Electronic Supplementary Material (ESI) for Chemical Communications

1,3-Dipolar cycloaddition of 4-platinumisochromenyliums with an olefin and tandem insertion into benzylic C-H bond

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1. Preparation of substrates 1a-s:

The enynones **1a-s** were synthesized according to the literature reported procedure using sonogashira reaction of aromatic bromoaldehydes with benzyloxyalkynes or 1-hexyne followed by Grignard reaction with bromoalkenes and then Jones oxidation.[1]

2. Platinum–catalysed cyclizaton of enynones 1a-s:

To a solution of enynone (**1a-s**, 0.1 mmol) in 0.5 mL of dried solvent taken in 5 mL test tube, catalyst (5 mol %) was added. The reaction mixture was stirred for 1-24 h either at room temperature or in a preheated oil bath (60-100 ^{o}C). The reaction was monitored periodically by TLC. The solvent was removed under vacuum on completion of reaction and purified using column chromatography to afford pure product.

For the intermolecular reaction, the enynones (**1q-s**, 0.1 mmol) and *N*-ethylmaleic imide (0.1 mmol) was dissolved in 0.5 mL of dry toluene. Platinum(II) chloride (5 mol %) was added to it and the reaction mixture was stirred in a preheated oil bath at 60 ^{o}C for 5 h. On completion of the reaction analyzed with TLC, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude products (**2q** and **2s**) were purified by column chromatography using hexane and ethyl acetate.

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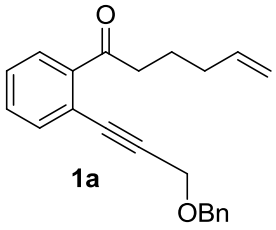
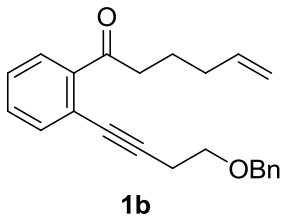
[1] a) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Letters* **1975**, *50*, 4467; b) K. R. Roesch and R. C. Larock *J. Org. Chem.*, **2002**, *67*, 86; c) N. Asao, K. Sato, Menggenbateer, and Y. Yamamoto, *J. Org. Chem.* **2005**, *70*, 3682.

3. Spectroscopic data of compounds:



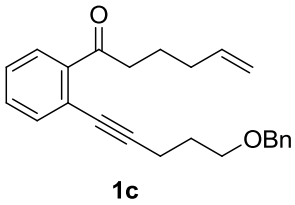
1a

1a: IR (NaCl, cm^{-1}) 3065, 3031, 2935, 2856, 2250, 1690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.55 (m, 1H), 7.45-7.29 (m, 7H), 5.82-5.75 (m, 1H), 5.01 (d, J = 17.6 Hz, 1H), 4.96 (d, J = 11.6 Hz, 1H), 4.70 (s, 2H), 4.43 (s, 2H), 3.06 (t, J = 7.2 Hz, 2H), 2.15-2.10 (m, 2H), 1.83 (quint, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.18, 141.62, 138.12, 137.48, 134.20, 130.92, 128.57, 128.53, 128.28, 128.07, 128.02, 120.62, 115.36, 90.46, 85.27, 71.81, 57.99, 41.17, 33.25, 23.47; HRMS *m/z* calcd for $C_{22}H_{23}O_2$ [M+1] 319.1698, found 319.1696.



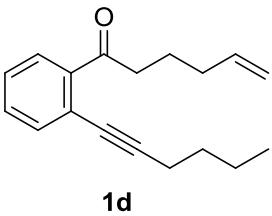
1b

1b: IR (NaCl, cm^{-1}) 3065, 3031, 2931, 2864, 2230, 1684; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.48 (m, 1H), 7.40-7.33 (m, 5H), 7.31-7.28 (m, 2H), 5.84-5.74 (m, 1H), 5.01 (d, J = 17.6Hz, 1H), 4.97 (d, J = 10.4 Hz, 1H), 4.59 (s, 2H), 3.69 (t, J = 6.8 Hz, 2H), 3.07 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 6.8 Hz, 2H), 2.10 (q, J = 7.2 Hz, 2H), 1.79 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.93, 141.71, 138.20, 138.07, 133.98, 130.76, 128.53, 127.95, 127.90, 127.81, 127.78, 121.52, 115.26, 92.59, 80.43, 73.12, 68.23, 41.42, 33.29, 23.53, 21.24; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1856.



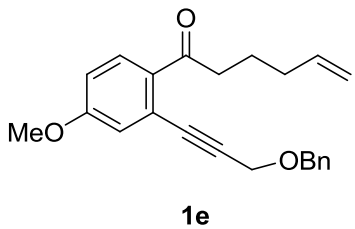
1c

1c : IR (NaCl, cm^{-1}) 3064, 3030, 2931, 2859, 2229, 1688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.2 Hz, 1H), 7.43 (m, 1H), 7.39-7.31 (m, 6H), 7.30-7.27 (m, 1H), 5.84-5.74 (m, 1H), 5.02 (d J = 16.0, 1H), 4.97 (d, J = 10.4 Hz, 1H), 4.54 (s, 2H), 3.63 (t, J = 6.4 Hz, 2H), 3.06 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.90 (quint, J = 6.4 Hz, 2H), 1.81 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.93, 141.63, 138.47, 138.13, 133.91, 130.68, 128.43, 127.84, 127.67, 127.62, 121.76, 115.26, 95.37, 79.73, 73.06, 68.83, 41.40, 33.28, 28.79, 23.52, 16.66; HRMS *m/z* calcd for $C_{24}H_{27}O_2$ [M+1] 347.2011, found 347.2010.



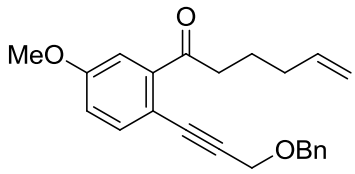
1d

1d : IR (NaCl, cm^{-1}) 3066, 2958, 2933, 2228, 1693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 1H), 7.47 (m, 1H), 7.39-7.30 (m, 2H), 5.86-5.76 (m, 1H), 5.03 (d, J = 17.2, 1H), 4.98 (d, J = 10.4 Hz, 1H), 3.10 (t, J = 7.6 Hz, 2H), 2.45 (t, J = 7.2 Hz, 2H), 2.13 (t, J = 6.4 Hz, 2H), 1.82 (t, J = 7.2 Hz, 2H), 1.60 (m, 2H), 1.52-1.45 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.29, 141.75, 138.22, 133.87, 130.70, 127.87, 127.64, 121.95, 115.25, 96.30, 79.46, 41.57, 33.35, 30.67, 23.59, 22.21, 19.50, 13.75; HRMS *m/z* calcd for $C_{18}H_{23}O$ [M+1] 255.1749, found 255.1751.



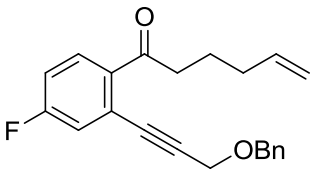
1e

1e : IR (NaCl, cm^{-1}) 3068, 3031, 2939, 2844, 2249, 1680; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 1H), 7.42-7.29 (m, 5H), 7.04 (d, J = 2.0 Hz, 1H), 6.90 (dd, J = 8.8, 2.0 Hz, 1H), 5.84-5.74 (m, 1H), 5.01 (d, J = 17.6 Hz, 1H), 4.96 (d, J = 10.0 Hz, 1H), 4.71 (s, 2H), 4.45 (s, 2H), 3.85 (s, 3H), 3.05 (t, J = 7.2 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.82 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.75, 161.56, 138.24, 137.45, 133.35, 130.94, 128.54, 128.26, 127.99, 123.08, 118.95, 115.23, 114.70, 90.49, 85.75, 71.86, 58.04, 55.63, 40.54, 30.30, 23.69; HRMS *m/z* calcd for $C_{23}H_{25}O_3$ [M+1] 349.1804, found 349.1802.



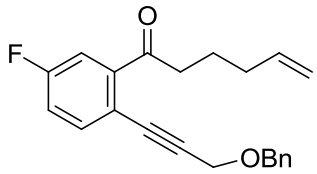
1f

1f : IR (NaCl, cm^{-1}) 3068, 3031, 2939, 2843, 2229, 2182, 1692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 1H), 7.40-7.29 (m, 5H), 7.12 (d, J = 2.8 Hz, 1H), 6.96 (dd, J = 9.6, 2.8 Hz, 1H), 5.82-5.75 (m, 1H), 5.01 (dd, J = 17.2, 1.6 Hz, 1H), 4.96 (d, J = 10.0 Hz, 1H), 4.67 (s, 2H), 4.41 (s, 2H), 3.85 (s, 3H), 3.08 (t, J = 7.6 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.82 (quint, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.34, 159.61, 143.22, 138.13, 137.49, 135.66, 128.56, 128.24, 128.00, 117.08, 115.34, 113.03, 112.68, 89.96, 85.16, 71.77, 58.06, 55.63, 41.38, 33.26, 23.49; HRMS *m/z* calcd for $C_{23}H_{25}O_3$ [M+1] 349.1804, found 349.1801.



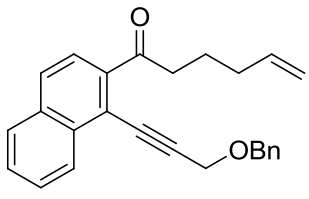
1g

1g : IR (NaCl, cm^{-1}) 3071, 3032, 2936, 2859, 1691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 8.8, 6.0 Hz, 1H), 7.41-7.30 (m, 5H), 7.22 (dd, J = 9.0, 2.4 Hz, 1H), 7.09 (td, J = 8.4, 2.8 Hz, 1H), 5.83-5.73 (m, 1H), 5.01 (d, J = 18.4 Hz, 1H), 4.97 (d, J = 11.2 Hz, 1H), 4.69 (s, 2H), 4.43 (s, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.82 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.11, 163.60 (d, J = 251.7 Hz), 137.98, 137.44 (d, J = 3.3 Hz), 137.29, 130.85 (d, J = 9.4 Hz), 128.50, 128.18, 127.99, 123.32 (d, J = 10.3 Hz), 120.83 (d, J = 23.1 Hz), 115.88 (d, J = 19.4 Hz), 115.33, 91.81, 84.28 (d, J = 2.5 Hz), 71.88, 57.81, 40.86, 33.13, 23.39; HRMS *m/z* calcd for $C_{22}H_{22}FO_2$ [M+1] 337.1604, found 337.1605.



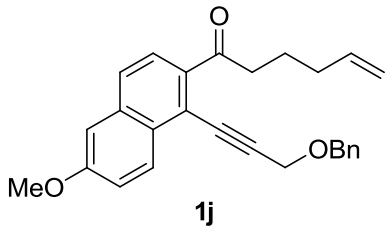
1h

1h : IR (NaCl, cm^{-1}) 3071, 3032, 2934, 2856, 2225, 1697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 8.6, 5.2 Hz, 1H), 7.41-7.31 (m, 6H), 7.14 (td, J = 8.4, 2.8 Hz, 1H), 5.81-5.75 (m, 1H), 5.01 (d, J = 17.6 Hz, 1H), 4.97 (d, J = 11.2 Hz, 1H), 4.68 (s, 2H), 4.41 (s, 2H), 3.06 (t, J = 6.8 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.82 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.77, 162.19 (d, J = 250.6 Hz), 143.62 (d, J = 6.3 Hz), 137.98, 137.39, 136.22 (d, J = 7.8 Hz), 128.59, 128.23, 128.06, 118.31 (d, J = 21.8 Hz), 116.72 (d, J = 3.5 Hz), 115.49, 115.25 (d, J = 23.2 Hz), 90.33, 84.22, 71.92, 57.94, 41.16, 33.17, 23.31; HRMS *m/z* calcd for $C_{22}H_{22}FO_2$ [M+1] 337.1604, found 337.1601.



1i

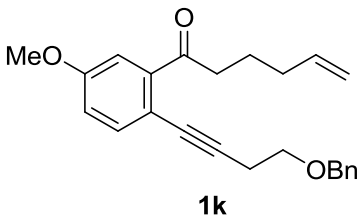
1i : IR (NaCl, cm^{-1}) 3064, 3032, 2934, 2861, 2216, 1690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.65-7.58 (m, 3H), 7.45-7.31 (m, 5H), 5.85-5.75 (m, 1H), 5.01 (d, J = 17.2, 1H), 4.97 (d, J = 10.4 Hz, 1H), 4.77 (s, 2H), 4.60 (s, 2H), 3.19 (t, J = 7.2 Hz, 2H), 2.15 (q, J = 7.2 Hz, 2H), 1.87 (quint, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.57, 140.76, 138.13, 137.43, 133.96, 133.45, 129.00, 128.63, 128.31, 128.10, 127.99, 127.91, 127.79, 127.34, 124.06, 118.40, 115.39, 96.73, 82.93, 71.97, 58.19, 41.92, 33.32, 23.66; HRMS *m/z* calcd for $C_{26}H_{25}O_2$ [M+1] 369.1855, found 369.1855.



1j

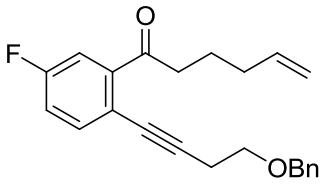
1j : IR (NaCl, cm^{-1}) 3066, 2936, 2218, 1685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 9.2 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.65(d, J = 8.8 Hz, 1H), 7.44-7.24 (m, 6H), 7.12 (d, J = 2.4 Hz, 1H), 5.85-5.75 (m, 1H), 5.01 (dd, J = 17.2, 1.6 Hz, 1H), 4.96 (d, J = 10.0 Hz, 1H), 4.77 (s, 2H), 4.58 (s, 2H), 3.93 (s, 3H), 3.17 (t, J = 7.2 Hz, 2H), 2.15 (q, J = 6.8 Hz, 2H), 1.87 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.74, 159.26, 138.19, 138.14, 137.43, 135.69, 129.11, 128.85, 128.59, 128.27, 128.05, 127.60, 125.02,

120.48, 118.71, 115.30, 106.02, 96.50, 83.25, 71.95, 58.19, 55.51, 41.66, 33.33, 23.75; HRMS *m/z* calcd for $C_{27}H_{27}O_3$ [M+1] 399.1960, found 399.1962.



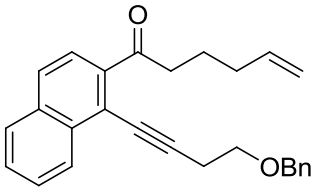
1k

1k : IR (NaCl, cm^{-1}) 3068, 3031, 2935, 2862, 2229, 1684; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 1H), 7.36-7.28 (m, 5H), 7.09 (d, J = 2 Hz, 1H), 6.93 (dd, J = 8.4, 2.8 Hz, 1H), 5.84-5.73 (m, 1H), 5.01 (dd, J = 17.2, 2.0 Hz, 1H), 4.97 (d, J = 10.0 Hz, 1H), 4.58 (s, 2H), 3.83 (s, 3H), 3.68 (t, J = 7.2 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.2 Hz, 2H), 2.10 (q, J = 7.2 Hz, 2H), 1.79 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.77, 159.05, 143.02, 138.17, 138.05, 135.30, 128.47, 127.75, 127.73, 117.17, 115.20, 113.72, 112.59, 90.89, 80.21, 73.05, 68.28, 55.49, 41.49, 33.26, 23.50, 21.17; HRMS *m/z* calcd for $C_{24}H_{27}O_3$ [M+1] 363.1960, found 363.1962.



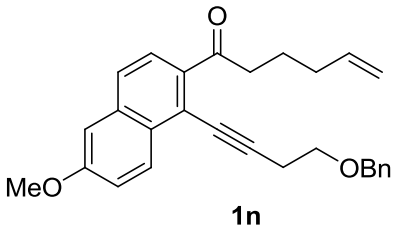
1l

1l : IR (NaCl, cm^{-1}) 3070, 2863, 2232, 1685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.6, 5.2 Hz, 1H), 7.35 (d, J = 4.4 Hz, 4H), 7.33-7.27 (m, 2H), 7.09 (td, J = 8.4, 2.8 Hz, 1H), 5.83-5.73 (m, 1H), 5.03 (d, J = 1.6 Hz, 1H), 4.97 (d, J = 10.8 Hz, 1H), 4.58 (s, 2H), 3.68 (t, J = 7.2 Hz, 2H), 3.07 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 2H), 2.10 (q, J = 6.8 Hz, 2H), 1.79 (quint, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.48, 161.85 (d, J = 249.5 Hz), 143.56 (d, J = 6.2 Hz), 138.09, 138.04, 135.99 (d, J = 7.7 Hz), 128.56, 127.87, 127.81, 118.17 (d, J = 21.9 Hz), 115.40, 115.19, 114.96, 92.50, 79.48, 73.17, 68.15, 41.38, 33.24, 23.40, 21.21; HRMS *m/z* calcd for $C_{23}H_{24}FO_2$ [M+1] 351.1760, found 351.1765.



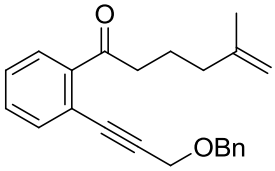
1m

1m : IR (NaCl, cm^{-1}) 3062, 3032, 2929, 2862, 2226, 1676; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (m, 1H), 7.85-7.80 (m, 2H), 7.62-7.53 (m, 3H), 7.40-7.28 (m, 5H), 5.85-5.75 (m, 1H), 5.02 (d, J = 16.8 Hz, 1H), 4.97 (d, J = 10.4 Hz, 1H), 4.64 (s, 2H), 3.81 (t, J = 6.8 Hz, 2H), 3.21 (t, J = 7.6 Hz, 2H), 2.94 (t, J = 6.4 Hz, 2H), 2.14 (q, J = 7.2 Hz, 2H), 1.85 (quint, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.16, 140.33, 138.24, 138.08, 134.02, 133.64, 128.58, 128.28, 128.18, 127.86, 127.83, 127.56, 127.50, 124.18, 119.60, 115.31, 99.20, 78.22, 73.27, 60.39, 42.05, 33.40, 23.76, 21.64; HRMS *m/z* calcd for $C_{27}H_{27}O_2$ [M+1] 383.2011, found 383.2010.



1n

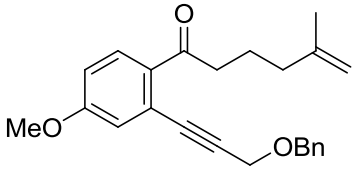
1n : IR (NaCl, cm^{-1}) 3065, 3030, 2933, 2861, 2226, 1670; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 9.6 Hz, 1H), 7.66 (dd, J = 19.2, 8.8 Hz, 2H), 7.40-7.28 (m, 5H), 7.18 (dd, J = 9.2, 2.8 Hz, 1H), 7.11(d, J = 2.4 Hz, 1H), 5.86-5.75 (m, 1H), 4.52 (dd, J = 17.2, 1.6 Hz, 2H), 4.63 (s, 2H), 3.94 (s,3H), 3.80 (t, J = 6.8 Hz, 2H), 3.20 (t, J = 7.6 Hz, 2H), 2.93 (t, J = 6.4 Hz, 2H), 2.13 (q, J = 7.2 Hz, 2H), 1.84 (quint, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.35, 159.17, 138.29, 138.05, 137.81, 135.70, 129.37, 129.03, 128.54, 127.83, 127.79, 126.94, 125.13, 120.11, 119.92, 115.21, 105.97, 98.98, 78.52, 73.21, 68.34, 55.48, 41.83, 33.40, 23.83, 21.60; HRMS *m/z* calcd for $C_{28}H_{29}O_3$ [M+1] 413.2117, found 413.21.



1o

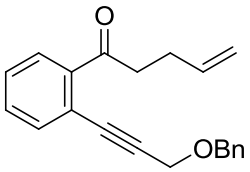
1o : IR (NaCl, cm^{-1}) 3066, 3031, 2936, 2230, 1691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.55 (m, 1H), 7.43-7.31 (m, 7H), 4.70 (s, 2H), 4.68 (d, J = 8.8 Hz, 2H), 4.43 (s, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.08 (t, J = 7.2 Hz, 2H), 1.87 (t, J = 7.2 Hz, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 202.98, 145.01, 141.48, 137.39, 134.09, 130.81, 128.45, 128.42, 128.16, 127.97, 127.89, 120.51, 110.62, 90.36, 85.21, 71.67, 57.87, 41.12, 37.09, 22.23, 22.02; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1856.



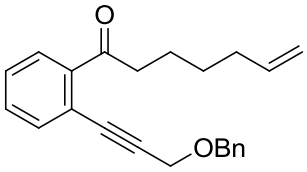
1p

1p : IR (NaCl, cm^{-1}) 3067, 2937, 2855, 2209, 1685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.42-7.31 (m, 5H), 7.04 (s, 1H), 6.90 (dd, *J* = 7.8, 2.0 Hz, 1H), 4.71 (s, 2H), 4.69 (d, *J* = 15.2 Hz, 2H), 4.45 (s, 2H), 3.85 (s, 3H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.08 (t, *J* = 7.2 Hz, 2H), 1.86 (t, *J* = 7.2 Hz, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.57, 161.49, 145.19, 137.43, 133.30, 130.87, 128.47, 128.19, 127.92, 123.01, 118.91, 114.60, 110.53, 90.44, 85.72, 71.80, 57.99, 55.54, 40.56, 37.20, 22.29; HRMS *m/z* calcd for $C_{24}H_{27}O_3$ [M+1] 364.2038, found 364.2041.



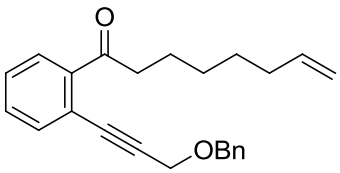
1q

1q : IR (NaCl, cm^{-1}) 3066, 3032, 2929, 2857, 2250, 1691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.46-7.29 (m, 7H), 5.92-5.82 (m, 1H), 5.06 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.69 (s, 2H), 4.43 (s, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.48 (quint, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.46, 141.34, 137.41, 137.20, 134.21, 131.04, 128.55, 128.27, 128.17, 128.01, 120.66, 115.39, 90.62, 85.26, 71.81, 57.96, 41.04, 28.38 ; HRMS *m/z* calcd for $C_{21}H_{21}O_2$ [M+1] 305.1542, found 305.1547.



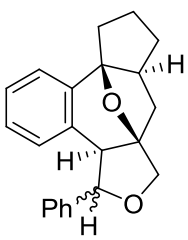
1r

1r : IR (NaCl, cm^{-1}) 3066, 3032, 2933, 2858, 2248, 1691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6Hz, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.45-7.29 (m, 7H), 5.81-5.75 (m, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 10.4 Hz, 1H), 4.69 (s, 2H), 4.43 (s, 2H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.07 (q, *J* = 6.8 Hz, 2H), 1.73 (quint, *J* = 7.2 Hz, 2H), 1.45 (quint, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.22, 141.62, 138.54, 137.44, 134.11, 130.83, 128.50, 128.20, 127.99, 127.95, 120.54, 114.69, 90.41, 85.23, 71.74, 57.94, 41.75, 33.63, 28.56, 23.87; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1859.



1s

1s : IR (NaCl, cm^{-1}) 3066, 3032, 2930, 2856, 2249, 1691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.45-7.31 (m, 7H), 5.83-5.73 (m, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.0 Hz, 1H), 4.69 (s, 2H), 4.43 (s, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.03 (q, *J* = 6.4 Hz, 2H),1.72 (quint, *J* = 7.6 Hz, 2H), 1.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.55, 141.63, 138.93, 137.43, 134.16, 130.88, 128.54, 128.52, 128.26, 128.04, 128.00, 120.58, 114.47, 90.39, 85.28, 71.78, 57.96, 41.83, 33.67, 38.83, 28.79, 24.29; HRMS *m/z* calcd for $C_{24}H_{27}O_2$ [M+1] 347.2011, found 347.2016.

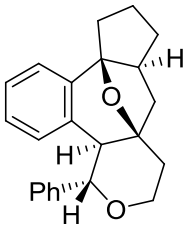


2a

2a (1:3 α/β mixture) : For α, IR (NaCl, cm^{-1}) 3065, 3032, 2951, 2868, 2247; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 5H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.16-7.12 (m, 1H), 6.98-6.94 (m, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 4.86 (d, *J* = 10.0 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 4.23 (d, *J* = 10.0Hz, 1H), 2.94 (d, *J* = 9.6 Hz, 1H), 2.51-2.50 (m, 1H), 2.42-2.30 (m, 2H), 2.15-2.08 (m, 2H), 2.01-1.92 (m, 1H), 1.89-1.81 (m, 2H), 1.51-1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.43, 140.44, 132.07, 129.31, 128.54, 128.9, 128.02, 126.70, 126.47, 121.20, 93.53, 90.56, 87.40, 74.93, 56.33, 52.60, 41.27, 34.87, 33.31, 26.13;

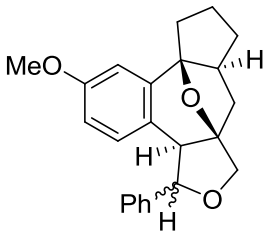
HRMS *m/z* calcd for $C_{22}H_{23}O_2$ [M+1] 319.1698, found 319.1699.

For β, IR (NaCl, cm^{-1}) 3065, 3031, 2954, 2867, 2248; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.19 (m, 2H), 7.07-7.01 (m, 4H), 6.95-6.91 (m, 1H), 6.83-6.79 (m, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.48 (d, *J* = 10.4 Hz, 1H), 4.33 (d, *J* = 10.0 Hz, 1H), 4.06 (d, *J* =10.4 Hz, 1H), 3.50 (d, *J* =10.0 Hz, 1H), 2.49-2.42 (m, 1H), 2.30-2.23 (m, 2H), 2.16-2.04 (m, 2H), 1.99-1.89 (m, 1H), 1.87-1.80 (m, 2H), 1.49-1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.23, 139.81, 133.20, 131.10, 129.23, 127.37, 127.19, 125.92, 125.60, 120.57, 92.73, 89.53, 86.56, 74.70, 52.14, 52.02, 40.63, 34.73, 33.17, 25.97.



2b

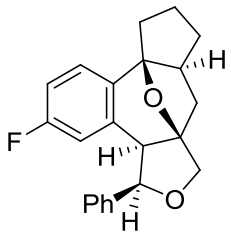
2b :IR (NaCl, cm^{-1}) 3063, 3031, 2950, 2866, 2244; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.28 (m, 3H), 7.14-7.12 (m, 3H), 7.07-7.02 (m, 1H), 6.71-6.67 (m, 1H), 5.74 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 10.0 Hz, 1H), 4.04-4.01 (m, 2H), 2.73 (d, *J* = 10.0 Hz, 1H), 2.53-2.46 (m, 1H), 2.28-2.05 (m, 6H), 1.99-1.79 (m, 3H), 1.65-1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.37, 140.98, 132.13, 131.84, 128.61, 128.09, 127.96, 126.71, 125.34, 121.05, 94.51, 83.41, 81.54, 65.26, 56.58, 52.84, 44.30, 38.15, 34.60, 32.23, 26.49; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1858.



2f

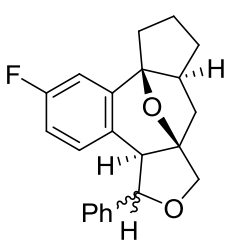
2f (1:3 α/β mixture) : For α, IR(NaCl, Cm^{-1}) 3063, 3031, 2950, 2869, 2246, ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 5H), 6.77 (d, *J* =2.4 Hz, 1H), 6.52-6.49 (m, 1H), 6.28 (d, *J* =8.8 Hz, 1H), 4.80 (d, *J* =9.6 Hz, 1H), 4.33 (d, *J* =10.0 Hz, 1H), 4.22 (d, *J* =10.4 Hz, 1H), 3.76 (s, 3H), 2.87 (d, *J* =9.6 Hz, 1H), 2.50-2.44 (m, 1H), 2.40-2.34 (m, 1H), 2.30-2.24 (m, 1H), 2.15-2.05 (m, 2H), 1.99-1.91 (m, 1H), 1.88-1.83 (m, 2H), 1.48-1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.34, 143.80, 140.47, 130.24, 128.53, 128.24, 127.99, 124.01, 110.94, 107.95, 93.53, 90.64, 87.56, 74.90, 55.77, 55.32, 52.51, 41.23, 34.82, 33.36, 26.11; HRMS *m/z* calcd for $C_{23}H_{25}O_3$ [M+1] 349.1804, found 349.1809.

For β, IR (NaCl, cm^{-1}) 3064, 3030, 2954, 2868, 2250, ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.18 (m, 2H), 7.08-7.02 (m, 3H), 6.62 (d, *J* = 2.8 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 6.38-6.35 (m, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 4.32 (d, *J* =10.0 Hz, 1H), 4.04 (d, *J* =10.0 Hz, 1H), 3.68 (s, 3H), 3.44 (d, *J* =10.0 Hz, 1H), 2.47-2.41 (m, 1H), 2.28-2.17 (m, 2H), 2.15-2.54 (m, 2H), 1.98-1.88 (m, 1H), 1.86-1.78 (m, 2H), 1.48-1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.31, 143.47, 139.86, 131.91, 129.18, 127.41, 127.13, 125.11, 110.78, 106.98, 92.71, 89.59, 86.62, 74.60, 55.15, 51.92, 51.43, 40.55, 34.65, 33.22, 25.93.



2g

2g : IR (NaCl, cm^{-1}) 3064, 3032, 2955, 2865, 2245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 2H), 7.10-7.05 (m, 3H), 7.01 (dd, *J* =7.2, 6.0 Hz, 1H), 6.61 (td, *J* = 8.6, 2.4 Hz, 1H), 6.26 (dd, *J* = 4.7, 2.4 Hz, 1H), 5.45 (d, *J* = 10.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 4.04 (d, *J* = 9.6 Hz, 1H), 3.46 (d, *J* = 9.6 Hz, 1H), 2.45-2.38 (m, 1H), 2.30-2.18 (m, 2H), 2.15-2.04 (m, 2H), 1.99-1.89 (m, 1H), 1.86-1.80 (m, 2H), 1.48-1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.72 (d, *J* = 242.4 Hz), 139.28, 138.06 (d, *J* = 2.8 Hz), 139.57 (d, *J* = 7.7 Hz), 128.96, 127.45, 127.39, 121.96 (d, *J* = 11.1 Hz), 117.50 (d, *J* = 21.5 Hz), 112.14 (d, *J* = 21.0 Hz), 92.27, 89.17, 86.14, 74.44, 52.06, 51.78, 40.34, 34.54, 33.21, 25.73; HRMS *m/z* calcd for $C_{22}H_{22}FO_2$ [M+1] 337.1604, found 337.1607.

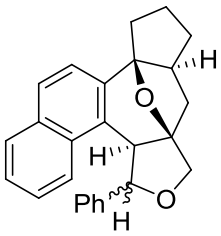


2h

2h (1:3 α/β mixture) : For α, IR (NaCl, cm^{-1}) 3066, 3033, 2945, 2866, 2234; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33(m, 5H), 6.91 (dd, *J* = 4.8, 2.4 Hz, 1H), 6.64 (td, *J* = 8.6, 2.8 Hz, 1H), 6.29 (dd, *J* = 5.6, 4.1 Hz, 1H), 4.79 (d, *J* = 9.6 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 4.23 (d, *J* = 10.4 Hz, 1H), 2.88 (d,

J = 10.0 Hz, 1H), 2.51-2.44 (m, 1H), 2.41-2.33 (m, 1H), 2.27-2.19 (m, 1H), 2.16-2.05 (m, 2H), 2.01-1.95 (m, 1H), 2.88-1.81 (m, 2H), 1.50-1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.57(d, *J* = 244.0 Hz), 144.72 (d, *J* = 6.3 Hz), 140.03, 130.70 (d, *J* = 7.9 Hz), 128.63, 128.44, 127.96, 127.54 (d, *J* = 3.0 Hz), 113.06 (d, *J* = 21.0 Hz), 108.72 (d, *J* = 22.2Hz), 93.26, 90.58, 87.36, 74.80, 55.73, 52.48, 41.22, 34.77, 33.38, 26.06; HRMS *m/z* calcd for $C_{22}H_{22}FO_2$ [M] 336.1526, found 337.1528.

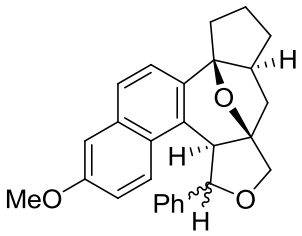
For β, IR (NaCl, cm^{-1}) 3065, 3031, 2955, 2866, 2231; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.16 (m, 2H), 7.06-7.03 (m, 3H), 6.77 (d, *J* = 9.6 Hz, 1H), 6.50 (d, *J* = 6.4 Hz, 2H), 5.44 (d, *J* = 10.0 Hz, 1H), 4.33 (d, *J* =10.0 Hz, 1H), 4.04 (d, *J* =10.0 Hz, 1H), 3.44 (d, *J* =9.6 Hz, 1H), 2.47-2.40 (m, 1H), 2.28-2.23 (m, 1H), 2.16-2.04 (m, 3H), 1.98-1.89 (m, 1H), 1.85-1.79 (m, 2H), 1.48-1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.59 (d, *J* = 243.5 Hz), 144.24 (d, *J* = 6.4 Hz), 139.47, 132.28 (d, *J* = 7.9 Hz), 129.03, 128.74 (d, *J* = 23.0 Hz), 127.40, 127.22, 112.55 (d, *J* = 21.2 Hz), 107.88 (d, *J* = 22.2 Hz), 92.29, 89.46, 86.36, 74.43, 51.81, 51.37, 40.34, 34.51, 33.14, 25.76.



2i

2i (1:3 α/β mixture) : For α, IR (NaCl, cm^{-1}) 2949, 2866, 2388; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.68 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.29-7.17 (m, 6H), 6.74-6.70 (m, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.07 (d, *J* = 9.2 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 4.30 (d, *J* = 10.0 Hz, 1H), 3.49 (d, *J* = 9.2 Hz, 1H), 2.60-2.53 (m, 1H), 2.45-2.43 (m, 1H), 2.36-2.18 (m, 3H), 2.05-1.96 (m, 1H), 1.94-1.90 (m, 2H), 1.52-1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.02, 139.21, 132.87, 132.81, 128.72, 128.11, 128.05, 127.73, 127.66, 127.63, 124.94, 124.91, 127.75, 120.28, 94.04, 91.34, 88.18, 75.15, 55.37, 53.90, 38.64, 34.94, 33.46, 26.81; HRMS *m/z* calcd for $C_{26}H_{25}O_2$ [M+1] 369.1855, found 369.1856.

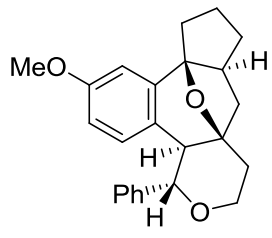
For β, IR (NaCl, cm^{-1}) 3061, 2953, 2864, 2245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.47-7.43 (m, 1H), 7.35-7.31 (m, 1H), 7.26-7.24 (m, 2H), 7.12-7.10 (m, 2H), 6.78-6.76 (m, 2H), 5.85 (d, *J* = 9.6 Hz, 1H), 4.42 (d, *J* = 9.6 Hz, 1H), 4.20 (d, *J* = 9.6 Hz, 1H), 3.92 (d, *J* = 9.2 Hz, 1H), 2.45-2.37 (m, 2H), 2.30-2.25 (m, 1H), 2.21-2.10 (m, 2H), 2.02-1.95 (m, 1H), 1.92-1.86 (m, 2H), 1.51-1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.81, 139.50, 132.37, 132.31, 128.69, 128.54, 127.01, 126.70, 126.58, 125.78, 125.01, 124.89, 119.97, 93.14, 89.75, 86.00, 75.11, 53.19, 51.14, 39.47, 34.88, 33.26, 26.62.



2j

2j (1:3 α/β mixture) : For α, IR (NaCl, cm^{-1}) 3061, 3032, 2951, 2868, 2247; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.30-7.23 (m, 5H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 9.6 Hz, 1H), 6.39-6.36 (m, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 4.42 (d, *J* = 9.6 Hz, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 3.82 (s, 3H), 3.43 (d, *J* = 9.6 Hz, 1H), 2.57-2.50 (m, 1H), 2.45-2.39 (m, 1H), 2.35-2.15 (m, 3H), 2.04-1.85 (m, 3H), 1.52-1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.70, 141.91, 136.95, 134.12, 128.77, 128.14, 127.68, 127.59, 127.55, 126.53, 126.43, 120.82, 117.32, 105.86, 93.98, 91.27, 88.13, 75.16, 55.49, 55.25, 53.81, 38.59, 34.91, 33.40, 26.73; HRMS *m/z* calcd for $C_{27}H_{27}O_3$ [M+1] 399.1960, found 399.1961.

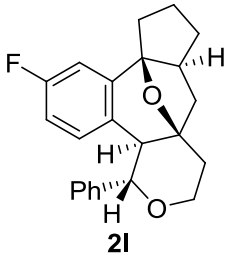
For β, IR (NaCl, cm^{-1}) 3062, 3029, 2954, 2865, 2246; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.13-7.10 (m, 3H), 6.94-6.93 (m, 1H), 6.80-6.79 (m, 3H), 5.80 (d, *J* = 9.6 Hz, 1H), 4.41 (d, *J* = 9.6 Hz, 1H), 4.18 (d, *J* = 10.4 Hz, 1H), 3.86 (s, 3H), 2.43-2.35 (m, 2H), 2.29-2.24 (m, 1H), 2.20-2.08 (m, 2H), 2.02-1.84 (m, 4H), 1.50-1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.89, 139.83, 137.39, 133.57, 128.79, 128.71, 127.81, 126.75, 126.67, 126.46, 125.80, 120.53, 118.47, 106.44, 93.14, 89.73, 86.07, 75.14, 55.35, 53.18, 51.19, 39.46, 34.90, 33.26, 26.61.



2k

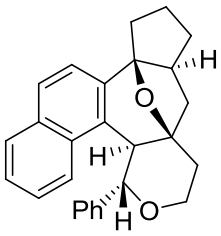
2k : IR (NaCl, cm^{-1}) 3063, 3032, 2950, 2866, 2245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.18 (m, 5H), 6.68 (d, *J* =2.8 Hz, 1H), 6.26-6.23 (m, 1H), 5.65 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 10.0 Hz, 1H),

4.02-3.99 (m, 2H), 3.71 (s, 3H), 2.67 (d, *J* = 10.0 Hz, 1H), 2.47-2.39 (m, 1H), 2.27-2.05 (m, 5H), 1.98-1.78 (m, 3H), 1.61 (d, *J* = 11.6 Hz, 1H), 1.56-1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.27, 142.80, 141.15, 132.79, 128.73, 128.66, 128.08, 127.80, 124.27, 110.09, 107.34, 94.52, 83.54, 81.66, 65.27, 56.45, 55.19, 52.09, 44.42, 38.19, 34.64, 32.39, 26.53; HRMS *m/z* calcd for $C_{24}H_{27}O_3$ [M] 362.1882, found 363.1881.



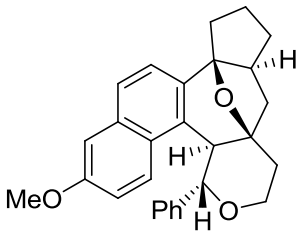
2l

2l : IR (NaCl, cm^{-1}) 3067, 3033, 2940, 2866, 2235; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.15 (m, 5H), 6.85-6.81 (m, 1H), 6.40-6.36 (m, 1H), 5.69-5.65 (m, 1H), 4.46 (d, *J* = 9.6 Hz, 1H), 4.02-3.99 (m, 2H), 2.68 (d, *J* = 10.0Hz, 1H), 2.42-2.35 (m, 1H), 2.27-2.04 (m, 5H), 1.99-1.79 (m, 3H), 1.65-1.60 (m, 1H), 1.56-1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.63 (d, *J* = 243.7 Hz), 143.64 (d, *J* = 6.1 Hz), 140.73, 132.25 (d, *J* = 7.7 Hz), 128.59, 128.55 (d, *J* = 3.3 Hz), 128.45, 128.09 (d, *J* = 7.9 Hz), 127.72 (d, *J* = 3.1 Hz), 112.02 (d, *J* = 20.8 Hz), 94.20 (d, *J* = 2.0 Hz), 83.36, 81.63, 65.22, 56.50, 52.25, 44.23, 38.02, 34.55, 32.32, 26.43; HRMS *m/z* calcd for $C_{23}H_{24}FO_2$ [M+1] 351.1760, found 351.1766.



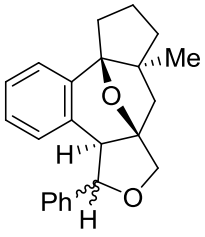
2m

2m : IR (NaCl, cm^{-1}) 3058, 3033, 2949, 2867, 2245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.08-7.05 (m, 1H), 6.94-6.64 (m, 7H), 4.80 (d, *J* = 9.2 Hz, 1H), 4.16-4.14 (m, 2H), 3.31 (d, *J* = 9.6 Hz, 1H), 2.70-2.63 (m, 1H), 2.36-2.04 (m, 5H), 1.95-1.83 (m, 3H), 1.64 (d, *J* = 12.0 Hz, 1H), 1.59-1.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.92, 138.09, 133.39, 132.03, 128.03, 127.52, 127.47, 127.34, 127.27, 126.98, 124.30, 123.94, 123.57, 119.97, 94.64, 83.47, 82.26, 65.49, 57.63, 50.63, 50.14, 44.04, 38.44, 34.34, 32.02, 26.76; HRMS *m/z* calcd for $C_{27}H_{27}O_2$ [M] 382.1933, found 382.1938.



2n

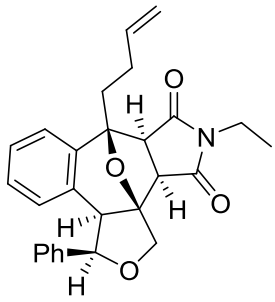
2n : IR (NaCl, cm^{-1}) 3053, 2947, 2864, 2228; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 6.98-6.75 (m, 7H), 6.34-6.30 (m, 1H), 4.79 (d, *J* = 9.2 Hz, 1H), 4.15-4.13 (m, 2H), 3.79 (s, 3H), 3.24 (d, *J* = 9.2 Hz, 1H), 2.68-2.61 (m, 1H), 2.34-2.04 (m, 5H), 1.95-1.82 (m, 3H), 1.63 (d, *J* = 12.4 Hz, 1H), 1.58-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.05, 140.94, 135.95, 133.24, 129.01, 128.17, 127.50, 127.41, 127.30, 127.27, 127.22, 126.24, 125.14, 120.58, 116.89, 94.59, 83.44, 82.19, 65.46, 27.59, 55.29, 50.38, 44.05, 38.50, 34.33, 31.97, 26.69; HRMS *m/z* calcd for $C_{28}H_{29}O_3$ [M+1] 413.2117, found 413.2122.



2o

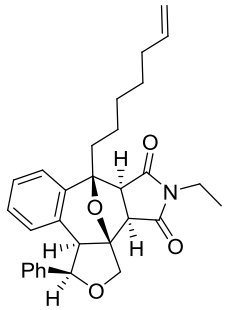
2o (1:2 α/β mixture) : For α, IR (NaCl, cm^{-1}) 3064, 3031, 2954, 2869, 2245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 5H), 7.18-7.212 (m, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 7.2 Hz, 1H), 4.87 (d, *J* = 9.6 Hz, 1H), 4.30 (d, *J* = 10.0 Hz, 1H), 4.21 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 9.6 Hz, 1H), 2.36-2.28 (m, 1H), 2.24 (d, *J* = 12.8 Hz, 1H), 2.17-2.06 (m, 2H), 1.92 (d, *J* = 13.2 Hz, 2H), 1.88-1.80 (m, 1H), 1.70-1.64 (m, 1H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.52, 139.46, 132.39, 129.12, 128.57, 128.30, 128.01, 126.71, 126.27, 123.58, 95.58, 88.69, 87.40, 75.33, 56.77, 54.90, 48.99, 43.43, 32.31, 25.98, 23.58; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1854.

For β, IR (NaCl, cm^{-1}) 3064, 3031, 2951, 2869, 2245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.33 (m, 5H), 7.30-7.24 (m, 2H), 7.22-7.19 (m, 2H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.4 Hz, 1H), 3.95 (d, *J* = 11.6 Hz, 1H), 3.87 (d, *J* =11.6 Hz, 1H), 2.47-2.39 (m, 1H), 2.31 (d, *J* = 7.6 Hz, 1H), 2.29-2.22 (m, 1H), 2.18-2.10 (m, 2H), 2.09-1.88 (m, 2H), 1.69-1.64 (m, 1H), 0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.56, 136.03, 134.40, 128.50, 128.45, 127.76, 127.62, 127.33, 126.74, 124.61, 121.72, 93.31, 73.12, 69.96, 63.32, 47.57, 36.39, 30.01, 26.62, 24.91, 22.62, 19.00.



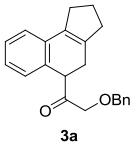
2q

2q: IR (NaCl, cm^{-1}) 2977, 2231, 1700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-6.93 (m, 9H), 5.82-5.72 (m, 1H), 5.56 (d, J = 10.0 Hz, 1H), 4.98-4.92 (m, 2H), 4.77 (d, J =11.2 Hz, 1H), 4.24 (d, J =10.8 Hz, 1H), 3.62-3.54 (m, 3H,) 3.21 (ABq, $\Delta\delta$ = 25.4 Hz, J = 7.2 Hz, 2H), 2.61-2.53 (m, 1H), 1.82-1.74 (m, 2H), 1.62-1.56 (m, 1H), 1.21-1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.46, 174.51, 139.56, 139.48, 138.23, 131.30, 128.09, 127.30, 127.26, 127.23, 127.10, 122.87, 114.51, 88.30, 84.85, 84.23, 72.83, 57.77, 52.25, 50.45, 34.25, 32.11, 28.25, 13.25; HRMS *m/z* calcd for $C_{27}H_{28}NO_4$ [M+1] 430.2018, found 430.2023.



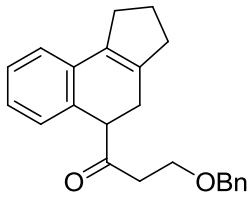
2s

2s : IR (NaCl, cm^{-1}) 3073, 3034, 2934, 2855, 2226, 1697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-6.91 (m, 9H), 5.84-5.74 (m, 1H), 5.55 (d, J = 9.2 Hz, 1H), 4.99-4.92 (m, 2H), 4.76 (d, J = 10.8 Hz, 1H), 4.24 (d, J =10.8Hz, 1H), 3.61-3.54 (m, 3H,) 3.19 (ABq, $\Delta\delta$ = 29.8 Hz, J = 7.6 Hz, 2H), 2.49-2.42 (m, 1H), 1.99 (d, J =6.0 Hz, 2H), 1.67-1.62 (m, 1H), 1.30-1.17 (m, 7H), 1.07-1.04 (m, 1H), 0.88-0.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.43, 174.53, 139.73, 139.47, 138.88, 131.10, 130.49, 128.05, 127.12, 127.06, 127.02, 126.98, 114.26, 88.07, 85.04, 84.15, 72.75, 57.69, 52.11, 50.35, 34.11, 33.66, 32.91, 29.41, 28.77, 23.90, 13.14; HRMS *m/z* calcd for $C_{30}H_{34}NO_4$ [M+1] 472.2488, found 472.2492.



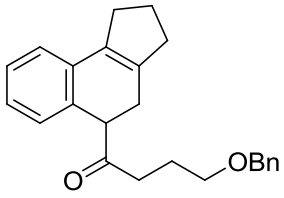
3a

3a : IR (NaCl, cm^{-1}) 3061, 3029, 2922, 2843, 1722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 6H), 7.19 (d, J =7.2 Hz, 1H) 7.14-7.11 (m, 1H), 7.05 (d, J =7.2 Hz, 1H), 4.48 (ABq, $\Delta\delta$ = 13.8 Hz, J = 11.6 Hz, 2H), 4.01 (ABq, $\Delta\delta$ = 50.8 Hz, J = 17.6 Hz, 2H), 3.84 (dd, J = 2.8 Hz, J = 7.6 Hz, 1H), 2.78 (d, J = 17.6 Hz, 1H), 2.63-2.46 (m, 5H), 2.05-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.95, 139.08, 137.29, 134.18, 133.63, 131.13, 128.62, 128.54, 128.14, 128.04, 126.44, 123.21, 73.38, 73.21, 49.73, 36.34, 30.87, 26.69, 22.38; HRMS *m/z* calcd for $C_{22}H_{23}O_2$ [M+1] 319.1698, found 319.1698.



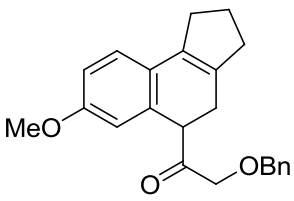
3b

3b : IR (NaCl, cm^{-1}) 3061, 3029, 2869, 2249, 1710; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 7H), 7.15-7.04 (m, 2H), 4.43 (s, 2H), 3.73-3.57 (m, 3H), 2.82 (d, J = 17.2 Hz, 1H), 2.76-2.43 (m, 7H), 2.02-1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.04, 139.23, 138.28, 134.12, 133.37, 131.82, 128.98, 128.45, 127.92, 127.80, 126.36, 123.13, 73.34, 65.68, 52.88, 40.32, 36.35, 30.89, 26.42, 22.39; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1857.



3c

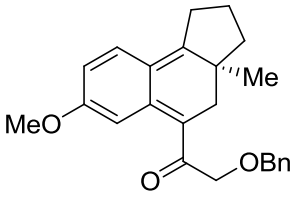
3c : IR (NaCl, cm^{-1}) 3061, 3028, 2928, 2846, 1708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (m, 7H), 7.16-7.12 (m, 1H), 7.05 (d, J = 7.2 Hz, 1H) 4.40 (s, 2H), 3.70 (dd, J = 5.1, 2.8 Hz, 1H), 3.35 (t, J = 5.6 Hz, 2H), 2.64 (m, 1H), 2.05-2.43 (m, 7H), 2.02-1.95 (m, 2H), 1.83-1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.80, 139.29, 138.58, 134.12, 133.38, 132.23, 128.91, 128.47, 127.84, 127.70, 127.65, 126.30, 123.10, 72.83, 69.31, 52.60, 36.71, 36.39, 30.90, 26.68, 23.90, 22.41; HRMS *m/z* calcd for $C_{24}H_{27}O_2$ [M+1] 347.2011, found 347.2012.



3e

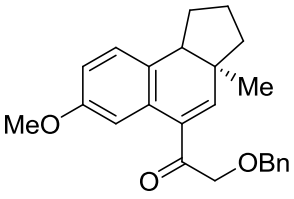
3e : IR (NaCl, cm^{-1}) 3063, 3031, 2937, 2841, 2249, 1724; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 5H), 6.98 (m, 1H), 6.78-6.76 (m, 2H), 4.49 (ABq, $\Delta\delta$ = 11.6 Hz, J = 5.2 Hz, 2H), 4.03(q, J = 18.0 Hz, 2H), 4.03(dd, J = 4.0, 2.8 Hz, 1H), 3.78 (s, 3H), 2.72 (d, J = 16.8 Hz, 1H), 2.60-2.44 (m, 5H), 2.05-1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.92, 158.28, 137.32, 135.94, 133.30, 132.78, 126.55, 128.16, 128.05, 127.44, 124.25, 115.31, 112.45, 73.27, 73.23, 55.48,

50.23, 36.19, 31.02, 26.81, 22.44; HRMS *m/z* calcd for $C_{23}H_{25}O_3$ [M+1] 349.1804, found 349.1805.



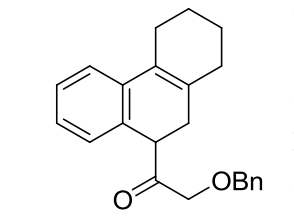
pre-3p

pre-3p: IR (NaCl, cm^{-1}) 3074, 3043, 2938, 2252, 1729; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 1H), 7.33 (m, 4H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.46 (s, 1H), 5.89 (s, 1H), 4.58 (q, *J* = 12.4 Hz, 2H), 4.22 (s, 3H), 3.74 (s, 3H), 2.59-2.50 (m, 1H), 2.43-2.37 (m, 1H), 2.12-2.05 (m, 1H), 1.95-1.90 (m, 1H), 1.74-1.68 (m, 2H), 1.28 (d, *J* = 11.2 Hz, 1H), 1.00 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.21, 158.86, 144.83, 137.28, 133.04, 128.61, 128.10, 128.00, 127.29, 124.99, 119.42, 114.18, 112.63, 73.39, 73.15, 55.41, 49.51, 44.55, 40.43, 40.15, 30.18, 21.87; HRMS *m/z* calcd for $C_{24}H_{27}O_3$ [M+1] 364.2038, found 364.2041.



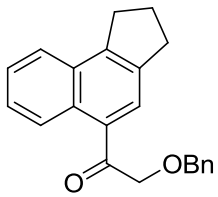
3p

3p: IR (NaCl, cm^{-1}) 3064, 3032, 2935, 28682, 2251, 1723; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 1H), 7.37-7.33 (m, 4H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.50 (s, 1H), 5.88 (s, 1H), 4.63 (s, 2H), 4.32 (q, *J* = 16.8 Hz, 2H), 3.98 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H), 2.54 (d, *J* = 14.0 Hz, 1H), 2.50-2.46 (m, 1H), 2.39-2.32 (m, 1H), 2.05-1.99 (m, 1H), 1.90-1.85 (m, 1H), 1.70-1.63 (m, 1H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.36, 158.53, 145.36, 137.27, 128.67, 128.25, 128.20, 128.13, 128.05, 126.75, 125.19, 119.81, 115.02, 114.51, 74.67, 73.57, 55.39, 49.97, 44.94, 41.33, 38.52, 29.90, 22.76; HRMS *m/z* calcd for $C_{24}H_{27}O_3$ [M+1] 364.2038, found 364.2044.



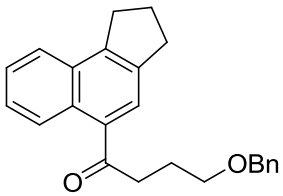
3r

3r: IR (NaCl, cm^{-1}) 3061, 3029, 2928, 1722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 6H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.16-7.11 (m, 2H), 4.48 (ABq, $\Delta\delta$ = 18.0 Hz, *J* = 7.0 Hz, 2H), 4.00 (ABq, $\Delta\delta$ = 62.8Hz, *J* = 31.4Hz, 2H), 3.66 (q, *J* = 9.6 Hz, 1H), 2.57-2.38 (m, 4H), 2.20(d, *J* =14.8 Hz, 2H), 2.07(d, *J* =18.4Hz, 1H), 1.85-1.73 (m, 2H), 1.63-1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.83, 137.39, 136.69, 133.37, 131.31, 128.55, 128.43, 128.13, 128.05, 128.03, 126.65, 126.28, 122.24, 73.66, 73.24, 49.09, 31.04, 30.98, 25.29, 22.99, 22.77; HRMS *m/z* calcd for $C_{23}H_{25}O_2$ [M+1] 333.1855, found 333.1854.



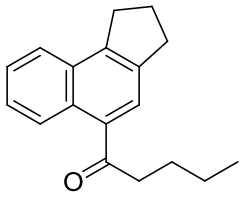
4a

4a: IR (NaCl, cm^{-1}) 3062, 3031, 2849, 2845, 2247, 1688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (m, 1H), 7.84 (m, 1H), 7.74 (s, 1H), 7.55 (m, 2H), 7.40-7.29 (m, 5H), 4.75 (s, 2H), 4.72 (s, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.78 (quint, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.47, 145.79, 139.44, 137.45, 131.88, 131.04, 129.67, 128.64, 128.26, 128.12, 127.13, 126.65, 126.38, 125.51, 124.81, 74.13, 73.45, 33.73, 31.88, 24.48; HRMS *m/z* calcd for $C_{22}H_{21}O_2$ [M+1] 317.1542, found 317.1544.



4c

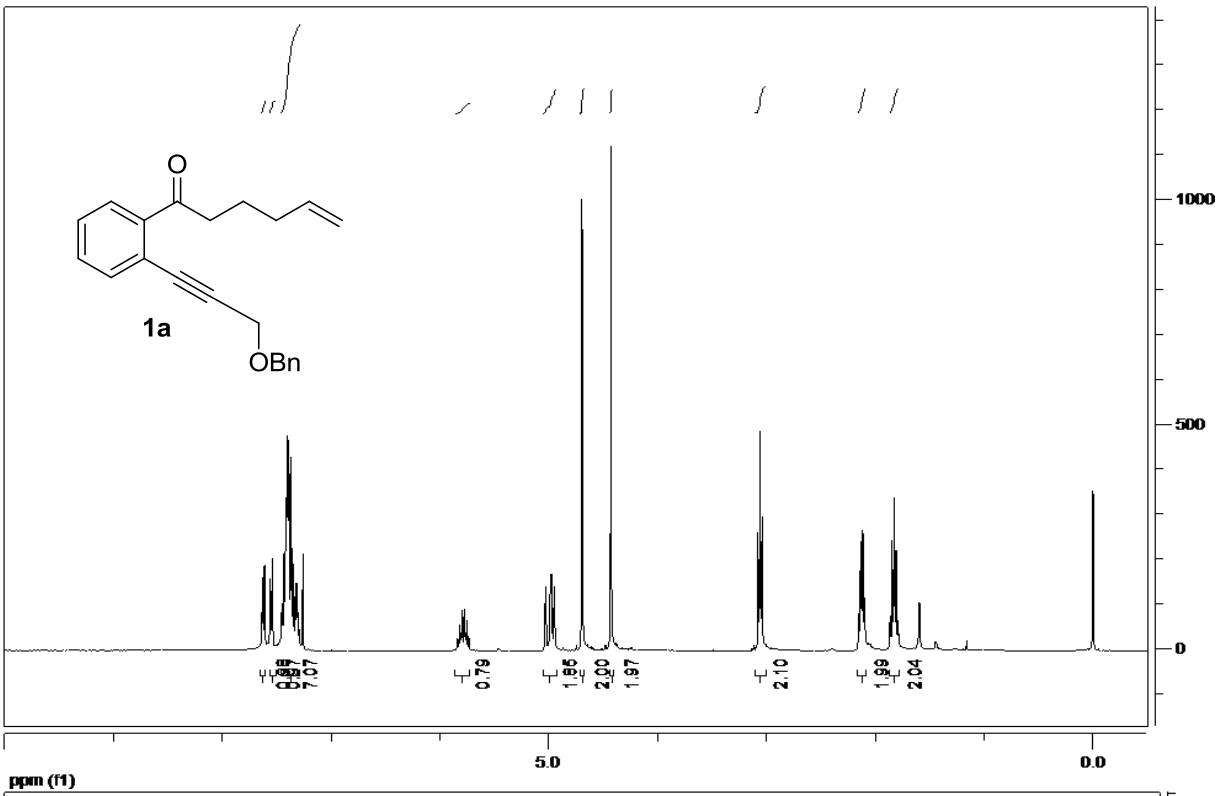
4c: IR (NaCl, cm^{-1}) 3062, 3031, 2927, 2851, 2249, 1676; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (m, 1H), 7.84-7.82 (m, 2H), 7.54-7.48 (m, 2H), 7.33-7.27 (m, 5H), 4.51 (s, 2H), 3.61 (d, *J* = 5.6 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.28 (quint, *J* = 7.6 Hz, 2H), 2.13 (quint, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.26, 144.80, 139.57, 138.56, 135.21, 130.99, 129.53, 128.50, 127.79, 127.69, 126.75, 126.63, 126.45, 125.25, 124.74, 73.04, 69.57, 38.80, 33.80, 31.83, 25.02, 24.52; HRMS *m/z* calcd for $C_{24}H_{25}O_2$ [M+1] 345.1855, found 345.1858.

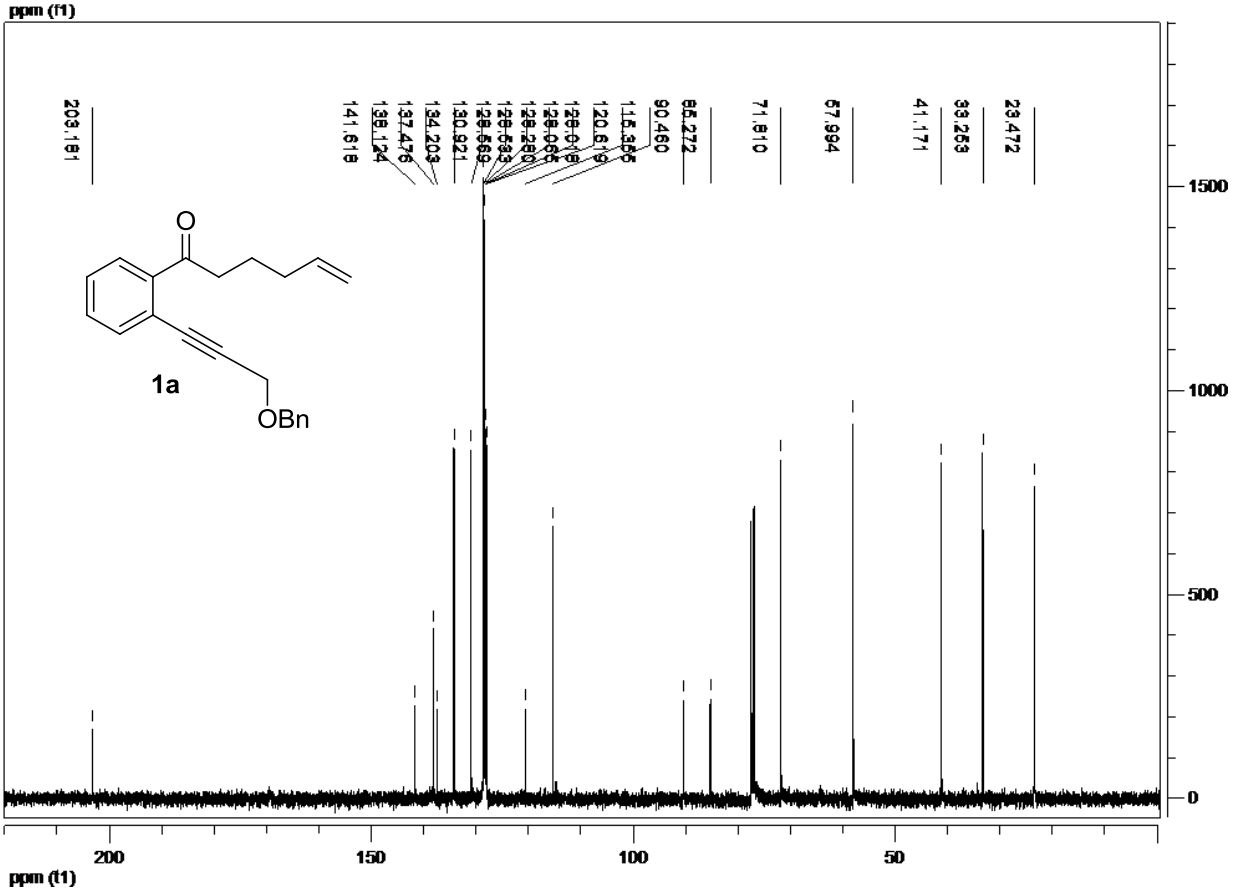


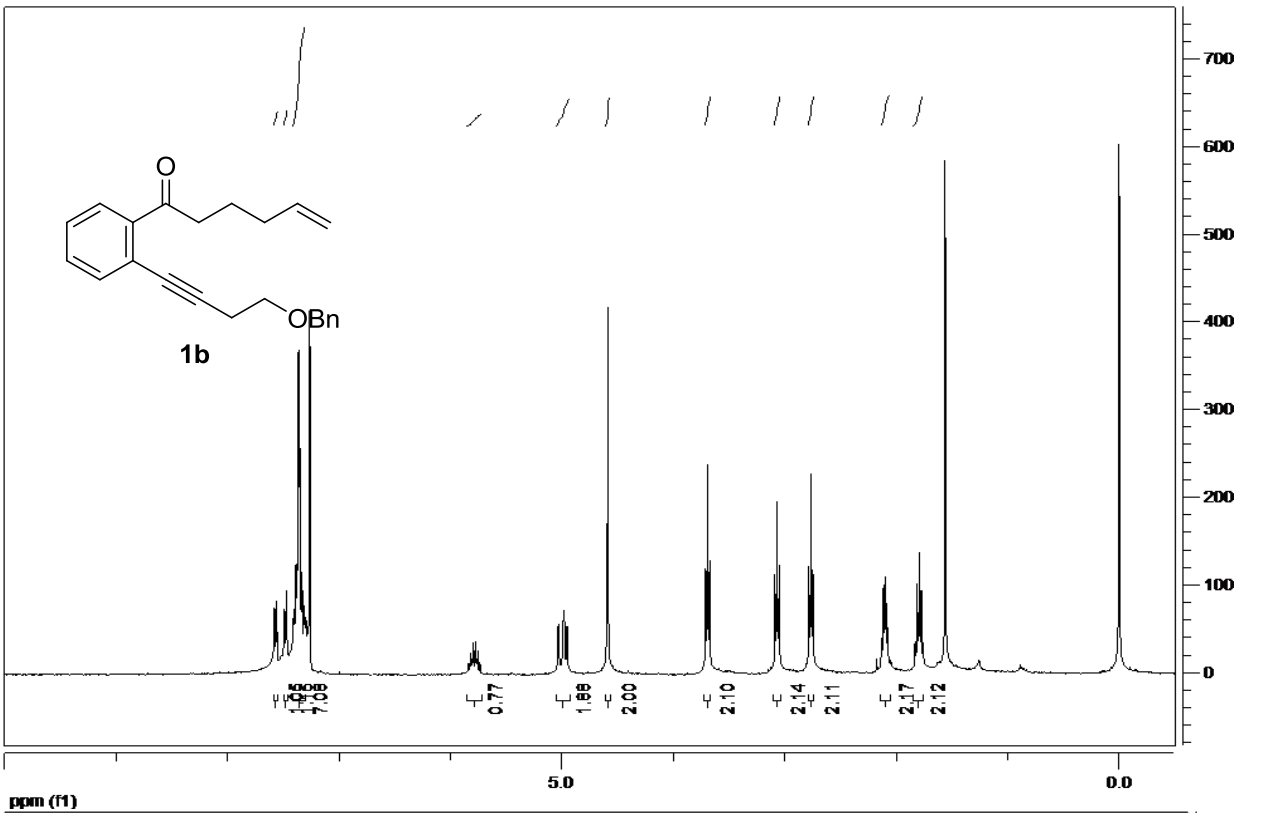
4d

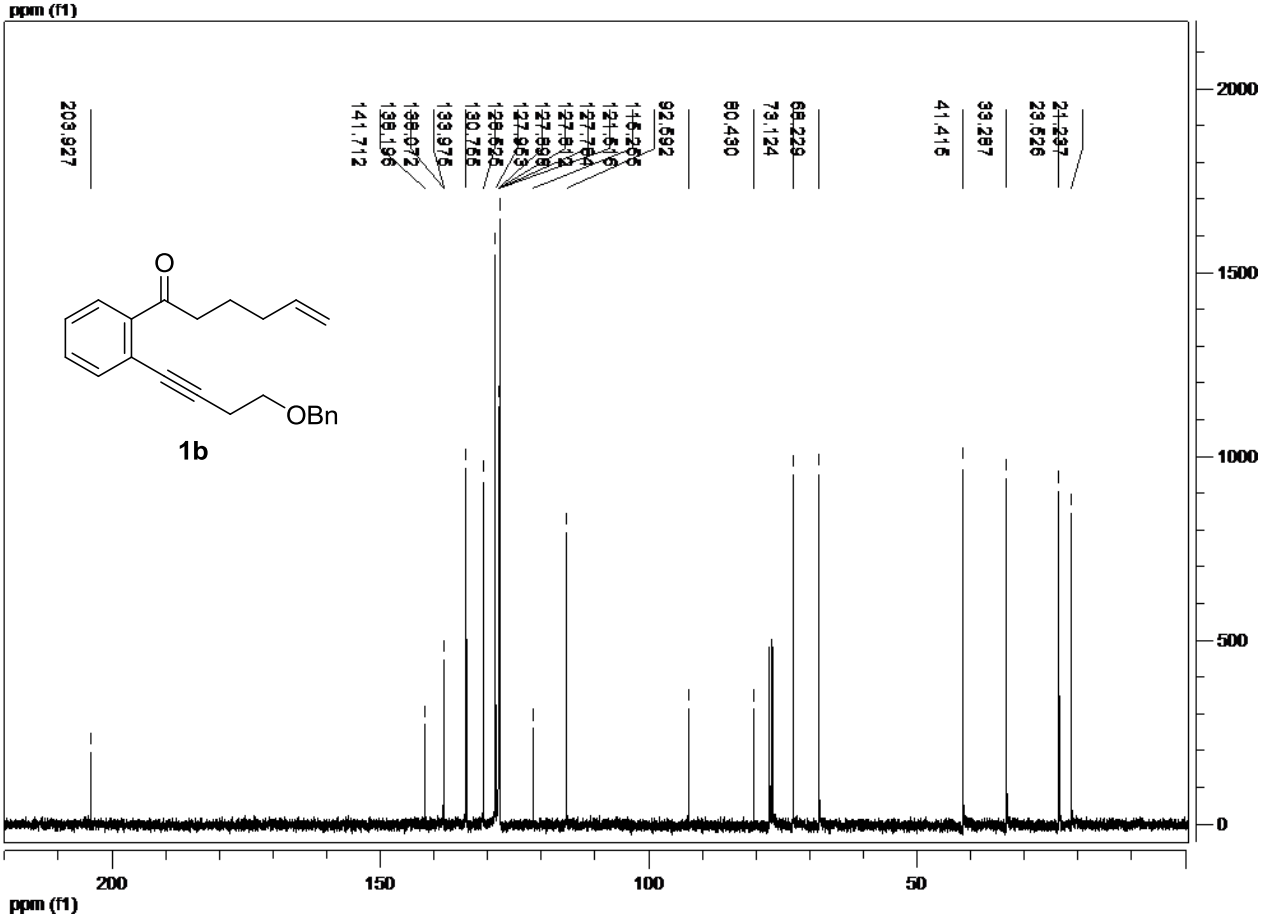
4d : IR (NaCl, cm^{-1}) 3062, 2956, 2869, 1677; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (m, 1H), 7.83 (m, 1H), 7.78 (s, 1H), 7.55-7.51 (m, 2H), 3.30 (t, J = 7.6 Hz, 2H), 3.15 (t, J = 7.2 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.28 (quint, J = 7.6 Hz, 2H), 1.77 (quint, J = 7.6 Hz, 2H), 1.48-1.39 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.37, 144.60, 139.59, 135.47, 131.00, 129.54, 126.70, 126.60, 16.45, 124.91, 124.75, 42.12, 33.82, 31.80, 27.18, 24.51, 22.67, 14.13; HRMS *m/z* calcd for $C_{18}H_{20}O$ [M+1] 255.1749, found 255.1745.

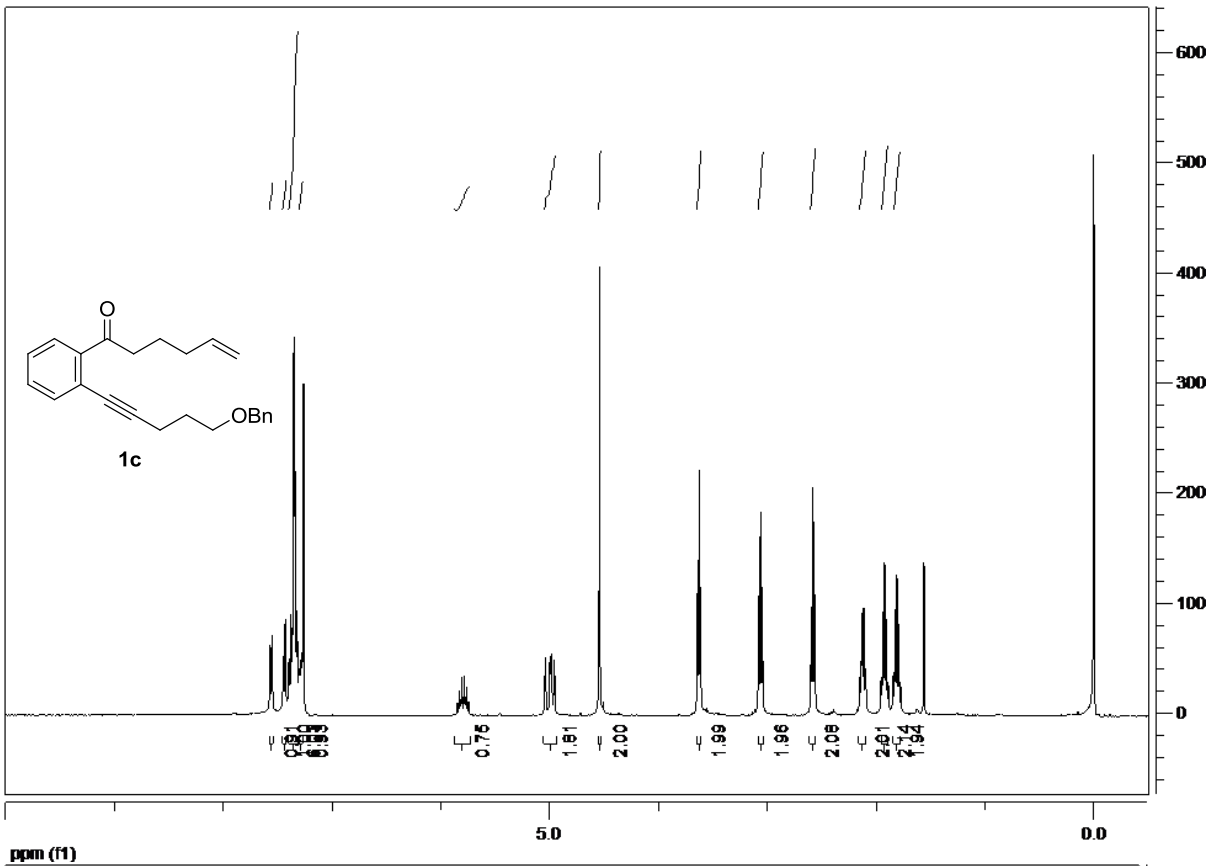
4. ^{1}H and ^{13}C spectra of compounds:

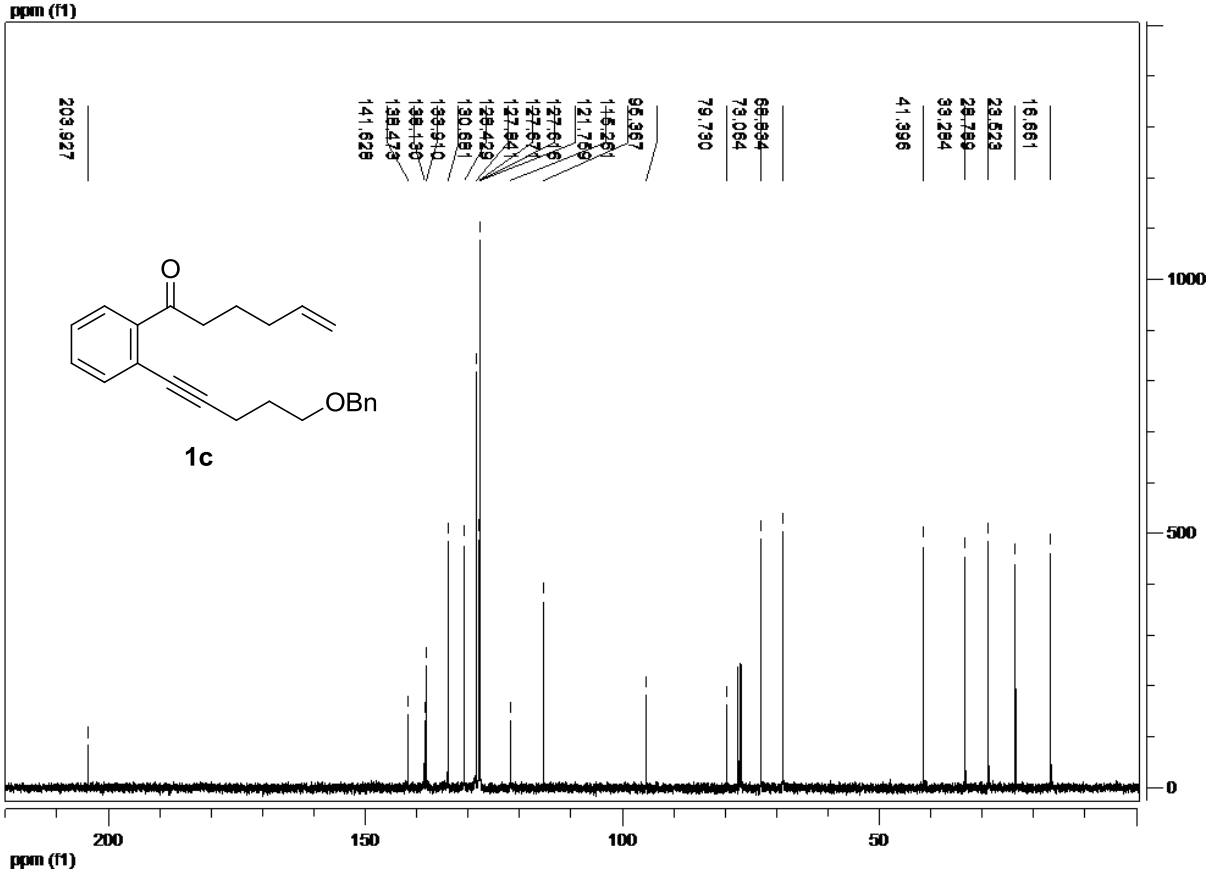


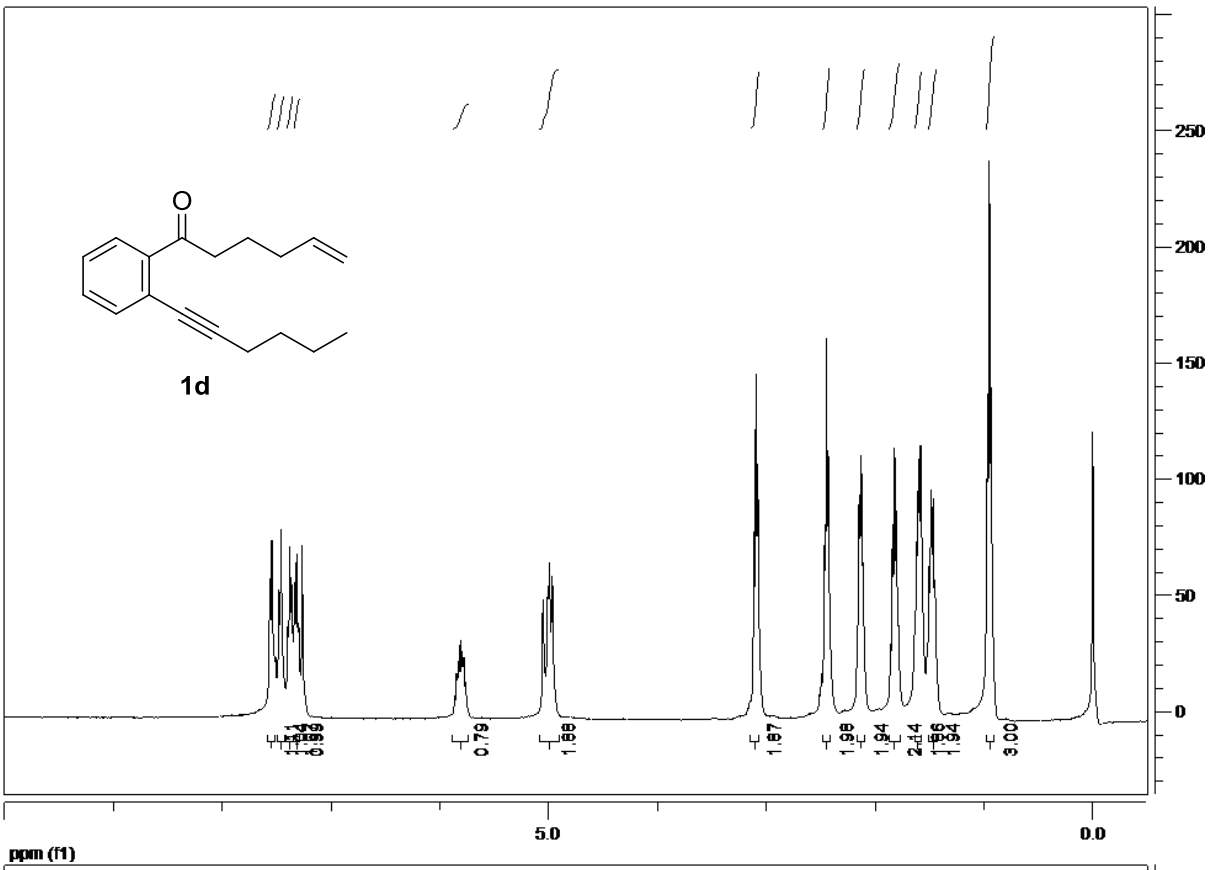


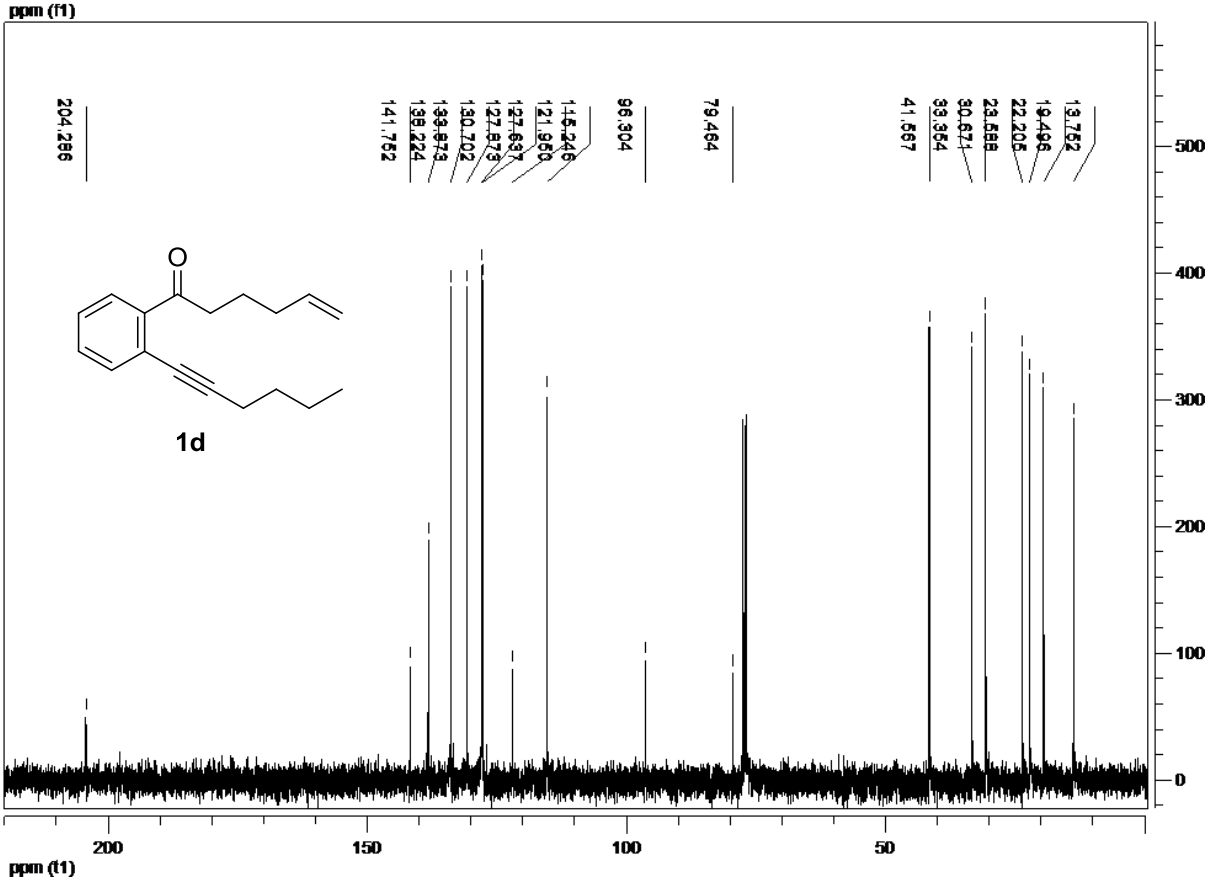


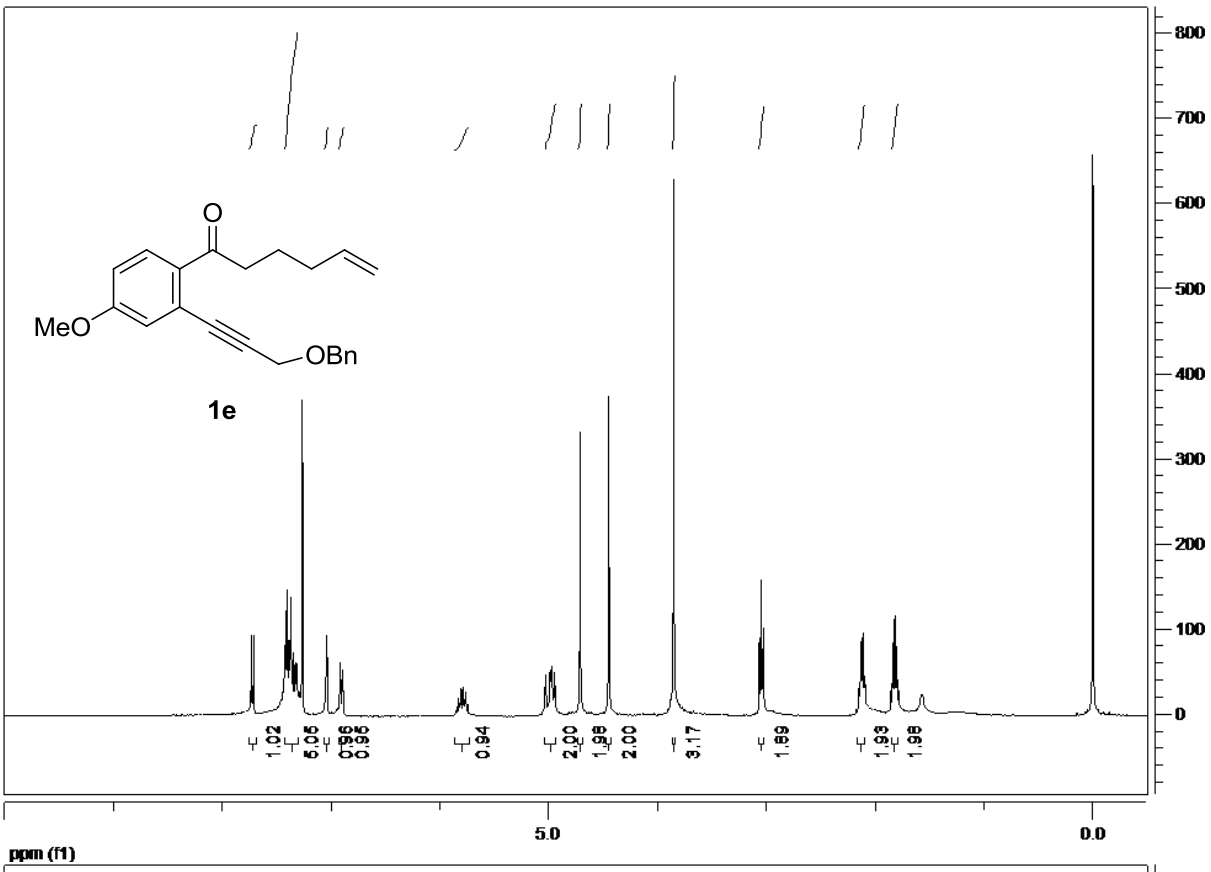


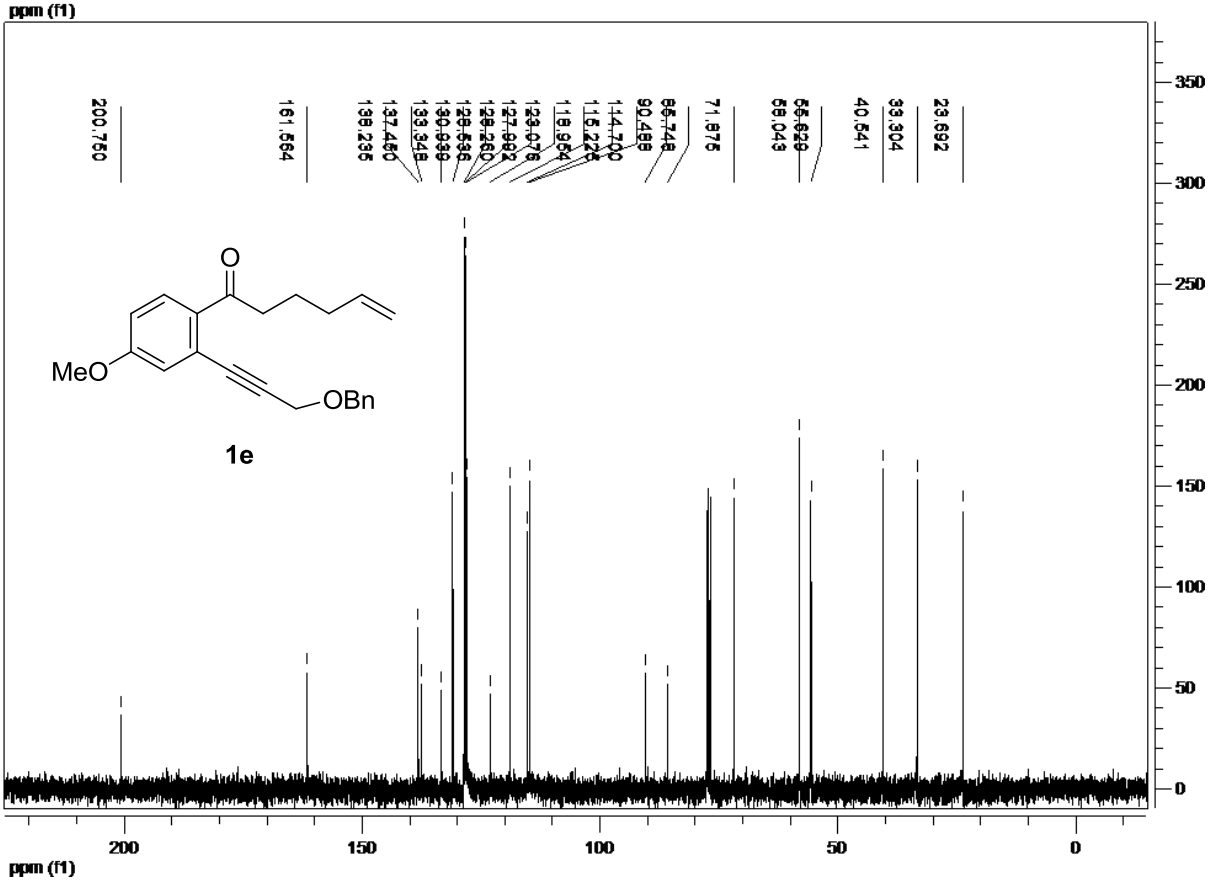


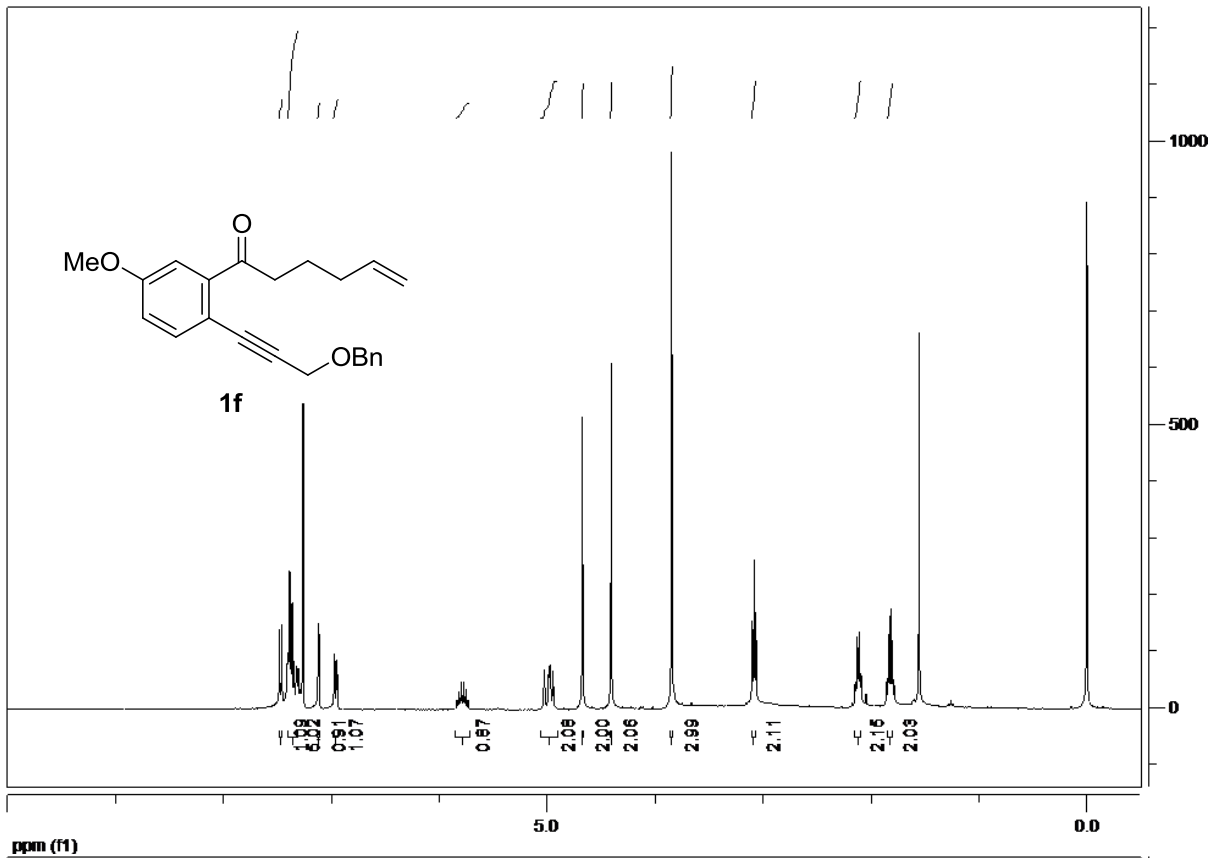


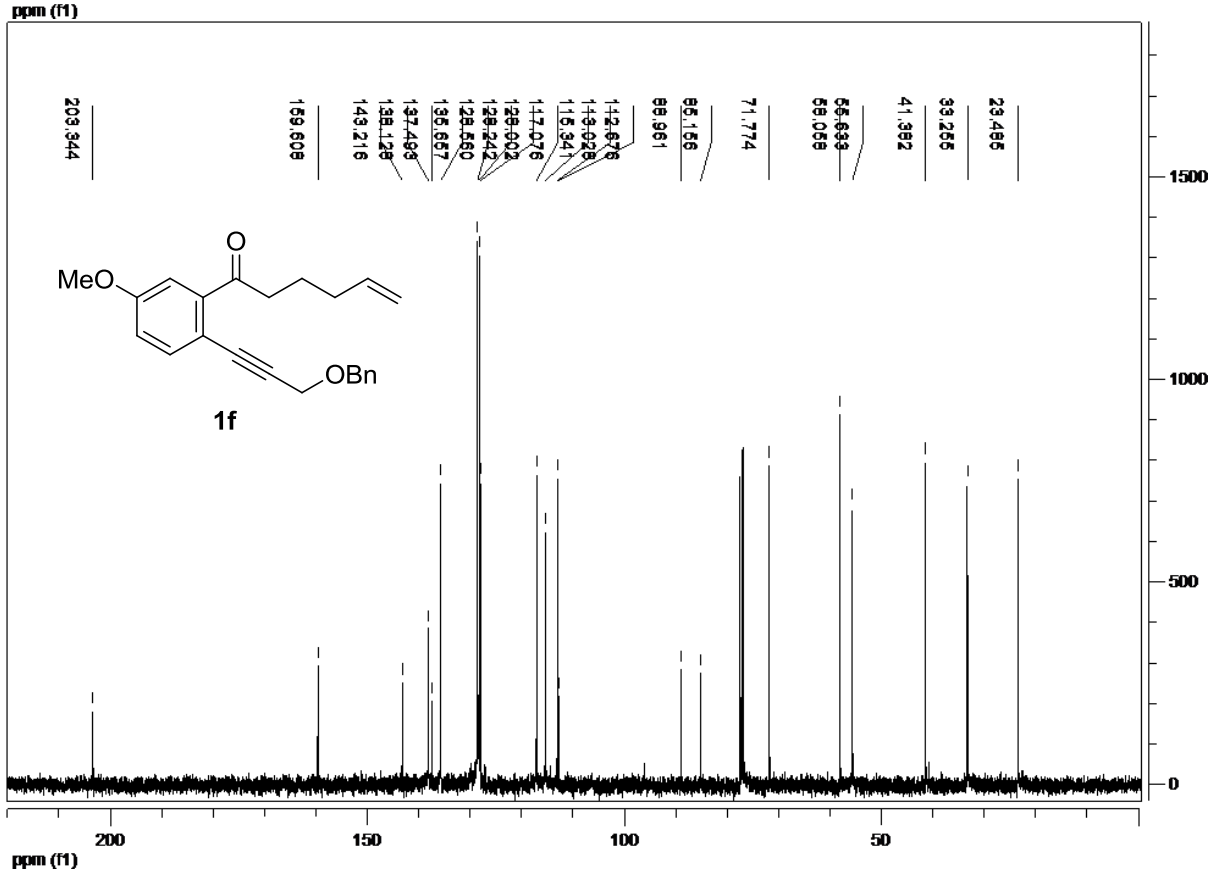


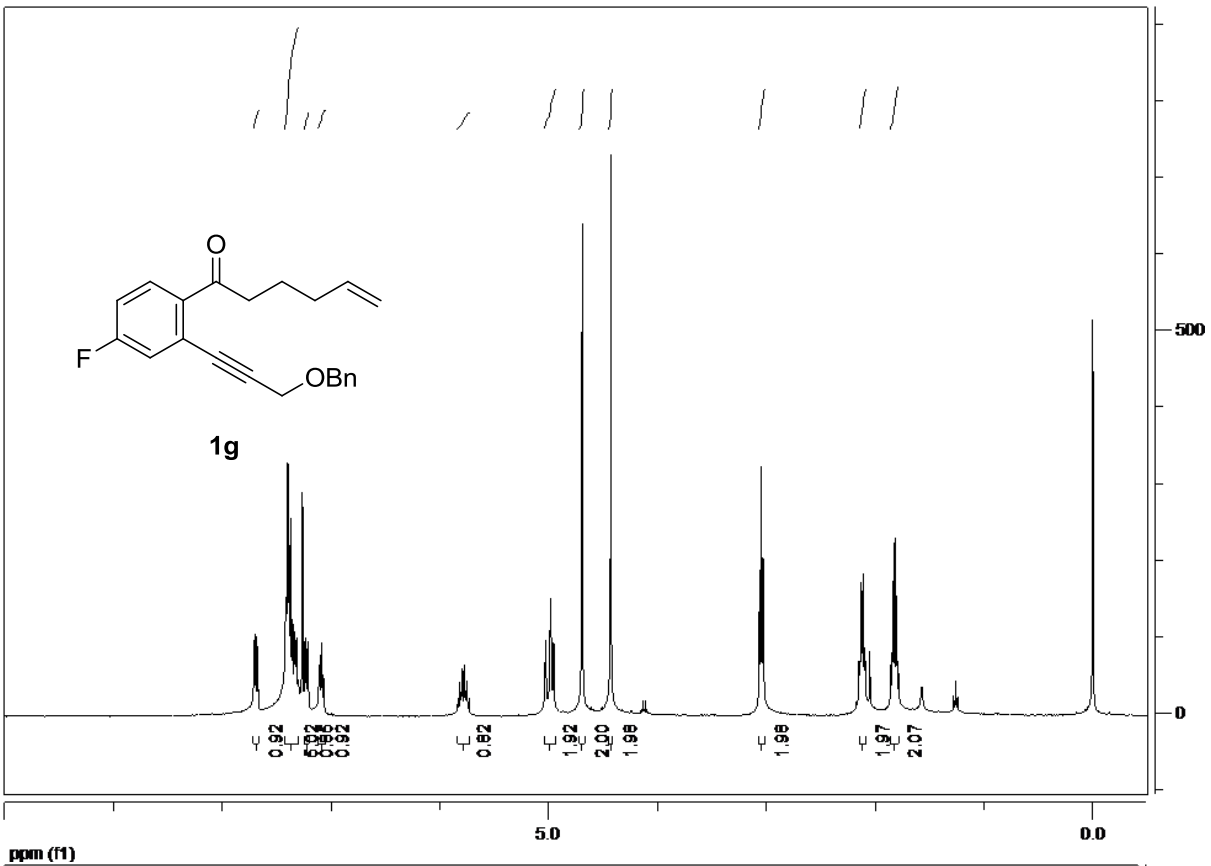


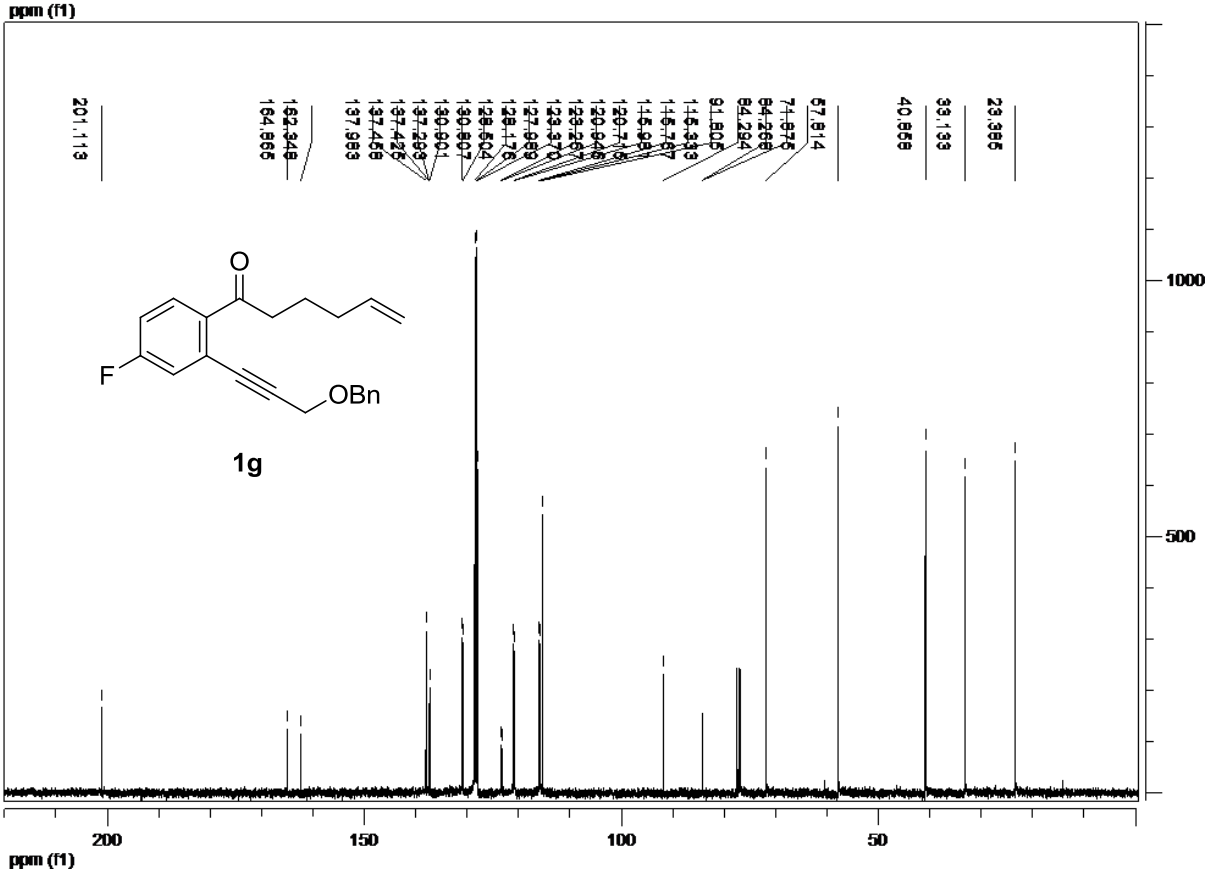


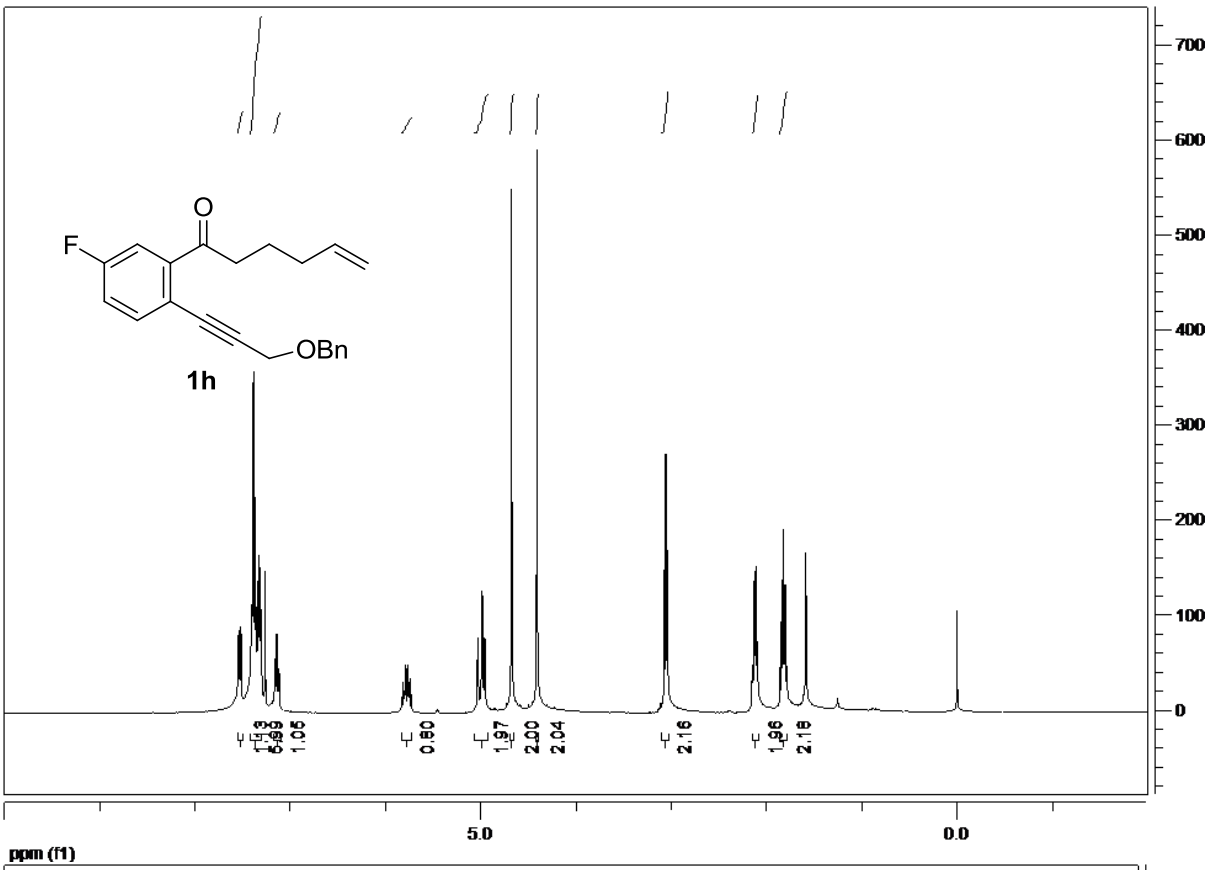


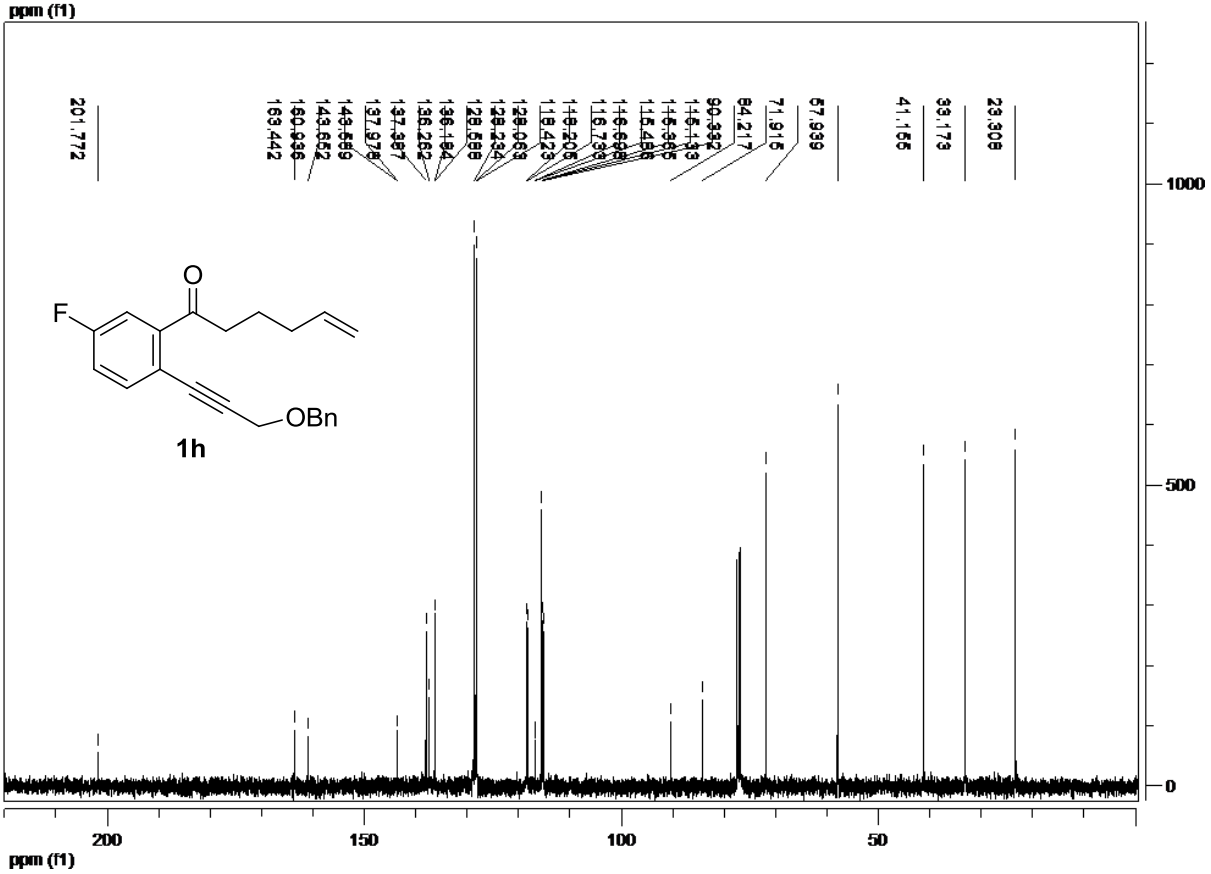


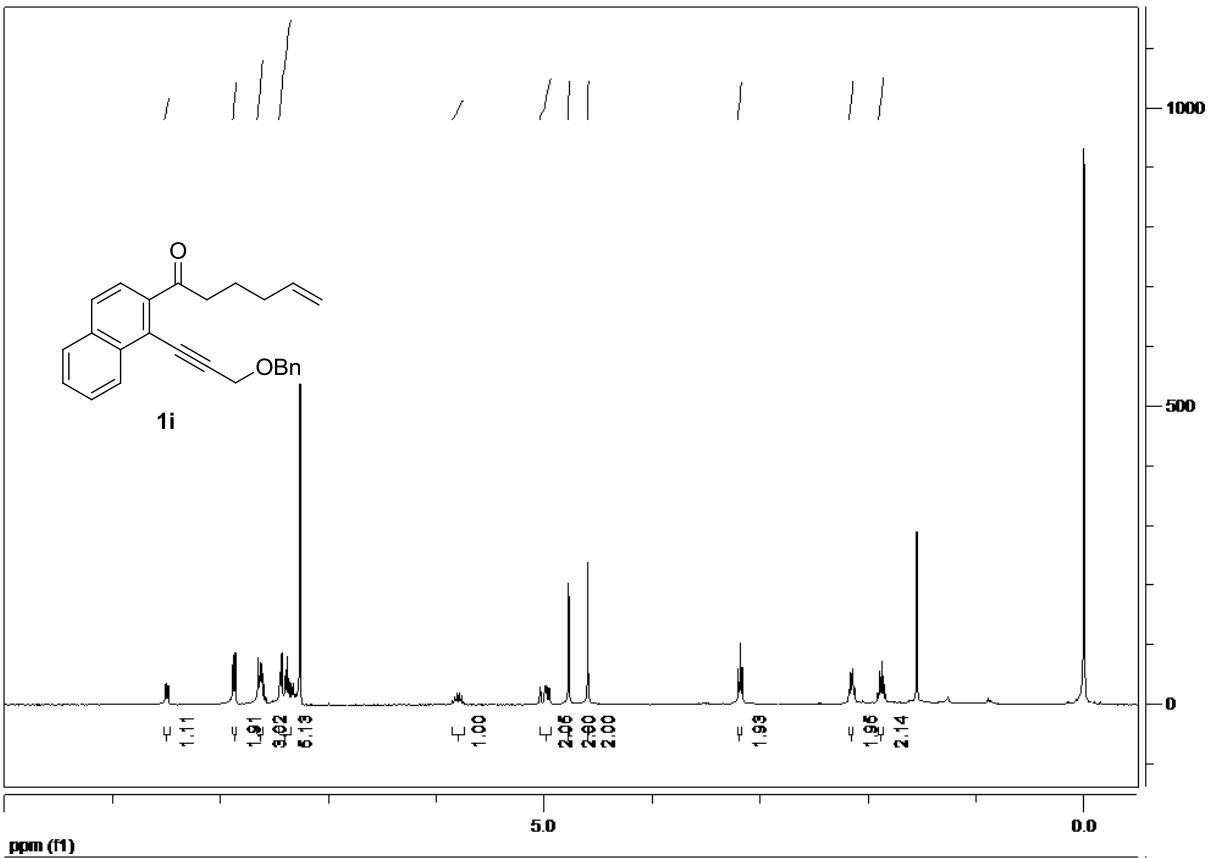


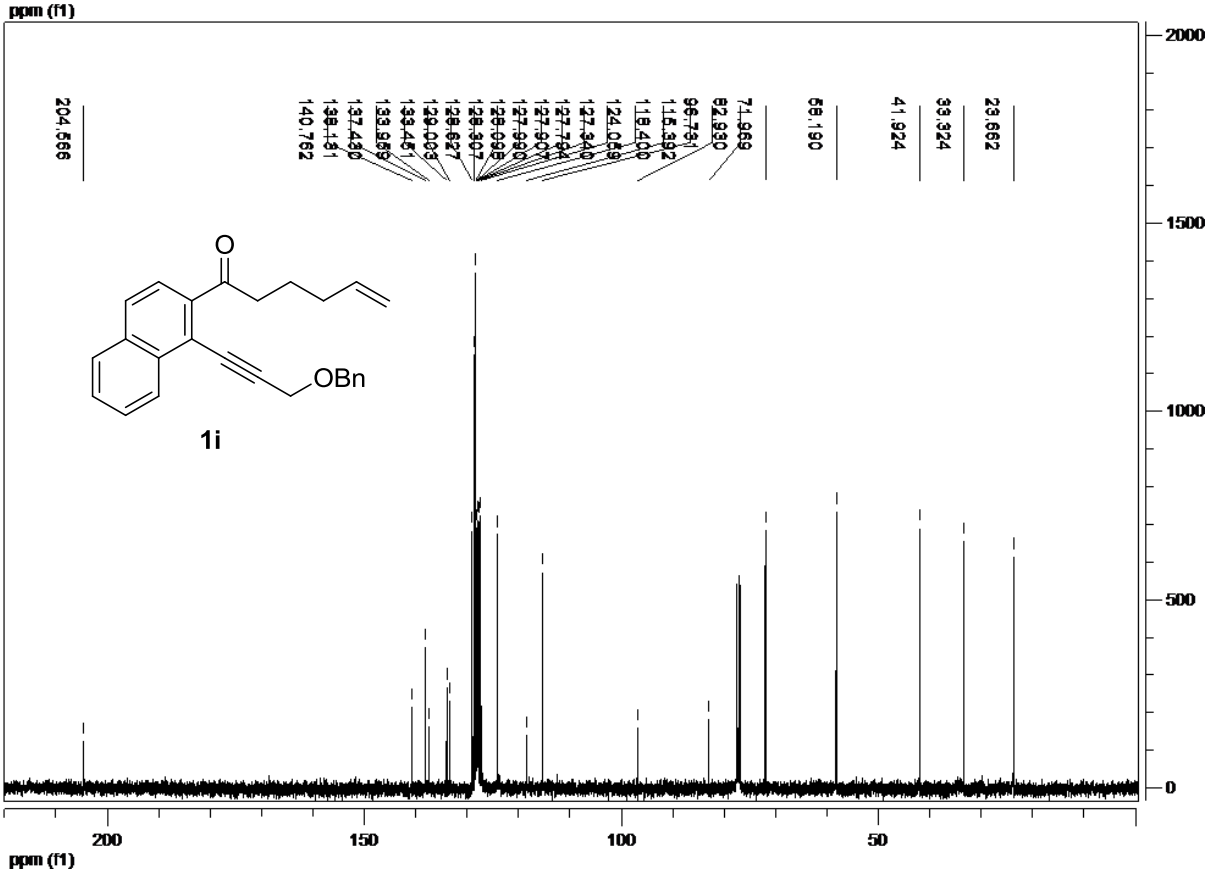


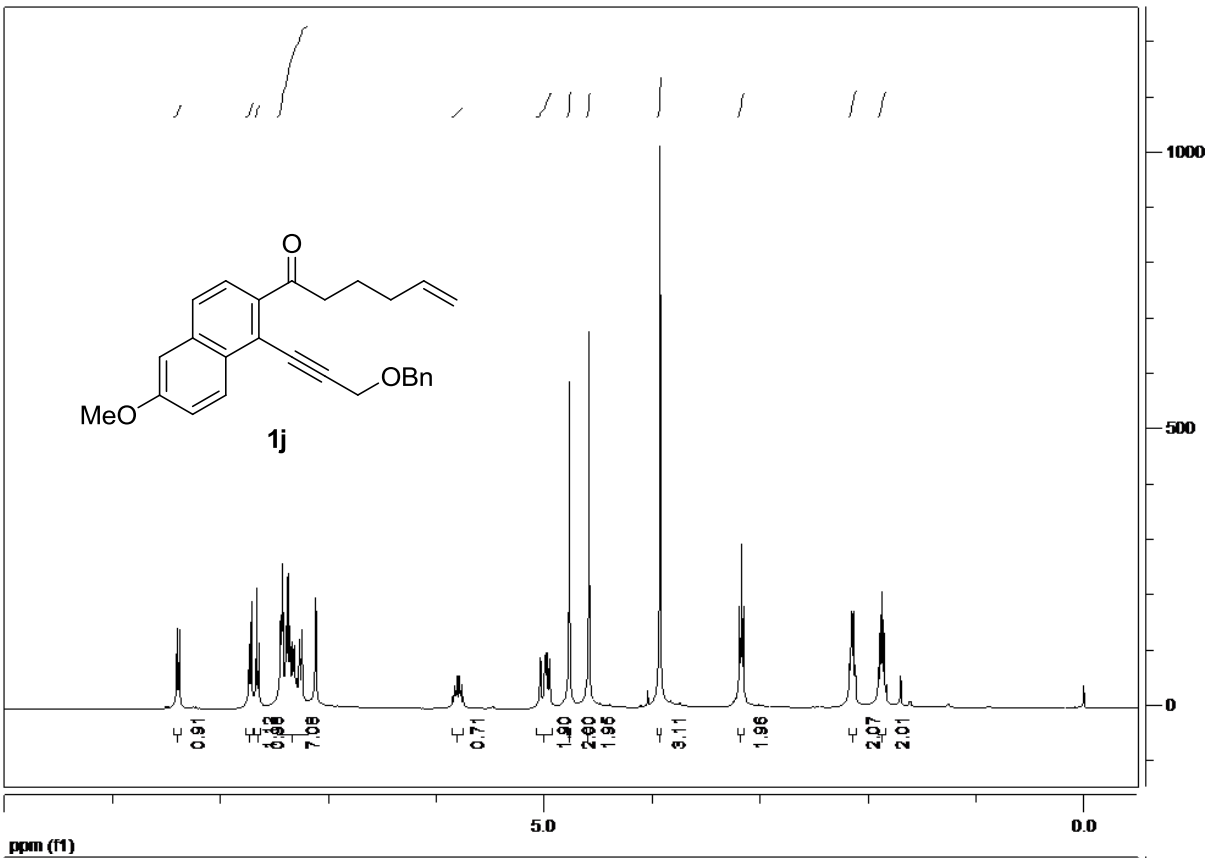


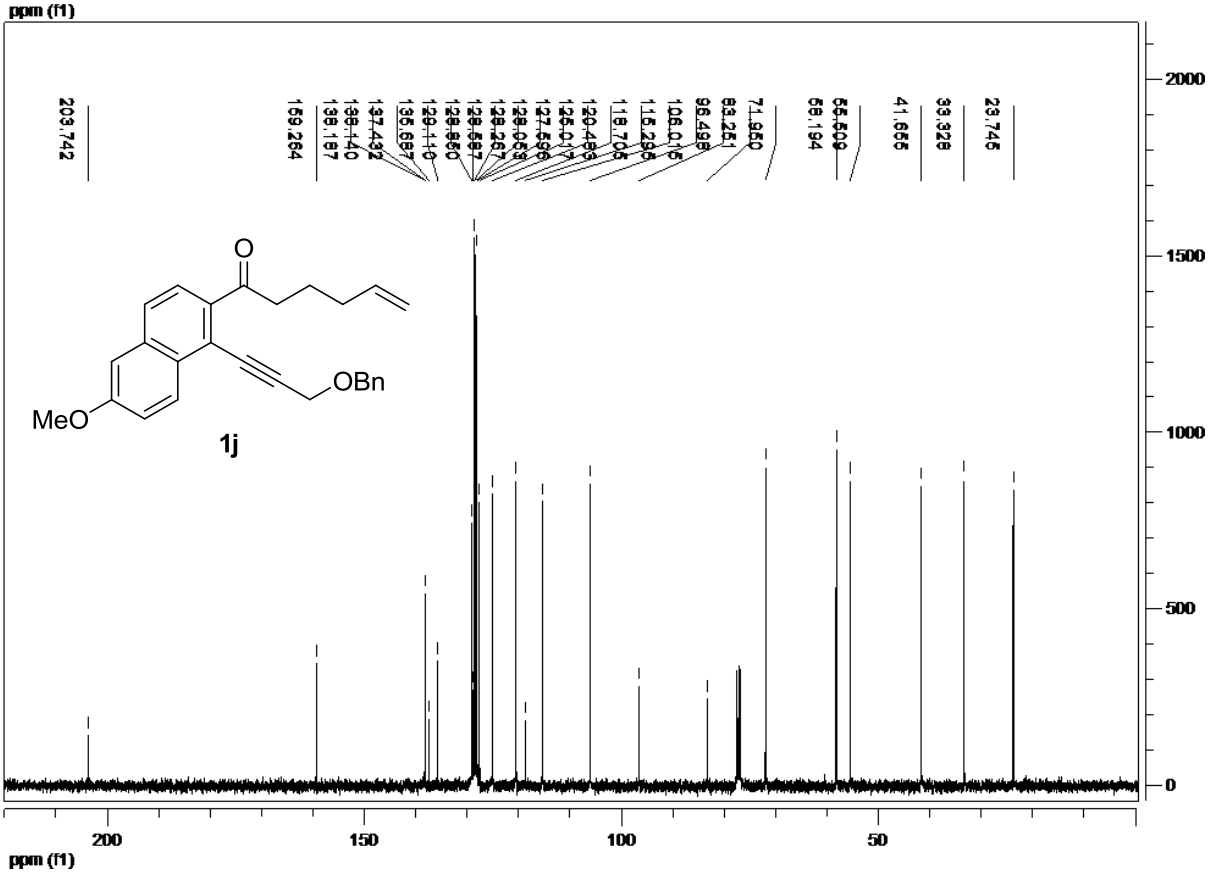


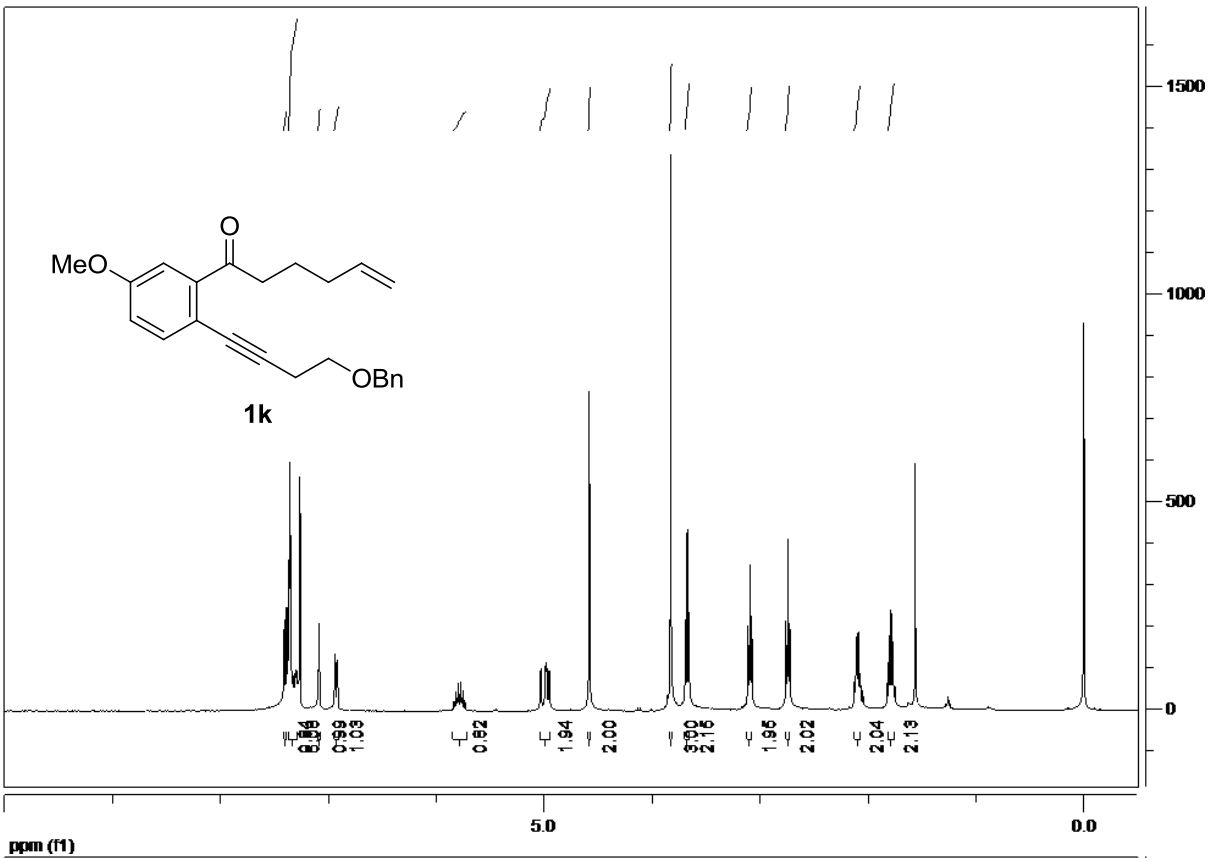


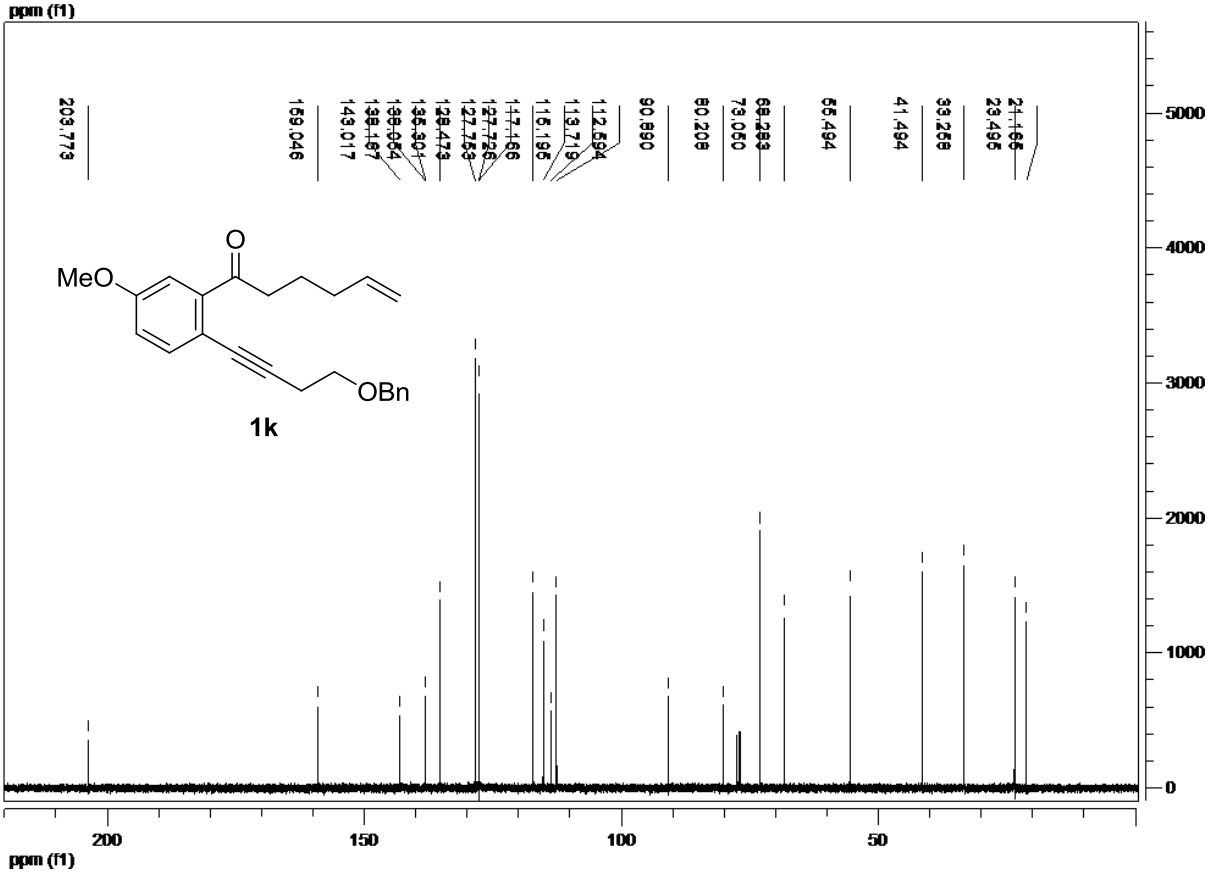


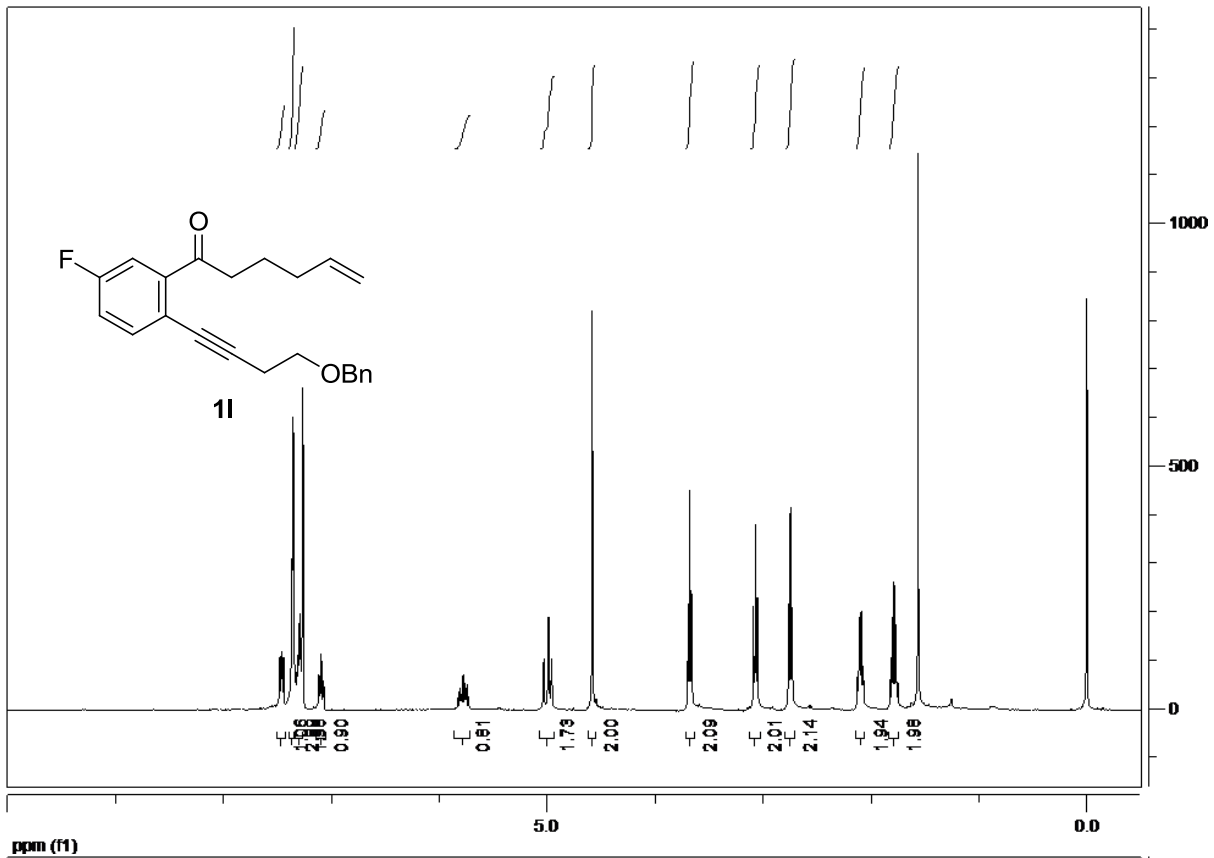


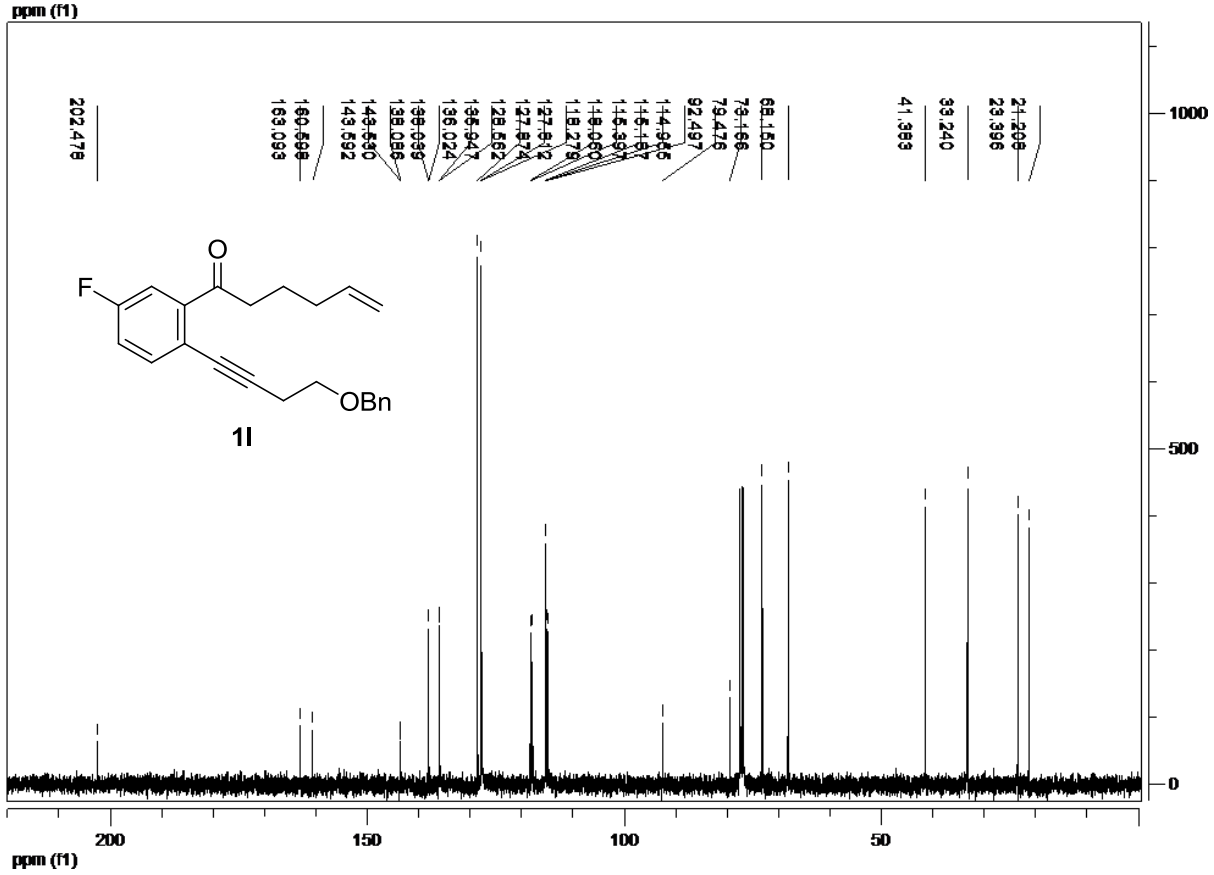


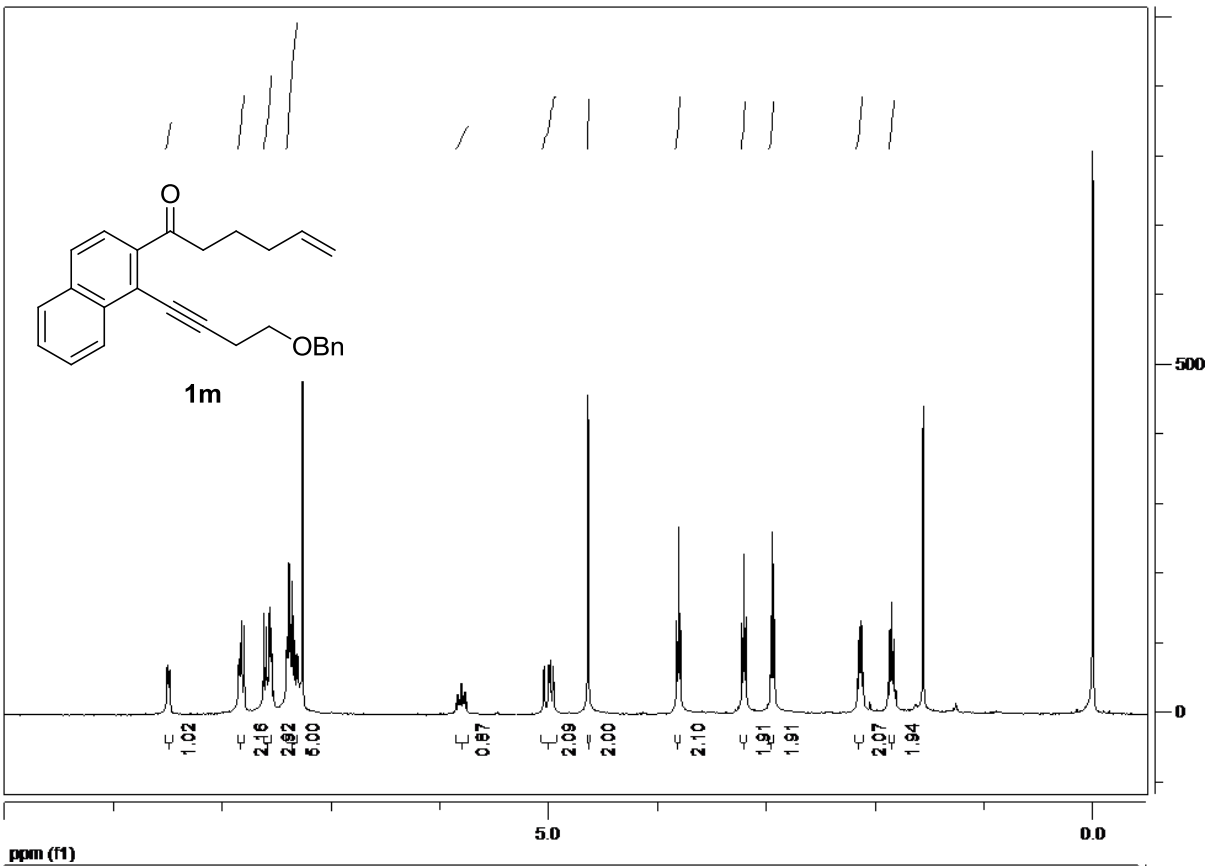


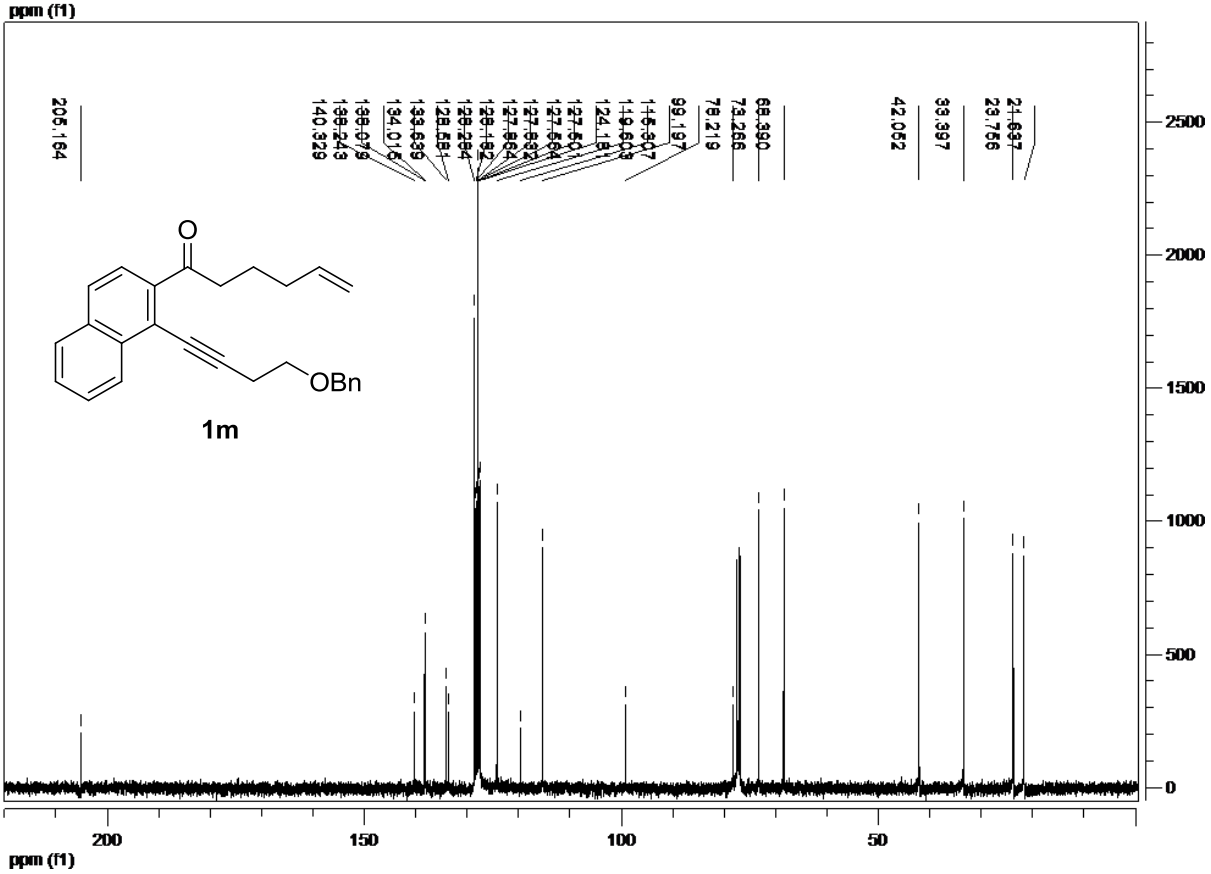


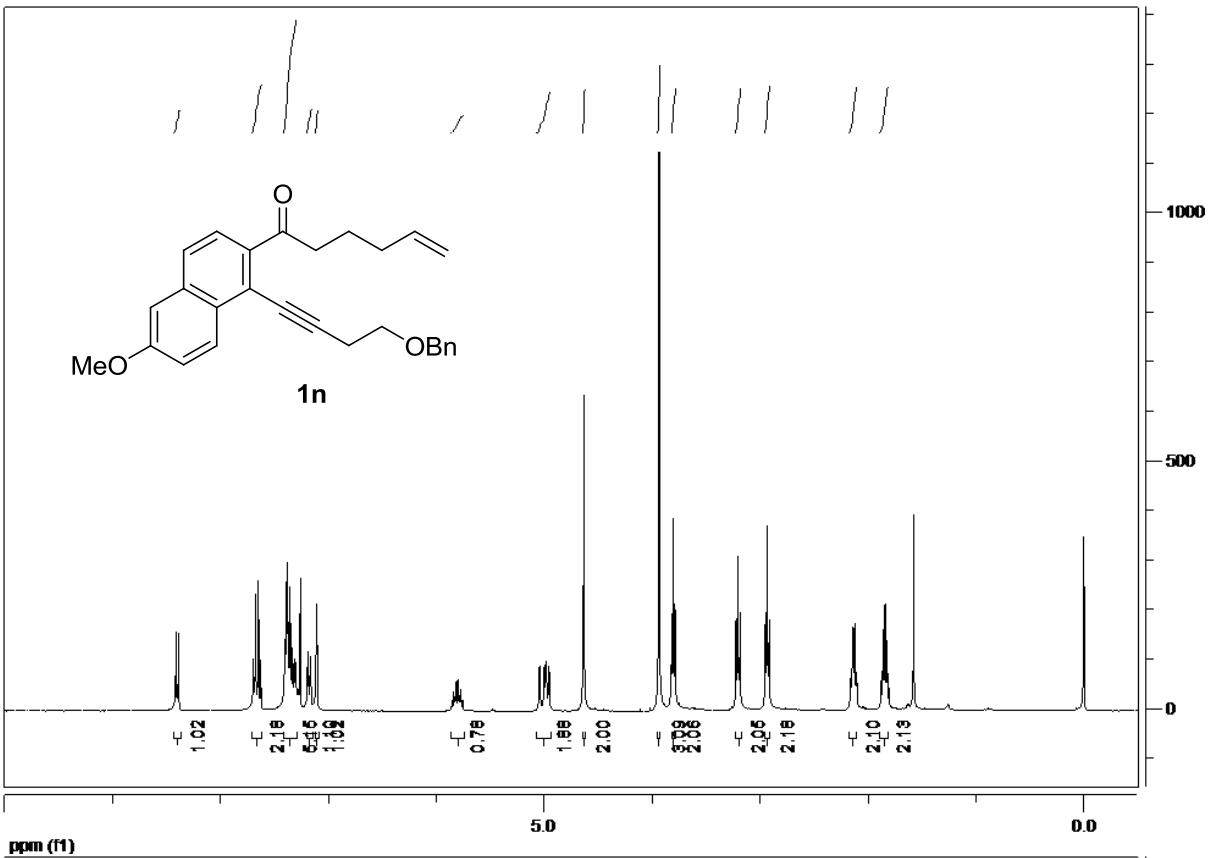


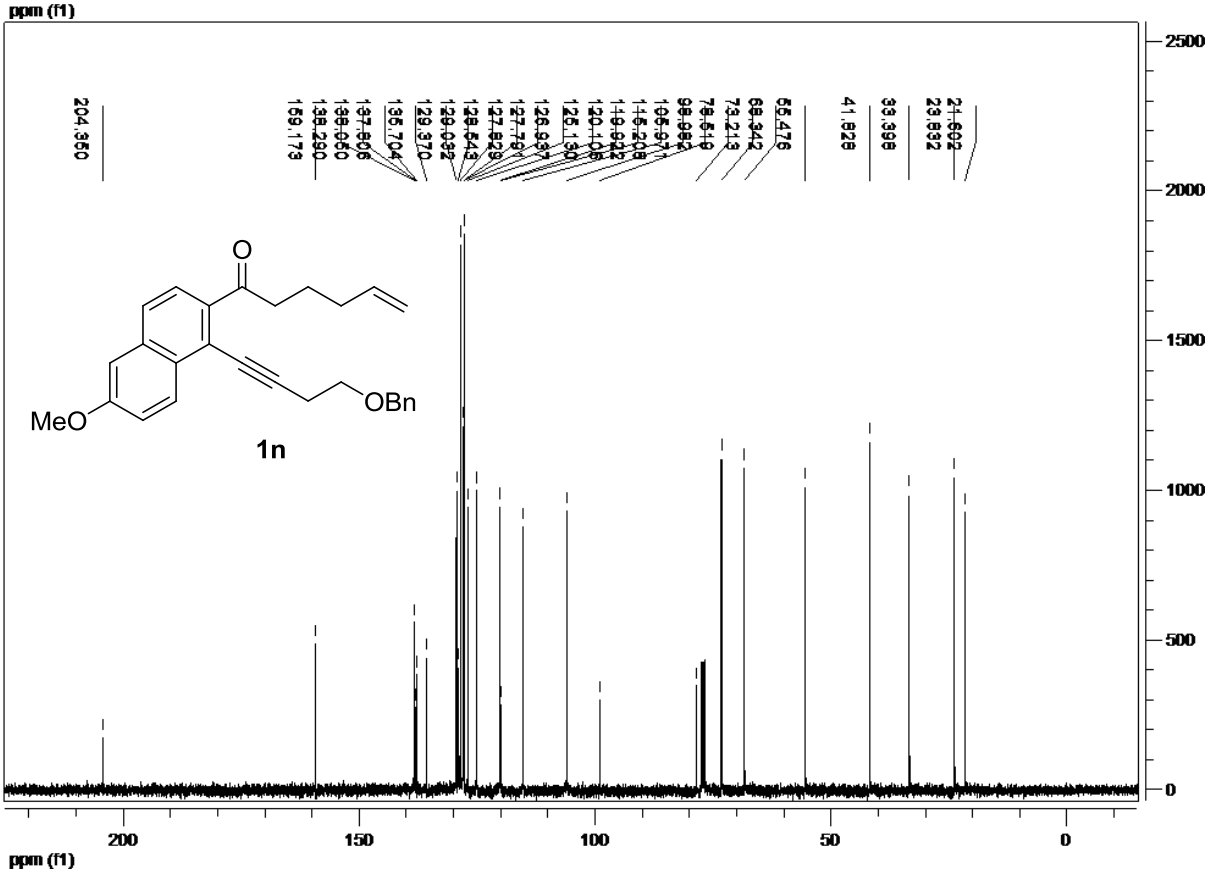


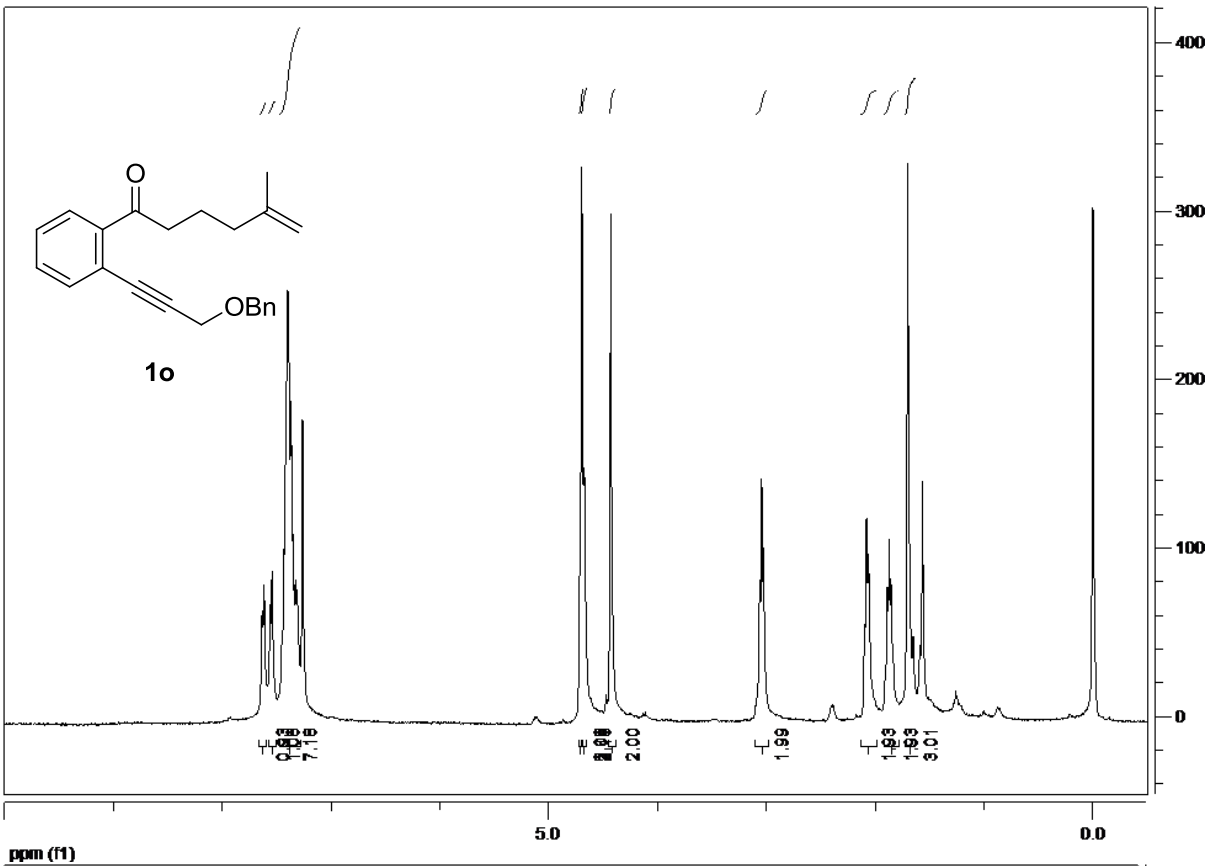


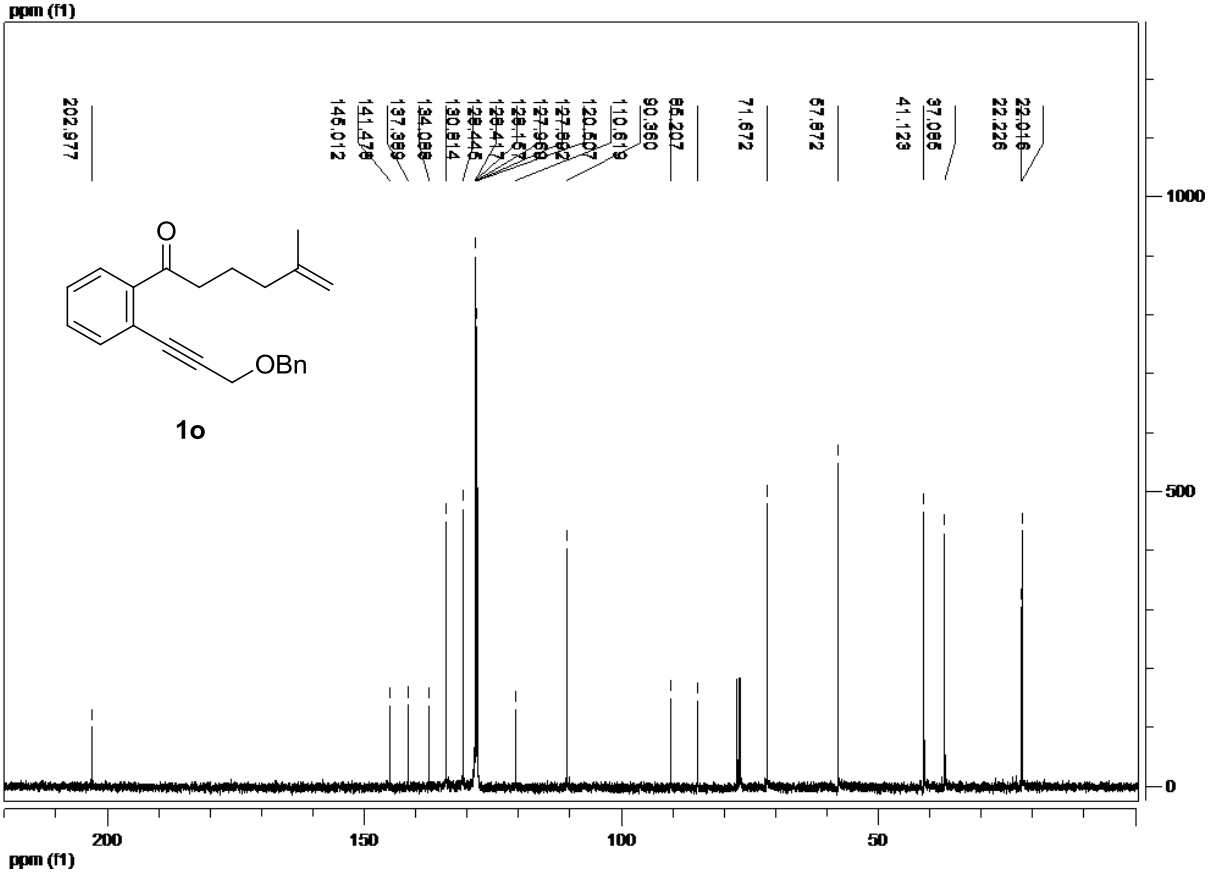


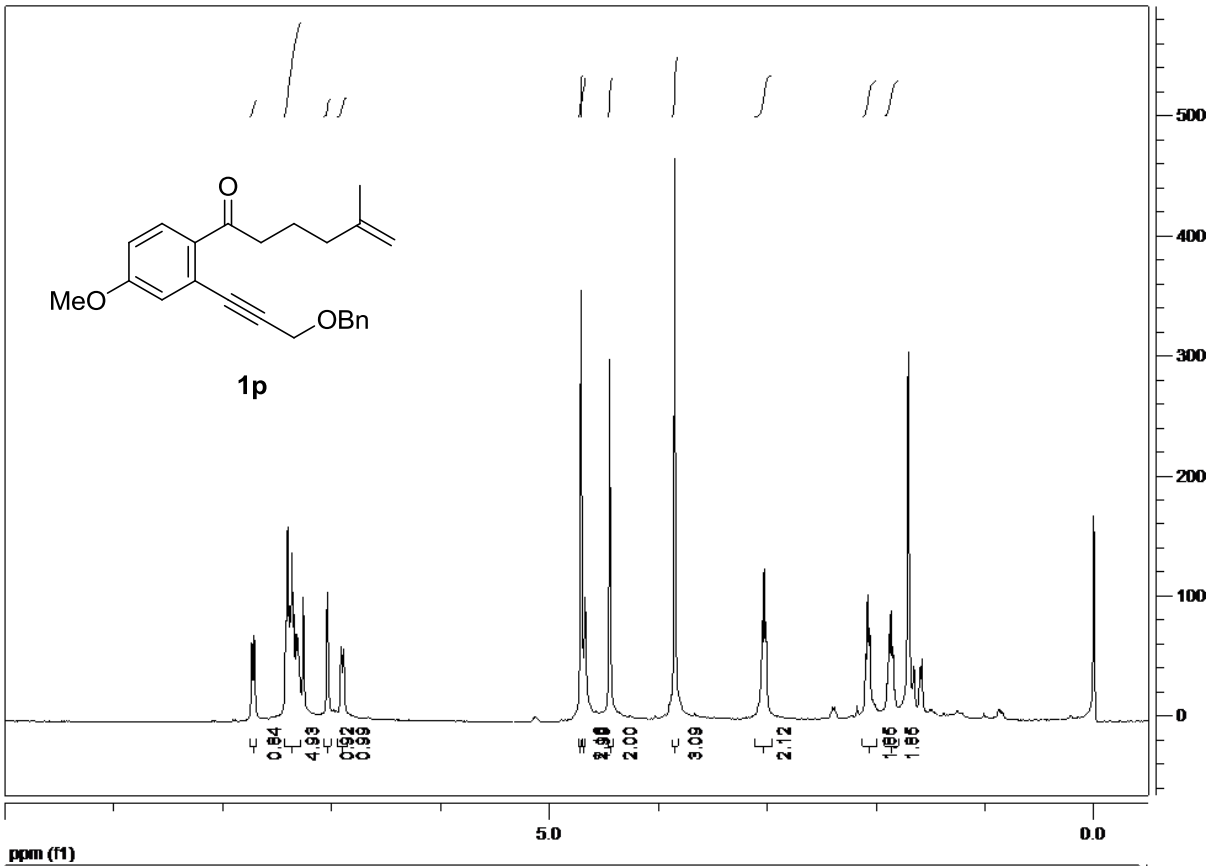


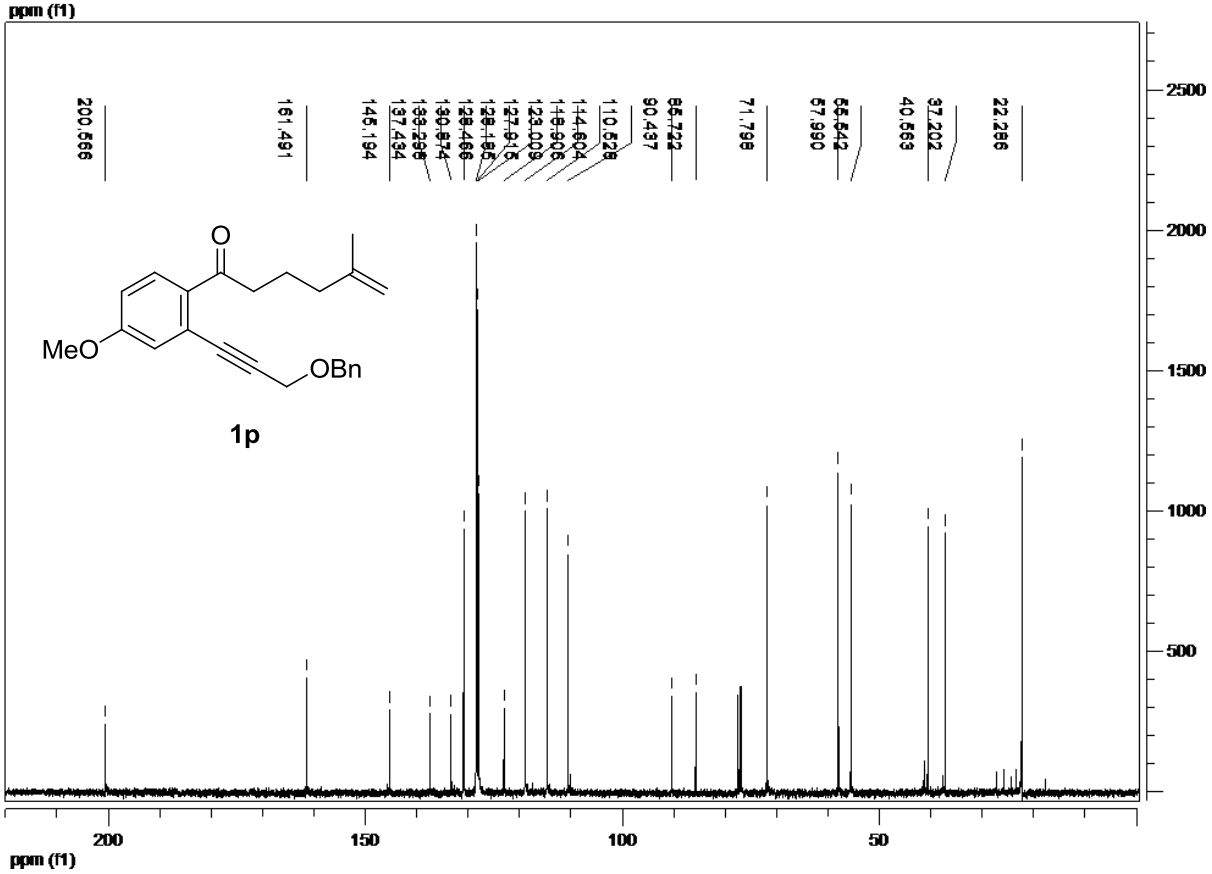


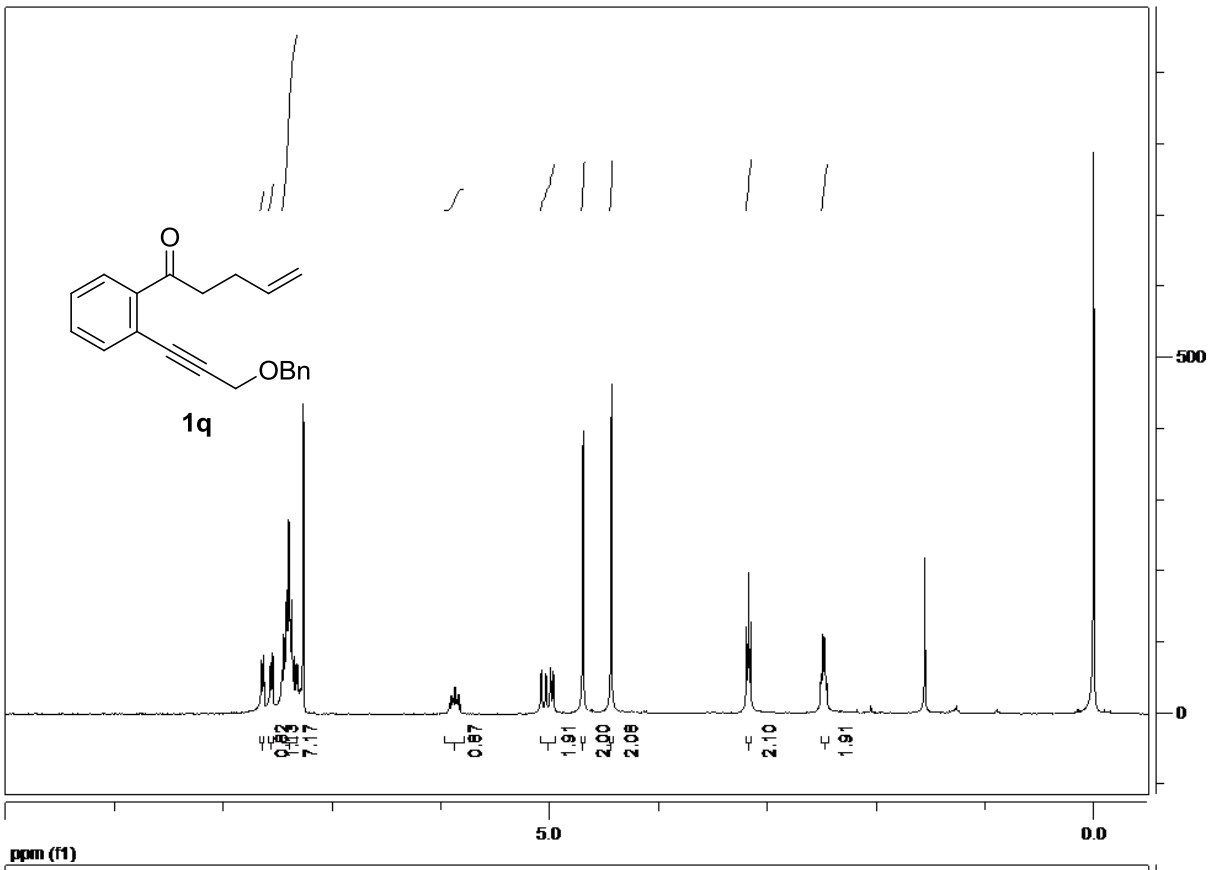


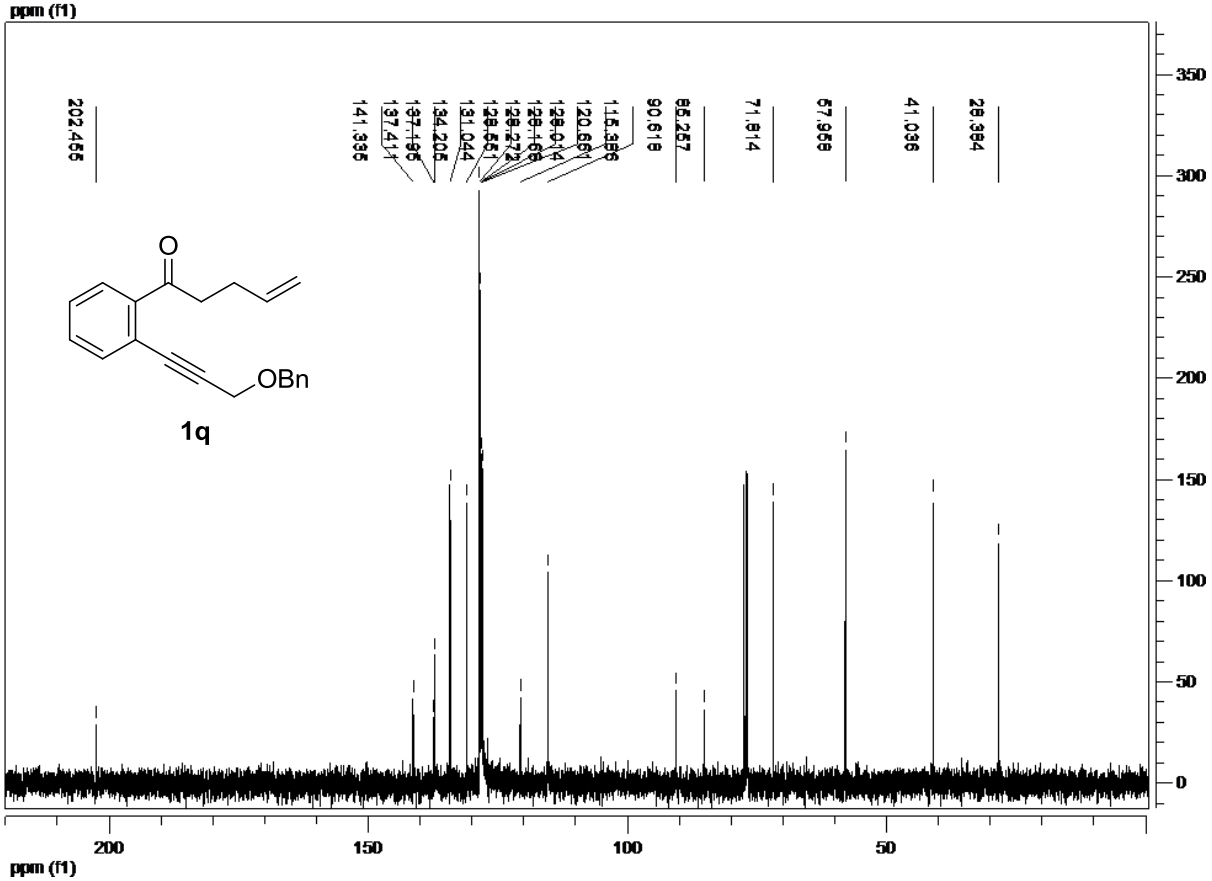


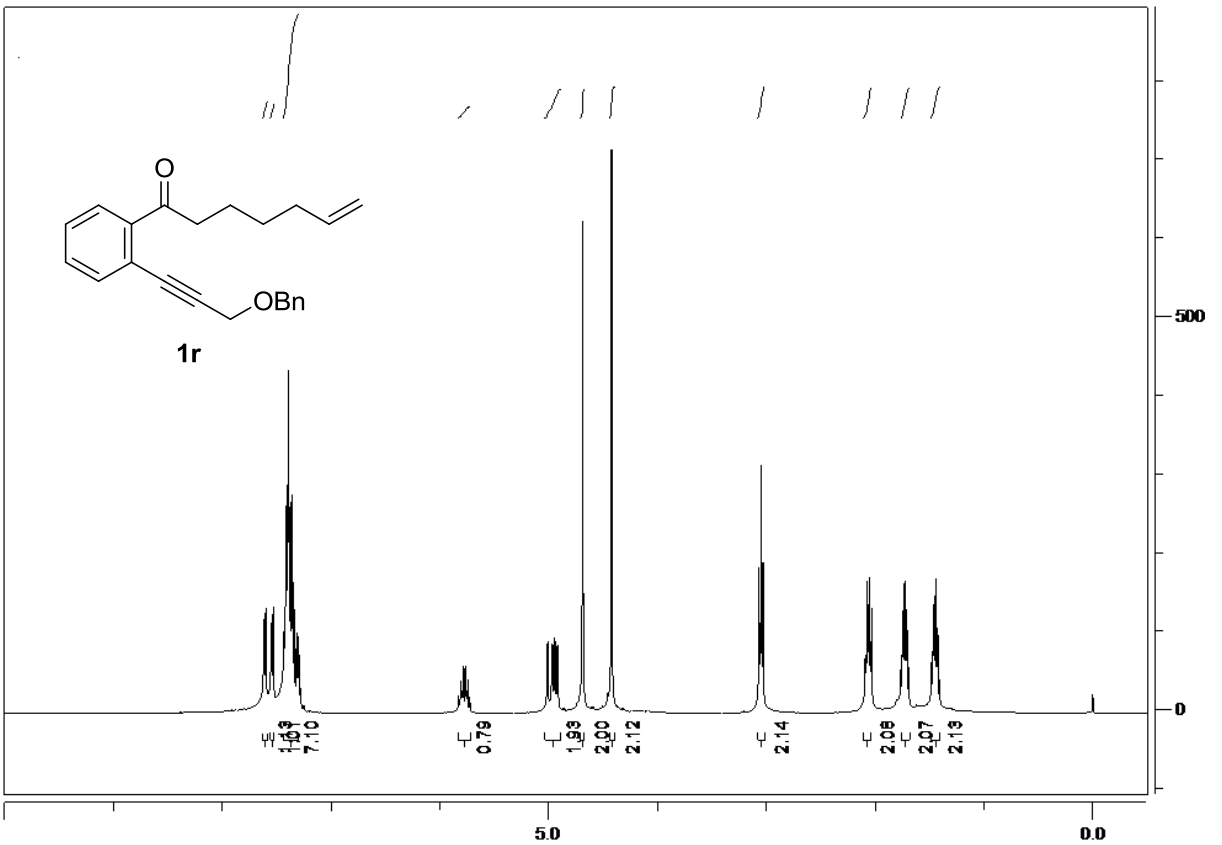


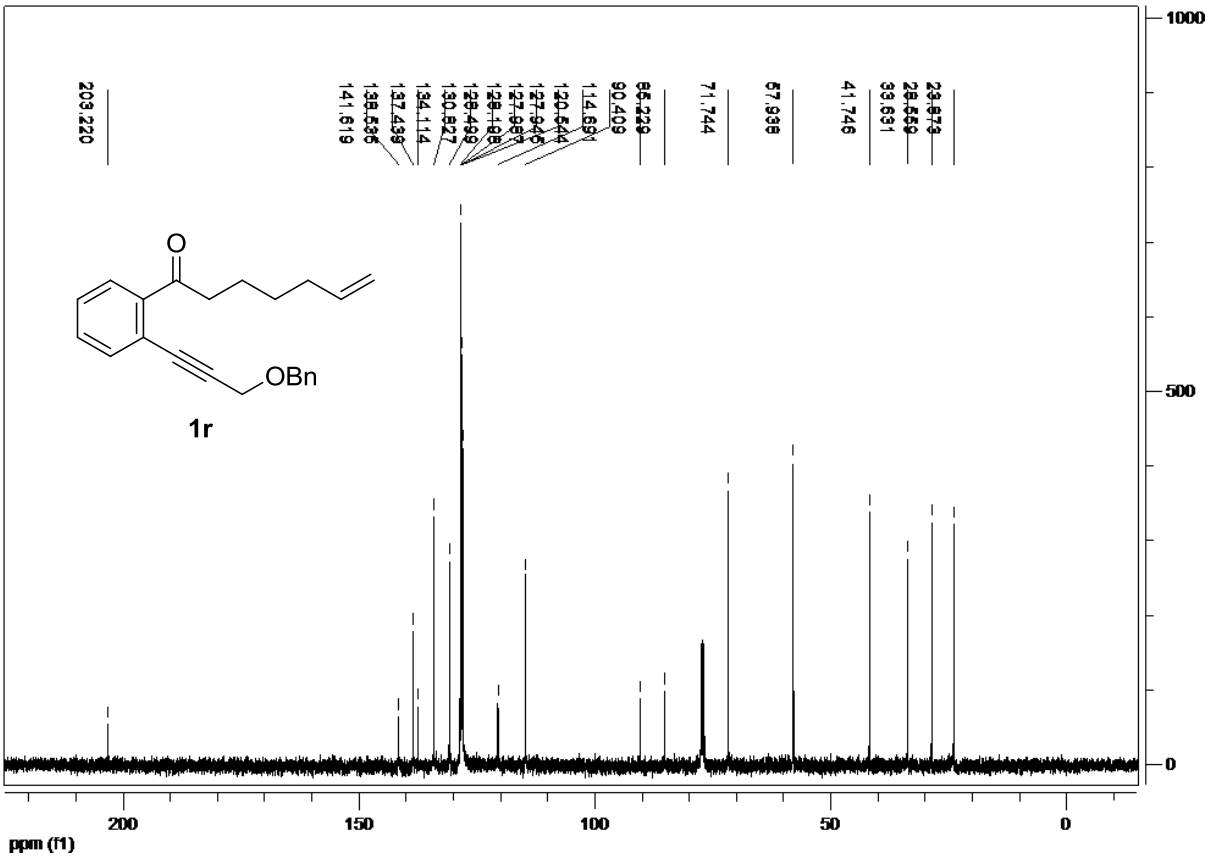


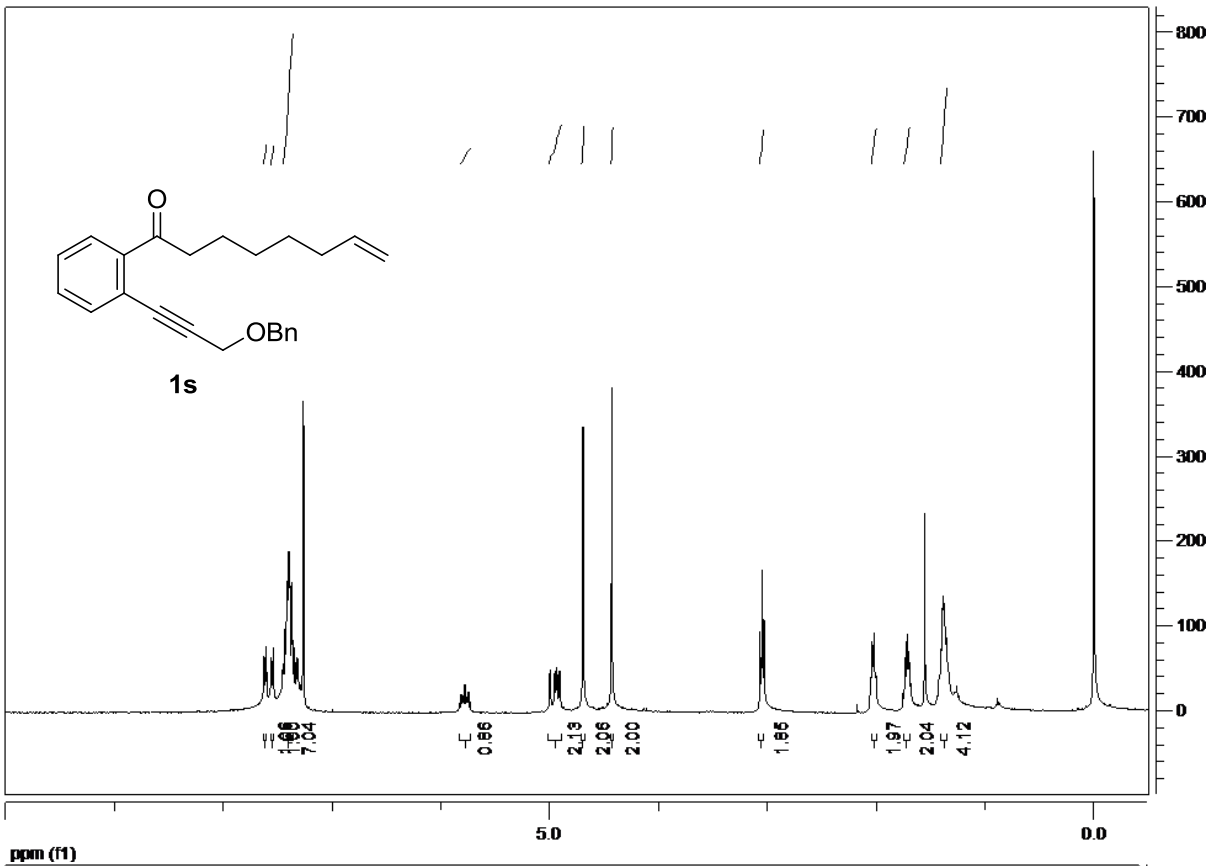


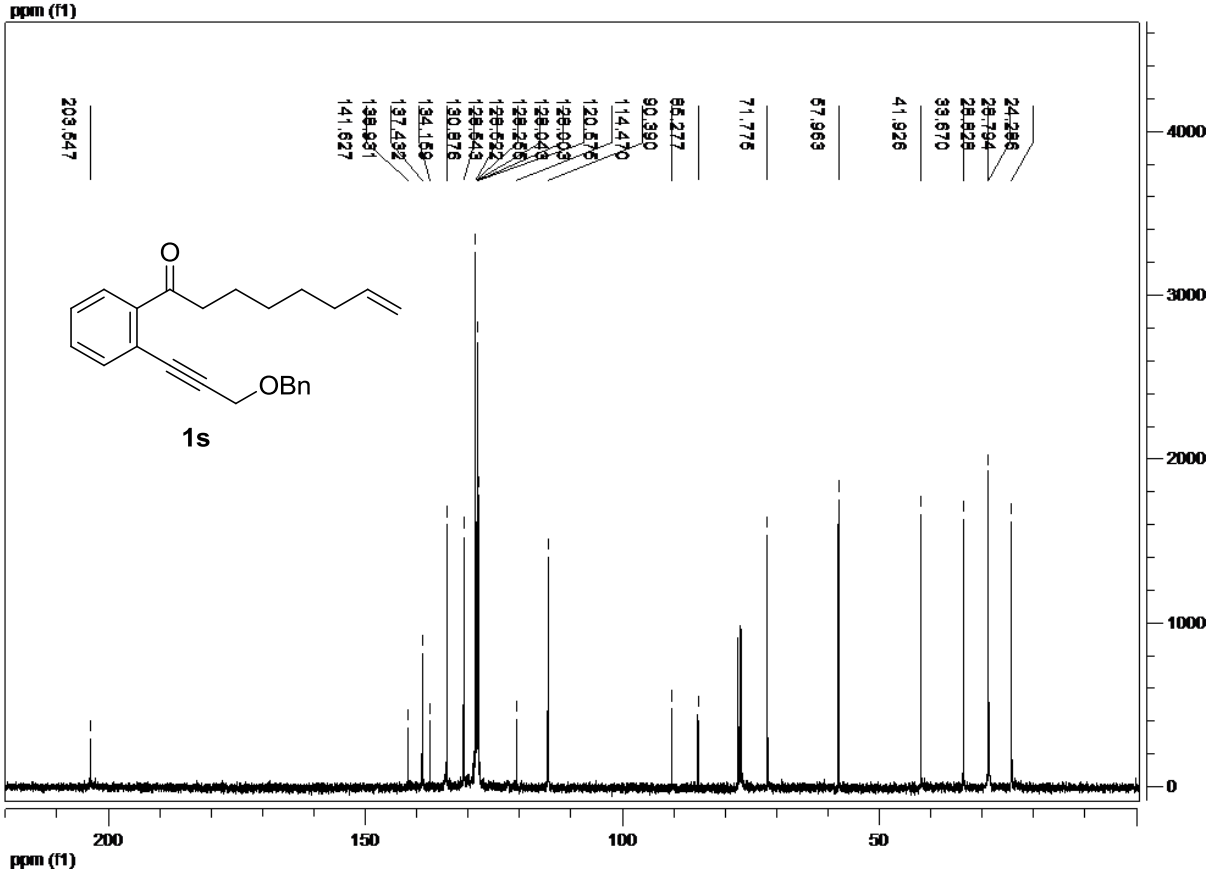


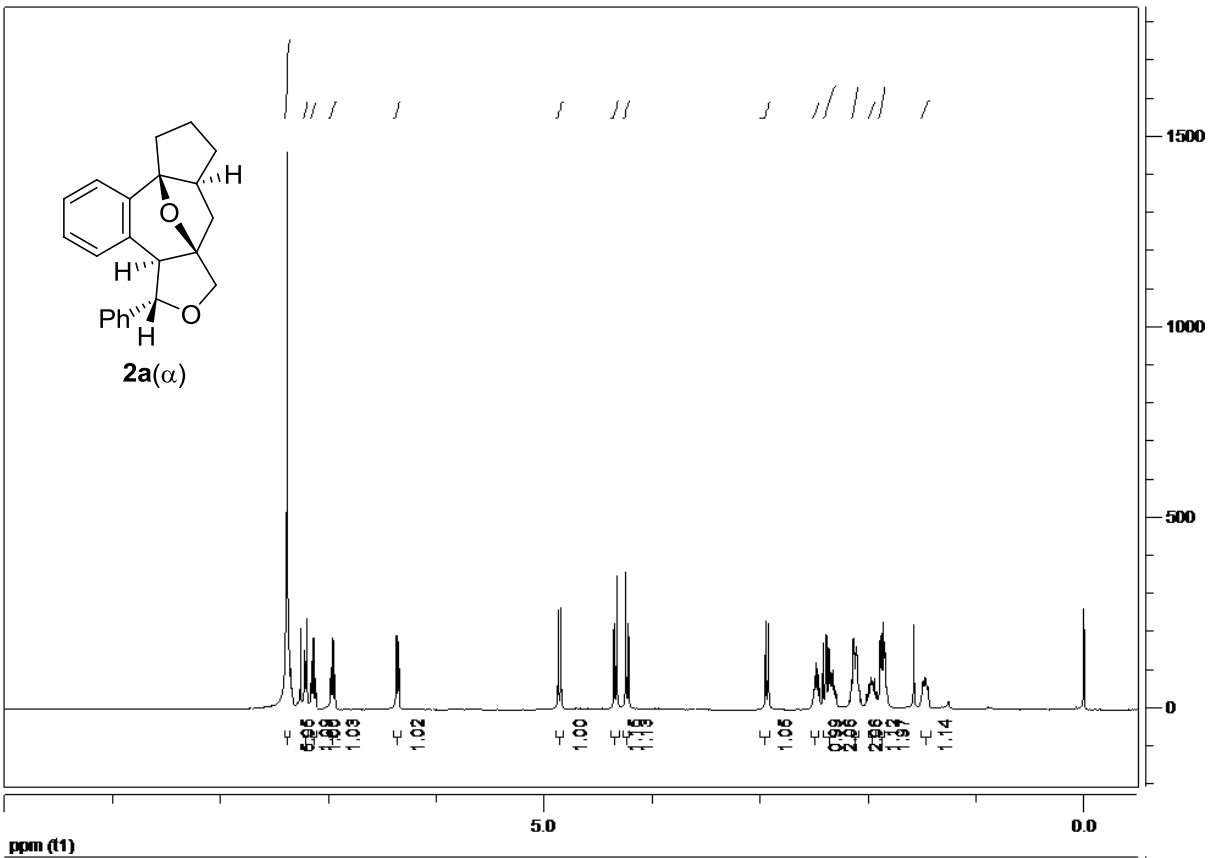


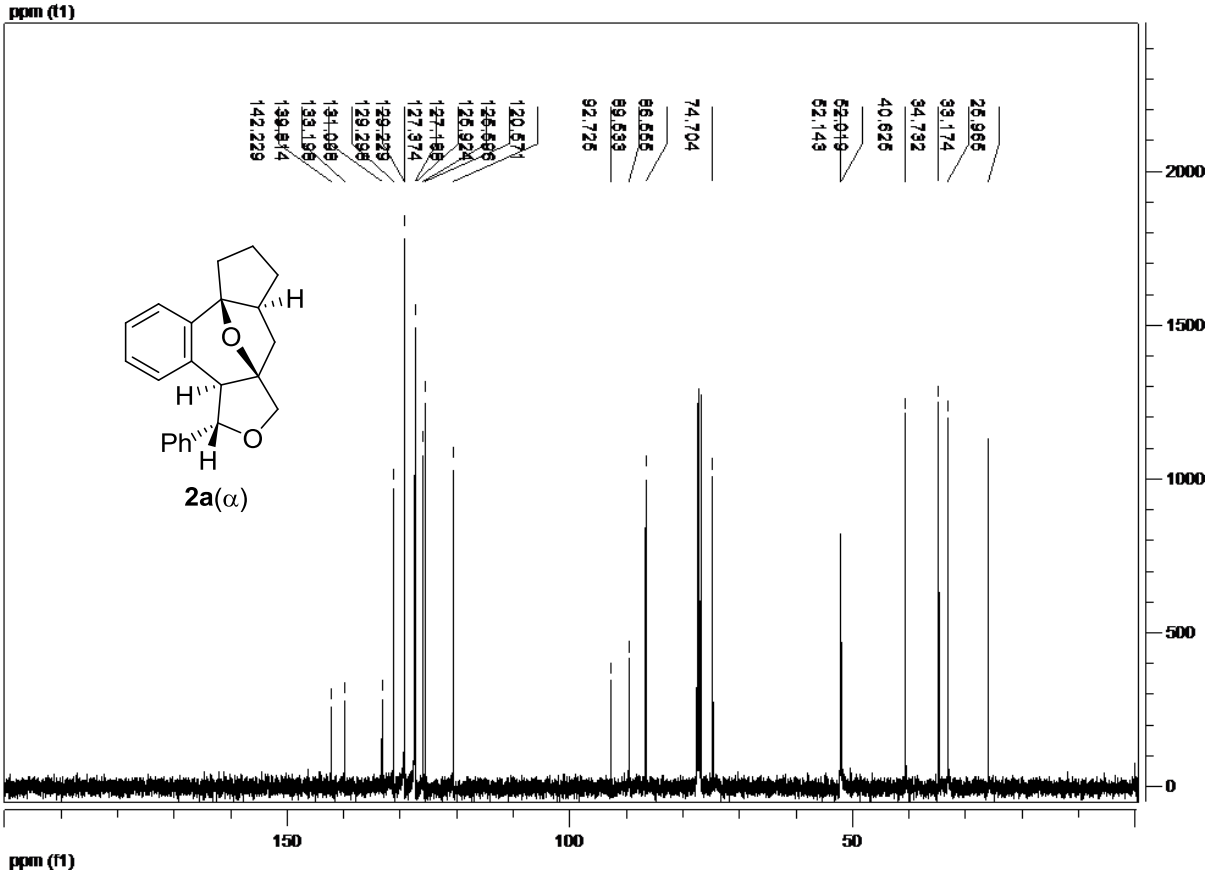


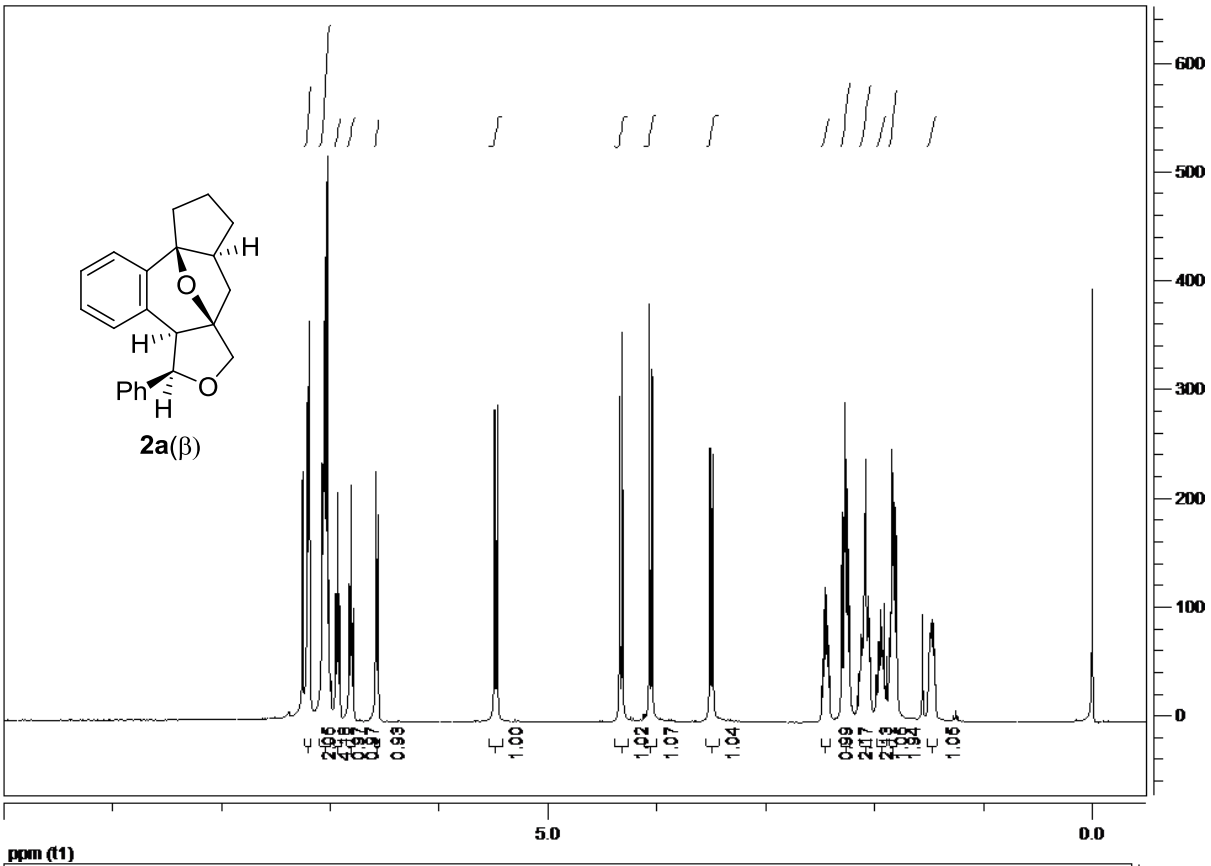


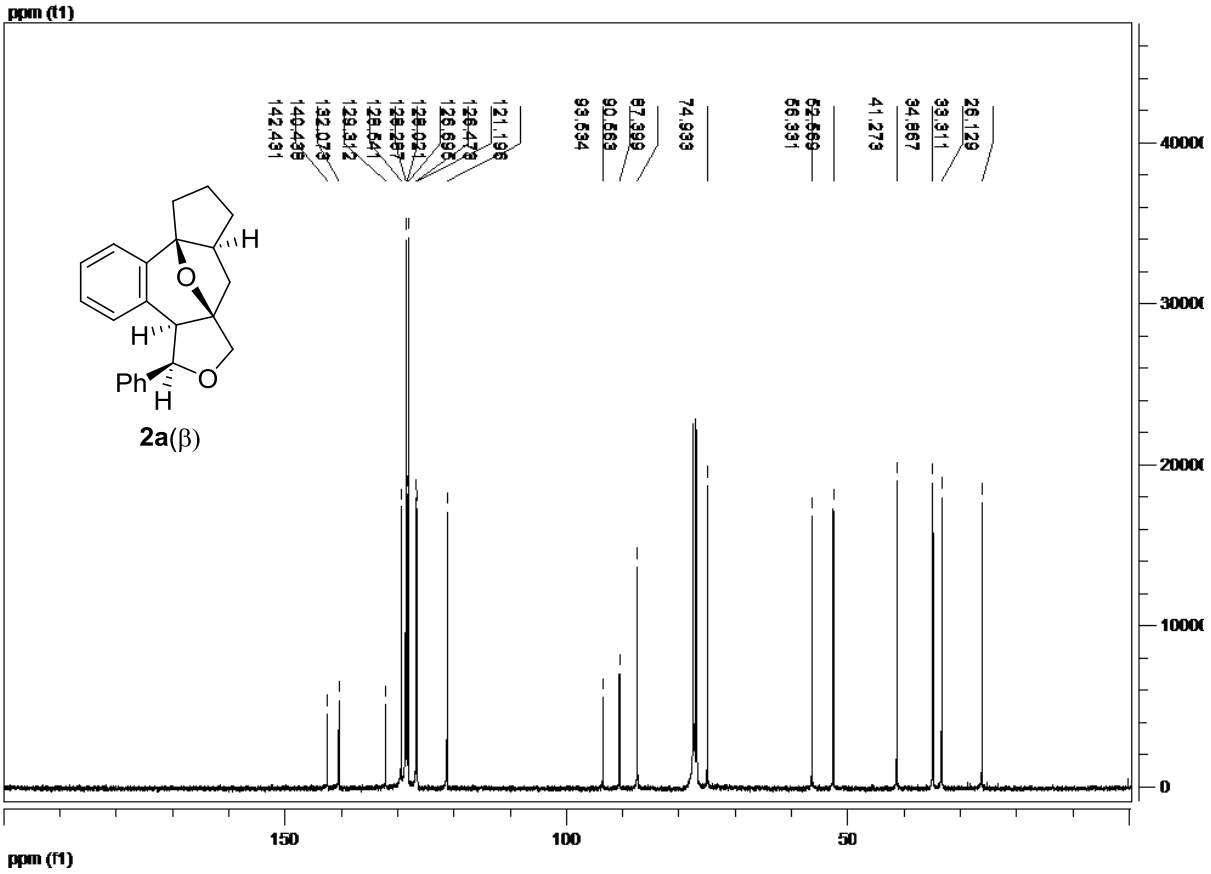


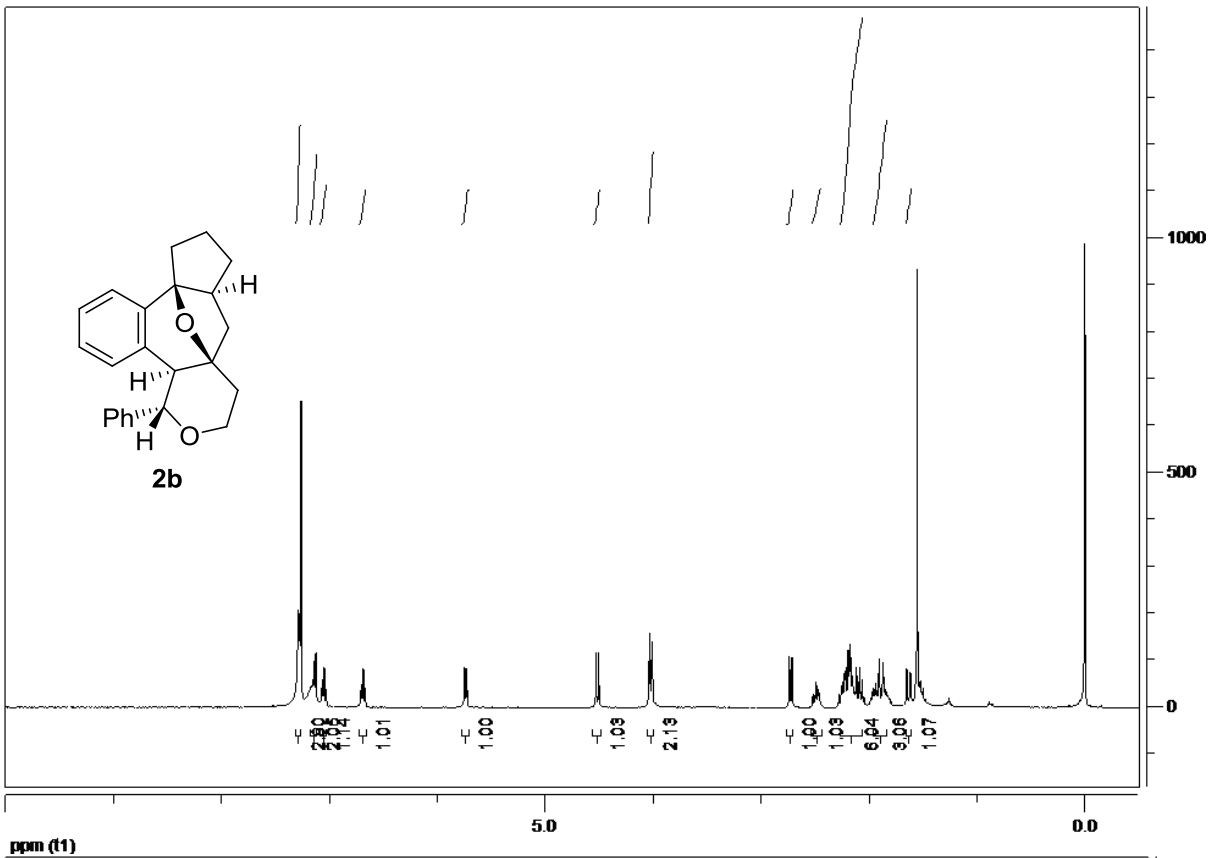


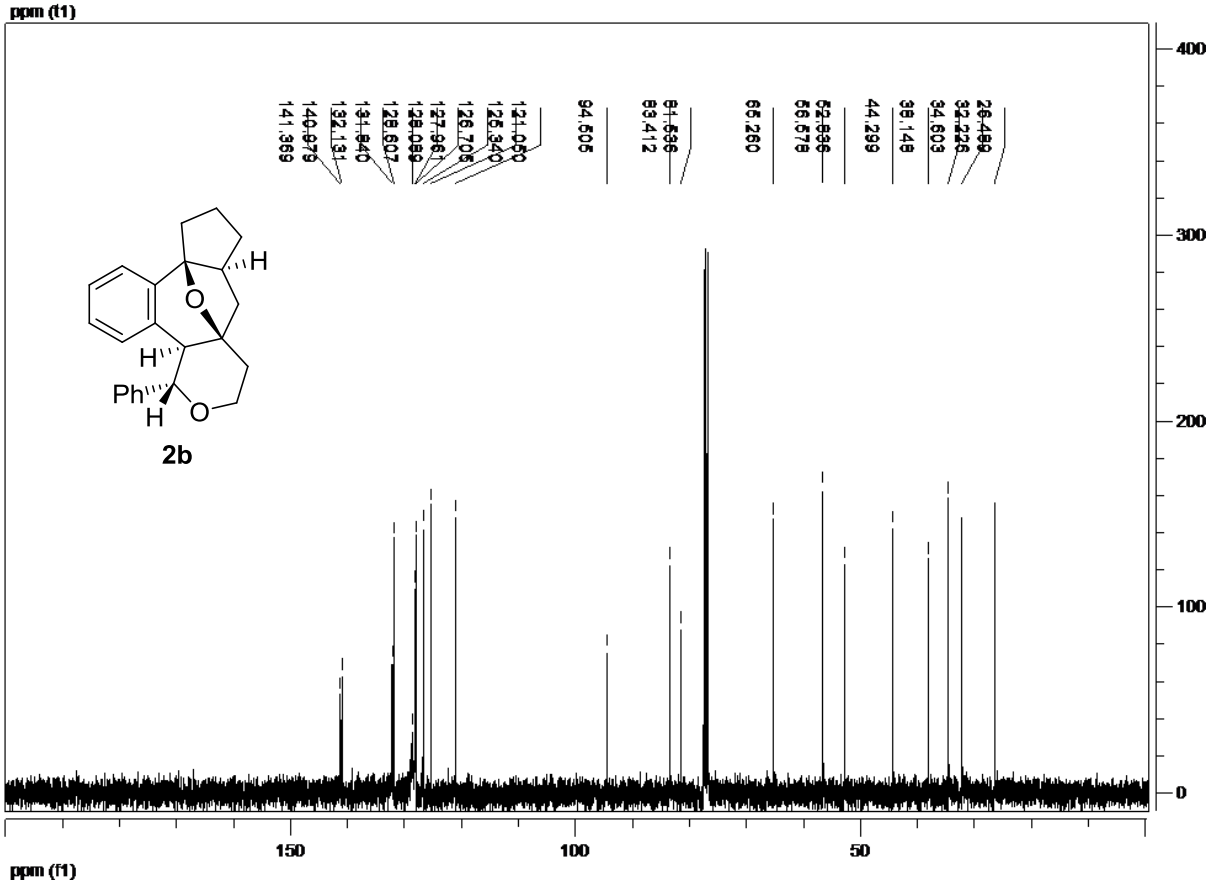


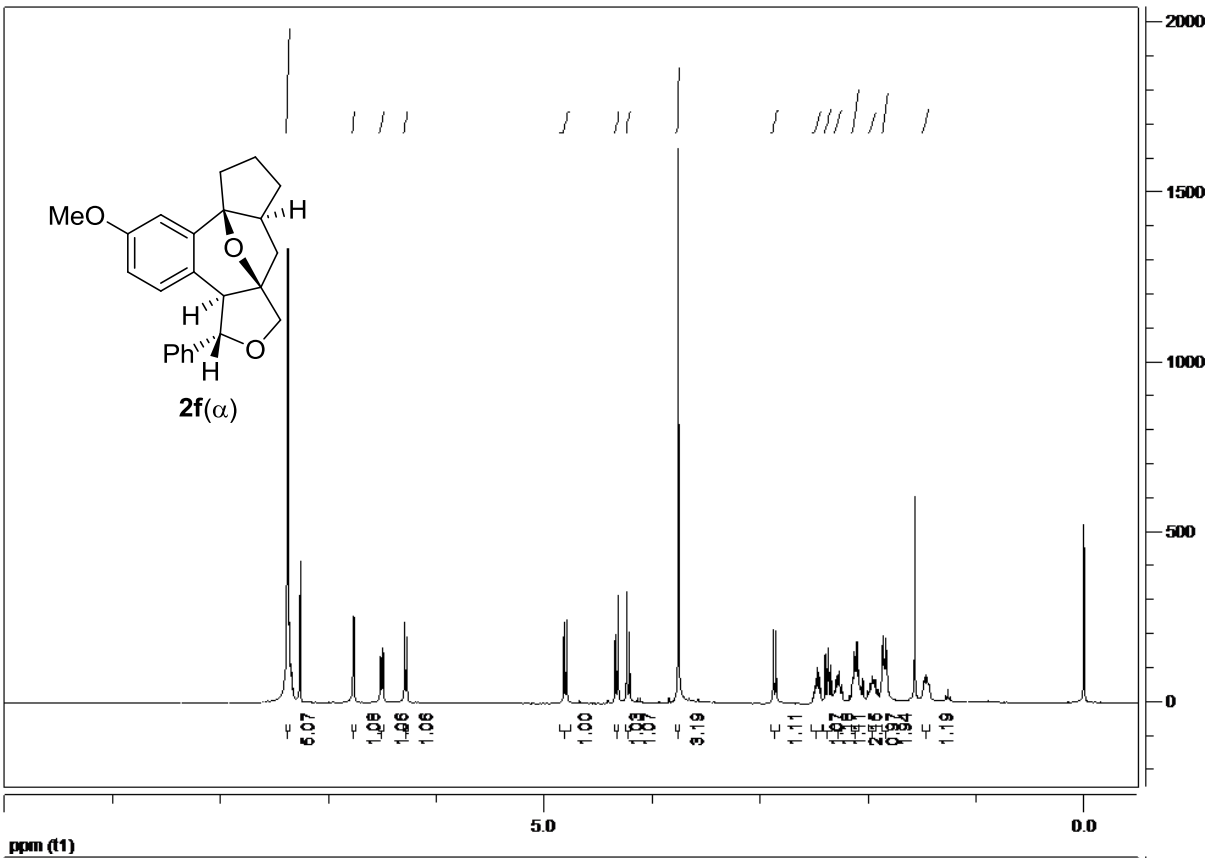


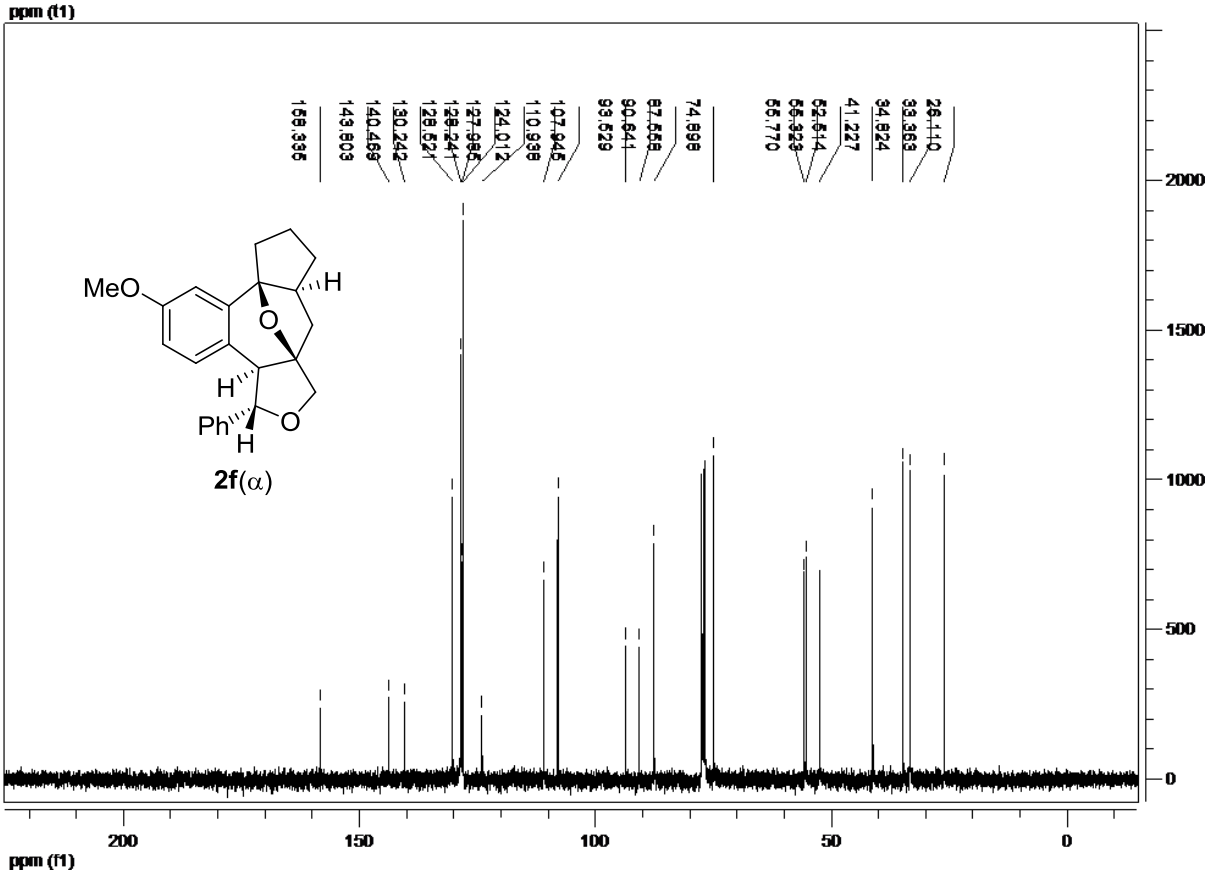


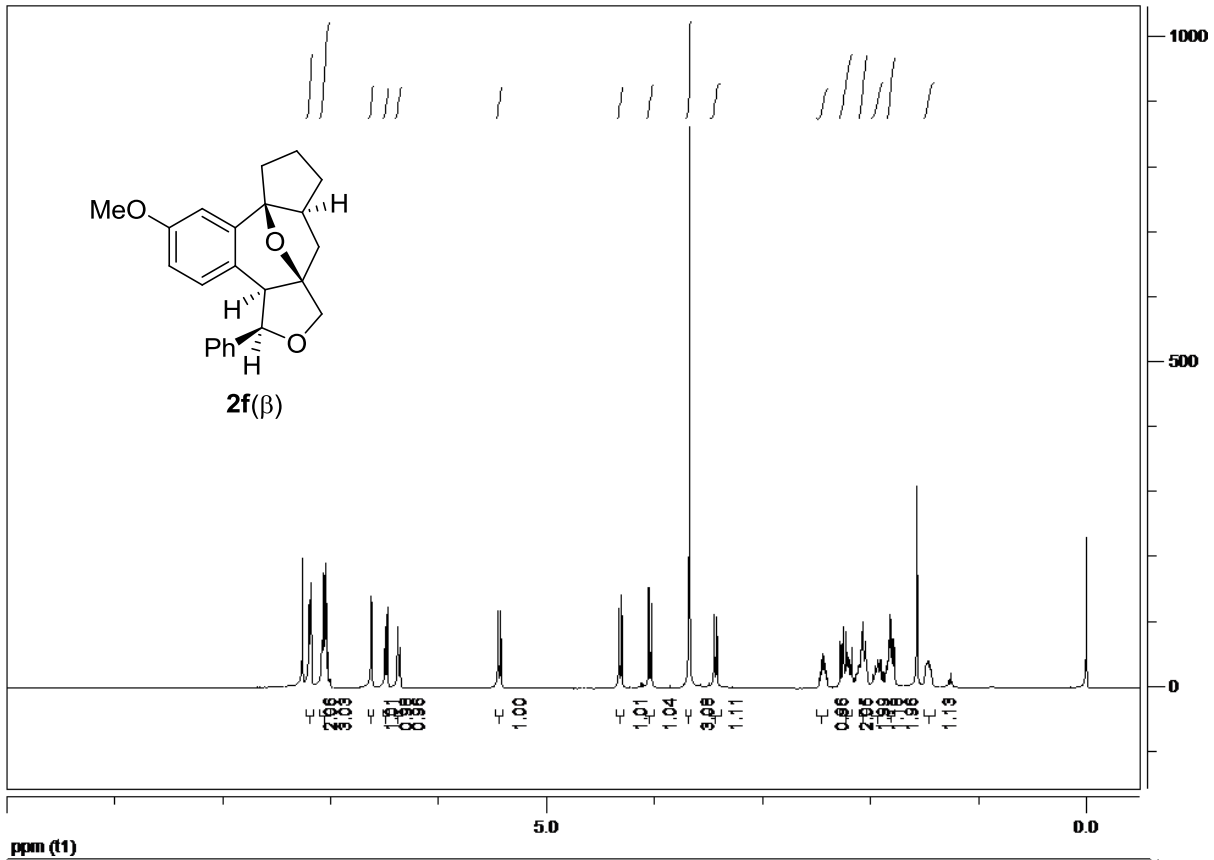


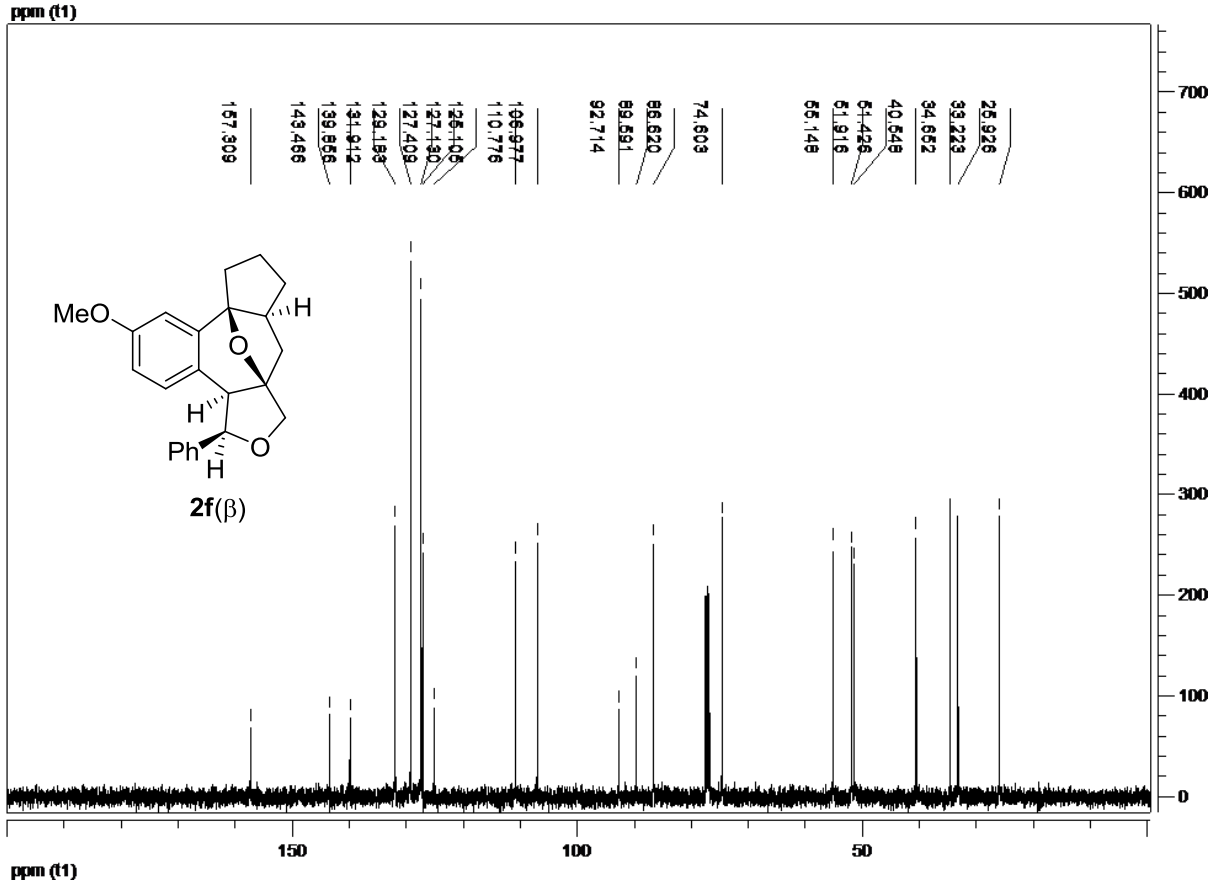


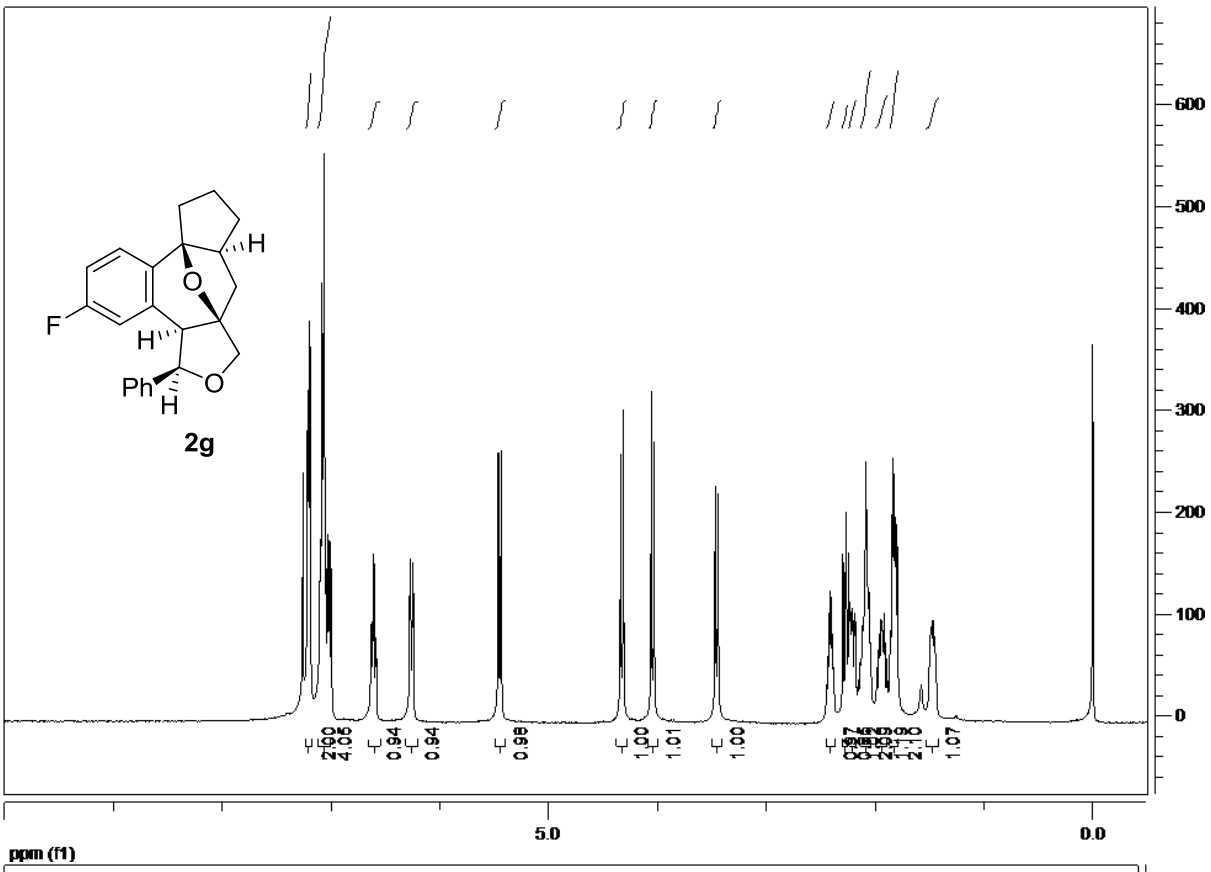


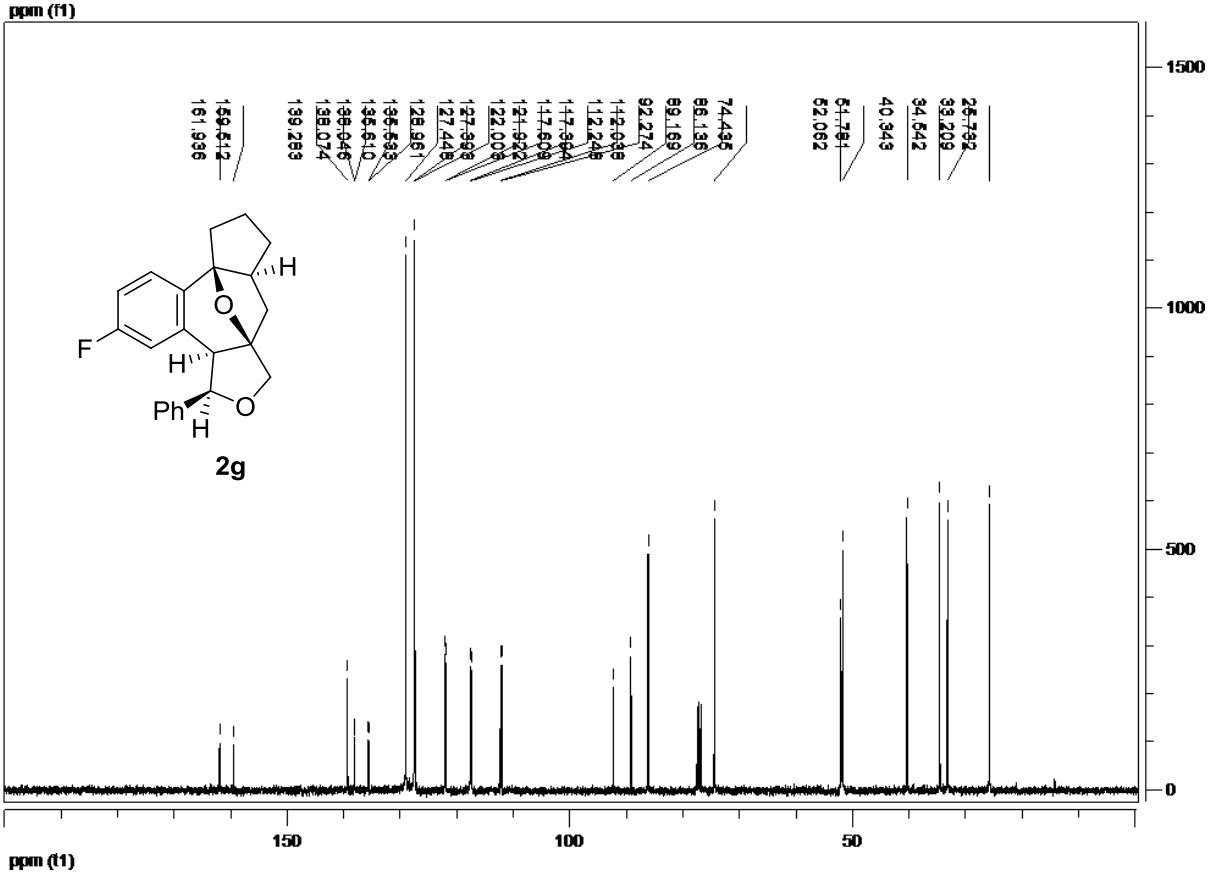


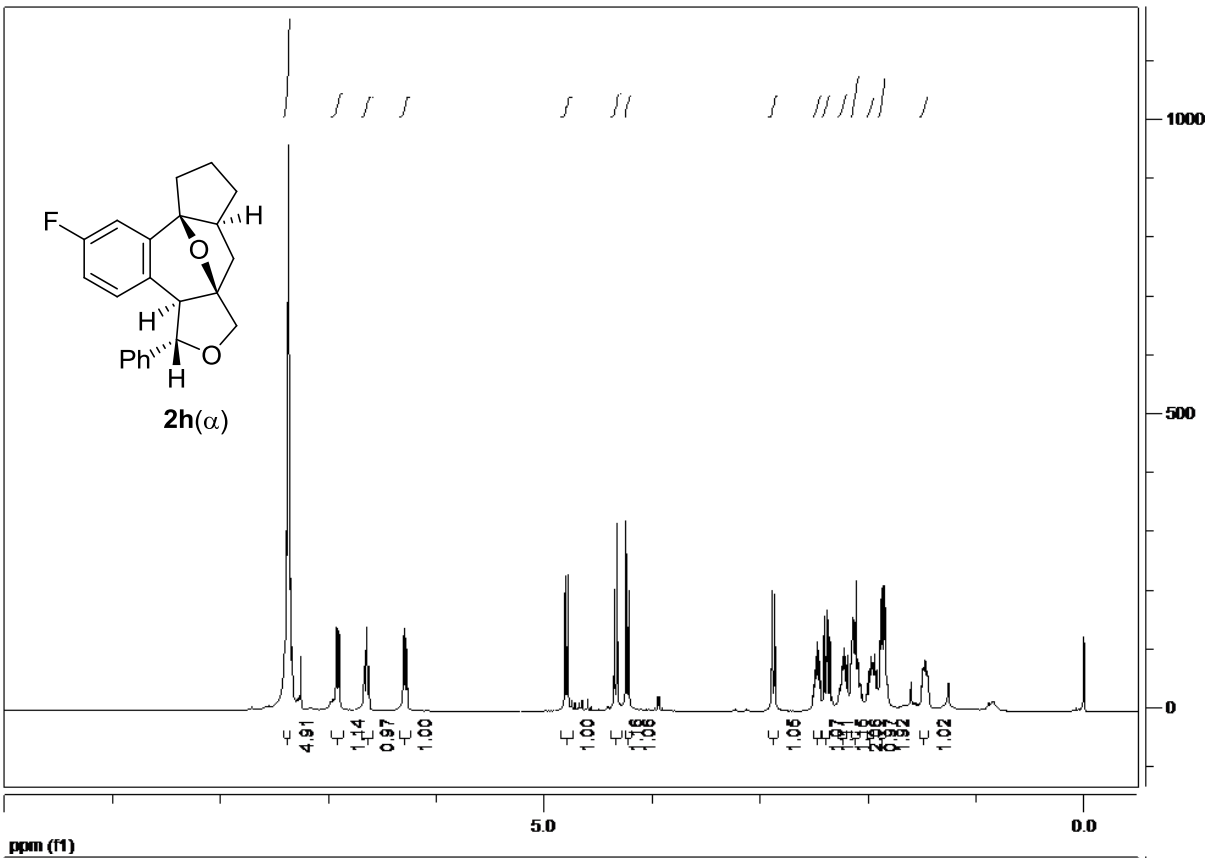


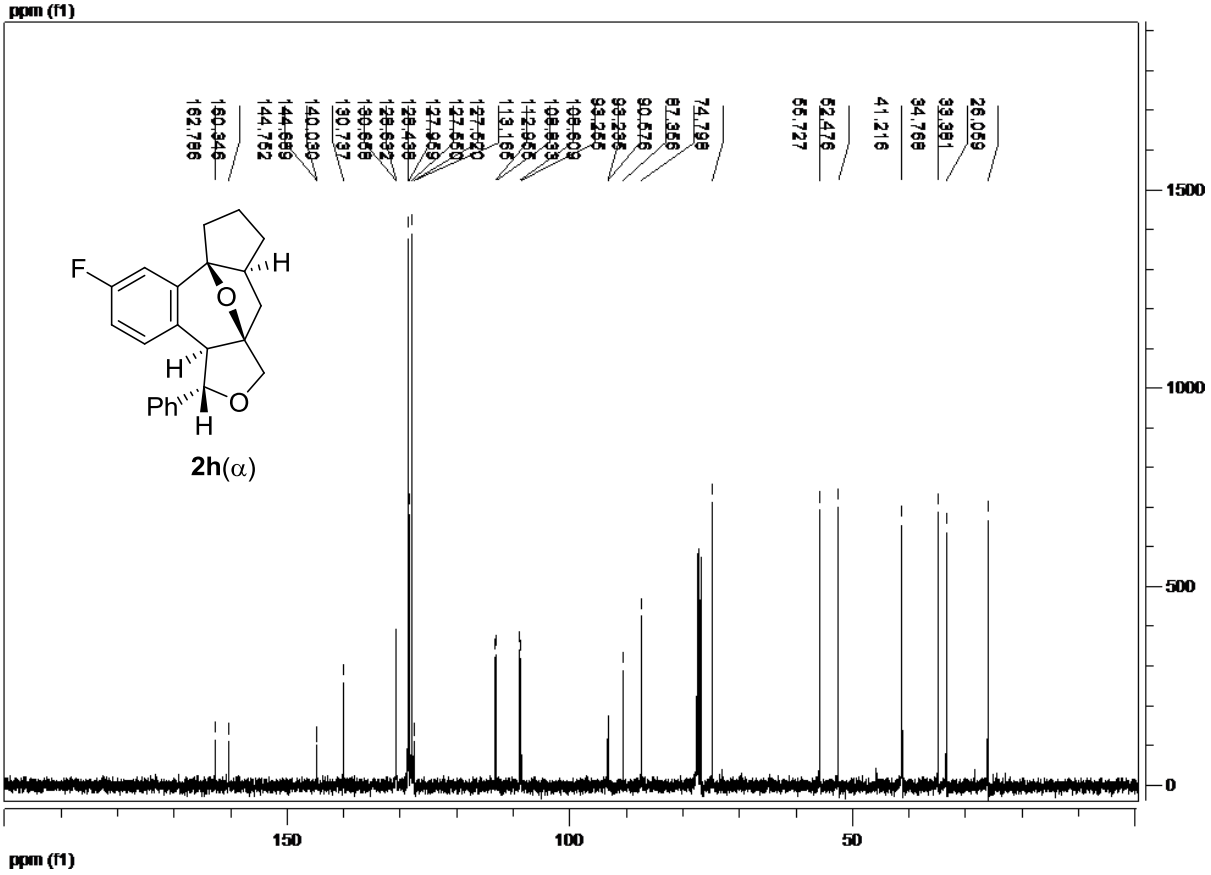


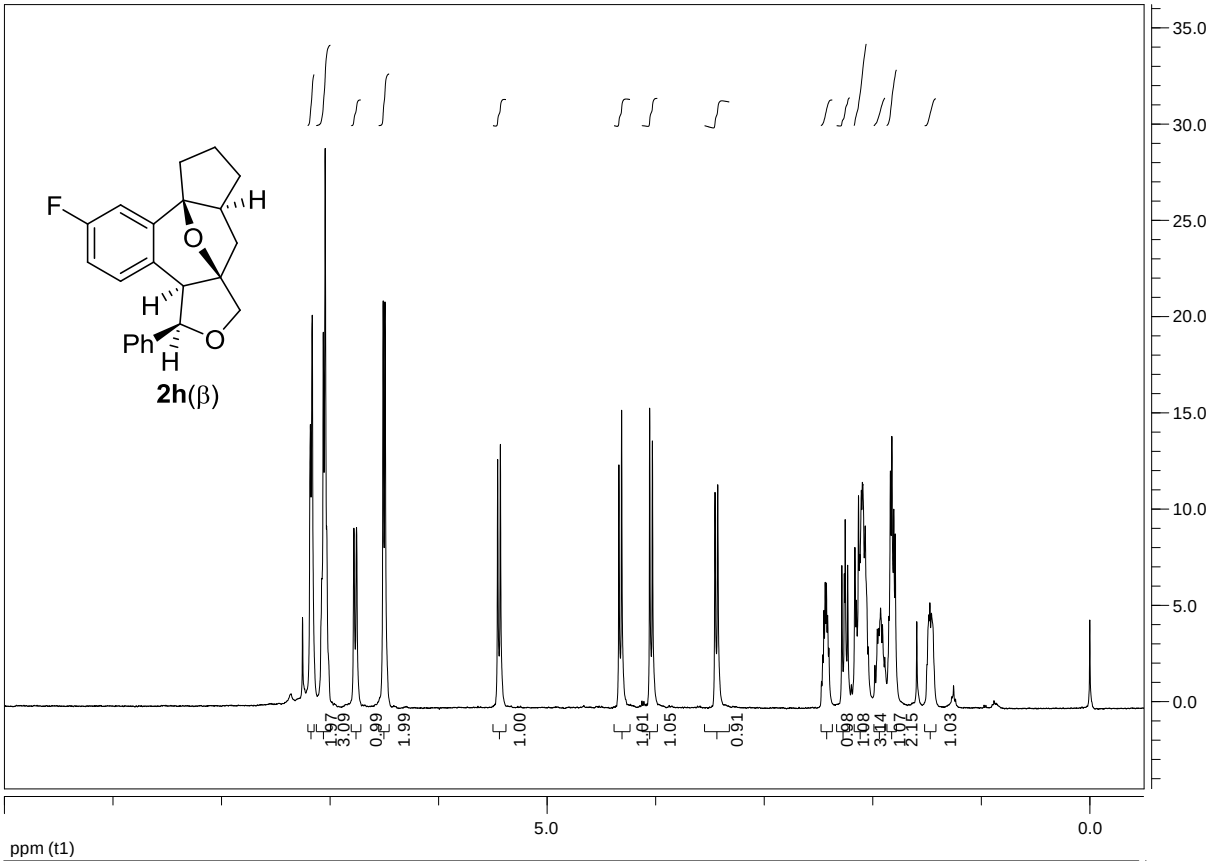


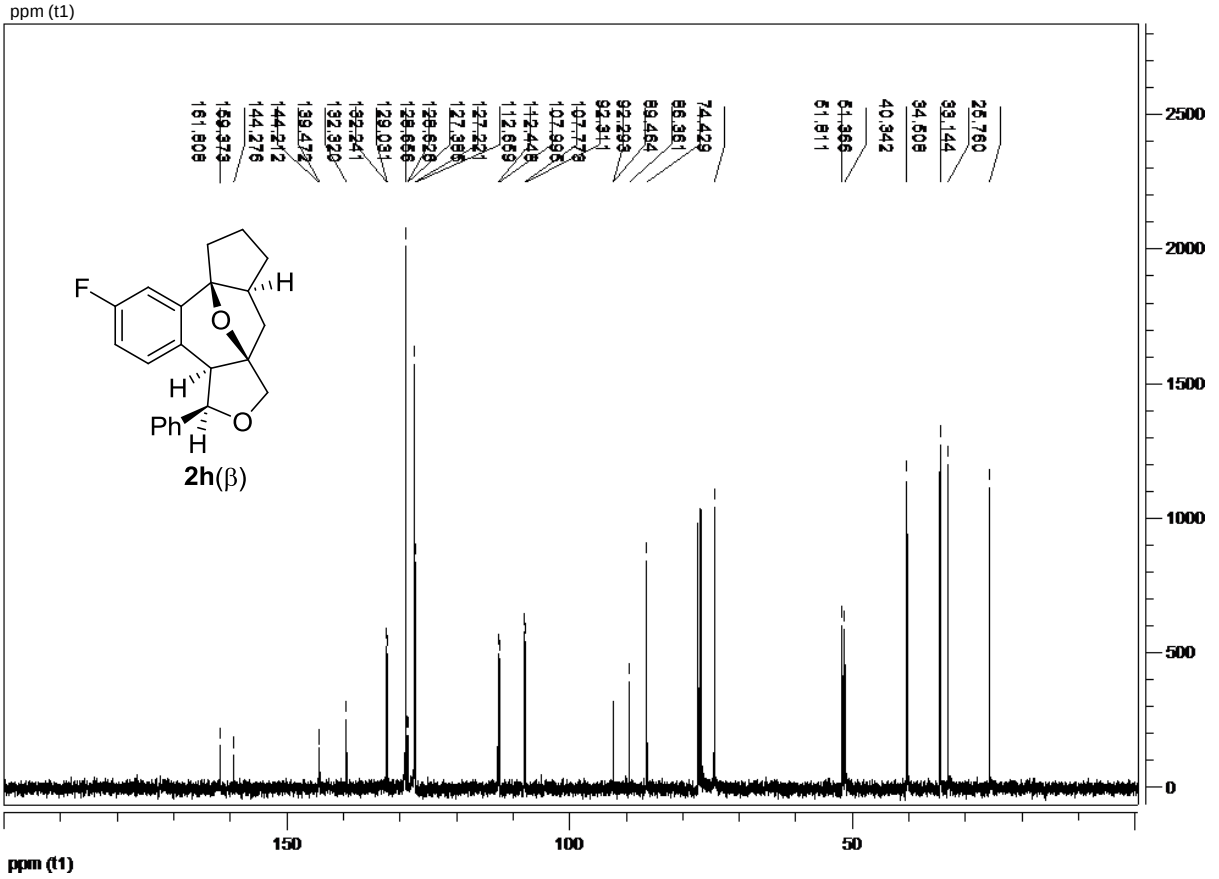


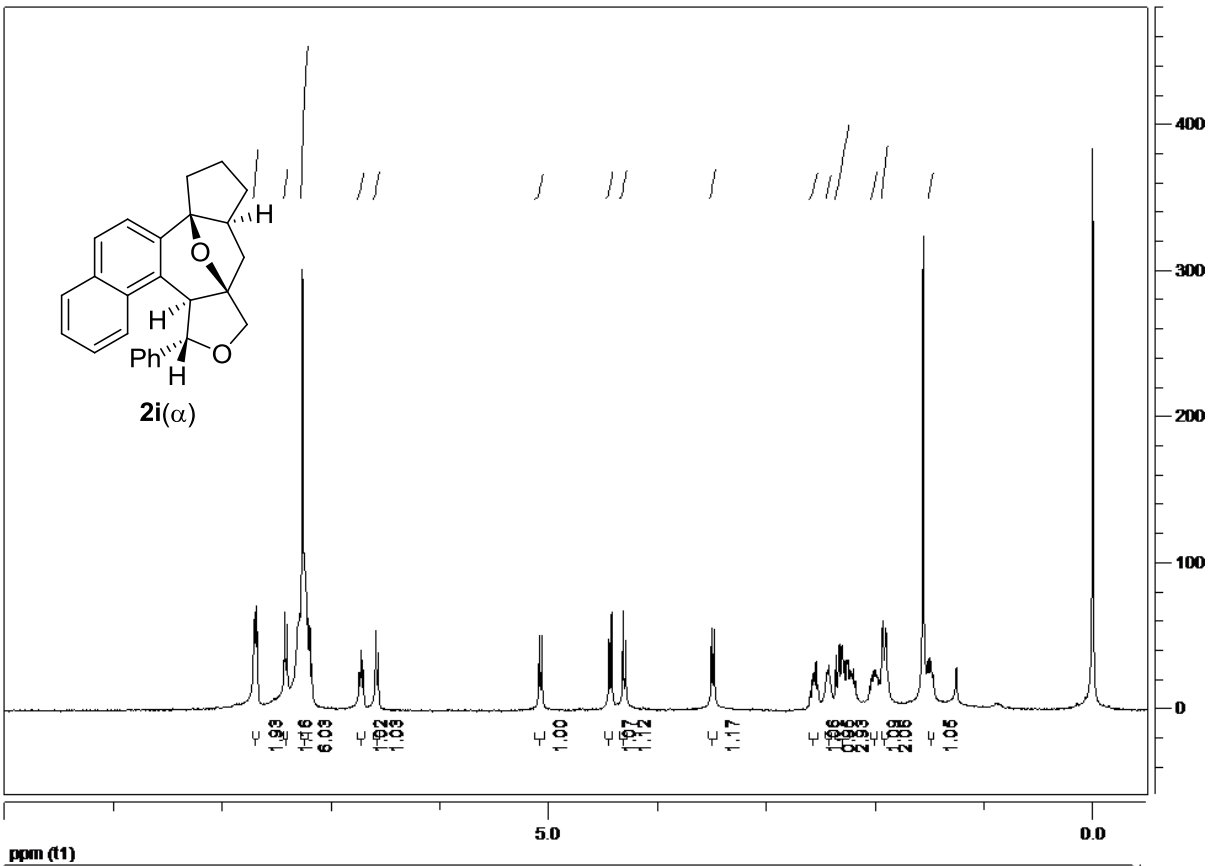


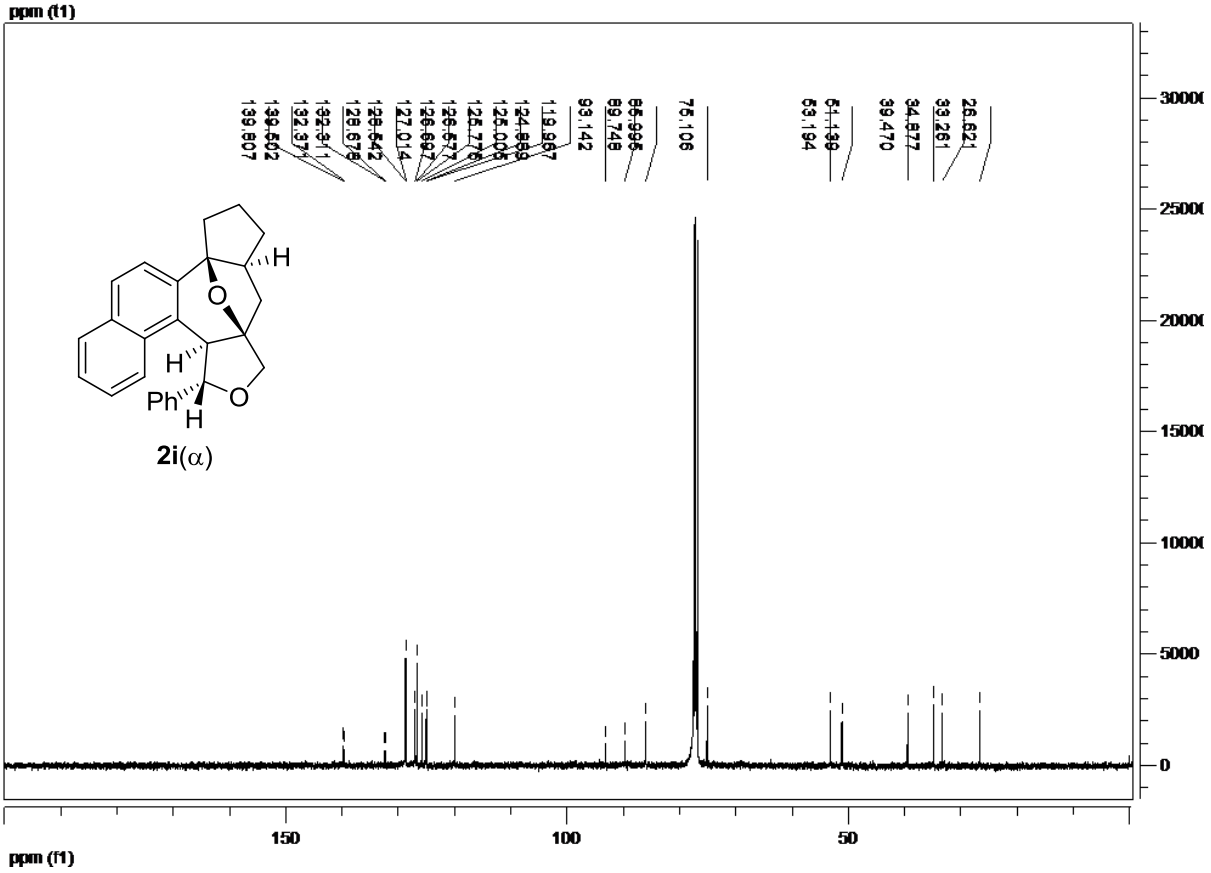


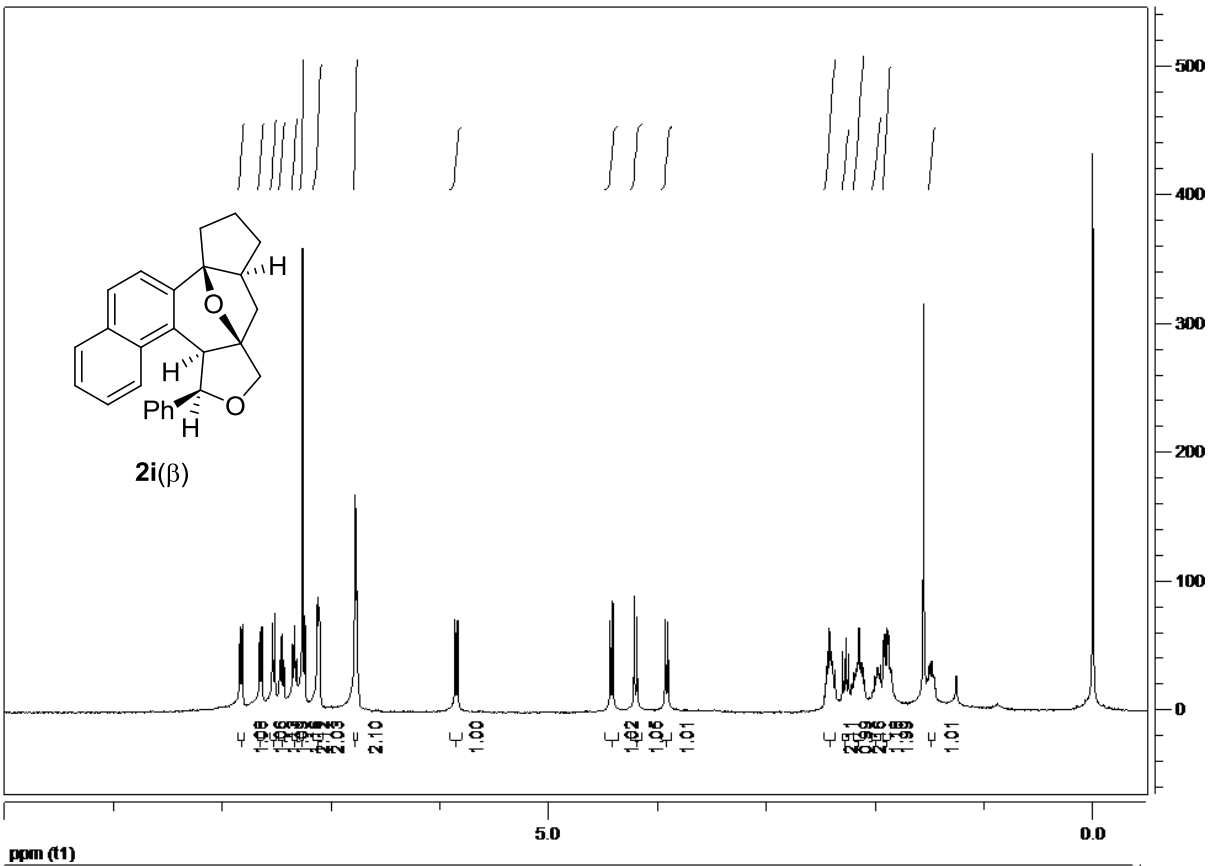




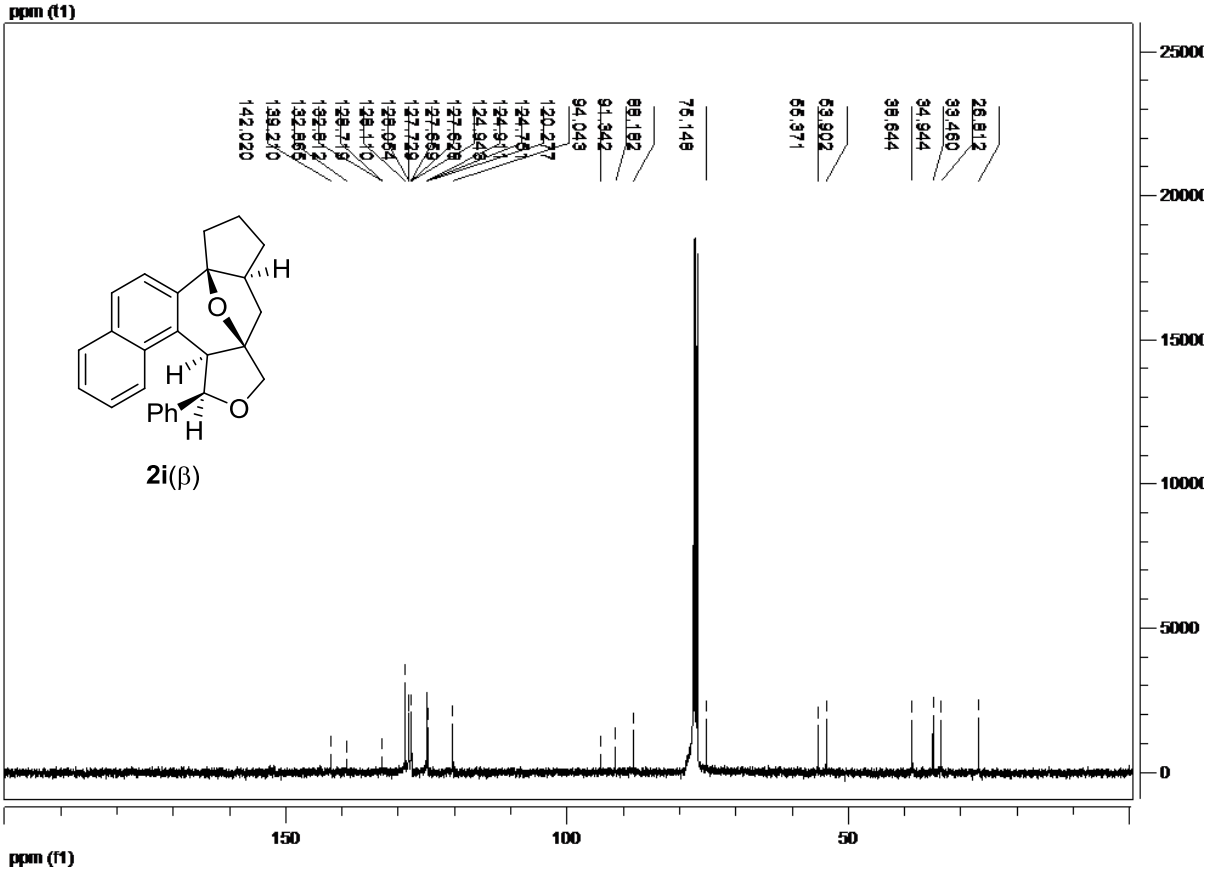








2i(β)



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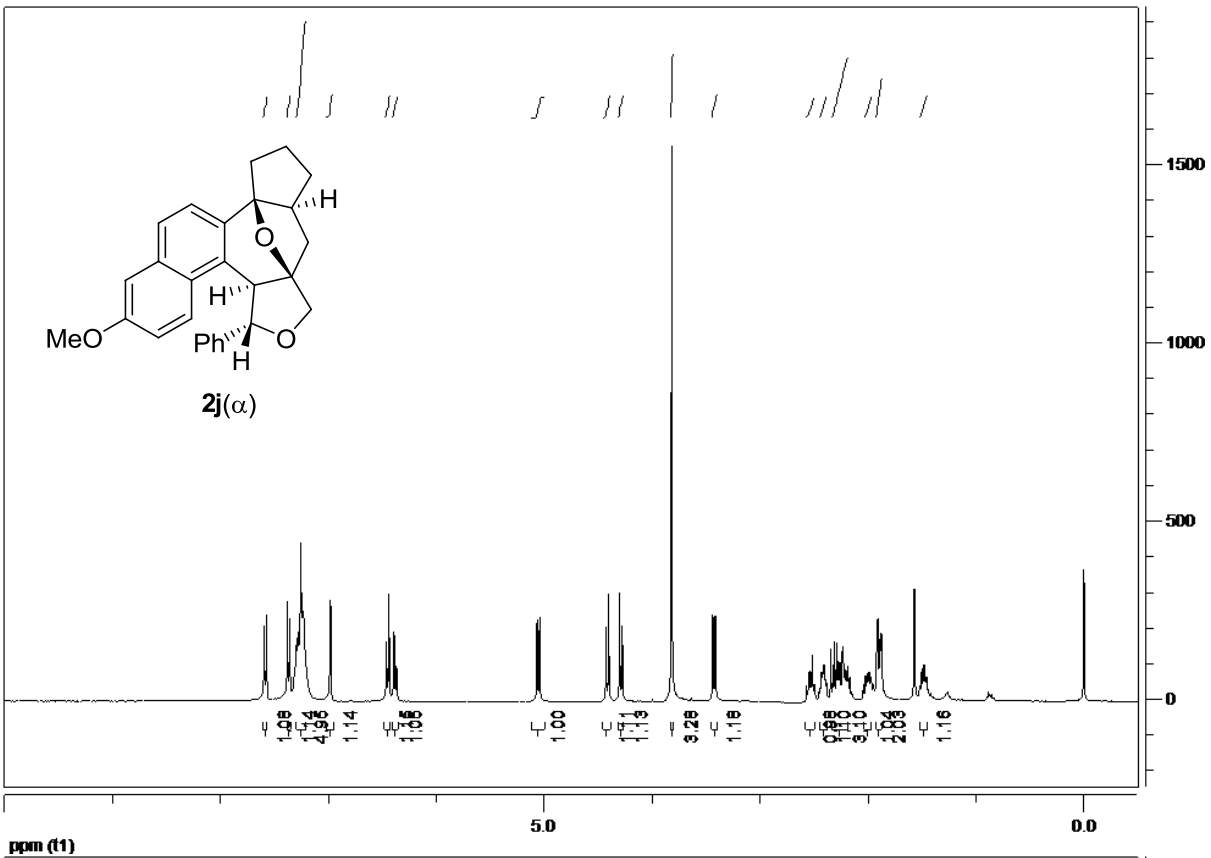
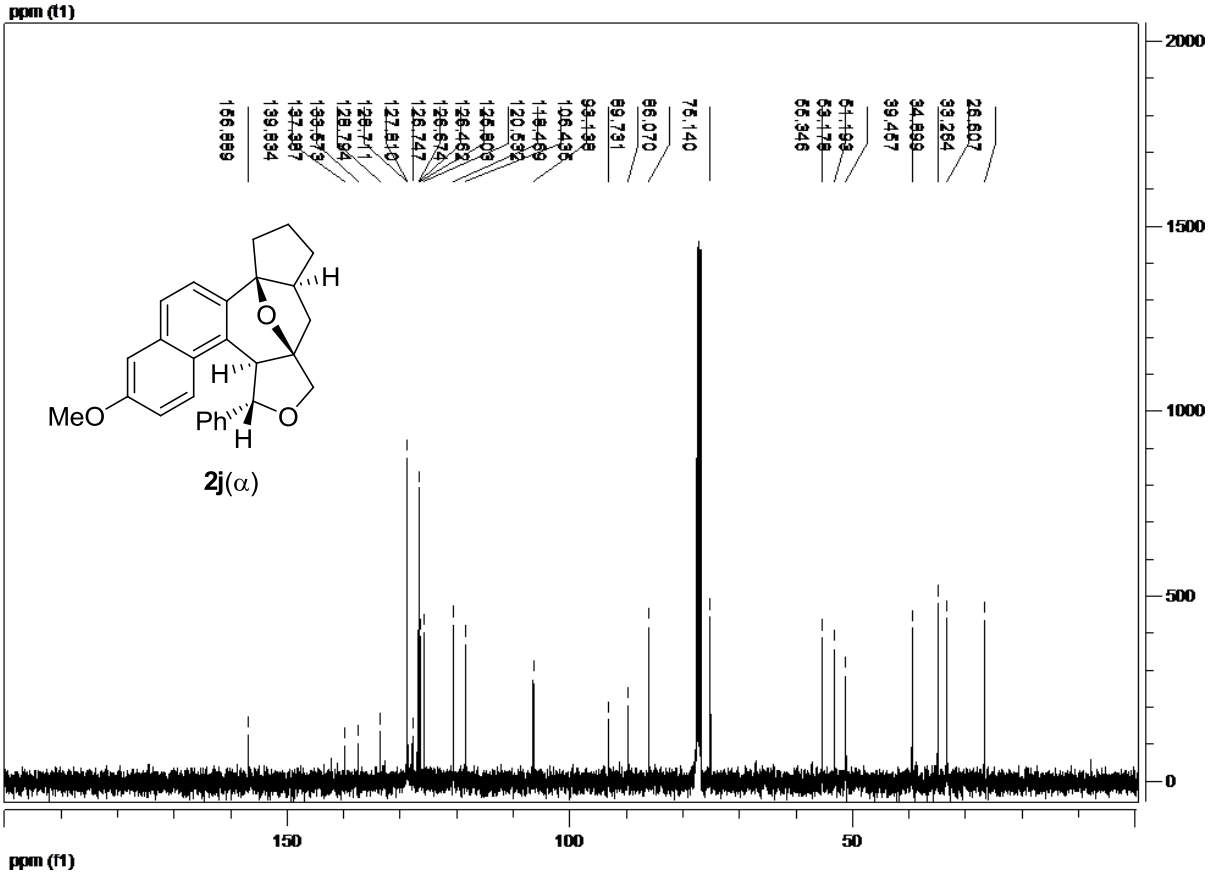
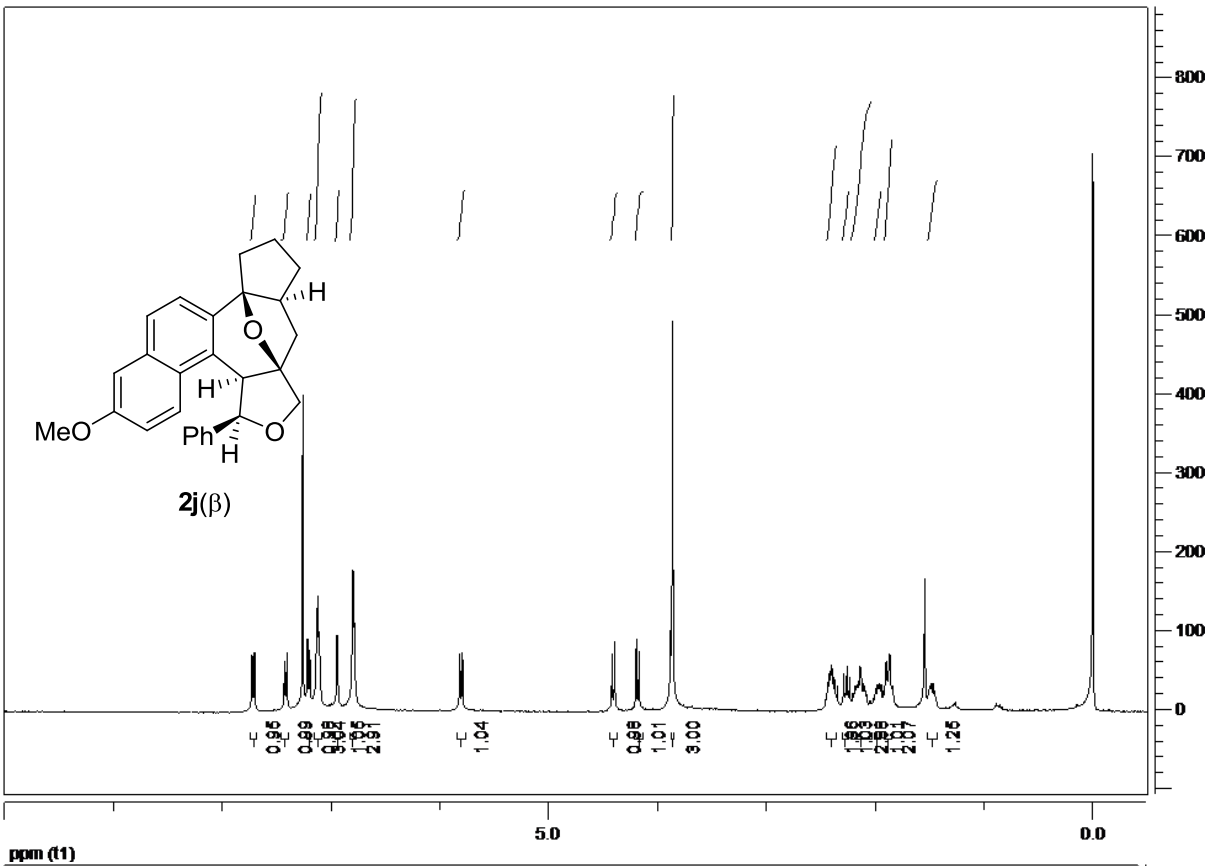
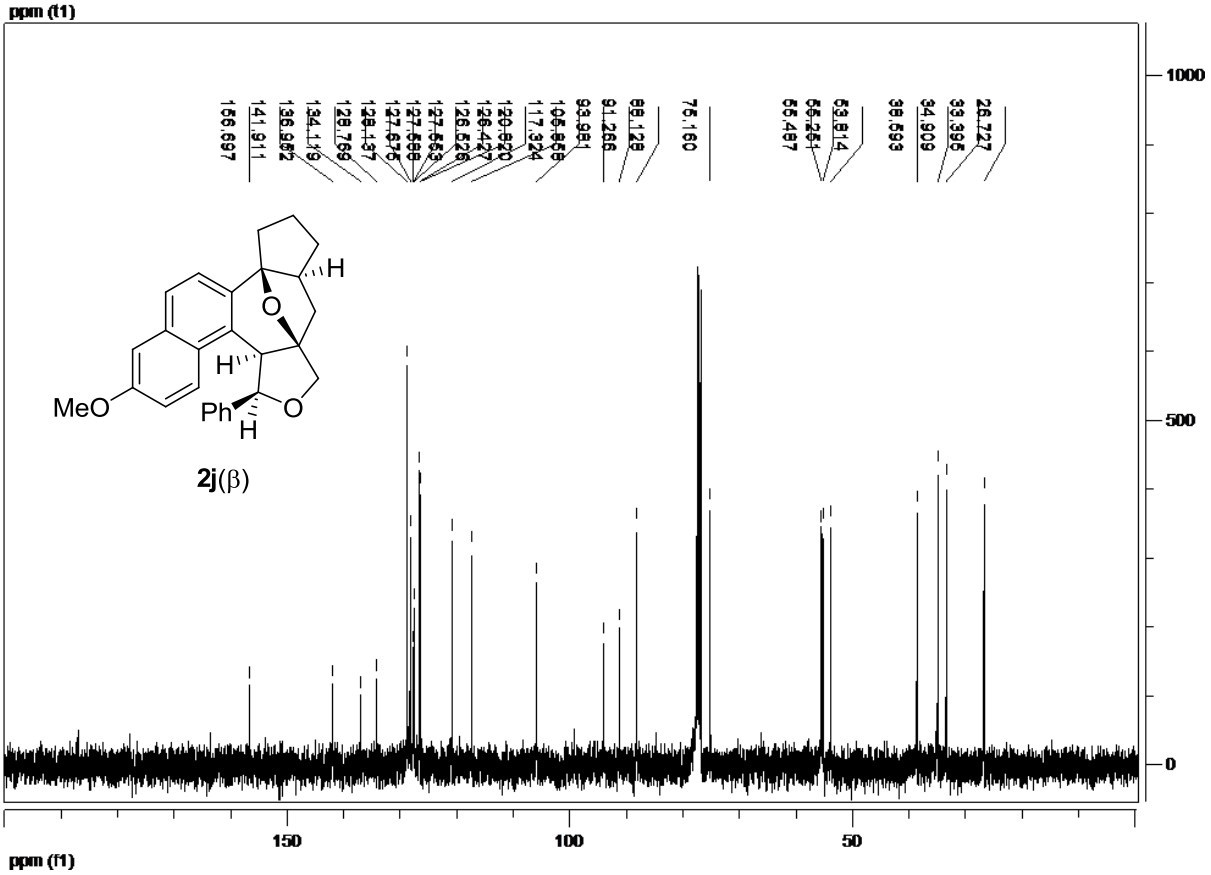
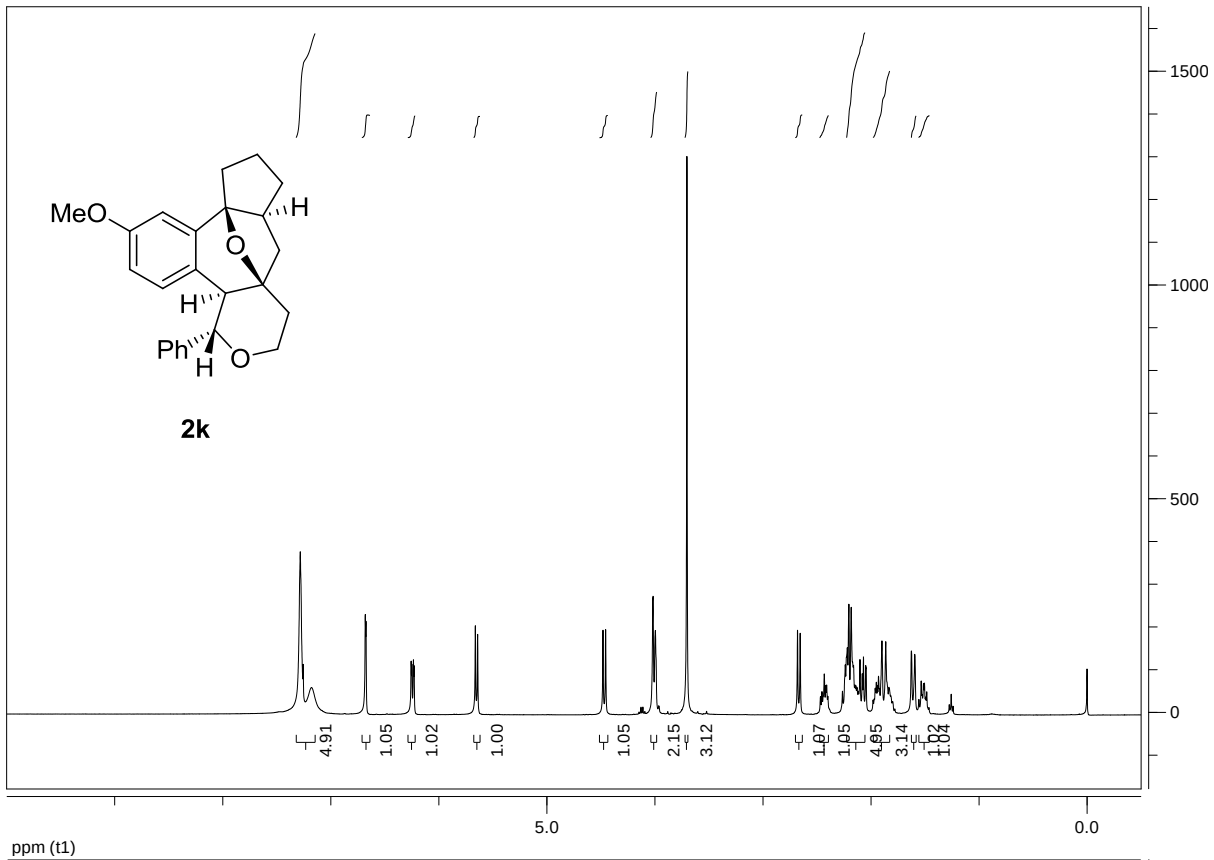
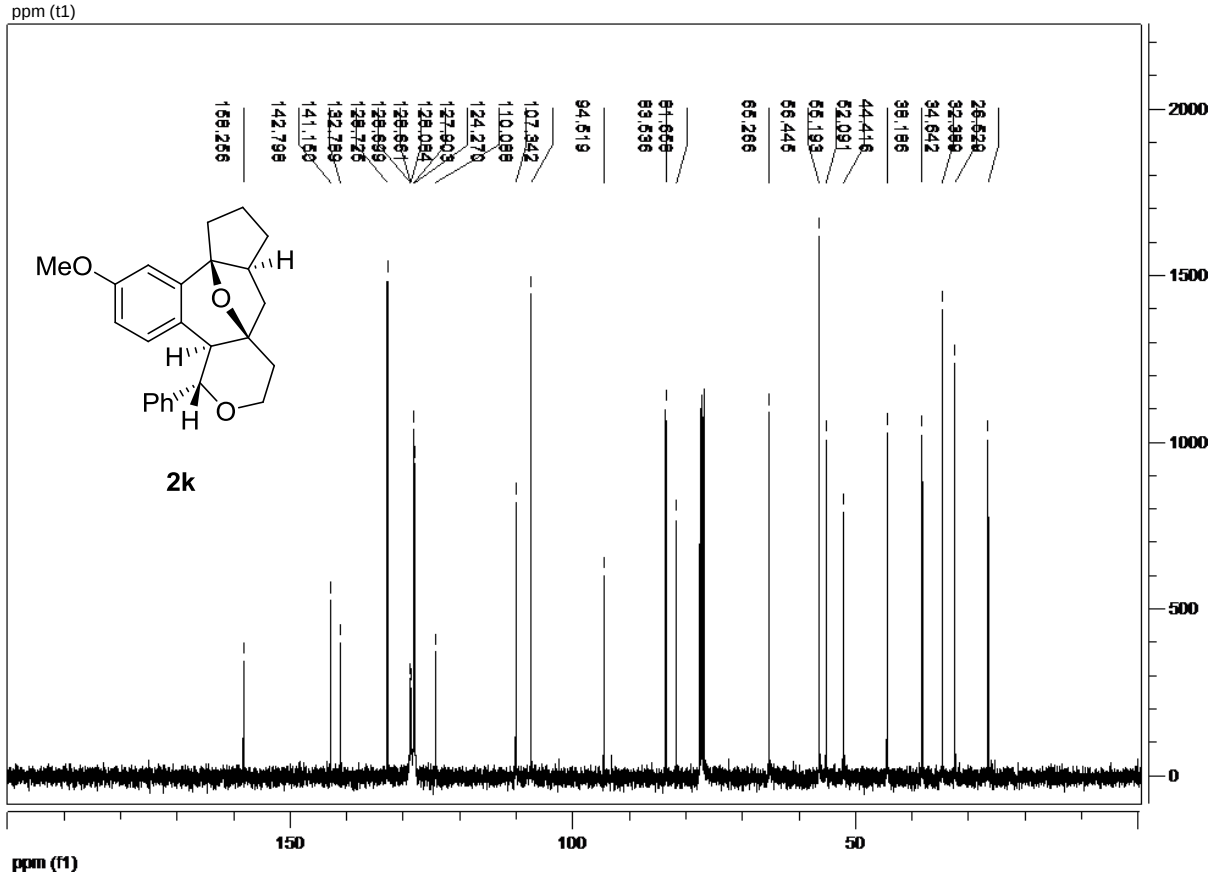


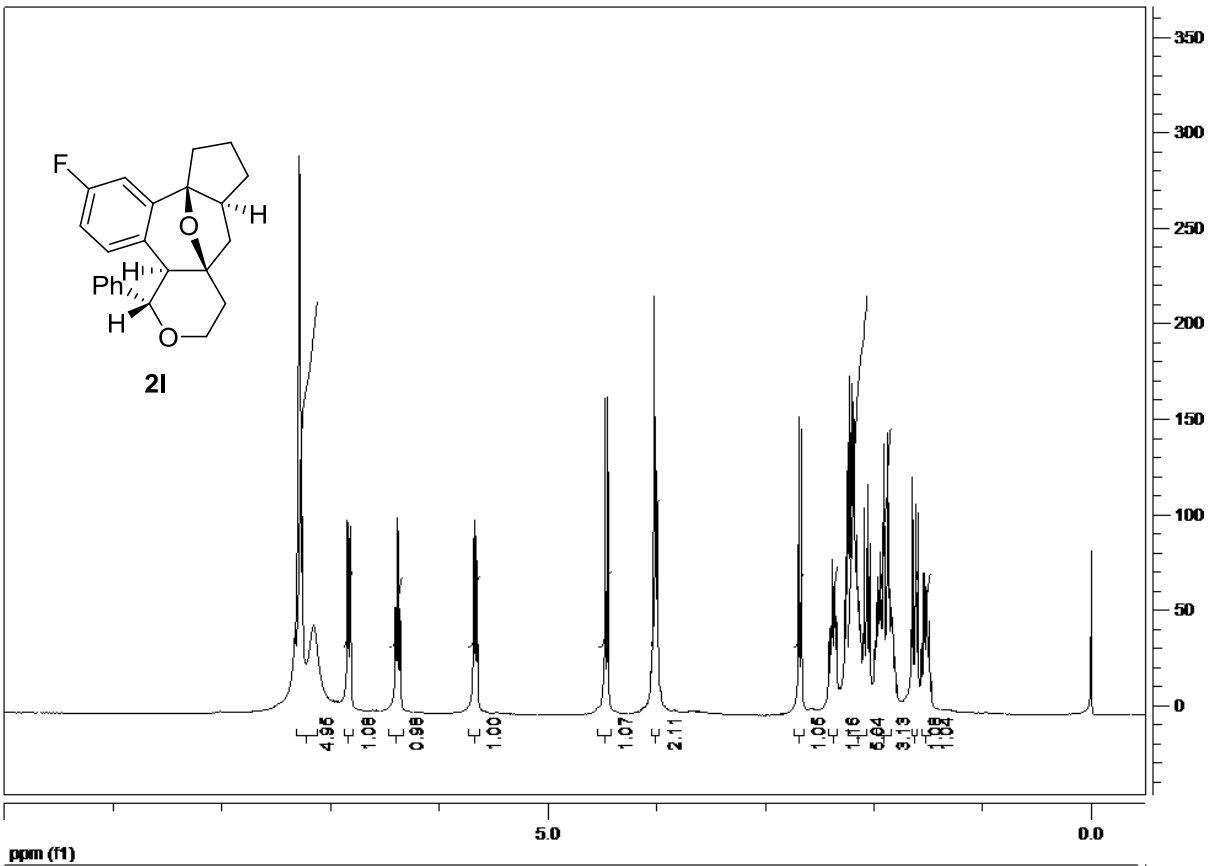


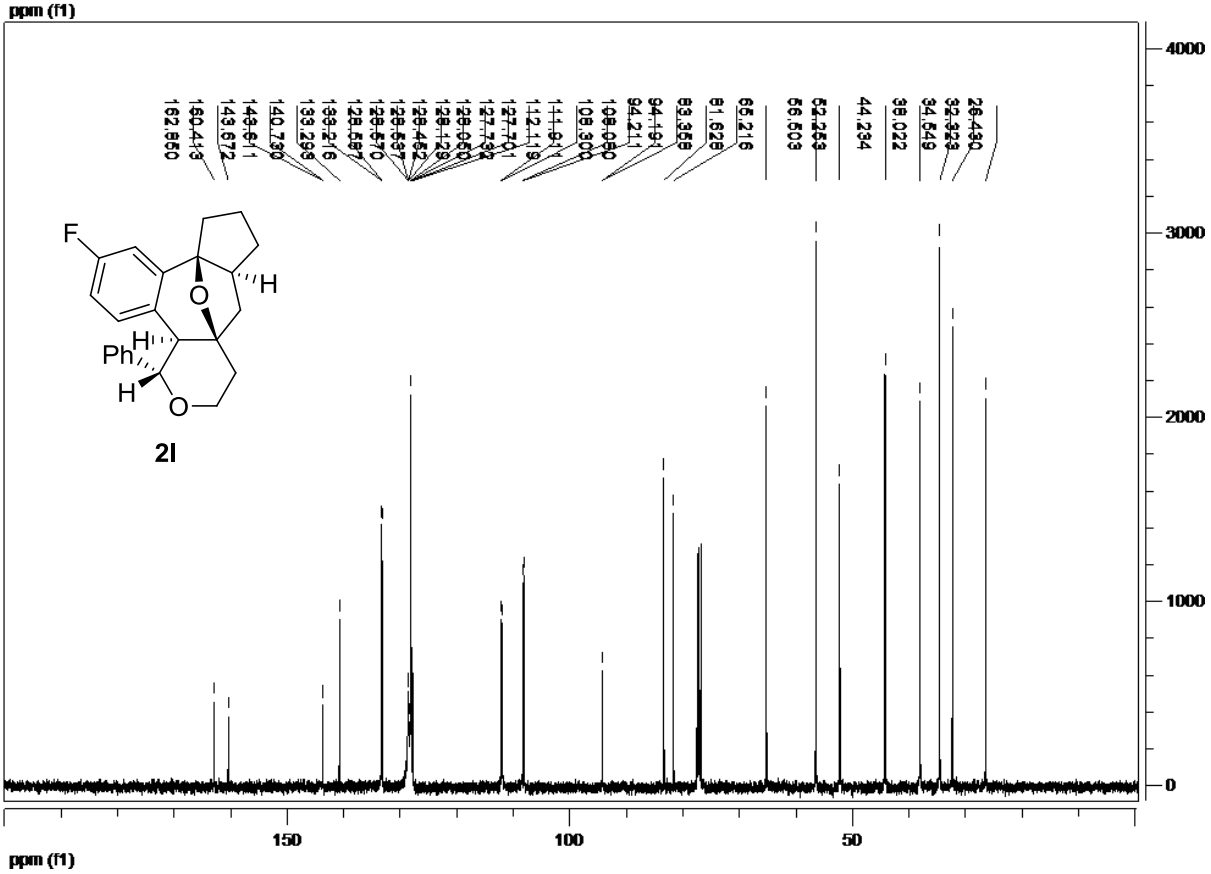


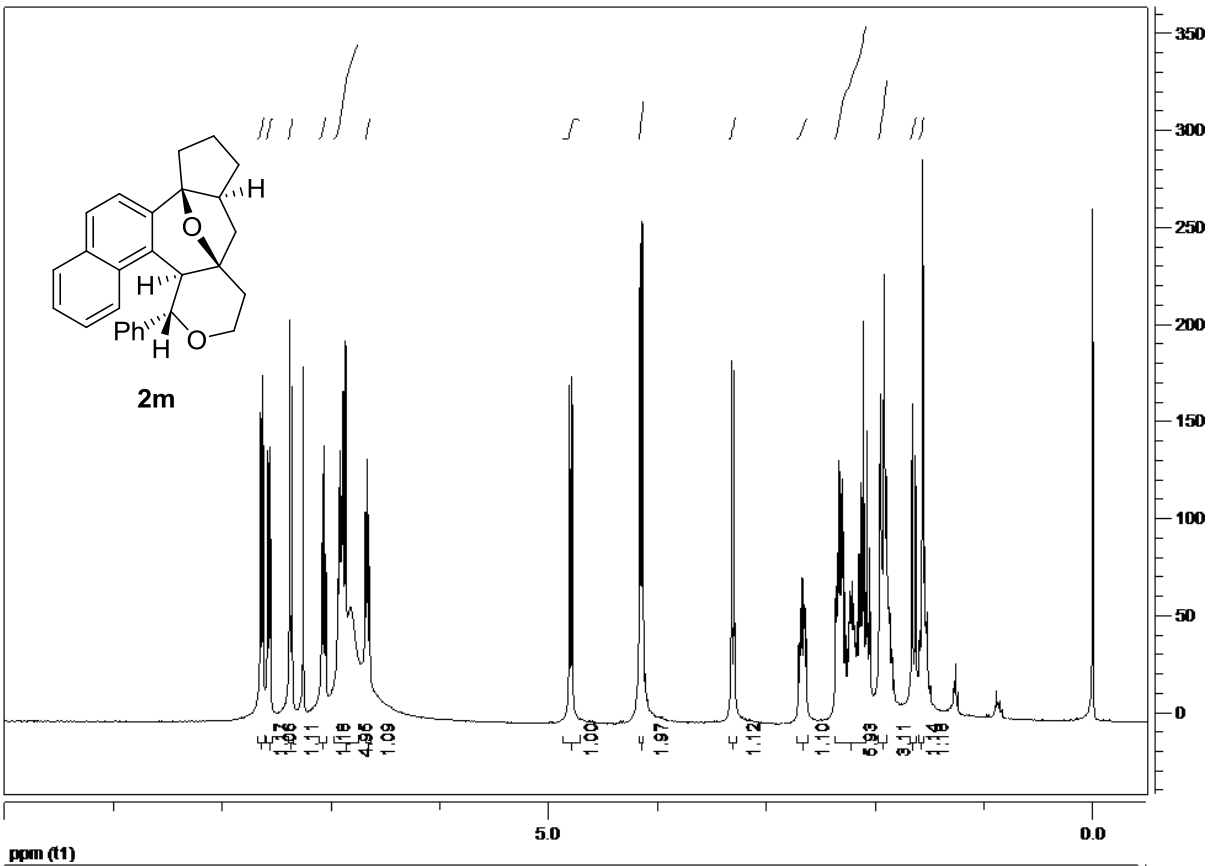


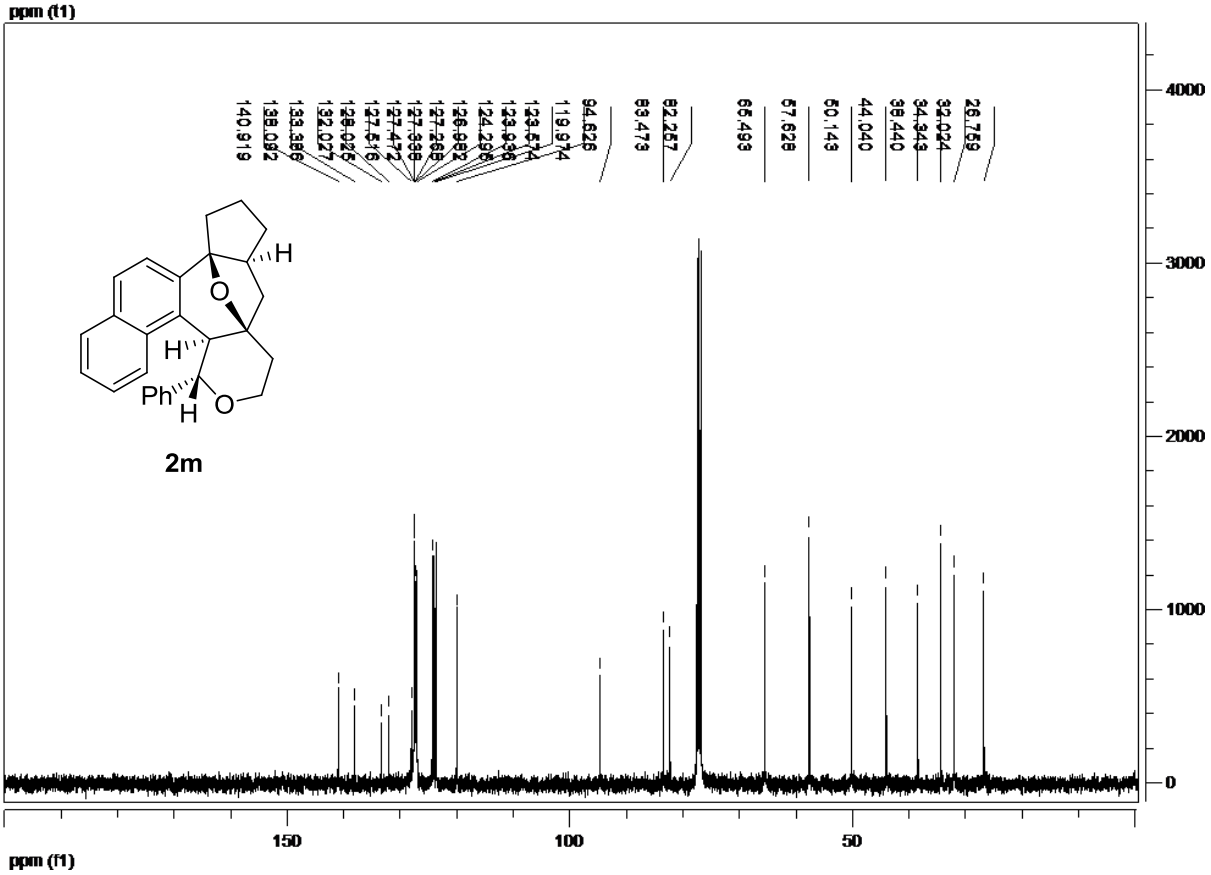


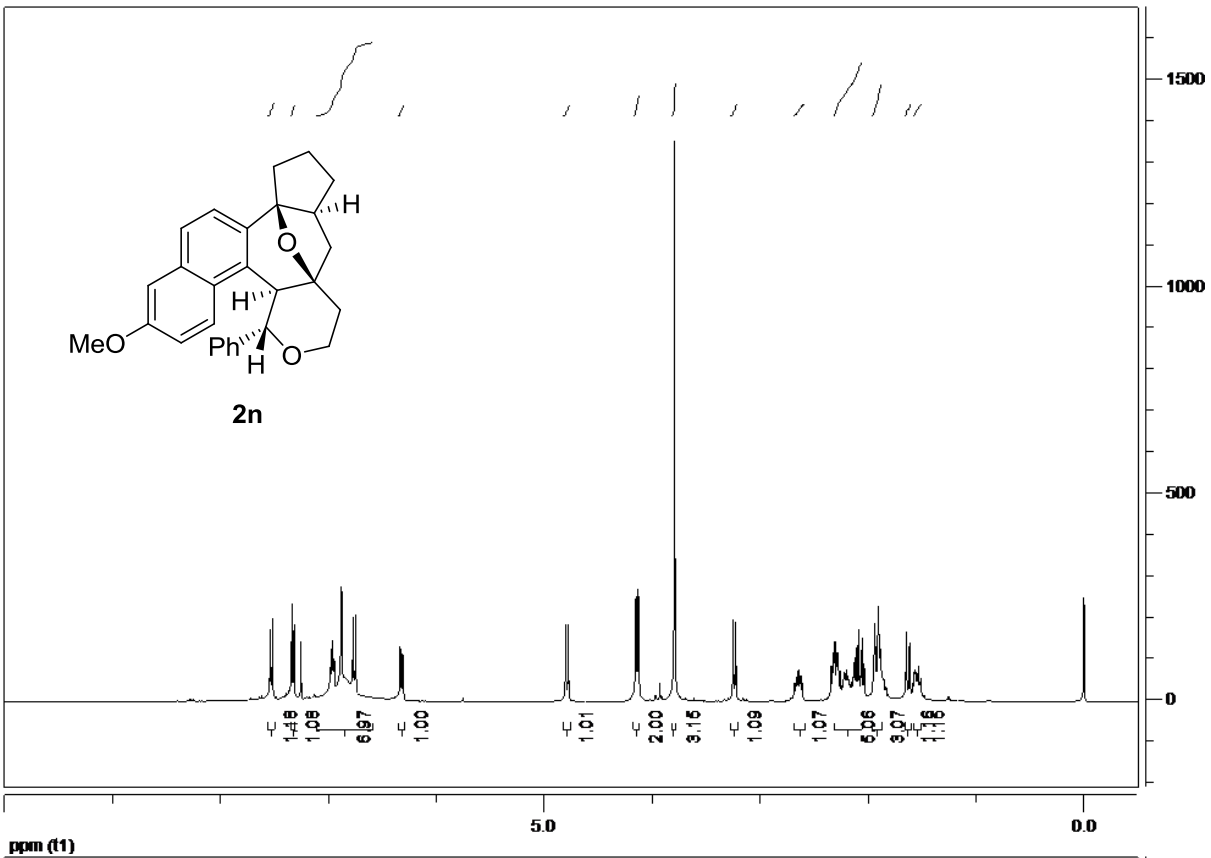


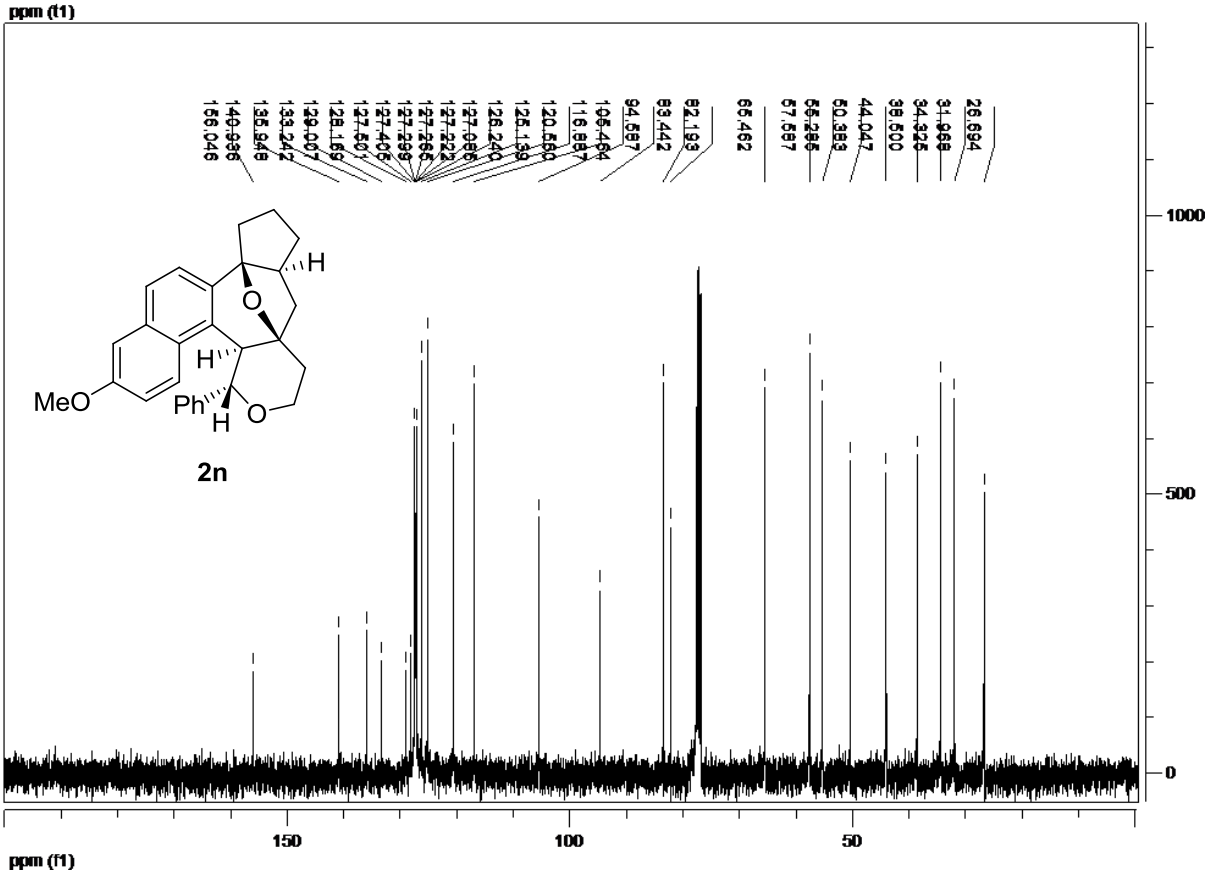


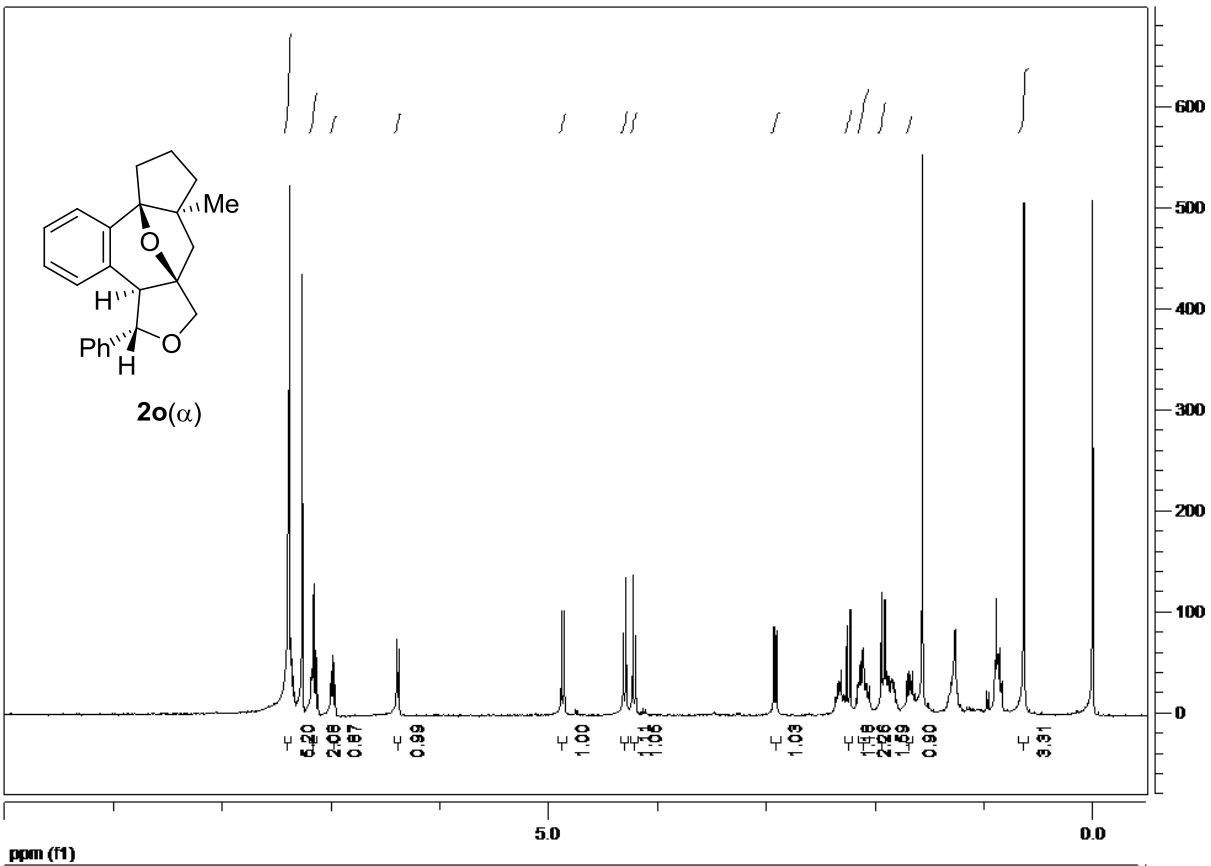


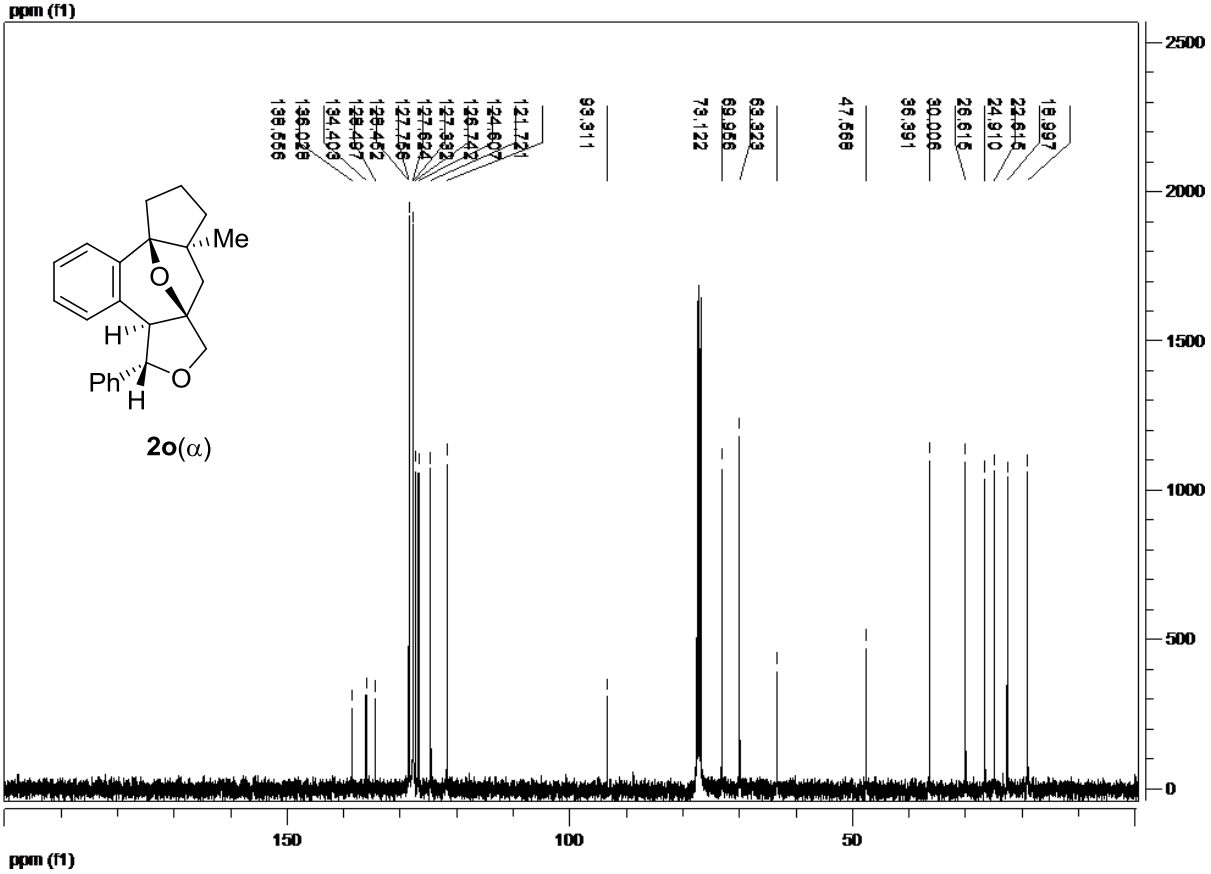


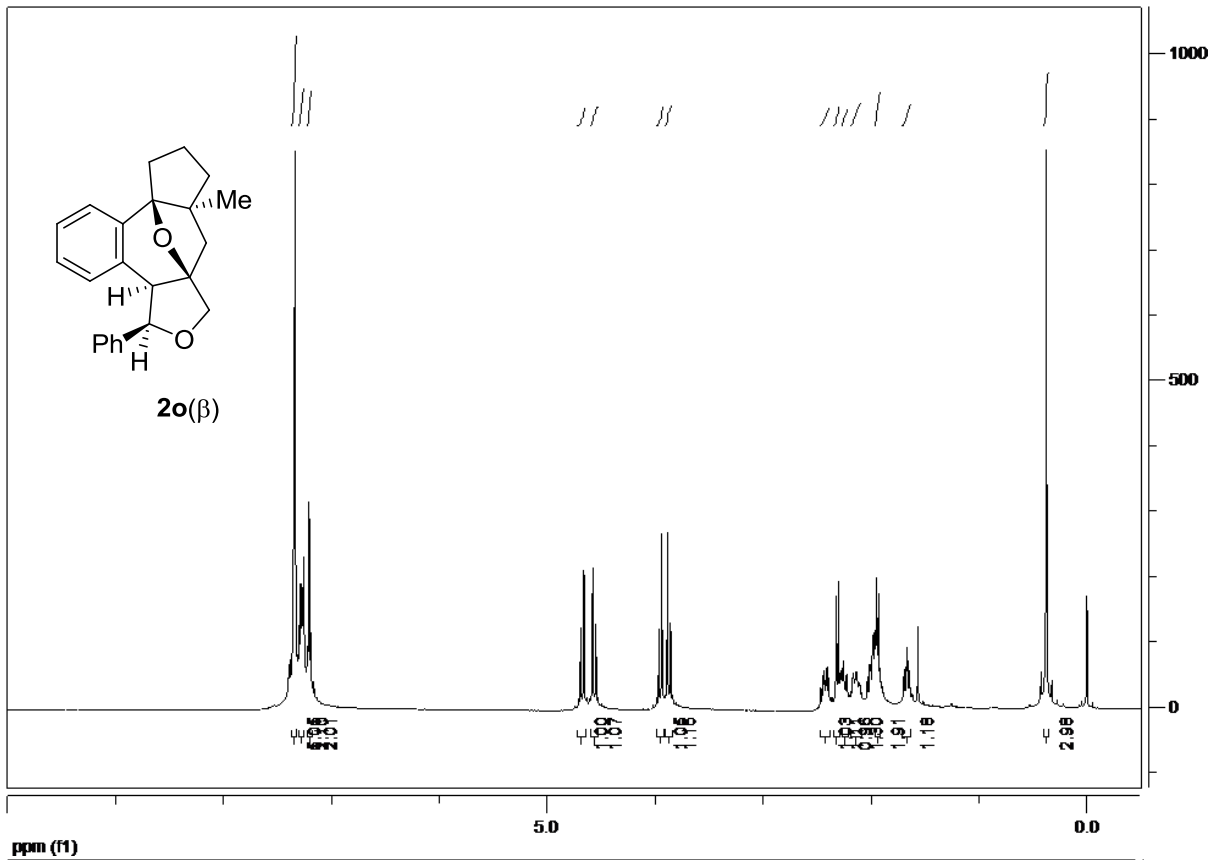




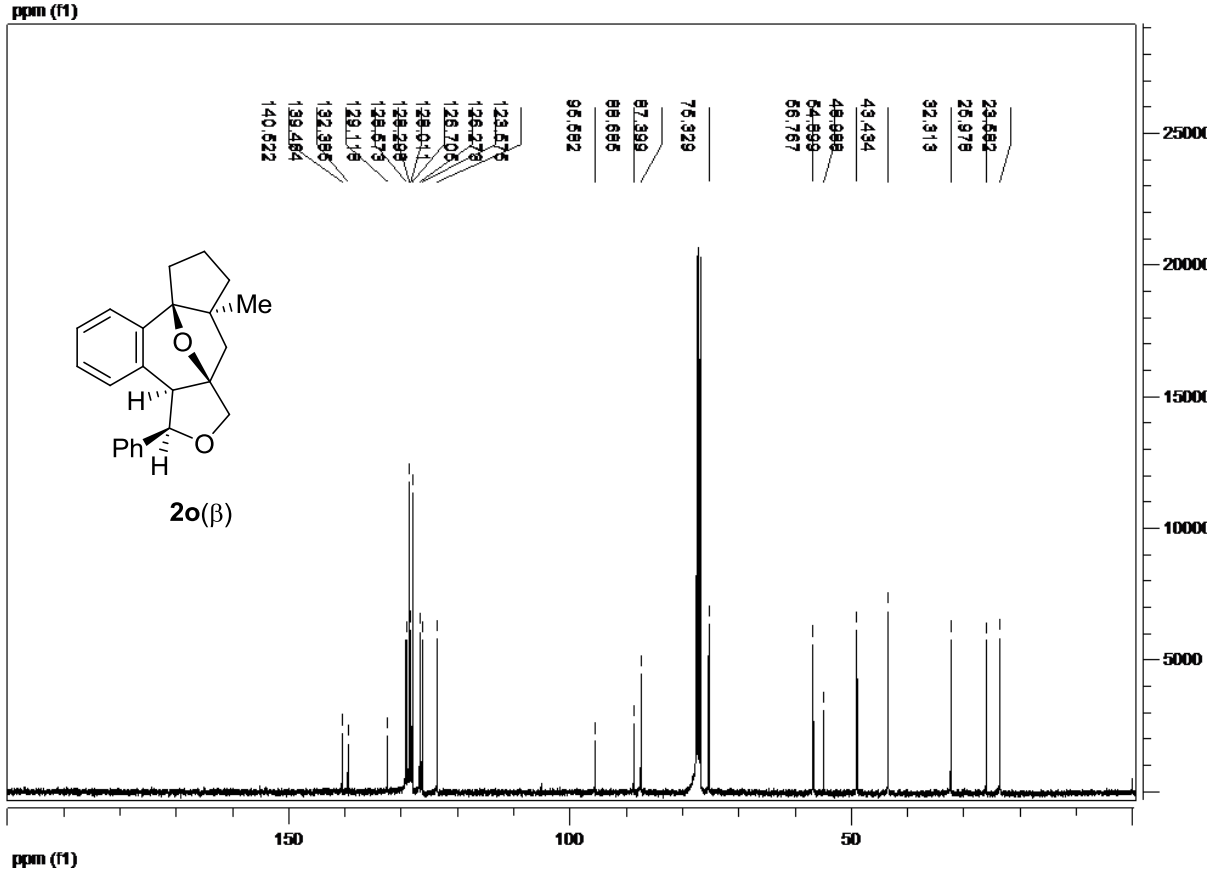








2o(β)



2o(β)