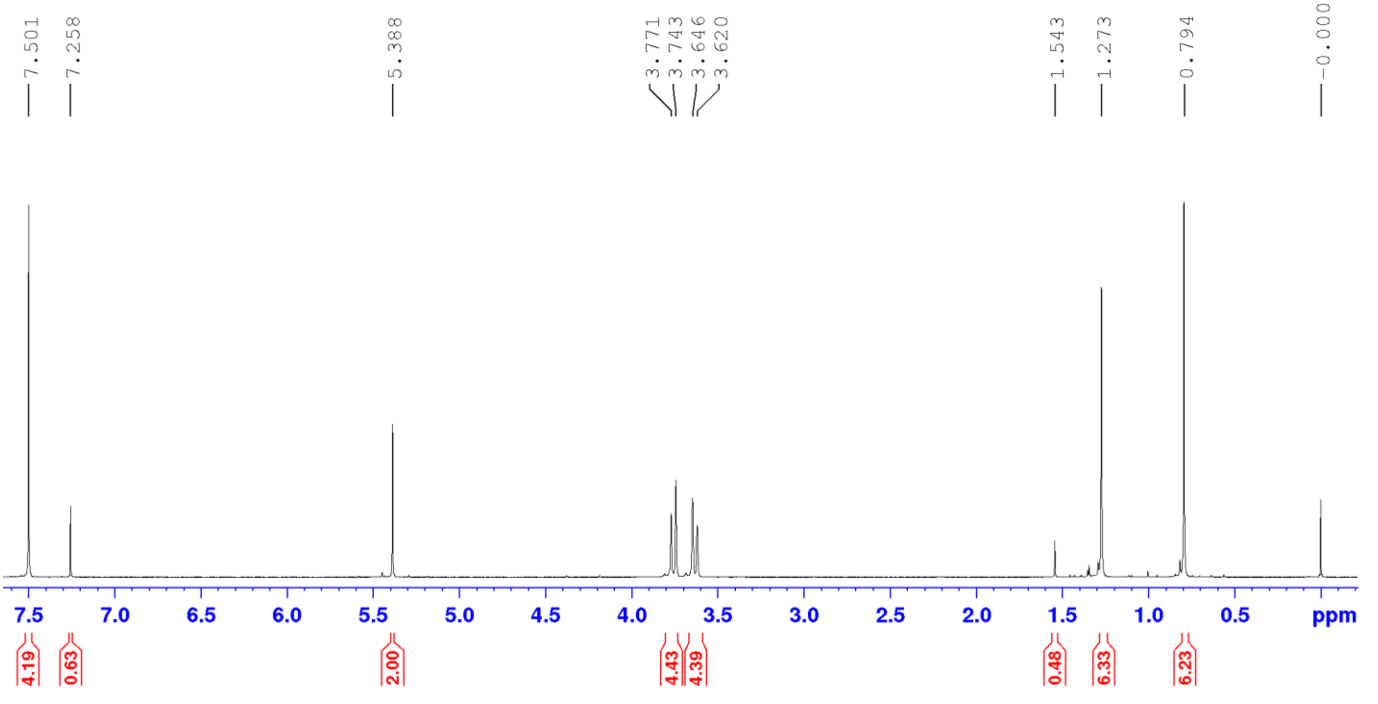
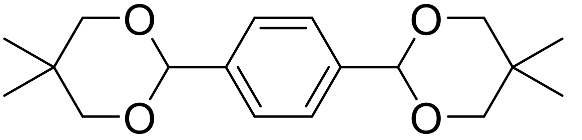


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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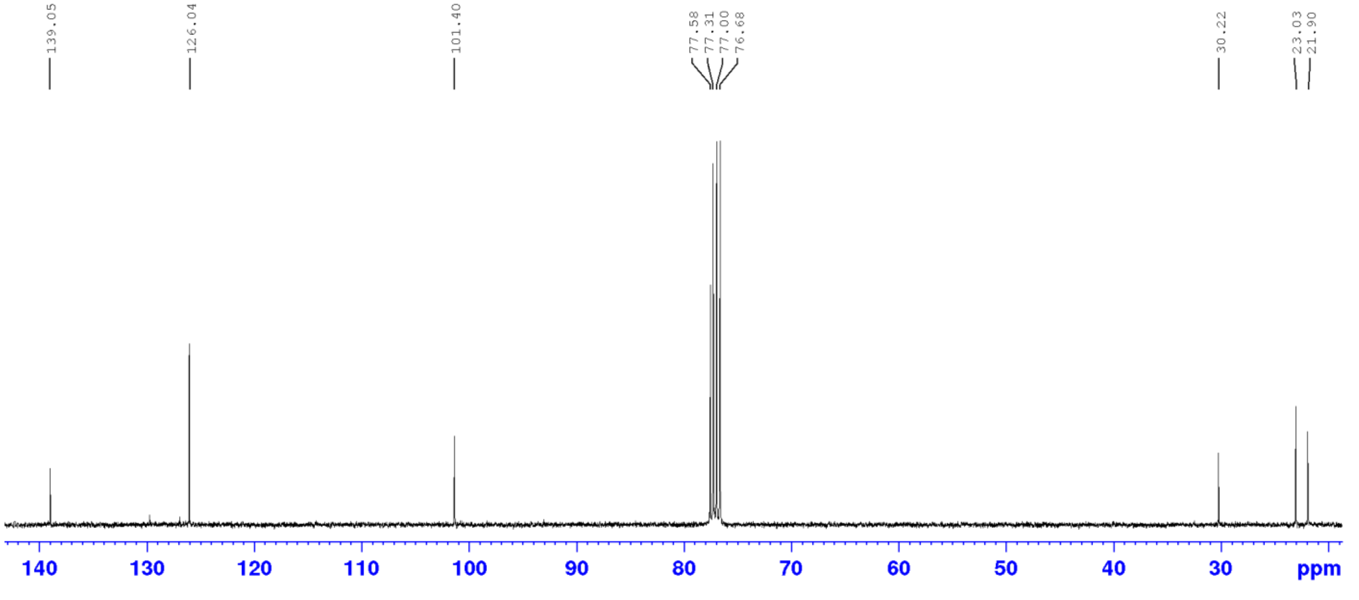

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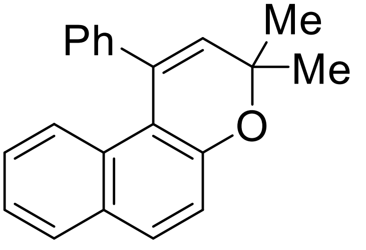

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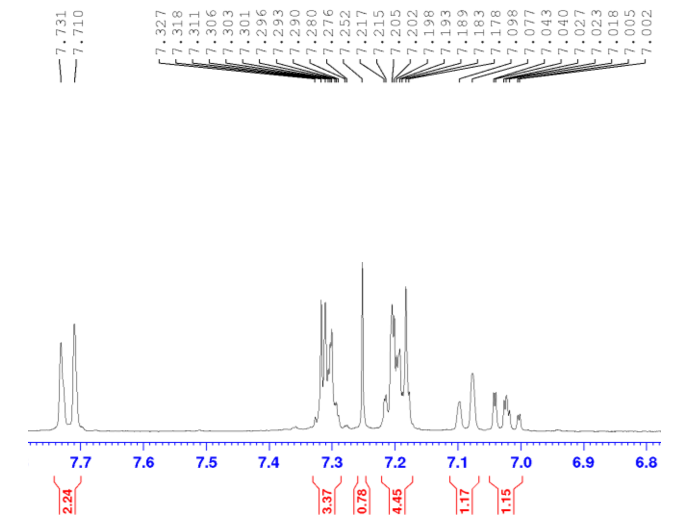

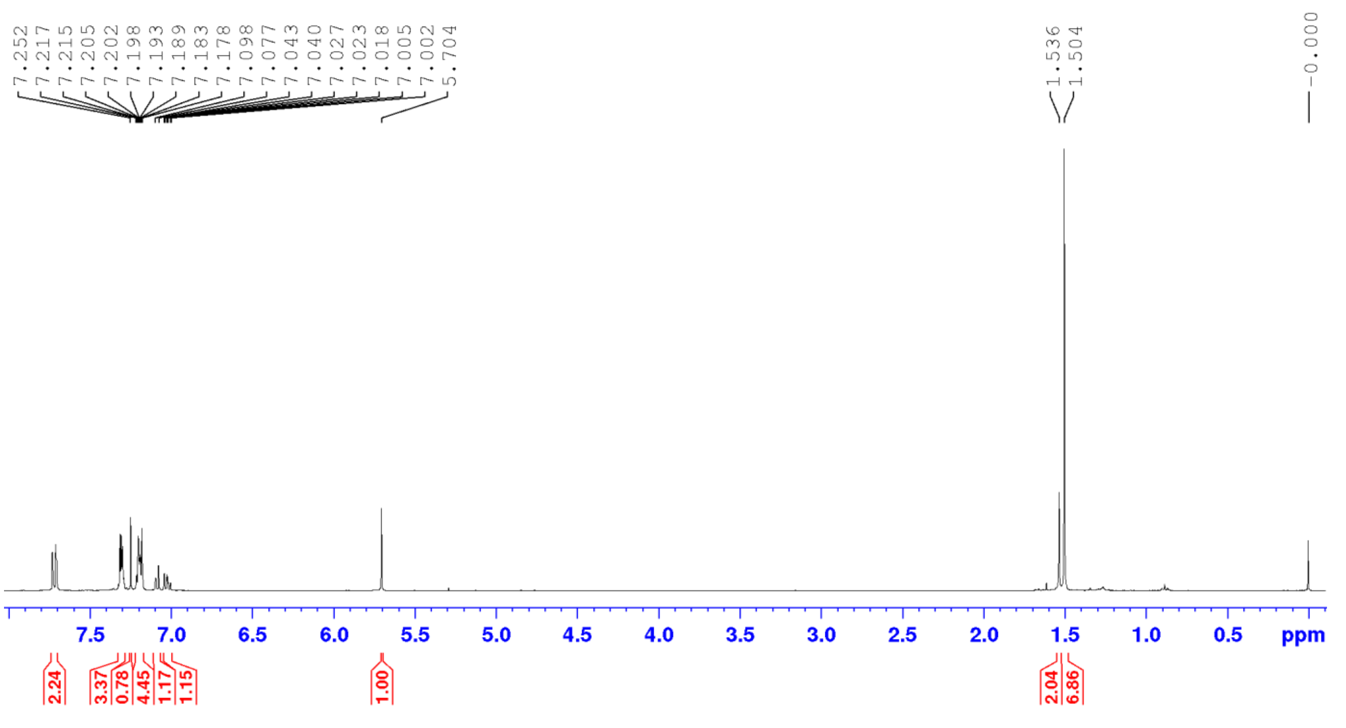

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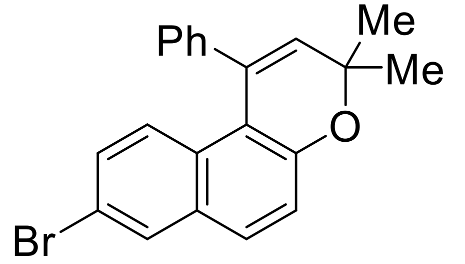

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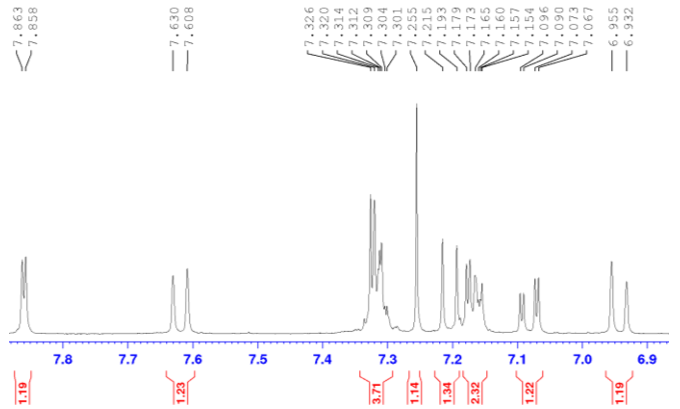
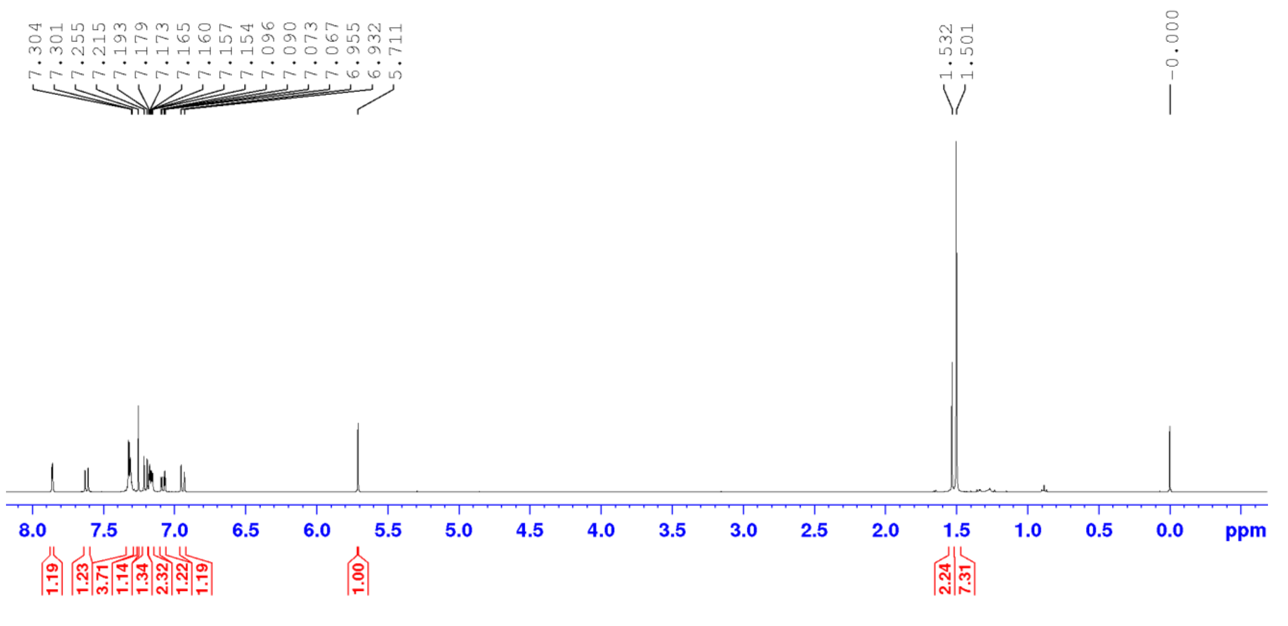
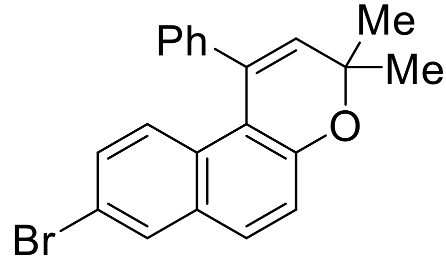




$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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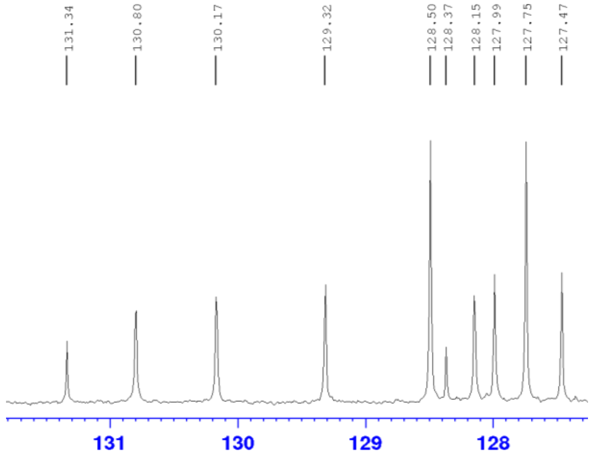
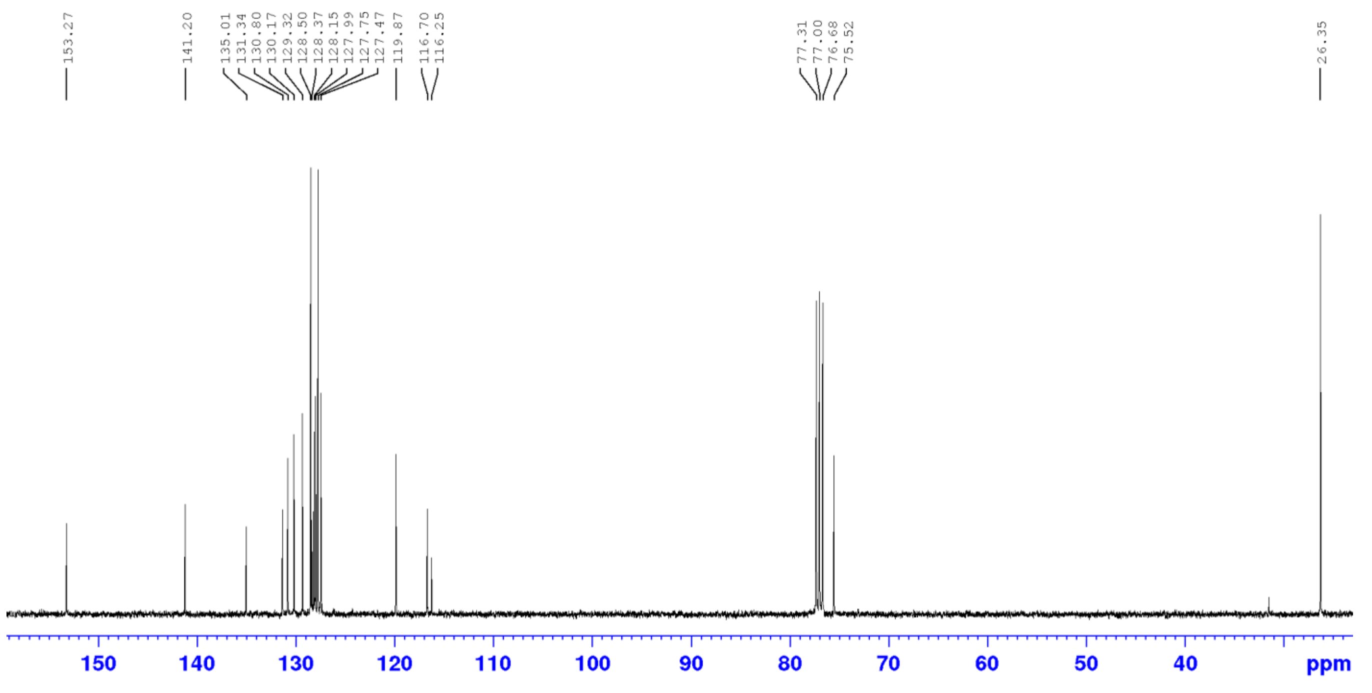
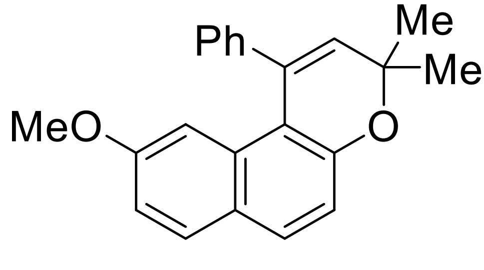




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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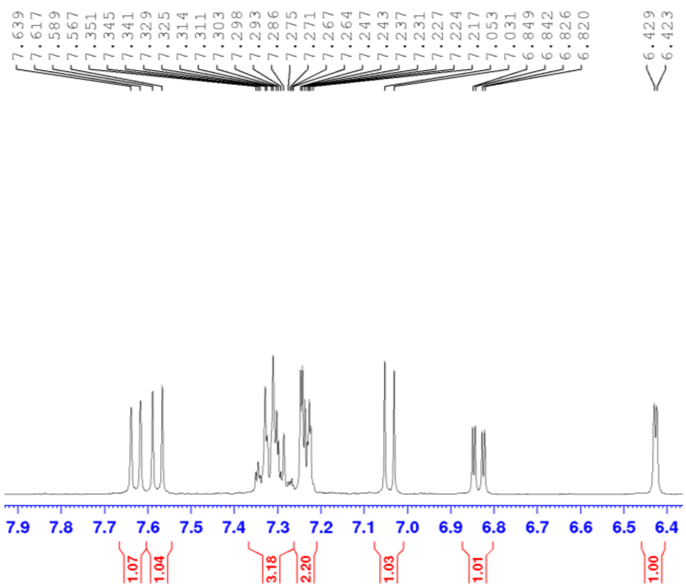
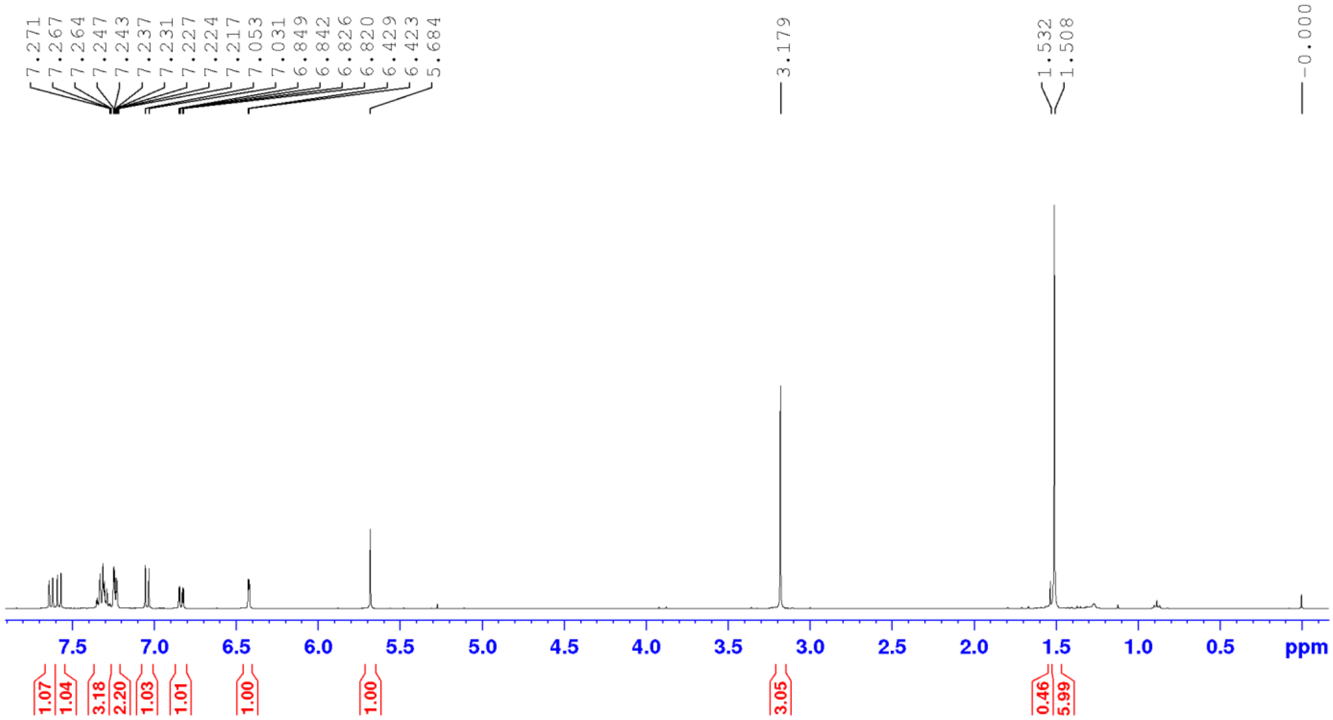
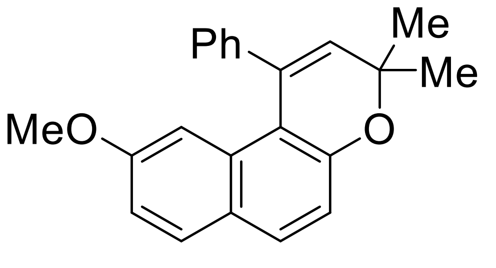




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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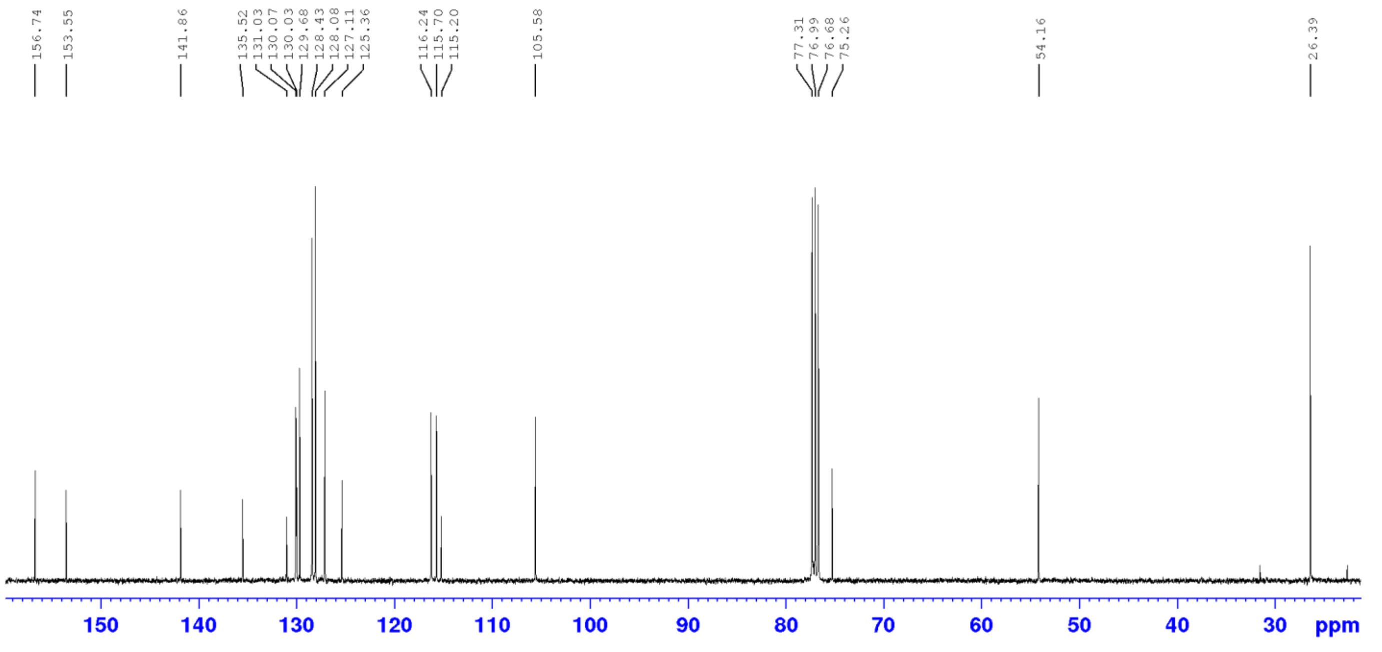

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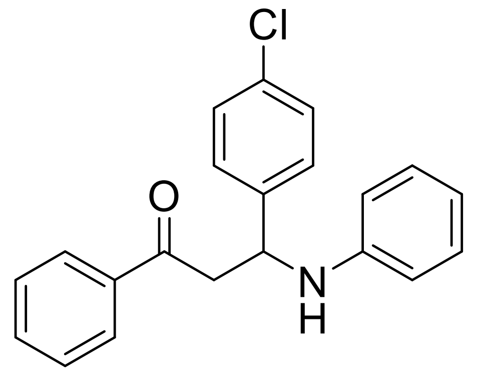

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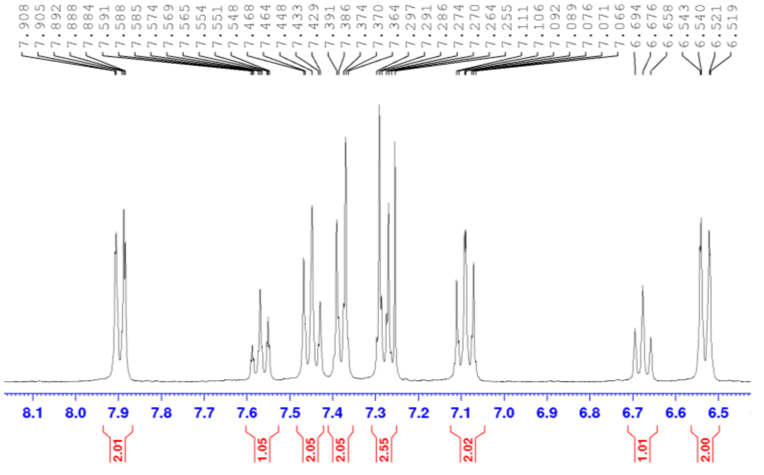
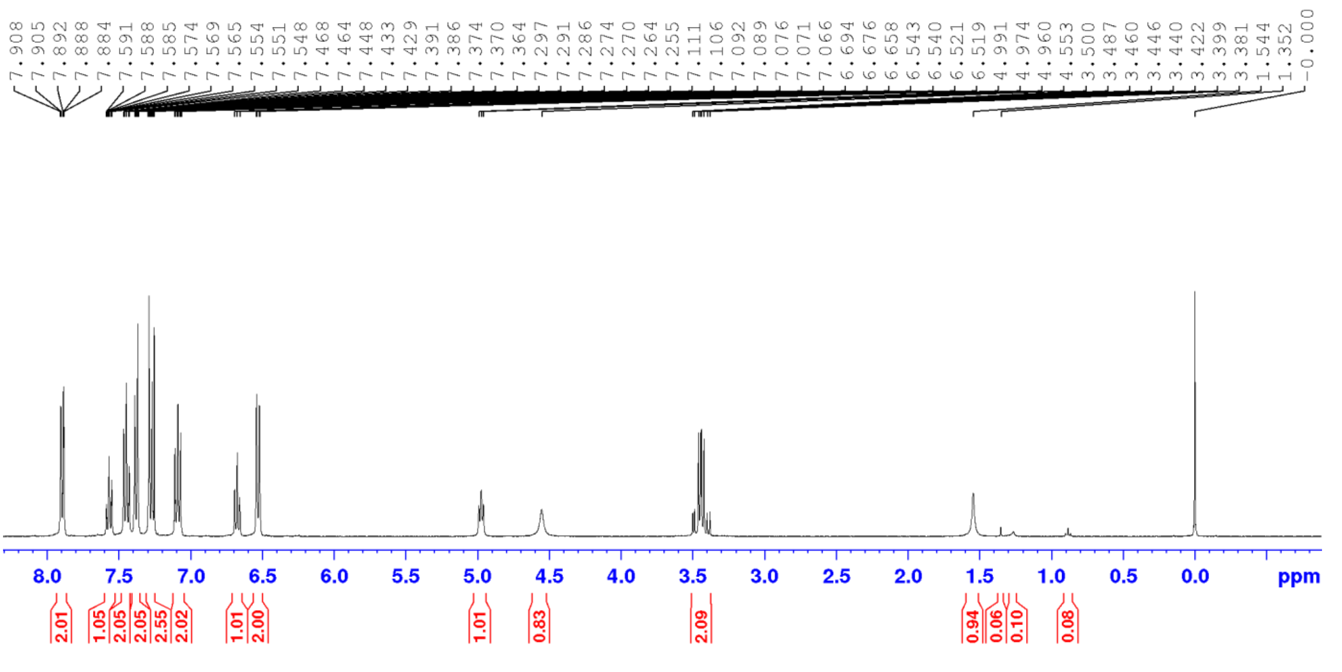
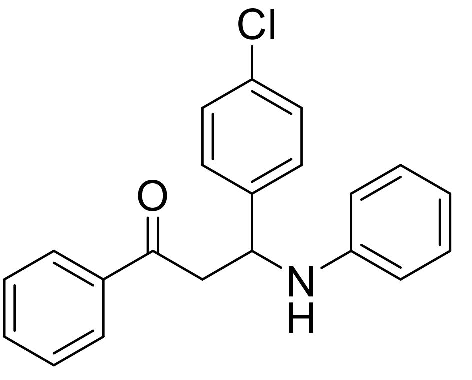




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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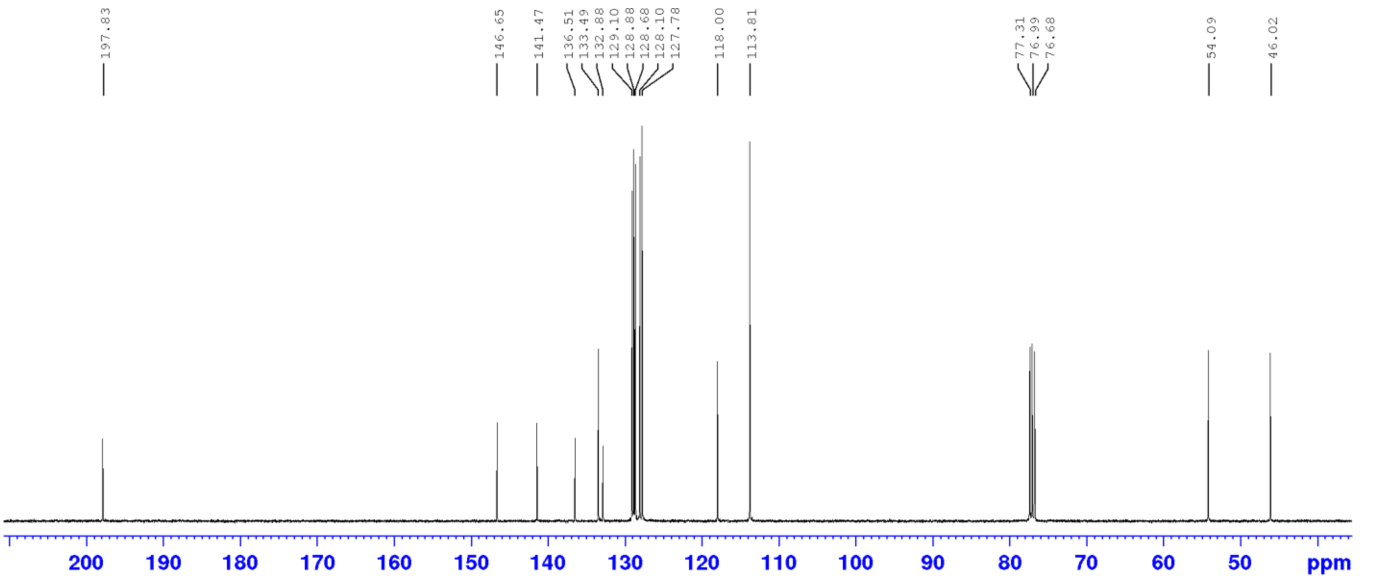
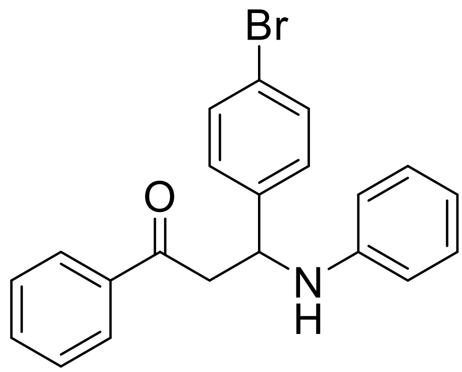


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



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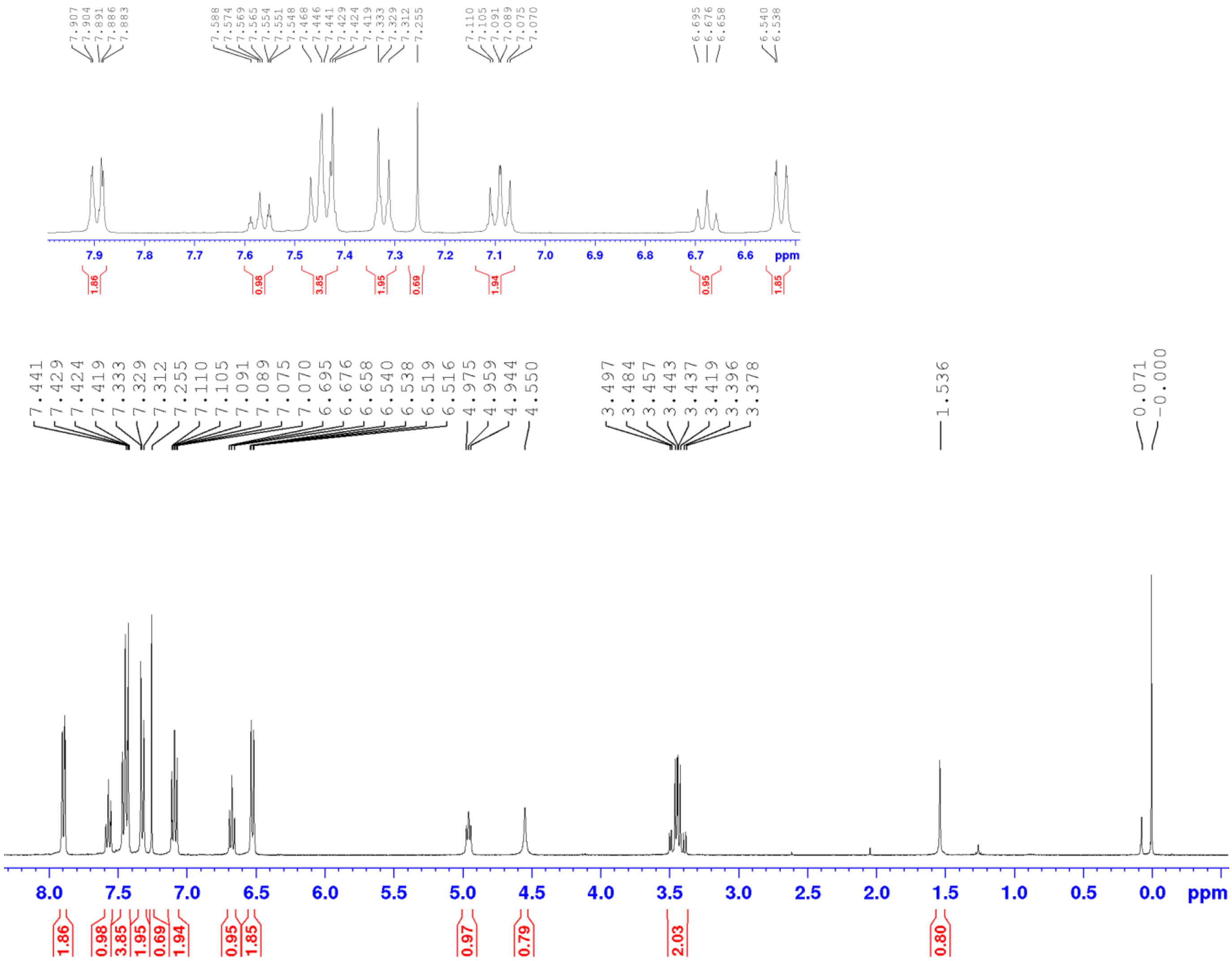
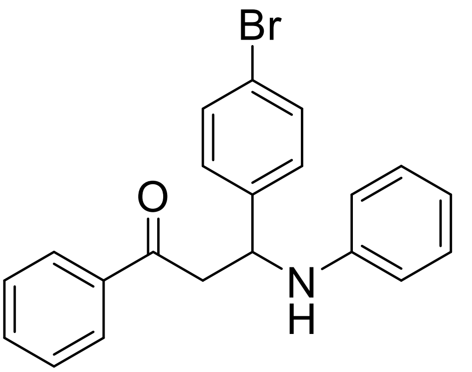


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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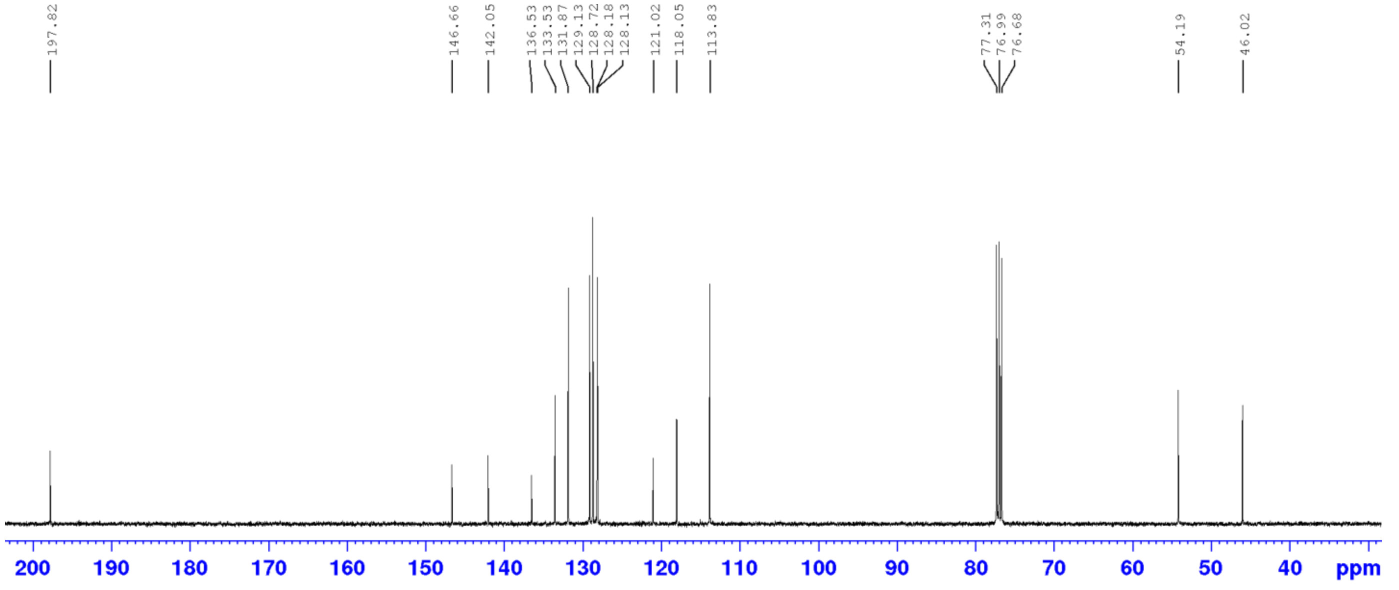
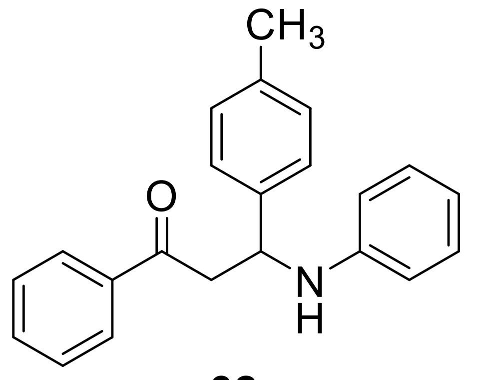


[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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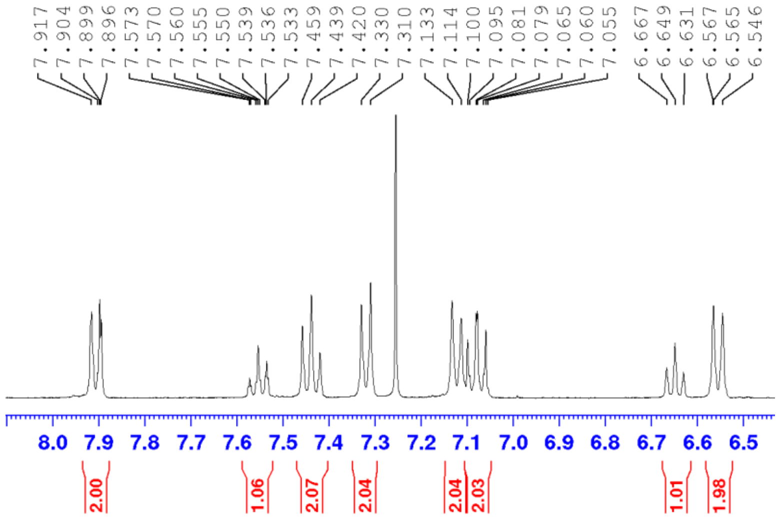

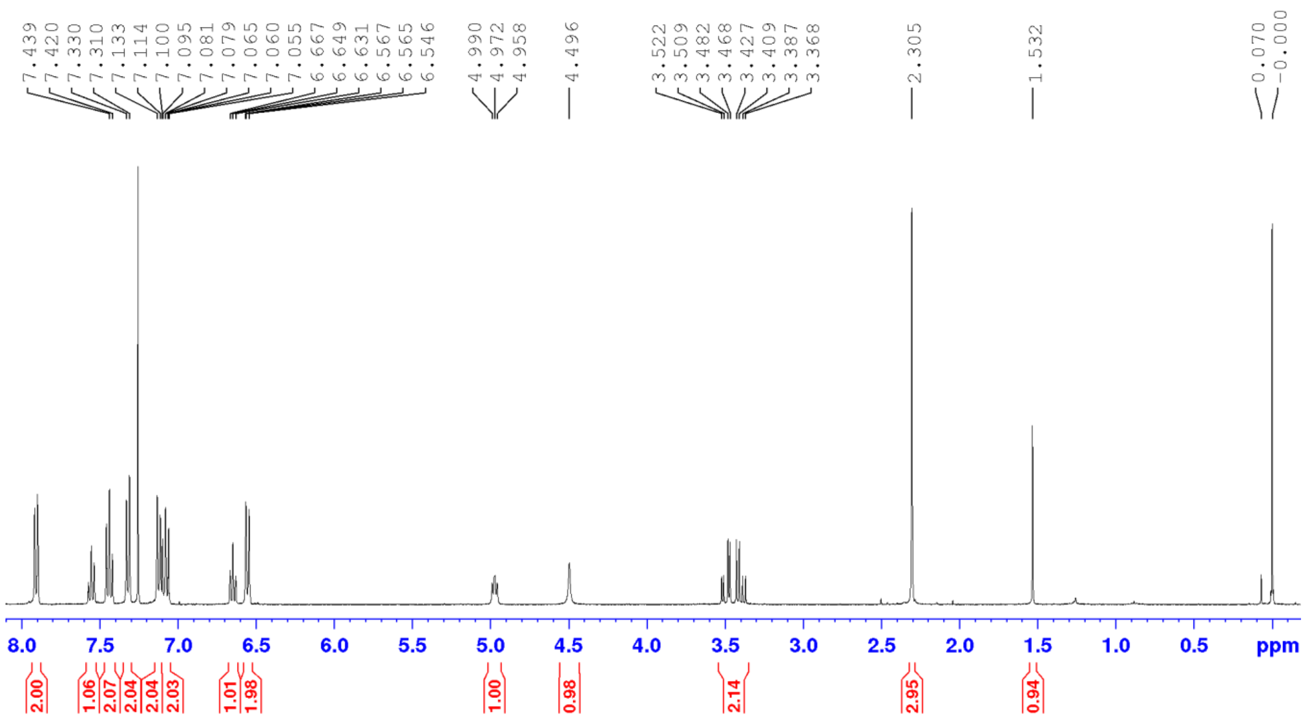

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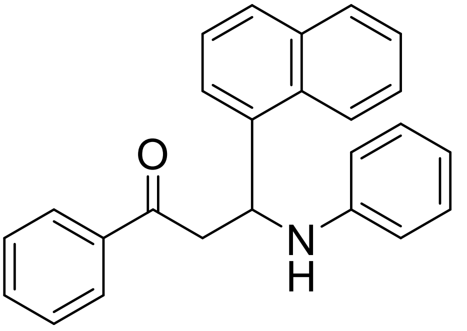

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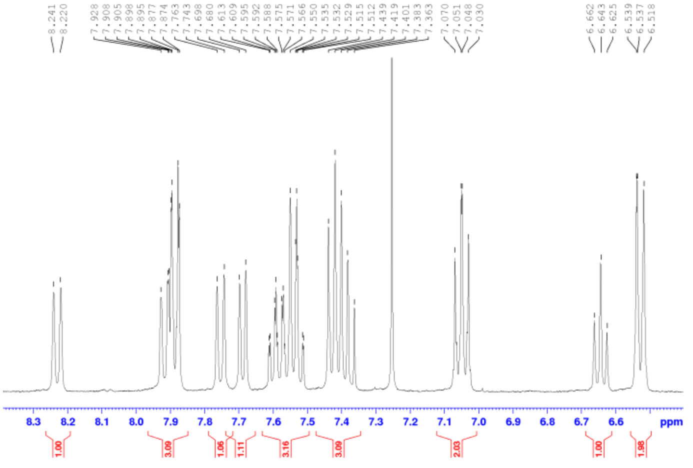
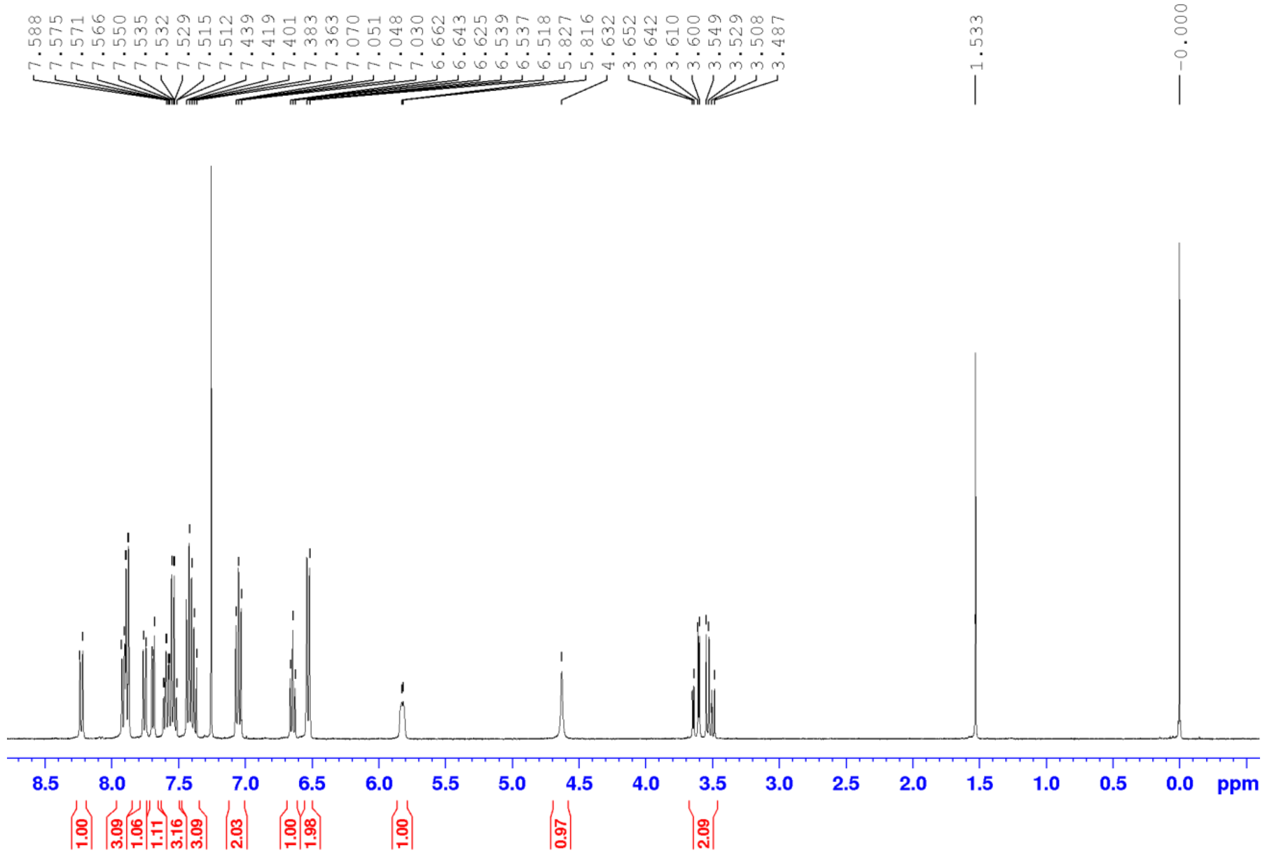
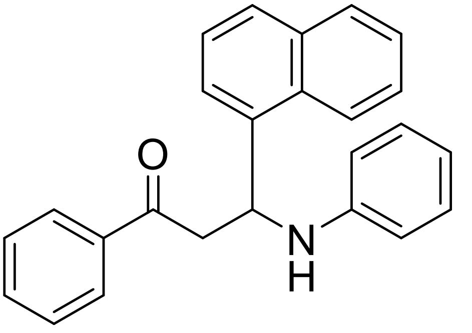




$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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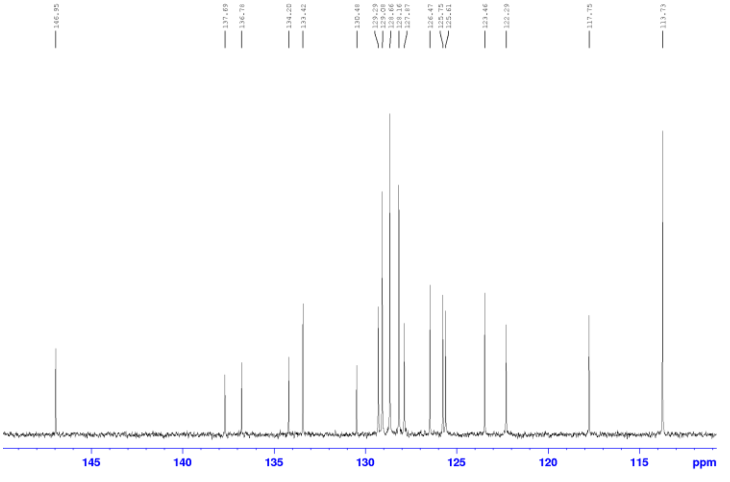

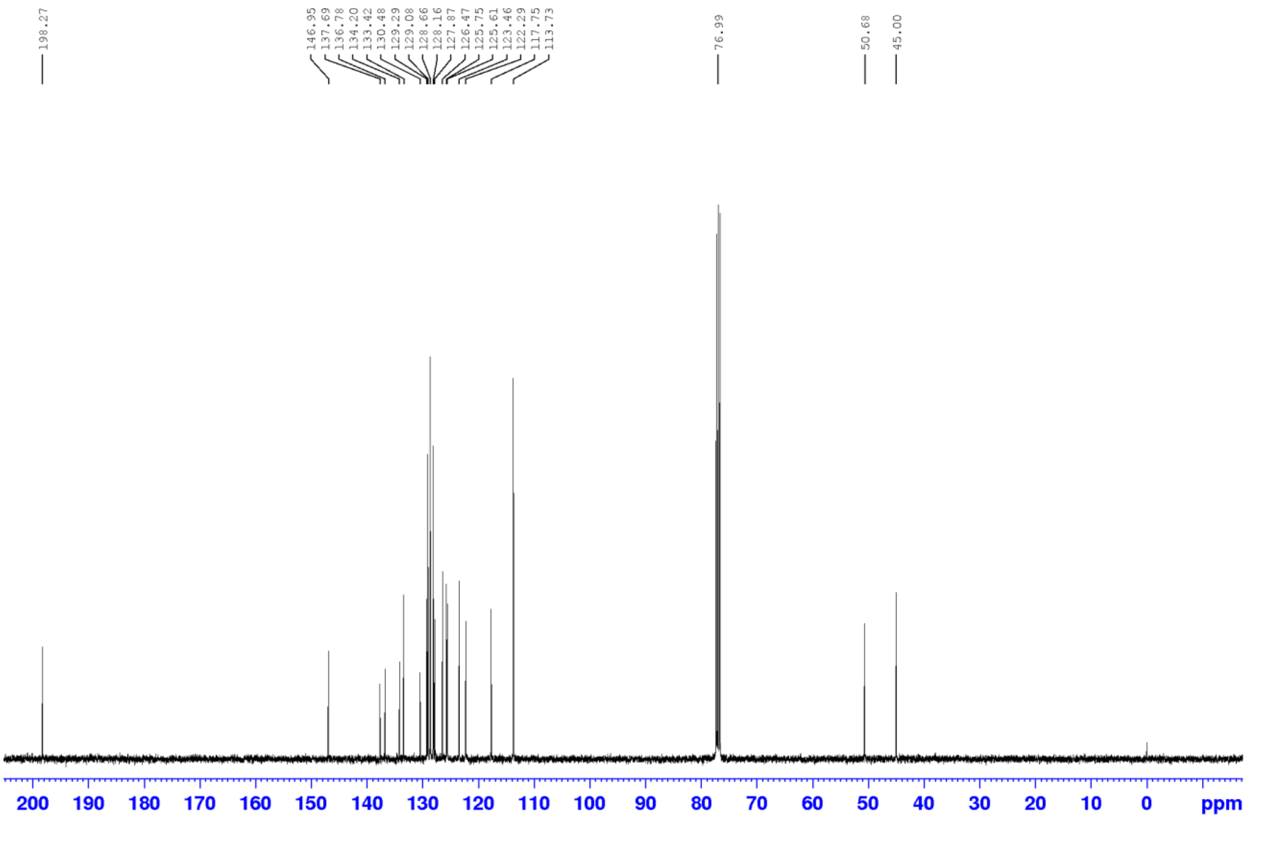

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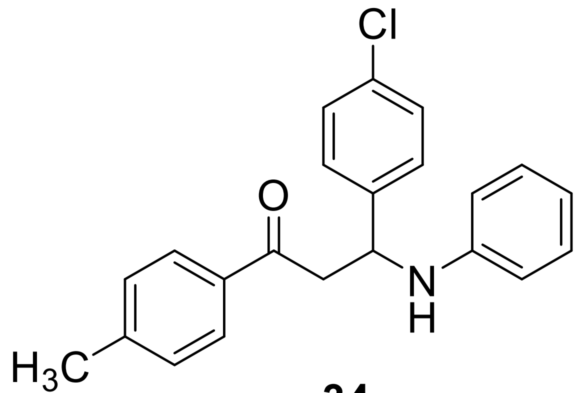

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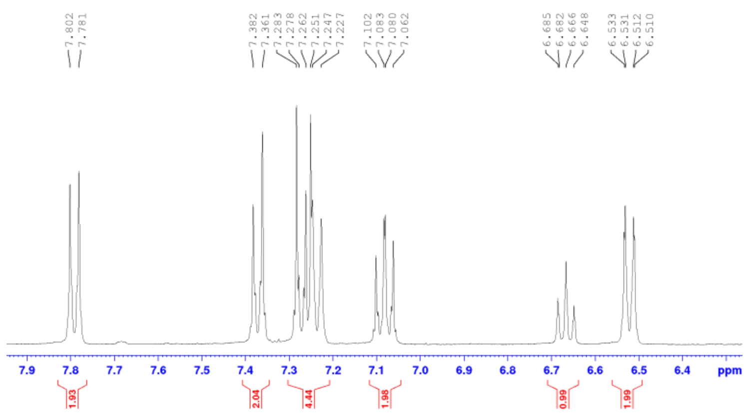
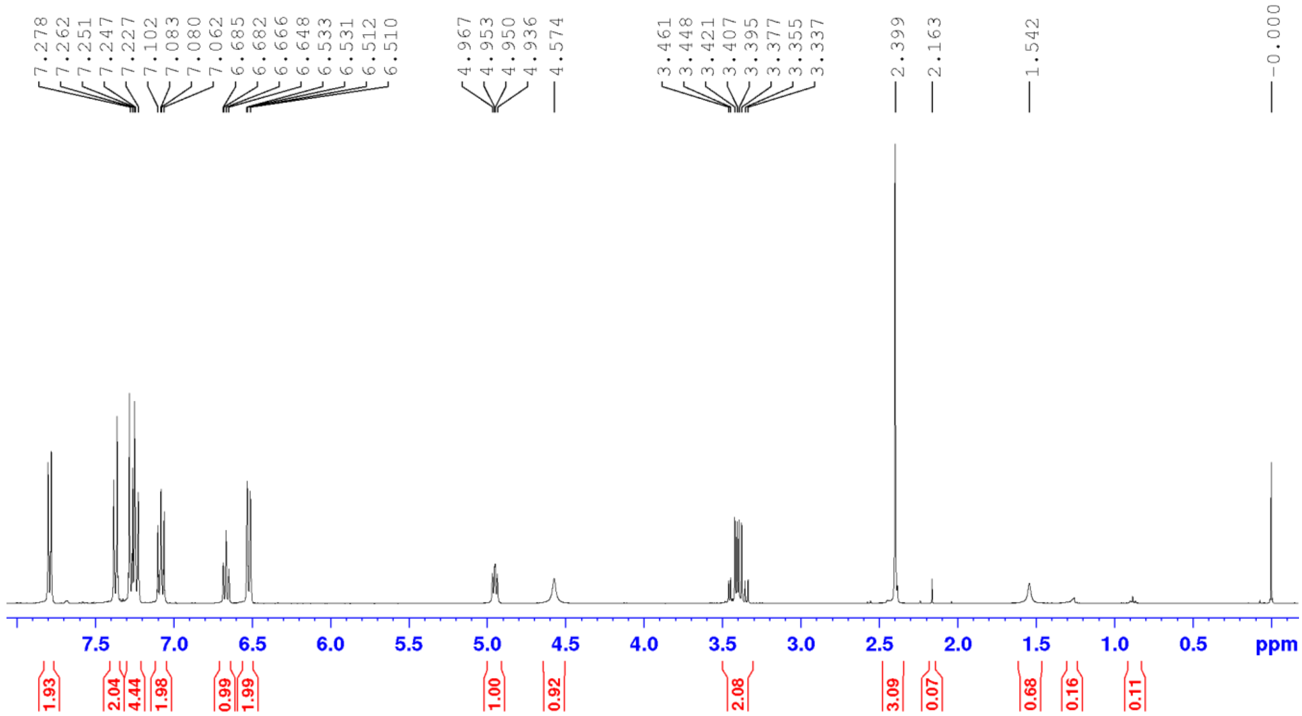
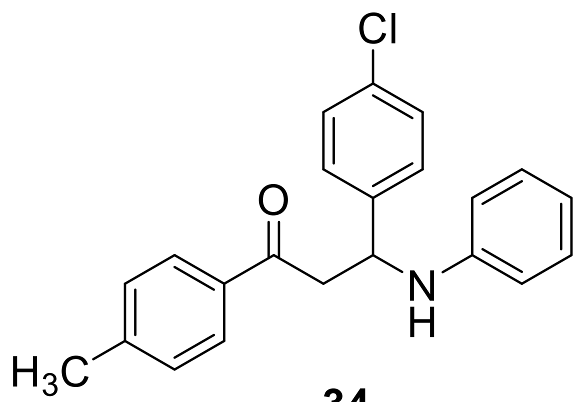




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



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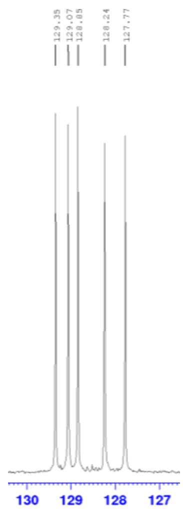
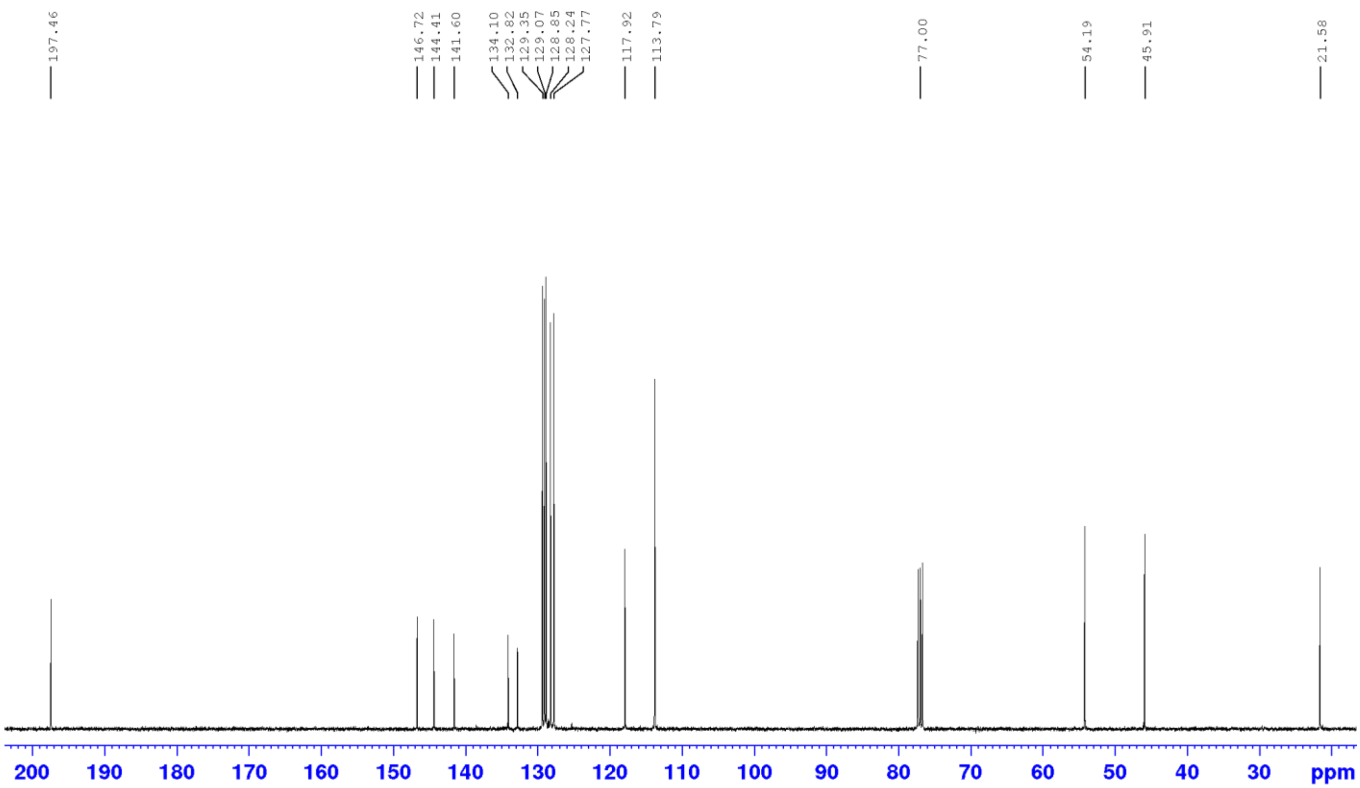
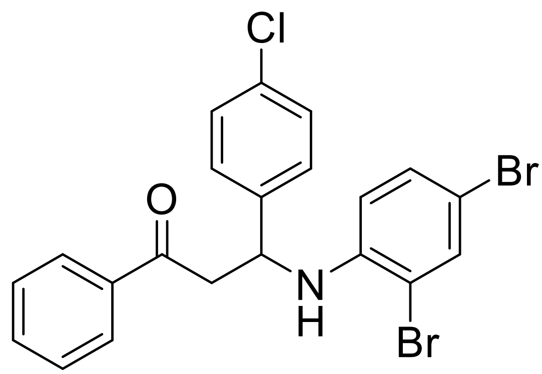




[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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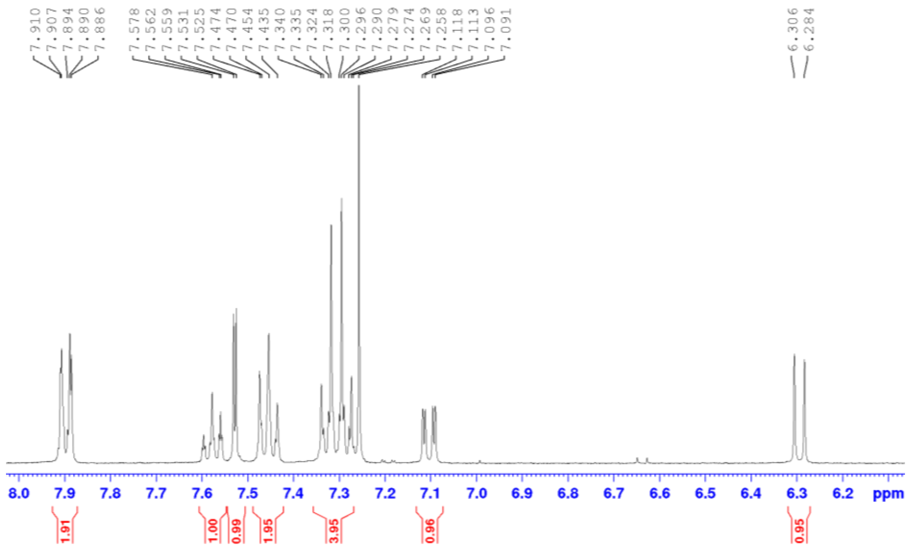
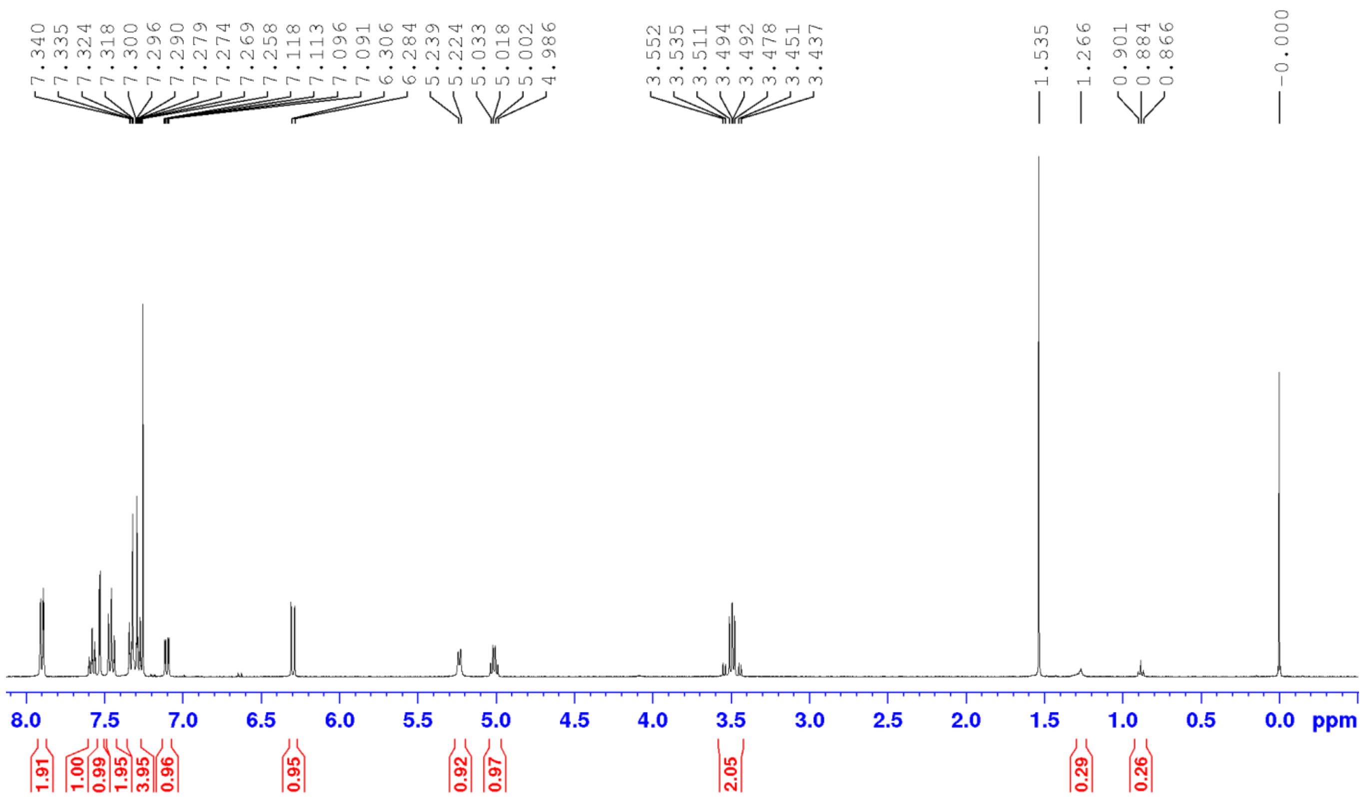
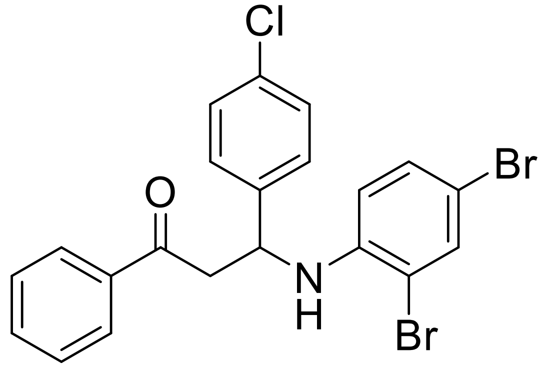




[1]H NMR (400 MHz, $CDCl_3$, 298 K)



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