

Supporting Information

Regioselective Access of Dibenzo[*c,f*]oxocine Framework via Cyclocarbopalladation/Cross-Coupling Cascade Reactions and Reductive Heck Strategy

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Experimental:

General Information – Materials and Equipments:

Melting points were determined in open capillaries and are uncorrected. IR spectra were run for KBr discs (and neat for liquid samples) on AIM-8800 infrared microscope connected to a Shimadzu IR Affinity FT-IR spectrometer (ν_{\max} in cm^{-1}) and NMR spectra were recorded on a Bruker-Daltonics Avance-400 spectrometer operating at 400 MHz (^1H) or 100 MHz (^{13}C), with the residual protic solvent used as the internal standard. Elemental analysis experiments were performed at the Institute of Inorganic Chemistry at the University of Würzburg. Mass spectra were recorded on a Bruker Daltonics micOTOF focus instrument. Silica gel (60-120 mesh) and (230-400 mesh) were used for chromatographic separation. Petroleum-ether refers to the fraction between 60 °C and 80 °C.

General procedure for the preparation of compound **5a,b**:

Sodium hydride (230 mg, 9.6 mmol) was washed free of mineral oil (3 hexane washings) and treated with DMF (15 mL) followed by a solution of 2-iodobenzylalcohol (1.5 g, 6.4 mmol) in DMF (10 mL). After H_2 evolution had ceased, solid 2-bromobenzyl bromide (1.6 g, 6.4 mmol) was added and the reaction mixture was stirred at room temperature for 16 hours followed by stirring at 70 °C for 2 additional hours. The reaction mixture was cooled to room temperature, poured into 2N HCl (50 mL), and extracted with ether (3 x 30 mL). The combined organics were washed with brine (50 mL), dried over MgSO_4 , and concentrated under reduced pressure, and purified using flash column chromatography on silica gel (elution with 11% diethyl ether in hexanes) to give benzylic ether **5a** as a white crystalline solid. Compound **5b** was also prepared using the same procedure.

1-bromo-2-((2-iodobenzyloxy)methyl)benzene (**5a**):

Colorless gummy, Yield 88%, IR (KBr): 1588, 1576 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ_{H} = 7.84 (dd, 1H, J = 8.0, 1.2 Hz), 7.52-7.60 (m, 3H), 7.33-7.40 (m, 2H), 7.17 (dt, 1H, J = 7.6, 2.0 Hz), 7.01 (dt, 1H, J = 7.2, 1.6 Hz), 4.72 (s, 2H), 4.64 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 140.3, 139.2, 137.4, 132.5, 129.2, 129.1, 129.0, 128.8, 128.2, 127.4, 122.6, 97.7, 76.5, 72.0. MS (EI): m/z = 403 $[\text{M}+\text{H}]^+$. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{BrIO}$: C, 41.72; H, 3.00%. Found: C, 41.86; H, 3.09%.

1-bromo-2-((2-iodobenzyloxy)methyl)-4-methoxybenzene (**5b**):

Colorless gummy, Yield 88%, IR (KBr): 1583, 1567 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ_{H} = 7.84 (d, 1H, J = 7.6 Hz), 7.52 (d, 1H, J = 7.2 Hz), 7.35-7.44 (m, 2H), 7.17 (s, 1H), 7.01 (t, 1H, J = 7.6 Hz), 6.73 (d, 1H, J = 8.8 Hz), 4.67 (s, 2H), 4.64 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 159.0, 140.2,

139.2, 138.4, 133.0, 129.2, 128.8, 128.2, 114.6, 114.4, 112.6, 97.8, 76.5, 71.9, 55.5. MS (EI): $m/z = 433$ $[M+H]^+$. Anal. Calcd. for $C_{15}H_{14}BrIO_2$: C, 41.60; H, 3.26%. Found: C, 41.74; H, 3.33%.

General procedure for the preparation of starting materials 6a-i:

A mixture of compound **5a** (403 mg, 1 mmol), phenylacetylene (98 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 5 mol%), CuI (9.5 mg, 5 mol%) and dry Et_3N (2 ml) in dry DMF (5 ml) was stirred at room temperature for 4 h. After completion of the reaction as monitored by TLC, the reaction mixture was cooled and water (5 mL) was added and then extracted with $CHCl_3$ (3 x 15 mL). The organic extract was washed with water (2 x 10 mL) followed by brine (10 mL) and subsequently the organic layer was dried over $MgSO_4$. Further concentration furnished a crude mass which was purified by column chromatography over silica-gel. Elution of the column with petroleum ether-ethyl acetate (9:1) mixture afforded the product **6a**. Similarly other alkynes were treated with compounds **5a,b** to produce the corresponding substrates **6b-i**.

1-bromo-2-(((2-(phenylethynyl)benzyl)oxy)methyl)benzene (6a):

Brown gummy, yield = 82%, IR (KBr): 2230, 1585 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.49-7.60$ (m, 6H), 7.26-7.39 (m, 6H), 7.11-7.15 (m, 1H), 4.90 (s, 2H), 4.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_C = 139.8, 137.7, 132.4, 132.0, 131.5, 129.1, 128.8, 128.6, 128.4, 128.3, 127.7, 127.40, 127.38, 123.1, 122.6, 121.8, 93.9, 87.0, 72.0, 70.8$. MS (EI): $m/z = 377$ $[M+H]^+$. Anal. Calcd. for $C_{22}H_{17}BrO$: C, 70.04; H, 4.54%. Found: C, 70.11; H, 4.61%.

1-bromo-4-methoxy-2-(((2-(phenylethynyl)benzyl)oxy)methyl)benzene (6b):

Brown gummy, yield = 87%, IR (KBr): 3278, 2229, 1599 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.60$ (d, 1H, $J = 7.6$ Hz), 7.56 (d, 1H, $J = 7.6$ Hz), 7.50-7.52 (m, 2H), 7.29-7.42 (m, 6H), 7.17 (d, 1H, $J = 2.8$ Hz), 6.70 (dd, 1H, $J = 8.8, 3.2$ Hz), 4.92 (s, 2H), 4.70 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_C = 159.0, 139.7, 138.7, 132.9, 132.0, 131.5, 128.5, 128.34, 128.32, 127.7, 127.4, 123.1, 121.9, 114.7, 114.3, 112.6, 94.0, 87.0, 71.8, 70.9, 55.4$. MS (EI): $m/z = 407$ $[M+H]^+$. Anal. Calcd. for $C_{23}H_{19}BrO_2$: C, 67.82; H, 4.70%. Found: C, 67.85; H, 4.79%.

1-bromo-2-(((2-((4-methoxyphenyl)ethynyl)benzyl)oxy)methyl)benzene (6c):

Pale brown gummy, yield = 86%, IR (KBr): 3290, 2228, 1597 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.57-7.60$ (m, 2H), 7.52-7.55 (m, 2H), 7.44 (td, 2H, $J = 9.2, 2.4$ Hz), 7.35 (dt, 1H, $J = 7.6, 1.6$ Hz), 7.27-7.31 (m, 2H), 7.12-7.16 (m, 1H), 6.88 (td, 2H, $J = 8.8, 2.8$ Hz), 4.90 (s, 2H), 4.73 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_C = 159.7, 139.6, 137.7, 133.0, 132.4, 131.9, 129.1, 128.8, 128.2, 127.6, 127.40, 127.37, 122.6, 122.2, 115.3, 114.0, 94.0, 85.7, 72.0, 70.9, 55.3$. MS (EI): $m/z = 407$ $[M+H]^+$. Anal. Calcd. for $C_{23}H_{19}BrO_2$: C, 67.82; H, 4.70%. Found: C, 67.89; H, 4.77%.

1-bromo-4-methoxy-2-(((2-((4-methoxyphenyl)ethynyl)benzyl)oxy)methyl)benzene (6d):

White solid, yield = 86%, mp. 94-96 °C, IR (KBr): 3289, 2221, 1596 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.57 (dd, 1H, *J* = 7.6, 0.8 Hz), 7.52 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.39-7.47 (m, 3H), 7.35 (dt, 1H, *J* = 7.6, 1.2 Hz), 7.29 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.16 (d, 1H, *J* = 7.2 Hz), 6.87 (td, 2H, *J* = 9.2, 2.8 Hz), 6.69 (dd, 1H, *J* = 8.4, 3.2 Hz), 4.90 (s, 2H), 4.69 (s, 2H), 3.84 (s, 3H), 3.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_C = 159.7, 159.1, 139.5, 138.7, 134.0, 133.0, 132.9, 131.9, 128.2, 127.6, 127.4, 122.2, 115.2, 114.7, 114.2, 114.1, 114.0, 112.6, 94.0, 85.7, 71.8, 70.9, 55.4, 55.3. MS (EI): *m/z* = 437 [M+H]⁺. Anal. Calcd. for C₂₄H₂₁BrO₃: C, 65.91; H, 4.84%. Found: C, 65.89; H, 4.87%.

1-bromo-4-methoxy-2-((2-(pent-1-ynyl)benzyloxy)methyl)benzene (6e):

Brown gummy, yield = 80%, IR (KBr): 3288, 2989, 2933, 2230, 1599 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.54 (d, 1H, *J* = 7.6 Hz), 7.42 (d, 2H, *J* = 8.4 Hz), 7.31 (dt, 1H, *J* = 8.0, 1.2 Hz), 7.23 (dt, 1H, *J* = 7.6, 1.2 Hz), 7.17 (d, 1H, *J* = 3.2 Hz), 6.72 (dd, 1H, *J* = 8.8, 3.2 Hz), 4.82 (s, 2H), 4.66 (s, 2H), 3.80 (s, 3H), 2.42 (t, 2H, *J* = 7.2 Hz), 1.63 (sextet, 2H, *J* = 7.2 Hz), 1.05 (t, 3H, *J* = 7.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C = 159.1, 139.5, 138.8, 132.9, 132.0, 127.7, 127.4, 127.2, 122.6, 114.5, 114.3, 112.5, 95.1, 78.3, 71.7, 70.9, 55.4, 22.2, 21.5, 13.6. MS (EI): *m/z* = 373 [M+H]⁺. Anal. Calcd. for C₂₀H₂₁BrO: C, 64.35; H, 5.67%. Found: C, 64.44; H, 5.69%.

1-bromo-2-((2-(hept-1-ynyl)benzyloxy)methyl)benzene (6f):

Brown gummy, yield = 82%, IR (KBr): 2965, 2936, 2229, 1596 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.54-7.60 (m, 3H), 7.42 (d, 1H, *J* = 8.4 Hz), 7.29-7.38 (m, 2H), 7.23 (t, 1H, *J* = 7.6 Hz), 7.14-7.19 (m, 1H), 4.83 (s, 2H), 4.71 (s, 2H), 2.44 (t, 2H, *J* = 7.2 Hz), 1.61 (quint, 2H, *J* = 7.2 Hz), 1.32-1.49 (m, 4H), 0.93 (t, 3H, *J* = 7.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C = 139.6, 137.8, 132.4, 132.0, 128.9, 128.8, 127.7, 127.4, 127.3, 127.2, 122.6, 122.5, 95.3, 78.1, 71.9, 70.9, 31.1, 28.5, 22.2, 19.5, 14.0. MS (EI): *m/z* = 371 [M+H]⁺. Anal. Calcd. for C₂₁H₂₃BrO: C, 67.93; H, 6.24%. Found: C, 67.99; H, 6.40%.

1-bromo-2-((2-(hept-1-ynyl)benzyloxy)methyl)-4-methoxybenzene (6g):

Brown gummy, yield = 84%, IR (KBr): 2988, 2930, 2234, 1594 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.54 (d, 1H, *J* = 7.2 Hz), 7.42 (d, 2H, *J* = 8.4 Hz), 7.31 (dt, 1H, *J* = 7.6, 1.2 Hz), 7.23 (dt, 1H, *J* = 7.6, 1.2 Hz), 7.17 (d, 1H, *J* = 2.8 Hz), 6.72 (dd, 1H, *J* = 8.8, 3.2 Hz), 4.82 (s, 2H), 4.66 (s, 2H), 3.80 (s, 3H), 2.43 (t, 2H, *J* = 7.2 Hz), 1.61 (quint, 2H, *J* = 7.6 Hz), 1.31-1.48 (m, 4H), 0.93 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C = 159.1, 139.6, 138.8, 132.9, 132.0, 127.7, 127.4, 127.2, 122.7, 114.5, 114.2, 112.5, 95.3, 78.1, 71.8, 70.9, 55.4, 31.1, 28.4, 22.2, 19.5, 14.0. MS (EI): *m/z* = 401 [M+H]⁺. Anal. Calcd. for C₂₂H₂₅BrO₂: C, 65.84; H, 6.28%. Found: C, 65.91; H, 6.30%.

((2-((2-bromobenzyloxy)methyl)phenyl)ethynyl)trimethylsilane (6h):

Yellow gummy, yield = 78%, IR (KBr): 3281, 2219, 1598 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.53-7.58 (m, 3H), 7.48 (dd, 1H, *J* = 7.6, 1.2 Hz), 7.31-7.37 (m, 2H), 7.23 (dd, 1H, *J* = 7.6, 1.2 Hz), 7.15 (dt,

1H, $J = 7.6, 1.6$ Hz), 4.82 (s, 2H), 4.70 (s, 2H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): $\delta_{\text{C}} = 140.3, 137.7, 132.4, 132.3, 129.1, 128.8, 128.7, 127.5, 127.4, 127.2, 122.6, 121.7, 102.5, 99.1, 71.9, 70.7, -0.03$. MS (EI): $m/z = 373$ $[\text{M}+\text{H}]^+$. Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{BrOSi}$: C, 61.12; H, 5.67%. Found: C, 61.19; H, 5.73%.

((2-((2-bromo-5-methoxybenzyloxy)methyl)phenyl)ethynyl)trimethylsilane (6i):

Brown gummy, yield = 79%, IR (KBr): 3288, 2967, 2232, 1597 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.55$ (d, 1H, $J = 8.0$ Hz), 7.48 (d, 1H, $J = 7.6$ Hz), 7.42 (d, 1H, $J = 8.4$ Hz), 7.35 (t, 1H, $J = 7.6$ Hz), 7.23 (d, 1H, $J = 7.6$ Hz), 7.15 (d, 1H, $J = 2.8$ Hz), 6.71 (dd, 1H, $J = 8.8, 3.2$ Hz), 4.83 (s, 2H), 4.66 (s, 2H), 3.80 (s, 3H), 0.25 (s, 9H), 0.93 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3): $\delta_{\text{C}} = 159.1, 140.2, 138.7, 132.9, 132.3, 128.7, 127.4, 127.2, 121.7, 114.6, 114.3, 112.6, 102.5, 99.2, 71.9, 70.7, 55.4, -0.06$. MS (EI): $m/z = 403$ $[\text{M}+\text{H}]^+$. Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{BrOSi}$: C, 59.55; H, 5.75%. Found: C, 59.59; H, 5.83%.

General procedure for the cyclocarbopalladation of compounds 6a-d to afford dibenzo[*c,f*]oxocines 7a-g:

$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (6.2 mg, 3 mol%), xantphos (13.9 mg, 4 equiv. to Pd), organoboron reagent (0.3 mmol), and substrate **6** (0.2 mmol) were dissolved in DMF (2 mL). Then K_3PO_4 (85 mg, 0.4 mmol) was added followed by distilled water (0.4 mL) and allowed to continuous heating at 80 °C. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled and then diluted with EtOAc (40 mL), washed with water (2 x 40 mL), dried over MgSO_4 and concentrated under reduced pressure. The resulted crude material was subjected to purification via column chromatography or other suitable purification procedure.

12-(diphenylmethylene)-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (7a):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **7a**. Yellow solid, yield = 92%, mp. 102-104 °C, IR (KBr): 2965, 2925, 1614, 1527 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.14$ -7.17 (m, 6H), 7.01-7.11 (m, 10H), 6.97 (d, 2H, $J = 7.2$ Hz), 4.83 (bs, 2H), 4.57 (bs, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta_{\text{C}} = 142.1, 140.8, 139.4, 137.8, 131.0, 130.4, 127.3, 127.0, 126.3, 126.1, 71.7$. HRMS (ESI $[\text{M}+\text{Na}]^+$): for $\text{C}_{28}\text{H}_{22}\text{O}$ calcd 397.1568; found 397.1564.

12-(diphenylmethylene)-3-methoxy-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (7b):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent followed by recrystallization/washing with diethyl ether to deliver pure **7b**. White solid, yield = 92%, mp. 194-196 °C, IR (KBr): 2955, 2933, 1611, 1525 cm^{-1} , ^1H NMR (400 MHz,

CDCl₃): δ_{H} = 7.12-7.16 (m, 5H), 7.00-7.11 (m, 9H), 6.96 (d, 1H, J = 7.6 Hz), 6.62 (dd, 1H, J = 8.4, 2.8 Hz), 6.51 (d, 1H, J = 2.4 Hz), 4.72 (bs, 2H), 4.60 (bs, 2H), 3.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_{C} = 157.8, 142.32, 142.27, 140.4, 139.8, 139.2, 137.5, 131.9, 130.9, 130.4, 129.3, 128.0, 127.4, 127.3, 127.2, 127.1, 126.2, 126.02, 125.97, 112.5, 112.4, 71.8, 71.6, 55.1. HRMS (ESI [M+Na]⁺): for C₂₉H₂₄O₂ calcd 427.1674; found 427.1672.

12-((4-methoxyphenyl)(phenyl)methylene)-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (7c):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **7c**. Brown gummy, yield = 94%, IR (KBr): 2939, 2929, 1622, 1533 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.28-7.34 (m, 3H), 7.14-7.16 (m, 4H), 7.03-7.10 (m, 7H), 6.92 (dd, 1H, J = 6.4, 2.0 Hz), 6.61 (td, 2H, J = 4.8, 2.8 Hz), 4.85 (bs, 2H), 4.55 (bs, 2H), 3.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_{C} = 157.7, 142.5, 141.4, 140.0, 139.7, 137.84, 137.76, 136.9, 135.5, 134.6, 133.2, 131.6, 131.0, 130.5, 130.3, 130.0, 129.4, 127.6, 127.3, 127.2, 127.12, 127.05, 126.2, 126.0, 113.5, 112.7, 71.7, 71.5, 55.0. HRMS (ESI [M+Na]⁺): for C₂₉H₂₄O₂ calcd 427.1674; found 427.1671.

(*E*)-3-methoxy-12-((4-methoxyphenyl)(phenyl)methylene)-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (7d):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **7d**. Yellow gummy, yield = 90%, IR (KBr): 2948, 2923, 1611, 1529 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.11-7.14 (m, 3H), 6.99-7.09 (m, 8H), 6.95 (d, 1H, J = 7.6 Hz), 6.60-6.66 (m, 3H), 6.53 (d, 1H, J = 2.0 Hz), 4.74 (bs, 2H), 4.56 (bs, 2H), 3.72 (s, 3H), 3.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_{C} = 157.7, 157.6, 142.6, 140.0, 139.6, 139.2, 137.5, 137.1, 134.8, 132.3, 131.9, 131.6, 131.0, 130.4, 127.3, 127.2, 126.1, 126.0, 112.8, 112.6, 112.4, 71.9, 71.5, 55.1, 55.0. HRMS (ESI [M+Na]⁺): for C₃₀H₂₆O₃ calcd 457.1780; found 457.1756.

(*Z*)-3-methoxy-12-((4-methoxyphenyl)(phenyl)methylene)-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (7e):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **7e**. Off white gummy, yield = 92%, IR (KBr): 2949, 2922, 1612, 1525 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.02-7.16 (m, 11H), 6.98 (d, 1H, J = 7.6 Hz), 6.59-6.63 (m, 3H), 6.50 (d, 1H, J = 2.4 Hz), 4.76 (bs, 2H), 4.53 (bs, 2H), 3.70 (s, 3H), 3.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_{C} = 157.68, 157.65, 142.7, 140.1, 139.2, 137.5, 137.1, 134.7, 132.2, 132.0, 131.6, 130.9, 130.5, 127.33, 127.27, 127.1, 126.1, 126.0, 125.9, 112.8, 112.7, 112.5, 77.2, 71.7, 55.1, 55.0. HRMS (ESI [M+Na]⁺): for C₃₀H₂₆O₃ calcd 457.1780; found 457.1755.

12-(bis(4-methoxyphenyl)methylene)-3-methoxy-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (7f):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **7f**. Brown gummy, yield = 88%, IR (KBr): 2958, 2923, 1614, 1532 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.07-7.14 (m, 2H), 7.01-7.05 (m, 6H), 6.96 (d, 1H, J = 7.6 Hz), 6.59-6.65 (m, 5H), 6.52 (d, 1H, J = 2.0 Hz), 4.77 (bs, 2H), 4.52 (bs, 2H), 3.71 (s, 6H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} = 157.60, 157.57, 140.3, 139.2, 138.9, 137.5, 136.6, 135.1, 135.0, 132.5, 132.0, 131.6, 131.0, 127.3, 127.1, 126.0, 112.70, 112.65, 112.6, 112.4, 71.7, 71.5, 55.1, 54.98, 54.96. HRMS (ESI $[\text{M}+\text{Na}]^+$): for $\text{C}_{31}\text{H}_{28}\text{O}_4$ calcd 487.1885; found 487.1885.

(Z)-3-methoxy-12-((4-methoxyphenyl)(4-nitrophenyl)methylene)-7,12-dihydro-5H-dibenzo[c,f]oxocine (7g):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **7g**. Yellow gummy, yield = 76%, IR (KBr): 2954, 2931, 1630, 1535 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.94 (td, 2H, J = 8.8, 2.4 Hz), 7.29-7.32 (m, 2H), 7.14-7.16 (m, 2H), 7.05-7.07 (m, 2H), 6.97-7.01 (m, 4H), 6.62 (td, 2H, J = 8.8, 3.2 Hz), 6.52 (d, 1H, J = 2.4 Hz), 4.80 (bs, 2H), 4.49 (bs, 2H), 3.71 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} = 159.8, 158.2, 158.1, 150.0, 145.7, 142.7, 139.6, 138.9, 137.1, 135.2, 133.3, 131.6, 131.5, 131.3, 131.0, 130.6, 130.1, 127.5, 127.3, 126.6, 123.3, 122.73, 122.67, 113.10, 113.05, 112.5, 72.1, 71.1, 55.1, 55.0. HRMS (ESI $[\text{M}]^+$): for $\text{C}_{30}\text{H}_{25}\text{NO}_5$ calcd 479.1733; found 479.1710.

General procedure for the reductive Heck cyclization of substrates 6a-i into dibenzo[c,f]oxocines 8a-i:

Substrates **6** (0.2 mmol) was dissolved in DMF (2mL) followed by addition of $\text{Pd}(\text{PPh}_3)_4$ (4.6 mg, 0.004 mmol), HCOONa (40.8 mg, 0.6 mmol) and distilled water (0.4 mL) and heated at under continuous stirring at 100 °C for 3-4h. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was diluted with EtOAc (40 mL), washed with water (2 x 40 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with petroleum ether - EtOAc (19:1) as eluent to give pure **8**.

12-benzylidene-7,12-dihydro-5H-dibenzo[c,f]oxocine (8a):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8a**. Off white solid, yield = 82%, mp. 134-136 °C, IR (KBr): 2861, 1623, 1602 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.47 (d, 1H, J = 7.2 Hz), 7.19-7.34 (m, 5H), 7.05-7.15 (m, 5H), 6.94-6.96 (m, 2H), 6.64 (s, 1H), 4.87 (s, 2H), 4.75 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} = 144.6, 142.1, 138.3, 137.4, 136.9, 129.9, 129.1, 128.9, 128.6, 128.3, 128.1, 127.9, 127.4, 127.0, 126.7, 73.0, 70.3. HRMS (ESI $[\text{M}+\text{Na}]^+$): for $\text{C}_{22}\text{H}_{18}\text{O}$ calcd 321.1255; found 321.1245.

(Z)-12-benzylidene-3-methoxy-7,12-dihydro-5H-dibenzo[c,f]oxocine (8b):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent followed by recrystallization/washing with diethyl ether to deliver pure **8b**. Off white solid, yield = 86%, mp. 176-178 °C, IR (KBr): 2954, 2925, 1604 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.38 (d, 1H, *J* = 8.4 Hz), 7.21-7.28 (m, 3H), 7.07-7.11 (m, 4H), 6.90-6.92 (m, 2H), 6.83 (dd, 1H, *J* = 8.4, 2.8 Hz), 6.59 (s, 2H), 4.85 (s, 2H), 4.68 (s, 2H), 3.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_C = 158.5, 144.1, 139.7, 137.9, 137.2, 137.0, 134.8, 130.1, 129.8, 128.9, 128.6, 128.4, 128.1, 127.8, 127.3, 126.6, 112.7, 112.4, 73.1, 70.3, 55.3. HRMS (ESI [M+Na]⁺): for C₂₃H₂₀O₂ calcd 351.1361; found 351.1359.

12-(4-methoxybenzylidene)-7,12-dihydro-5H-dibenzo[c,f]oxocine (8c):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8c**. Pale yellow gummy, yield = 84%, IR (KBr): 2962, 2932, 1601 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.46 (d, 1H, *J* = 7.2 Hz), 7.23-7.32 (m, 4H), 7.16-7.21 (m, 2H), 7.04-7.07 (m, 1H), 6.86 (d, 2H, *J* = 8.8 Hz), 6.66 (td, 2H, *J* = 8.8, 2.8 Hz), 6.58 (s, 1H), 4.86 (s, 2H), 4.73 (s, 2H), 3.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_C = 158.3, 144.2, 138.2, 137.5, 133.0, 131.2, 130.7, 129.8, 129.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.1, 126.9, 126.2, 113.6, 73.0, 70.3, 55.1. HRMS (ESI [M+Na]⁺): for C₂₃H₂₀O₂ calcd 351.1361; found 351.1358.

(Z)-3-methoxy-12-(4-methoxybenzylidene)-7,12-dihydro-5H-dibenzo[c,f]oxocine (8d):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent followed by recrystallization/washing with diethyl ether to deliver pure **8d**. Brown solid, yield = 81%, mp. 164-166 °C, IR (KBr): 2944, 2945, 1605 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.39 (d, 1H, *J* = 8.4 Hz), 7.27-7.30 (m, 2H), 7.23-7.25 (m, 1H), 7.13-7.14 (m, 1H), 6.82-6.85 (m, 3H), 6.65 (td, 2H, *J* = 8.8, 2.8 Hz), 6.60 (s, 1H), 6.55 (s, 1H), 4.86 (s, 2H), 4.68 (s, 2H), 3.78 (s, 3H), 3.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ_C = 158.4, 158.2, 141.8, 139.6, 138.0, 137.2, 130.1, 129.7, 129.0, 128.2, 127.6, 127.2, 113.6, 112.7, 73.0, 70.2, 55.3, 55.1. HRMS (ESI [M+Na]⁺): for C₂₄H₂₂O₃ calcd 381.1467; found 381.1465.

(Z)-12-butylidene-3-methoxy-7,12-dihydro-5H-dibenzo[c,f]oxocine (8e):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8e**. Pale yellow gummy, yield = 80%, IR (KBr): 2931, 1600 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.16-7.29 (m, 4H), 7.06 (d, 1H, *J* = 7.2 Hz), 6.78 (dd, 1H, *J* = 8.4, 2.4 Hz), 6.57 (s, 1H), 5.69 (t, 1H, *J* = 7.2 Hz), 4.85 (s, 2H), 4.62 (s, 2H), 3.76 (s, 3H), 1.86 (q, 2H, *J* = 7.6 Hz), 1.42 (sextet, 2H, *J* = 7.6 Hz), 0.89 (t, 3H, *J* = 7.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C = 158.3,

142.8, 138.9, 137.0, 130.4, 130.1, 129.4, 128.6, 128.2, 127.9, 126.8, 112.6, 73.1, 70.0, 55.3, 31.0, 22.8, 13.9. HRMS (ESI [M+H]⁺): for C₂₀H₂₂O₂ calcd 295.1698; found 295.1692.

12-hexylidene-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (8f):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8f**. Pale yellow gummy, yield = 80%, IR (KBr): 2928, 1602 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.27-7.35 (m, 2H), 7.20-7.25 (m, 2H), 7.13-7.19 (m, 2H), 7.08 (d, 1H, *J* = 7.2 Hz), 7.01 (d, 1H, *J* = 8.4 Hz), 5.73 (t, 1H, *J* = 7.2 Hz), 4.86 (s, 2H), 4.66 (s, 2H), 1.88 (q, 2H, *J* = 7.6 Hz), 1.36-1.44 (m, 2H), 1.23-1.28 (m, 4H), 0.86 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C = 137.6, 137.2, 130.8, 130.2, 129.4, 129.3, 128.5, 128.3, 128.2, 127.8, 127.6, 126.9, 126.6, 72.3, 69.7, 53.4, 31.5, 29.3, 28.9, 22.5, 14.0. HRMS (ESI [M+Na]⁺): for C₂₁H₂₄O calcd 315.1725; found 315.1718.

(*Z*)-12-hexylidene-3-methoxy-7,12-dihydro-5H-dibenzo[*c,f*]oxocine (8g):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8g**. Off white gummy, yield = 82%, IR (KBr): 2932, 1604 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.16-7.30 (m, 4H), 7.07 (d, 1H, *J* = 7.2 Hz), 6.79 (dd, 1H, *J* = 8.4, 2.4 Hz), 6.57 (s, 1H), 5.70 (t, 1H, *J* = 7.6 Hz), 4.86 (s, 2H), 4.63 (s, 2H), 3.76 (s, 3H), 1.88 (q, 2H, *J* = 7.6 Hz), 1.40 (quint, 2H, *J* = 7.2 Hz), 1.26 (sextet, 4H, *J* = 3.6 Hz), 0.86 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C = 158.2, 142.5, 138.9, 137.0, 134.6, 130.4, 130.0, 129.6, 128.2, 127.8, 126.8, 112.5, 73.2, 69.9, 55.2, 31.5, 29.3, 28.9, 22.5, 14.0. HRMS (ESI [M+Na]⁺): for C₂₂H₂₆O₂ calcd 345.1830; found 345.1815.

((5H-dibenzo[*c,f*]oxocin-12(7H)-ylidene)methyl)trimethylsilane (8h):

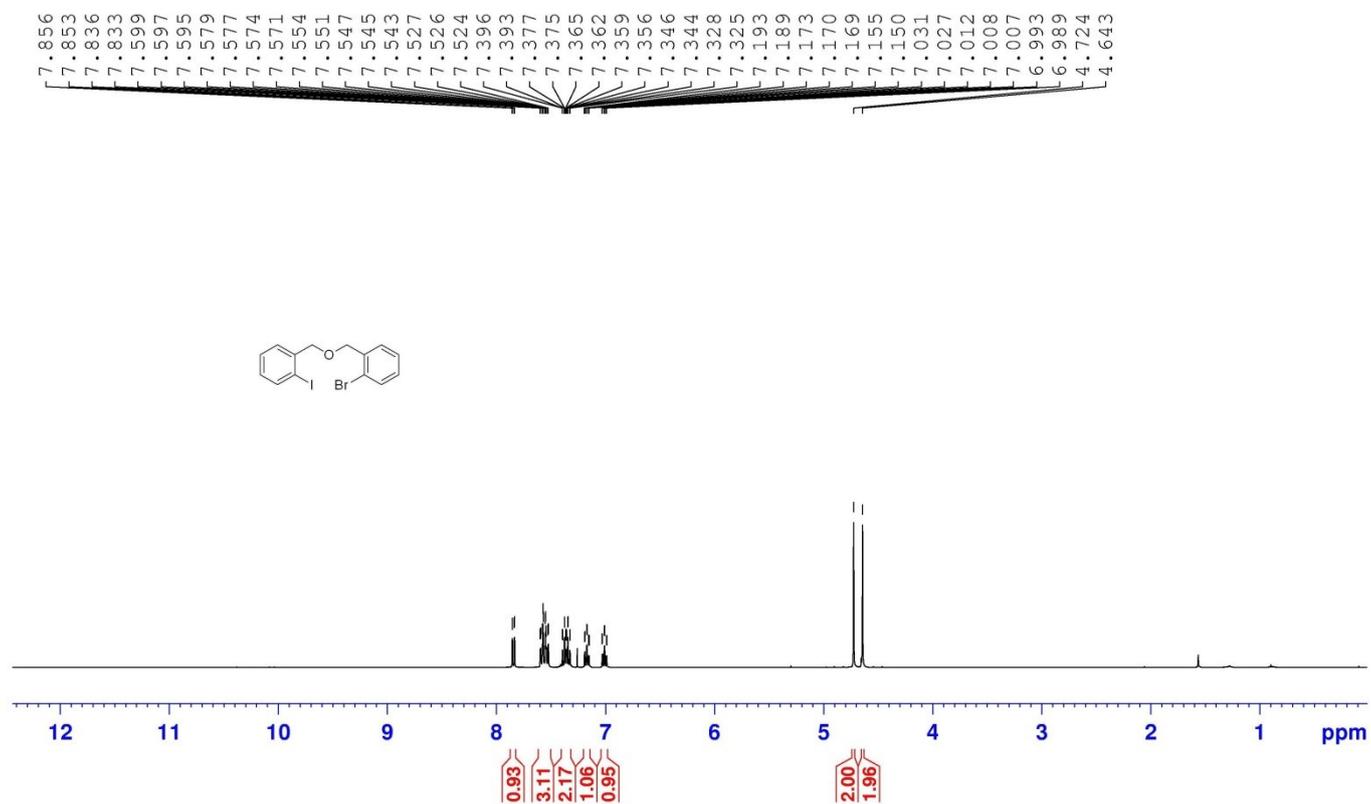
The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8h**. Pale yellow gummy, yield = 74%, IR (KBr): 2955, 2932, 1601 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.50-7.56 (m, 2H), 7.39-7.43 (m, 3H), 7.31 (dt, 2H, *J* = 7.6, 1.6 Hz), 7.14 (d, 1H, *J* = 7.2 Hz), 6.09 (s, 1H), 5.07 (s, 2H), 4.83 (s, 2H), 0.00 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ_C = 160.1, 137.2, 130.4, 129.3, 128.40, 128.35, 128.2, 127.83, 127.79, 127.6, 127.3, 127.0, 126.3, 73.5, 70.1, -0.44. HRMS (ESI [M+Na]⁺): for C₁₉H₂₂OSi calcd 317.1338; found 317.1333.

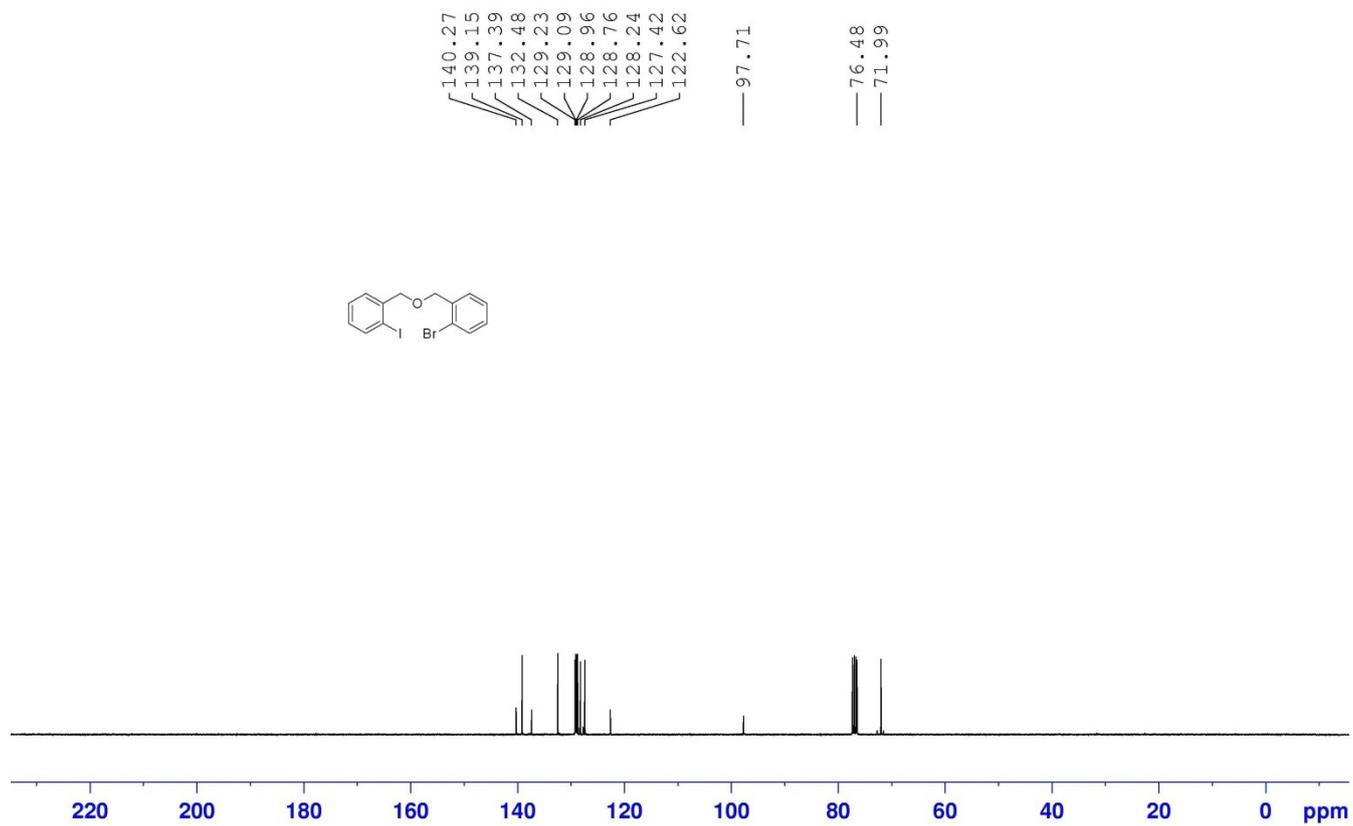
(*Z*)-((3-methoxy-5H-dibenzo[*c,f*]oxocin-12(7H)-ylidene)methyl)trimethylsilane (8i):

The material obtained after workup was subjected to column chromatography on silica gel with petroleum ether/EtOAc (19:1) as eluent to deliver pure **8i**. Pale yellow gummy, yield = 77%, IR (KBr): 2949, 2927, 1605 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ_H = 7.35 (d, 1H, *J* = 8.4 Hz), 7.23-7.29 (m, 2H), 7.14-7.17 (m, 1H), 7.09-7.12 (m, 1H), 6.81 (dd, 1H, *J* = 8.4, 2.8 Hz), 6.55 (s, 1H), 5.91 (s, 1H), 4.93 (s, 2H), 4.64 (s, 2H), 3.78 (s, 3H), -0.15 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ_C = 159.7, 158.5, 138.4, 136.9, 130.4,

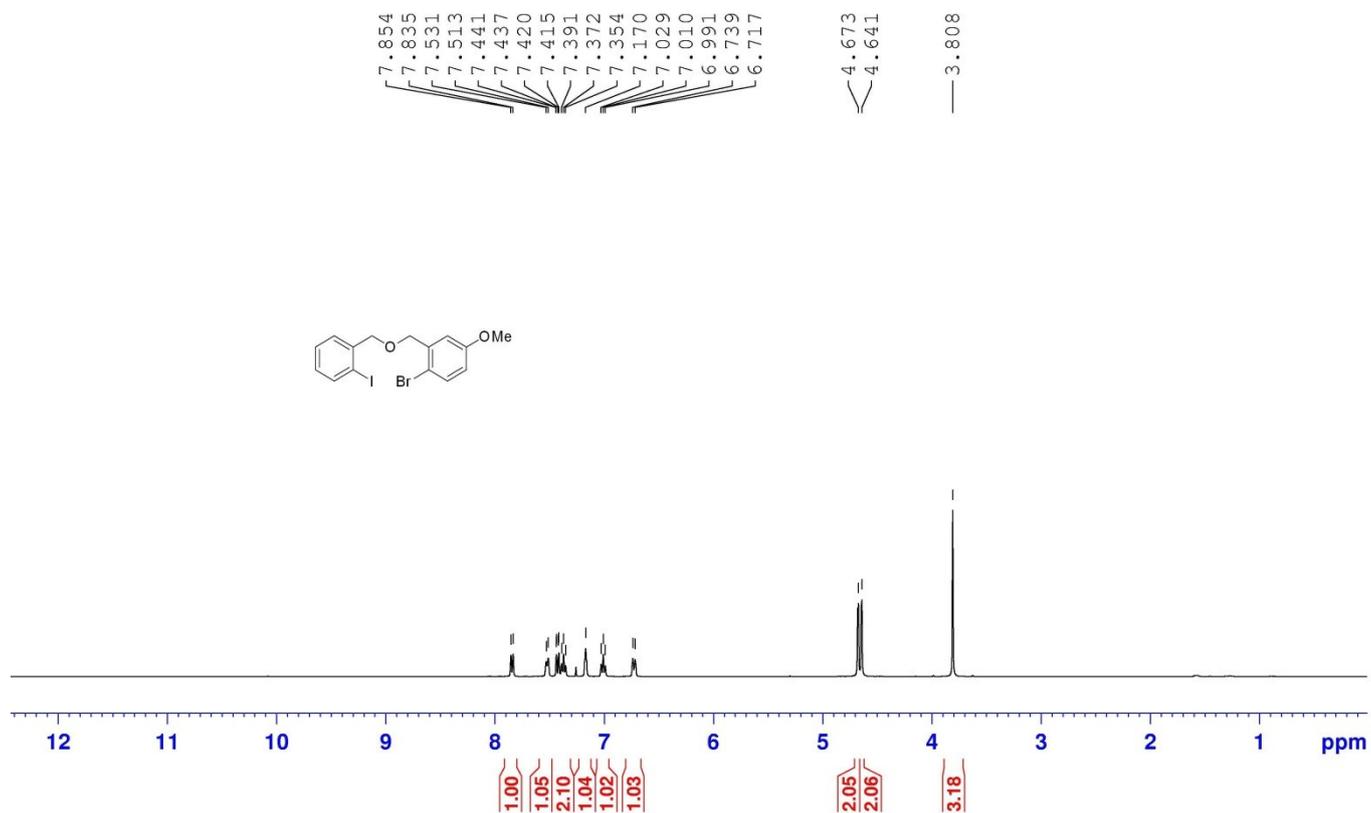
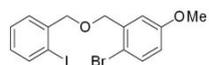
129.6, 129.4, 127.8, 127.4, 127.1, 126.8, 112.8, 112.6, 111.9, 73.5, 69.9, 55.3, -0.42. HRMS (ESI [M+Na]⁺): for C₂₀H₂₄O₂Si calcd 347.1443; found 347.1433.

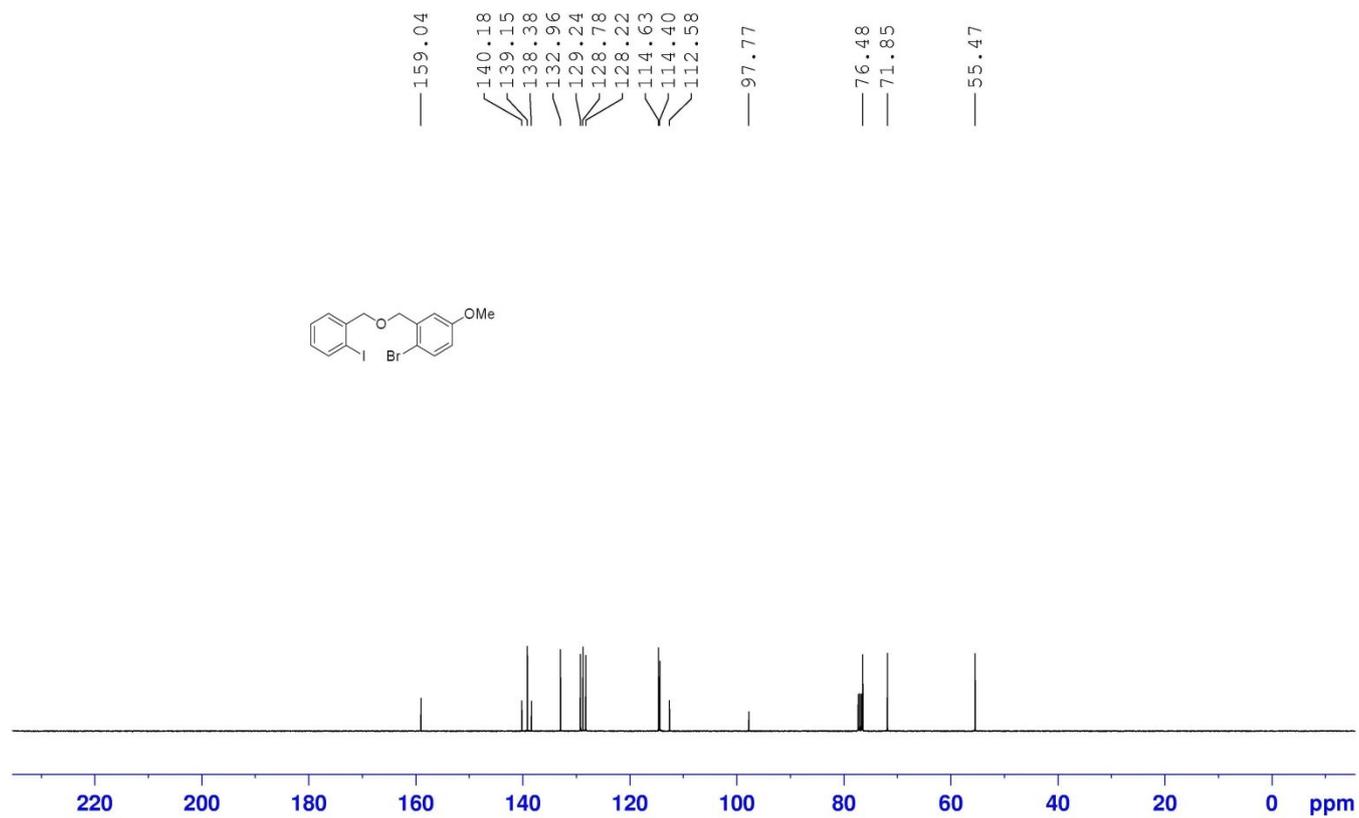
¹H and ¹³C spectra of compound 5a:



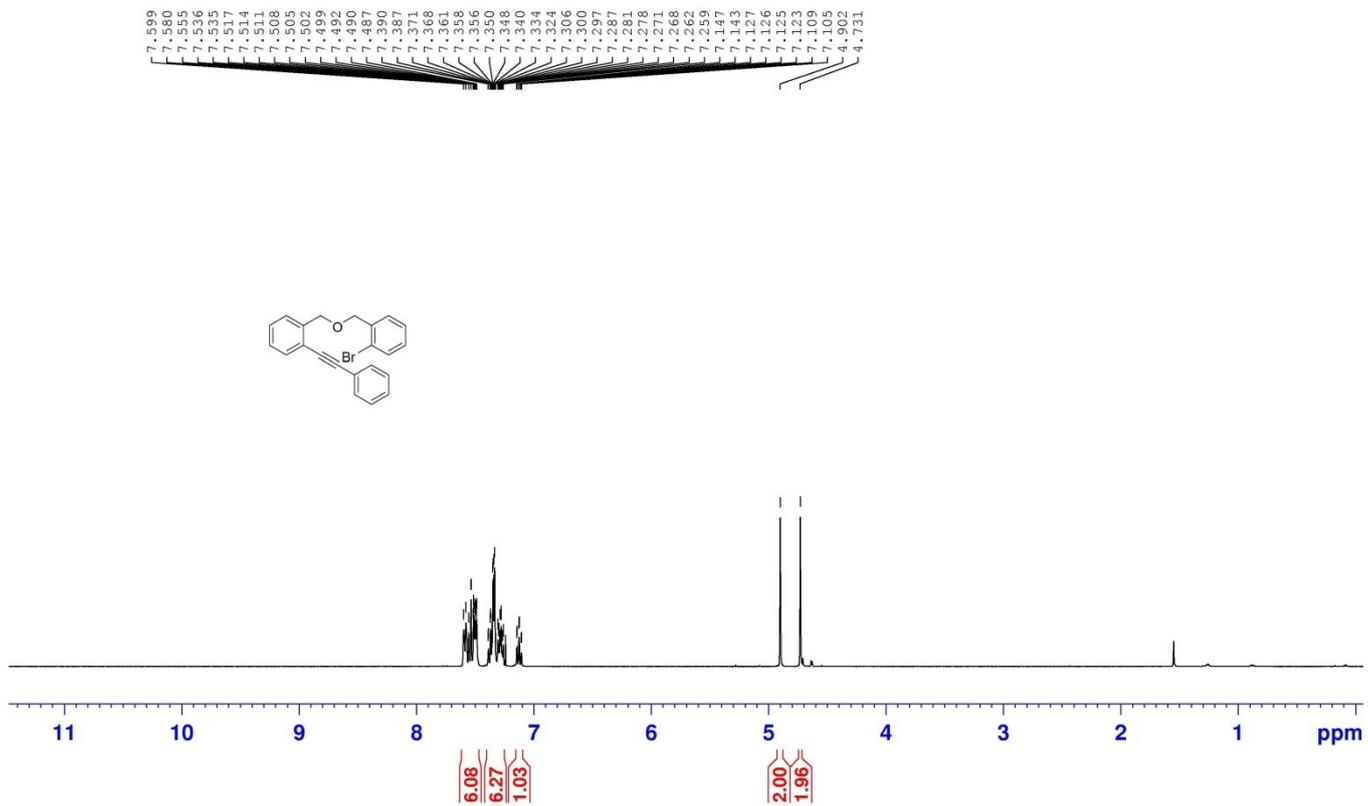


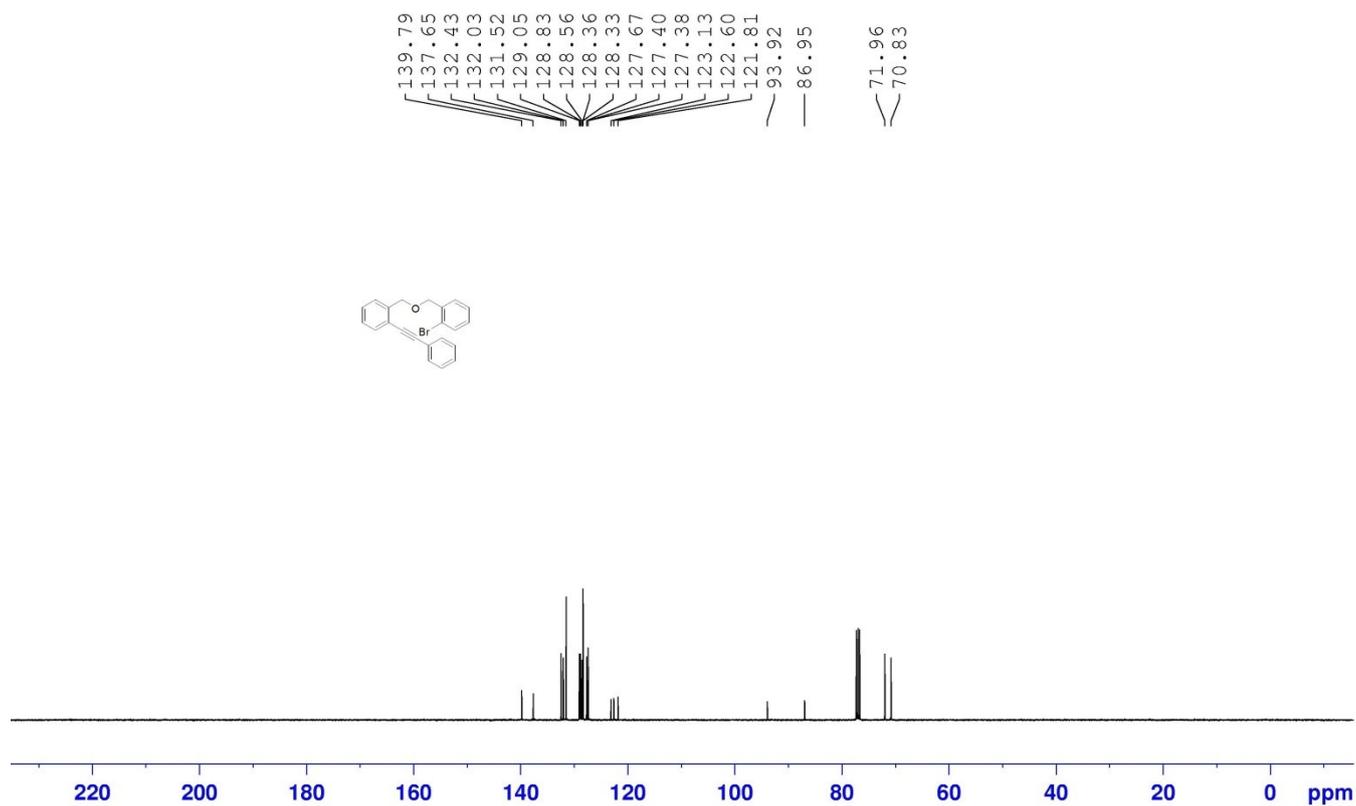
^1H and ^{13}C spectra of compound 5b:



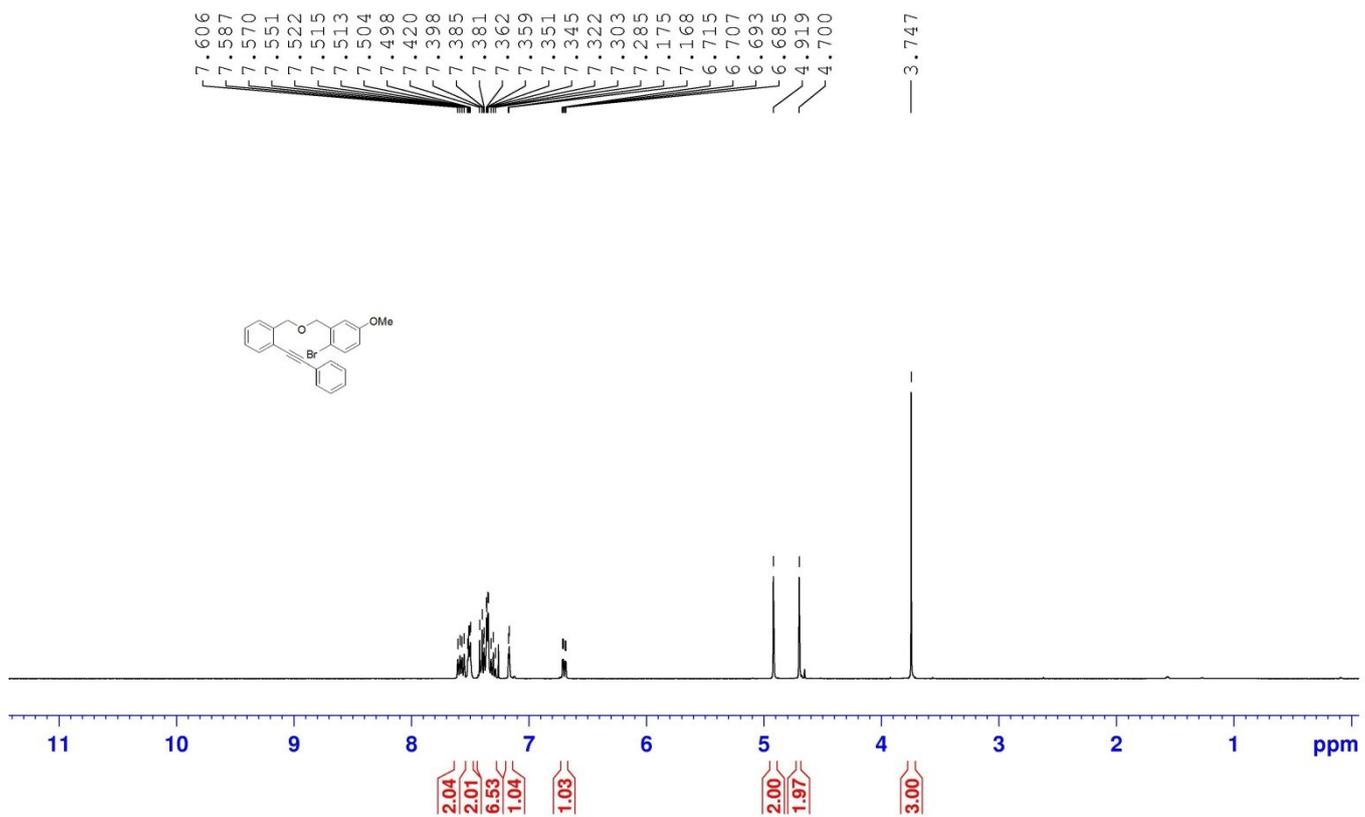


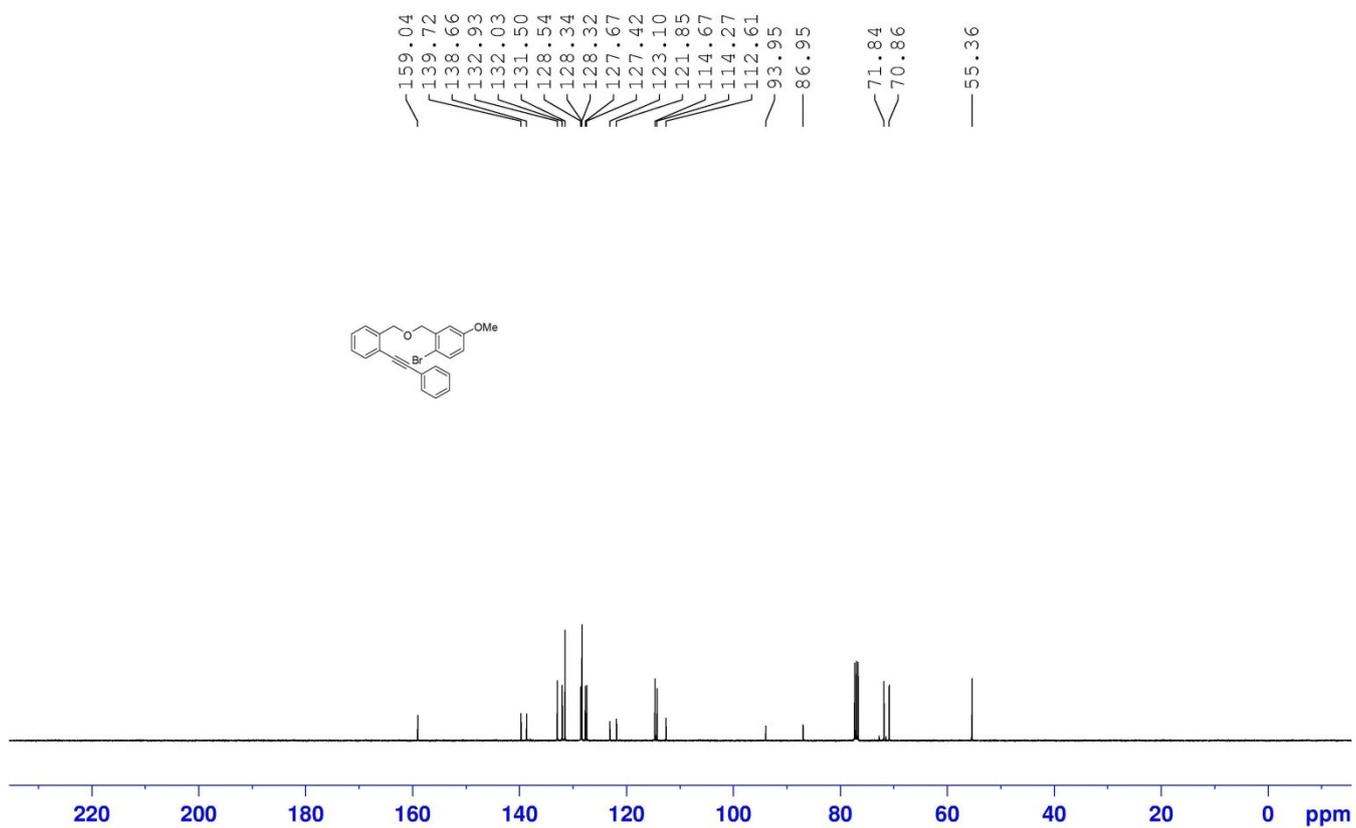
¹H and ¹³C spectra of compound 6a:



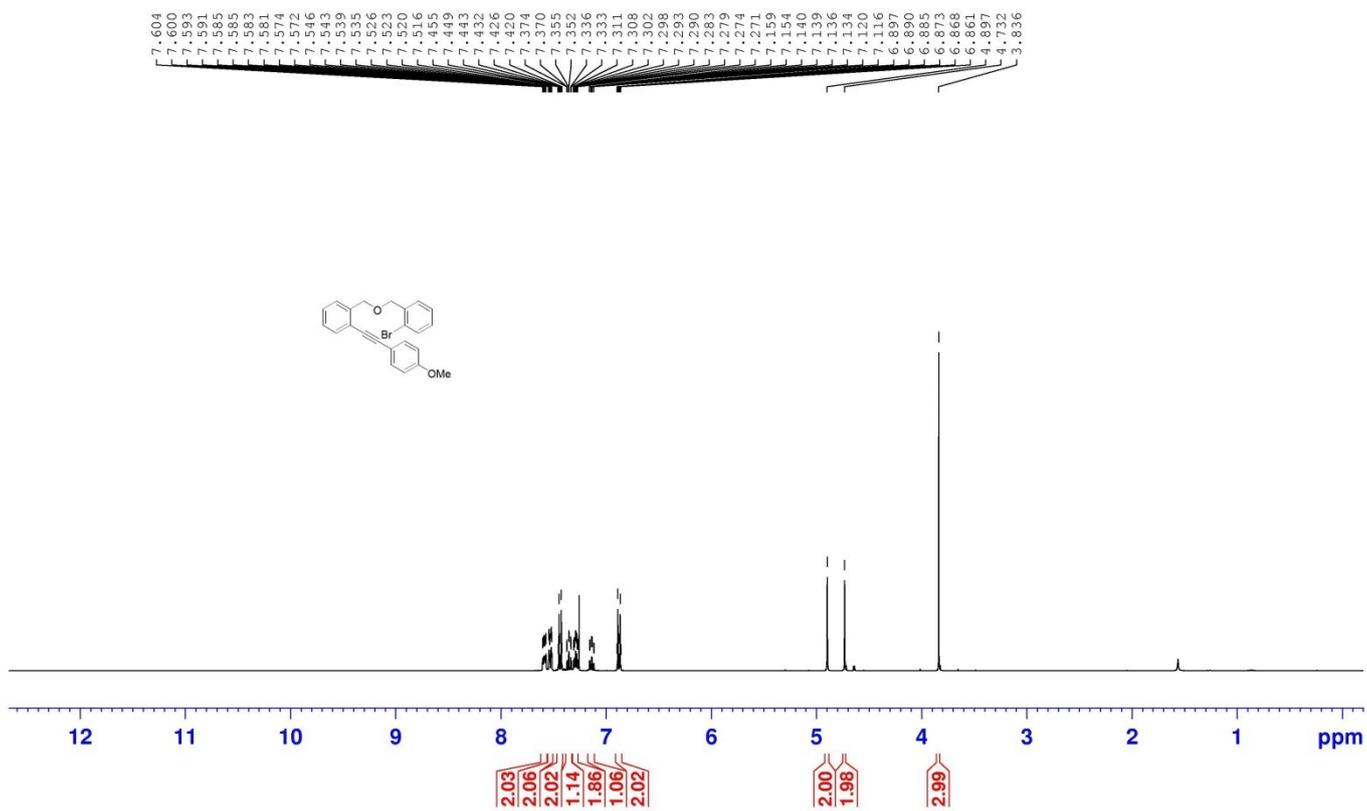


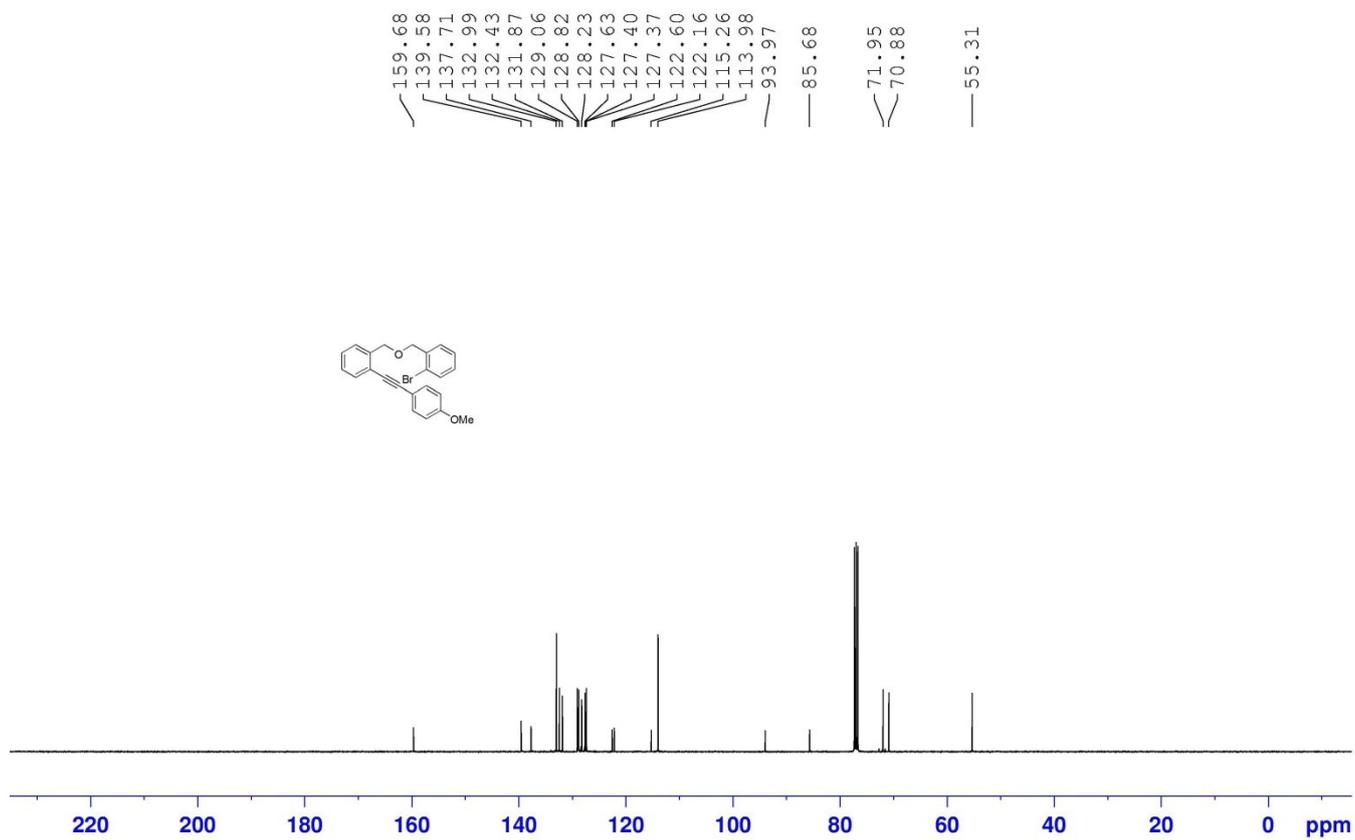
¹H and ¹³C spectra of compound 6b:



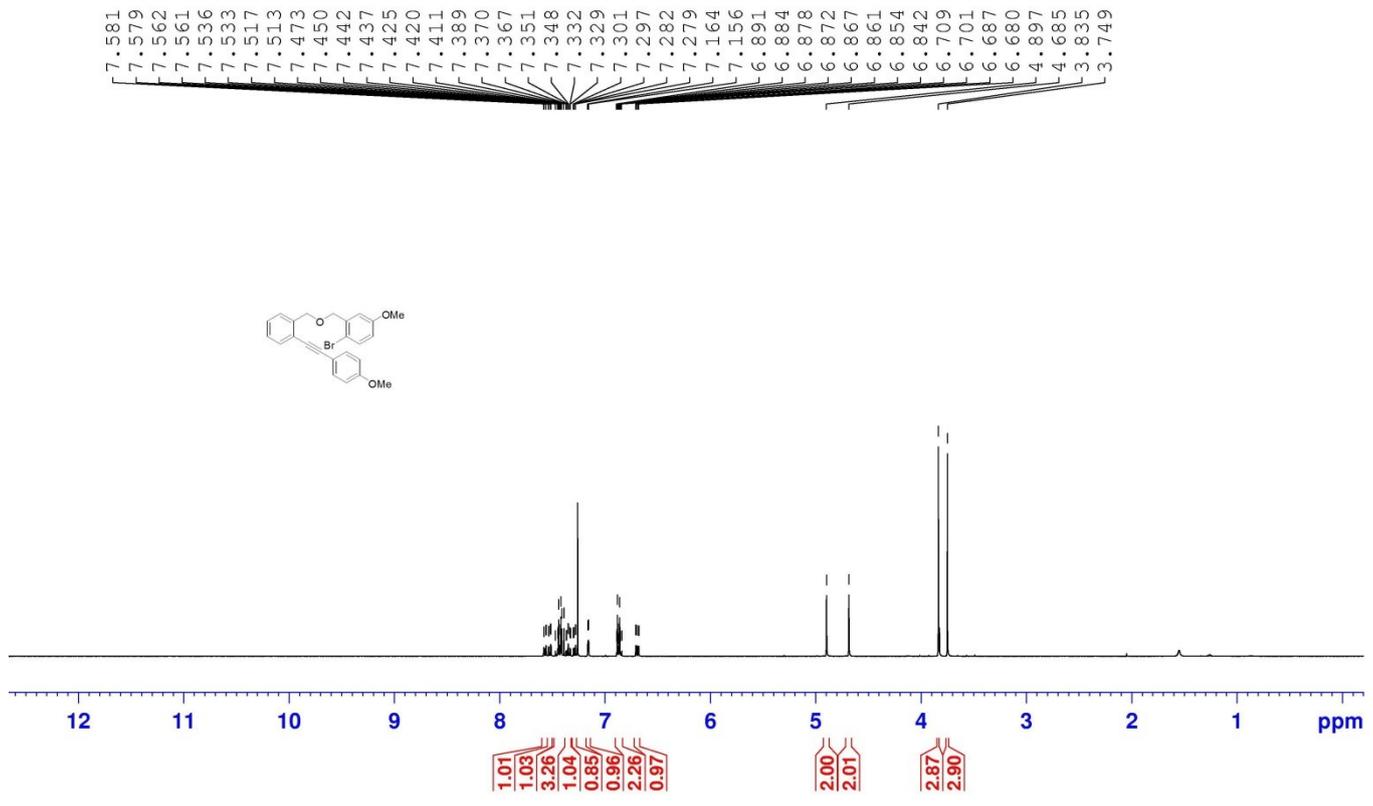


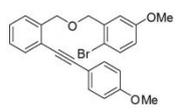
¹H and ¹³C spectra of compound 6c:



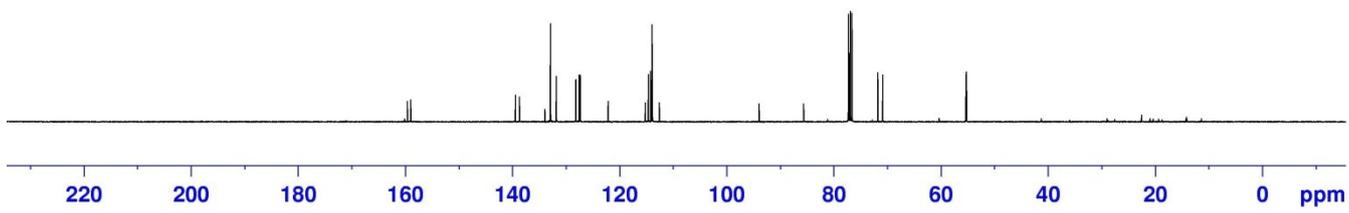


^1H and ^{13}C spectra of compound 6d:

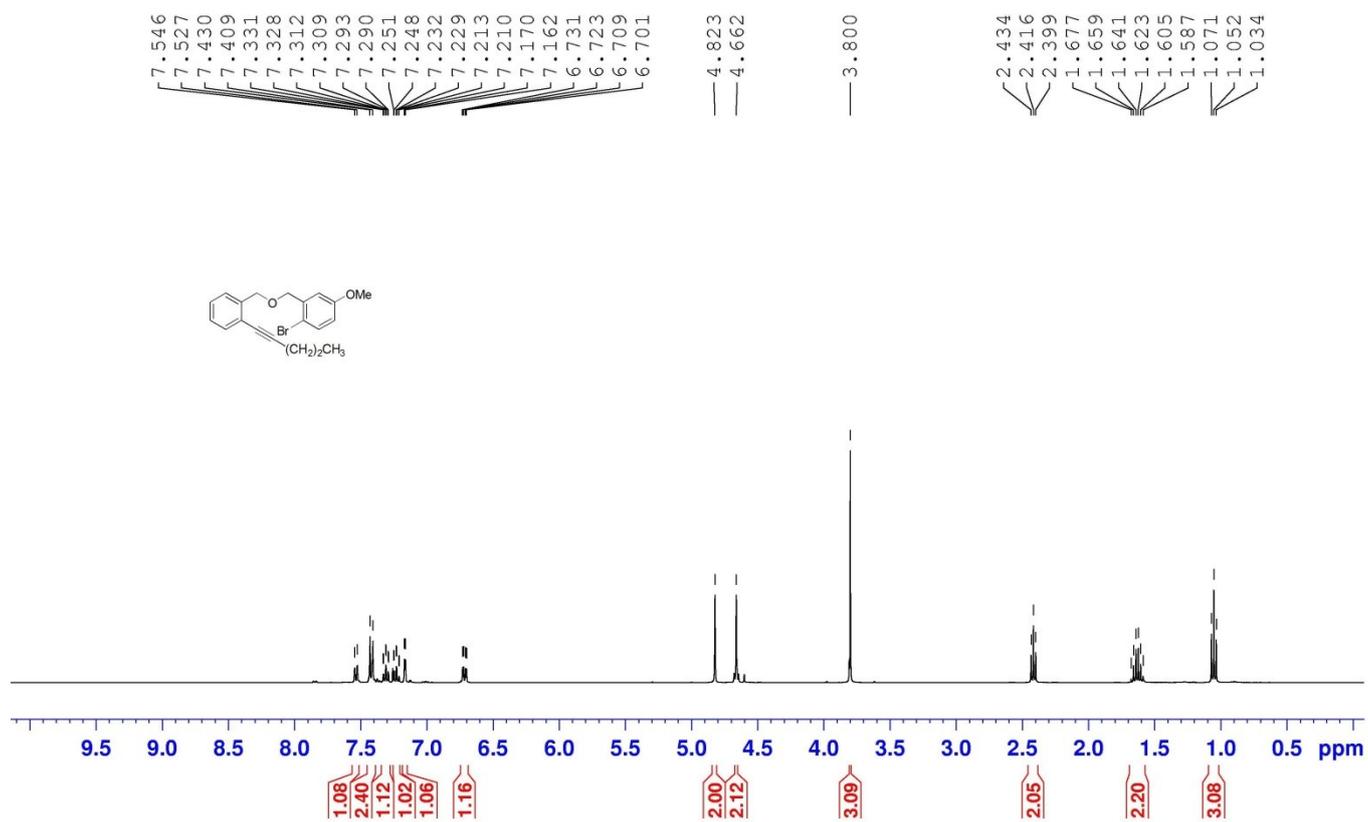


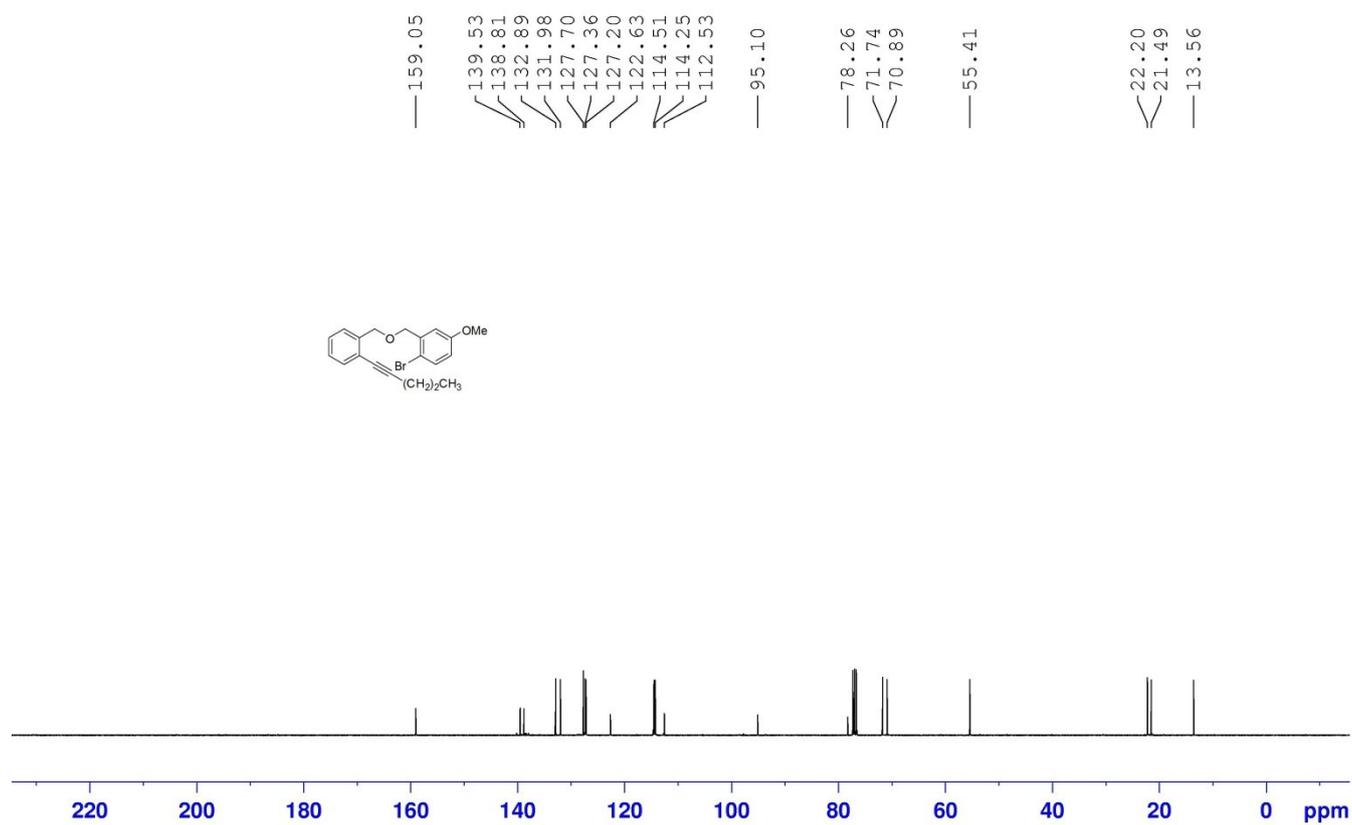


159.68
159.06
139.50
138.73
134.01
132.97
132.93
131.86
128.21
127.63
127.39
122.21
115.24
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112.61
94.01
85.68
71.84
70.92
55.39
55.30

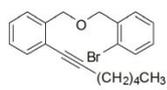


¹H and ¹³C spectra of compound 6e:





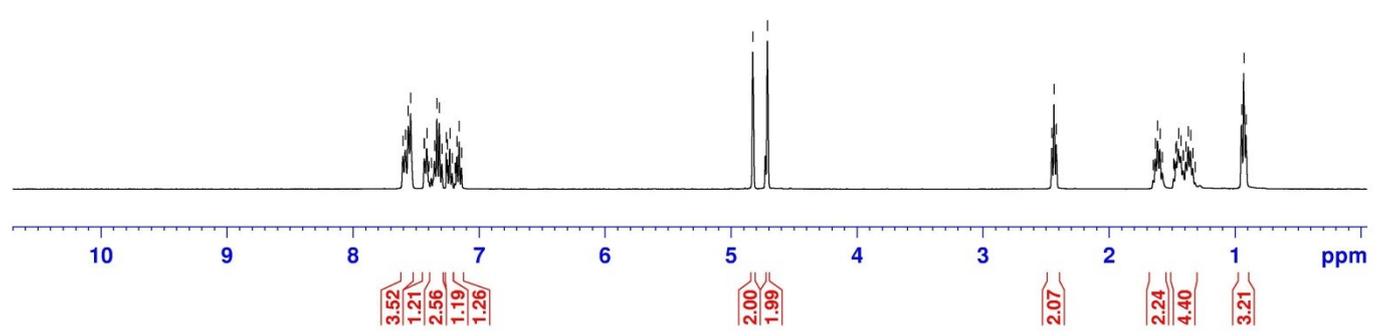
^1H and ^{13}C spectra of compound 6f:

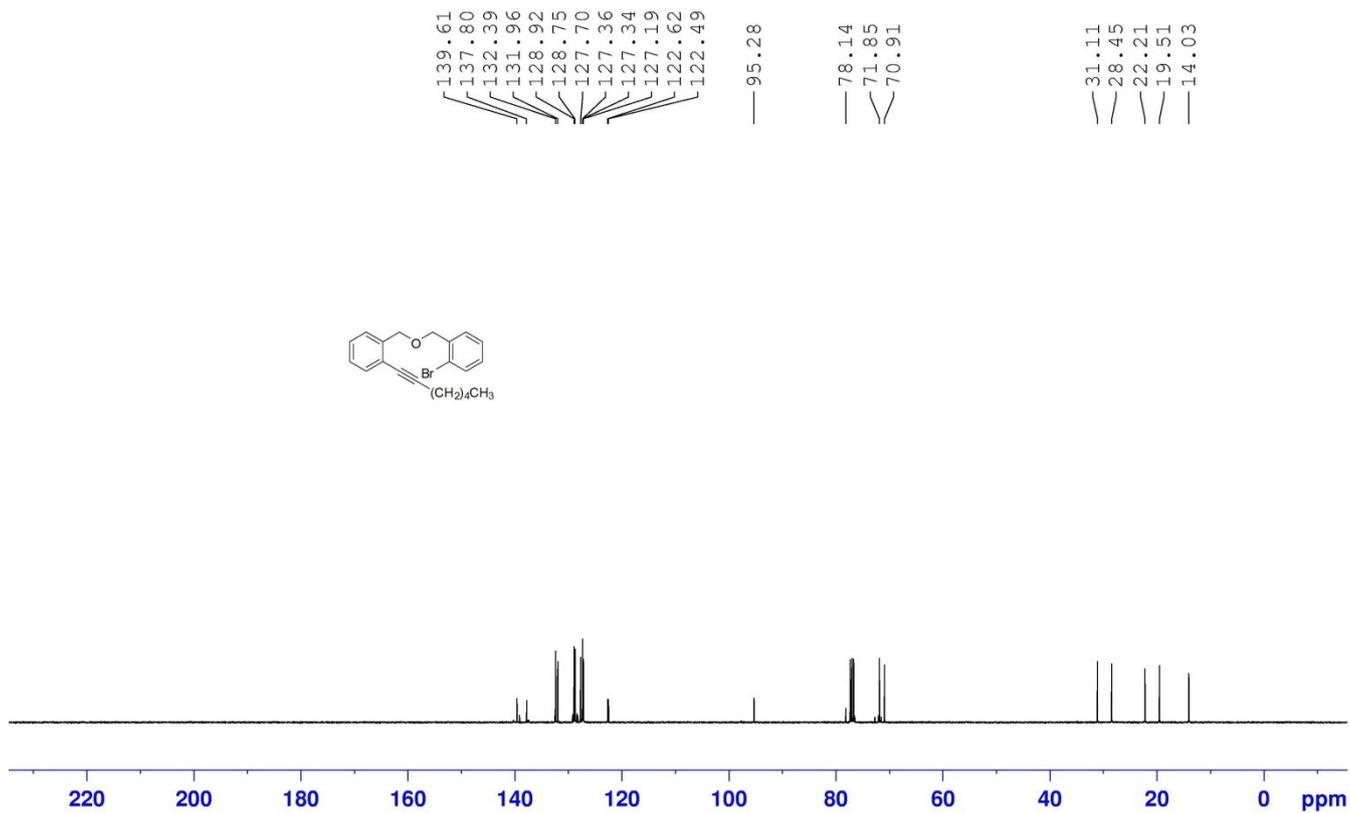


7.603
7.584
7.562
7.542
7.495
7.433
7.414
7.399
7.378
7.353
7.334
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7.294
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7.251
7.232
7.213
7.191
7.176
7.158
7.138

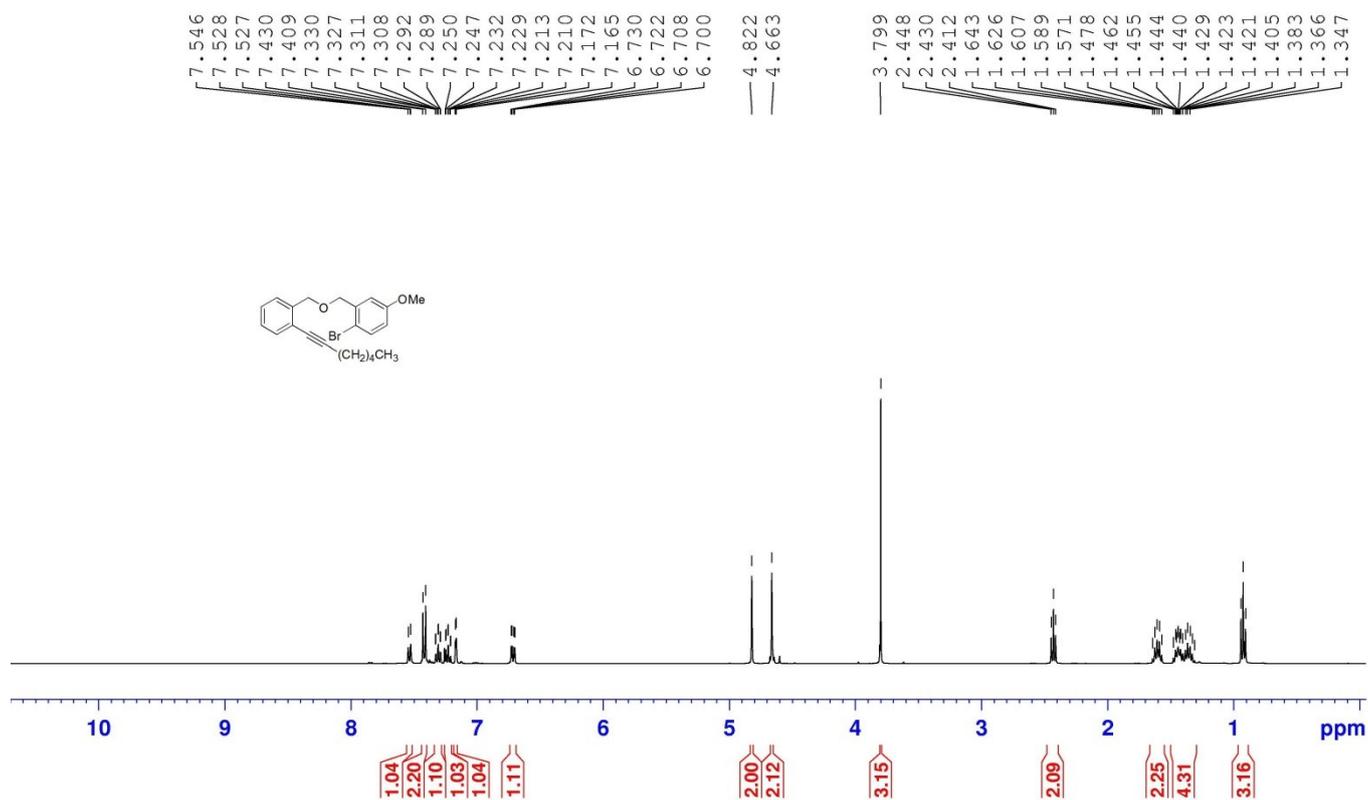
4.827
4.711

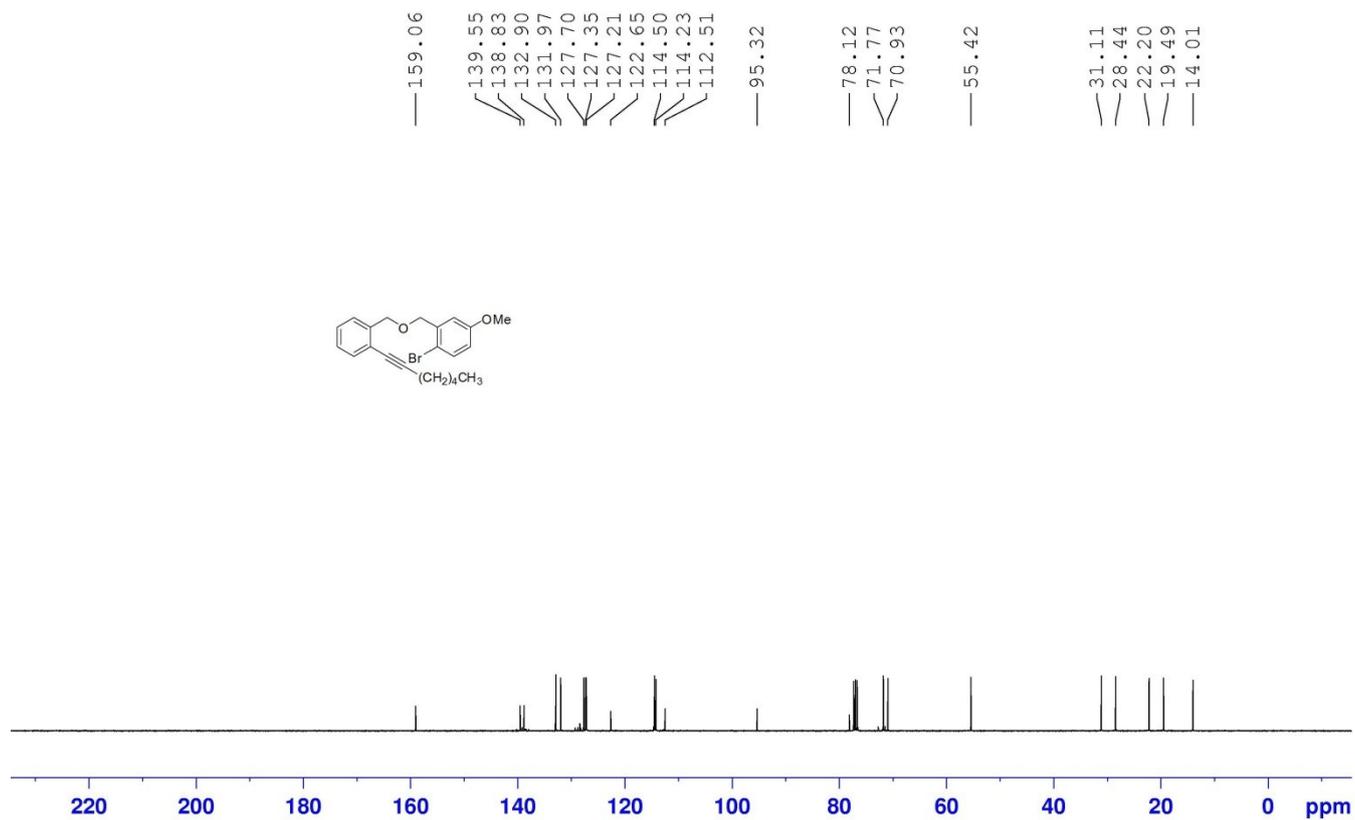
2.454
2.436
2.418
1.650
1.633
1.614
1.596
1.578
1.487
1.482
1.470
1.465
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1.365
1.348
1.336
1.318
0.949
0.930
0.912



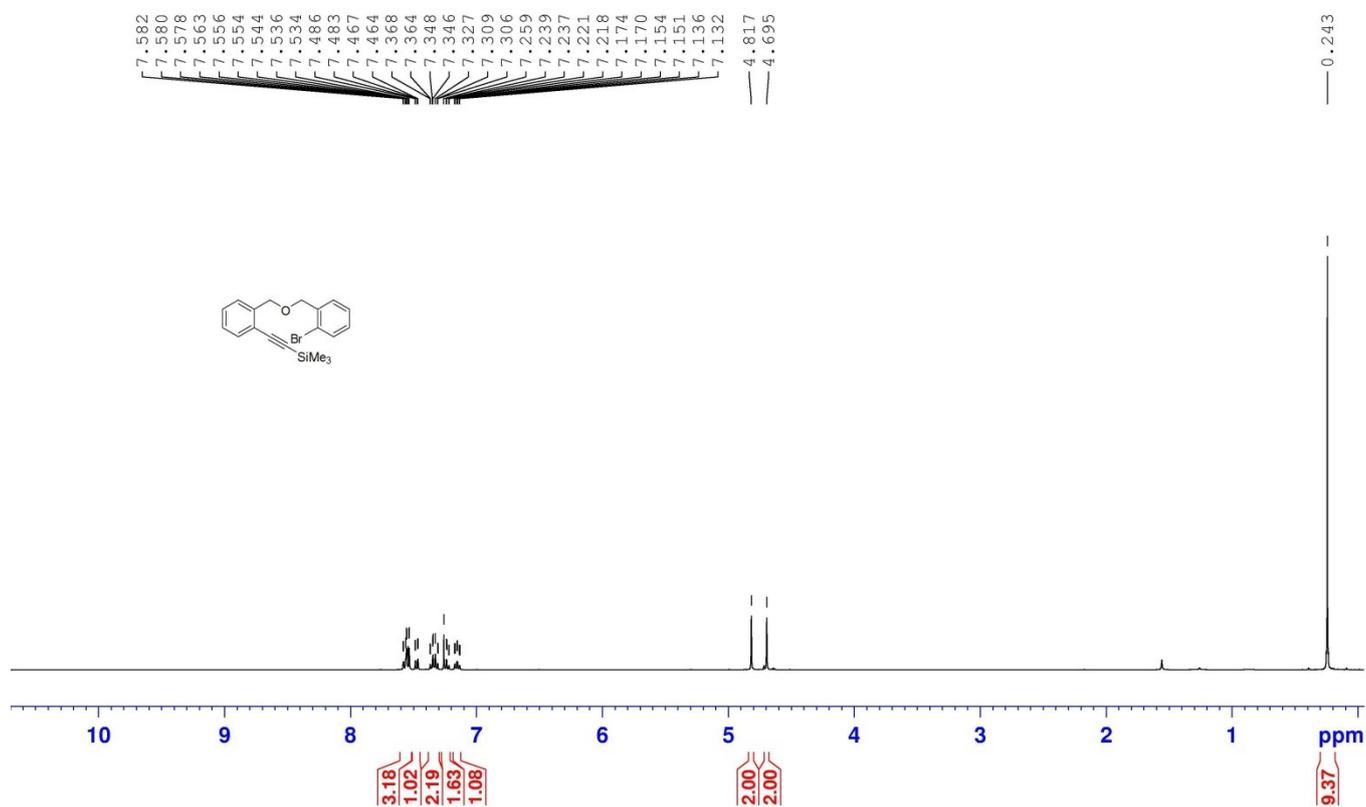


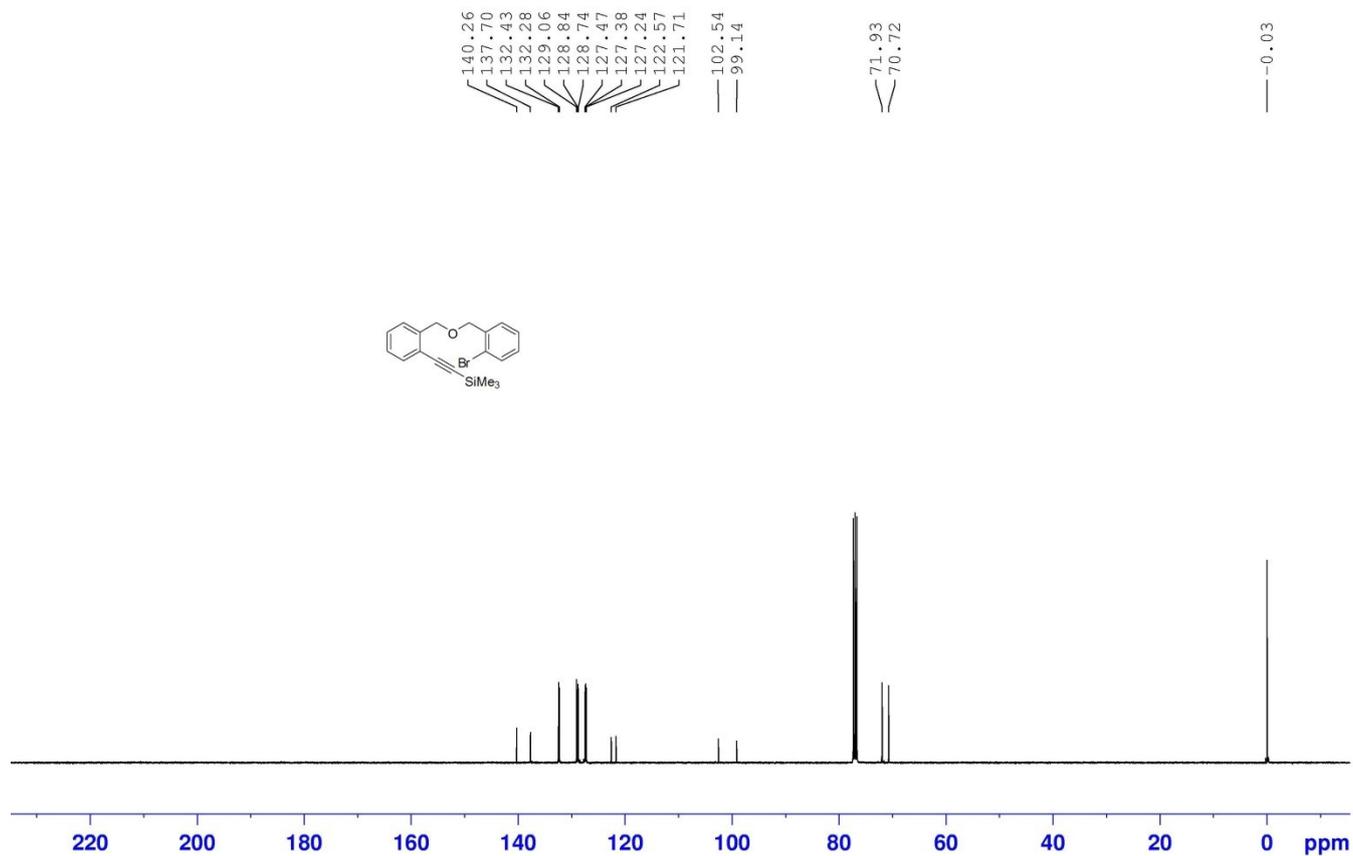
^1H and ^{13}C spectra of compound 6g:



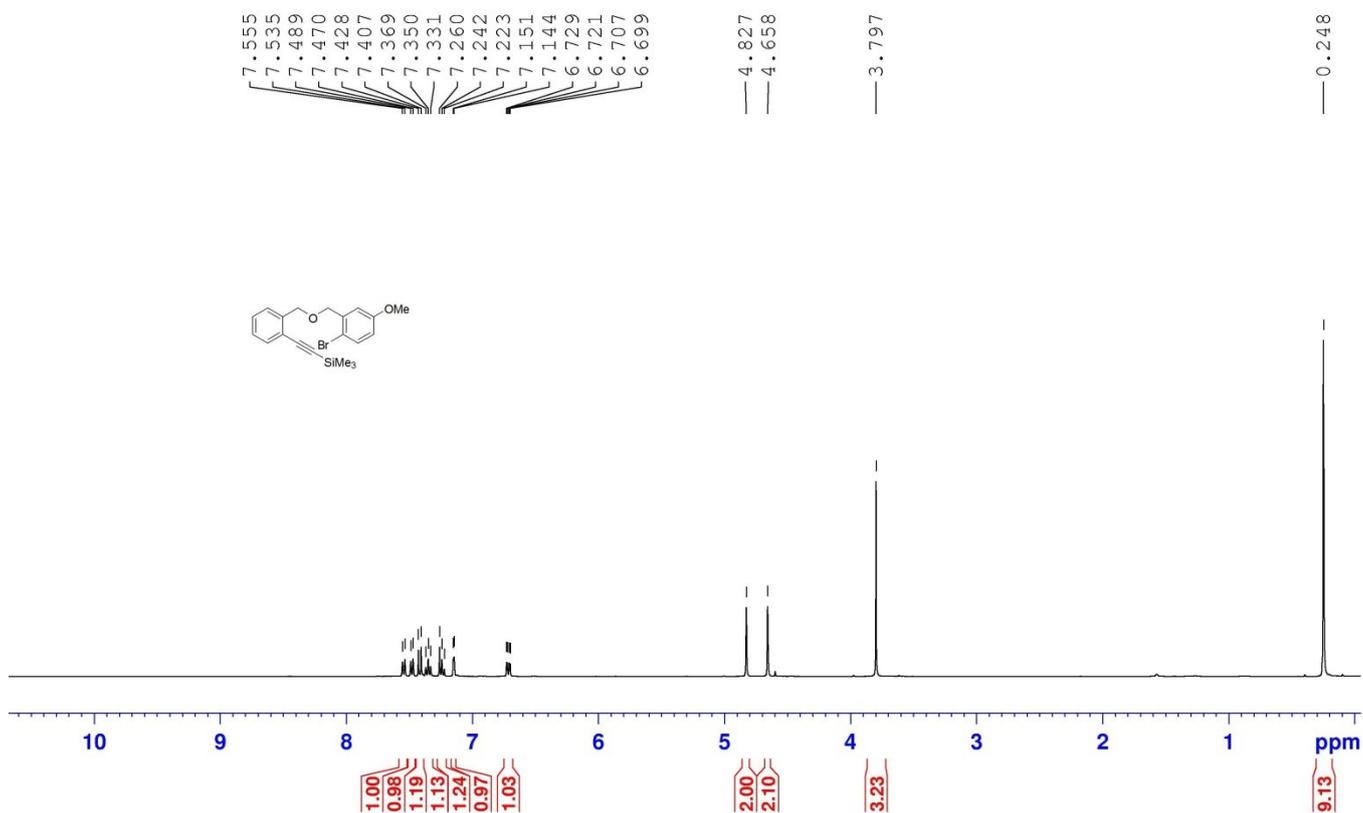


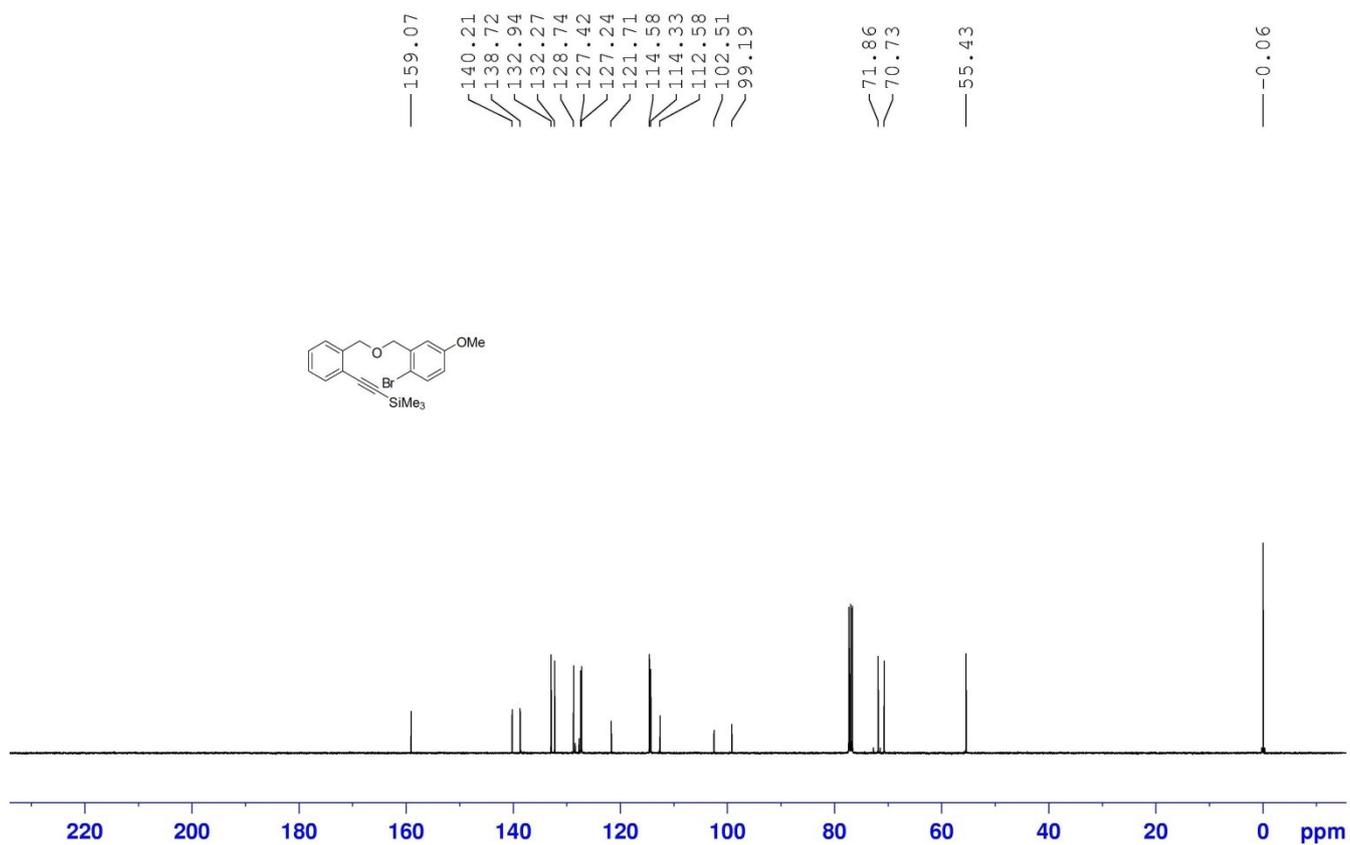
^1H and ^{13}C spectra of compound 6h:



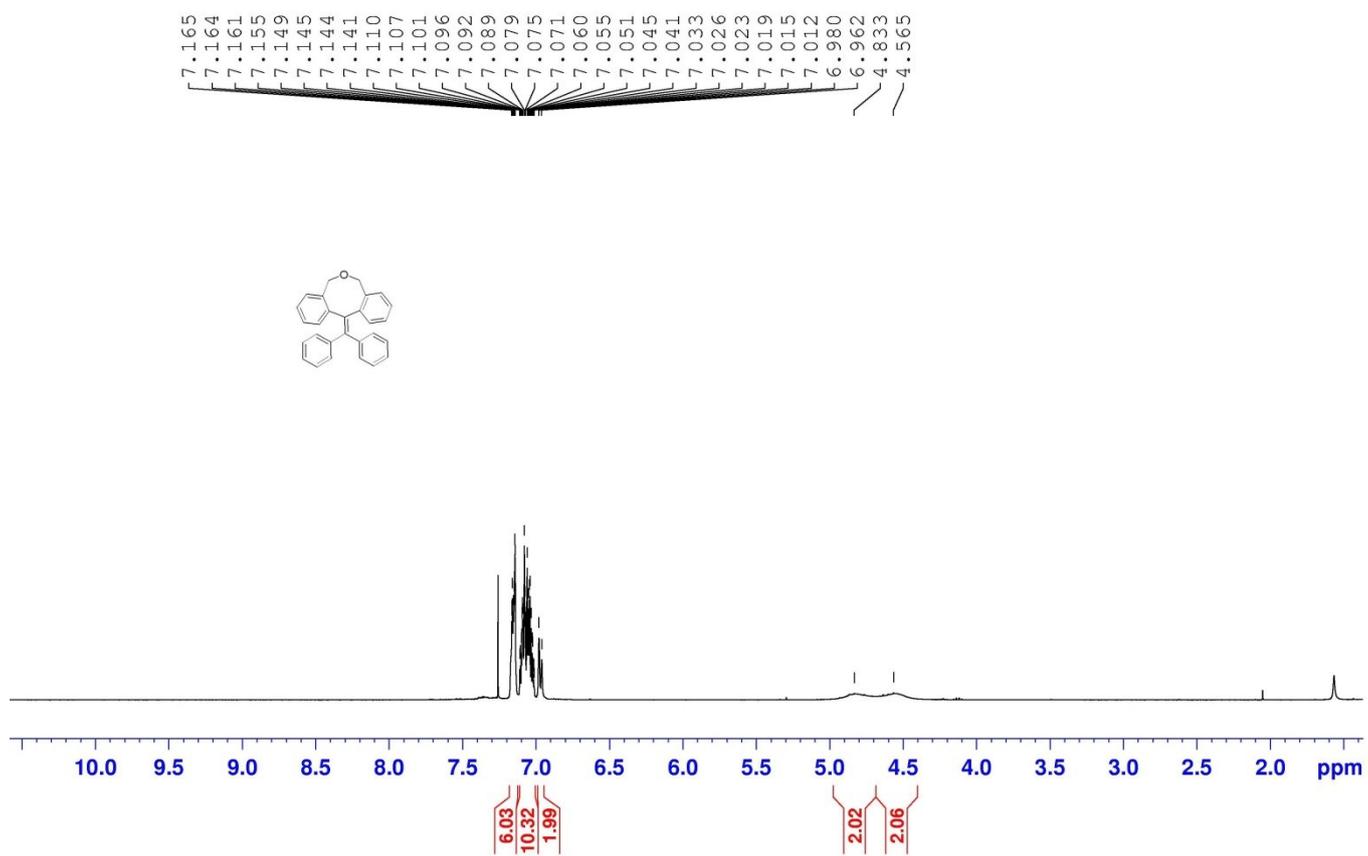


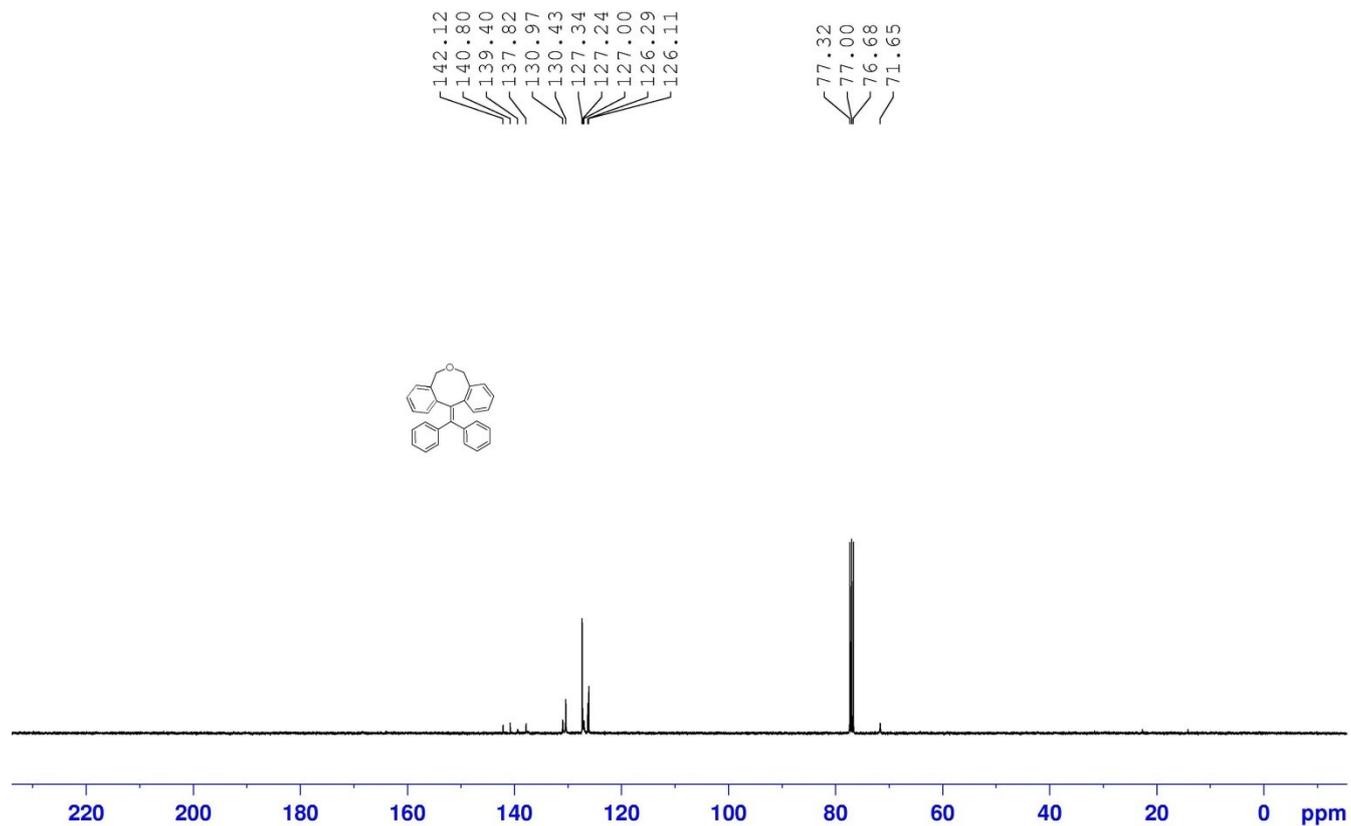
¹H and ¹³C spectra of compound 6i:



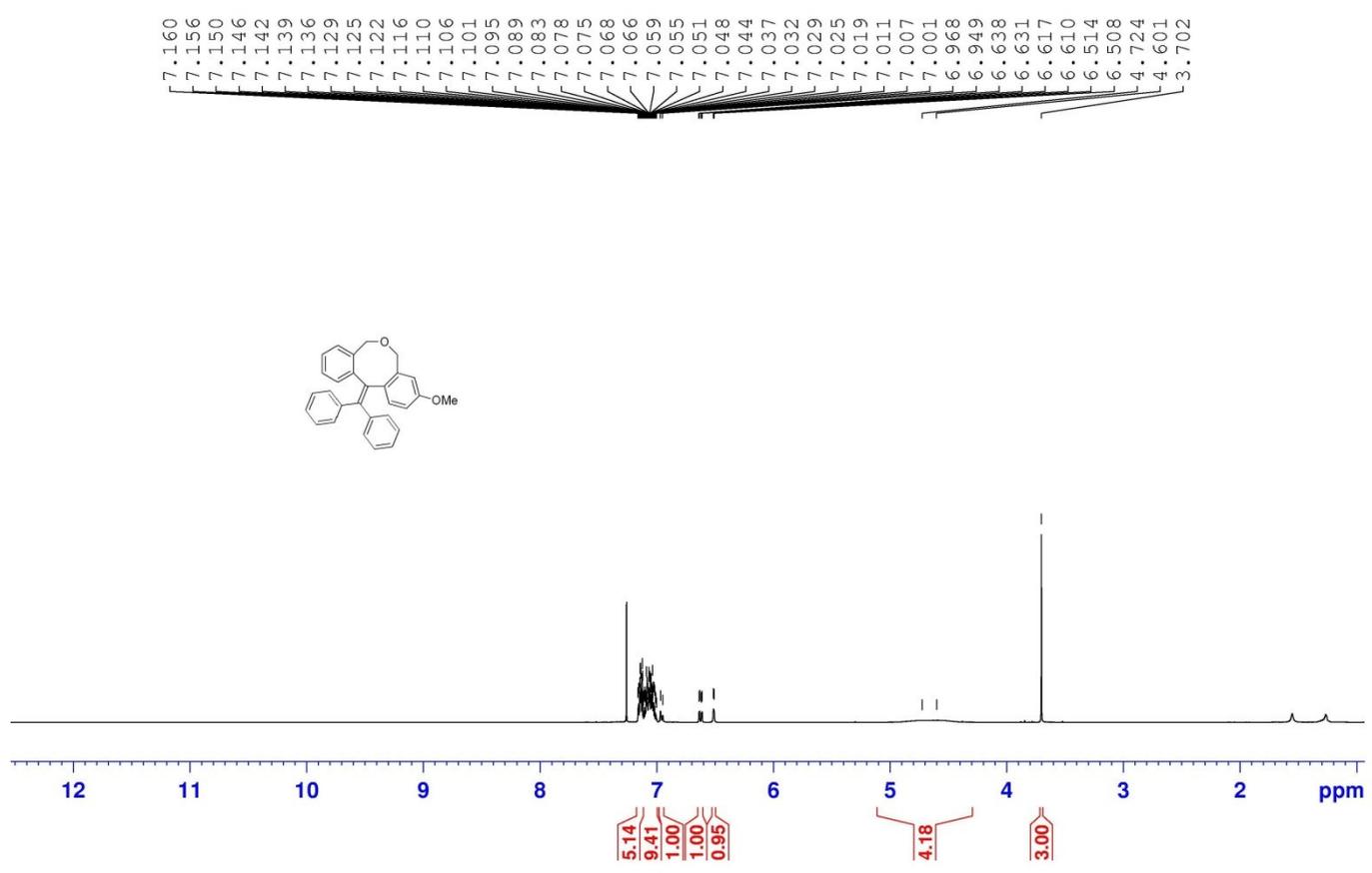


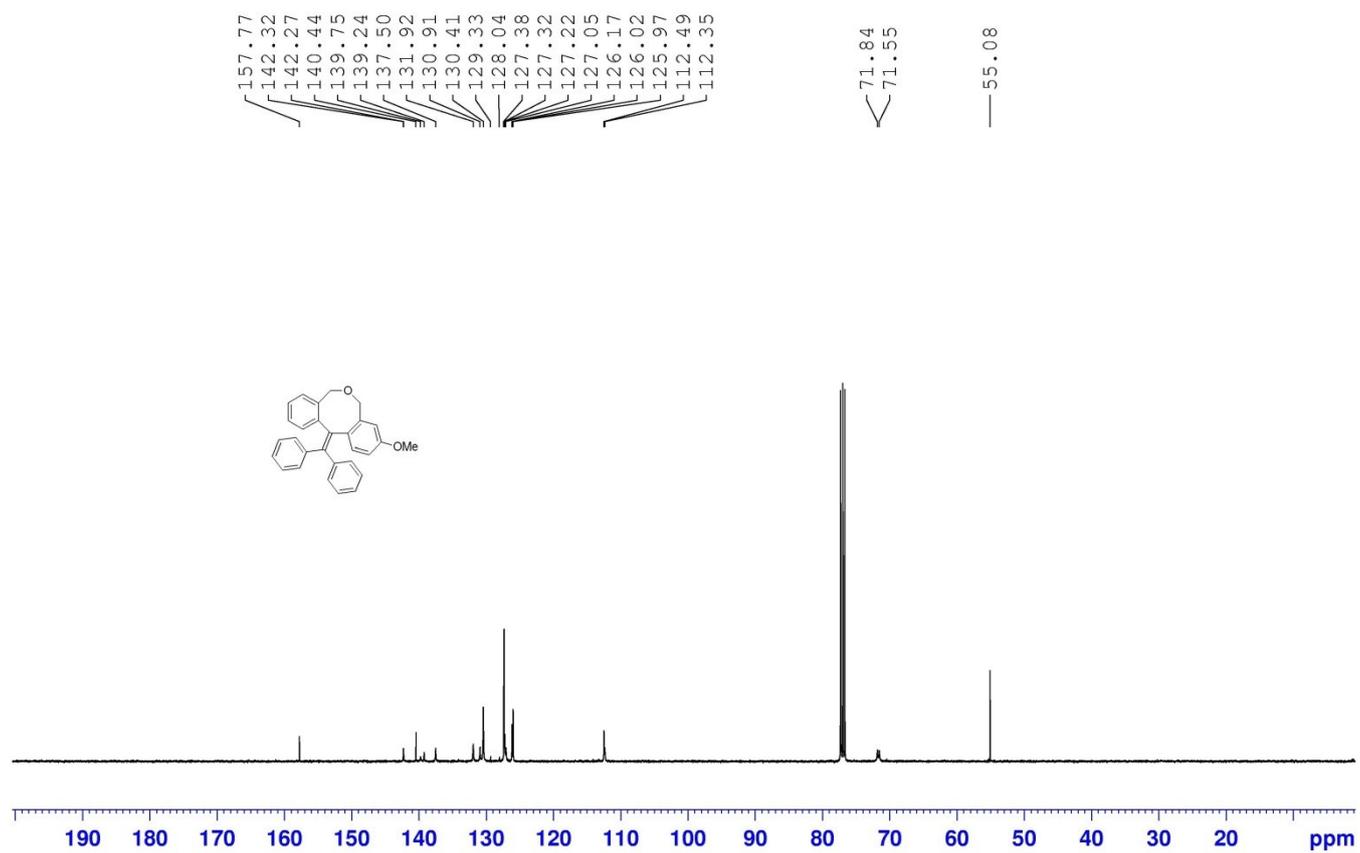
¹H and ¹³C spectra of compound 7a:



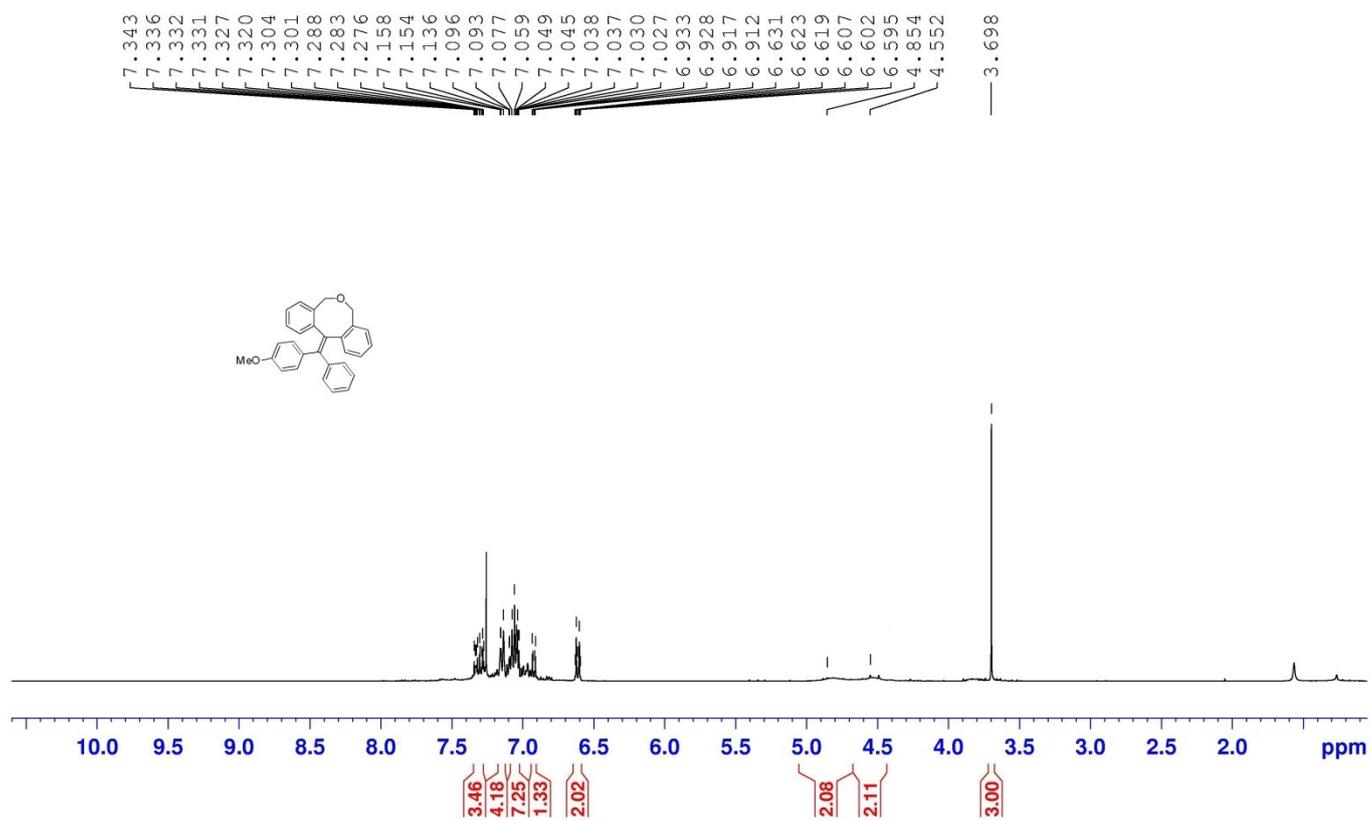


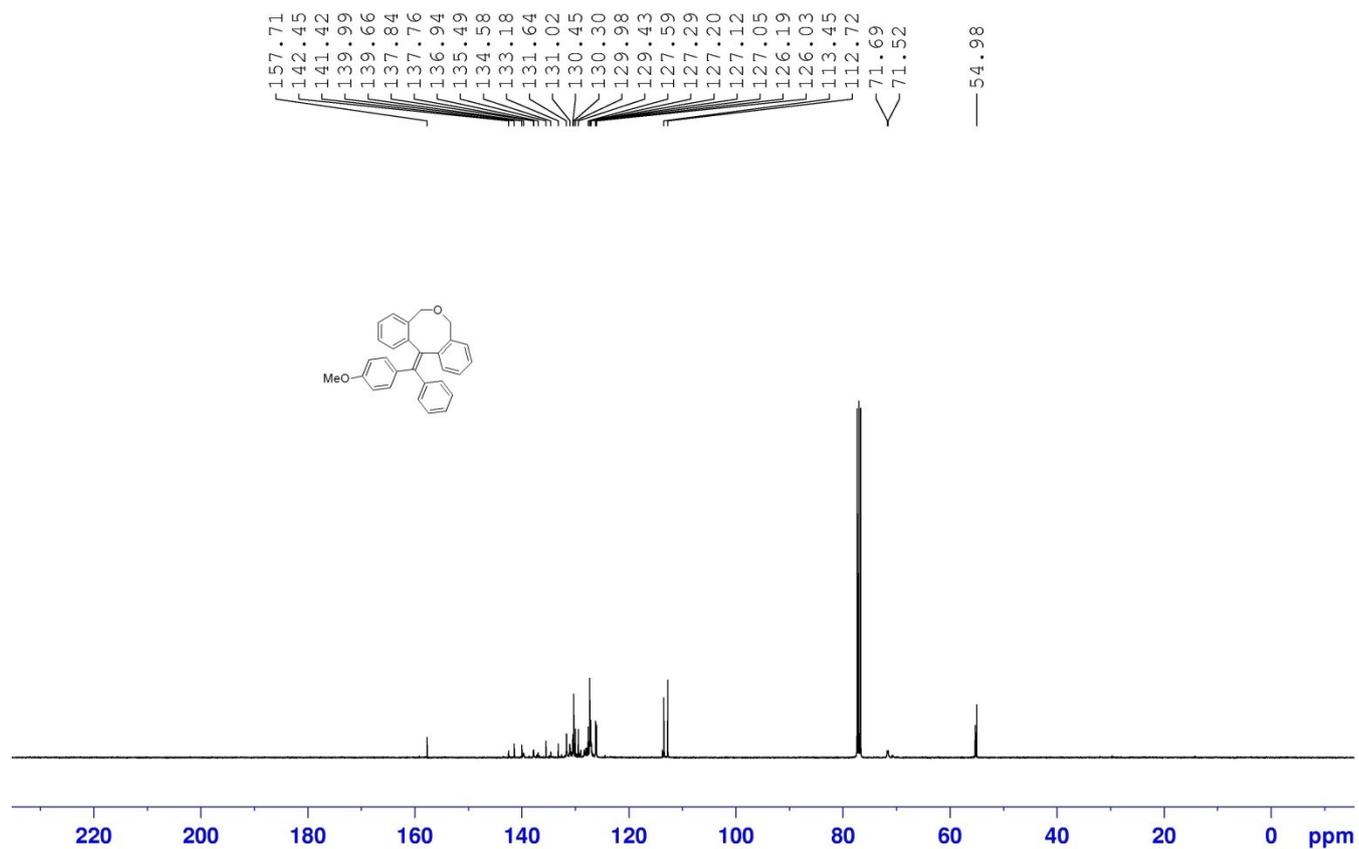
¹H and ¹³C spectra of compound 7b:



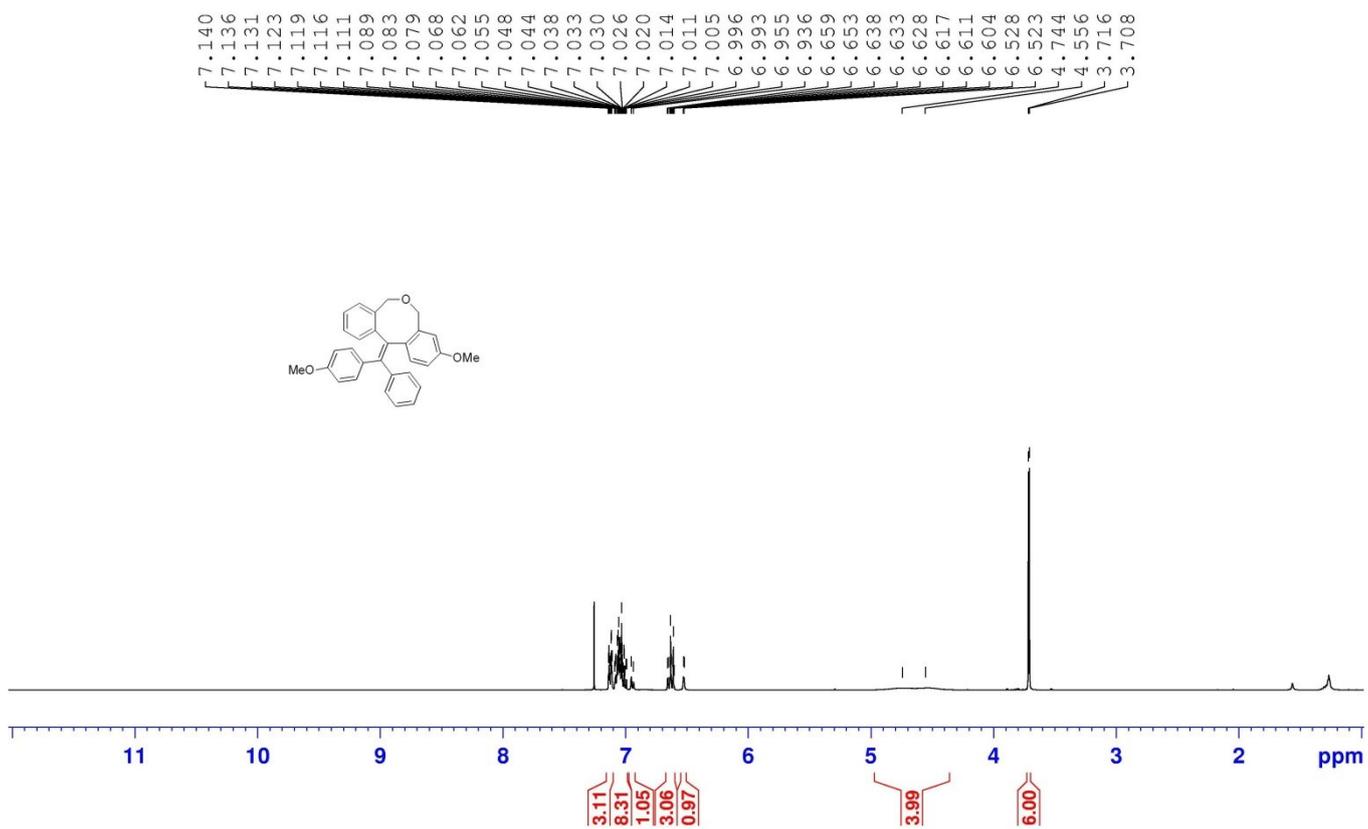


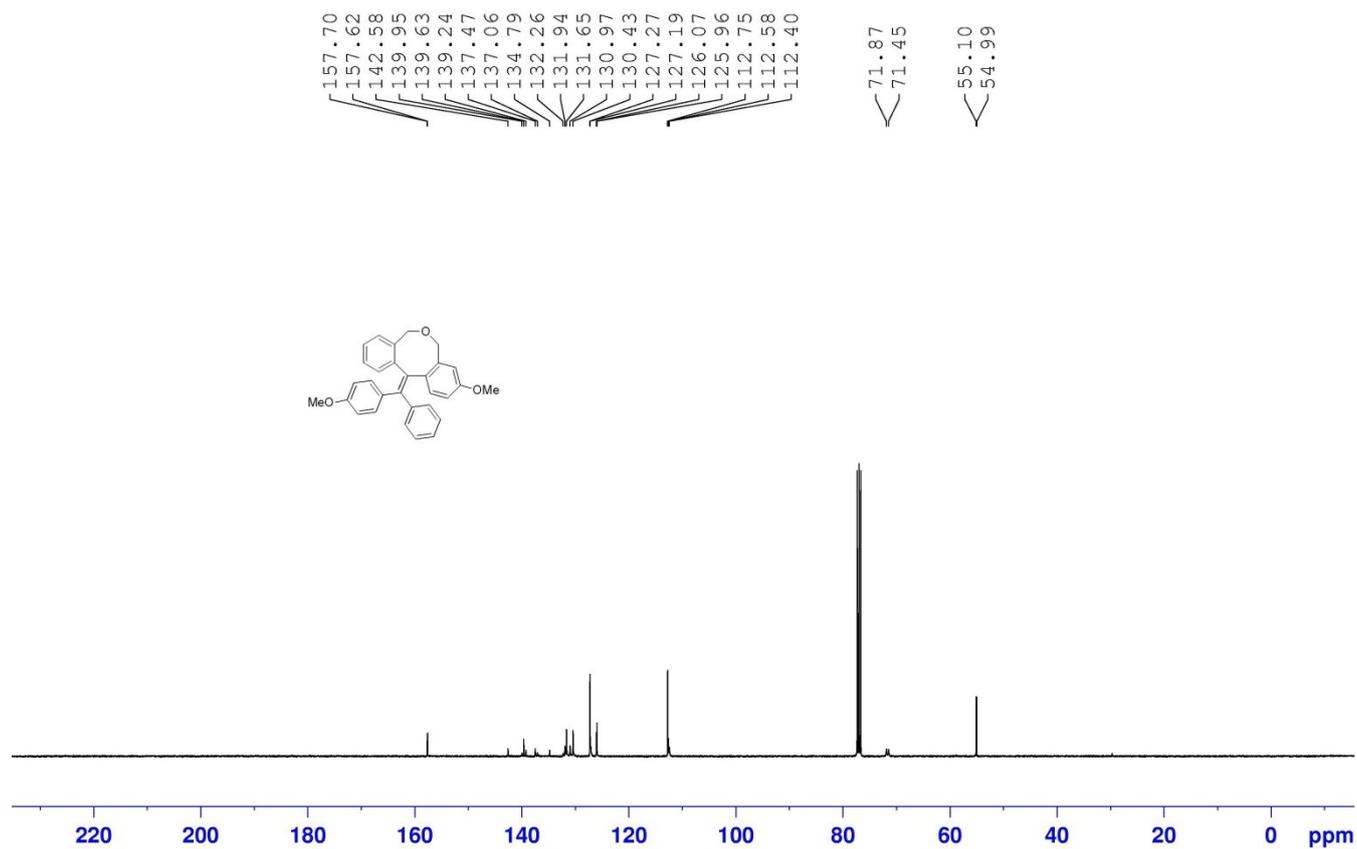
^1H and ^{13}C spectra of compound 7c:



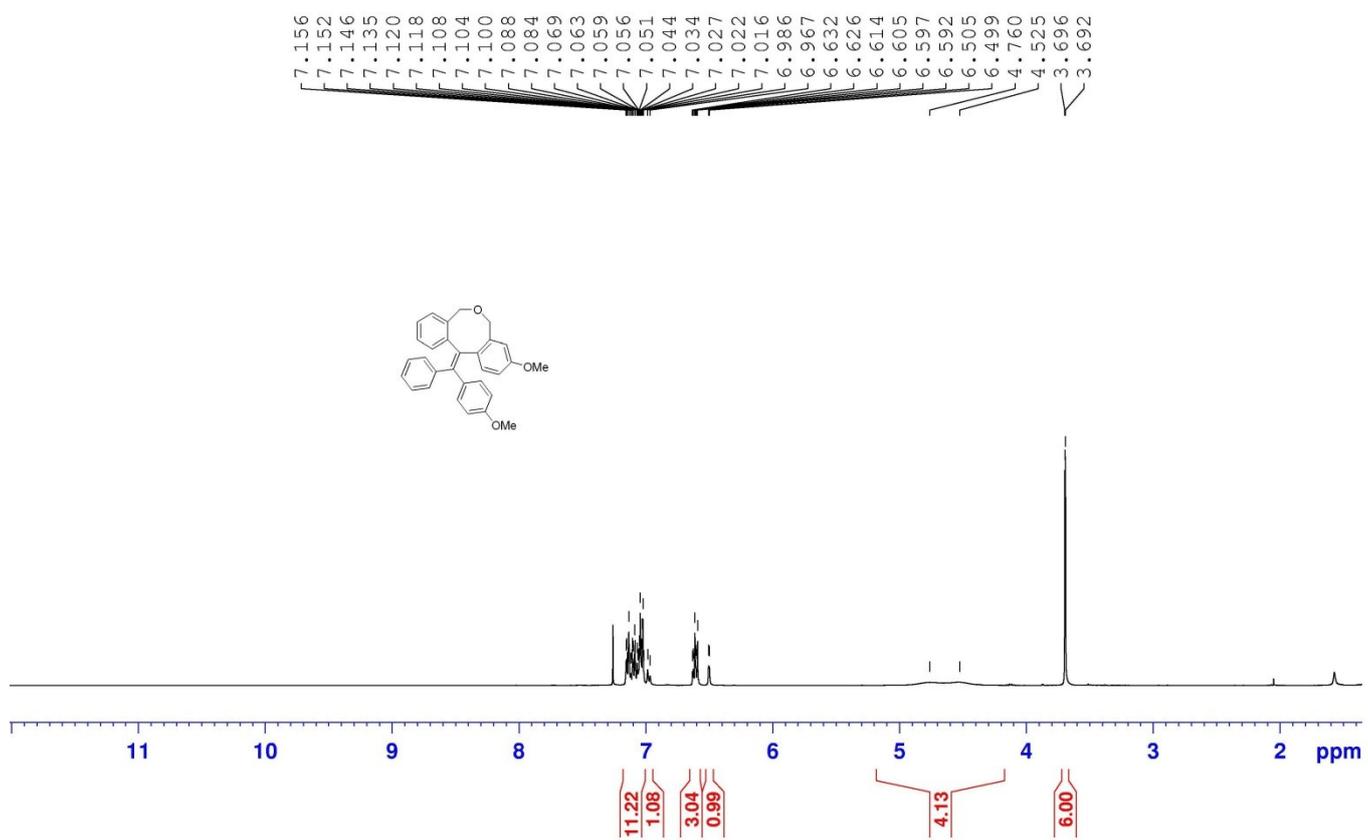


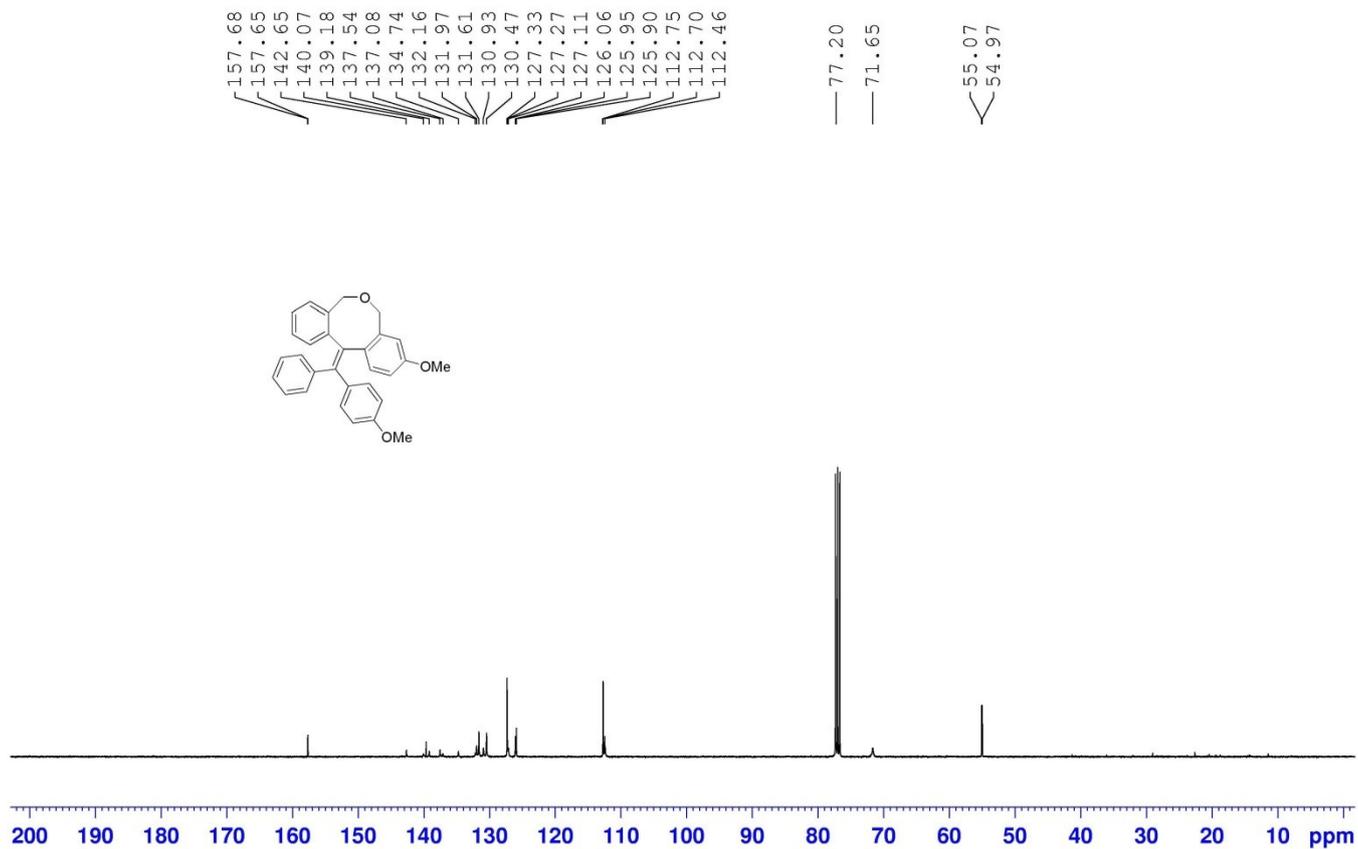
^1H and ^{13}C spectra of compound 7d:



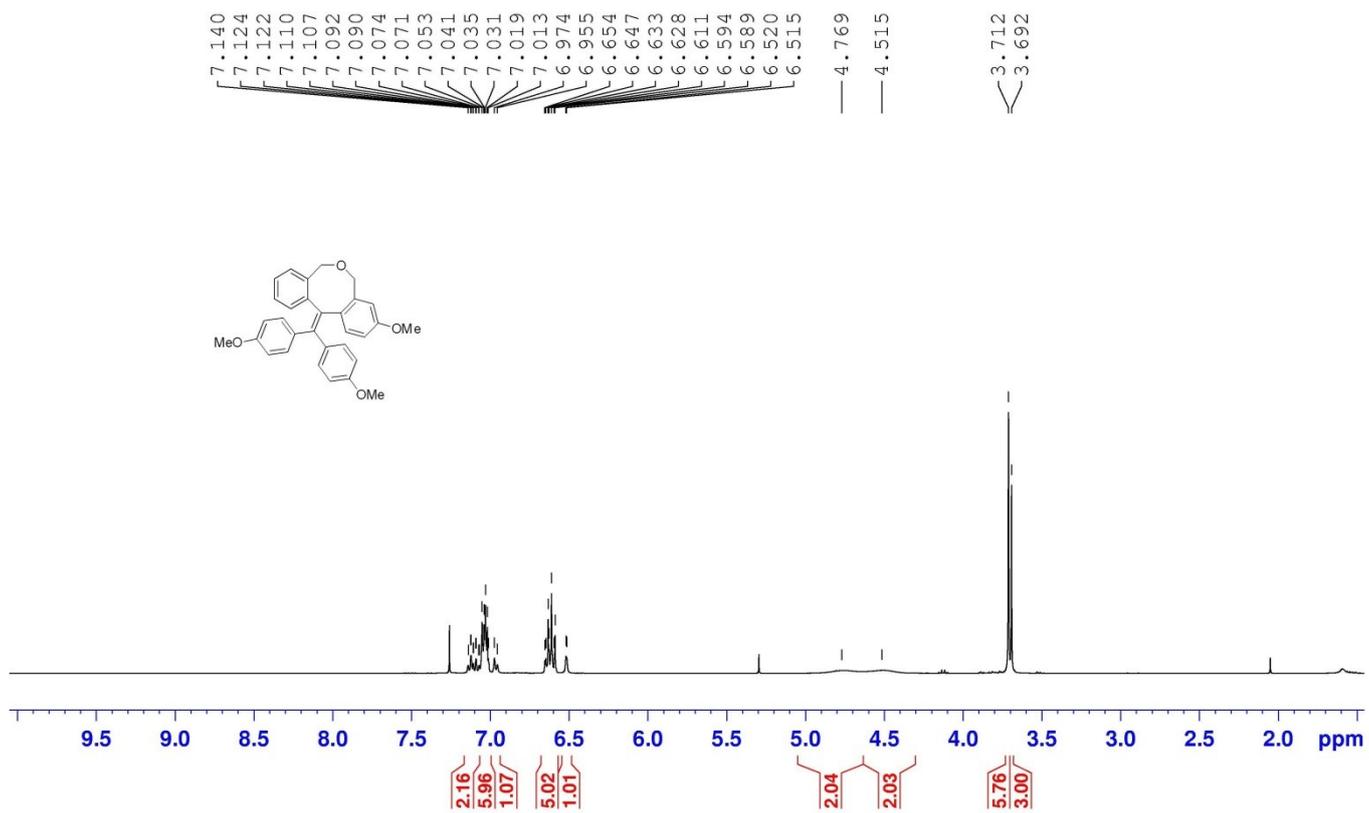


¹H and ¹³C spectra of compound 7e:





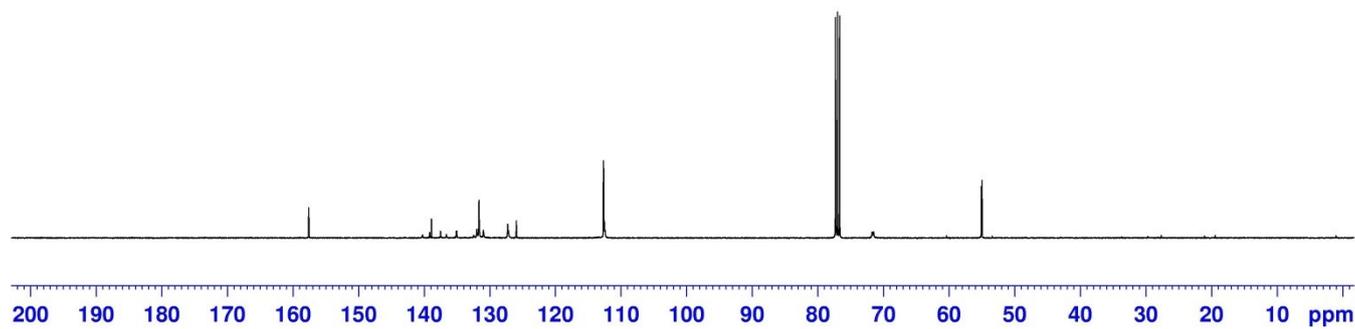
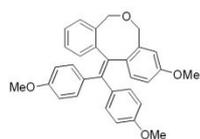
^1H and ^{13}C spectra of compound 7f:



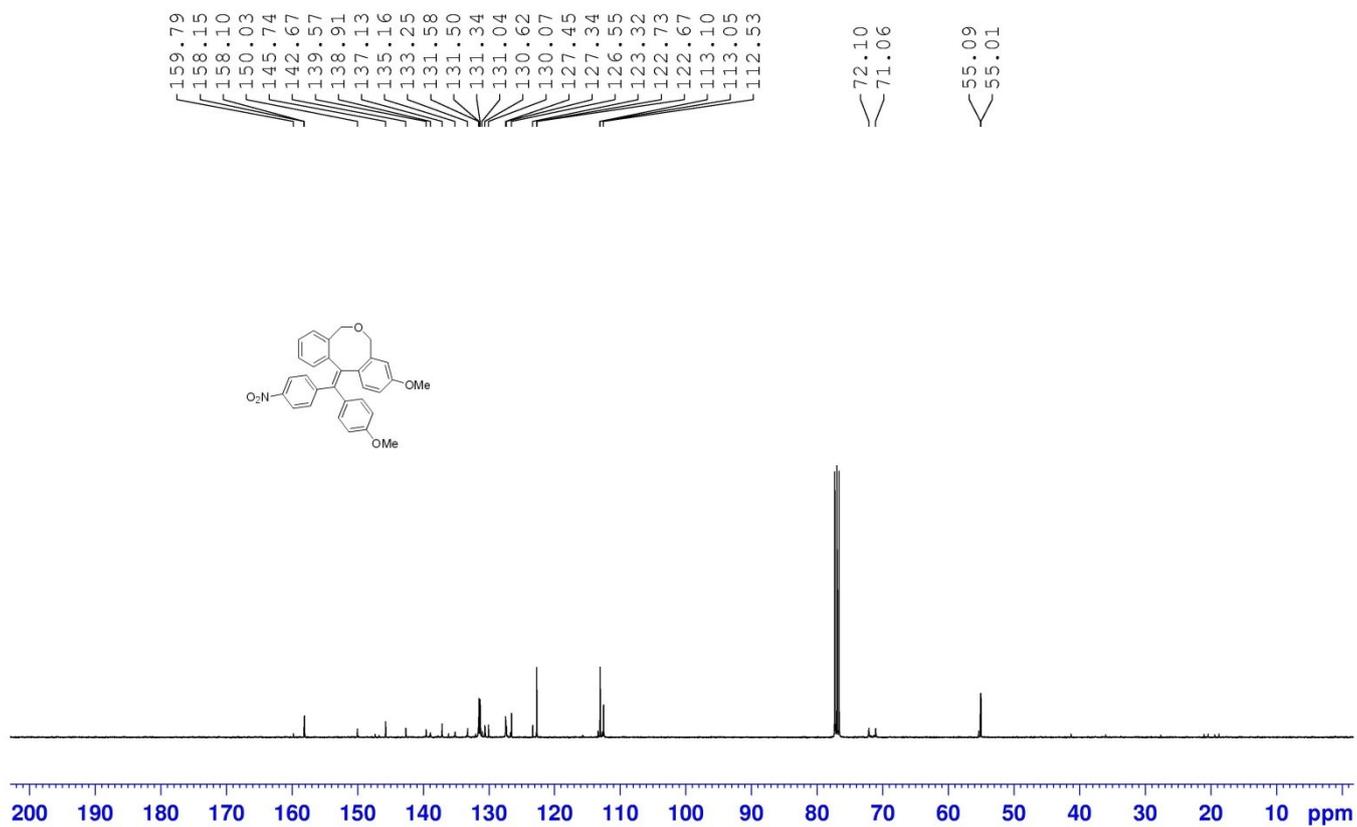
157.60
157.57
140.25
139.17
138.89
137.50
136.61
135.11
135.04
132.46
131.98
131.64
130.97
127.28
127.14
125.96
112.70
112.65
112.55
112.44

71.71
71.48

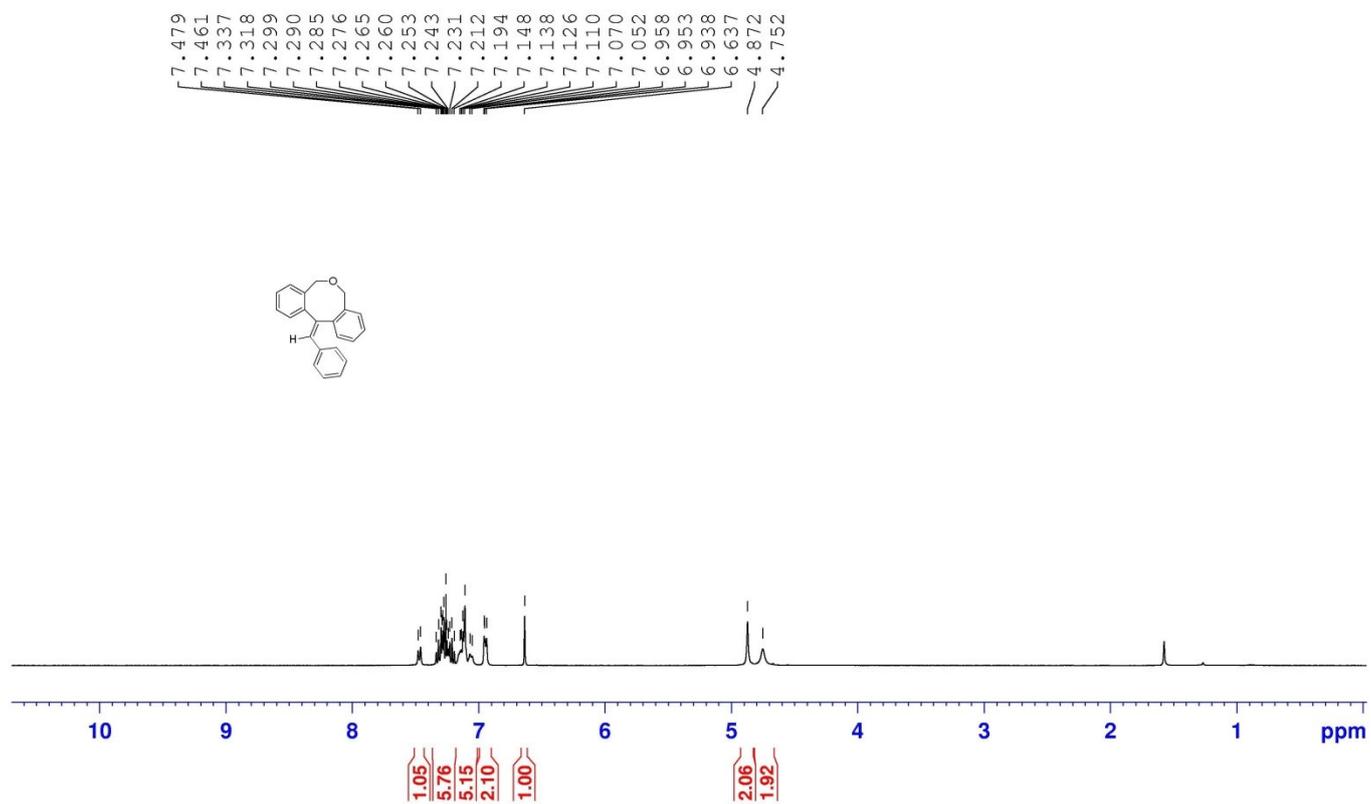
55.08
54.98
54.96

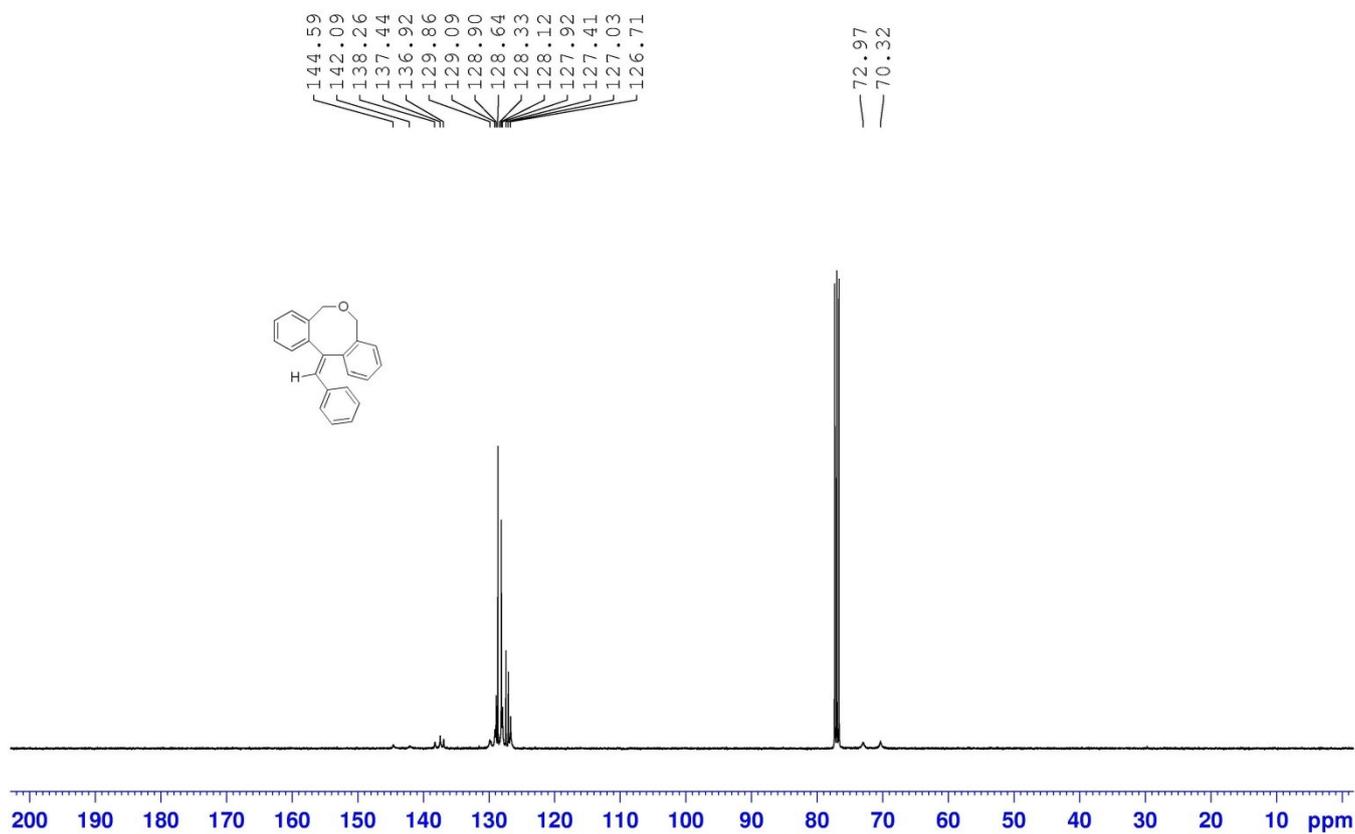


^1H and ^{13}C spectra of compound 7g:

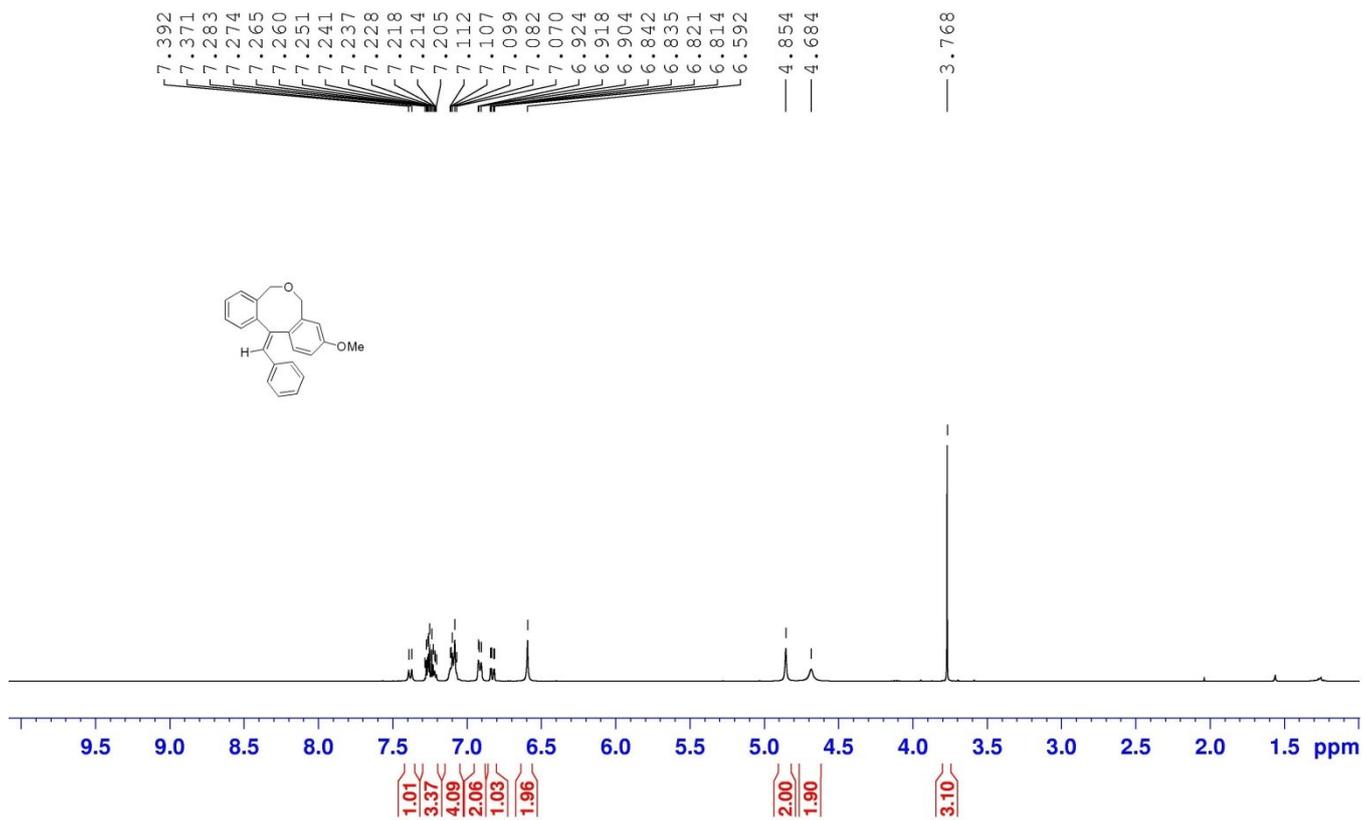


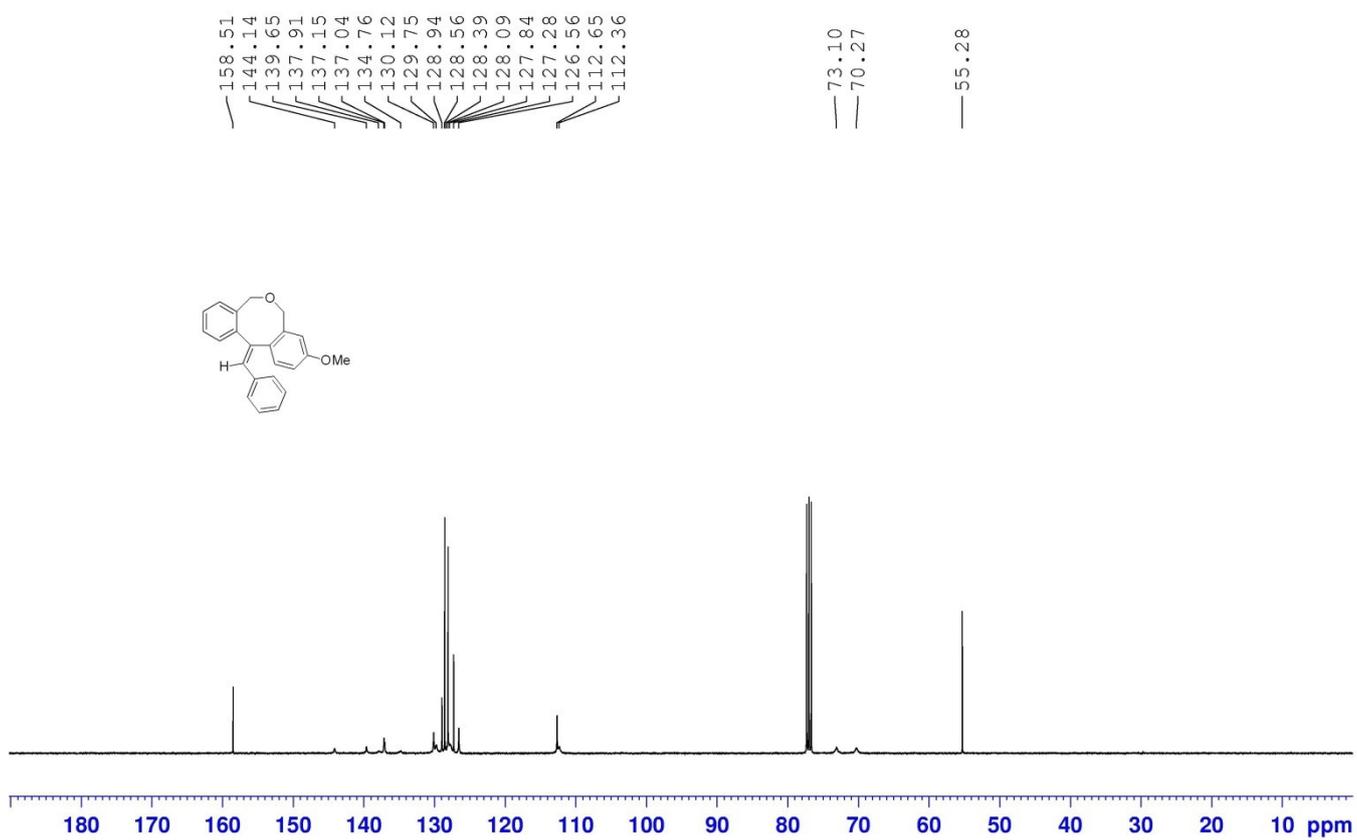
¹H and ¹³C spectra of compound 8a:



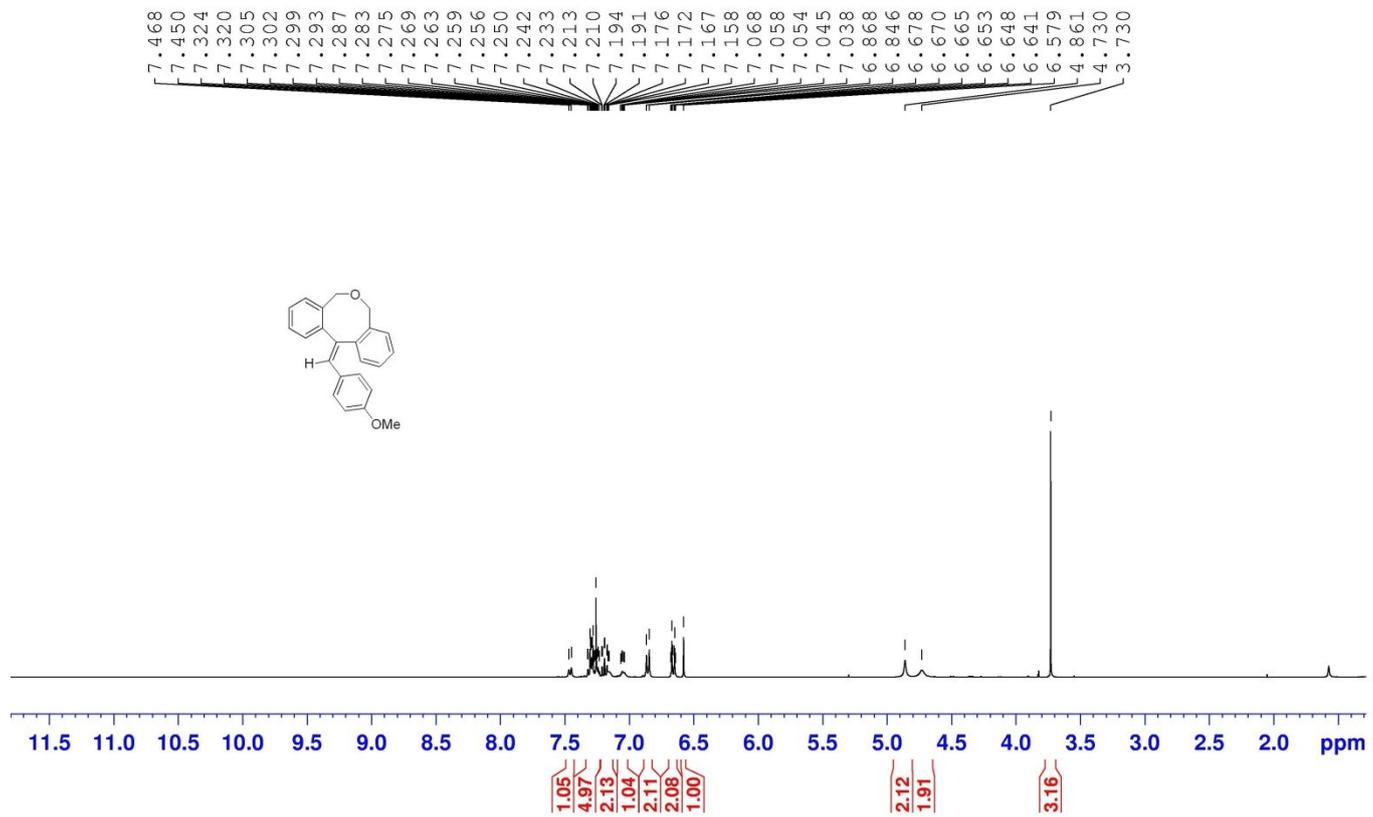


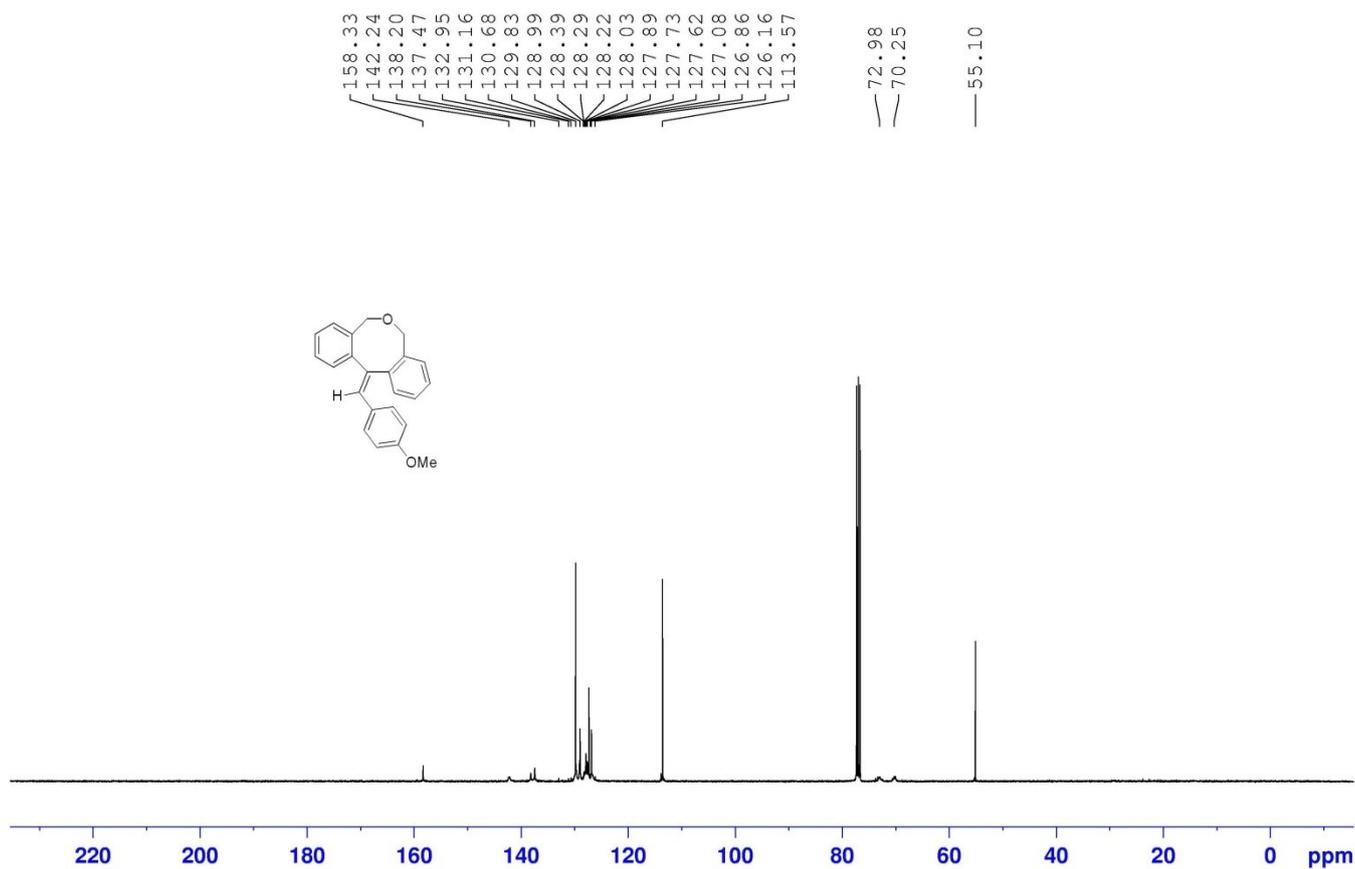
¹H and ¹³C spectra of compound 8b:



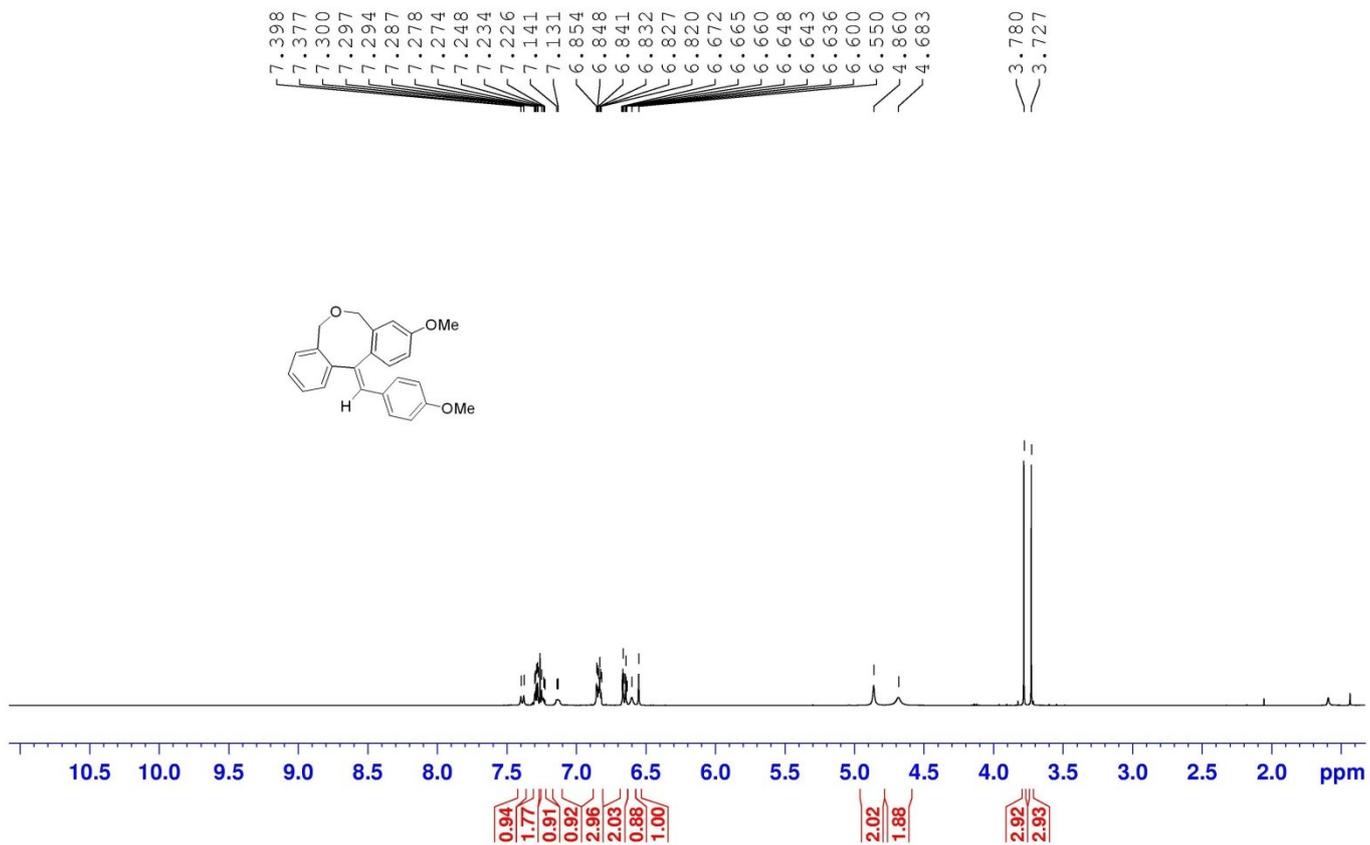


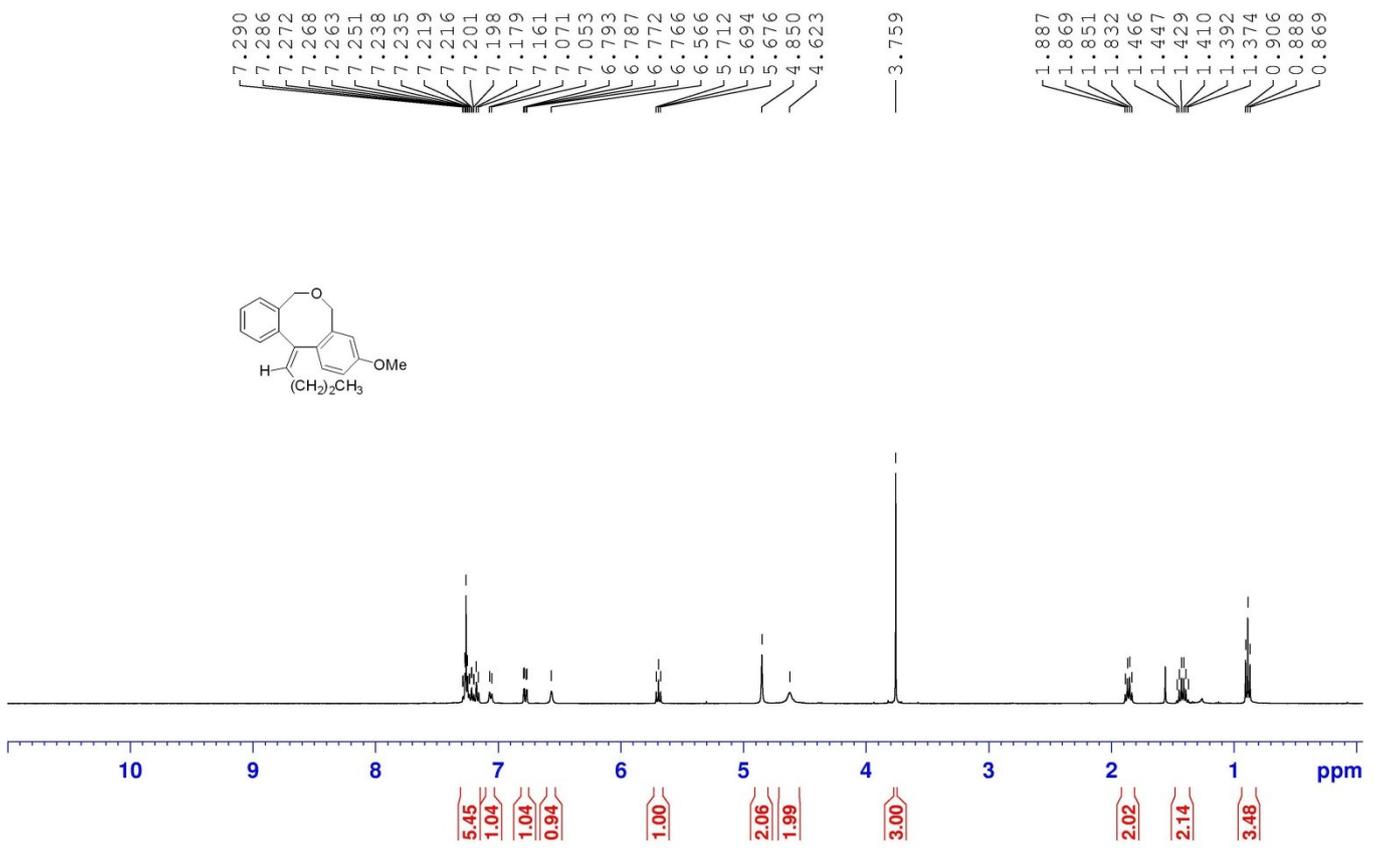
¹H and ¹³C spectra of compound 8c:

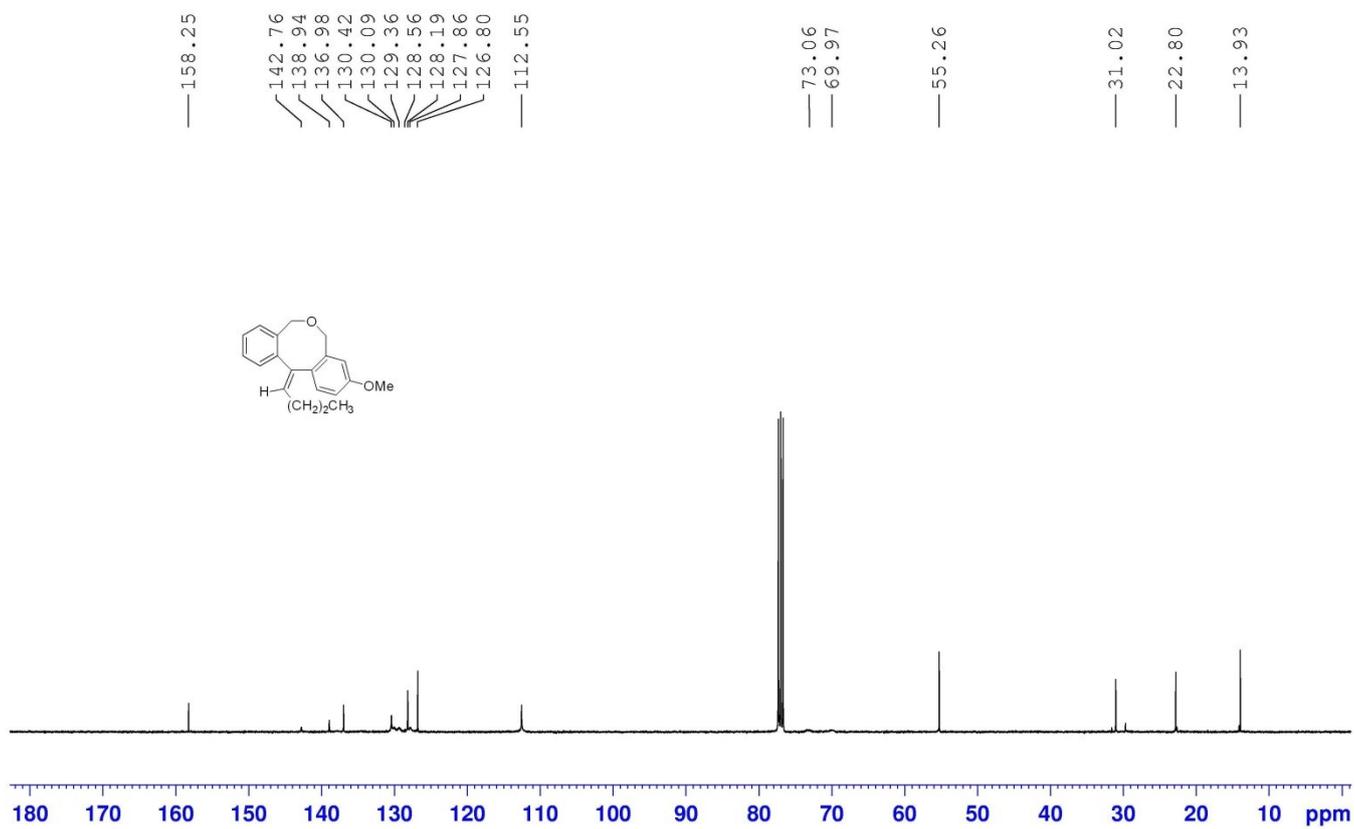




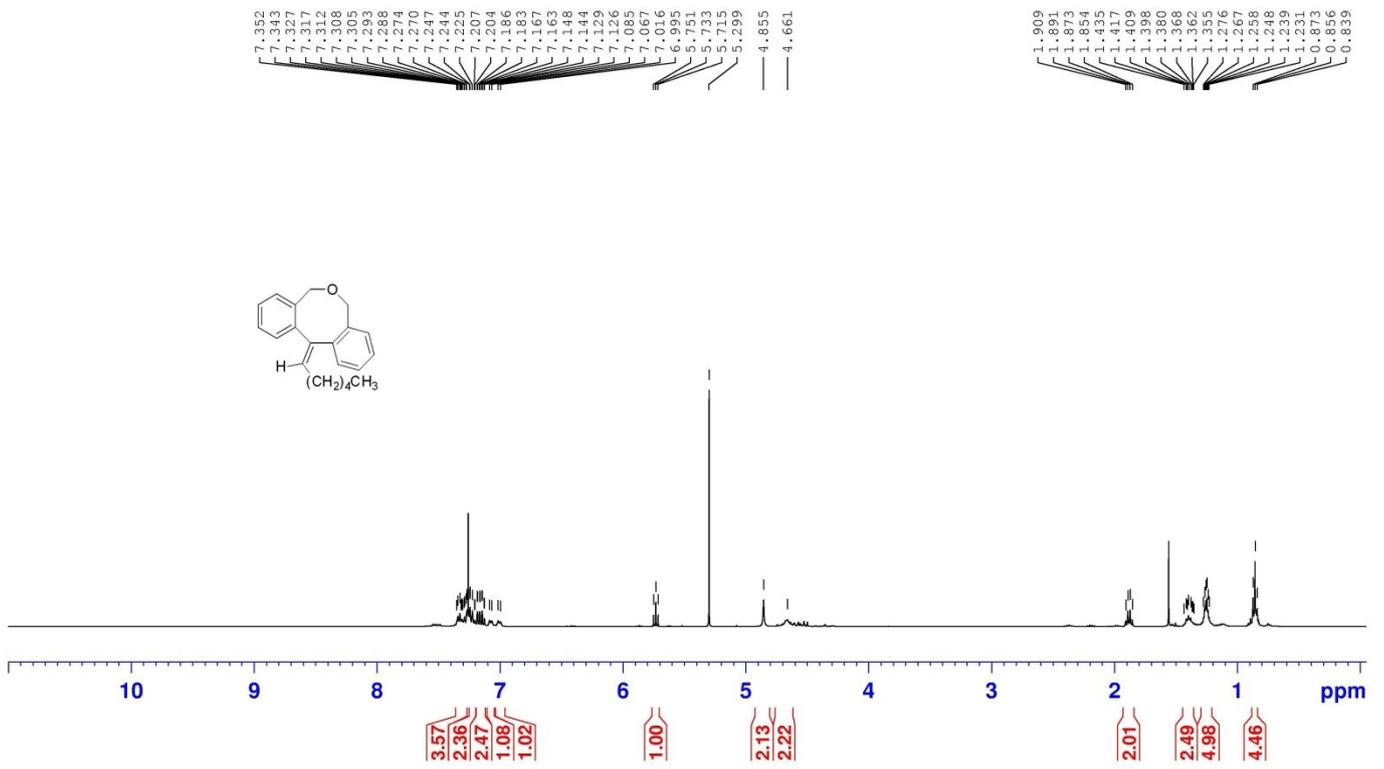
¹H and ¹³C spectra of compound 8d:

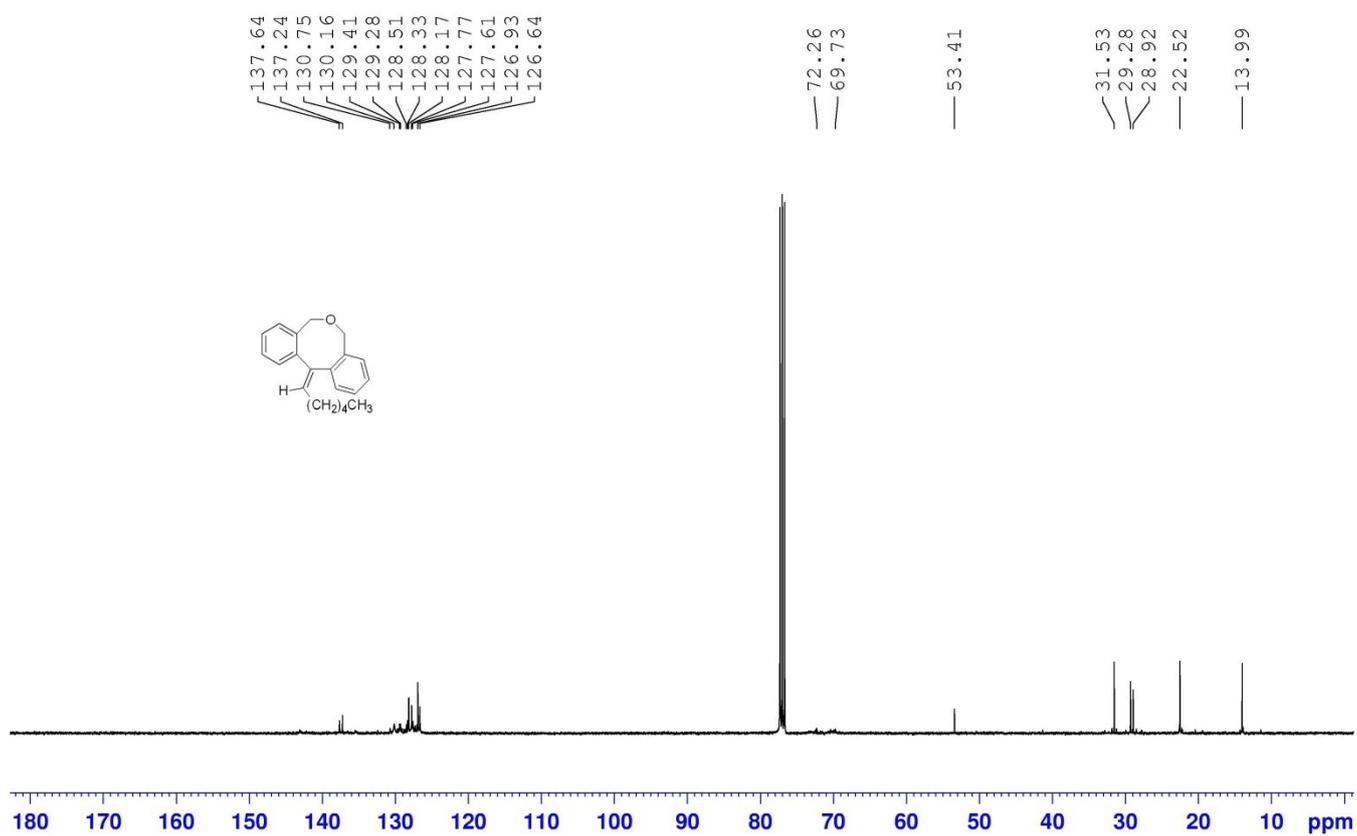




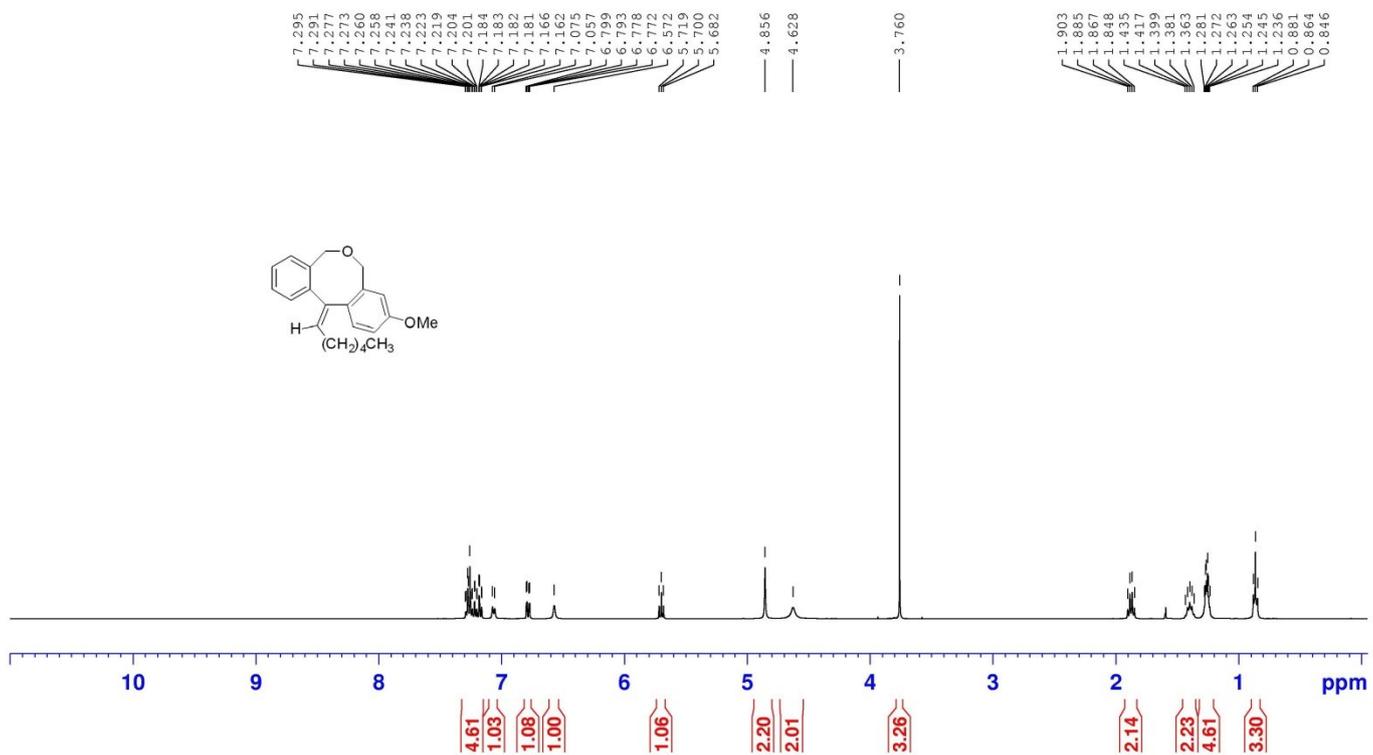


¹H and ¹³C spectra of compound 8f:





^1H and ^{13}C spectra of compound 8g:

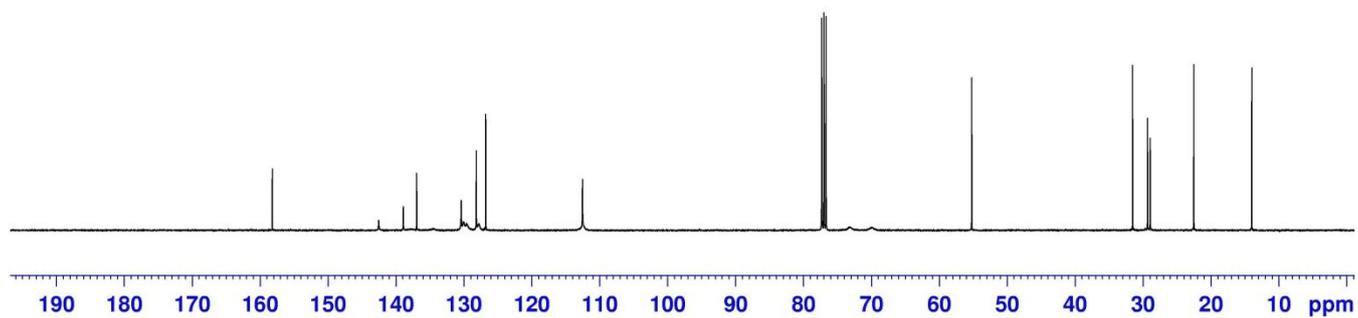
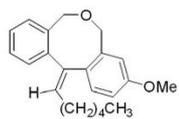


— 158.23
142.54
138.93
136.97
134.60
130.40
130.03
129.60
128.17
127.79
126.80
— 112.54

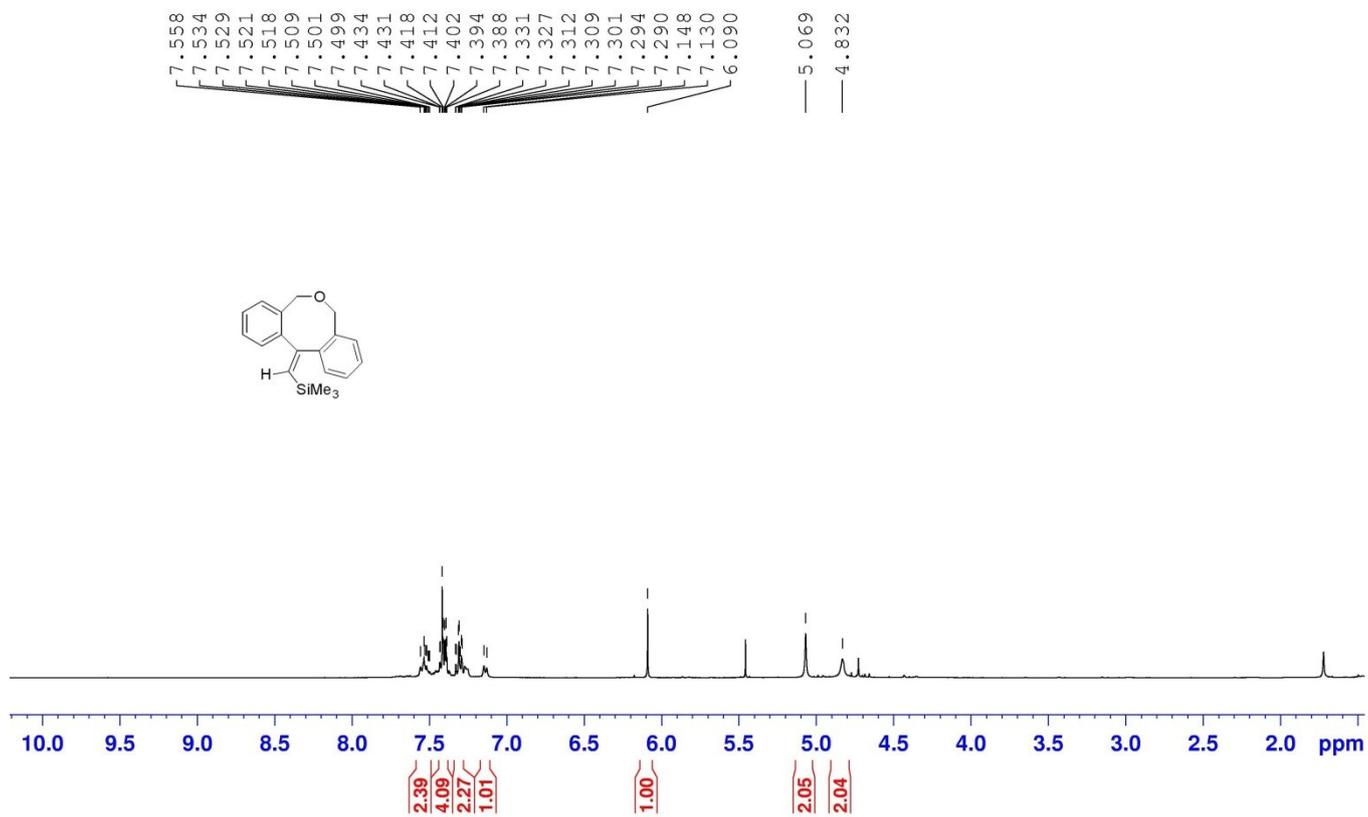
— 73.17
— 69.88

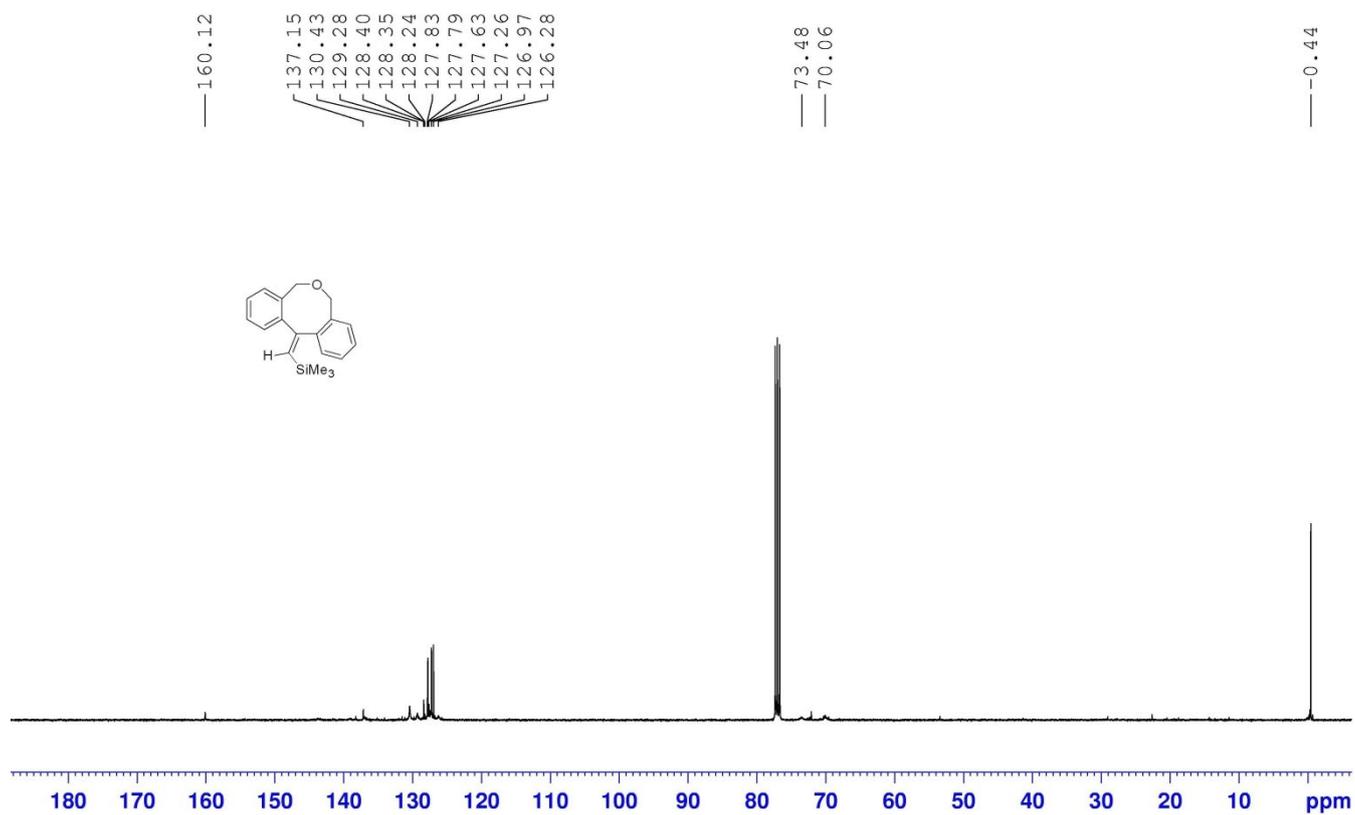
— 55.23

31.52
29.32
28.93
— 22.51
— 13.98

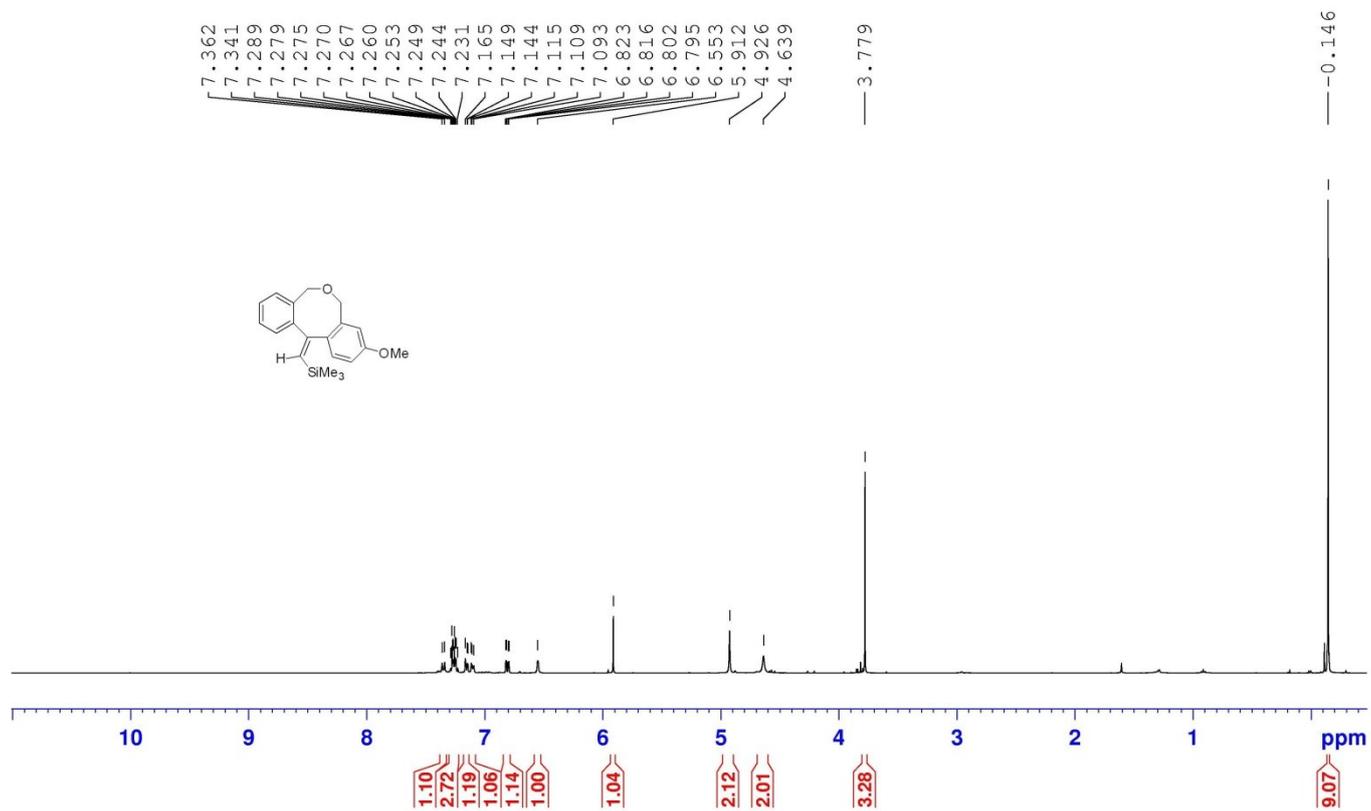


¹H and ¹³C spectra of compound 8h:





^1H and ^{13}C spectra of compound 8i:



159.72
158.48
138.36
136.85
130.37
129.64
129.40
127.80
127.37
127.13
126.83
112.77
112.62
111.87

73.54
69.86

55.25

-0.42

