Supplementary Information

Au(I)-Catalyzed Triple Bond Alkoxylation/Vinyl-Vinyl Aromaticity-Driven Cascade Cyclization to Naphthalenes

Yongxiang Liu,* Jia Guo, Yang Liu, Xiaoyu Wang,Yanshi Wang, Xinyu Jia, Gaofei Wei, Lizhu Chen, Jianyong Xiao, Maosheng Cheng*

Key Laboratory of Structure-Based Drug Design and Discovery (Shenyang Pharmaceutical University), Ministry of Education, Shenyang 110016, P. R. China

Institute of Drug Research in Medicine Capital of China (Shenyang Pharmaceutical University), Benxi, 117000, P. R. China

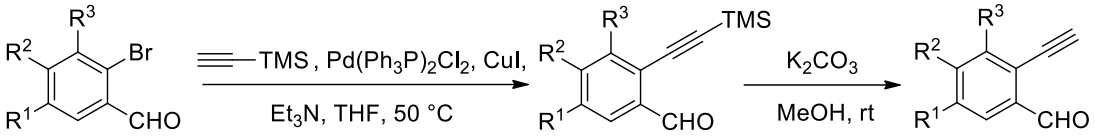
*Corresponding author. Tel.: +86 414 5864056; Fax: +86 414 5864056; E-mail: yongxiang.liu@ syphu.edu.cn

Table of Contents:

I. General Information

Unless otherwise noted, reagents were obtained commercially and used without further purification. THF was distilled from sodium-benzophenone under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 ECO silica gel. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to $CDCl_3$. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. Melting points were tested on Thomas Hoover capillary melting point apparatus. Compounds were detected by monitoring UV absorbance at 254 nm.

II. General Preparation of 2-Ethynylbenzaldehyde Derivatives (7a-7g)

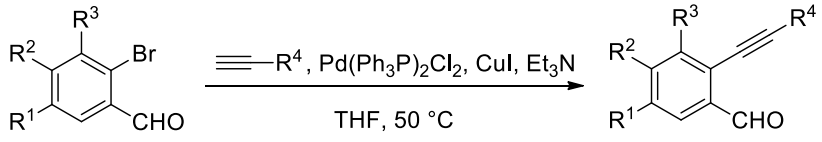


7a-7g

To a solution of the corresponding 2-bromobenzaldehyde (1 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et_3N (5 mmol, 0.7 mL) in dry THF was added the appropriate acetylene (2 mmol, 0.3 mL). The resulting mixture was heated at 50 ℃ for 12 hours. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product 2-[(trimethylsilyl)ethynyl]benzaldehyde. Then the product obtained above was dissolved in MeOH and treated with K_2CO_3 (2 mmol, 276.4 mg). After being stirred at room temperature for 1 hour, the reaction mixture was diluted with water and extracted with CH_2Cl_2 (three times). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to yield products **7a-7g**.

Spectral data were consistent with those reported in the literatures. [1-6]

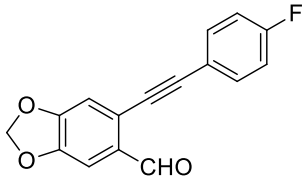
III. General Preparation of 2-Alkynylbenzaldehyde Derivatives (7h-7l) and Characterization Data



7h-7l

To a solution of the corresponding 2-bromobenzaldehyde (1 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et_3N (5 mmol, 0.7 mL) in dry THF was added the appropriate acetylene (1.2 mmol). The resulting mixture was heated at 50 ℃ for 12 hours. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired products **7h-7l**.

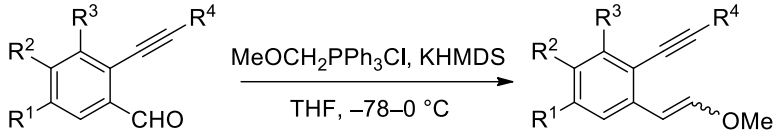
Spectral data were consistent with those reported in the literature. [1]



7l

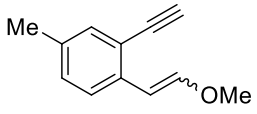
4, 5-Methylenedioxy-2-(2-phenylethynyl) benzaldehyde (7l): TLC (petroleum ether: ethyl acetate, 30:1, v/v): R_f=0.3; yellowish solid, Mp 138–139 ℃; 85%; ^1H NMR (600 MHz, $CDCl_3$) δ = 10.44 (s, 1H), 7.51 (dd, J = 8.4 Hz, 5.5 Hz, 2H), 7.35 (s, 1H), 7.06 (t, J = 8.6 Hz, 2H), 6.99 (s, 1H), 6.08 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 190.0, 163.0 (d, J = 249.4 Hz), 152.5, 148.9, 133.7 (d, J = 8.4 Hz), 133.7 (d, J = 8.4 Hz), 132.3, 123.5, 118.6 (d, J = 3.5 Hz), 116.0 (d, J = 22.0 Hz), 116.0 (d, J = 22.0 Hz), 112.1, 106.3, 102.6, 94.2, 84.7; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{10}O_3F$ $[M+H]^+$ 269.0608, Found 269.0608; IR (thin film, cm^{-1}): 3712, 3816, 3734, 3619, 1542, 1457, 805.

IV. General Preparation of 1, 5-Enyne Substrates (1-1k) and Characterization Data



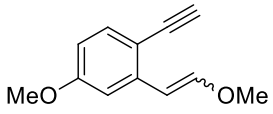
7 R^4 = H, aryl **1-1k**

To a suspension of (methoxymethyl)triphenylphosphonium chloride (2 mmol, 685.6 mg) in anhydrous THF was added 1 M solution of KHMDS in anhydrous THF (1.8 mmol, 1.8 mL) at –78 ℃. The mixture was stirred at –78 ℃ for 0.5 h, and then a solution of 2-alkynylbenzaldehyde (1 mmol) in anhydrous THF was added. The reaction was allowed to warm up to 0 ℃ over 3 h, and then hexane was added. The resulting mixture was filtered through Celite and thoroughly washed with hexane. The filtrate was concentrated *in vacuo* and the residue was diluted with hexane. The resulting mixture was filtered through Celite again to remove the remaining triphenylphosphine oxide. After evaporation to dryness, the crude vinyl ether was purified by silica gel chromatography eluting with petroleum ether/ethyl acetate to yield the products.
Spectral data were consistent with those reported in the literature. [7-8]



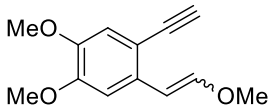
1a

2-Ethynyl-1-(2-methoxyvinyl)-4-methylbenzene (1a): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; yellowish oil, 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.2 Hz, 1H, *Z*), 7.29 (s, 1H, *Z* + 1H, *E*), 7.25 (d, J = 8.1 Hz, 1H, *E*), 7.13 – 7.09 (m, 1H, *Z* + 1H, *E*), 7.06 (d, J = 8.0 Hz, 1H, *E*), 6.24 (d, J = 13.0 Hz, 1H, *E*), 6.20 (d, J = 7.2 Hz, 1H, *Z*), 5.77 (d, J = 7.2 Hz, 1H, *Z*), 3.78 (s, 3H, *Z*), 3.72 (s, 3H, *E*), 3.28 (s, 1H, *E*), 3.26 (s, 1H, *Z*), 2.29 (s, 3H, *Z*), 2.29 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 149.9 (*E*), 148.6 (*Z*), 136.0 (*E*), 135.2 (*Z*), 135.2 (*Z*), 135.2 (*E*), 133.7 (*E*), 133.2 (*Z*), 130.2 (*E*), 129.8 (*Z*), 128.6 (*Z*), 123.6 (*E*), 119.7 (*Z*), 119.4 (*E*), 103.2 (*E*), 103.0 (*Z*), 83.0 (*Z*), 82.8 (*Z*), 81.1 (*E*), 80.8 (*E*), 60.9 (*Z*), 59.7 (*E*), 21.0 (*Z*), 20.9 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{12}H_{13}O$ $[M+H]^+$ 173.0961, Found 173.0962; IR (thin film, cm^{-1}): 3854, 3807, 3675, 2923, 1700,1652, 1638, 1635, 1558, 1465, 1457, 1090, 833, 748, 682.



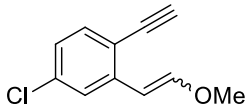
1b

1-Ethynyl-4-methoxy-2-(2-methoxyvinyl)benzene (1b): TLC (petroleum ether:ethyl acetate, 30:1, v/v): R_f=0.25; yellowish oil (1: 0.5 *E*/*Z*), 72%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (d, J = 2.6 Hz, 1H, *Z*), 7.40 (d, J = 8.5 Hz, 1H, *E* + 1H, *Z*), 7.15 (d, J = 13.0 Hz, 1H, *E*), 6.86 (d, J = 2.5 Hz, 1H, *E*), 6.66 (dd, J = 8.5 Hz, 2.4 Hz, 1H, *Z* + 1H, *E*), 6.24 (dd, J = 10.1 Hz, 5.5 Hz, 1H, *Z* + 1H, *E*), 5.79 (d, J = 7.2 Hz, 1H, *Z*), 3.82 (s, 3H, *Z*), 3.81 (s, 3H, *E*), 3.80 (s, 3H, *Z*), 3.73 (s, 3H, *E*), 3.24 (s, 1H, *E*), 3.22 (s, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.1 (*E*), 159.9 (*Z*), 150.6 (*E*), 149.6 (*Z*), 140.5 (*E*), 139.4 (*Z*), 134.7 (*E*), 134.0 (*Z*), 113.9 (*Z*), 112.5 (*Z*), 112.2 (*E*), 111.8 (*Z*), 111.7 (*E*), 108.8 (*E*), 103.4 (*E*), 103.1 (*Z*), 82.9 (*Z*), 82.7 (*Z*), 80.1 (*E*), 79.9 (*E*), 61.1 (*Z*), 56.7 (*E*), 55.4(*E*), 55.3 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{12}H_{13}O_2$ $[M+H]^+$ 189.0910, Found 189.0909; IR (thin film, cm^{-1}): 3744, 3628, 1700, 1652, 1507, 720, 688, 676



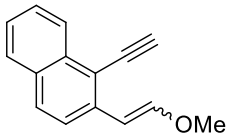
1c

1-Ethynyl-4,5-dimethoxy-2-(2-methoxyvinyl)benzene (1c): TLC (petroleum ether:ethyl acetate, 10:1): R_f=0.3; yellowish solid (1: 0.6 *E*/*Z*), Mp 80–82 ℃; 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (s, 1H, *Z*), 7.06 (d, *J* = 13.0 Hz, 1H, *E*), 6.94 (s, 1H, *Z*), 6.93 (s, 1H, *E*), 6.79 (s, 1H, *E*), 6.21 (d, *J* = 13.0 Hz, 1H, *E*), 6.16 (d, *J* = 7.2 Hz, 1H, *Z*), 5.74 (d, *J* = 7.2 Hz, 1H, *Z*), 3.89 (s, 3H, *E* + 3H, *Z*), 3.85 (s, 3H, *Z*), 3.85 (s, 3H, *E*), 3.79 (s, 3H, *Z*), 3.71 (s, 3H, *E*), 3.25 (s, 1H, *E*), 3.24 (s, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 150.1 (*E*), 149.5 (*Z*), 149.4 (*E*), 147.9 (*E*), 147.1 (*Z*), 146.7 (*Z*), 132.7 (*E*), 132.2 (*Z*), 115.2 (*E*), 114.8 (*Z*), 112.1 (*Z*), 111.5 (*Z*), 111.5 (*E*), 106.4 (*E*), 103.4 (*E*), 103.1 (*Z*), 82.9 (*Z*), 82.8 (*Z*), 80.2 (*E*), 79.9 (*E*), 61.0 (*Z*), 56.6 (*E*), 56.1 (*E*), 56.0 (*Z*), 56.0 (*E*), 55.9 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{13}H_{15}O_3$ $[M+H]^+$ 219.1016, Found 219.1016; IR (thin film, cm^{-1}): 3874, 3850, 3821, 3750, 1685, 1652, 1560, 744, 683.



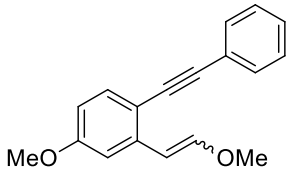
1e

4-Chloro-1-ethynyl-2-(2-methoxyvinyl) benzene (1e): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; yellowish solid (1: 0.5 *E*/*Z*), Mp 91–93 ℃; 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 2.1 Hz, 1H, *Z*), 7.37 (d, *J* = 8.3 Hz, 1H, *E* + 1H, *Z*), 7.33 (d, *J* = 2.0 Hz, 1H, *E*), 7.14 (d, *J* = 13.0 Hz, 1H, *E*), 7.06 (dt, *J* = 8.3Hz, 2.3 Hz, 1H, *E* + 1H, *Z*), 6.28 (d, *J* = 7.2 Hz, 1H, *Z*), 6.19 (d, *J* = 13.0 Hz, 1H, *E*), 5.75 (d, *J* = 7.2 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.73 (s, 3H, *E*), 3.33 (s, 1H, *E*), 3.31 (s, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 151.4 (*E*), 150.4 (*Z*), 140.6 (*E*), 139.5 (*Z*), 135.1 (*E*), 134.8 (*Z*), 134.4 (*E*), 133.8 (*Z*), 128.5 (*Z*), 125.6 (*Z*), 125.6 (*E*), 123.6 (*E*), 118.2 (*Z*), 118.0 (*E*), 102.6 (*E*), 102.1 (*Z*), 82.3 (*Z* + *E*), 82.1 (*E*), 81.7 (*Z*), 61.3 (*Z*), 56.9 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{11}H_{10}OCl$ $[M+H]^+$ 193.0414, Found 193.0415; IR (thin film, cm^{-1}): 3854, 3670, 1734, 1700, 1685, 1539, 841, 754, 676.



1f

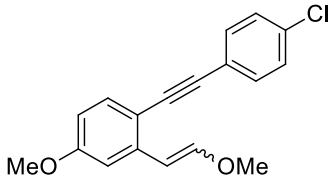
1-Ethynyl-2-(2-methoxyvinyl) naphthalene (1f): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.25; yellowish oil (1: 0.5 *E*/*Z*), 74%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 8.6 Hz, 1H, *Z*), 8.35 (d, *J* = 8.4 Hz, 1H, *E*), 8.27 (d, *J* = 8.8 Hz, 1H, *Z*), 7.79 (d, *J* = 8.8 Hz, 1H, *Z*), 7.77 (d, *J* = 8.6 Hz, 1H, *E* + 1H, *Z*), 7.72 (d, *J* = 8.7 Hz, 1H, *E*), 7.58 – 7.53 (m, 1H, *E* + 1H, *Z*), 7.52 (d, *J* = 8.7 Hz, 1H, *E*), 7.45 (m, 1H, *E* + 1H, *Z*), 7.31 (d, *J* = 13.0 Hz, 1H, *E*), 6.59 (d, *J* = 13.0 Hz, 1H, *E*), 6.33 (d, *J* = 7.2 Hz, 1H, *Z*), 6.08 (d, *J* = 7.2 Hz, 1H, *Z*), 3.84 (s, 3H, *Z*), 3.80 (s, 3H, *E*), 3.78 (s, 1H, *E*), 3.77 (s, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 151.4 (*E*), 149.9 (*Z*), 137.8 (*E*), 137.6 (*Z*), 134.3 (*E*) 134.0 (*Z*), 131.5 (*E*), 131.4 (*Z*), 129.1 (*E*), 128.5 (*Z*), 128.1 (*E*), 128.1 (*Z*), 127.3 (*E*), 127.0 (*Z*), 126.5 (*Z*), 126.4 (*Z*), 126.1 (*E*), 125.8 (*Z*), 125.6 (*E*), 121.6 (*E*), 116.0 (*Z*), 115.4 (*E*), 104.3 (*E*), 104.0 (*Z*), 87.2 (*E*), 87.1 (*E*), 80.8 (*Z*), 80.6 (*Z*), 61.1 (*Z*), 56.8 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0961, Found 209.0962; IR (thin film, cm^{-1}): 3852, 3650, 1717, 1696, 1653, 1534, 1520, 720, 684.



1g

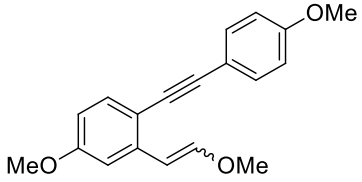
4-Methoxy-2-(2-methoxyvinyl)-1-(phenylethynyl)benzene (1g): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.3; yellowish oil (0.6: 1 *E*/*Z*), 74%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 2.6 Hz, 1H, *Z*), 7.56 – 7.49 (m, 2H, *Z* + 2H *E*), 7.44 (d, *J* = 8.5 Hz, 1H, *Z* + 1H, *E*), 7.38 – 7.29 (m, 3H, *Z* + 3H, *E*), 7.20 (d, *J* = 13.0 Hz, 1H, *E*), 6.89 (d, *J* = 2.5 Hz, 1H, *E*), 6.72 – 6.70 (m, 1H, *Z* + 1H, *E*), 6.34 (d, *J* = 13.0 Hz, 1H, *E*),

6.28 (d, *J* = 7.2 Hz, 1H, *Z*), 5.89 (d, *J* = 7.2 Hz, 1H, *Z*), 3.84 (s, 3H, *Z*), 3.83 (s, 3H, *E*), 3.82 (s, 3H, *Z*), 3.76 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.9 (*E*), 159.6 (*Z*), 150.5 (*E*), 149.5(*Z*), 139.8 (*E*), 138.8 (*Z*), 134.0 (*E*), 133.4 (*Z*), 131.5 (*Z*), 131.5 (*Z*),131.4 (*E*), 131.4 (*E*), 128.5 (*E*), 128.5 (*E*), 128.4 (*Z*), 128.4 (*Z*),128.0 (*E*), 127.9 (*Z*), 124.0 (*Z*), 124.0 (*E*), 113.9 (*Z*), 113.7 (*E*), 113.4 (*E*), 111.9 (*Z*), 111.8 (*E*), 109.0 (*Z*), 103.7 (*E*), 103.4 (*Z*), 92.5 (*Z*), 92.2 (*Z*), 88.7 (*E*), 88.6 (*E*), 61.1 (*Z*), 56.7 (*E*), 55.4 (*E*), 55.4 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ 265.1223, Found 265.1221; IR (thin film, cm^{-1}): 3838, 3676, 2921, 1734, 1700, 1560, 1540, 767, 679.



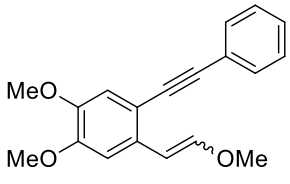
1h

1-((4-Chlorophenyl)ethynyl)-4-methoxy-2-(2-methoxyvinyl)benzene (1h): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.2; yellowish solid (1: 0.7 *E*/*Z*), Mp 77–79 ℃; 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 2.5 Hz, 1H, *Z*), 7.45 – 7.41 (m, 2H, *E* + 2H, *Z*), 7.37 – 7.29 (m, 3H, *E* + 3H, *Z*), 7.18 (d, *J* = 12.9 Hz, 1H, *E*), 6.89 (d, *J* = 2.5 Hz, 1H, *E*), 6.71 (ddd, *J* = 8.5 Hz, 2.4 Hz, 1.2 Hz, 1H, *Z* + 1H, *E*), 6.29 (d, *J* = 12.0 Hz, 7.7 Hz, 1H, *E* + 1H, *Z*), 5.84 (d, *J* = 7.2 Hz, 1H, *Z*), 3.84 (s, 3H, *Z*), 3.83 (s, 3H, *E*), 3.82 (s, 3H, *Z*), 3.75 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.0 (*E*), 159.8 (*Z*), 150.6 (*E*), 149.6 (*Z*), 139.9 (*E*), 138.8 (*Z*), 134.0 (*E*), 133.4 (*Z*), 132.7 (*Z*), 132.6 (*E*), 132.7 (*Z*), 132.6 (*E*), 128.8 (*E*), 128.7 (*Z*), 128.8 (*E*), 128.7 (*Z*), 128.6 (*Z*), 128.6 (*E*), 122.5 (*Z*), 122.5 (*E*), 114.0 (*Z*), 113.3 (*Z*), 113.0 (*E*), 111.9 (*Z*), 111.9 (*E*), 109.0 (*E*), 103.7 (*E*), 103.2 (*Z*), 91.4 (*E*), 91.1 (*E*), 89.7 (*Z*), 89.6 (*Z*), 61.1 (*Z*), 56.8 (*E*), 55.4 (*E*), 55.3 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{18}H_{16}O_2Cl$ $[M+H]^+$ 299.0833, Found 299.0856; IR (thin film, cm^{-1}): 3852, 3815, 3744, 3668, 3646, 1696, 1675, 1576, 1560, 1558, 696, 678.



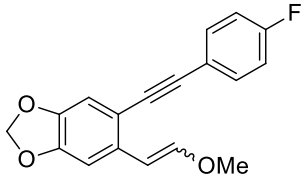
1i

4-Methoxy-1-((4-methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)benzene (1i): TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.3; yellowish solid (1: 0.5 *E*/*Z*), Mp 83–85 ℃; 65%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 2.6 Hz, 1H, *Z*), 7.47 – 7.44 (m, 2H, *E* + 2H, *Z*), 7.42 (d, *J* = 8.5 Hz, 1H, *E* + 1H, *Z*), 7.18 (d, *J* = 13.0 Hz, 1H, *E*), 6.91 – 6.85 (m, 3H, *E* + 2H, *Z*), 6.70 (dd, *J* = 8.5, 2.4 Hz, 1H, *E* + 1H, *Z*), 6.33 (d, *J* = 13.0 Hz, 1H, *E*), 6.27 (d, *J* = 7.2 Hz, 1H, *Z*), 5.88 (d, *J* = 7.2 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.83 (s, 3H, *Z*), 3.82 (s, 6H, *E*), 3.81 (s, 3H, *Z*), 3.75 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.6 (*E*), 159.5 (*E*), 159.4 (*Z*), 159.4 (*Z*), 150.4 (*E*), 149.4 (*Z*), 139.5 (*E*), 138.6 (*Z*), 133.8 (*E*), 133.2 (*Z*), 132.9 (*Z*), 132.8 (*E*), 132.9 (*Z*), 132.8 (*E*), 116.2 (*Z*), 116.1 (*E*), 114.1 (*E*), 114.1 (*Z*), 114.1 (*E*), 114.1 (*Z*), 114.0 (*Z*), 113.9 (*E*), 113.7 (*Z*), 111.8 (*Z*), 111.6 (*E*), 108.9 (*E*), 103.8 (*E*), 103.5 (*Z*), 92.4 (*E*), 92.1 (*Z*), 87.2 (*Z*), 87.1 (*E*), 61.0 (*Z*), 56.7 (*E*), 55.4 (*E* + *Z*), 55.4 (*E*), 55.3 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1329, Found 295.1300; IR (thin film, cm^{-1}): 3891, 3854, 3744, 3735, 3674, 2920, 1701, 1695, 1685, 718, 676.



1j

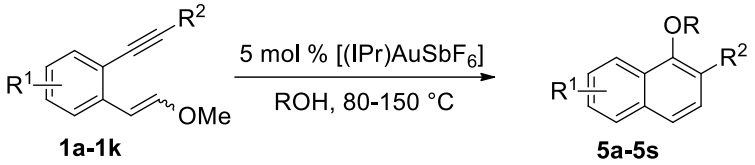
1, 2-Dimethoxy-4-(2-methoxyvinyl)-5-(phenylethynyl) benzene (1j): TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.25; yellowish oil (1: 0.7 *E*/*Z*); 63% ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72 (s, 1H, *Z*), 7.54 – 7.49 (m, 5H, *Z*), 7.33 (m, 5H, *E*), 7.09 (d, *J* = 13.0 Hz, 1H, *E*), 6.98 (s, 1H, *Z*), 6.98 (s, 1H, *E*), 6.82 (s, 1H, *E*), 6.30 (d, *J* = 13.0 Hz, 1H, *E*), 6.18 (d, *J* = 7.2 Hz, 1H, *Z*), 5.83 (d, *J* = 7.2 Hz, 1H, *Z*), 3.90 (s, 3H, *E*), 3.90 (s, 3H, *Z*), 3.88 (s, 3H, *E*), 3.88 (s, 3H, *Z*), 3.80 (s, 3H, *Z*), 3.73 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 149.8 (*E*), 149.2 (*Z*), 149.2 (*E*), 147.8 (*E*), 147.2 (*Z*), 146.9 (*Z*), 132.0 (*E*), 131.7 (*Z*), 131.5 (*Z*), 131.5 (*Z*), 131.4 (*E*), 131.4 (*E*), 128.5 (*E*), 128.5 (*E*), 128.4 (*Z*), 128.4 (*Z*), 128.1 (*E*), 128.0 (*Z*), 123.9 (*Z*), 123.8 (*E*), 114.7 (*E*), 114.2 (*Z*), 113.3 (*Z*), 112.7 (*E*), 111.6 (*Z*), 106.7 (*E*), 103.8 (*E*), 103.5 (*Z*), 92.6 (*E*), 92.3 (*Z*), 88.7 (*E*), 88.6 (*Z*), 60.9 (*Z*), 56.6 (*E*), 56.1 (*E*), 56.0 (*Z*), 56.0 (*E*), 55.9 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1329, Found 295.1331; IR (thin film, cm^{-1}) 3838, 3816, 3676, 1700, 1696, 1576, 1560, 1540, 747, 683.



1k

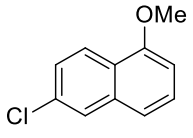
5-((4-Fluorophenyl)ethynyl)-6-(2-methoxyvinyl)benzo[*d*][1,3]dioxole (1k): TLC (petroleum ether:ethyl acetate, 30:1, v/v): R_f=0.2; yellowish solid (1: 0.4 *E*/*Z*), Mp 97–98 ℃; 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (s, 1H, *Z*), 7.51 – 7.45 (m, 2H, *E* + 2H, *Z*), 7.07 – 7.00 (m, 3H, *E* + 2H, *Z*), 6.92 (s, 1H, *Z*), 6.91 (s, 1H, *E*), 6.83 (s, 1H, *E*), 6.31 (d, *J* = 12.9 Hz, 1H, *E*), 6.18 (d, *J* = 7.2 Hz, 1H, *Z*), 5.96 (s, 2H, *Z*), 5.95 (s, 2H, *E*), 5.81 (d, *J* = 7.2 Hz, 1H, *Z*), 3.79 (s, 3H, *Z*), 3.72 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.5 (d, *J* = 247.8 Hz, *E*), 149.5 (*E*), 148.6 (*E*), 148.1 (*Z*), 148.0 (*Z*), 145.7 (*E*), 145.3 (*Z*), 133.6 (*E*), 133.3 (d, *J* = 8.3 Hz, *Z*), 133.3 (d, *J* = 8.3 Hz, *Z*), 133.2 (d, *J* = 8.3 Hz, *E*), 133.2 (d, *J* = 8.3 Hz, *E*), 132.9 (*Z*), 119.9 (d, *J* = 3.5 Hz, *Z*), 119.8 (d, *J* = 3.5 Hz, *E*), 115.8 (d, *J* = 21.9 Hz, *E*), 115.8 (d, *J* = 21.9 Hz, *E*), 115.7 (d, *J* = 21.9 Hz, *Z*), 115.7 (d, *J* = 21.9 Hz, *Z*), 114.1 (*Z*), 113.5 (*E*), 111.6 (*E*), 111.3 (*Z*), 108.9 (*Z*), 103.9 (*E*), 103.8 (*E*), 103.4 (*Z*), 101.4 (*E*), 101.4 (*Z*), 91.6 (*E*), 91.3 (*Z*), 88.4 (*Z*), 88.1 (*E*), 60.9 (*Z*), 56.8 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{18}H_{13}O_3Na$ $[M+Na]^+$ 319.0741, Found 319.0738; IR (thin film, cm^{-1}): 3854, 3821, 3802, 3752, 3671, 1700, 1684, 1653, 1635, 694, 686.

V. Characteration Data of Naphthalenes



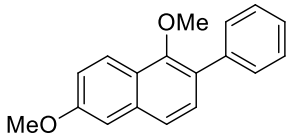
1a-1k **5a-5s**

General procedure for Au(I)-catalyzed cascade cyclization for the synthesis of naphthalenes: The 1,5-enyne substrate (1 mmol) and the [(IPr)$AuSbF_6$] (0.05 mmol, 36.9 mg) in ROH (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, evacuated, filled with nitrogen, and heated with stirring at 80–150 ℃ for 30–120h. The reaction mixture was cooled, filtered through a plug of silica gel. The filtrate was concentrated and the obtained residue was purified by flash column chromatography to afford the naphthalene.



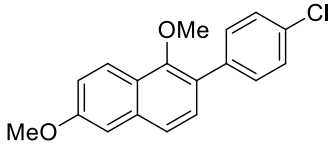
5e

6-Chloro-1-methoxynaphthalene (5e): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.2; white solid, Mp 46–47 ℃; 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.20 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 1.6 Hz, 1H), 7.41 (m, 2H), 7.33 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.6, 135.3, 132.5, 127.4, 126.3, 126.1, 124.1, 124.0, 119.4, 104.2, 55.7; HRMS (ESI): *m/z*: Calcd for $C_{11}H_{10}OCl$ $[M+H]^+$ 193.0414, Found 193.0417; IR (thin film, cm^{-1}): 3750, 3745, 1701, 1653, 1558, 1507, 761, 749, 676.



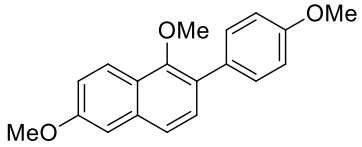
5g

1,6-Dimethoxy-2-phenylnaphthalene (5g): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.2; yellowish solid, Mp 112–114 ℃; 50%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.15 (d, J = 9.1 Hz, 1H), 7.68 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.48 – 7.45 (m, 3H), 7.36 (t, J = 7.3 Hz, 1H), 7.20 (dd, J = 9.1 Hz, 2.0 Hz, 1H), 7.17 (br.s, 1H), 3.95 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.2, 153.6, 139.0, 135.8, 129.5, 129.5, 129.5, 128.5, 128.5, 127.7, 127.0, 124.4, 123.9, 122.9, 119.0, 106.0, 61.3, 55.5; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ 265.1223, Found 265.1199; IR (thin film, cm^{-1}): 3854, 3821, 3752, 1700, 1685, 1653, 1635, 1507, 743, 728, 687.



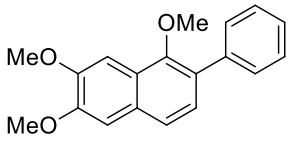
5h

2-(4-Chlorophenyl)-1,6-dimethoxynaphthalene (5h): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.3; yellowish solid, Mp 118–120 ℃; 51%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 (d, J = 9.1 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.42 (m, 3H), 7.21 (dd, J = 9.1 Hz, 2.1 Hz, 1H), 7.16 (s, 1H), 3.95 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.4, 153.6, 137.3, 136.0, 133.0, 130.8, 130.8, 129.0, 128.7, 128.7, 126.5, 124.4, 123.9, 123.1, 119.2, 106.0, 61.4, 55.5; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{16}O_2Cl$ $[M+H]^+$ 299.0833, Found 299.0728; IR (thin film, cm^{-1}): 3852, 3815, 3744, 3734, 3688, 3674, 1700, 1695, 1652, 1558, 1507, 714, 678.



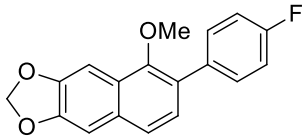
5i

1,6-Dimethoxy-2-(4-methoxyphenyl)naphthalene (5i): TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.2; yellowish solid, Mp 107–108 ℃; 30%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 (d, J = 9.1 Hz, 1H), 7.64 – 7.60 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 9.1 Hz, 2.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 7.02 – 6.97 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.8, 158.1, 153.3, 135.5, 131.3, 130.5, 130.5, 129.5, 128.8, 124.3, 124.0, 122.9, 118.9, 114.0, 114.0, 106.0, 61.1, 55.5, 55.4; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1328, Found 295.1330; IR (thin film, cm^{-1}): 3837, 3832, 3647, 1696, 1675, 1558, 1542, 747, 728, 688.



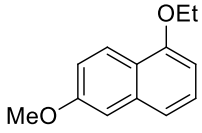
5j

1, 6, 7-Trimethoxy-2-phenylnaphthalene (5j): TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.3; yellowish solid, Mp 101–103 ℃; 50%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (d, J = 7.4 Hz, 2H), 7.52 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (m, 2H), 7.15 (s, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 152.3, 150.1, 150.0, 139.1, 130.3, 129.5, 129.5, 128.5, 128.5, 128.3, 127.1, 127.0, 124.1, 122.5, 106.5, 101.3, 60.9, 56.1, 56.1HRMS (ESI): *m/z*: Calcd for $C_{19}H_{18}O_3Na$ $[M+Na]^+$ 317.1148, Found 317.1150; IR (thin film, cm^{-1}): 3891, 3854, 3821, 3752, 3744, 1700, 1685, 1653, 1635, 1506, 743, 745, 677.



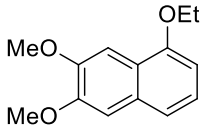
5k

6-(4-Fluorophenyl)-5-methoxynaphtho[2,3-*d*][1,3]dioxole (5k): TLC (petroleum ether:ethyl acetate, 40:1, v/v): R_f=0.3; yellow solid, Mp 120–122 ℃; 50%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.64 (m, 2H), 7.50 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.14 (m, 3H), 6.07 (s, 2H), 3.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.2 (d, J = 244.8 Hz), 152.8, 148.4, 148.2, 134.8 (d, J = 3.5 Hz), 131.7, 131.0 (d, J = 7.8 Hz), 131.0 (d, J =7.8 Hz), 127.8, 127.0, 125.5, 123.3, 115.4 (d, J = 21.2 Hz), 115.4 (d, J = 21.2 Hz), 104.1, 101.3, 99.2, 60.9; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{14}O_3F$ $[M+H]^+$ 297.0921, Found 297.0915; IR (thin film, cm^{-1}): 3854, 3821, 3816, 3801, 3671, 1700, 1696, 1653, 1560, 1539, 835, 694, 686.



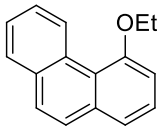
5l

1-Ethoxy-6-methoxynaphthalene (5l): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.2; white solid, Mp 63–65 ℃; 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.21 (d, J = 9.1 Hz, 1H), 7.39 – 7.28 (m, 1H), 7.16 – 7.07 (m, 1H), 6.68 (dd, J = 7.0 Hz, 0.9 Hz, 1H), 4.20 (q, J = 7.0 Hz, 1H), 3.92 (s, 1H), 1.54 (t, J = 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.2, 155.1, 136.0, 126.8, 124.0, 121.0, 119.2, 117.5, 105.8, 103.0, 63.8, 55.3, 15.0; HRMS (ESI): *m/z*: Calcd for $C_{13}H_{15}O_2$ $[M+H]^+$ 203.1067, Found 203.1010; IR (thin film, cm^{-1}): 3854, 3821, 1685, 1653, 1617, 1596, 1432, 1373, 747, 696.



5m

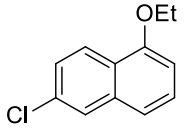
1-Ethoxy-6, 7-dimethoxynaphthalene (5m): TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.2; white solid, Mp 103–104 ℃; 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.09 (s, 1H), 6.72 (d, J = 7.5 Hz, 1H), 4.21 (q, J = 7.0 Hz, 2H), 4.03 (s, 3H), 4.00 (s, 3H), 1.55 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 153.9, 149.9, 149.0, 130.5, 124.4, 120.9, 118.8, 106.4, 103.8, 101.2, 63.8, 56.0, 55.9, 15.1; HRMS (ESI): *m/z*: Calcd for $C_{14}H_{17}O_3$ $[M+H]^+$ 233.1200, Found 233.1200; IR (thin film, cm^{-1}): 3860, 3854, 3836, 3732, 3611, 1683, 1558, 835, 743, 728, 681.



5n

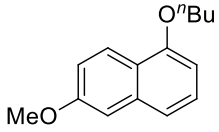
4-Ethoxyphenanthrene (5n): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; colorless oil, 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.80 (d, J = 8.6 Hz, 1H), 7.89 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.64 (ddd, J = 8.6 Hz, 7.0 Hz, 1.6 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.52 (d, J =

6.9 Hz, 2H), 7.16 (t, *J* = 6.6 Hz, 1H), 4.36 (q, *J* = 6.9 Hz, 2H), 1.72 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.3, 134.8, 132.9, 130.7, 128.8, 128.4, 128.1, 127.3, 126.6, 126.5, 125.9, 121.6, 120.9, 109.3, 64.8, 15.3; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{14}OK$ $[M+K]^+$ 261.1271, Found 261.1271; IR (thin film, cm^{-1}): 3881, 3854, 3749, 3646, 3612, 1675, 1559, 1539, 792, 683.



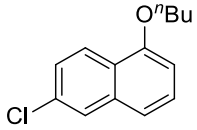
5o

6-Chloro-1-ethoxynaphthalene (5o): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; white solid, Mp 51–52 ℃; 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.20 (q, *J* = 6.9 Hz, 2H), 1.55 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.0, 135.4, 132.4, 127.4, 126.2, 125.9, 124.2, 124.1, 119.2, 105.0, 63.9, 15.0; HRMS (ESI): *m/z*: Calcd for $C_{12}H_{12}OCl$ $[M+H]^+$ 207.0571, Found 207.0571; IR (thin film, cm^{-1}): 3851, 3801, 3749, 3647, 1700, 1635, 1539, 1505, 746, 729, 679.



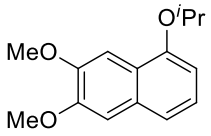
5p

1-Butoxy-6-methoxynaphthalene (5p): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.25; white solid, Mp 46–47 ℃; 65%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 9.0 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.11 (m, 1H), 6.69 – 6.67 (m, 1H), 4.13 (t, *J* = 6.4 Hz, 1H), 3.92 (s, 1H), 1.90 (tt, *J* = 12.7 Hz, 6.4 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.2, 155.3, 136.0, 126.9, 124.0, 121.09, 119.1, 117.5, 105.8, 102.9, 67.9, 55.4, 31.6, 19.6, 14.1; HRMS (ESI): *m/z*: Calcd for $C_{15}H_{19}O_2$ [M+H]+ 231.1380, Found 231.1377; IR (thin film, cm^{-1}): 3870, 3807, 3801, 3750, 1653, 1557, 774, 685.



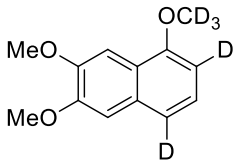
5q

1-Butoxy-6-chloronaphthalene (5q): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; colorless oil, 60%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 1H), 1.97 – 1.82 (m, 1H), 1.60 (dd, *J* = 15.0 Hz, 7.5 Hz, 1H), 1.03 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.1, 135.4, 132.4, 127.5, 126.2, 125.9, 124.2, 124.1, 119.2, 104.9, 68.1, 31.5, 19.6, 14.1; HRMS (ESI): *m/z*: Calcd for $C_{14}H_{16}OCl$ $[M+H]^+$ 235.0884, Found 235.0885; IR (thin film, cm^{-1}): 3815, 3743, 3674, 1652, 780, 675.



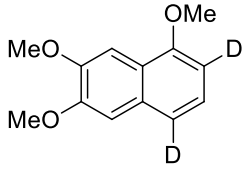
5r

1-Isopropoxy-6,7-dimethoxynaphthalene (5r): TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.2; white solid, Mp 71–73 ℃; 50%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.54 (s, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.09 (s, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 4.73 (dt, *J* = 12.1 Hz, 6.0 Hz, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 152.9, 149.9, 149.0, 130.7, 124.4, 121.8, 118.7, 106.3, 105.6, 101.5, 70.6, 56.0, 55.9, 22.4, 22.4; HRMS (ESI): *m/z*: Calcd for $C_{15}H_{18}O_3Na$ $[M+Na]^+$ 269.1148, Found 269.1152; IR (thin film, cm^{-1}): 3734, 3711,1652, 1635, 1542, 1507, 841, 743.



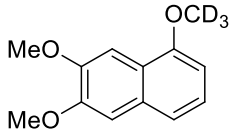
5c-D

d5-1,6,7-Trimethoxynaphthalene (5c-D): TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.3; white solid, Mp 120–121 ℃; 79%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.54 (s, 1H), 7.25 (s, 1H), 7.10 (s, 1H), 4.02 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.6, 149.9, 149.1, 130.4, 124.2, 120.7, 118.7 (t), 106.3, 102.5 (t), 101.1, 56.0, 55.9; HRMS (ESI): *m/z*: Calcd for $C_{13}H_{10}O_3D_5$ $[M+H]^+$ 224.1330, Found 224.1310; IR (thin film, cm^{-1}): 3891, 3854, 3821, 3752, 3744, 1700, 1653, 1635, 1506, 826, 745, 677.



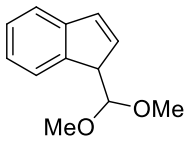
5c-D-1

d2-1,6,7-Trimethoxynaphthalene (5c-D-1): TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.3; white solid, Mp 120–121 ℃; 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.54 (s, 1H), 7.25 (s, 1H), 7.10 (s, 1H), 4.02 (s, 3H), 4.00 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.6, 149.9, 149.1, 130.4, 124.2, 120.7, 118.7 (t), 106.4, 102.5 (t), 101.1, 56.0, 55.9, 55.6; HRMS (ESI): *m/z*: Calcd for $C_{13}H_{13}O_3D_2$ $[M+H]^+$ 221.1147, Found 221.1151; IR (thin film, cm^{-1}): 3890, 3855, 3821, 3752, 3744, 1700, 1655, 1635, 1506, 826, 745, 679.



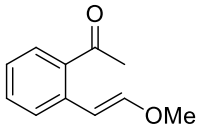
5c-D-2

d3-1,6,7-Trimethoxynaphthalene (5c-D-2): TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.3; white solid, Mp 120–121 ℃; 74%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.54 (s, 1H),7.29 (br.d, *J* = 8.0 Hz, 1H), 7.26 (m, 1H), 7.10 (s, 1H), 6.72 (dd, *J* = 7.4, 0.8 Hz,), 4.02 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.6, 149.9, 149.1, 130.4, 124.4, 120.7, 118.79, 106.4, 102.8, 101.1, 56.0, 55.9, 54.8 (t); HRMS (ESI): *m/z*: Calcd for $C_{13}H_{12}O_3D_3$ $[M+H]^+$ 222.1209, Found 222.1211; IR (thin film, cm^{-1}): 3891, 3853, 3821, 3755, 3744, 1700, 1653, 1636, 1506, 826, 745, 677.



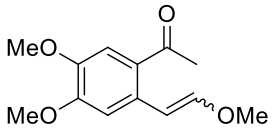
3

1-(Dimethoxymethyl)-1H-indene (3): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; yellowish oil, 42 %; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.88 (dd, *J* = 5.5 Hz, 1.5 Hz, 1H), 6.48 (dd, *J* = 5.6 Hz, 1.8 Hz, 1H), 4.07 (d, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 8.0 Hz, 1H), 3.48 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.1, 143.2, 135.0, 133.1, 127.2, 125.1, 125.0, 121.1, 105.7, 54.5, 53.8, 53.7; HRMS (ESI): *m/z*: Calcd for $C_{12}H_{14}O_2Na$ $[M+Na]^+$ 213.0886, Found 213.0874; IR (thin film, cm^{-1}): 3400, 2880, 2700, 1696, 1476, 1400, 748.



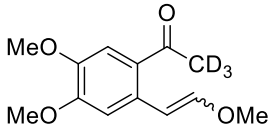
6

(*E*)-1-(2-(2-Methoxyvinyl) phenyl)ethanone (6): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.25; colorless oil, 61%; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.71 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.41 (td, J = 7.8 Hz, 1.1 Hz, 1H), 7.25 (td, J = 7.7 Hz, 1.1 Hz, 1H), 7.14 (d, J = 12.9 Hz, 1H), 6.38 (d, J = 12.9 Hz, 1H), 3.63 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 202.1, 150.9, 135.9, 134.8, 131.4, 129.3, 125.7, 125.4, 103.2, 56.5, 30.0; HRMS (ESI): *m/z*: Calcd for $C_{11}H_{13}O_2$ $[M+H]^+$ 77.0910, Found 177.0913; IR (thin film, cm^{-1}): 3675, 3668, 3647, 1696, 1576, 1558, 1539, 748, 680.



6c

(*E*/*Z*)-1-(4, 5-Dimethoxy-2-(2-methoxyvinyl) phenyl)ethanone (6c): TLC (petroleum ether:ethyl acetate, 10:1, v/v): R_f=0.3; white solid (1: 0.4 *E*/*Z*), Mp 66–68 ℃; 93%; ^{1}H NMR (600 MHz, CD_3OD) δ = 7.56 (s, 1H, *Z*), 7.29 (s, 1H, *E*), 7.22 (s, 1H, *Z*), 6.98 (d, J = 12.9 Hz, 1H, *E*), 6.94 (s, 1H, *E*), 6.55 (d, J = 12.8 Hz, 1H, *E*), 6.19 (d, J = 7.3 Hz, 1H, *Z*), 5.83 (d, J = 7.3 Hz, 1H, *Z*), 3.88 (s, 3H, *E*), 3.85 (s, 3H, *E*), 3.85 (s, 3H, *Z*), 3.84 (s, 3H, *Z*), 3.74 (s, 3H, *Z*), 3.67 (s, 3H, *E*), 2.54 (s, 3H, *E*), 2.53 (s, 3H, *Z*); ^{13}C NMR (150 MHz, CD_3OD) δ = 203.7 (*Z*), 202.9 (*E*), 153.6 (*Z*), 152.6 (*Z*), 151.5 (*E*), 149.4 (*E*), 148.2 (*E*), 147.8 (*Z*), 132.9 (*E*), 130.9 (*Z*), 130.8 (*Z*), 129.2 (*E*), 114.8 (*E*), 114.4 (*Z*), 113.8 (*Z*), 110.5 (*E*), 105.4 (*E*), 103.9 (*Z*), 60.9 (*Z*), 56.9 (*E*), 56.7 (*E*), 56.6 (*Z*), 56.4 (*E*), 56.2 (*Z*), 29.9 (*E*), 29.9 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{13}H_{16}O_4Na$ $[M+Na]^+$ 259.0941, Found 259.0939; IR (thin film, cm^{-1}): 3890, 3864, 3853, 3836, 3751, 3690, 3668, 3687, 1750, 1729, 1695, 1560, 1558, 1541, 786, 683.



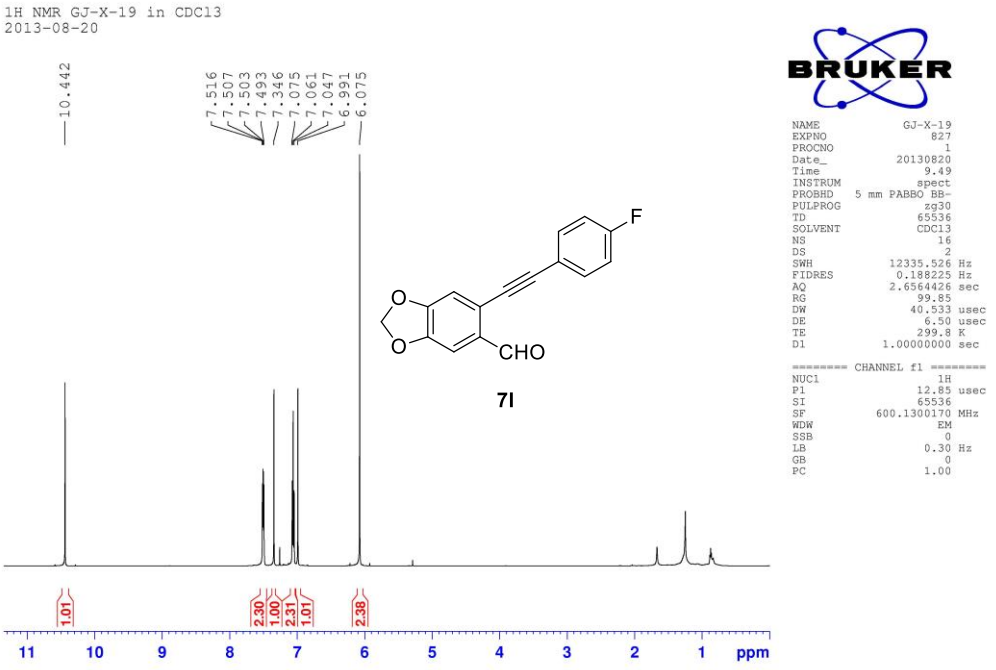
6c-D

d3-(*E*/*Z*)-1-(4,5-Dimethoxy-2-(2-methoxyvinyl)phenyl)ethanone (6c-D): TLC (petroleum ether:ethyl acetate, 10:1, v/v): R_f=0.25; white solid (1: 0.4 *E*/*Z*), Mp 58–59 ℃; 90%; ^{1}H NMR (600 MHz, CD_3OD) δ = 7.56 (s, 1H, *Z*), 7.29 (s, 1H, *E*), 7.22 (s, 1H, *Z*), 6.98 (d, J = 12.9 Hz, 1H, *E*), 6.94 (s, 1H, *E*), 6.56 (d, J = 12.8 Hz, 1H, *E*), 6.19 (d, J = 7.3 Hz, 1H, *Z*), 5.84 (d, J = 7.3 Hz, 1H, *Z*), 3.89 (s, 3H, *E*), 3.85 (s, 3H, *E*), 3.85 (s, 3H, *Z*), 3.84 (s, 3H, *Z*), 3.74 (s, 3H, *Z*), 3.68 (s, 3H, *E*); ^{13}C NMR (150 MHz, CD_3OD) δ = 203.8 (*Z*), 203.0 (*E*), 153.7 (*Z*), 152.7 (*Z*), 151.5 (*E*), 149.4 (*E*), 148.2 (*E*), 147.8 (*Z*), 132.9 (*E*), 130.9 (*Z*), 130.7 (*Z*), 129.2 (*E*), 114.8 (*E*), 114.4 (*Z*), 113.8 (*Z*), 110.5 (*E*), 105.4 (*E*), 103.9 (*Z*), 60.9 (*Z*), 56.9 (*E*), 56.7 (*E*), 56.6 (*Z*), 56.4 (*E*), 56.2 (*Z*), 30.5 (hepta, *E*), 29.3 (hepta, *Z*); HRMS (ESI): M/Z: Calcd for $C_{13}H_{13}O_3D_3Na$ $[M+Na]^+$ 262.1129, Found 262.1125; IR (thin film, cm^{-1}): 3821, 3752, 1700, 1652, 1635, 706, 693.

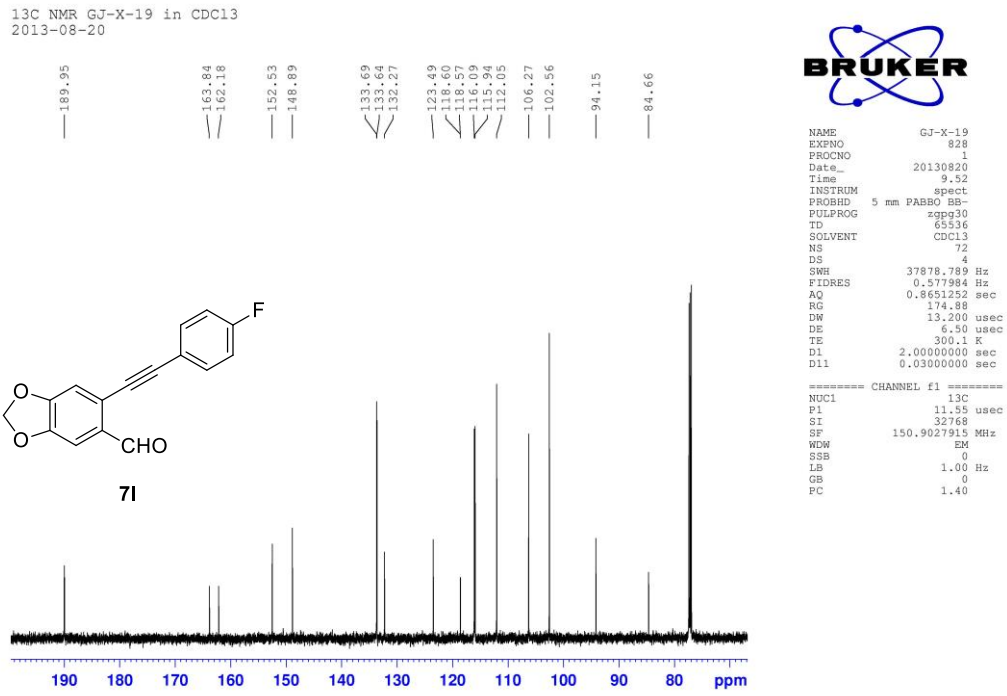
References

[1] Park, J. H.; Bhilare, S. V.; Youn, S. W. *Org*. *Lett*. **2011**, *13*, 2228.
[2] Ohta,Y.; Kubota,Y.; Watabe, T.; Chiba, H.; Oishi, S.; Fujii, N.; Ohno, H. *J*. *Org*. *Chem*. **2009**, *74*, 6299.
[3] Inga,C.; Rita,B.; Rokas, S. *Tetrahedron* **2011**, *67*, 706.
[4] Yoshida,K.; Shida, H.; Takahashi, H.; Yanagisawa, A. *Chem*. *Eur*. *J*. **2011**, *17*, 344.
[5] Li, M. M.; Xing, P.; Huang, Z. G.; Jiang, B. *Chin*. *J*. *Chem*. **2013**, *31*, 49.
[6] Jorg, B.; Norbert, L.; Thomas, M.; Wolfgang, E. *Chem*. *Ber*. **1994**, *12*, 247.
[7] Tsukamoto, H.; Ueno, T.; Kondo, Y. *J*. *Am*. *Chem*. *Soc*. **2006**, *128*, 1406.
[8] Enomoto, T.; Girard, A. L.; Yasui, Y.; Takemoto, Y. *J*. *Org*. *Chem*. **2009**, *74*, 9158.

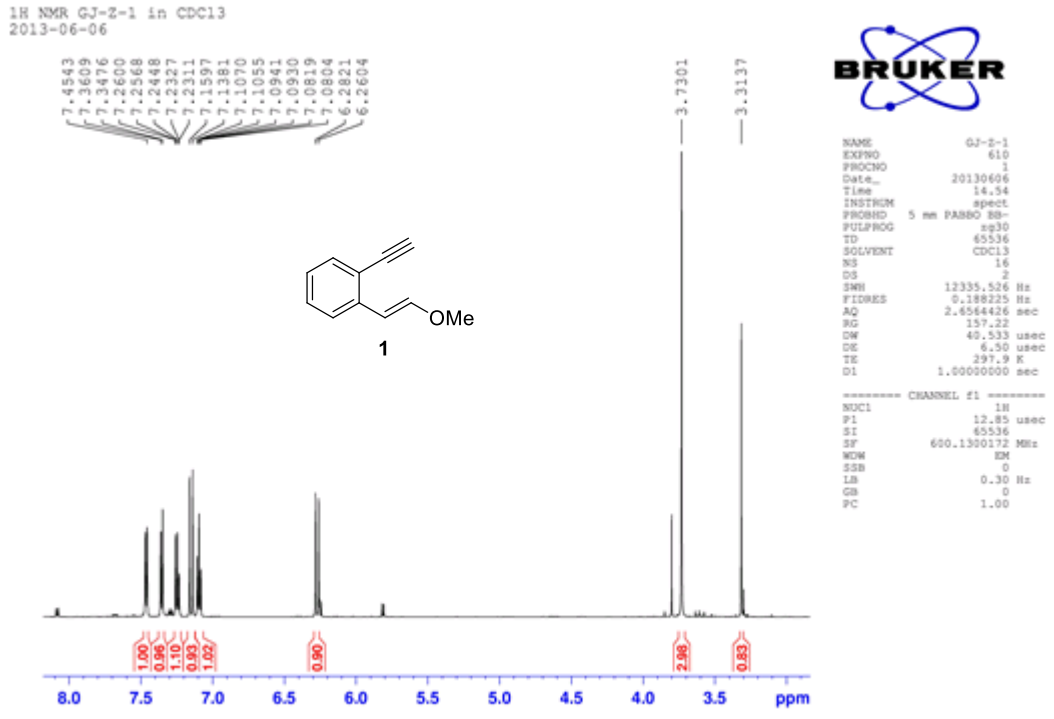
VII.NMR Spectra



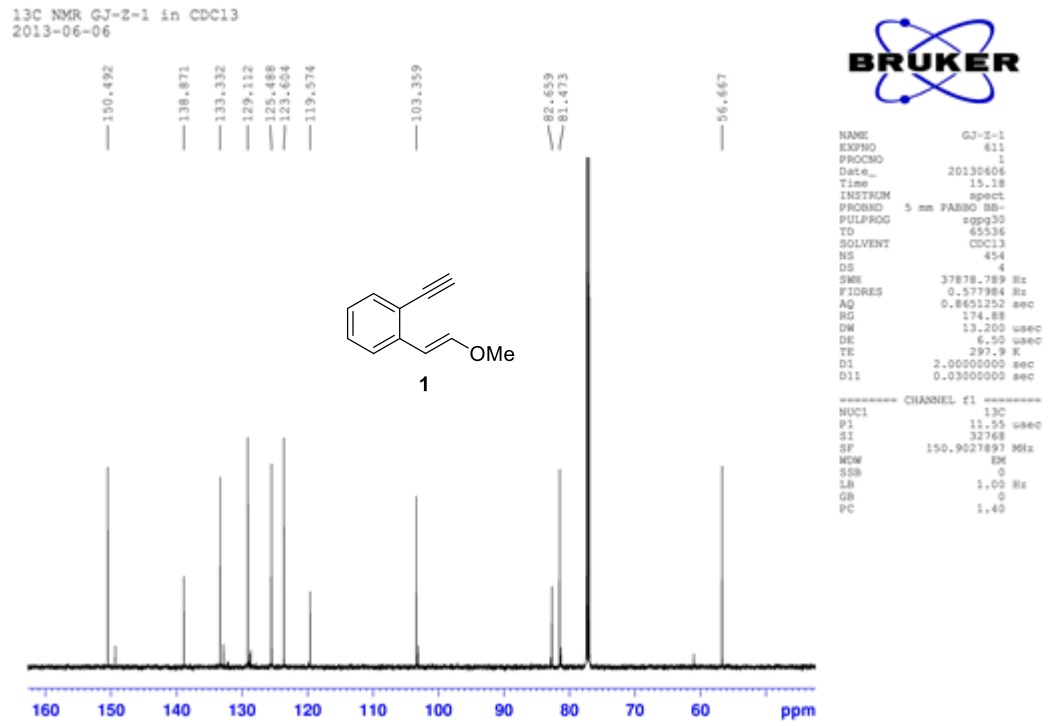
^{1}H NMR Spectrum of Compound **7l** ($CDCl_3$, 600 MHz)



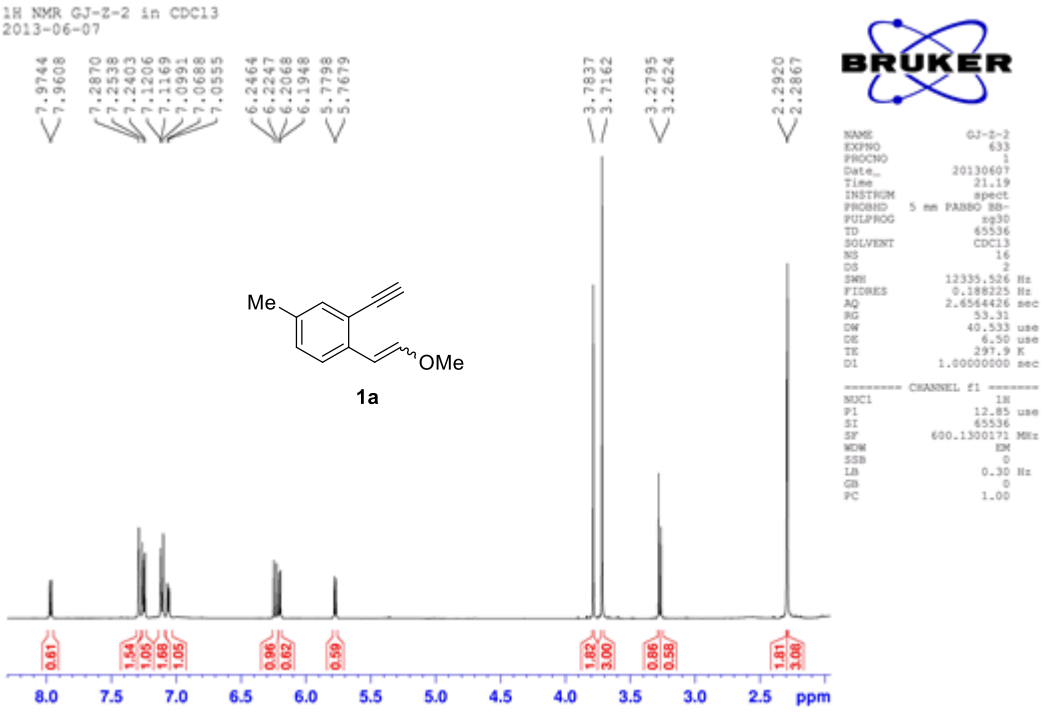
^{13}C NMR Spectrum of Compound **7l** ($CDCl_3$, 150 MHz)



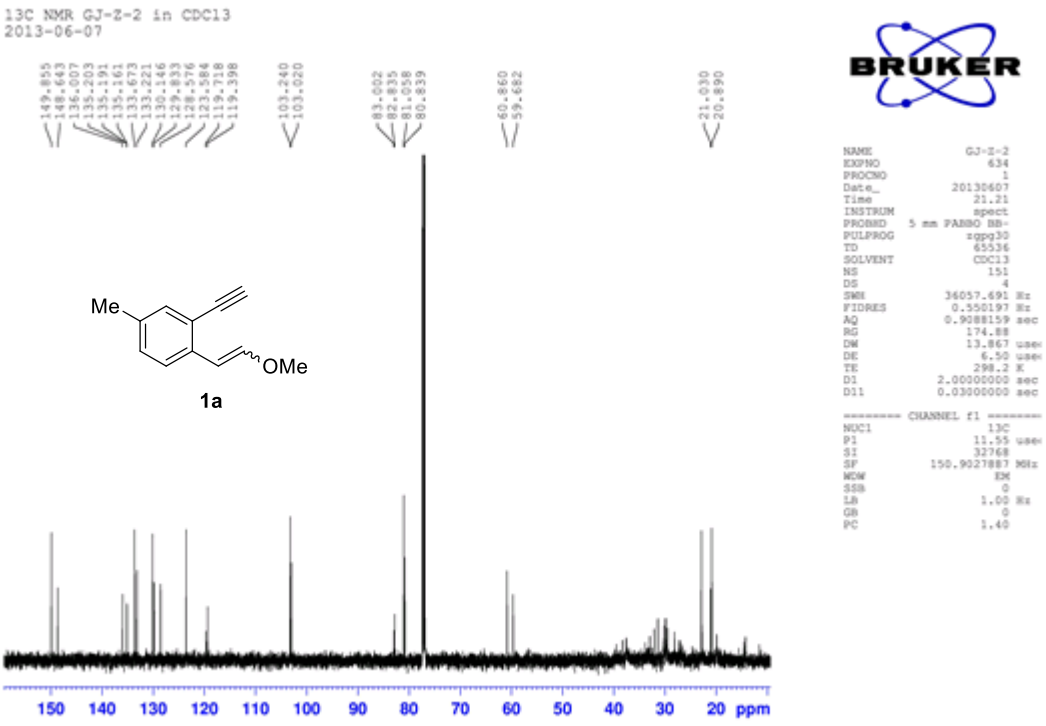
^{1}H NMR Spectrum of Compound **1** ($CDCl_3$, 600 MHz)



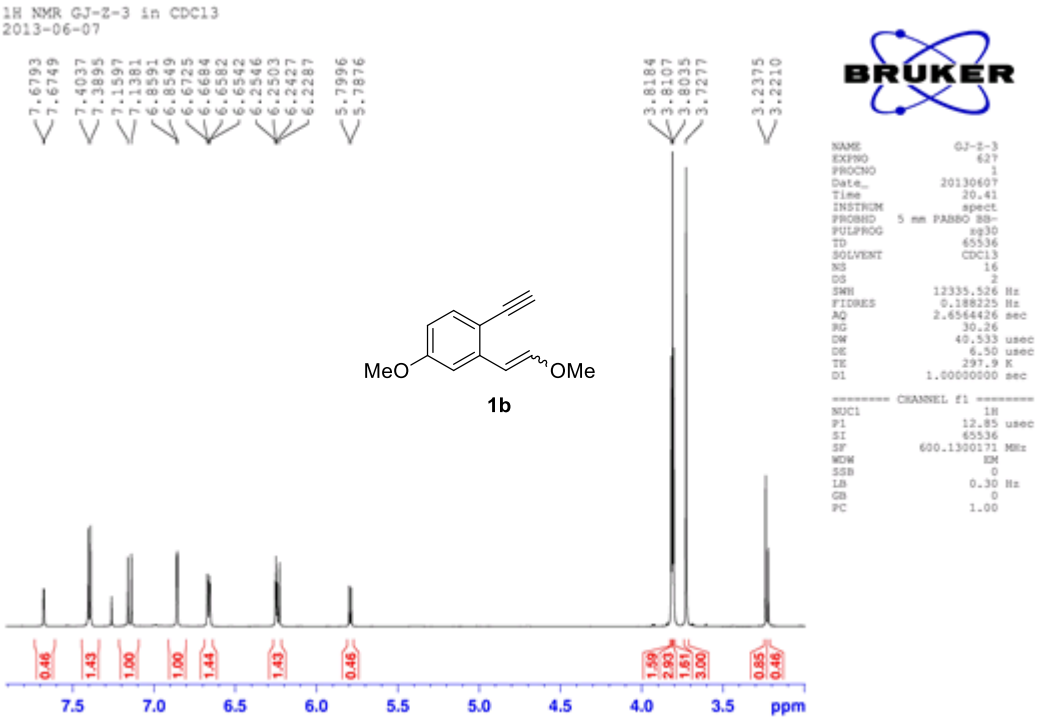
^{13}C NMR Spectrum of Compound **1** ($CDCl_3$, 150 MHz)



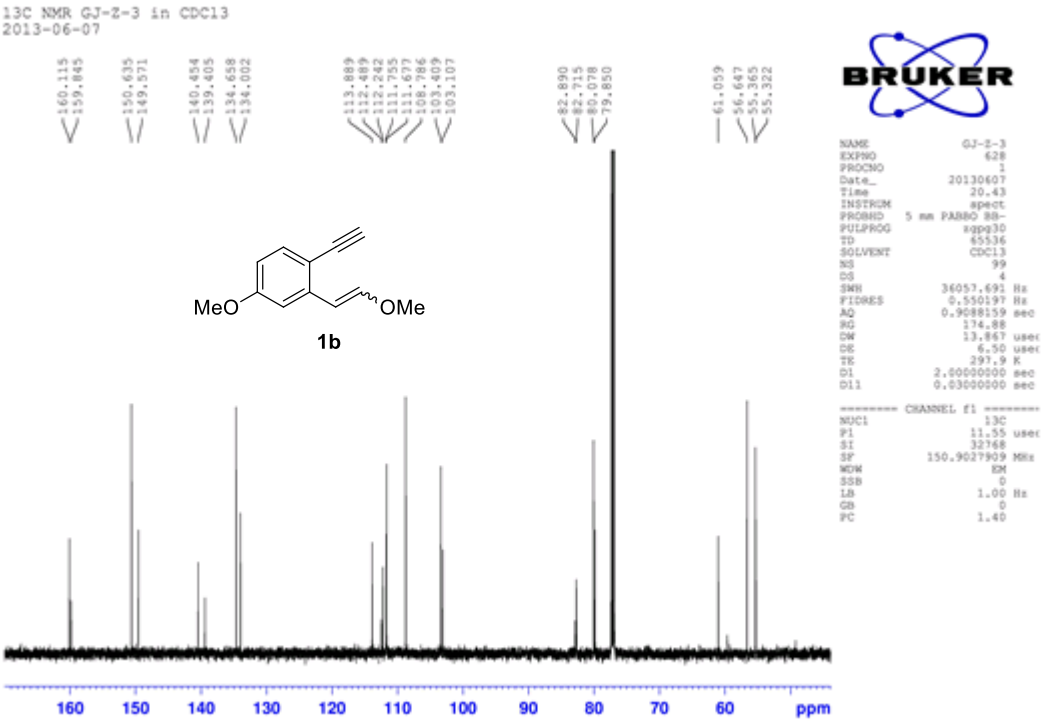
^{1}H NMR Spectrum of Compound **1a** ($CDCl_3$, 600 MHz)



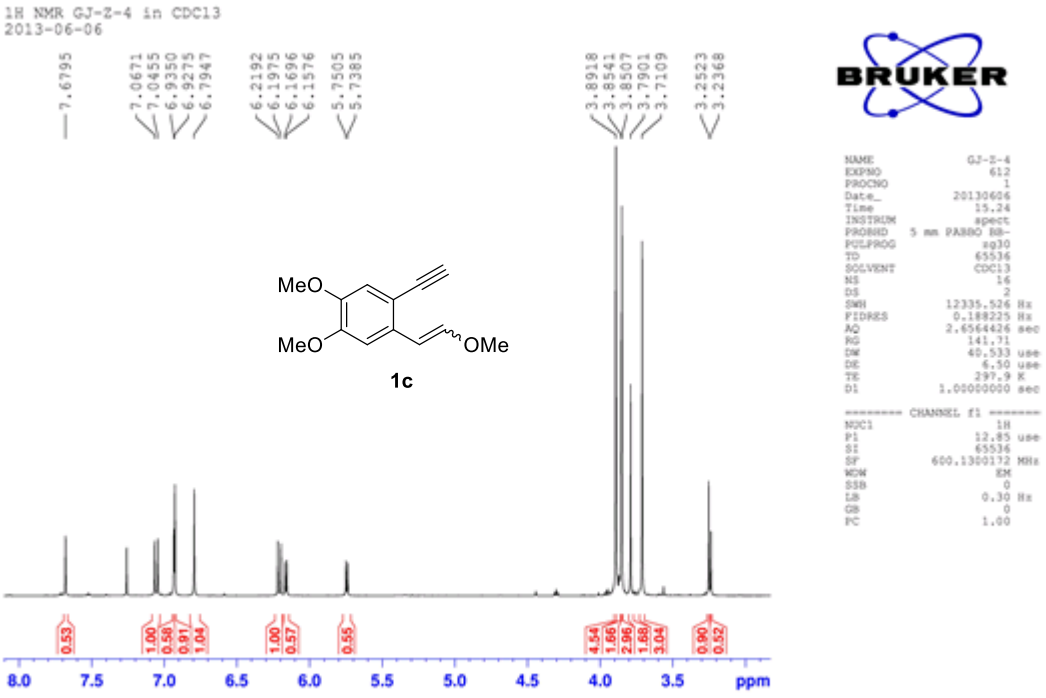
^{13}C NMR Spectrum of Compound **1a** ($CDCl_3$, 150 MHz)



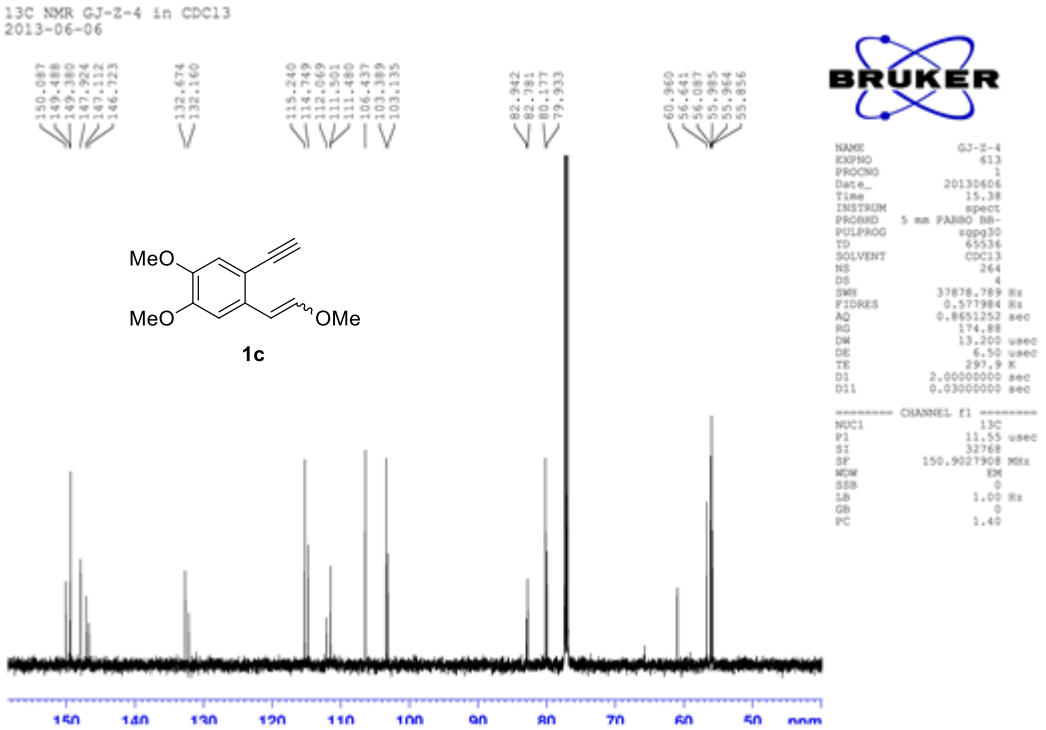
^{1}H NMR Spectrum of Compound **1b** ($CDCl_3$, 600 MHz)



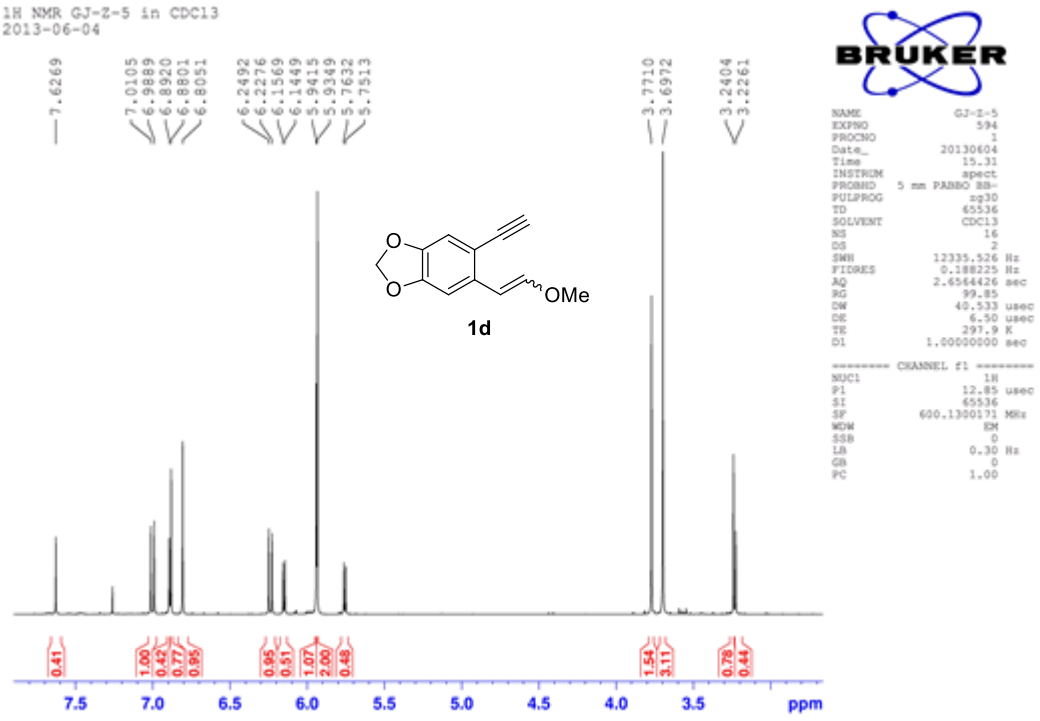
^{13}C NMR Spectrum of Compound **1b** ($CDCl_3$, 150 MHz)



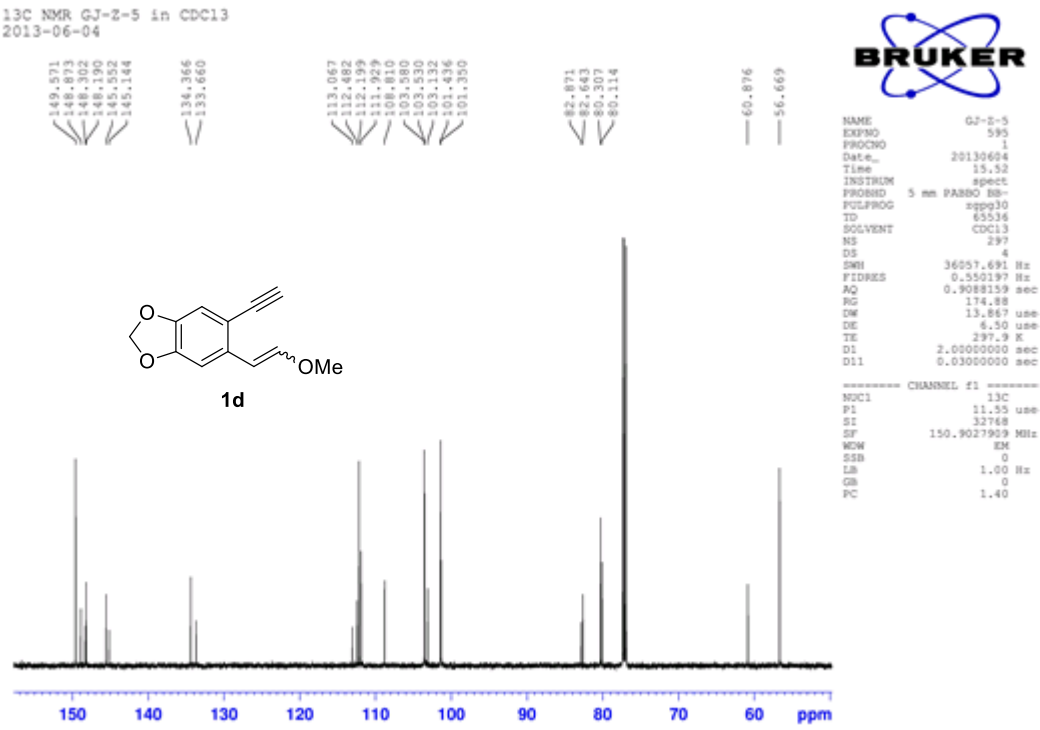
^{1}H NMR Spectrum of Compound **1c** ($CDCl_3$, 600 MHz)



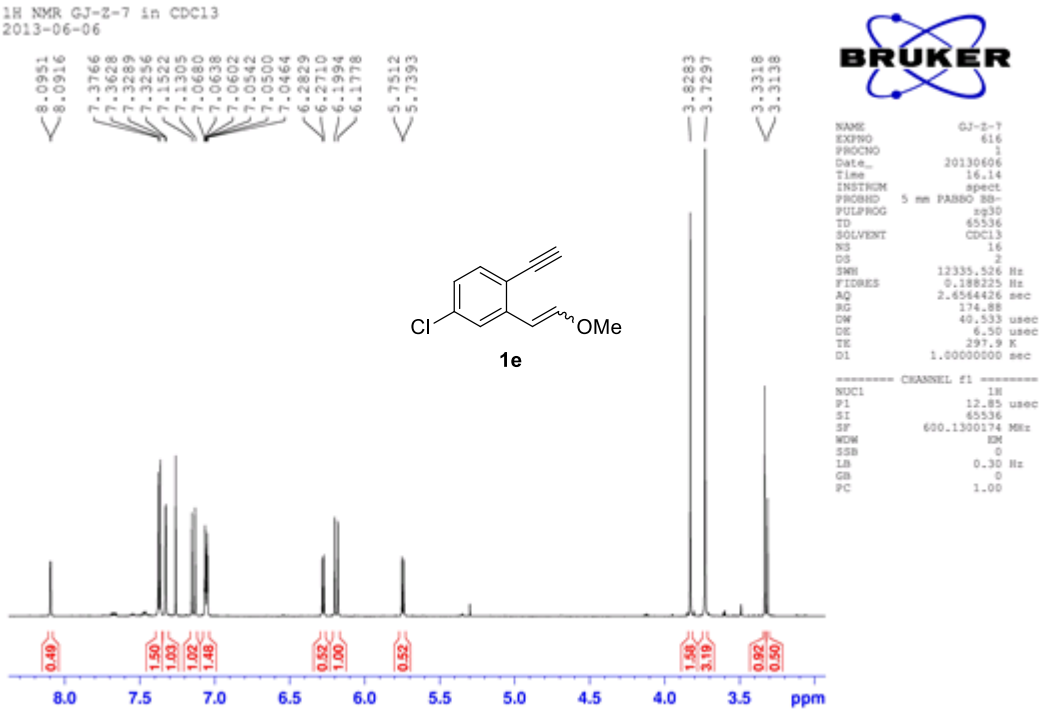
^{13}C NMR Spectrum of Compound **1c** ($CDCl_3$, 150 MHz)



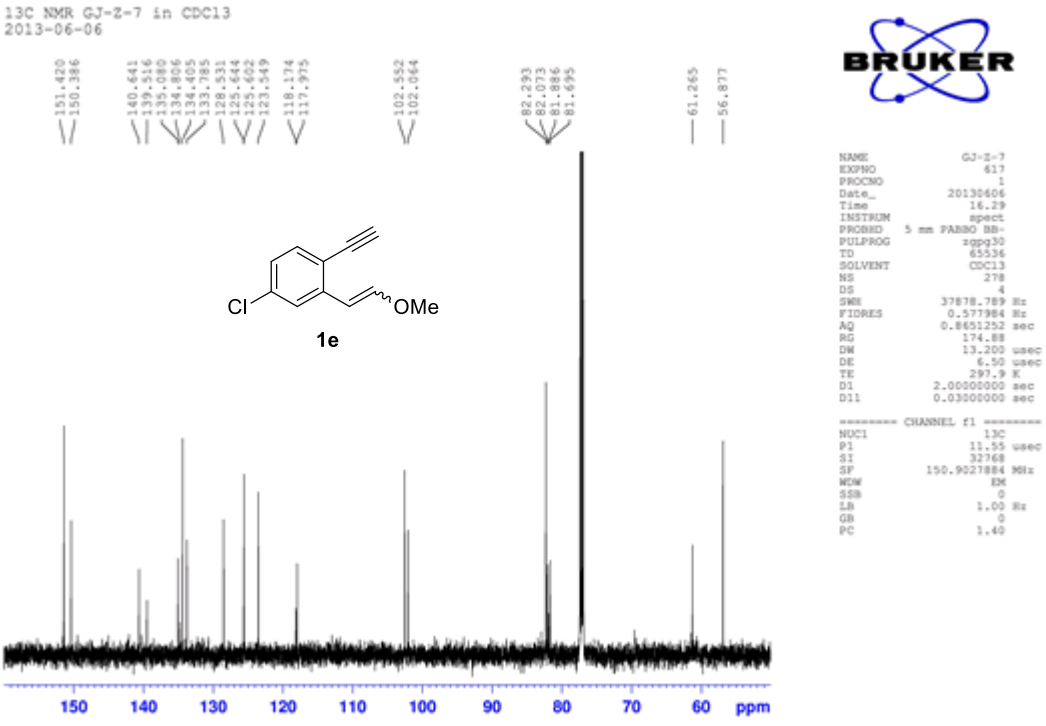
^{1}H NMR Spectrum of Compound **1d** ($CDCl_3$, 600 MHz)



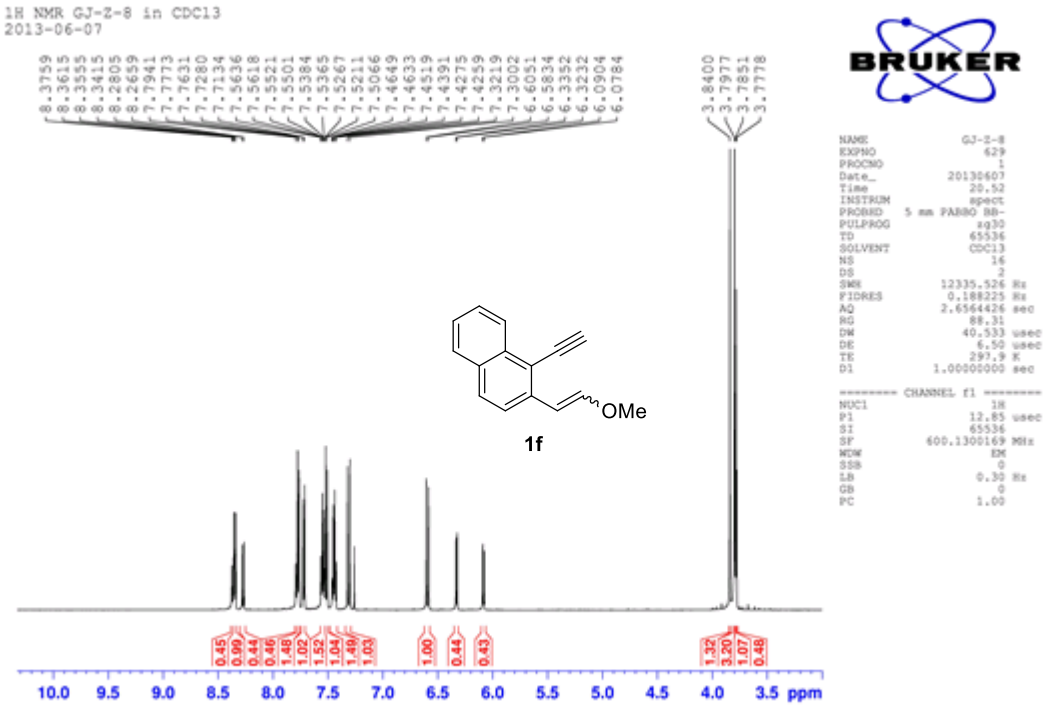
^{13}C NMR Spectrum of Compound **1d** ($CDCl_3$, 150 MHz)



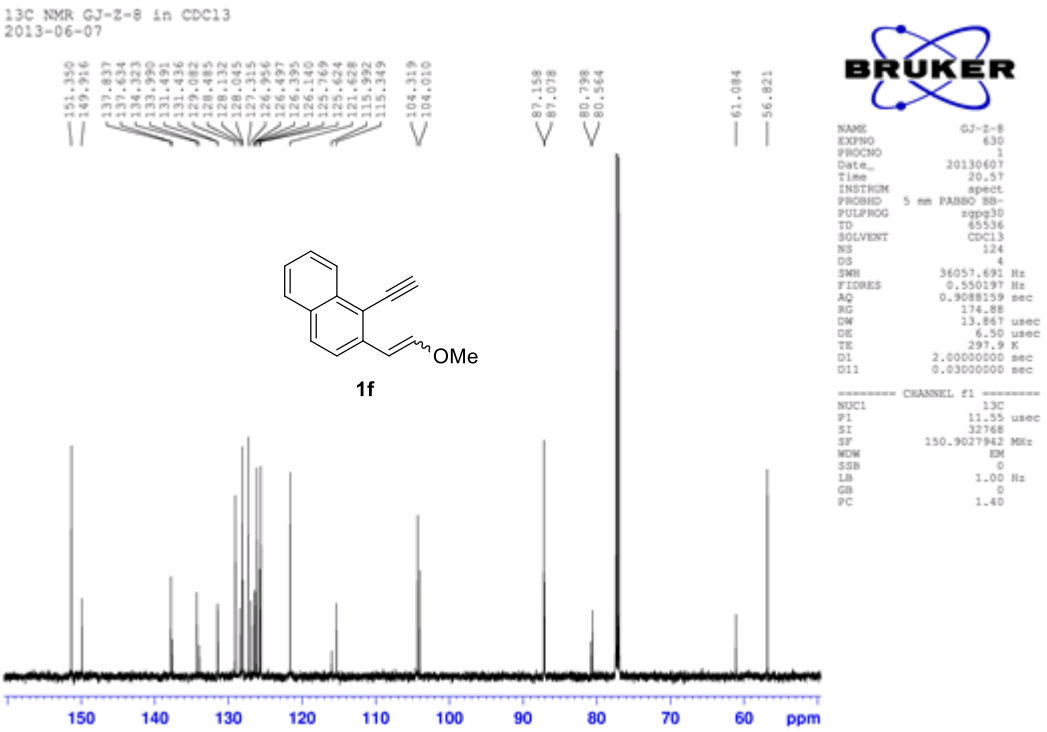
^{1}H NMR Spectrum of Compound **1e** ($CDCl_3$, 600 MHz)



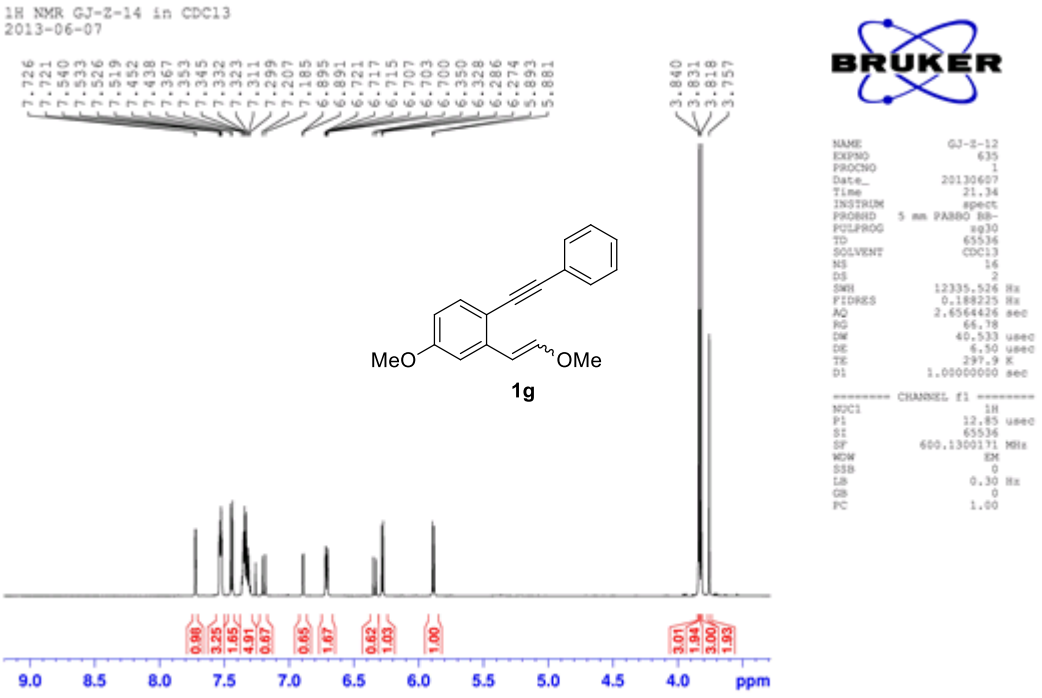
^{13}C NMR Spectrum of Compound **1e** ($CDCl_3$, 150 MHz)



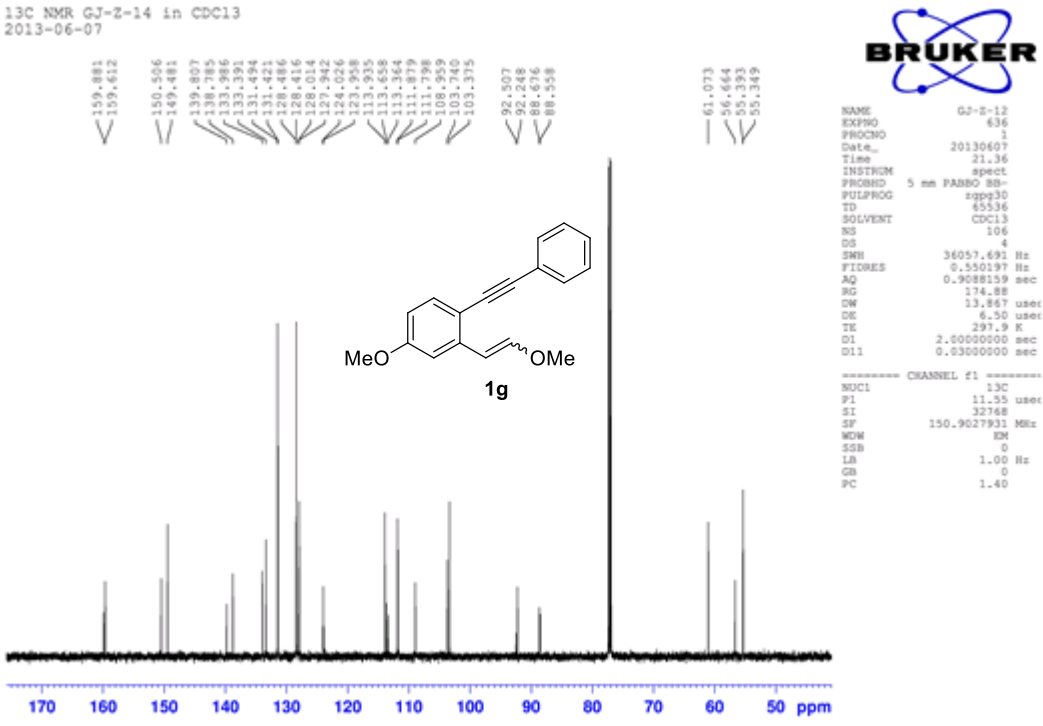
^{1}H NMR Spectrum of Compound **1f** ($CDCl_3$, 600 MHz)



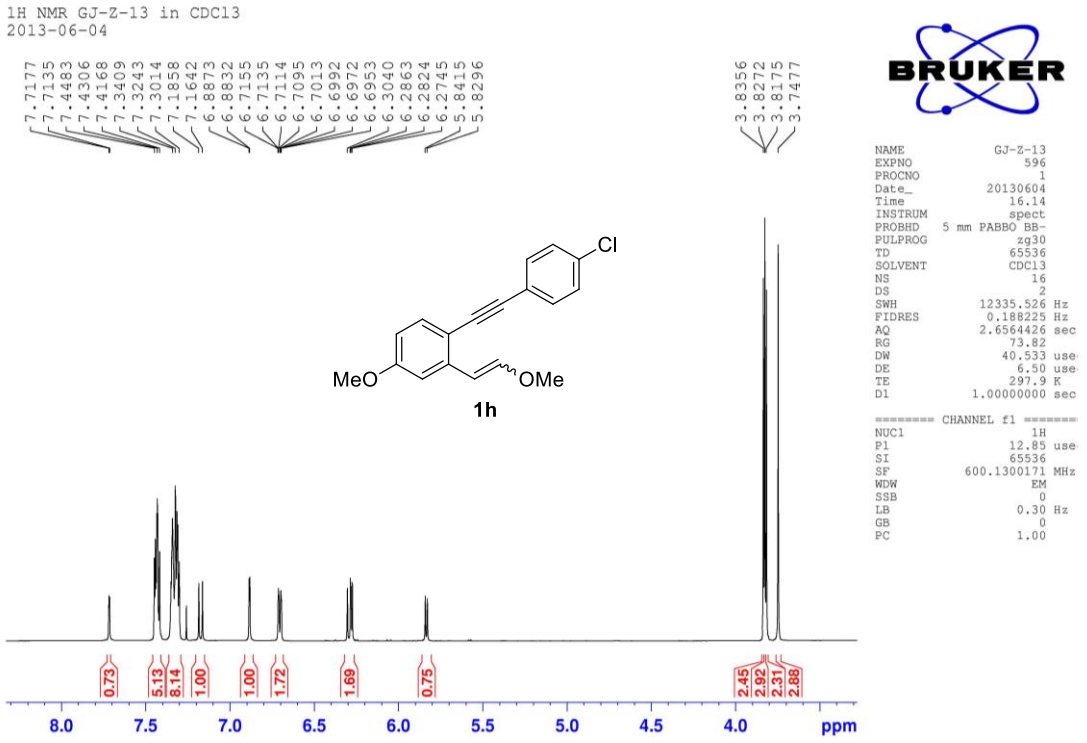
^{13}C NMR Spectrum of Compound **1f** ($CDCl_3$, 150 MHz)



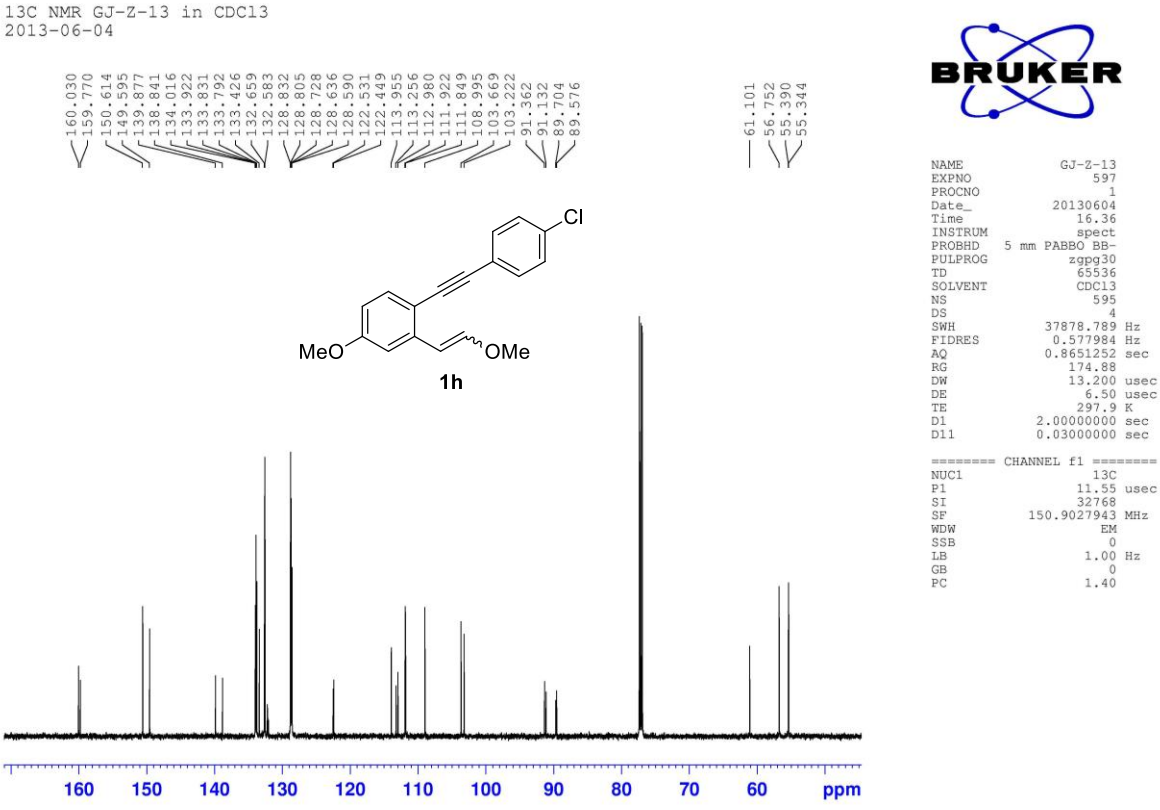
^{1}H NMR Spectrum of Compound **1g** ($CDCl_3$, 600 MHz)



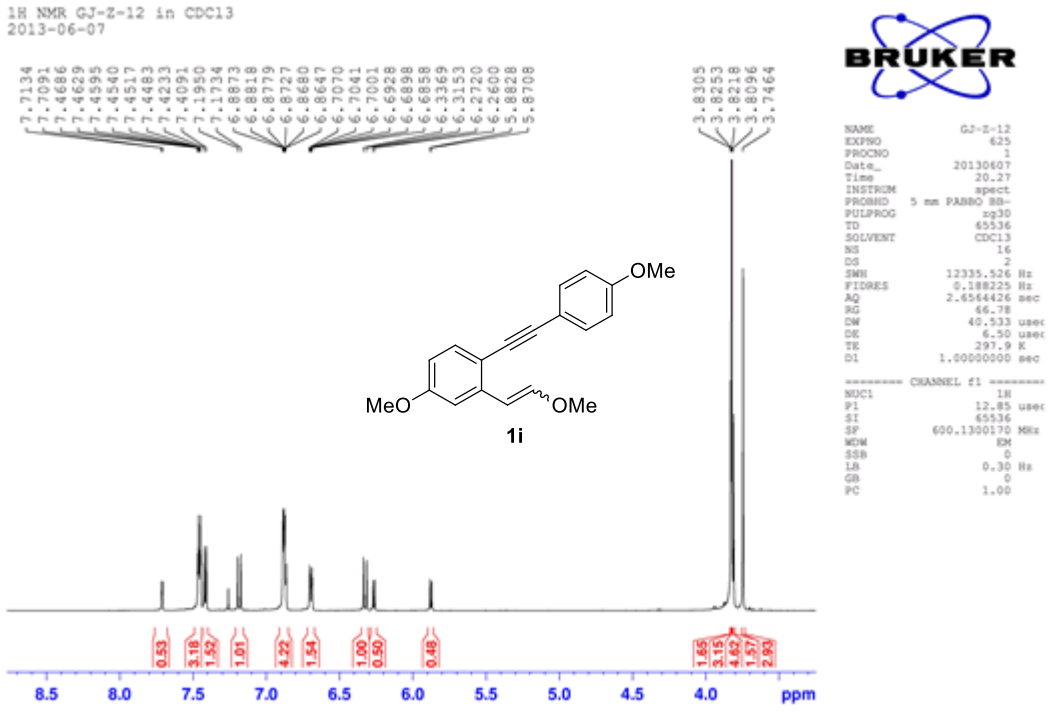
^{13}C NMR Spectrum of Compound **1g** ($CDCl_3$, 150 MHz)



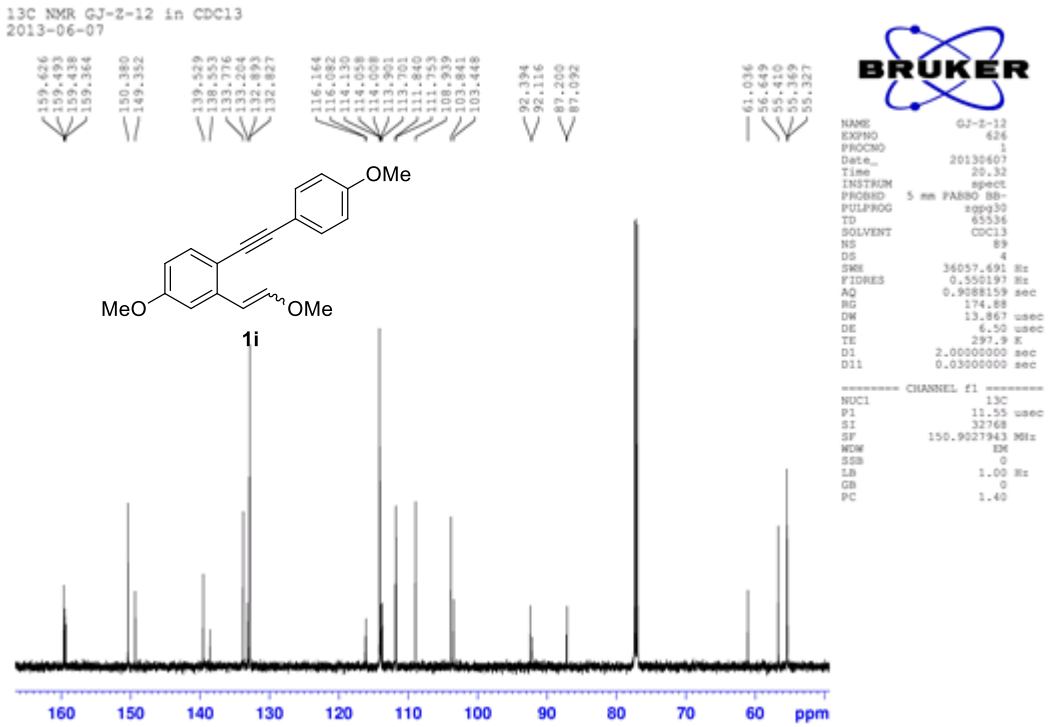
^{1}H NMR Spectrum of Compound **1h** ($CDCl_3$, 600 MHz)



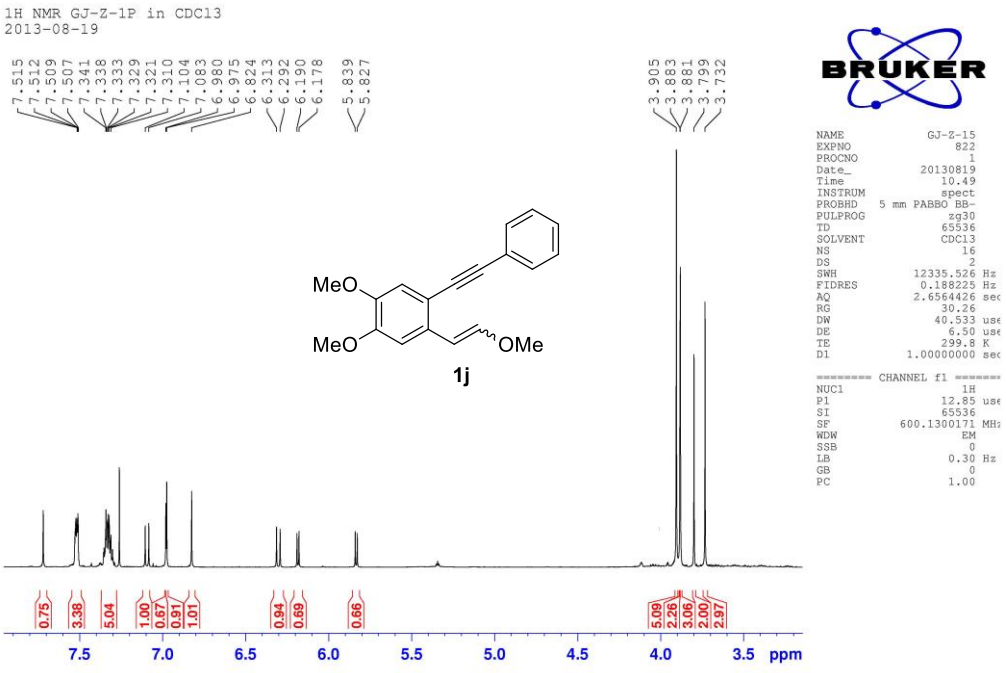
^{13}C NMR Spectrum of Compound **1h** ($CDCl_3$, 150 MHz)



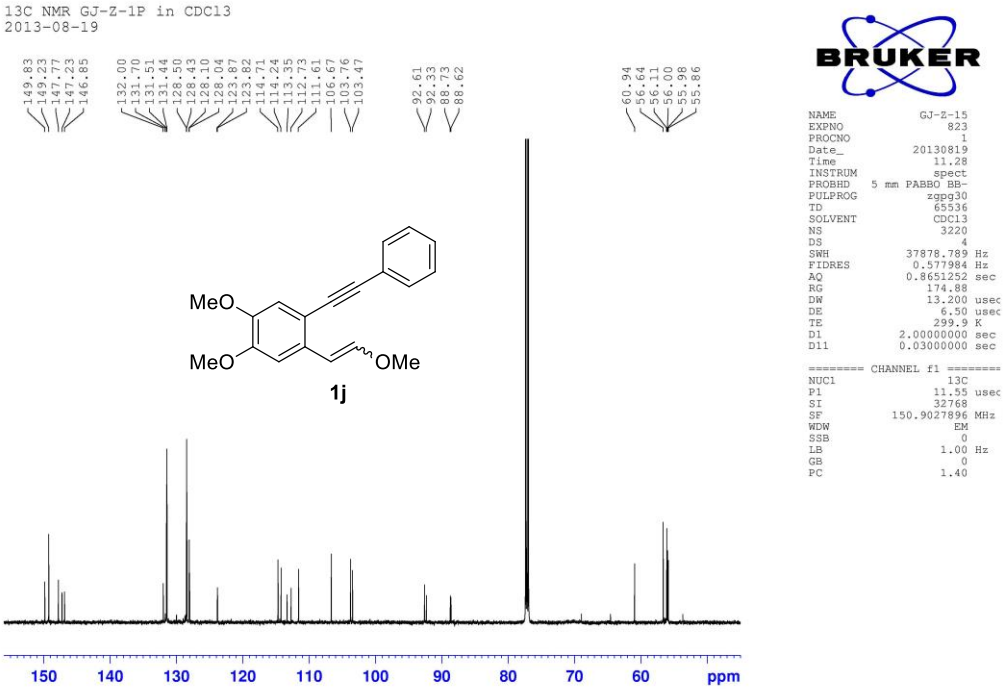
^{1}H NMR Spectrum of Compound **1i** ($CDCl_3$, 600 MHz)



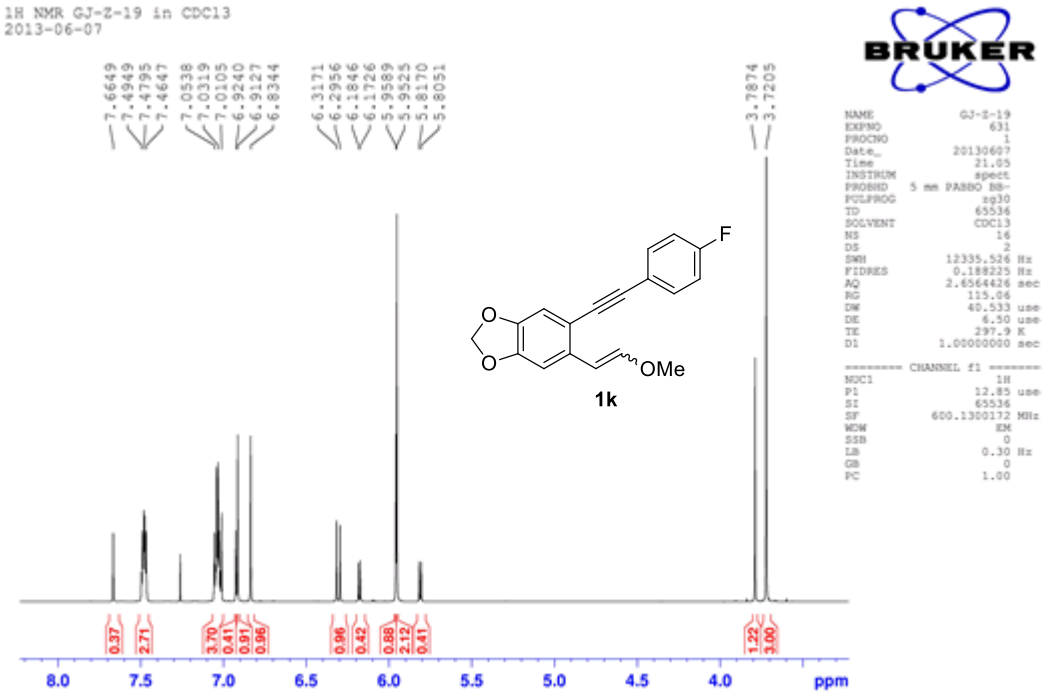
^{13}C NMR Spectrum of Compound **1i** ($CDCl_3$, 150 MHz)



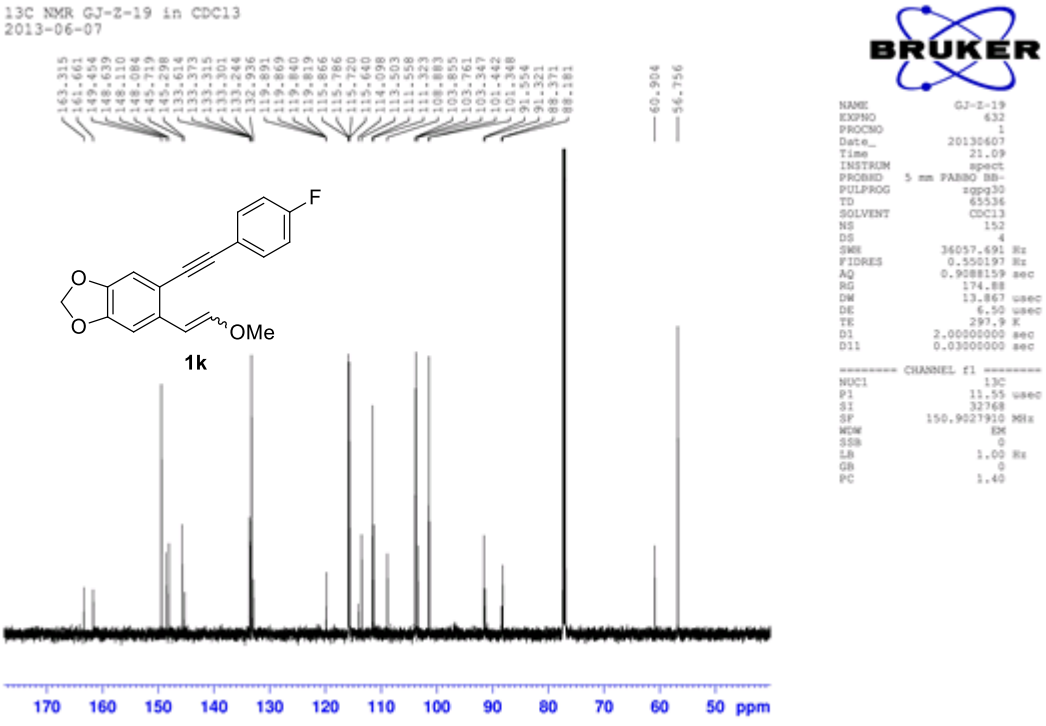
^{1}H NMR Spectrum of Compound **1j** ($CDCl_3$, 600 MHz)



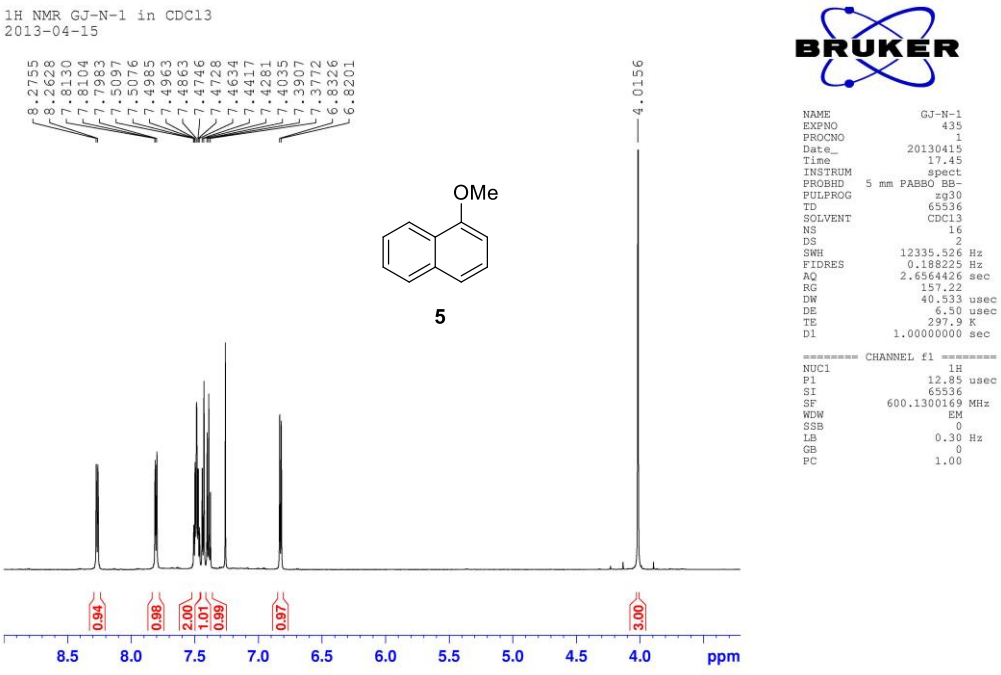
^{13}C NMR Spectrum of Compound **1j** ($CDCl_3$, 150 MHz)



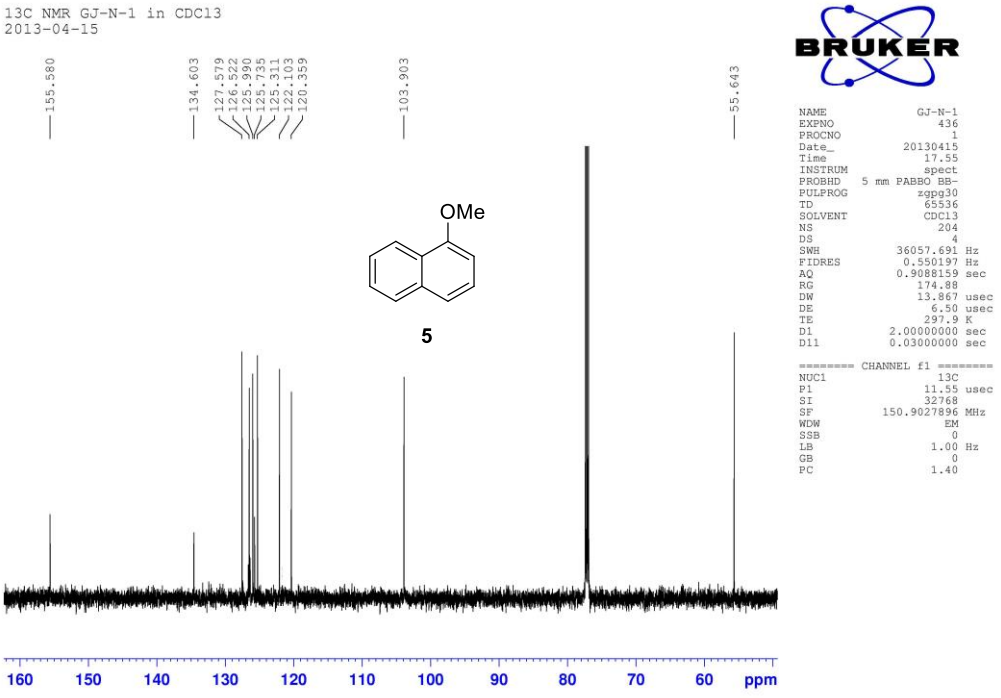
^{1}H NMR Spectrum of Compound **1k** ($CDCl_3$, 600 MHz)



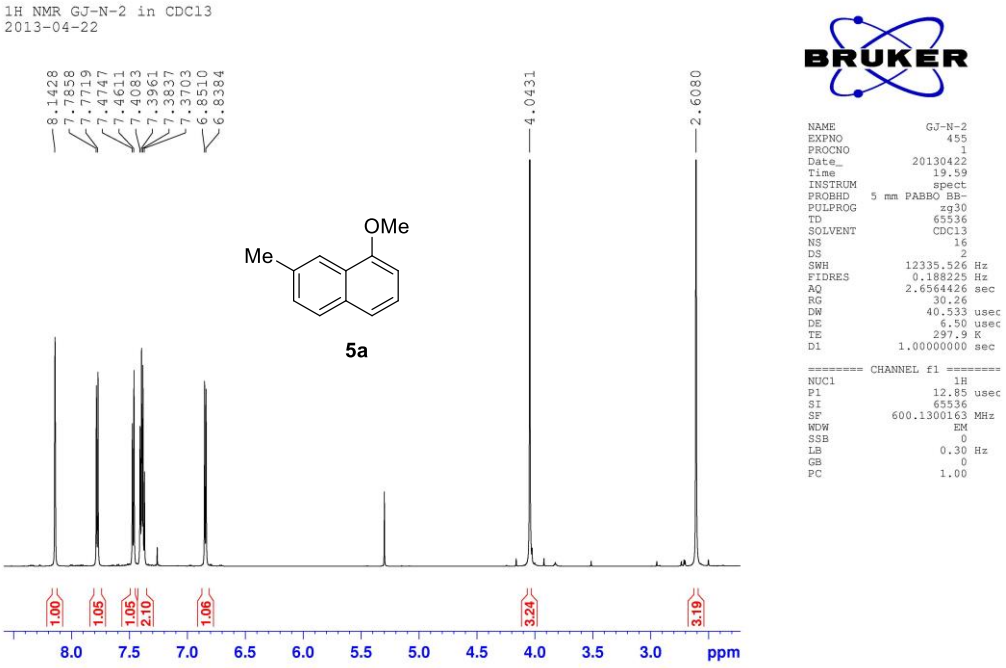
^{13}C NMR Spectrum of Compound **1k** ($CDCl_3$, 150 MHz)



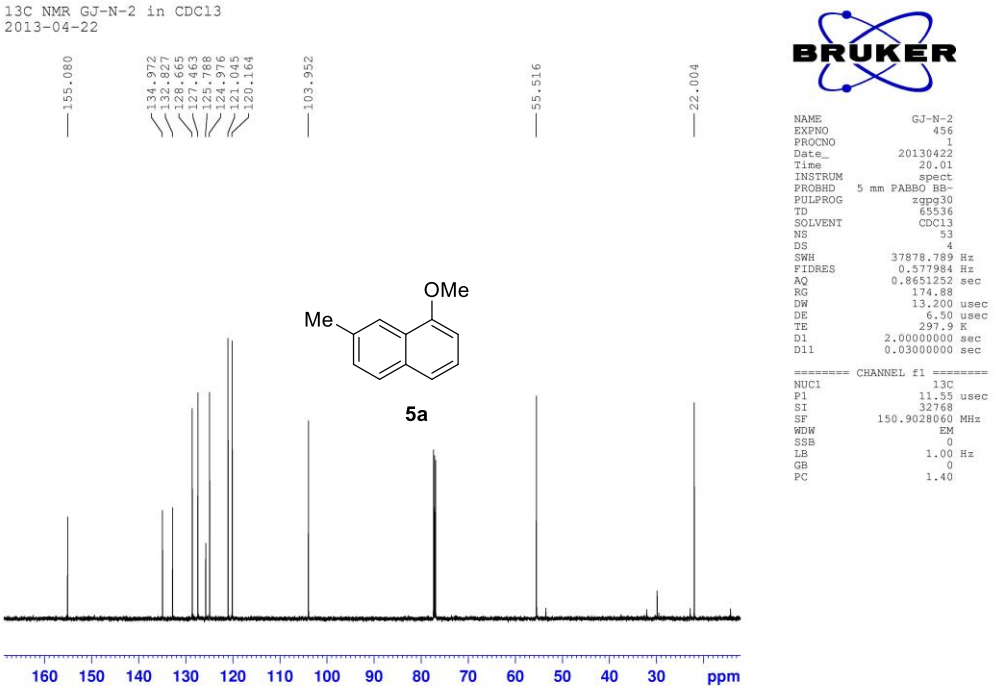
^{1}H NMR Spectrum of Compound **5** ($CDCl_3$, 600 MHz)



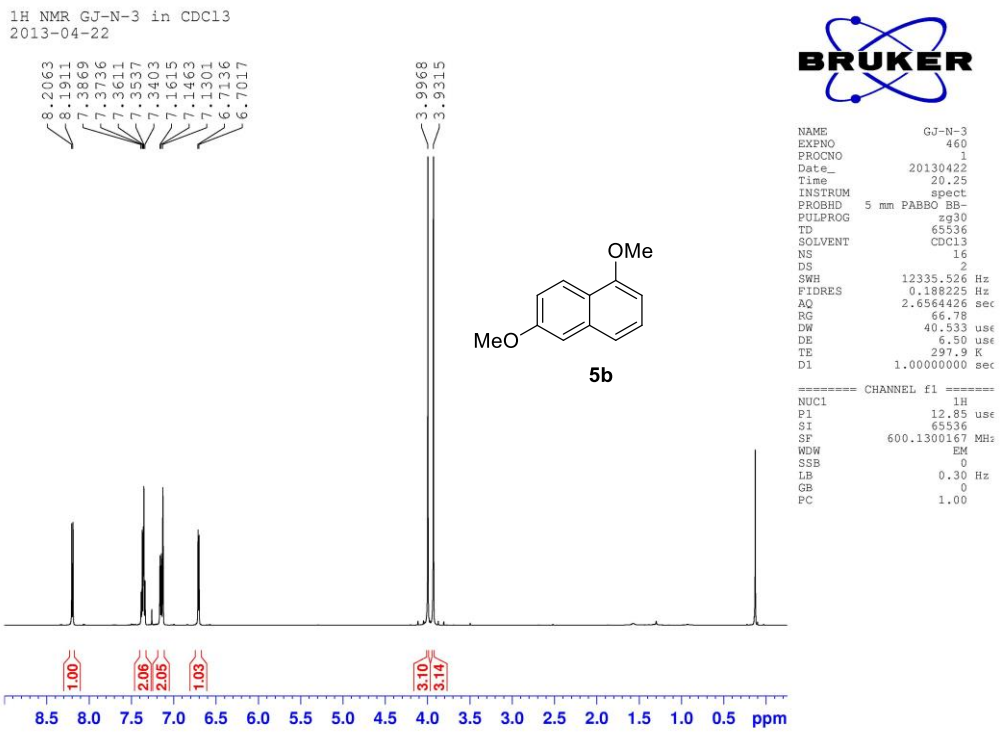
^{13}C NMR Spectrum of Compound **5** ($CDCl_3$, 150 MHz)



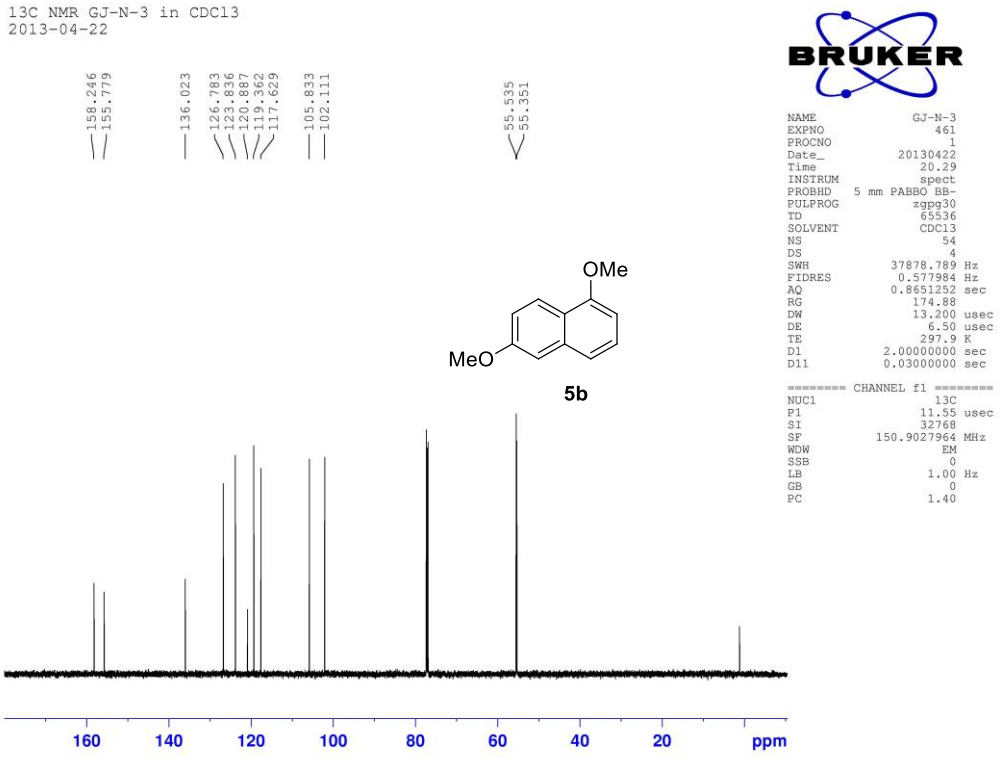
^{1}H NMR Spectrum of Compound **5a** ($CDCl_3$, 600 MHz)



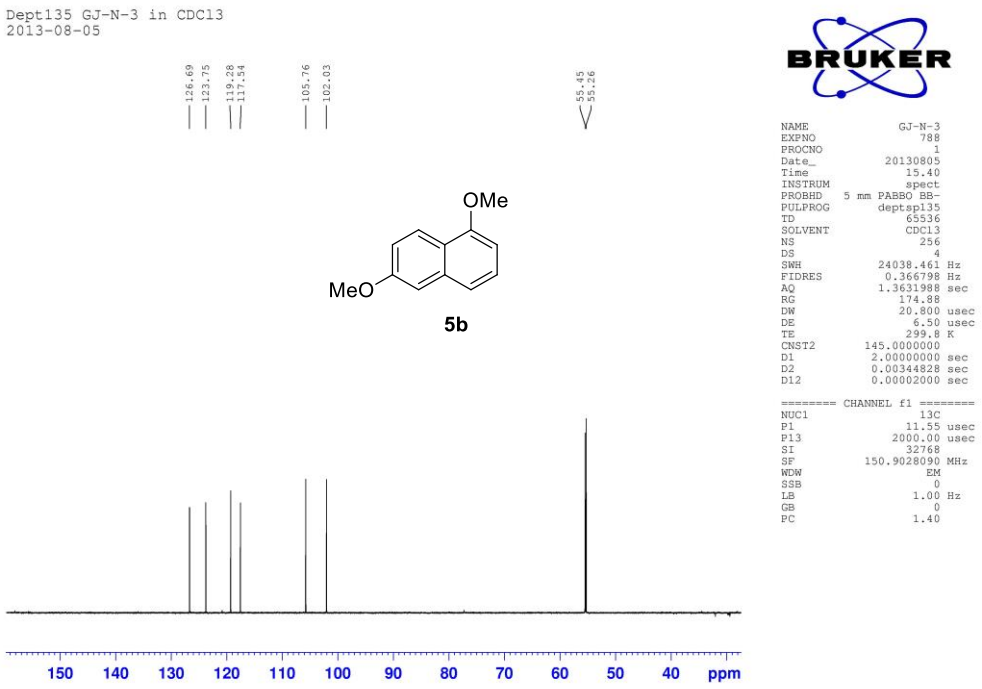
^{13}C NMR Spectrum of Compound **5a** ($CDCl_3$, 150 MHz)



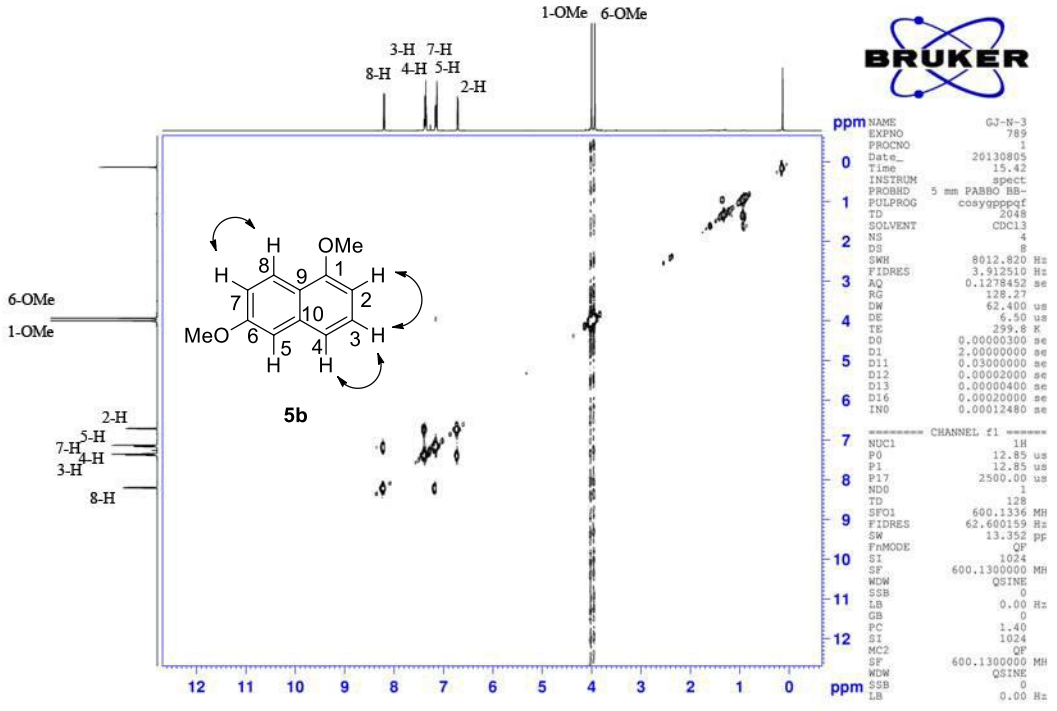
^{1}H NMR Spectrum of Compound **5b** ($CDCl_3$, 600 MHz)



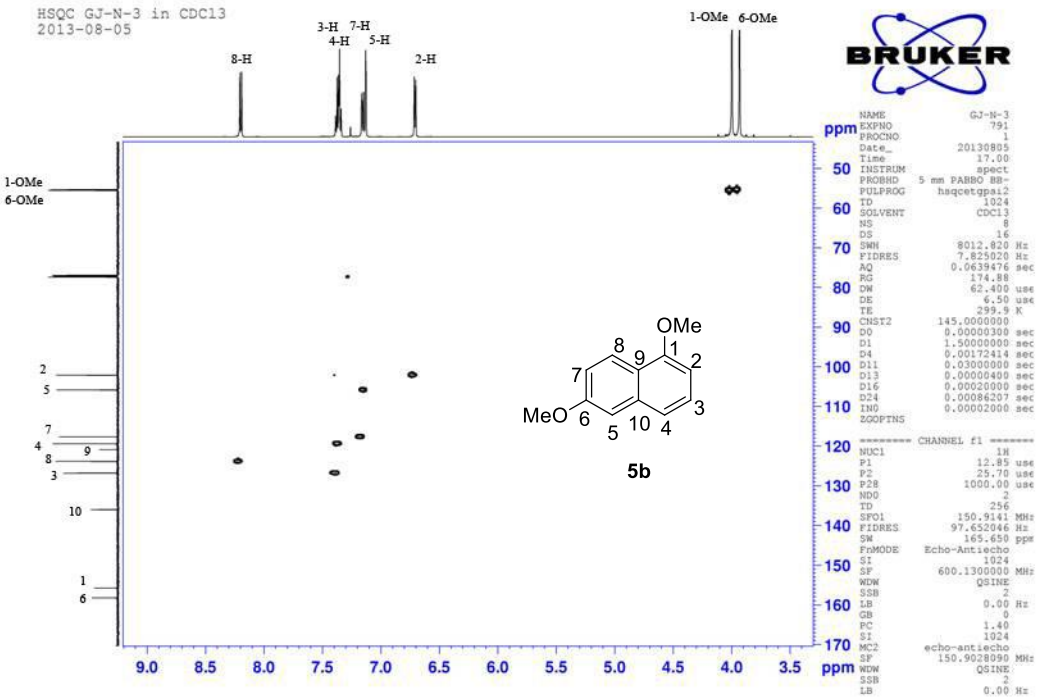
^{13}C NMR Spectrum of Compound **5b** ($CDCl_3$, 150 MHz)



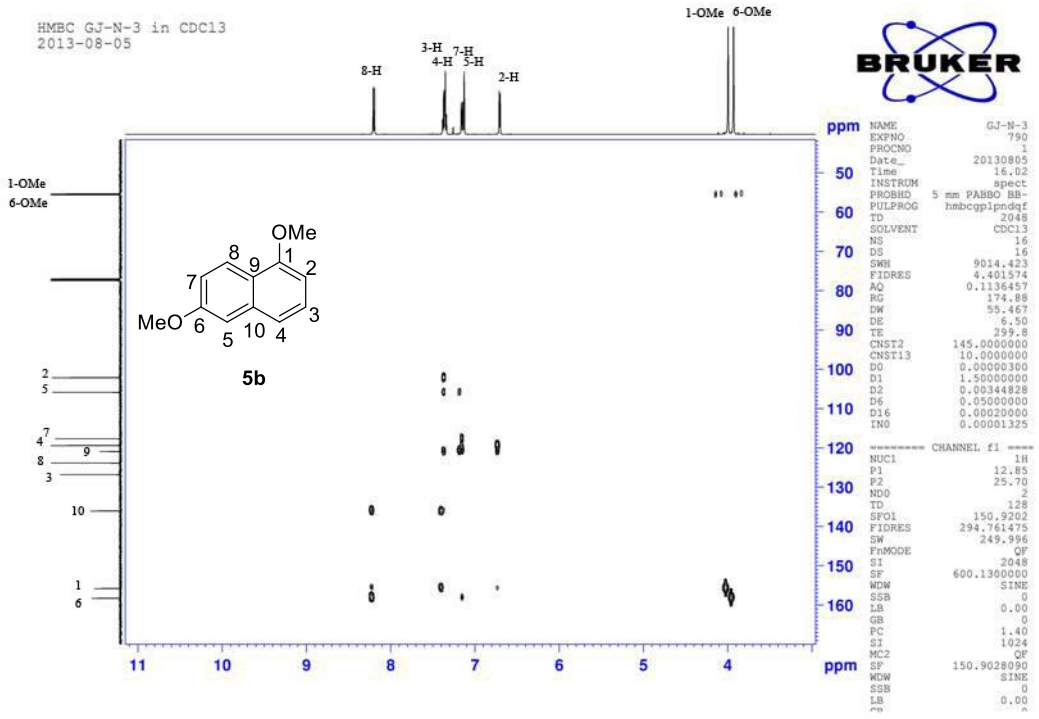
Dept135 ^{13}C NMR Spectrum of Compound **5b** ($CDCl_3$, 150 MHz)



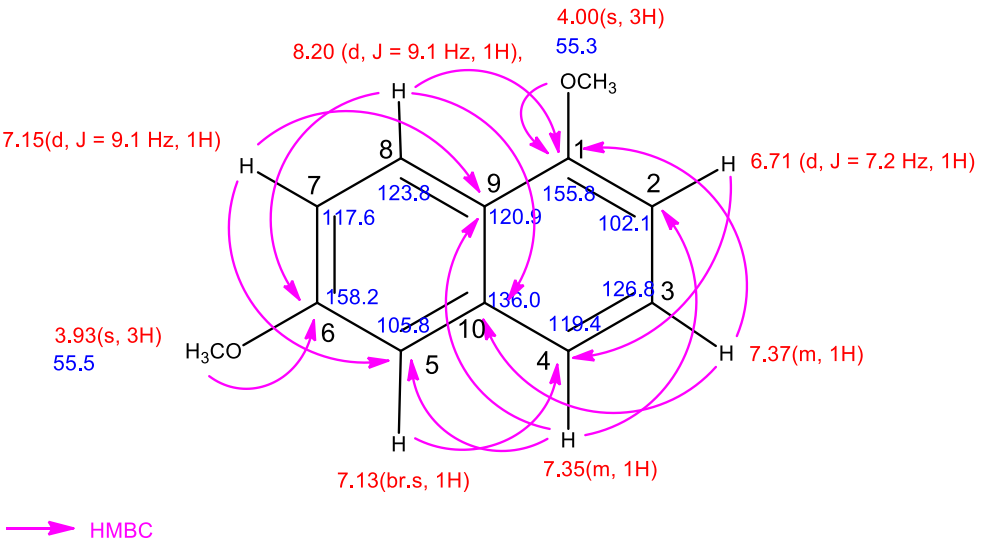
H-H COSY Spectrum of Compound **5b** ($CDCl_3$, 600 MHz)



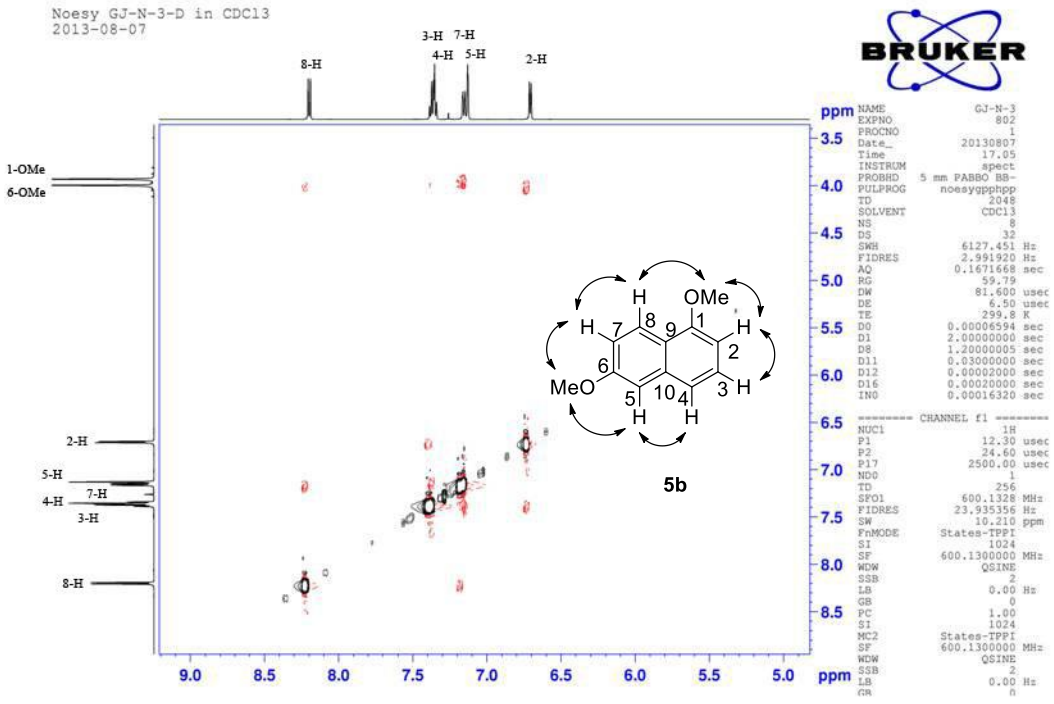
HSQC Spectrum of Compound **5b** ($CDCl_3$, 600 MHz)



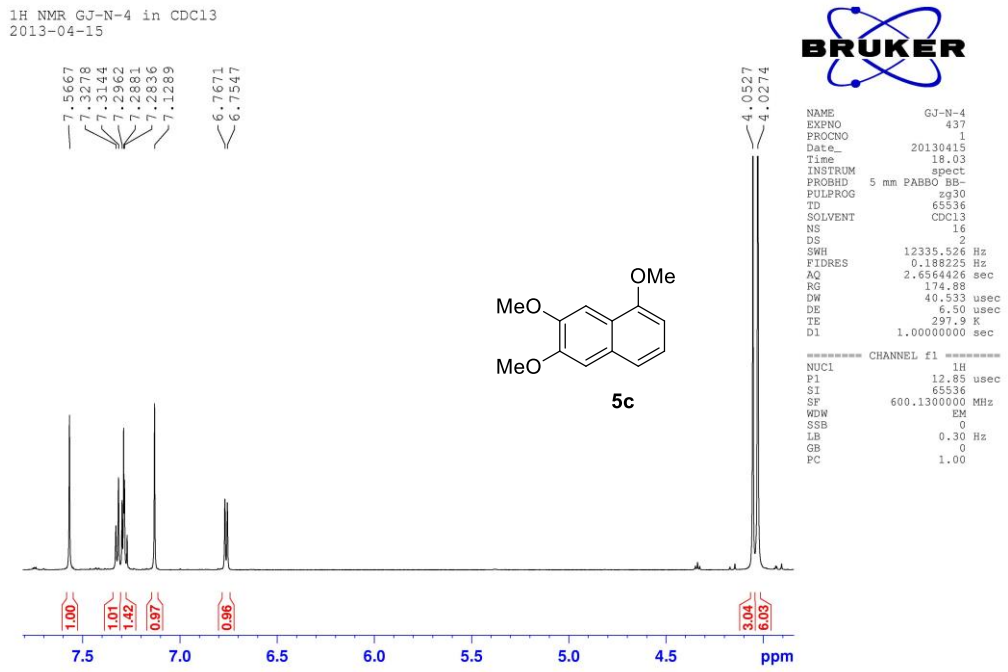
HMBC Spectrum of Compound **5b** ($CDCl_3$, 600 MHz)



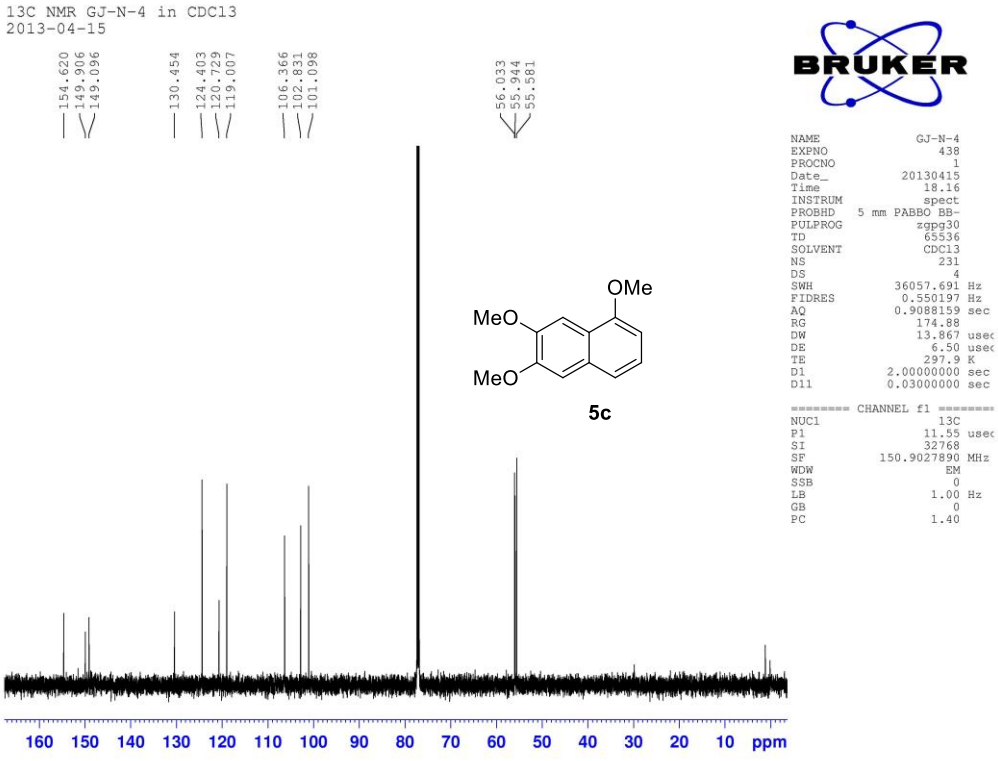
HMBC Spectrum of Compound **5b** ($CDCl_3$, 600 MHz)



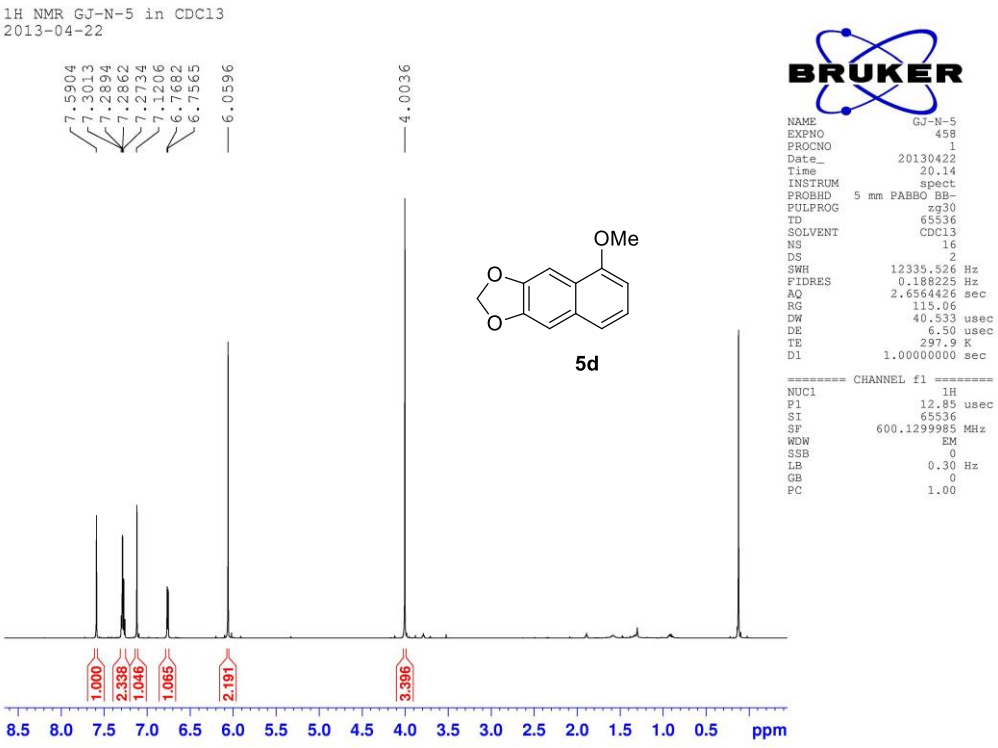
NOESEY Spectrum of Compound **5b** ($CDCl_3$, 600 MHz)



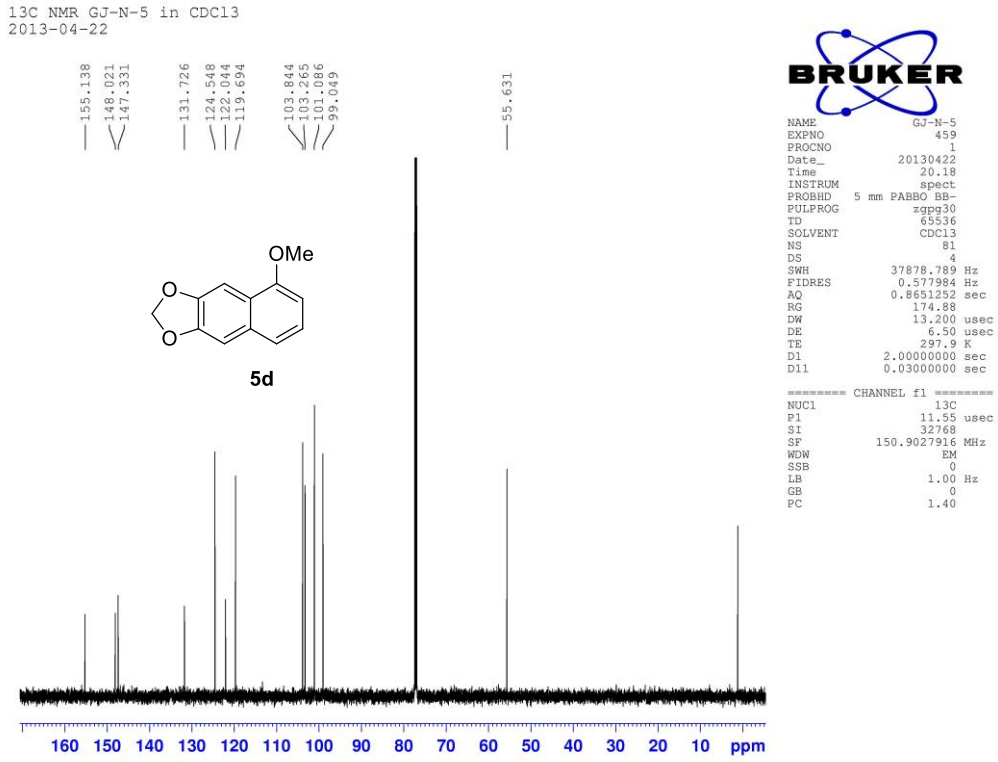
^{1}H NMR Spectrum of Compound **5c** ($CDCl_3$, 600 MHz)



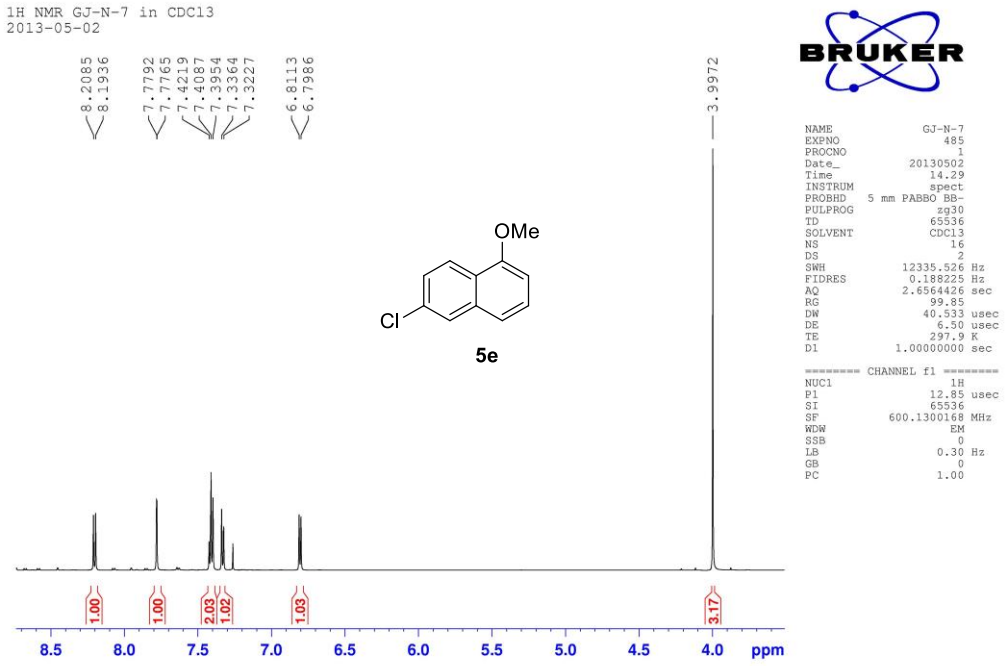
^{13}C NMR Spectrum of Compound **5c** ($CDCl_3$, 150 MHz)



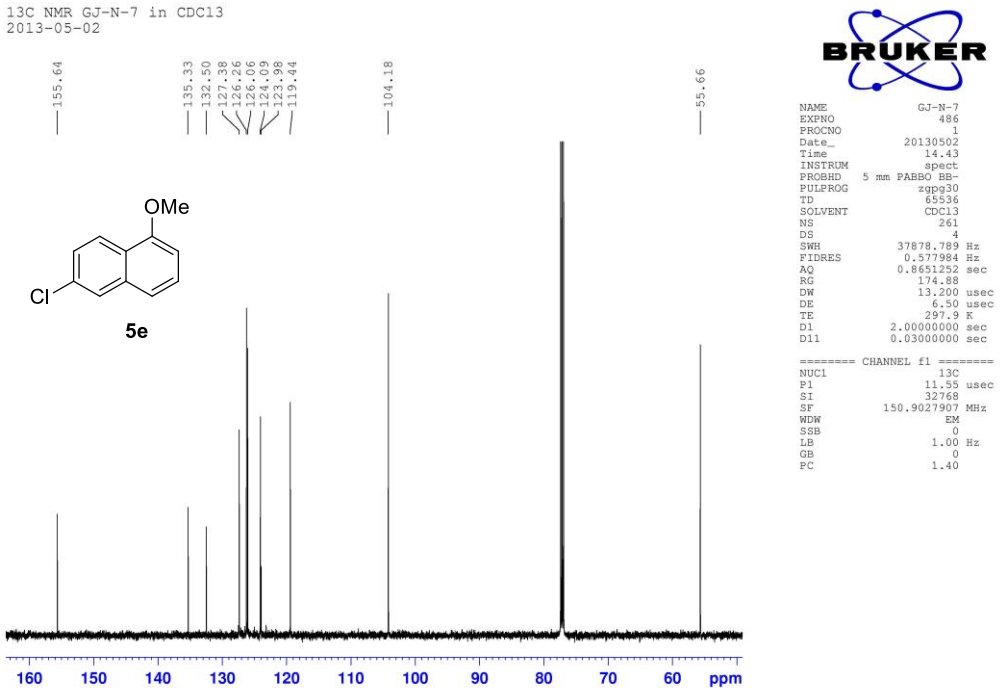
^{1}H NMR Spectrum of Compound **5d** ($CDCl_3$, 600 MHz)



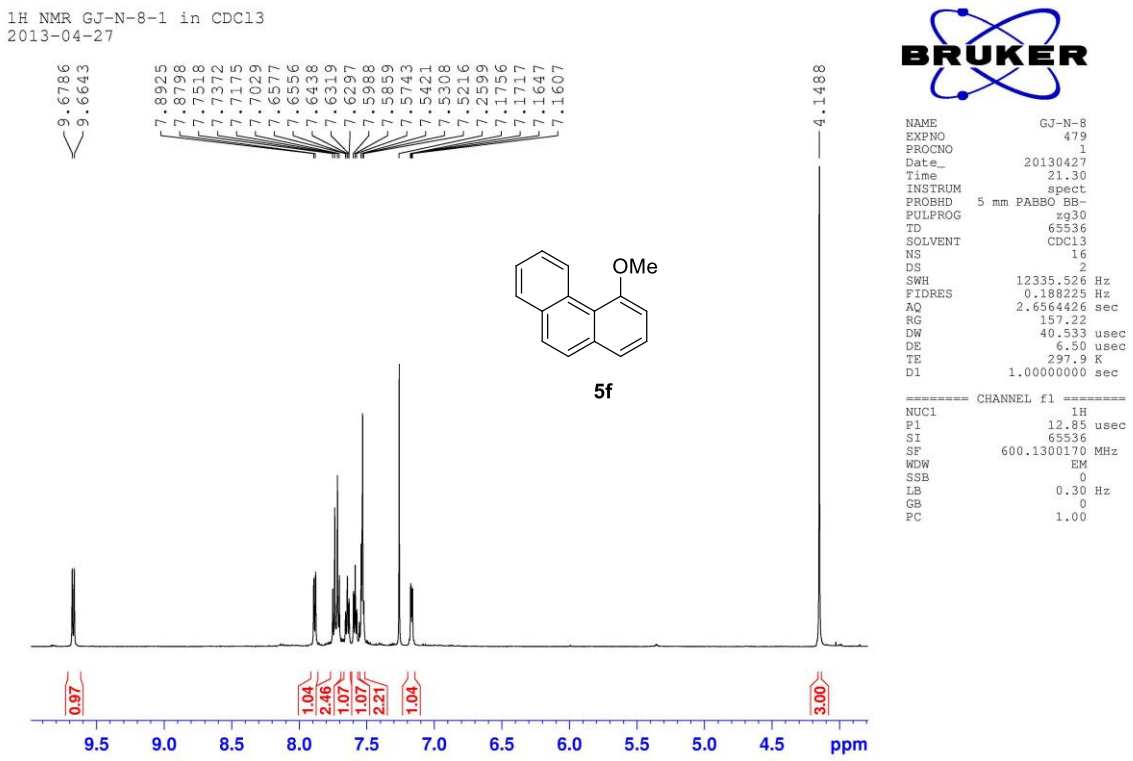
^{13}C NMR Spectrum of Compound **5d** ($CDCl_3$, 150 MHz)



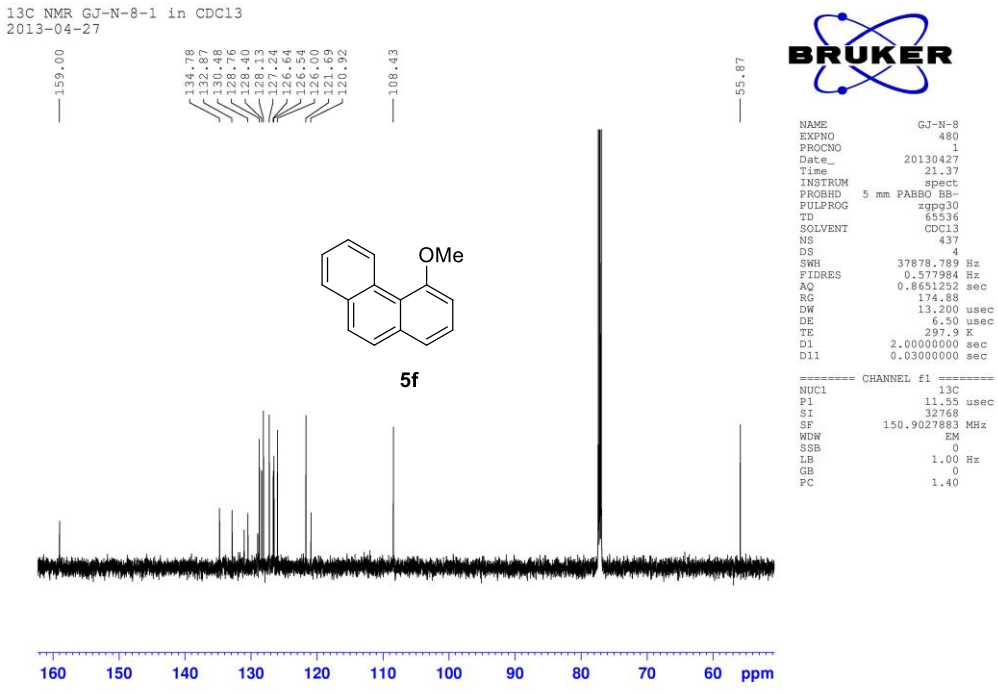
^{1}H NMR Spectrum of Compound **5e** ($CDCl_3$, 600 MHz)



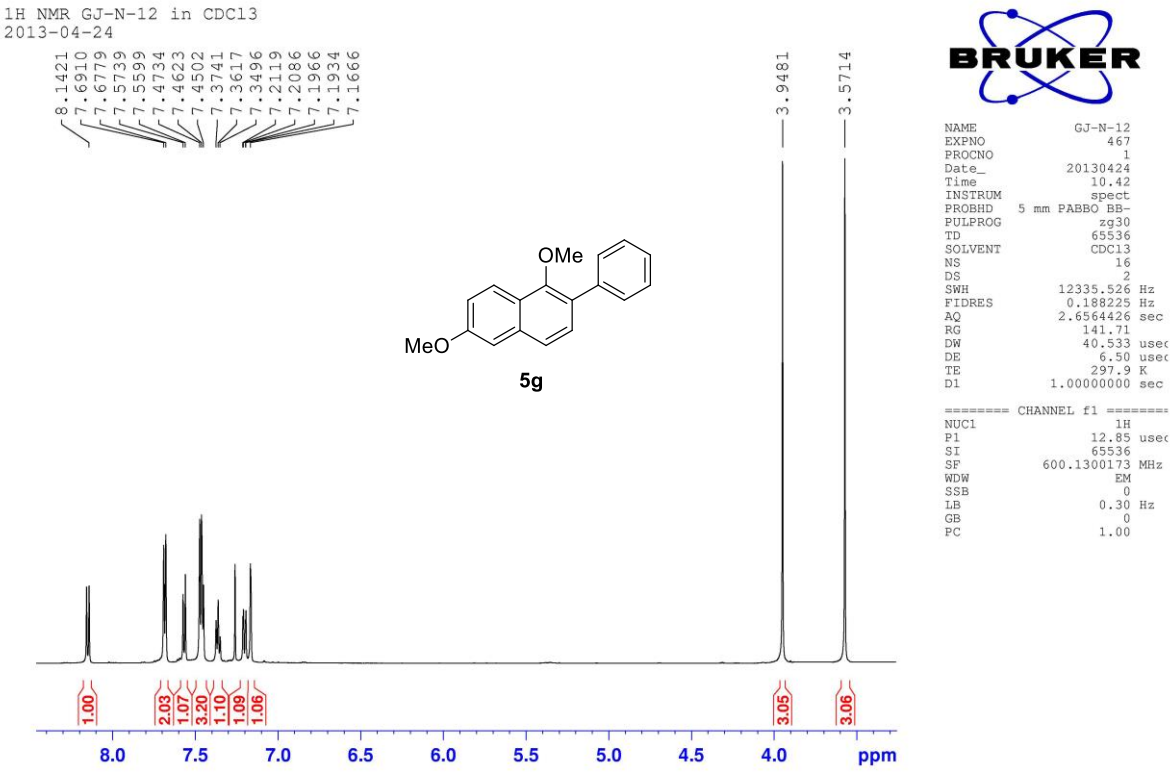
^{13}C NMR Spectrum of Compound **5e** ($CDCl_3$, 150 MHz)



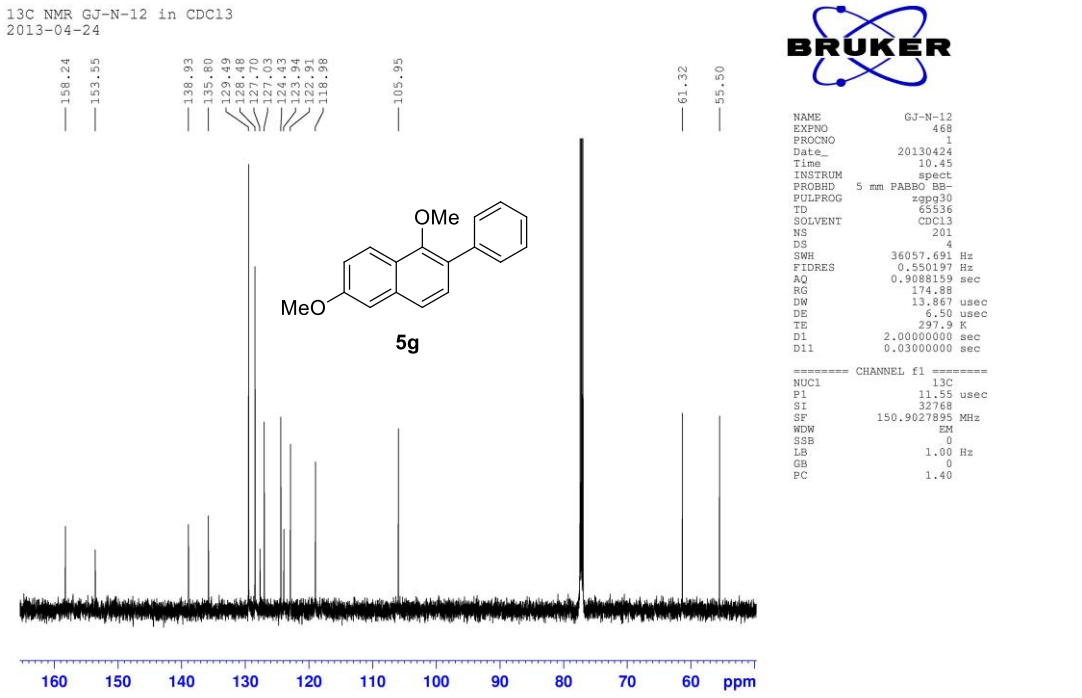
^{1}H NMR Spectrum of Compound **5f** ($CDCl_3$, 600 MHz)



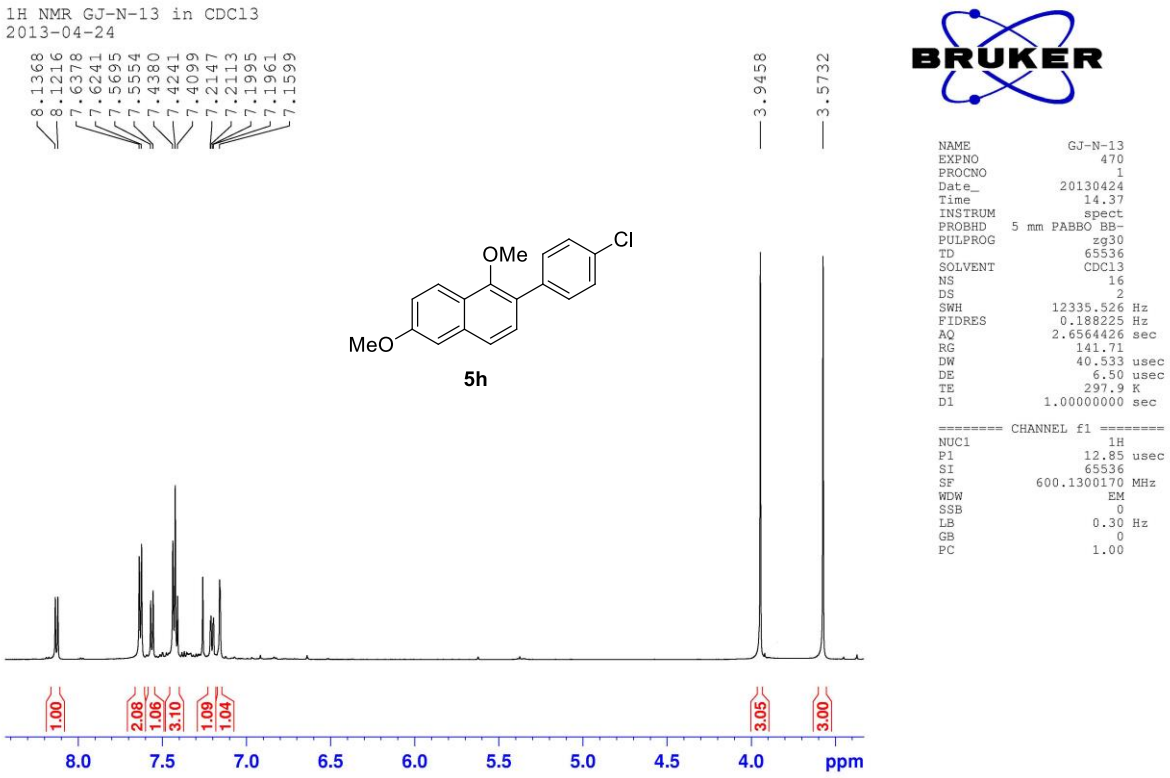
^{13}C NMR Spectrum of Compound **5f** ($CDCl_3$, 150 MHz)



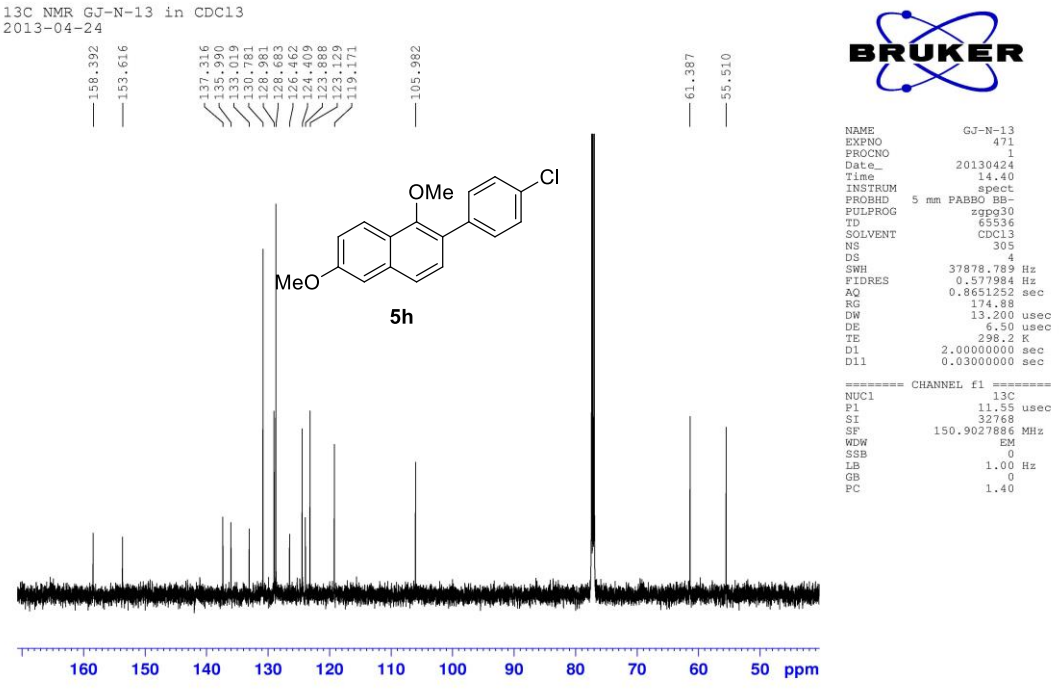
^{1}H NMR Spectrum of Compound **5g** ($CDCl_3$, 600 MHz)



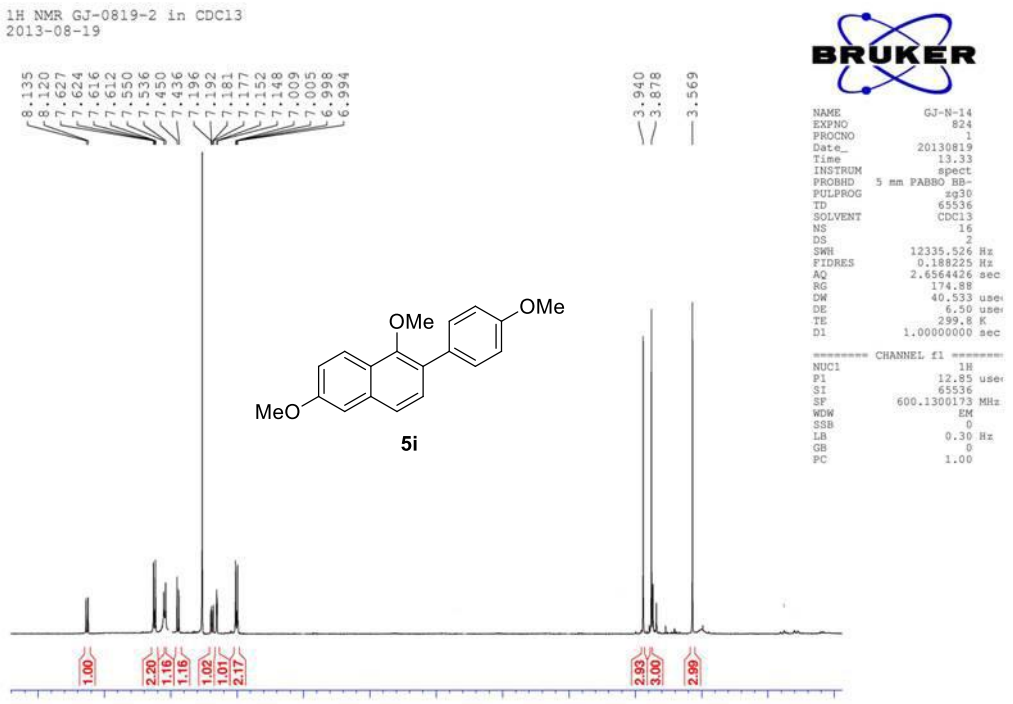
^{13}C NMR Spectrum of Compound **5g** ($CDCl_3$, 150 MHz)



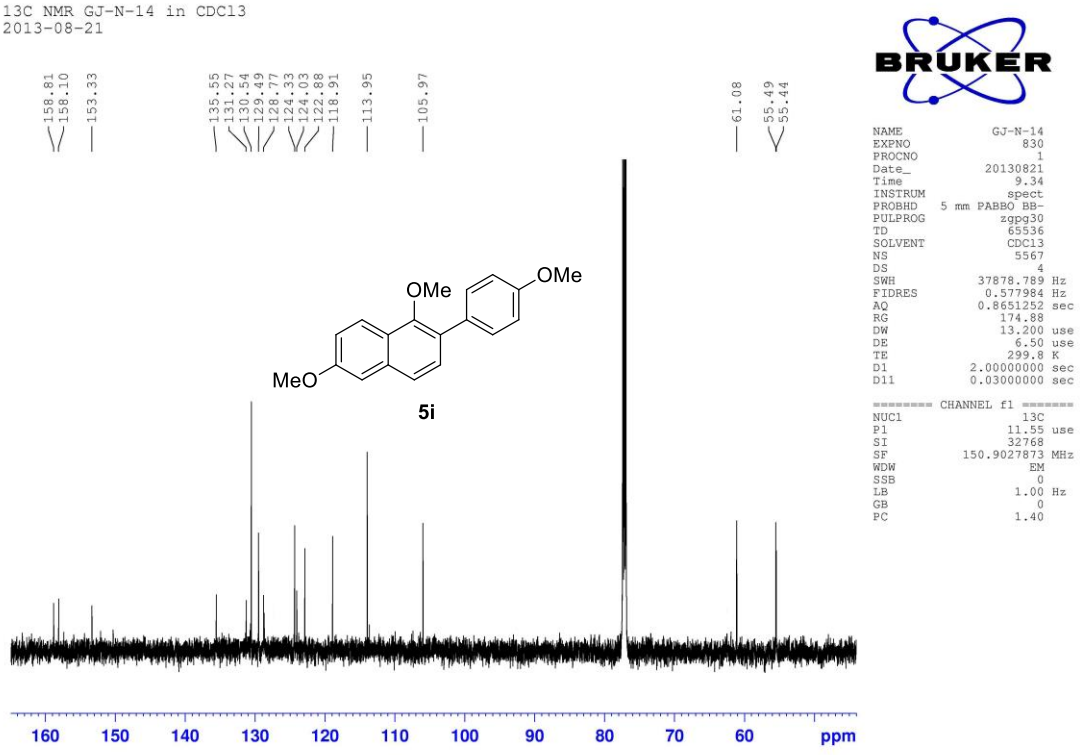
^{1}H NMR Spectrum of Compound **5h**($CDCl_3$, 600 MHz)



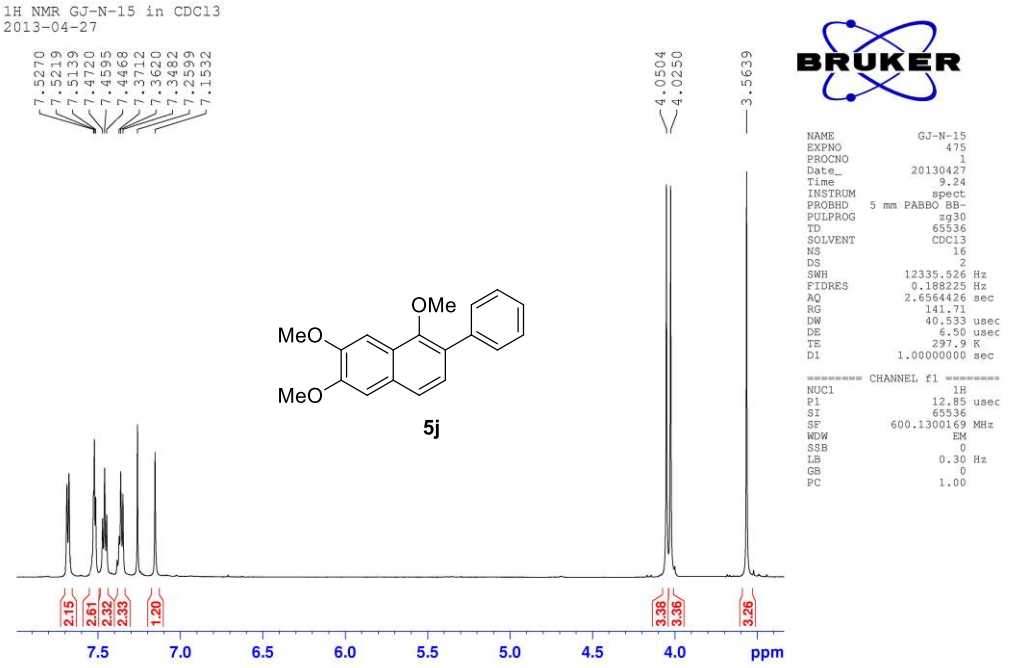
^{13}C NMR Spectrum of Compound **5h** ($CDCl_3$, 150 MHz)



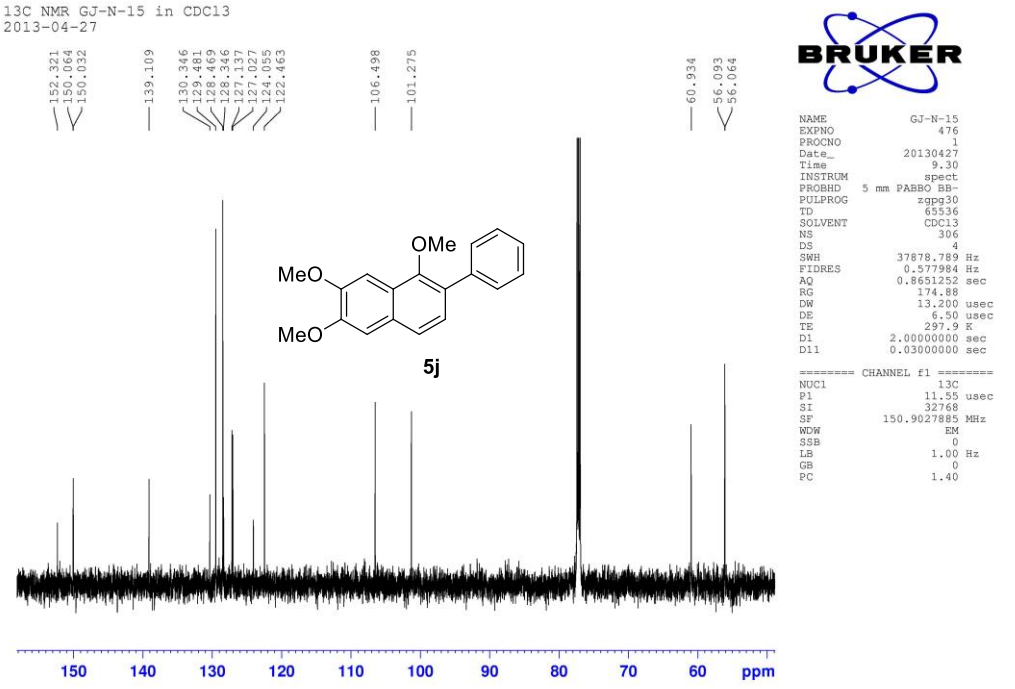
^{1}H NMR Spectrum of Compound **5i** ($CDCl_3$, 600 MHz)



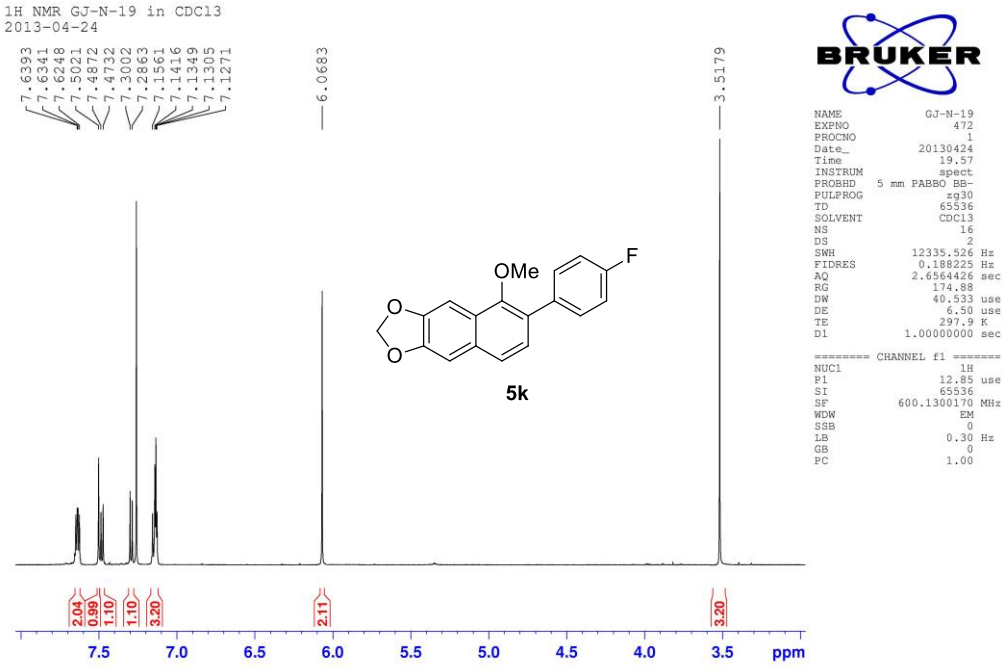
^{13}C NMR Spectrum of Compound **5i** ($CDCl_3$, 150 MHz)



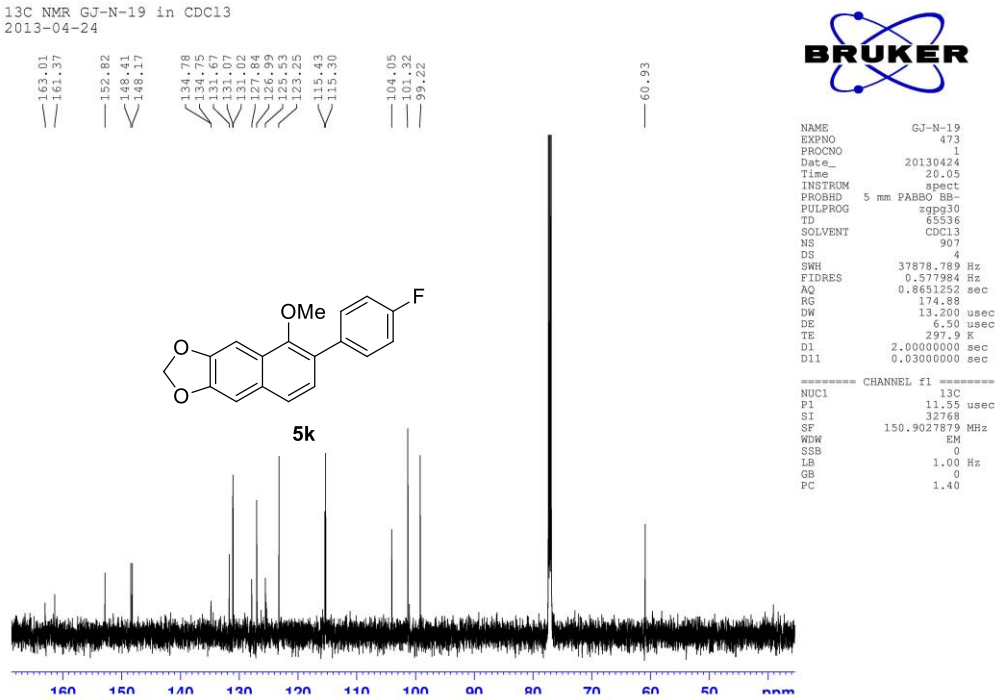
^{1}H NMR Spectrum of Compound 5**j** ($CDCl_3$, 600 MHz)



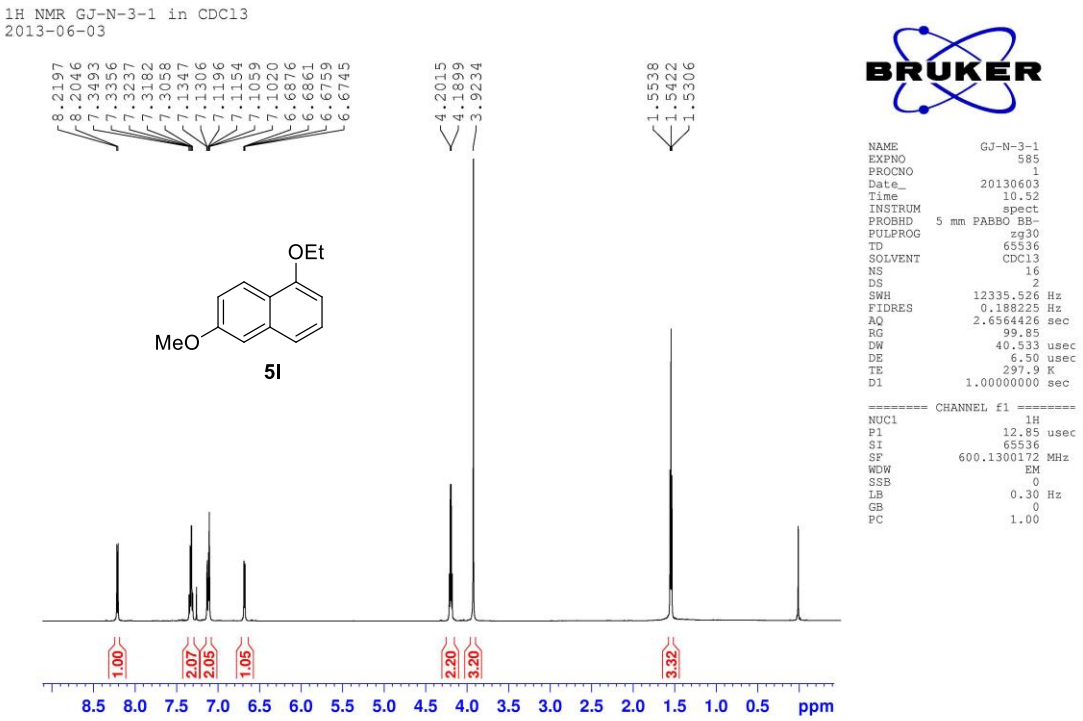
^{13}C NMR Spectrum of Compound 5**j** ($CDCl_3$, 150 MHz)



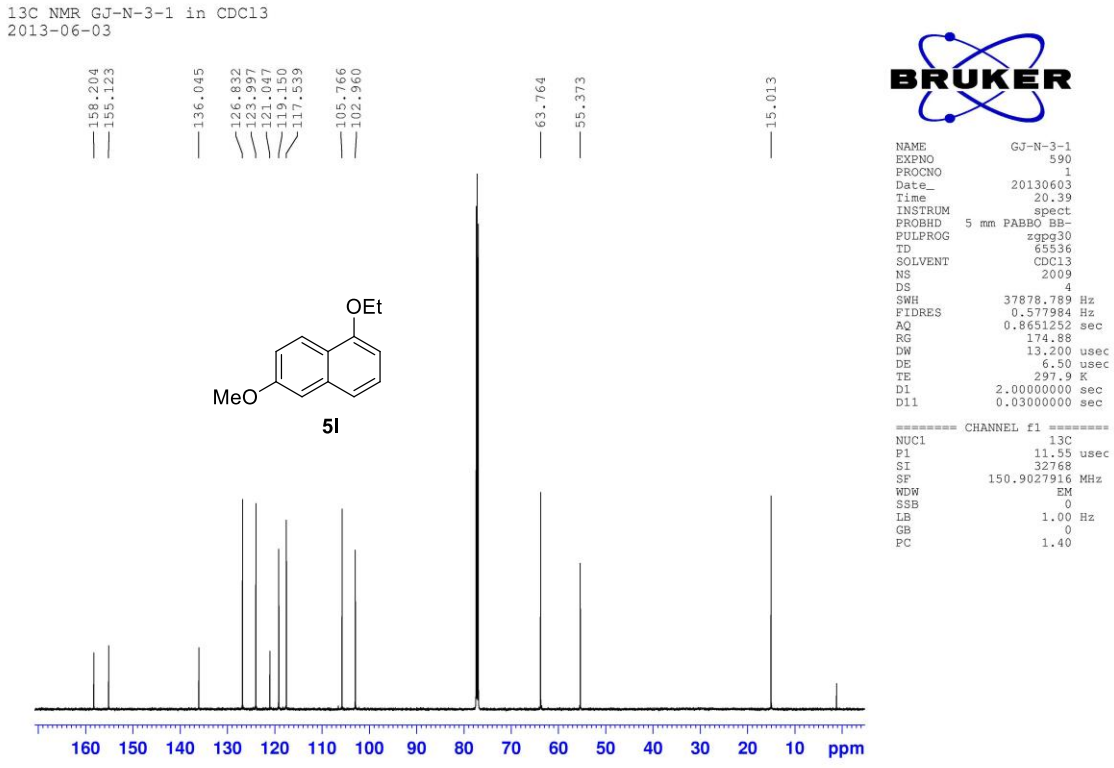
^{1}H NMR Spectrum of Compound **5k** ($CDCl_3$, 600 MHz)



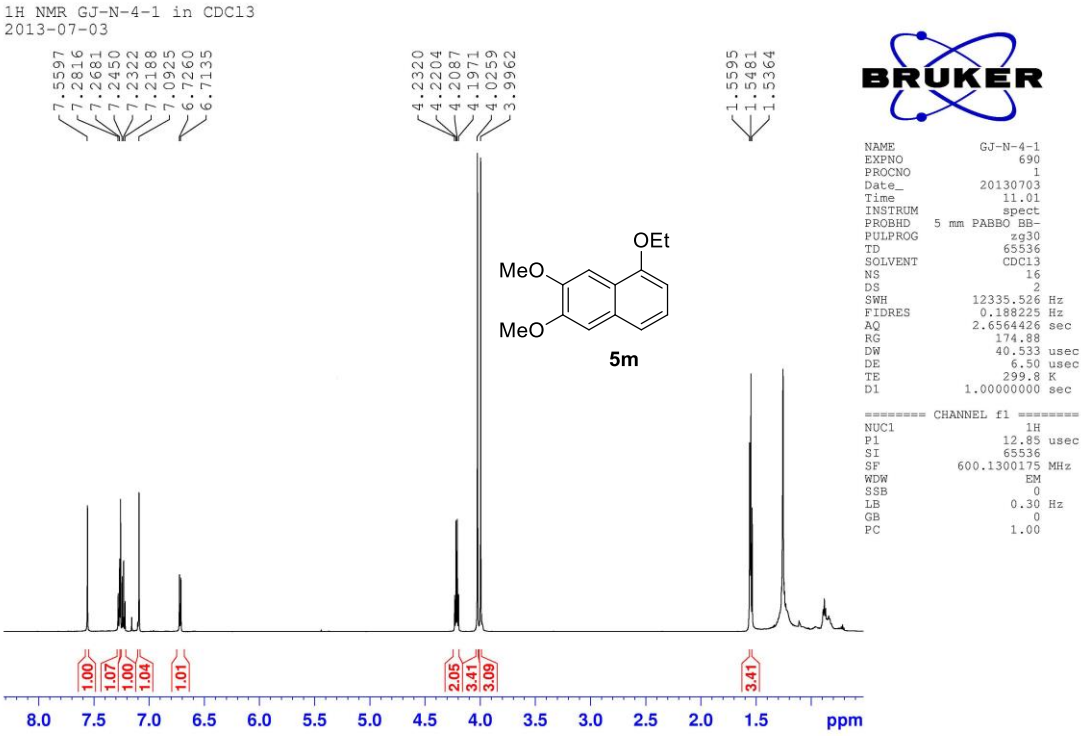
^{13}C NMR Spectrum of Compound **5k** ($CDCl_3$, 150 MHz)



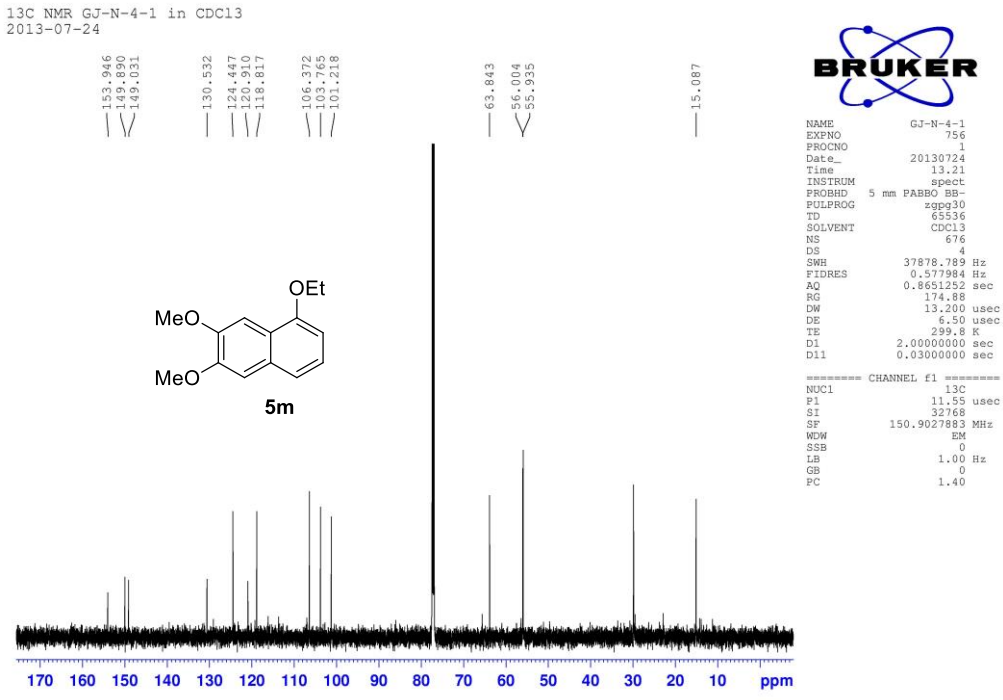
^{1}H NMR Spectrum of Compound **5l** ($CDCl_3$, 600 MHz)



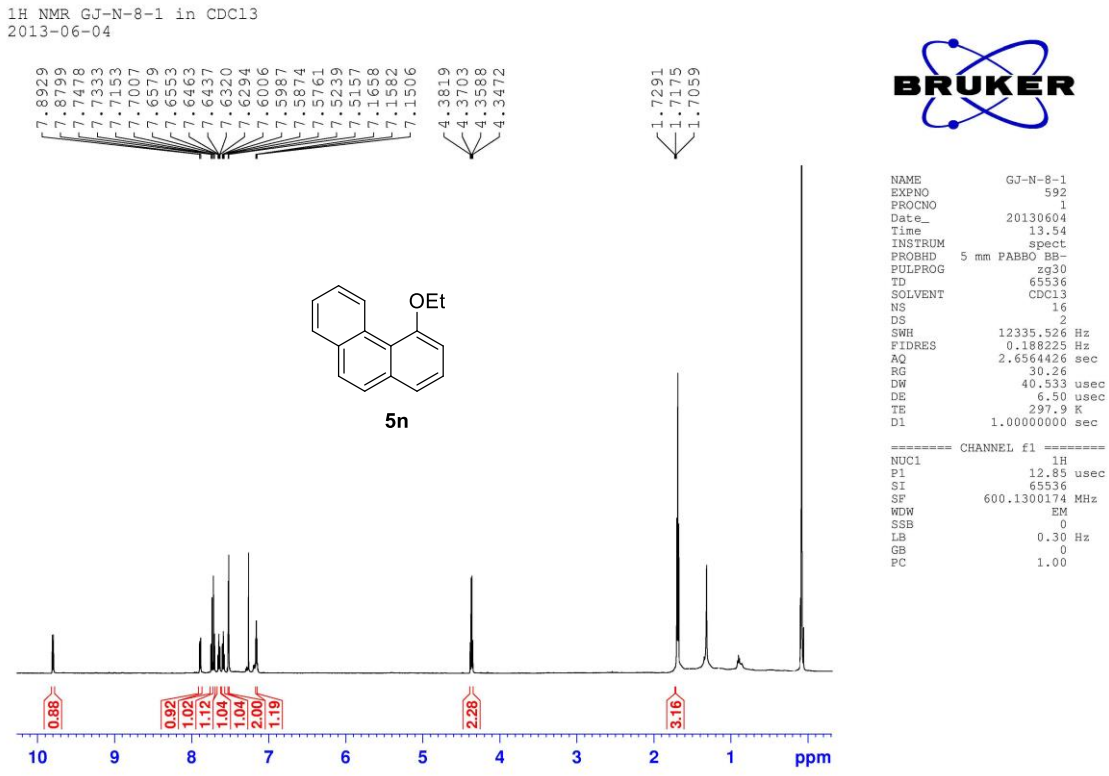
^{13}C NMR Spectrum of Compound **5l** ($CDCl_3$, 150 MHz)



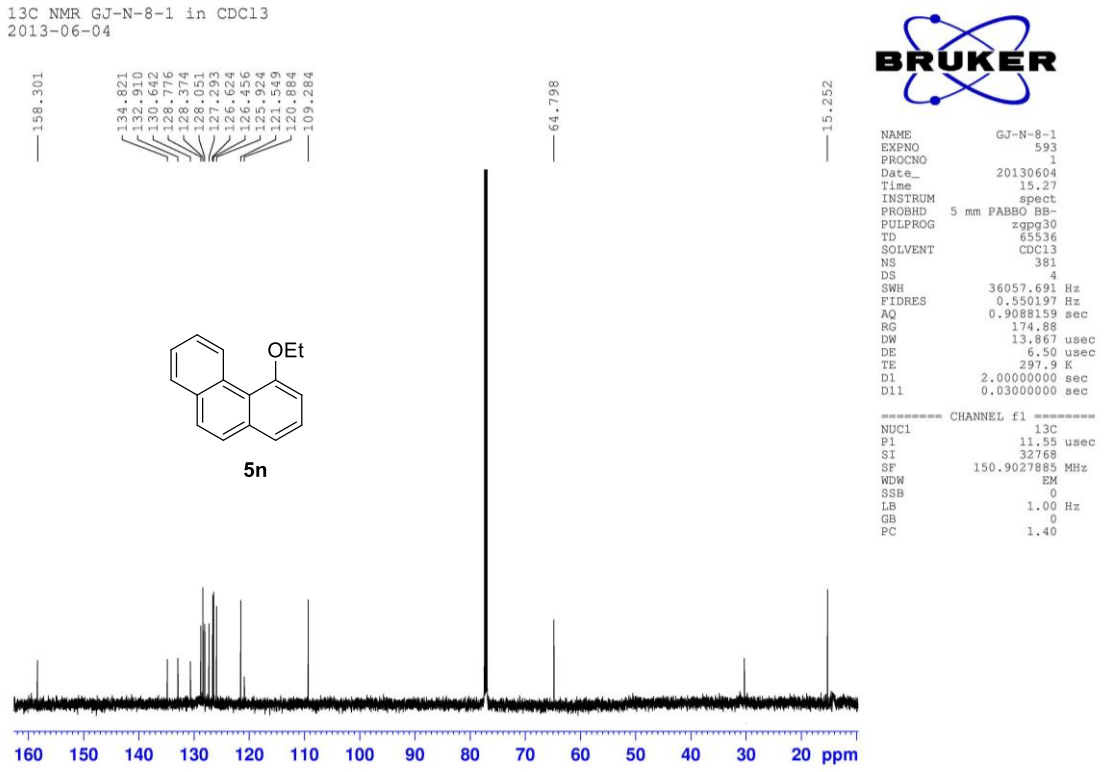
^{1}H NMR Spectrum of Compound **5m** ($CDCl_3$, 600 MHz)



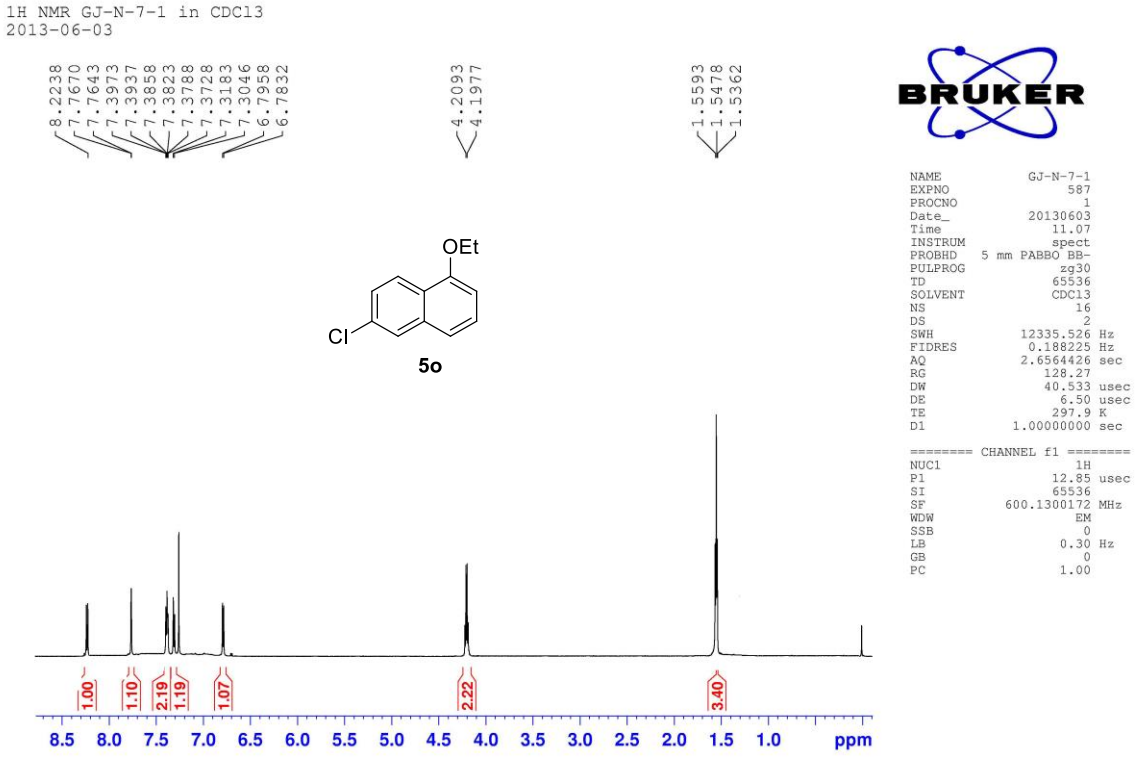
^{13}C NMR Spectrum of Compound **5m** ($CDCl_3$, 150 MHz)



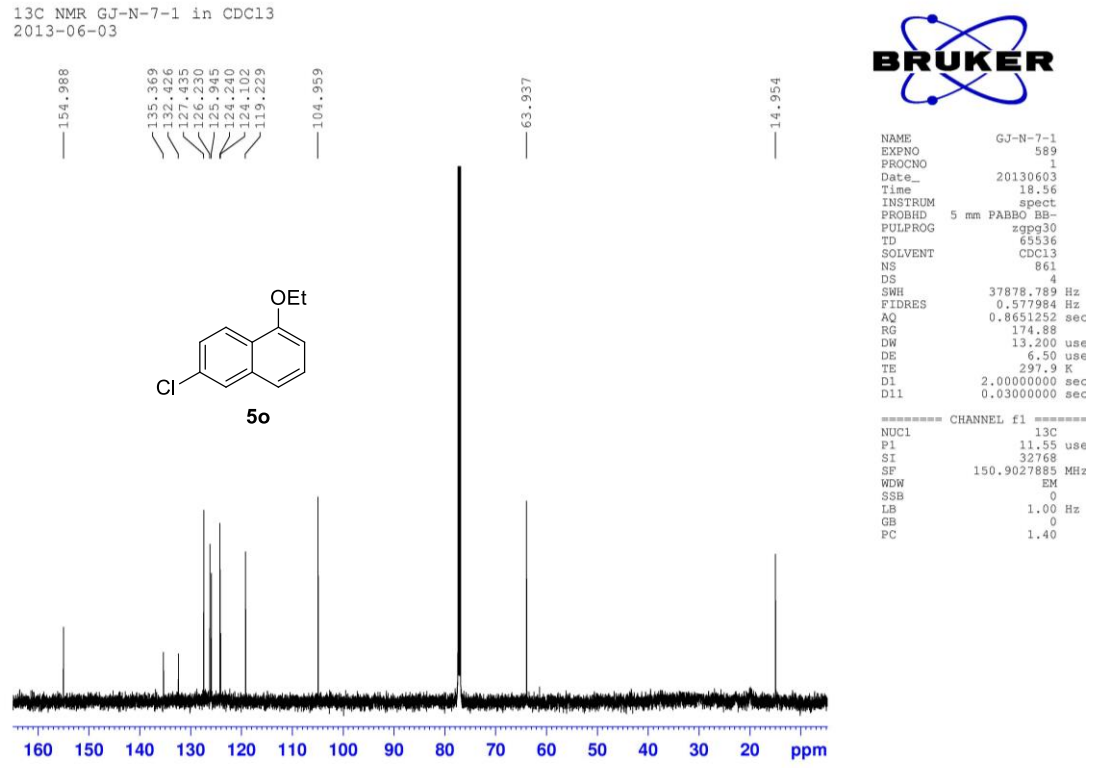
^{1}H NMR Spectrum of Compound **5n** ($CDCl_3$, 600 MHz)



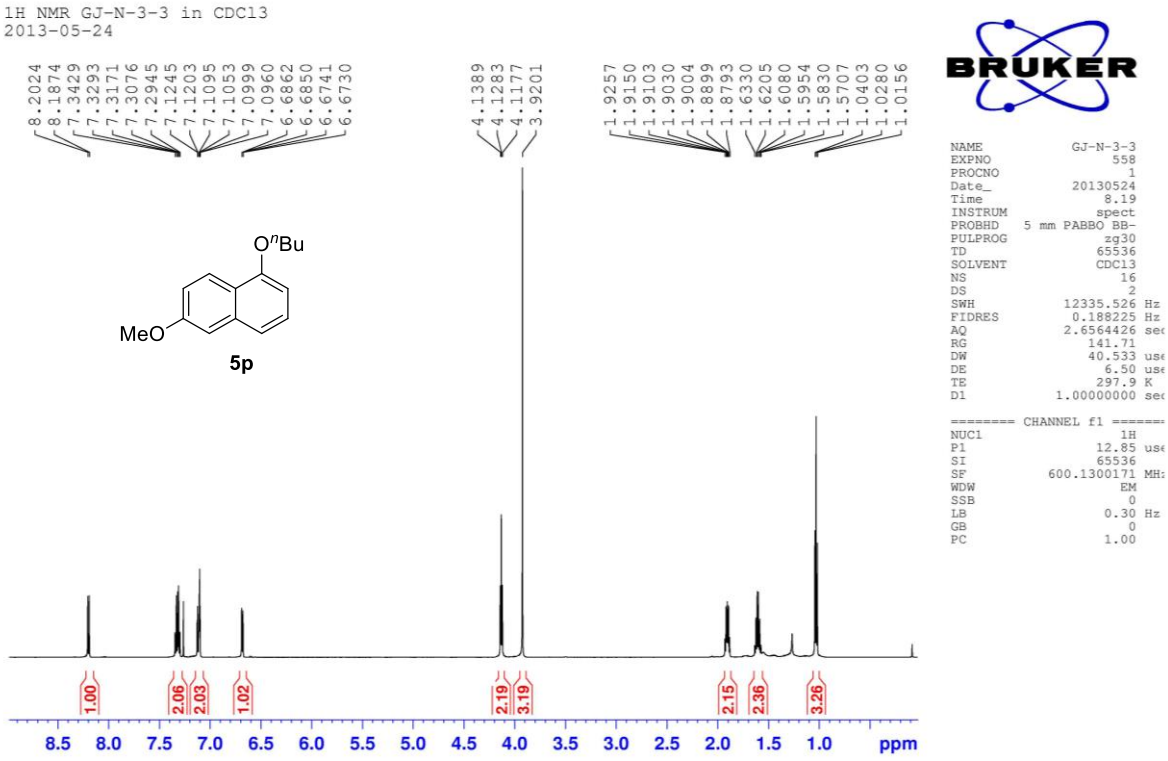
^{13}C NMR Spectrum of Compound **5n** ($CDCl_3$, 150 MHz)



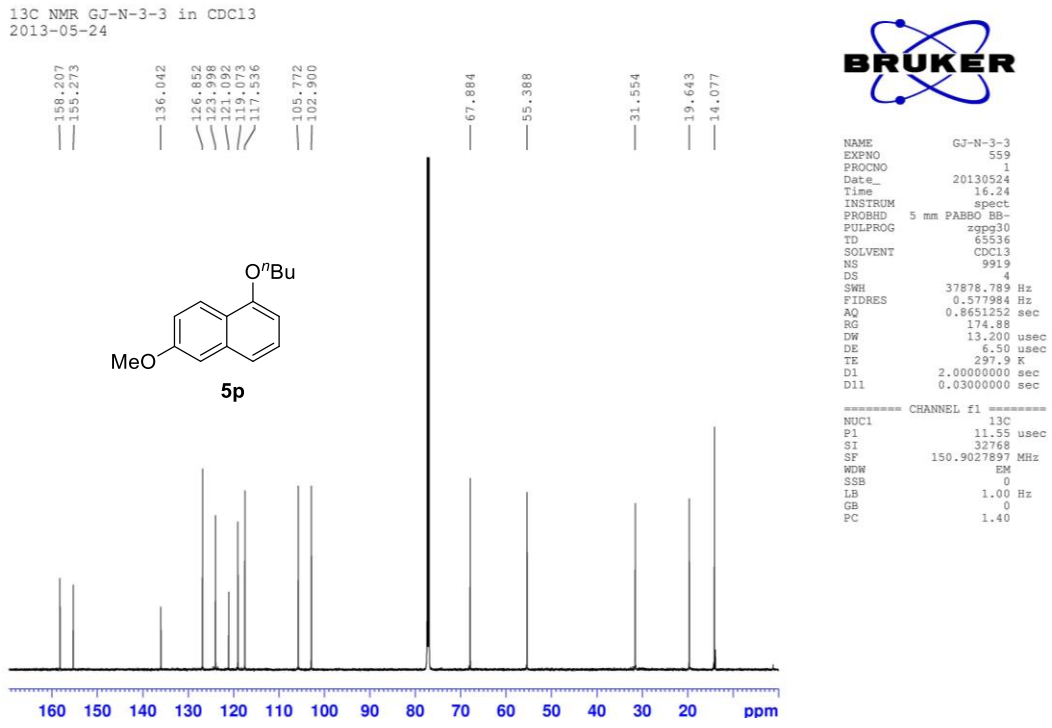
^{1}H NMR Spectrum of Compound **5o** ($CDCl_3$, 600 MHz)



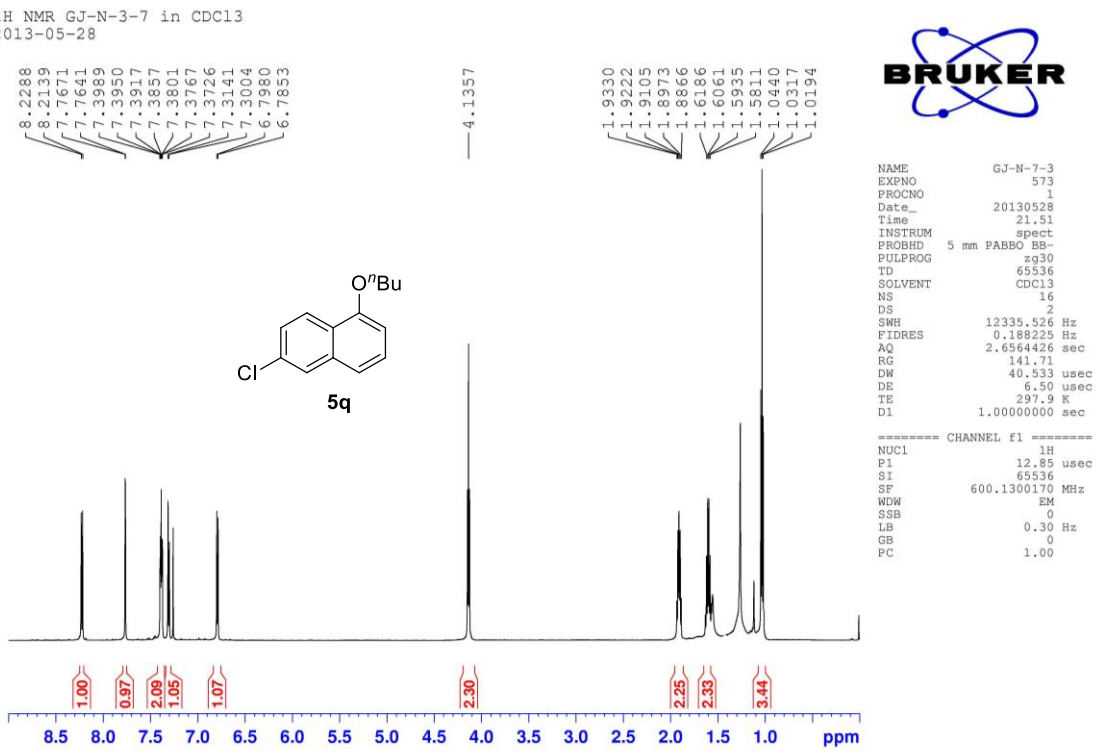
^{13}C NMR Spectrum of Compound **5o** ($CDCl_3$, 150 MHz)



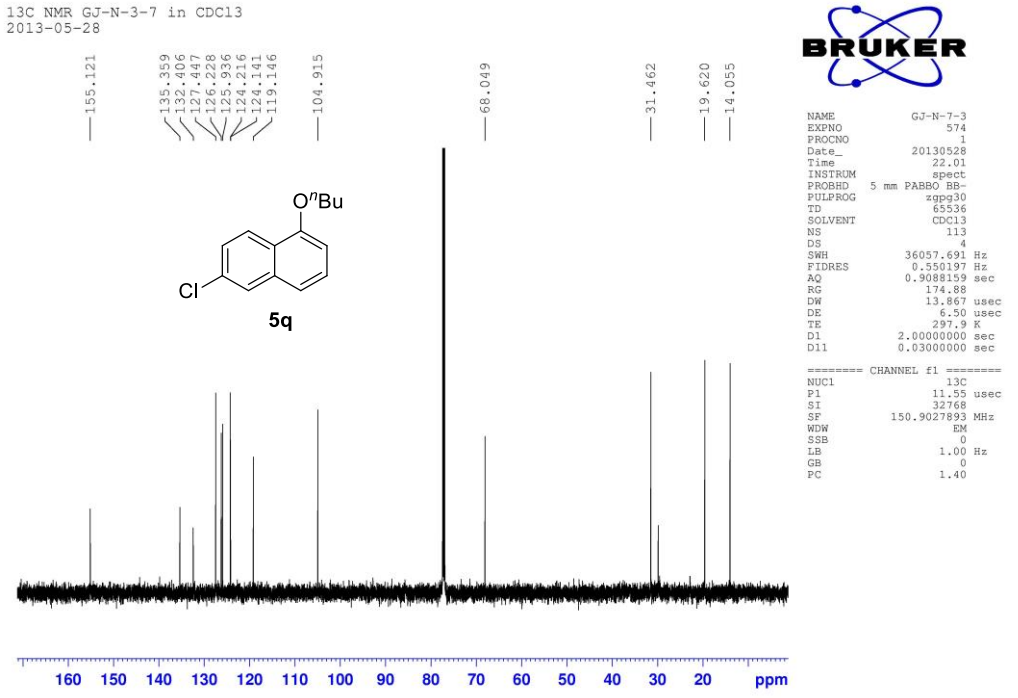
^{1}H NMR Spectrum of Compound **5p** ($CDCl_3$, 600 MHz)



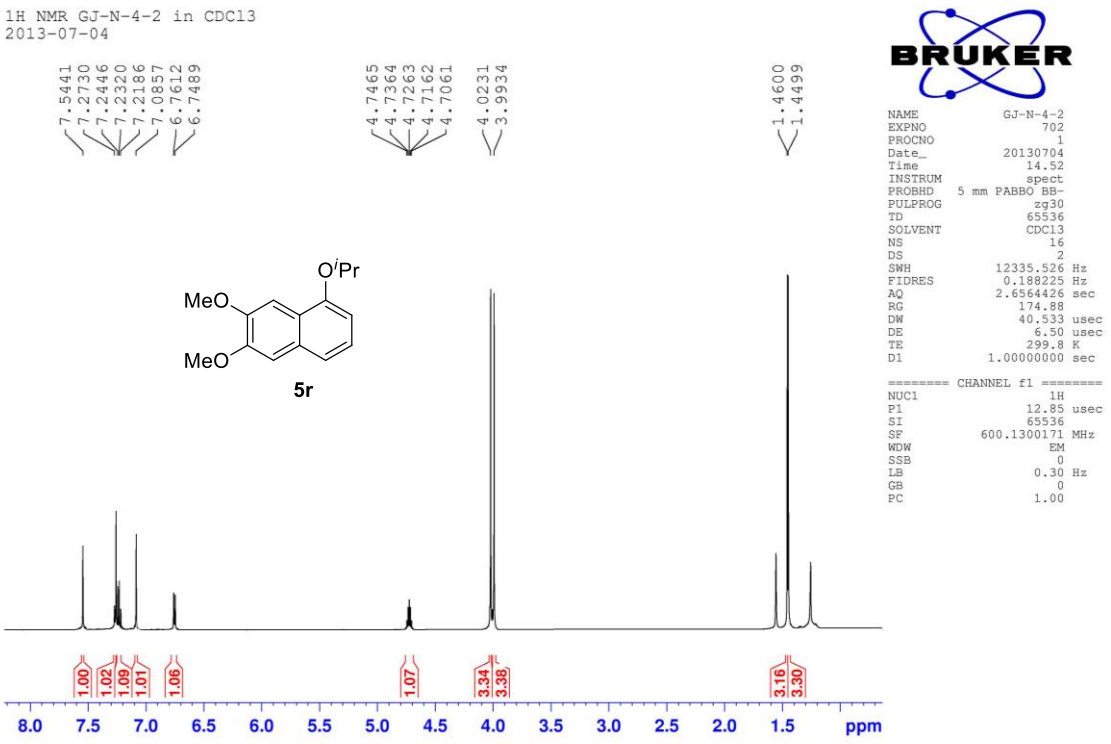
^{13}C NMR Spectrum of Compound **5p** ($CDCl_3$, 150 MHz)



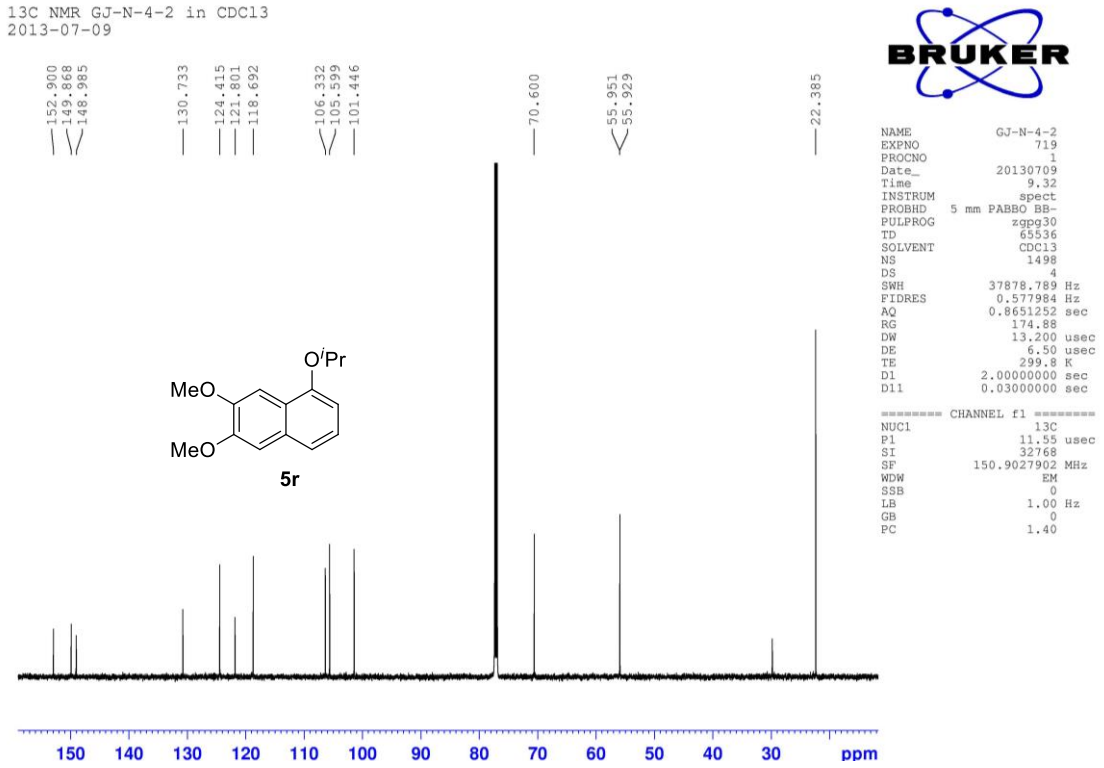
^{1}H NMR Spectrum of Compound **5q** ($CDCl_3$, 600 MHz)



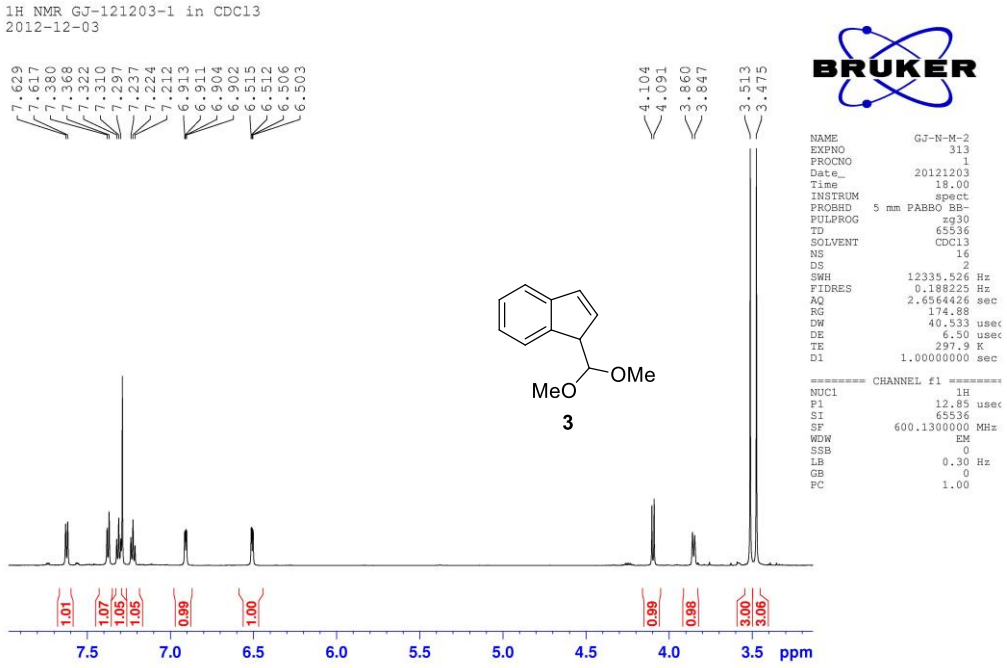
^{13}C NMR Spectrum of Compound **5q** ($CDCl_3$, 150 MHz)



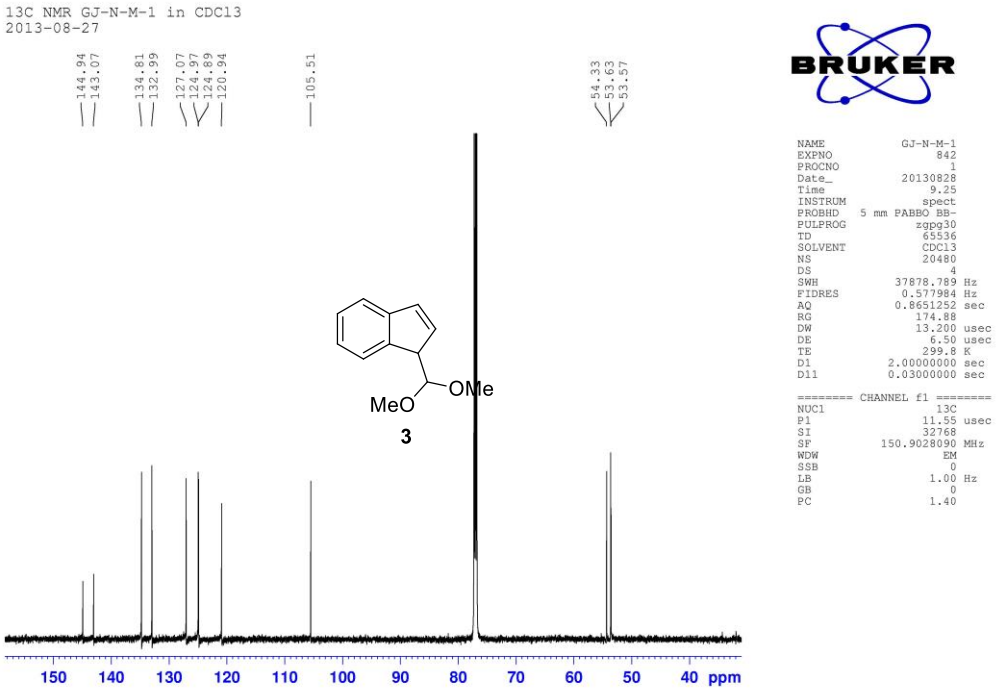
^{1}H NMR Spectrum of Compound **5r** ($CDCl_3$, 600 MHz)



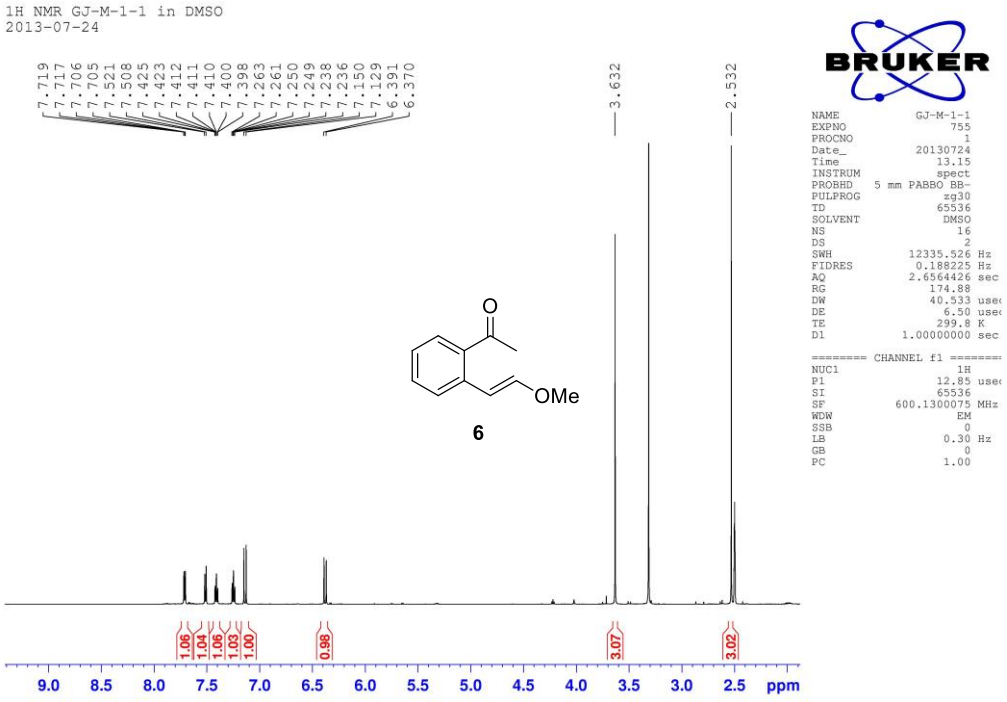
^{13}C NMR Spectrum of Compound **5r** ($CDCl_3$, 150 MHz)



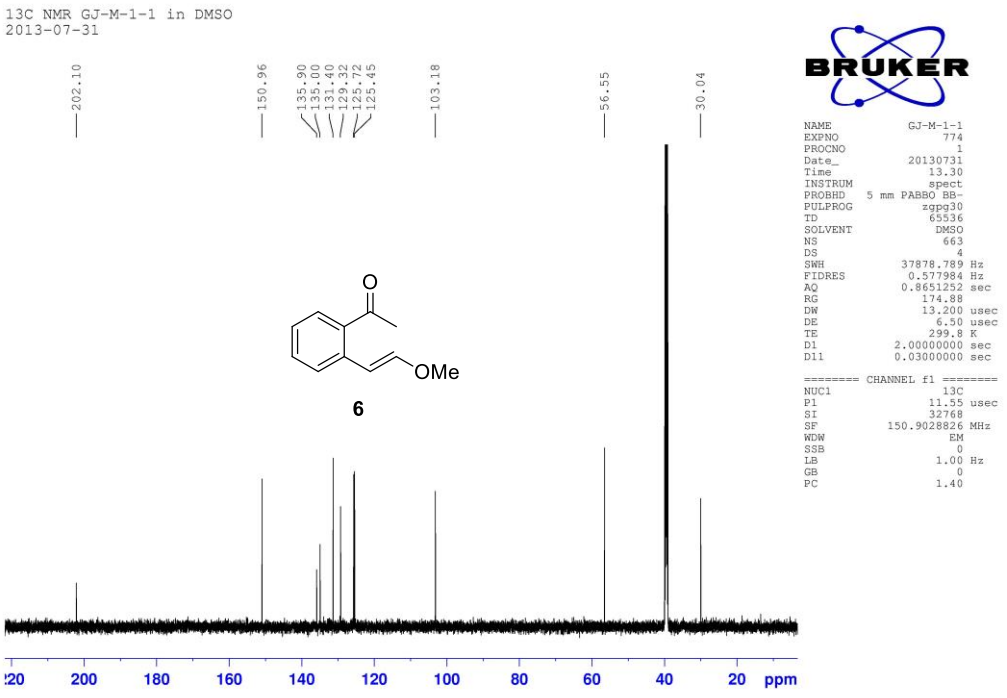
^{1}H NMR Spectrum of Compound **3** ($CDCl_3$, 600 MHz)



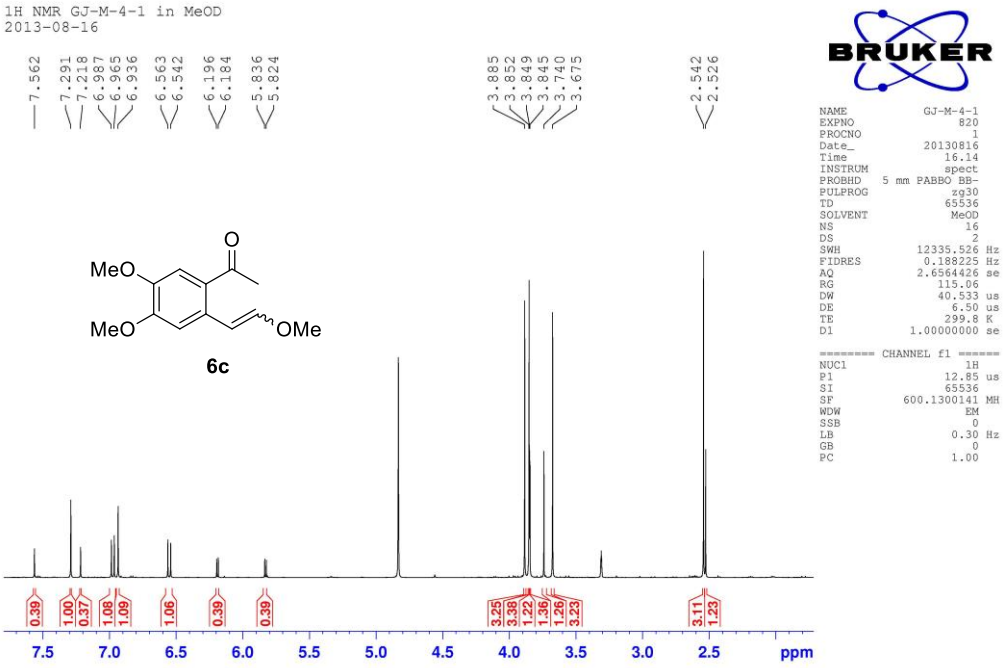
^{13}C NMR Spectrum of Compound **3** ($CDCl_3$, 150 MHz)



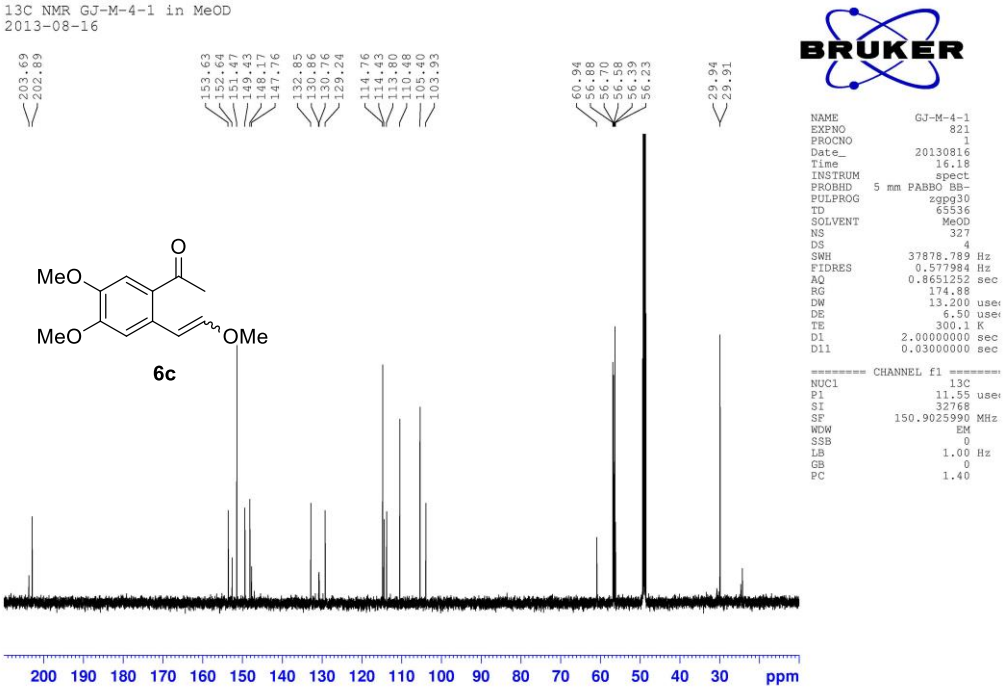
^{1}H NMR Spectrum of Compound **6** (DMSO-d_6, 600 MHz)



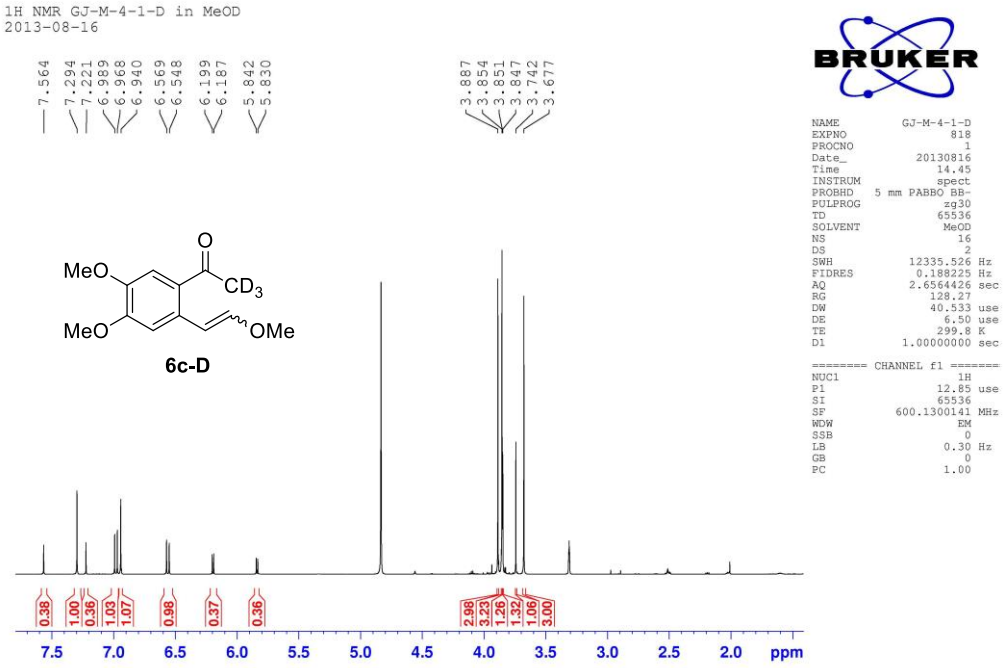
^{13}C NMR Spectrum of Compound **6** (DMSO-d_6, 150 MHz)



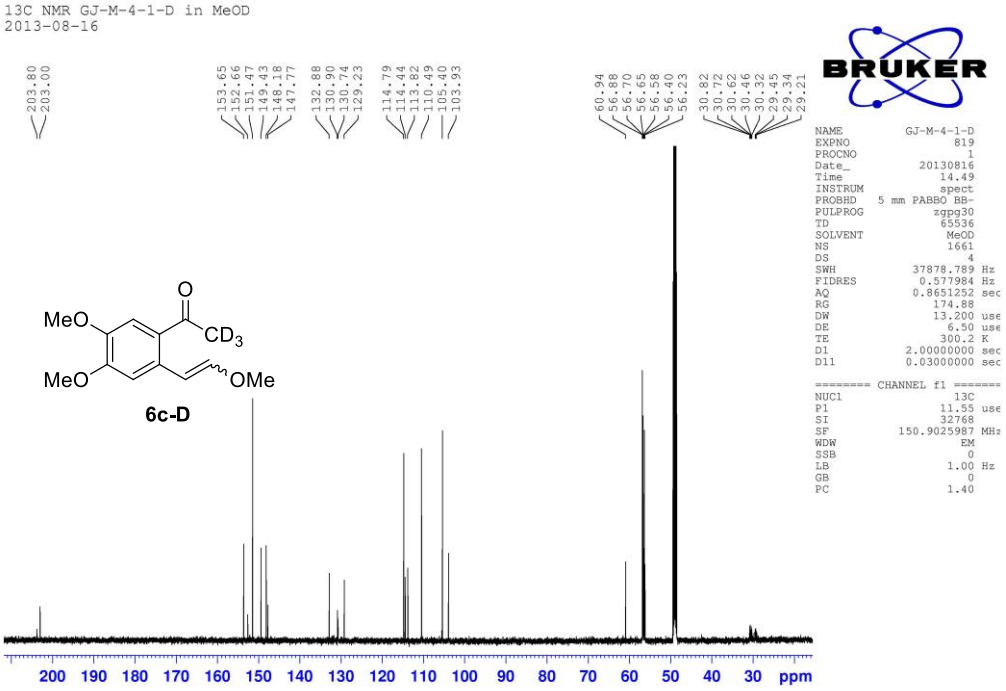
^{1}H NMR Spectrum of Compound **6c** (CD_3OD, 600 MHz)



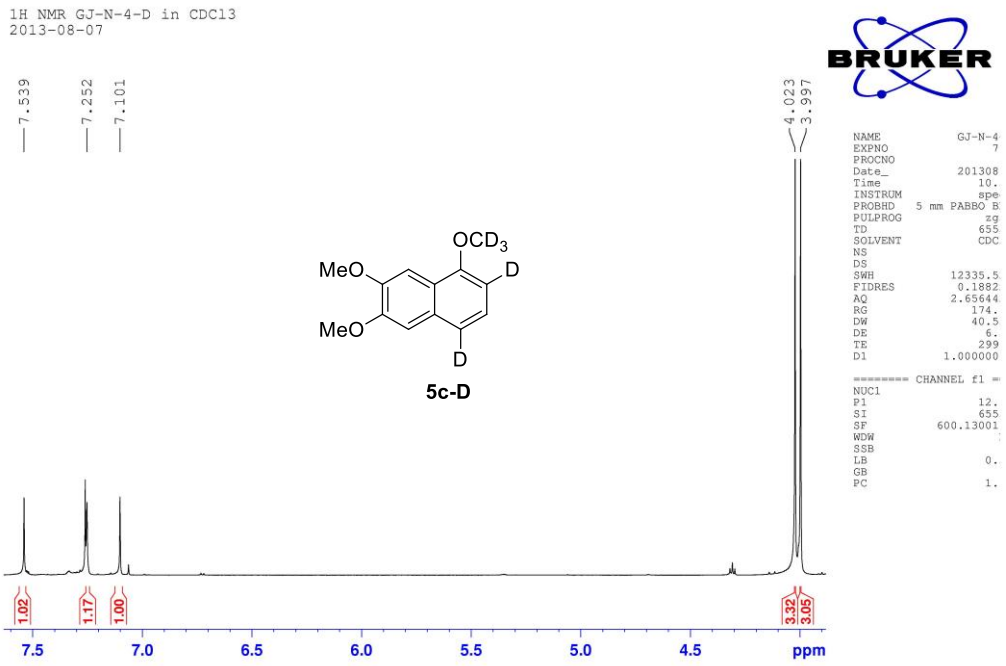
^{13}C NMR Spectrum of Compound **6c** (CD_3OD, 150 MHz)



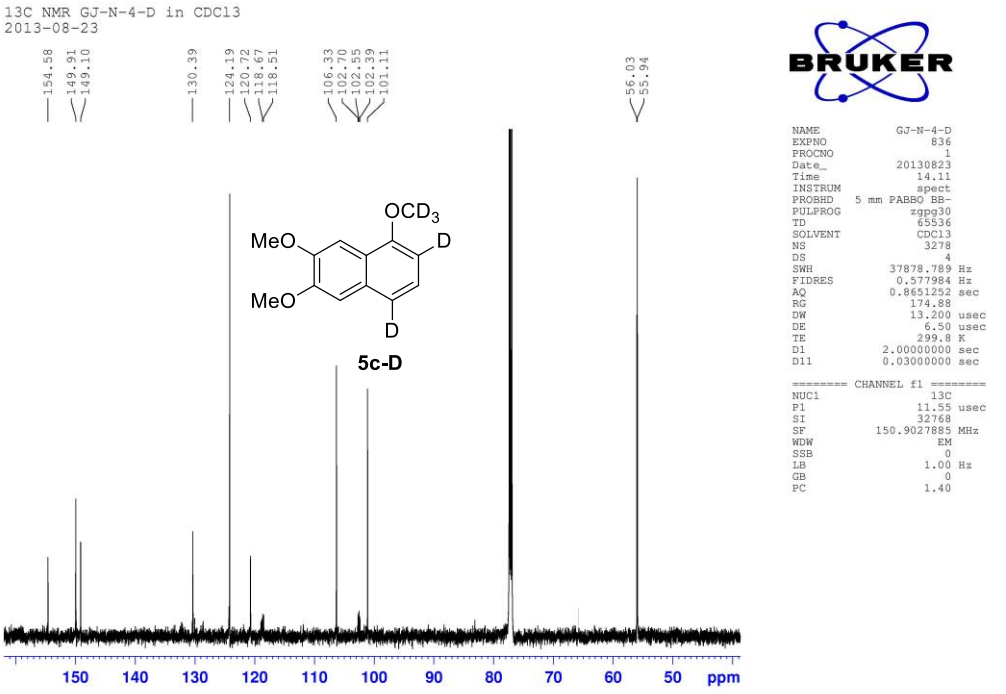
^{1}H NMR Spectrum of Compound **6c-D** (CD_3OD, 600 MHz)



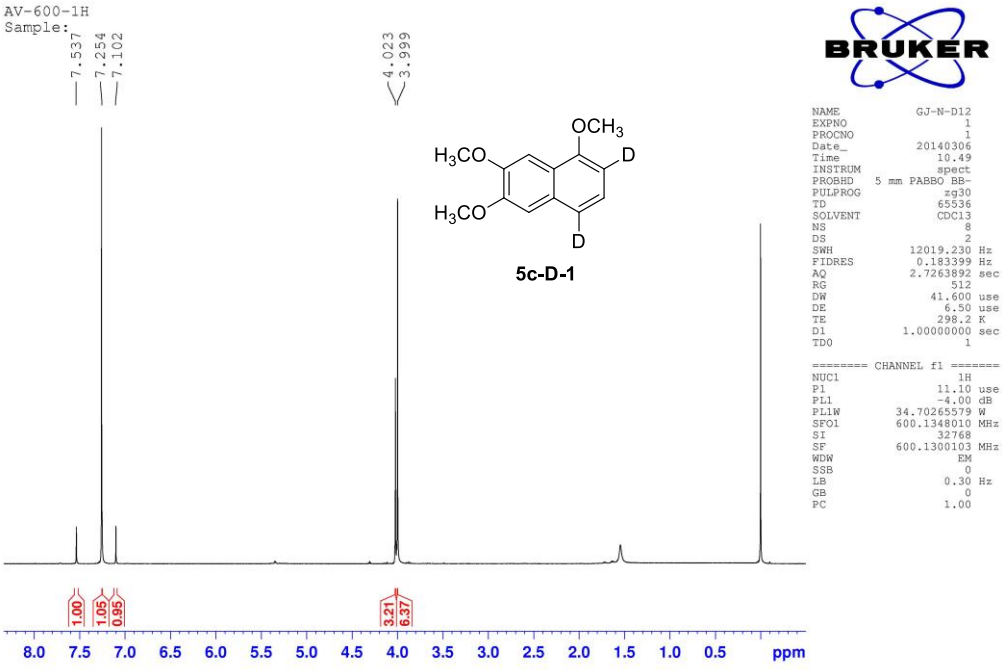
^{1}H NMR Spectrum of Compound **6c-D** (CD_3OD, 600 MHz)



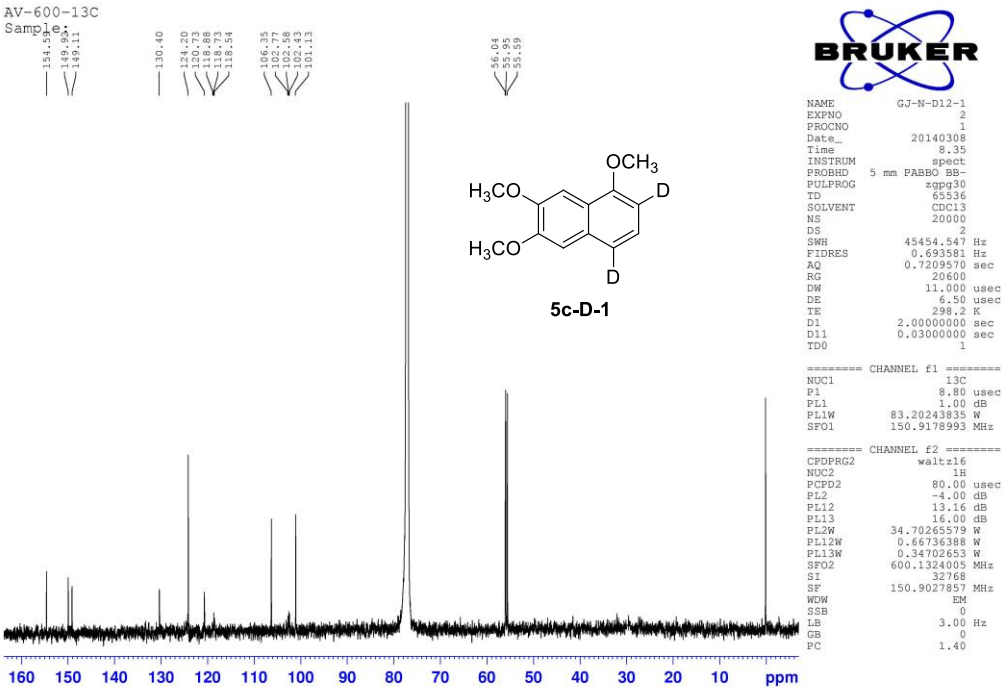
^{1}H NMR Spectrum of Compound **5c-D** ($CDCl_3$, 600 MHz)



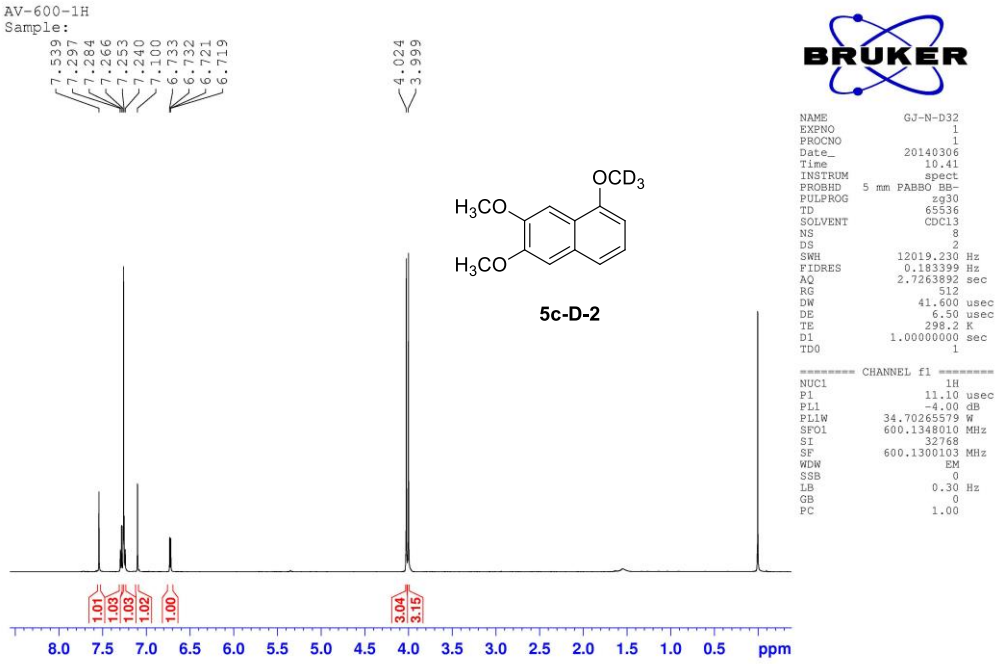
^{13}C NMR Spectrum of Compound **5c-D** ($CDCl_3$, 150 MHz)



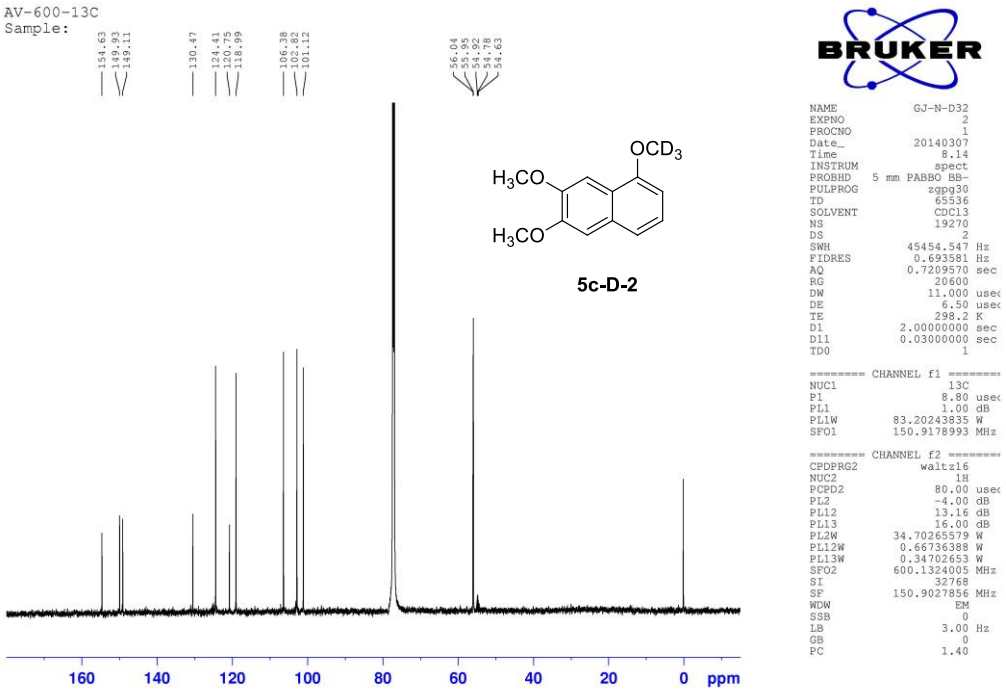
^{1}H NMR Spectrum of Compound **5c-D-1** ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of Compound **5c-D-1** ($CDCl_3$, 150 MHz)



^{1}H NMR Spectrum of Compound **5c-D-2** ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of Compound **5c-D-2** ($CDCl_3$, 150 MHz)