General Strategy for the Diverse Syntheses of Anhydrolandomycinone, Tetrangulol, and Landomycinone

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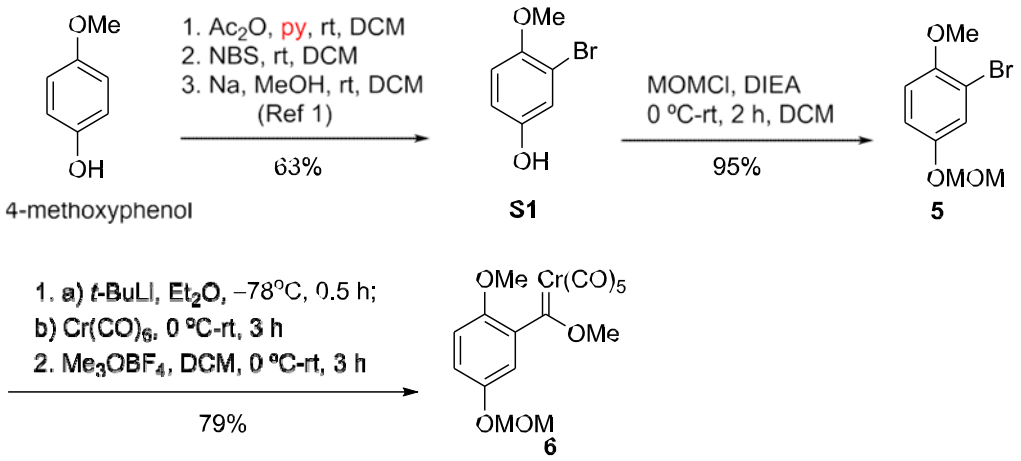
1. General Experimental

All the reactions were performed in oven- or flame-dried flasks under the nitrogen or argon atmosphere if anhydrous conditions were required. Reagents were purchased from Acros®, Alfa Aeser®, Sigma Aldrich® and some local chemical companies and used directly as supplied. Anhydrous solvents were used for the reactions unless otherwise stated. Aluminum plates (60 F-254) coated with silica-gel obtained from Merck were used for thin layer chromatography (TLC). Compounds were visualized under ultraviolet (UV) light and by staining with phosphomolybdic acid (PMA), or by *p*-anisaldehyde solution. Silica-gel (100-200 mesh) was used for flash column chromatography to purify all the compounds using head pressure by air releasing pump. 0.063-0.200 mm Silica gel for column chromatography was obtained from Merck (Geduran Si-60). Distilled solvents were used for purification of all compounds. ^{1}H NMR spectra were recorded on Varian UI (400 MHz) or Varian UI (600 MHz) spectrometers in $CDCl_3$ or Acetone-d_6 or DMSO-d_6 or Benzene-d_6 at ambient temperature. Chemical shifts of ^{1}H NMR spectra were reported to two decimal places in parts per million (ppm) with splitting recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin) and multiplet (m). Coupling constants, *J*, are calculated to one decimal in Hertz (Hz). ^{13}C NMR spectra were recorded on Varian (100 MHz) or Varian (150 MHz) spectrometers in $CDCl_3$ or Acetone-d_6 or DMSO-d_6 or Benzene-d_6 at ambient temperature with broadband decoupling. Chemical shifts of ^{13}C NMR spectra were reported to one decimal in ppm. All NMR chemical shifts were referenced to residual solvent peaks ($CDCl_3$: δ_H 7.26, δ_C 77.1; Acetone-d_6: δ_H 2.05, δ_C 29.8; DMSO-d_6: δ_H 2.50, δ_C 39.5; Benzene-d_6: δ_H 7.16, δ_C 128.0). High-resolution mass spectra were recorded on Joel Accurate Mass Q-Tof GCX instrument for electrospray ionization (ESI) and are reported as a ratio of mass to charge (*m/z*) in Daltons.

2. Experimental Section

2.1 Preparation of [(2-methoxy-5-methoxymethoxyphenyl)methoxymethylene] pentacarbonylchromium (6)

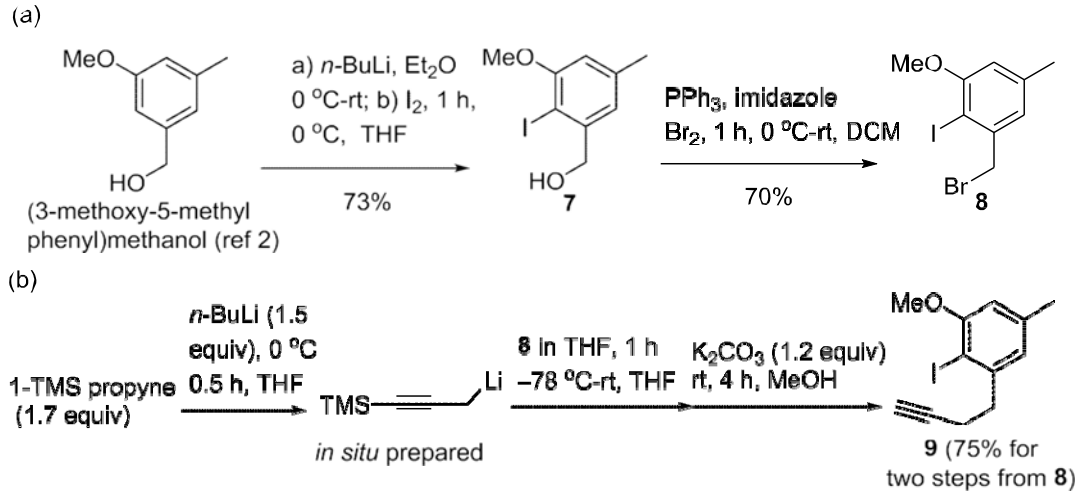


1-Bromo-2-methoxy-5-methoxymethoxybenzene 5. To the solution of 3-bromo-4-methoxyphenol[1] **S1** (10 g, 49.25 mmol) in dichloromethane (DCM) (175 mL) were added *N*,*N*-diisopropylethylamine (DIEA) (12.0 mL, 68.95 mmol), chloromethyl methyl ether (MOMCl) (4.1 mL, 54.17 mmol) dropwise at 0 °C. Then, the solution was raised to rt and stirred for 2 h. After completion of the reaction, the reaction mixture was diluted with DCM (100 mL), washed with satd. $NaHCO_3$ (100 mL), water (100 mL), brine (100 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo* for purification by flash silica-gel column chromatography (Elution: 5% EtOAc in hexanes) to furnish the product **5** (11.5 g, 95%) as colorless oil. **Analytical data for 5:** R_f = 0.43 (5% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.28 (d, J = 3.2 Hz, 1H), 6.96 (dd, J = 9.2 Hz, J = 3.2 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 5.09 (s, 2H), 3.84 (s, 3H), 3.46 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 151.5, 151.3, 121.9, 116.3, 112.6, 111.8, 95.3, 56.7, 56.0.

[(2-Methoxy-5-methoxymethoxyphenyl)methoxymethylene]pentacarbonylchromium 6. To the solution of **5** (5 g, 20.23 mmol) in ether (38 mL), *t*-butyl lithium solution (*t*-BuLi) (1.6 M in pentane, 13.9 mL, 22.25 mmol) was added dropwise at –78 °C. After 20 min, it was transferred to another cooled (0 °C) solution containing chromium hexacarbonyl ($Cr(CO)_6$, 5.34 g, 24.27 mmol) in ether (38 mL) *via* cannula. The resulting mixture was stirred at rt for 3 h. Then, ether

was evaporated under *vacuo* and the residue was dissolved in DCM (63 mL). To this suspension, trimethyloxonium tetrafluoroborate (4.93 g, 33.34 mmol) was added at 0 °C. Then, the reaction mixture was raised to rt and stirred for 3 h. The dark red solution was concentrated under *vacuo* to give the residue which on purification by flash silica-gel column chromatography (10 to 15% EtOAc in hexanes) furnish the title product **6** (6.4 g, 79%) as dark red solid. R_f = 0.27 (5% EtOAc in Hexanes), which was used for the Dötz benzannulation.

2.2 Synthesis of 1-(3-butynyl)-2-iodo-3-methoxy-5-methylbenzene 9



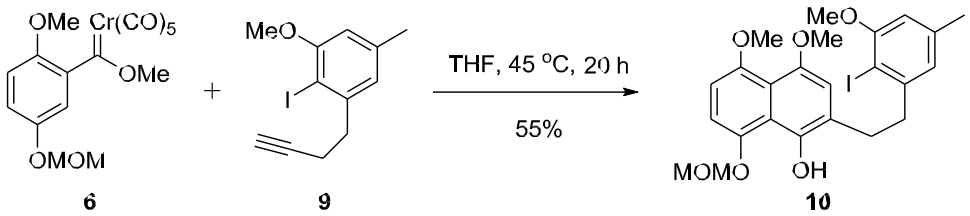
(2-Iodo-3-methoxy-5-methylphenyl)methanol 7: To the solution of (3-methoxy-5-methylphenyl)methanol (9 g, 59.13 mmol) in ether (383 mL), *n*-BuLi (1.6 M solution in hexanes, 92 mL, 0.14 mol) was added at 0 °C under N_2. After being stirred at rt for 4 h, the solution was cooled to 0 °C. Then, THF (120 mL) was added to the solution and the reaction mixture was stirred for 1 h, followed by the slow addition of I_2 (19.5 g, 76.86 mmol) dissolved in THF (60 mL). After being stirred at 0 °C for 30 min, the reaction mixture was poured into 20% $Na_2S_2O_{3(aq)}$ (200 mL). The organic layer was separated and washed with brine (150 mL), dried over $MgSO_4$, and concentrated in *vacuo*. The crystallization of crude residue with EtOAc/hexanes furnished product **7** (12.0 g, 73%) as white crystalline.[3] **Analytical data for 7:** R_f = 0.43 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 6.90 (m, 1H), 6.58 (d, *J* = 0.8 Hz, 1H), 4.64 (s, 2H), 3.86 (s, 3H), 2.33 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 157.8, 144.0, 139.7, 121.9, 111.2, 85.4, 69.6, 56.5, 21.4.

1-(Bromomethyl)-2-iodo-3-methoxy-5-methylbenzene 8: To a solution of triphenylphosphine (PPh_3) (6.5 g, 24.81 mmol) and imidazole (2.9 g, 43.14 mmol) in DCM (108 mL), bromine (Br_2) (1.25 mL, 24.6 mmol) was added in dropwise at 0 ºC. Supplementary amount of PPh_3 was added to complete conversion of Br_2 into Br_2–PPh_3 adduct. The solution of (2-iodo-3-methoxy-5-methylphenyl)methanol **7** (6 g, 21.57 mmol) in DCM (32 mL) was added to the above solution dropwise at 0 ºC. Then, the reaction mixture was stirred for 1 h at rt and quenched with satd. NH_4Cl (100 mL). The aqueous layer was extracted with DCM (50 mL × 2) and the combined organic layers were washed with satd. NH_4Cl (50 mL), brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo*. The crude solid was triturated with 15% EtOAc in hexanes (300 mL). Filtered off unwanted solid and the resulting filtrate was concentrated to furnish methylbenzene **8** (5.1 g, 70%) as a white glassy solid. **Analytical data for 8:** R_f = 0.75 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 6.93 (d, *J* = 1.2 Hz, 1H), 6.55 (d, *J* = 1.2 Hz, 1H), 4.62 (s, 2H), 3.85 (s, 3H), 2.32 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 158.3, 141.3, 139.8, 123.6, 111.8, 88.5, 56.6, 39.5, 21.2.

1-(3-Butynyl)-2-iodo-3-methoxy-5-methylbenzene 9: A solution of 1-TMS-propyne (3.32 mL, 22.4 mmol) in dry THF (40 mL) was treated dropwise with *n*-BuLi (1.6 M solution in hexanes, 12.3 mL, 19.8 mmol) at 0 ºC. The solution was stirred for 20-30 min, and transferred via cannula to another solution of **8** (from preceding step, 4.5 g, 13.2 mmol) in THF (16 mL) while maintaining at –78 ºC. After stirring at –78 ºC for 1 h, the reaction was allowed to reach rt and stirred for 1 h (TLC: R_f = 0.6, 10% EtOAc in Hexanes). The reaction was quenched with 5% HCl and the volatiles were removed under *vacuo*. The reaction was extracted with ether (50 mL × 3) and the combined organic layers were washed with water, brine and dried over $MgSO_4$. The mixture was filtered and evaporated to give crude TMS-protected alkyne which was used for next step without purification. The solution of TMS-protected alkyne in methanol (40 mL) was treated with K_2CO_3 (2.18 g, 15.82 mmol) and stirred for 4 h at room temperature. The reaction mixture was quenched with water (50 mL) and extracted with EtOAc (50 mL × 3). The combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude

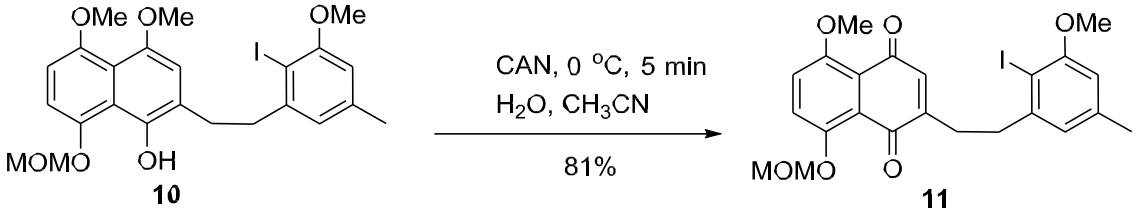
product was purified by flash silica-gel chromatography with 5% DCM in hexanes to furnish methylbenzene **9** (2.97 g, 75%) as a semi solid. **Analytical data for 9:** R_f = 0.53 (10% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 6.75 (d, *J* = 1.2 Hz, 1H), 6.51 (d, *J* = 1.2 Hz, 1H), 3.86 (s, 3H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.49 (td, *J* = 8.0 Hz, *J* = 2.8 Hz, 2H), 2.32 (s, 3H), 2.00 (t, *J* = 2.4 Hz, 1H); **δ_C (100 MHz, $CDCl_3$):** 158.1, 144.3, 139.2, 123.2, 110.1, 88.5, 83.5, 69.0, 56.5, 40.0, 21.4, 19.2; **HRMS (ESI)**: calcd for $C_{12}H_{14}IO^+$ $[M + H]^+$ 301.0084, found *m*/*z* 301.0086.

2.3 2-(2-Iodo-3-methoxy-5-methylphenethyl)-4,5-dimethoxy-8-(methoxymethoxy) naphthalen-1-ol (10)



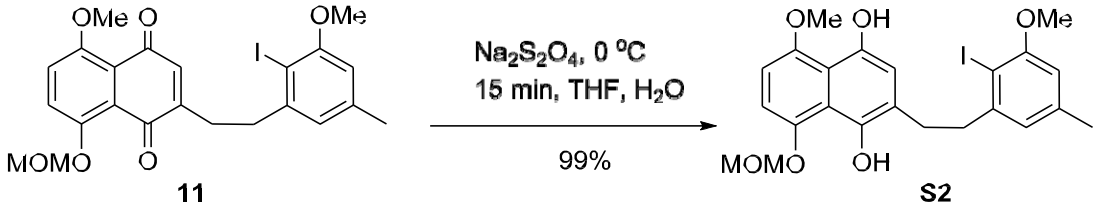
Chromium carbene **6** (3.01 g, 7.48 mmol) and alkyl alkyne **9** (2.69 g, 8.97 mmol) were mixed with anhydrous THF (185 mL) under N_2. The resulting dark red suspension was stirred for 20 h at 45 °C. Then, the solvent was evaporated under *vacuo* to give residue which on flash silica-gel chromatography with 20 to 25% EtOAc in hexanes provided naphthalen-1-ol product **10** (2.21 g, 55%) as light brown solid. **Analytical data for 10:** R_f = 0.3 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 9.66 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.83 (s, 1H), 6.76 (s, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.50 (s, 1H), 5.37 (s, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.59 (s, 3H), 3.14 – 3.08 (m, 2H), 3.02 – 2.98 (m, 2H), 2.29 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 158.0, 152.6, 149.1, 147.7, 146.4, 145.6, 139.1, 123.24, 123.20, 119.0, 117.7, 113.7, 109.6, 109.2, 105.7, 96.7, 88.8, 58.4, 57.2, 56.8, 56.5, 41.1, 31.1, 21.3; **HRMS (ESI)**: calcd for $C_{24}H_{27}INaO_6^+$ $[M + Na]^+$ 561.0745, found *m*/*z* 561.0739.

2.4 2-(2-Iodo-3-methoxy-5-methylphenethyl)-5-methoxy-8-(methoxymethoxy) naphthalene-1,4-dione (11):



A solution of **10** (2.1 g, 3.90 mmol) in CH_3CN (42 mL) was treated with cooled (0 °C) solution of ceric ammonium nitrate (1.49 g, 2.73 mmol) in H_2O (42 mL) at 0 °C. After stirring for 5 min at 0 °C, the reaction mixture was extracted with EtOAc (75 mL × 2). The combined organic layers were washed with satd. $NaHCO_3$ (100 mL), H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo* to give the crude residue for purification with flash silica-gel column chromatography (40 to 50% EtOAc in hexanes) to obtain naphthalene-1,4-dione **11** (1.65 g, 81%) as an orange glassy solid. **Analytical date for 11:** R_f = 0.25 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.48 (d, *J* = 9.6 Hz, 1H), 7.23 (d, *J* = 9.2 Hz, 1H), 6.68 (d, *J* = 1.2 Hz, 1H), 6.58 (s, 1H), 6.46 (d, *J* = 1.6 Hz, 1H), 5.24 (s, 2H), 3.93 (s, 3H), 3.82 (s, 3H), 3.54 (s, 3H), 2.98 – 2.94 (m, 2H), 2.77 – 2.72 (m, 2H), 2.25 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 184.9, 184.6, 158.0, 154.6, 150.9, 149.2, 144.8, 139.3, 135.5, 125.6, 123.1, 123.0, 120.9, 119.5, 109.9, 96.3, 88.6, 56.8, 56.6, 56.4, 39.3, 30.0, 21.2; **HRMS (ESI)**: calcd for $C_{23}H_{23}INaO_6^+$ $[M + Na]^+$ 545.0432, found *m*/*z* 545.0432.

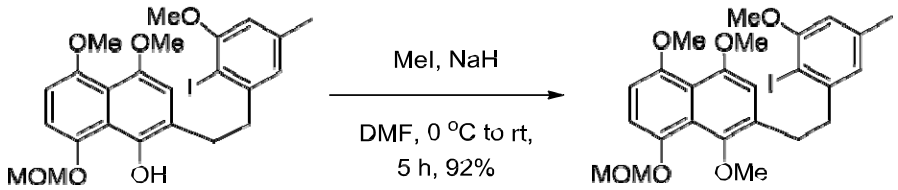
2.5 2-(2-Iodo-3-methoxy-5-methylphenethyl)-5-methoxy-8-(methoxymethoxy)naphthalen-1,2-diol (S2)



A solution of naphthalene-1,4-dione **11** (1.5 g, 2.87 mmol) in THF (57 mL) was treated with a solution of sodium dithionite (2.0 g, 11.48 mmol) in H_2O (57 mL) at 0 °C. After stirring for 15 min at same temperature, the solution was extracted with EtOAc (75 mL × 2). The combined

organic layers were washed with H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo* to give reduced naphthalene-1,2-diol **S2** (99% yield), which was used directly for hydroxyl protection. **Analytical data for S2:** R_f = 0.51 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 9.32 (s, 1H), 9.04 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 6.81 (d, *J* = 1.2 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 1.2 Hz, 1H), 5.36 (s, 2H), 3.99 (s, 3H), 3.87 (s, 3H), 3.58 (s, 3H), 3.10 – 3.05 (m, 2H), 2.99 – 2.94 (m, 2H), 2.32 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 158.0, 151.8, 148.4, 146.6, 146.5, 143.9, 139.1, 125.3, 123., 116.7, 115.2, 114.3, 109.6, 107.8, 102.7, 96.5, 88.7, 56.8, 56.5, 56.4, 41.2, 31.0, 21.3. This hydroquinone intermediate is unstable for mass spectrometry analysis.

2.6 2-(2-Iodo-3-methoxy-5-methylphenethyl)-1,4,5-trimethoxy-8-(methoxymethoxy) naphthalene (12a)

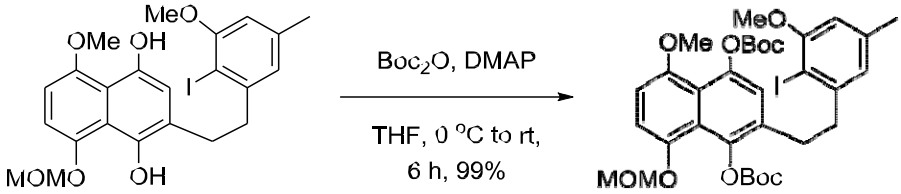


10 **12a**

Naphthalenetetrol substrate 12a: A solution of **10** (200 mg, 0.37 mmol) in DMF (7.5 mL) was treated slowly with 60% NaH in mineral oil (30 mg, 0.74 mmol) and MeI (35 µL, 0.55 mmol) at 0 ºC. The resulting reaction mixture was raised to rt and stirred for 5 h. Then, quenched with iced water (25 mL) and extracted with EtOAc (25mL × 2). The combined organic layers were washed with water (25 mL), brine (25 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography (Elution: DCM/EtOAc/hexanes, 4/0.5/5.5 gradient to 4/1/5) to afford naphthalenetetrol **12a** (188 mg, 92%) as a light brown solid. **Analytical data for 12a:** R_f = 0.32 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.11 (d, *J* = 8.8 Hz, 1H), 6.81 (s, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 1.2 Hz, 1H), 6.50 (d, *J* = 1.2 Hz, 1H), 5.17 (s, 2H), 3.914 (s, 3H), 3.908 (s, 3H), 3.88 (s, 3H), 3.78 (s, 3H), 3.61 (s, 3H), 3.13 – 3.09 (m, 2H), 3.06 – 3.02 (m, 2H), 2.29 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 158.0, 153.13, 153.11, 147.0, 146.6, 146.0, 139.1, 131.7,

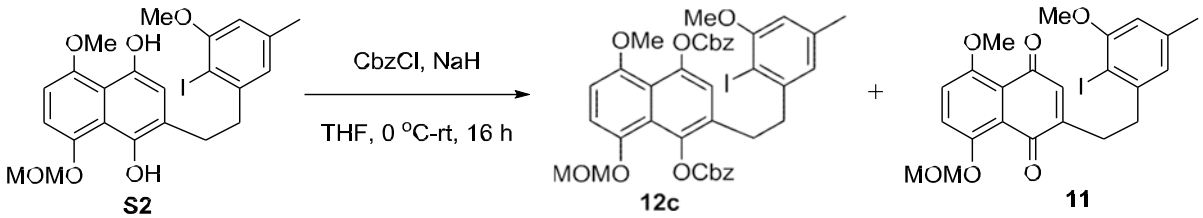
123.8, 123.2, 119.6, 115.8, 110.0, 109.7, 106.9, 98.0, 88.7, 62.4, 57.3, 57.2, 56.5, 56.4, 42.3, 30.7, 21.3; **HRMS (ESI)**: calcd for $C_{25}H_{29}INaO_6^+$ $[M + Na]^+$ 575.0901, found *m*/*z* 575.0900.

2.7 2-(2-Iodo-3-methoxy-5-methylphenethyl)-5-methoxy-8-(methoxymethoxy)naphthalene-1,4-diyl Bis(*t*-butylcarbonate) (12b)



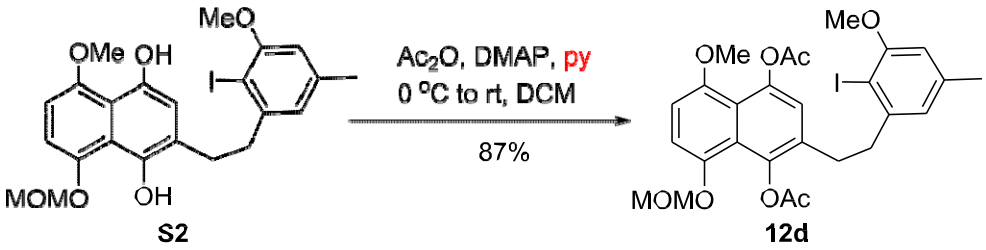
Naphthalenetetrol substrate 12b: To a solution of **S2** (385 mg, 0.73 mmol) in THF (10 mL) were added 4-dimethylaminopyridine (9 mg, 0.07 mmol) and di-*tert*-butyl dicarbonate (630 μL, 2.93 mmol) at 0 °C. After stirring 6 h at rt, the reaction was quenched with satd. NH_4Cl (50 mL) and extracted with EtOAc (50 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography with 30% EtOAc in hexanes to give precursor **12b** (526 mg, 99%) as a white foamy substance. **Analytical data for 12b**: R_f = 0.48 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.11 (d, *J* = 8.8 Hz, 1H), 7.08 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 1.2 Hz, 1H), 6.49 (d, *J* = 1.6 Hz, 1H), 5.23 (bs, 1H), 5.12 (bs, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.57 (s, 3H), 3.04 – 2.85 (m, 4H), 2.27 (s, 3H), 1.57 (s, 18H); **δ_C (100 MHz, $CDCl_3$):** 158.1, 152.2, 151.0, 146.5, 145.6, 144.4, 143.0, 141.9, 139.3, 131.8, 123.4, 123.0, 121.7, 120.5, 114.8, 109.8, 106.3, 97.2, 88.4, 82.9, 82.8, 56.6, 56.5, 56.3, 41.4, 30.9, 28.0, 27.9, 21.3; **HRMS (ESI)**: calcd for $C_{33}H_{41}INaO_{10}^+$ $[M + Na]^+$ 747.1637, found *m*/*z* 747.1643.

2.8 2-(2-Iodo-3-methoxy-5-methylphenethyl)-5-methoxy-8-(methoxymethoxy)naphthalene-1,4-diyl Bis(benzylcarbonate) (12c)



Naphthalenetetrol substrate 12c: A solution of **S2** (1.05 g, 2.00 mmol) in THF (20 mL) was treated with 60% NaH in mineral oil (0.96 g, 24.02 mmol) at 0 °C. After stirring for 30 min at 0 °C, benzyl chloroformate (3.42 mL, 24.02 mmol) was added. The resulting suspension was warmed to rt and stirred for 16 h. Then, the reaction was slowly quenched with ice and extracted with EtOAc (100 mL × 2). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The flash silica-gel column chromatography (20 to 30% EtOAc in hexanes) of crude residue provided protected naphthalenetetrol **12c** (1.3 g, 70%, recovery yield) along with naphthalenedione **11** (0.27 g, 26%) as a white foamy substance and orange solids respectively. **Analytical data for 12c:** R_f = 0.46 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.54 – 7.33 (m, 10H), 7.16 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 6.63 (d, *J* = 0.8 Hz, 1H), 6.51 (d, *J* = 1.2 Hz, 1H), 5.40 – 5.26 (m, 4H), 5.06 (bs, 1H), 4.89 (bs, 1H), 3.88 (s, 3H), 3.58 (s, 3H), 3.43 (s, 3H), 3.14 – 2.79 (m, 4H), 2.28 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 158.0, 153.8, 150.5, 146.3, 145.3, 144.7, 142.1, 139.3, 135.12, 135.08, 131.7, 129.0, 128.74, 128.67, 128.64, 128.59, 123.2, 122.4, 121.3, 120.1, 113.6, 109.9, 106.5, 96.3, 88.3, 70.27, 70.25, 56.5, 56.10, 56.05, 41.4, 30.8, 21.3; **HRMS (ESI)**: calcd for $C_{39}H_{37}INaO_{10}^+$ $[M + Na]^+$ 815.1324, found *m/z* 815.1322.

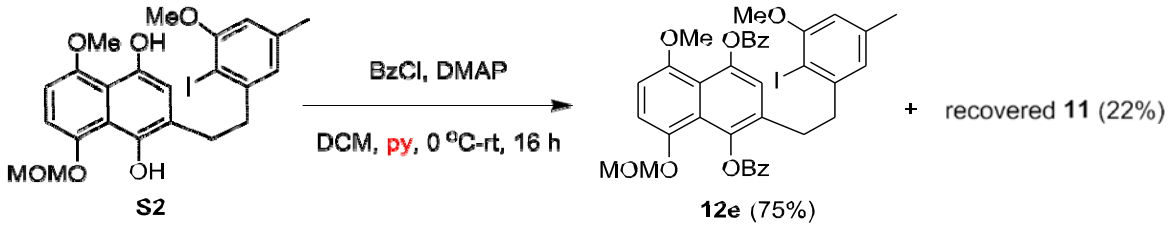
2.9 2-(2-Iodo-3-methoxy-5-methylphenethyl)-5-methoxy-8-(methoxymethoxy)-naphthalene-1,4-diyl Diacetate (12d)



Naphthalenetetrol substrate (12d): A solution of **S2** (178 mg, 0.34 mmol) in 3:1 DCM:pyridine (7.6 mL) was treated with DMAP (15 mg) and acetic anhydride (0.25 mL, 2.64 mmol) at 0 °C. Then, the reaction was allowed to reach rt and stirred for 1 h. The reaction was quenched with 5% HCl and extracted with DCM (20 mL × 2). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under

vacuo. The crude residue was purified by flash silica-gel column chromatography (Elution: 25% gradient to 30% EtOAc in hexanes) to give product **12d** (180 mg, 87%) as yellow solid. **Analytical data for 12d:** R_f = 0.41 (40% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.08 – 7.01 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 0.8 Hz, 1H), 6.49 (s, 1H), 5.15 (d, *J* = 5.6 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.51 (s, 3H), 3.10 – 2.94 (m, 2H), 2.94 – 2.83 (m, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 170.0, 169.7, 158.0, 150.4, 146.2, 145.4, 144.1, 141.4, 139.3, 131.4, 123.1, 122.3, 121.4, 120.2, 112.6, 109.8, 106.4, 96.4, 88.3, 56.6, 56.4, 56.2, 41.4, 30.8, 21.2, 21.1, 20.9; **HRMS (ESI)**: calcd for $C_{27}H_{29}INaO_8^+$ $[M + Na]^+$ 631.0799, found *m*/*z* 631.0800.

2.10 2-(2-Iodo-3-methoxy-5-methylphenethyl)-5-methoxy-8-(methoxymethoxy)-naphthalene-1,4-diyl Dibenzoate (12e)

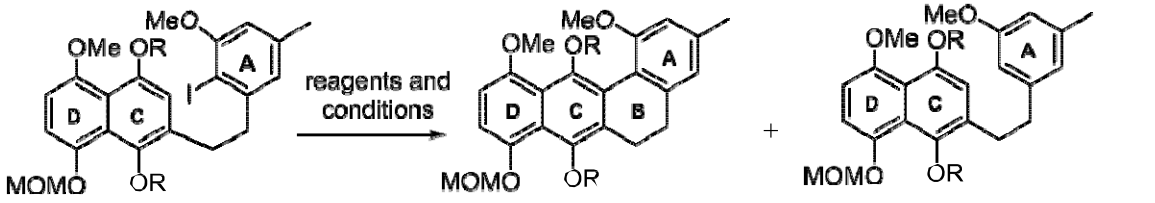


Naphthalenetetrol substrate 12e: To a solution of **S2** (278 mg, 0.53 mmol) in 3:1 DCM:pyridine (10.4 mL) were added DMAP (525 mg, 4.24 mmol) and benzoyl chloride (0.5 mL, 4.24 mmol) at 0 °C. The resulting white reaction mixture was warmed to rt and stirred for 16 h. Then, the reaction mixture was diluted with DCM (100 mL), washed with aqueous 1 N HCl solution (50 mL × 2), water (50 mL), brine (50 mL), and ried over Na_2SO_4. The crude products were purified by flash silica-gel column chromatography (Elution: 4/5.4/0.6, DCM/hexanes/EtOAc) to provide precursor **12e** (291 mg, 75%) along with naphthalenedione **11** (60 mg, 22%) as a white and an orange foamy substances respectively. **Analytical data for 12e**: R_f = 0.51 (4/5.3/0.7, DCM/hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 8.36 – 8.26 (m, 4H), 7.71 – 7.62 (m, 2H), 7.61 – 7.53 (m, 4H), 7.23 (s, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 1.2 Hz, 1H), 6.43 (d, *J* = 1.6 Hz, 1H), 4.82 (m, 2H), 3.82 (s, 3H), 3.52 (s, 3H), 3.16 (s, 3H), 3.15 – 2.91 (m, 4H), 2.16 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 165.9, 165.5, 158.0, 150.4, 146.7, 145.7, 144.7, 142.0, 139.3, 133.4, 133.2, 132.0, 130.5, 130.4, 128.6, 128.5, 123.3, 122.3, 121.9,

120.5, 111.5, 109.8, 106.3, 95.5, 88.4, 56.5, 56.2, 55.8, 41.8, 31.3, 21.2; **HRMS (ESI)**: calcd for $C_{37}H_{33}INaO_8^+$ $[M + Na]^+$ 755.1112, found *m*/*z* 755.1182.

2.11 Pd-catalyzed arylation

2.11.1 1,7,12-Trimethoxy-8-methoxymethoxy-3-methyl-5,6-dihydrobenz[*a*]anthracene (13a), 1,11-Dimethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Dicarbonates (13b, 13c), and 1,11-Dimethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Diacylates (13d, 13e)



12a, R = Me
12b, R = Boc
12c, R = Cbz
12d, R = Ac
12e, R = Bz

13a, R = Me
13b, R = Boc
13c, R = Cbz
13d, R = Ac
13e, R = Bz

14a, R = Me
14b, R = Boc
14c, R = Cbz (not isolated)
14d, R = Ac (not isolated)
14e, R = Bz (not isolated)

A thick glass reaction vessel was charged with protected naphthalenediol substrate (**12a**, **12b**, **12c, 12d,** or **12e,** 1.0 equiv.) and $NaHCO_3$(s) (12 equiv. w.r.t. $Pd(OAc)_2$). Then, added anhydrous *N*,*N*-dimethylacetamide to a naphthalenediol substrate (final concentration = 12 mM) and the solution was stirred for 10 min at rt under N_2. A pre-mixed solution of palladium acetate [$Pd(OAc)_2$] (equiv. specified in Table 1 of the article), $PCy_3 \cdot HBF_4$ (2 equiv. w.r.t. Pd cat) and pivaloyl acid [4 equiv. w.r.t. $Pd(OAc)_2$] in anhydrous *N*,*N*-dimethylacetamide (DMA) (final concentration of the Pd(II) catalyst = 35 mM) was added dropwise to the mixture. The reaction mixture was stirred at 95 ºC for 10-24 h. Then, the reaction mixture was quenched with water and extracted with EtOAc (× 2). The combined organic layers were washed with water, brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo* for purification with flash silica-gel column chromatography (DCM/EtOAc/hexanes) to give the products **12a-12e**.

1,7,11,12-Tetramethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene 13a: R_f = 0.472 (4/5/1, DCM/hexanes/EtOAc). Due to the difficult separation of **14a** from **13a** by flash chromatography, only partially assigned proton NMR spectrum was reported. **δ_H (400 MHz,**

$CDCl_3$): 7.06 (d, *J* = 8.4 Hz, Ar*H* at D ring), 6.80 (d, *J* = 8.4 Hz, 1H Ar*H* of D ring), 6.77 – 6.75 (broad d, 2H, Ar*H* at A ring), 6.23 – 6.18 (broad dd, *J* = 6.0, 14.4 Hz, 2H, CH_2 of MOM), 3.94 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.61 (s, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.44 – 3.40 (broad d, 1H), 2.82 – 2.78 (broad d, 1H), 2.56 (broad dt, 1H), 2.40 (s, 3H, CH_3 at A ring), 2.37 (broad signal overlapped with the CH_3 signal at 2.40 ppm, 1H). **HRMS (ESI)**: calcd for $C_{25}H_{28}NaO_6^+$ $[M + Na]^+$ 447.1778, found *m*/*z* 447.1772.

14a is slightly less polar than **13a** and thus we were able to isolate some **14a** for NMR analysis. For **14a**, R_f = 0.475 (4/5/1, DCM/Hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 7.11 (d, *J* = 8.4 Hz, Ar*H* at D ring), 6.76 (d, *J* = 8.8 Hz, 1H Ar*H* at D ring), 6.69 (s, 2H, including an Ar*H* of A ring and quinone-*H* at C ring), 6.62 (bs, 1H, Ar*H* at A ring), 6.58 (bs, 1H, Ar*H* at A ring), 5.18 (s, 2H, OCH_2 of MOM), 3.91 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 3.61 (s, 3H, CH_3), 3.07 (dd, *J* = 9.2, 10.8 Hz, 2H, methylene-CH_2), 3.91 (dd, *J* = 9.2, 10.8 Hz, 2H, methylene-CH_2), 2.32 (s, 3H, CH_3 at A ring); **δ_C (100 MHz, $CDCl_3$):** 159.8, 153.2, 153.1, 147.0, 146.7, 143.5, 139.4, 132.2, 123.9, 121.9, 119.6, 115.7, 111.2, 111.3, 110.1, 106.9, 98.0, 62.3, 57.4, 57.3, 56.5, 55.2, 37.3, 32.1, 21.6. **HRMS (ESI)**: calcd for $C_{25}H_{30}NaO_6^+$ $[M + Na]^+$ 449.1935, found *m*/*z* 449.1925.

1,11-Dimethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Bis(*t*-butylcarbonate) 13b: R_f = 0.46 (4/5.4/0.6, DCM/Hexanes/EtOAc); **δ_H (400 MHz, Benzene-d_6):** 6.99 (d, *J* = 8.4 Hz, 1H, Ar*H* at C10), 6.62 (s, 1H, Ar*H* at C2), 6.52 (s, 1H, Ar*H* at C4), 6.40 (broad d, 1H, Ar*H* at C8), 5.16 (broad d, *J* = 21.6 Hz, 2H, OCH_2 of MOM), 3.72 (s, 3H, OCH_3 at C1), 3.50 (s, 3H, OCH_3 at C11), 3.43 (s, 3H, OCH_3 of MOM), 3.33 (broad m, 2H, CH_2 at B ring), 2.81 – 2.27 (broad m, 2H, CH_2 at B ring), 2.17 (s, 3H, CH_3 at A ring), 1.44 (s, 9H, *t*Butyl-*H* at C ring), 1.19 (bs, 9H, *t*Butyl-*H* at C ring); **δ_C (100 MHz, Benzene-d_6):** 158.0 (C1), 152.1, 151.6, 147.3, 142.5, 140.2, 138.9, 132.2, 125.5, 122.2, 121.9, 120.8 (C4), 118.7, 113.5 (C10), 111.6 (C2), 107.6 (C9), 97.0 (OCH_2 of MOM), 81.9, 80.9, 56.8, 56.1, 55.7, 30.4 (*C*H_2 at B ring), 27.8, 27.6, 23.9 (*C*H_2 at B ring), 21.6 (*C*H_3 at C3); **HRMS (ESI)**: calcd for $C_{33}H_{40}NaO_{10}^+$ $[M + Na]^+$ 619.2514, found *m*/*z* 619.2542.

For **14b**: R_f = 0.49 (4/5.4/0.6, DCM/Hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 7.11 (d, *J* = 8.4 Hz, 1H, Ar*H* at D ring), 7.03 (s, 1*H*, ArH, quinone ^{1}H at C ring), 6.74 (d, *J* = 8.8 Hz, 1H, Ar*H* at D ring), 6.67 (s, 1H, Ar*H* at A ring), 6.59 (bs, 1H, Ar*H* at A ring), 6.57 (bs, 1H, Ar*H*), 5.22 (broad s, 1H, OCH_2 of MOM), 5.13 (broad s, 1H, OCH_2 of MOM), 3.89 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 3.57 (s, 3H, CH_3), 2.87 (broad m, 4H, methylene C$H_2 \times 2$), 2.31 (s, 3H, CH_3 at A ring), 1.57 (s, 18H, *t*Bu*H* × 2); **δ_C (100 MHz, $CDCl_3$):** 159.8, 152.2, 151.0, 146.5, 144.5, 143.0, 141.8, 139.5, 132.2, 123.0, 121.9, 121.6, 120.5, 114.7, 112.5, 110.1, 106.3, 97.1, 82.92, 82.87, 56.6, 56.3, 55.2, 36.3, 32.6, 27.93, 27.91, 21.6; **HRMS (ESI)**: calcd for $C_{33}H_{42}NaO_{10}^+$ $[M + Na]^+$ 621.2670, found *m*/*z* 621.2672.

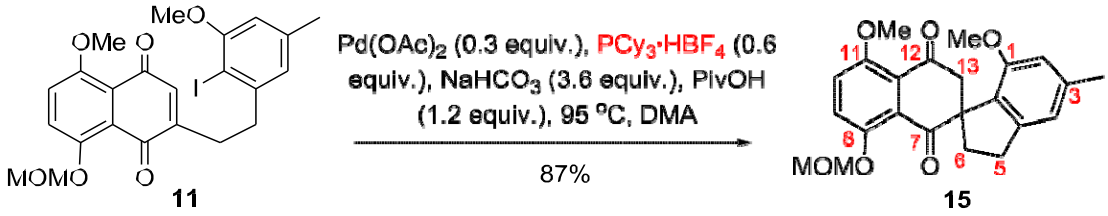
1,11-Dimethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Bis(benzylcarbonate) 13c: R_f = 0.59 (4/5/1, DCM/Hexanes/EtOAc); **HRMS (ESI)**: calcd for $C_{39}H_{36}NaO_{10}^+$ $[M + Na]^+$ 687.2201, found *m*/*z* 687.2215. ^{1}H and ^{13}C spectra for **13c** was completely indiscernible due to severe peak broadening and atypical splitting pattern.

1,11-Dimethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Diacetate 13d: R_f = 0.40 (30% EtOAc in hexane); **δ_H (600 MHz, $CDCl_3$):** 7.00 – 6.97 (broad m, 1H, Ar*H*), 6.70 – 6.69 (broad m, 3H, ArH), 5.17 – 5.09 (broad m, OCH_2 of MOM), 3.86 – 3.68 (broad m, 6H, OCH_3 × 2), 3.49 (s, 3H, OCH_3), 3.11 – 2.88 (broad m, 1H, CH_2 at B ring), 2.70 – 2.68 (broad d, 1H, CH_2 at B ring), 2.62 – 2.45 (broad m, 1H, CH_2 at B ring), 2.36 – 2.34 (broad m, 6H, CH_3 at A ring and CH_3C=O at C ring), 2.31 – 2.27 (broad m, 1H, CH_2 at B ring), 2.26 – 2.11 (broad d, 3H, CH_3C=O at C ring). Assignment of ^{13}C NMR spectrum for **13d** was difficult due to atypical splitting pattern. **HRMS (ESI)**: calcd for $C_{27}H_{28}NaO_8^+$ $[M + H]^+$ 503.1676, found *m*/*z* 503.1680.

1,11-Dimethoxy-8-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Dibenzoate 13e: R_f = 0.42 (4/5.4/0.6, DCM/hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 8.35 – 8.33 (d, *J* = 8.0 Hz, 4H, Ar*H* of Bz), 8.25 – 8.20 (m, 4H, Ar*H* of Bz), 7.69 – 7.48 (m, 12H, Ar*H* of Bz), 7.04 (t, *J* = 8.8 Hz, 2H, Ar*H*), 6.76 – 6.68 (m, 4H, Ar*H*), 6.56 (s, 1H, Ar*H* at A ring of one

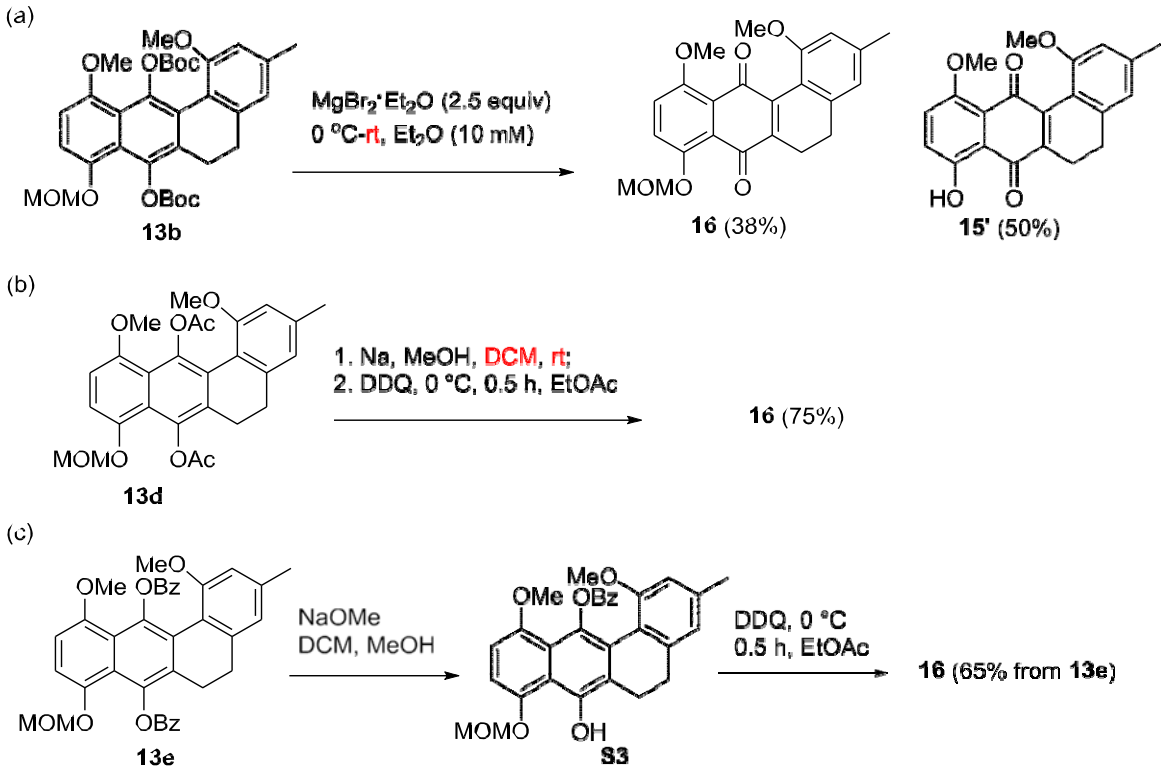
atropisomer), 6.49 (s, 1H, Ar*H* at A ring of other atropisomer), 5.17 – 5.09 (broad m, 4H, OCH_2 of MOM at two atropsiomers), 3.87 (splitting s, 3H, 3H, OCH_3 × 1), 3.55 (s, 3H, 3H, OCH_3 × 1), 3.49 (splitting s, 3H, OCH_3) 3.33 (broad s, 3H, OCH_3 × 1), 3.27 – 3.30 (broad d, 1H, CH_2 at B ring), 3.19 (broad s, 3H, OCH_3), 3.17 (broad s, 3H, OCH_3 × 1), 3.08 – 3.05 (broad d, 1H, CH_2 at B ring), 2.74 – 2.72 (broad m, 3H, CH_2 at B ring), 2.68 – 2.59 (broad m, 1H, CH_2 at B ring), 2.47 – 2.40 (broad m, 2H, CH_2 at B ring), 2.36 (s, 3H, CH_3 at C3 of one atropisomer), 2.29 (s, 3H, CH_3 at C3 of other atropisomer). The above spectroscopic data include the proton signals from the atropisomers of **13e**. Assignment of ^{13}C NMR spectrum for **13e** was difficult due to atypical splitting pattern. **HRMS (ESI)**: calcd for $C_{37}H_{33}O_8^+$ [M + H]$^+$ 605.2170, found *m*/*z* 605.2164.

2.11.2 Spiro compound (15)



Spiro compound (**15**) was obtained from **11** by using the general arylation protocol: R_f=0.37 (4/3/3, DCM/hexanes/EtOAc); **δ_H (600 MHz, $CDCl_3$)**: 7.42 (d, *J* = 9.6 Hz, 1H, H-10), 7.20 (d, *J* = 9.0 Hz, 1H, H-9), 6.68 (s, 1H, H-4), 6.51 (s, 1H, H-2), 5.13 (s, 1H, CH_3OCH_2O), 3.93 (s, 3H, OCH_3 at C11), 3.78 – 3.74 (d, *J* = 14.4 Hz, 1H, H13$_a$), 3.66 (s, 3H, OCH_3 at C1), 3.49 (s, 3H, CH_3OCH_2O), 2.97 (t, *J* = 7.4 Hz, 2H, H5), 2.82 – 2.78 (d, *J* = 14.4 Hz, 1H, H13$_b$), 2.48 – 2.40 (dt, *J* = 7.8, 12.0 Hz, 1H, H6$_a$), 2.32 (s, 3H, CH_3 at C3), 2.20 – 2.13 (dt, *J* = 7.8, 12.0 Hz, 1H, H6$_b$); **δ_C (150 MHz, $CDCl_3$):** 197.6 (C7), 195.6 (C12), 155.5 (C1), 153.2 (C11), 150.6 (C8), 145.8, 140.1 (C3), 129.0 (C4a), 127.1, 126.2, 125.9 (C10), 118.2 (C9), 117.8 (C4), 109.9 (C2), 97.2 (CH_3OCH_2O), 60.9 (quaternary C), 56.8 (OCH_3 at C11), 56.5 (CH_3OCH_2O at C8), 55.1 (OCH_3 at C1), 50.2 (C13), 37.3 (C6), 31.0 (C5), 21.8 (CH_3 at C3); **HRMS (ESI)**: calcd for $C_{23}H_{24}NaO_6^+$ [M + Na]$^+$ 419.1465, found *m*/*z* 419.1466.

2.11.3 1,11-Dimethoxy-8-methoxymethoxy-3-methyl-5,6-dihydrobenzo[*a*]anthracene-7,12-dione (16) from 13b, 13d, and 13e



From **13b**: To a solution of **13b** (256 mg, 0.43 mmol) in ether (43 mL, 10 mM), $MgBr_2 \cdot Et_2O$ (276 mg, 1.07 mmol) was added at 0 °C. After stirring at rt for 16 h, the reaction was quenched with satd. $NaHCO_3$ (75 mL). The resulting mixture was extracted with DCM (30 mL × 3) and the combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. The filtrate was kept at rt for 6 h to give dihydrobenz[*a*]anthracenedione **16** (65 mg, 38%) along with MOM-deprotected product **15′** (75 mg, 50%).

From **13d**: A solution of **13d** (58 mg, 0.12 mmol) in dry DCM (3.0 mL) was treated with the premade solution of NaOMe in MeOH (3.0 mL) at rt. After stirring for 19 h, the reaction was quenched with satd. NH_4Cl (20 mL). The aqueous layer was extracted with DCM (20 mL × 2) and the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo* to give the crude hydroquinone derivative which was used for next step without purification. To the solution of above crude residue in EtOAc (2.4 mL) was added DDQ (30 mg, 0.13 mmol) at 0 °C. After stirring for 30 min, the reaction mixture was

quenched with satd. $NaHCO_3$ (20 mL) and separated organic layer. The aqueous layer was extracted with EtOAc (10 mL × 2) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The residue was purified by flash silica-gel column chromatography (Elution: EtOAc/hexanes, 30% gradient to 50%) to give dihydrobenz[*a*]anthracenedione **16** (40 mg, 75%) as an orange glassy solid.

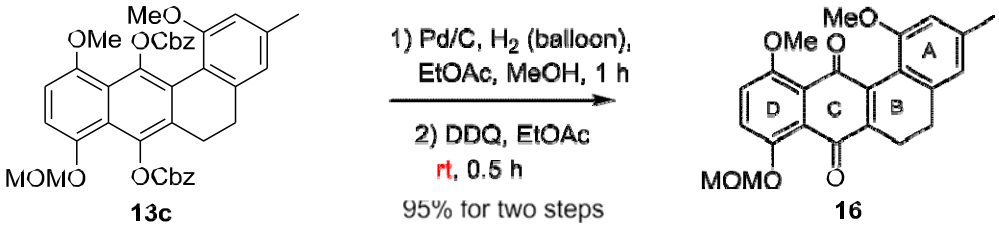
From **13e**: To solution of **13e** (60 mg, 0.09 mmol) in 1:1 MeOH:DCM (5 mL) was treated with sodium methoxide solution (25 wt% in MeOH, 1.98 mmol) at rt. After stirring for 3 h, the solution was neutralized with IR-120 amberlite acid resin and filtered. The filtrate was concentrated under *vacuo* to provide crude residue which was purified by flash silica-gel column chromatography (Elution: DCM/hexanes/EtOAc 4/5.5/0.5) to furnish **S3** (43 mg, 87%) as a white amorphous solid. **Analytical data for S3:** R_f = 0.47 (DCM/hexanes/EtOAc 4/5.4/0.6); **δ_H (600 MHz, $CDCl_3$):** 9.85 (s, O*H* at C7 of one atropisomer), 9.81 (s, O*H* at C7 of other atropisomer), 8.20 (d, *J* = 1.8 Hz, 2H, Ar*H* of Bz from one atropisomer), 8.17 (d, *J* = 1.8 Hz, 2H, Ar*H* of Bz from other atropisomer), 7.59 – 7.55 (m, 2H, Ar*H* of Bz from two atropisomers), 7.48 – 7.45 (m, 4H, Ar*H* of Bz from two atropisomers), 6.99 – 6.95 (m, 2H, Ar*H* at D ring of two atropisomers), 6.75 (s, 1H, Ar*H* at C4 of one atropisomer), 6.70 (s, 1H, Ar*H* at C4 of other atropisomer), 6.63 (d, *J* = 8.4 Hz, 1H, ArH at D ring of one atropisomer), 6.60 (d, *J* = 8.4 Hz, 1H, ArH at D ring of other atropisomer), 6.53 (s, 1H, Ar*H* at C2 of one atropisomer), 6.45 (s, 1H, Ar*H* at C2 of other atropisomer), 5.38 – 5.54 (m, 4H, OCH_2 of MOM from two atropisomers), 3.86 (s, 3H, OCH_3 at C1 of one atropisomer), 3.87 (s, 6H, OCH_3 × 2), 3.52 (s, 3H, OCH_3), 3.49 – 3.43 (m, 2H, CH_2 at B ring overlapped with signal at 3.37), 3.47 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3, at C1 of one atropisomer), 2.75 (d, *J* = 14.4 Hz, 2H, CH_2 at B ring), 2.67 (dt, *J* = 14.4, 3.0 Hz, 1H, CH_2 at B ring), 2.54 (dt, *J* = 14.4, 3.0 Hz, 1H, CH_2 at B ring), 2.35 (s, 3H, CH_3 at C3 of A ring from one atropisomer), 2.33 (m, 1H, CH_2 at B ring, overlapped with signal at 2.35), 2.30 (m, 1H, CH_2 at B ring, overlapped with signal at 2.28), 2.28 (s, 3H, CH_3 at C3 of A ring from other atropisomer). **δ_C (150 MHz, $CDCl_3$):** 166.0 (C=O from one atropisomer), 165.2 (C=O from other atropisomer), 157.1 (C1 of one atropisomer), 156.6 (C1 of other atropisomer), 151.6, 151.3, 147.34, 147.29, 146.8, 143.1, 142.8, 138.64, 138.60, 135.8, 135.5, 132.3, 131.7, 131.1, 130.1, 129.7, 128.1, 126.0,

125.5, 122.8, 120.4, 119.9, 118.3, 116.7, 116.6, 110.2, 109.8, 109.3, 109.0, 105.7, 105.5, 96.7 (O*C*H$_2$ of MOM of one atropisomer), 96.6 (O*C*H$_2$ of MOM of other atropisomer), 56.8, 56.2, 55.6, 55.1, 30.7, 30.6, 23.2, 22.8, 21.5. The above spectroscopic data include signals from two atropisomers of **13e**. **HRMS (ESI)**: calcd for $C_{30}H_{29}O_7^+$ $[M + H]^+$ 501.1908, found *m*/*z* 501.1917.

To a solution of **S3** (43 mg, 0.086 mmol) in EtOAc (2.4 mL) was added DDQ (30 mg, 0.13 mmol) at 0 °C. After stirring for 30 min, the reaction mixture was quenched with satd. $NaHCO_3$ (20 mL) and separated organic layer. The aqueous layer was extracted with EtOAc (10 mL × 2) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The residue was purified by flash silica-gel column chromatography (Elution: EtOAc/hexanes, 30% gradient to 50%) to give dihydrobenz[*a*]-anthracenedione **16** (29 mg, 83%).

Analytical data of 16: See next section 2.11

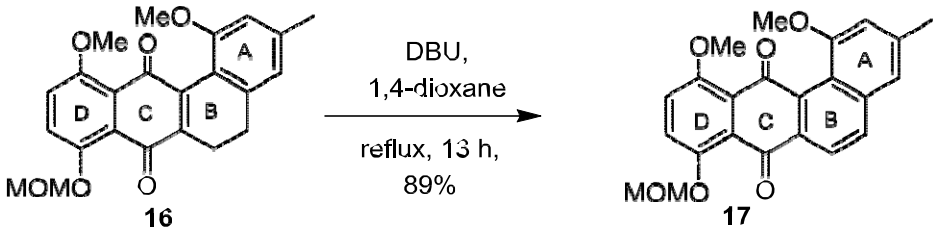
2.12 1,11-Dimethoxy-8-methoxymethoxy-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-dione (16)



To a stirred solution of **13c** (180 mg, 0.27 mmol) in 1:1 EtOAc:MeOH (54 mL, 5 mM) was added 10% Pd on charcoal (40 mg). After being treated with hydrogen for 1 h, the mixture was filtered. The filtrate was concentrated under *vacuo* to give the residue. To the solution of above residue in EtOAc (54 mL) was added DDQ (67 mg, 0.29 mmol). After stirring at rt for 1 h, the reaction was quenched with satd. $NaHCO_3$ solution (50 mL) and separated organic layer. The aqueous layer was extracted with EtOAc (25 mL) and the combined organic layers were washed with water, brine and, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The residue was purified by flash silica-gel column chromatography with 40% of EtOAc in hexanes to give dihydrobenz[*a*]anthracenedione **16** (101 mg, 95%) as a yellow amorphous solid.

Analytical data for 16: R_f = 0.23 (40% of EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.38 (d, *J* = 9.6 Hz, 1H, Ar*H* at C10 of D ring), 7.18 (d, *J* = 9.6 Hz, 1H, Ar*H* at C9 of D ring), 6.69 (s, 1H, Ar*H* at C4 of A ring), 6.67 (s, 1H, Ar*H* at C2 of A ring), 5.23 (s, 2H, OCH_2 of MOM), 3.94 (s, 3H, OCH_3 at C11), 3.80 (s, 3H, OCH_3 at C1), 3.53 (s, 3H, OCH_3), 2.71 (m, 4H, CH_2 × 2 at C5 and C6), 2.34 (s, 3H, CH_3 ar A ring); **δ_C (100 MHz, $CDCl_3$):** 184.4 (C=O), 183.0 (C=O), 157.2 (C1), 153.1 (C11), 150.3 (C8), 144.2, 142.0 (C3), 140.8, 140.3, 124.9, 123.9 (C10), 123.3, 121.3 (C4), 119.2 (C9), 117.5, 111.8 (C2), 96.5 (O*C*H$_2$ of MOM), 57.2 (O*C*H$_3$ at C11), 56.5 (O*C*H$_3$ of MOM), 56.2 (O*C*H$_3$ at C1), 28.3 (*C*H$_2$ at B ring), 21.9 (*C*H$_3$ at A ring), 19.4 (*C*H$_2$ at B ring); **HRMS (ESI)**: calcd for $C_{23}H_{22}NaO_6^+$ $[M + Na]^+$ 417.1309, found *m*/*z* 417.1312. The peak assignment is based on 2D COSY, HSQC, and HMBC NMR spectroscopy analysis.

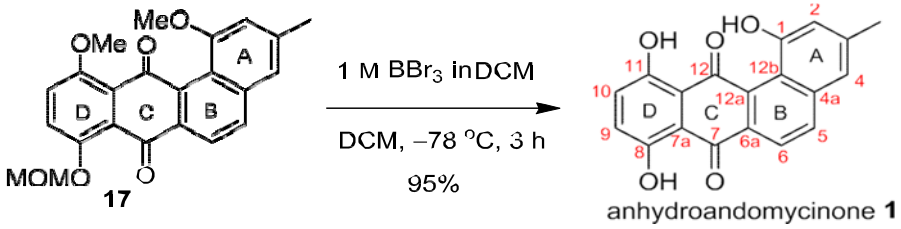
2.13 1,11-Dimethoxy-8-methoxymethoxy-3-methylbenz[*a*]anthracene-7,12-dione (17):



To a solution of **16** (80 mg, 0.20 mmol) in 1,4-dioxane (10 mL) was added DBU (0.41 mL, 2.80 mmol). The resulting reaction mixture was refluxed for 13 h. After the solution was cooled to rt, 0.5 N HCl (25 mL) was added, and product was extracted with DCM (2 × 30 mL).The combined organic layers were pooled and washed with water (25 mL), brine (25 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo* for purification with flash silica-gel chromatography (Elution: 40% of EtOAc in hexanes) to furnish benz[*a*]anthracenedione **17** (70 mg, 89%) as red glassy solid. **Analytical data for 17:** R_f = 0.67 (50% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 8.07 (d, *J* = 8.8 Hz, 1H, Ar*H* at B ring), 7.83 (d, *J* = 8.4 Hz, 1H, Ar*H* at B ring), 7.37 (d, *J* = 9.2 Hz, 1H, Ar*H* at C10 of D ring), 7.22 (broad s, 1H, Ar*H* at C4 of A ring), 7.20 (d, *J* = 9.2 Hz, 1H, Ar*H* at C9 of D ring), 6.84 (d, *J* = 1.2 Hz, 1H, Ar*H* at C2 of A ring), 5.28 (s, 2H, OCH_2 of MOM), 3.99 (s, 3H, OCH_3 at C11 of D ring), 3.98 (s, 3H, OCH_3 at C1 of A ring), 3.55 (s, 3H, OCH_3 of MOM), 2.50 (s, 3H, CH_3 at A ring); **δ_C (100 MHz, $CDCl_3$):** 187.1 (C=O at

C ring), 182.5 (C=O at C ring), 156.8 (C1), 152.1 (C11), 150.4 (C8), 140.4, 137.73, 137.70, 132.6, 131.4, 127.6, 124.1, 123.0 (C10), 122.1, 120.0 (C4), 119.2 (C9), 118.8, 110.8 (C2), 96.4 (OCH_2 of MOM), 57.3 (OCH_3 at C11), 56.5 (OCH_3 of MOM), 56.1 (OCH_3 at C1), 22.2; **HRMS (ESI)**: calcd for $C_{23}H_{20}NaO_6^+$ $[M + Na]^+$ 415.1152, found *m*/*z* 417.1149. The peak assignment is based on 2D COSY, HSQC, and HMBC NMR spectroscopy analysis.

2.14 5,6-Anhydrolandomycinone (1)



To a stirred solution of **17** (30 mg, 0.07 mmol) in DCM (4 mL) was added BBr_3 (1 M solution in DCM, 2 mL, 2.08 mmol) at –78 °C. After stirring at –78 °C for 1 h, the solution was warmed to –30 °C and stirred at –30 °C for 3 h. Then, the reaction was diluted with DCM (50 mL) and quenched with water (10 mL). The organic layer was successively washed with water (25 mL), brine (25 mL) and, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography (DCM/hexanes, 1/1) to provide 5,6-anhydrolandomycinone **1** (23 mg, 95%) as a brown-black solid.[5,6] **Analytical data for 1:** R_f = 0.47 (50% DCM in hexanes); **δ_H (400 MHz, $CDCl_3$):** 13.00 (s, 1H, OH at C8, correlation with C8 and C9 in HMBC), 12.50 (s, 1H, OH at C11, correlation with C11 and C10 in HMBC), 11.12 (s, 1H, OH at C1, correlation with C1 and C2 in HMBC), 8.34 (d, *J* = 8.4 Hz, 1H, H6, correlation with C6a, C7, and C12a in HMBC), 8.15 (d, *J* = 8.4 Hz, 1H, H5, correlation with C6 and C4a in HMBC), 7.36 (d, *J* = 9.6 Hz, H10, correlation with C11 and C11a in HMBC), 7.33 (d, *J* = 9.6 Hz, H9, correlation with C8 and C7a in HMBC), 7.28 (s, 1H, H4, correlation with C2 and C6a), 7.17 (s, 1H, H2, correlation with C1, C4, and C4a in HMBC), 2.50 (s, 3H, CH_3 at C3); **δ_C (100 MHz, $CDCl_3$):** 190.9 (C12), 186.2 (C7, correlation with H6 in HMBC), 159.0 (C11, correlation with OH at C11 and H10 in HMBC), 158.2 (C8, correlation with OH at C8 and H9 in HMBC), 155.1 (C1, correlation with OH at C1 and H2 in HMBC), 142.0 (C3, correlation with

C<u>*H*</u>$_3$ in HMBC), 139.2 (C6a correlation with H6 and H4 in HMBC), 138.3 (C5, correlation with H5 HSQC), 135.7 (C4a, correlation with H5 in HMBC), 131.6 (C12a, correlation with H6 in HMBC), 130.6 (C9, correlation with OH at C8), 130.4 (C10, correlation with OH at C11 in HMBC), 121.9 (C6, correlation with H6 in HSQC), 121.7 (C4, correlation with H2 in HSQC), 120.8 (C2, correlation with H2 in HSQC), 120.1 (C12b, correlation with OH at C1, H5, and H2 in HMBC), 113.7 (C7a, correlation with H9 in HMBC), 111.3(C11a, correlation with C10 in HMBC), 21.3 (*C*H$_3$ at C3, correlation with C<u>*H*</u>$_3$ in HSQC); **HRMS (ESI)**: calcd for $C_{19}H_{13}O_5^+$ $[M + H]^+$ 321.0757, found *m*/*z* 321.0754. ^{1}H assignment is based on 2D NMR experiments.

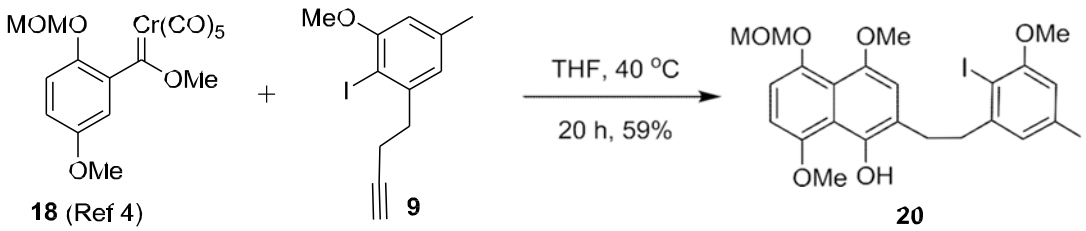
2.15 Table S1: Comparison of ^{1}H NMR spectroscopic data of anhydrolandomycinone 1 with the literature

^{1}H identity	δ_H data from present study (400 MHz, $CDCl_3$)	δ_H data from Kaliappan (400 MHz, $CDCl_3$)[5a]	δ_H data from Hsu (500 MHz, CD_2Cl_2)[5b]
H-2	7.17 (s)	7.19 (s)	7.08 (s)
CH_3 at C3	2.50 (s)	2.51 (s)	2.42 (s)
H-4	7.28 (s)	7.31 (s)	7.25 (s)
H-5	8.15 (d, *J* = 8.8)	8.17 (d, *J* = 8.5)	8.11 (d, *J* = 8.5)
H-6	8.34 (d, *J* = 8.4)	8.36 (d, *J* = 8.5)	8.26 (d, *J* = 8.5)
H-9	7.33 (d, *J* = 9.6)	7.36 (s)	7.27 (d, *J* = 9.5)
H-10	7.36 (d, *J* = 9.6)	7.36 (s)	7.29 (d, *J* = 9.5)
OH at C1	11.12 (s)	11.13 (s)	10.98 (s)
OH at C11	12.50 (s)	12.52 (S)	12.39 (s)
OH at C8	13.00 (s)	13.02 (s)	12.89 (s)

2.16 Table S2: Comparison of ^{13}C NMR spectroscopic data of anhydrolandomycinone 1 with the literature

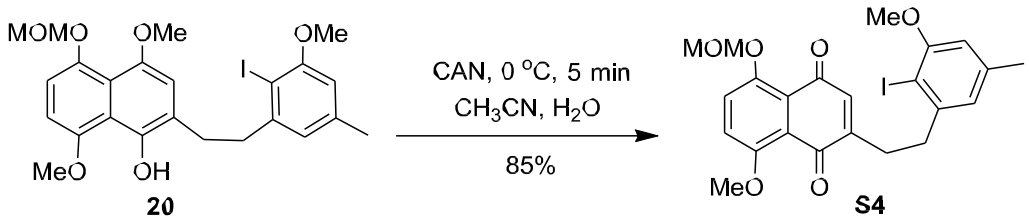
^{13}C identity	δ_C data (ppm) present study (150 MHz, $CDCl_3$)	δ_C data (ppm) from Kaliappan (100 MHz, $CDCl_3$)[5a]	δ_C data (ppm) from Hsu (125 MHz, $CDCl_3$)[5b]
C1 (at A ring)	155.1	155.2	154.2
C2 (at A ring)	120.8	121.8	119.1
C3 (at A ring)	142.0	142.5	141.3
C4 (at A ring)	121.7	122.0	121.0
C4a (at A/B ring)	120.1	120.2	120.8
C5 (at B ring)	138.3	138.4	137.5
C6 (at B ring)	121.9	120.9	119.7
C6a (at B/C ring)	139.2	139.3	138.4
C7 (at C ring)	186.2	186.3	185.5
C7a (at C/D ring)	113.7	113.8	113.0
C8 (at D ring)	158.2	158.3	157.3
C9 (at D ring)	130.6	130.7	129.7
C10 (at D ring)	130.4	130.5	129.5
C11 (at D ring)	159.0	159.1	158.1
C11a (at C/D ring)	111.3	111.4	110.5
C12 (at C ring)	190.9	191.1	190.2
C12a (at B/C ring)	131.6	131.7	130.8
C12b (at A/B ring)	135.7	135.8	135.0

2.17 2-(2-Iodo-3-methoxy-5-methylphenethyl)-4,8-dimethoxy-5-(methoxymethoxy) naphthalen-1-ol (20)



Chromium carbene **18** (2.0 g, 4.97 mmol) and alkyl alkyne **9** (1.79 g, 5.96 mmol) were mixed with anhydrous THF (98 mL) under N_2. The resulting dark red suspension was stirred for 20 h at 45 °C. Then, the solvent was evaporated under *vacuo* to give residue which on flash silica-gel chromatography with 20 to 25% EtOAc in hexanes provided naphthalen-1-ol **20** (1.57 g, 59%) as a light yellow solid. **Analytical data for 20:** R_f = 0.36 (20% DCM in hexanes); **δ_H (400 MHz, $CDCl_3$)**: 9.67 (s, 1H), 6.95 – 6.93 (d, *J* = 8.8 Hz, 1H), 6.82 (s, 1H), 6.76 (d, *J* = 1.2 Hz, 1H), 6.72 – 6.69 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 1.2 Hz, 1H), 5.13 (s, 2H), 4.01 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.60 (s, 3H), 3.11 – 3.07 (m, 2H), 3.01 – 2.97 (m, 2H), 2.29 (s, 3H); **δ_C (100 MHz, $CDCl_3$)**: 157.9, 151.8, 148.3, 148.0, 146.4, 146.0, 139.0, 123.2, 123.7, 120.1, 117.3, 114.5, 113.6, 109.6, 104.7, 98.0, 88.7, 58.0, 56.5, 56.4, 56.4, 41.1, 31.1, 21.2; **HRMS (ESI)**: calcd for $C_{24}H_{27}INaO_6^+$ $[M + Na]^+$ 561.0745, found *m*/*z* 561.0739.

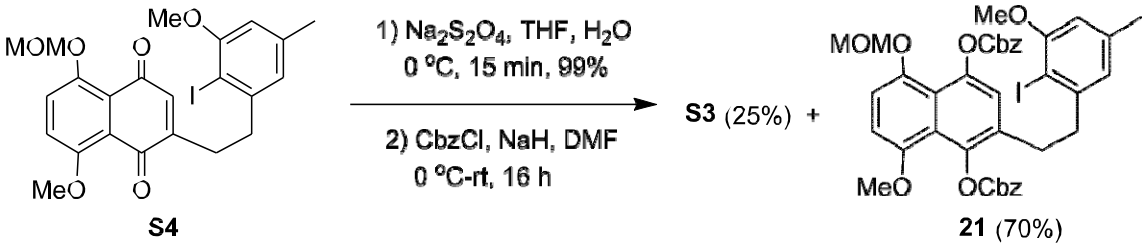
2.18 2-(2-Iodo-3-methoxy-5-methylphenethyl)-8-methoxy-5-(methoxymethoxy)naphthalene-1,4-dione S4



A solution of **20** (1.4 g, 2.60 mmol) in CH_3CN (31 mL) was treated with cooled (0 °C) solution of ceric ammonium nitrate (2.42 g, 4.42 mmol) in H_2O (31 mL) at 0 °C. After stirring for 5 min at 0 °C, the reaction mixture was extracted with EtOAc (75 mL × 2). The combined organic layers were washed with satd. $NaHCO_3$ (100 mL), water (100 mL), brine (50 mL) and dried over Na_2SO_4.

The crude residue was purified by flash silica-gel column chromatography (50% EtOAc in Hexanes) to give naphthalene-1,4-dione **S4** (1.13 g, 80%) as an orange powdery solid. **Analytical data for S4:** R_f = 0.3 (40% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.50 – 7.48 (d, *J* = 9.6 Hz, 1H), 7.27 – 7.25 (d, *J* = 9.2 Hz, 1H), 6.72 (d, *J* = 1.2 Hz, 1H), 6.61 (s, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 5.24 (s, 2H), 3.97 (s, 3H), 3.85 (s, 3H), 3.54 (s, 3H), 3.01 – 2.97 (m, 2H), 2.80 – 2.75 (m, 2H), 2.27 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 184.9, 184.8, 158.1, 155.1, 150.6, 149.9, 145.0, 139.4, 135.1, 125.9, 123.1, 122.9, 121.3, 119.5, 110.0, 96.4, 88.6, 56.8, 56.6, 56.5, 39.6, 30.2, 21.3; **HRMS (ESI)**: calcd for $C_{23}H_{23}INaO_6^+$ $[M + Na]^+$ 545.0432, found *m*/*z* 545.0431.

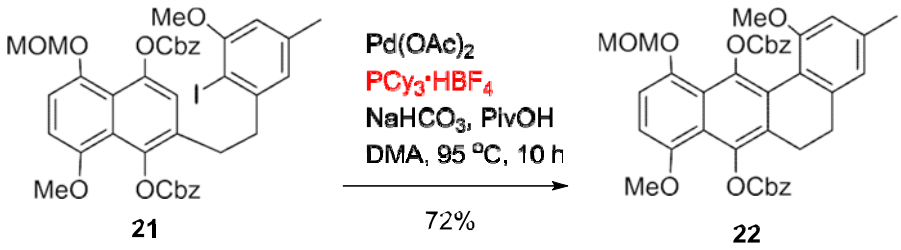
2.19 2-(2-Iodo-3-methoxy-5-methylphenethyl)-8-methoxy-5-(methoxymethoxy)-naphthalene-1,4-diyl Bis(benzylcarbonate) 21



A solution of **S4** (0.9 g, 1.72 mmol) in THF (34 mL) was treated with a solution of sodium dithionite (1.19 g, 6.89 mmol) in H_2O (34 mL) at 0 °C. After stirring for 15 min at same temperature, the solution was extracted with EtOAc (75 mL × 2). The combined organic layers were washed with H_2O (100 mL), brine (50 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo* to give the crude naphthalenetetrol, which was used for next step without purification. The solution of crude residue in THF (18 mL) was treated with 60% NaH in mineral oil (0.82 g, 20.64 mmol) at 0 °C. After stirring for 30 min at 0 °C, benzyl chloroformate (2.9 mL, 20.6 mmol) was added. The resulting mixture was warmed to room temperature and stirred for 16 h. Then, the reaction was slowly quenched with ice and extracted with EtOAc (100 mL × 2). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4. The flash silica-gel column chromatography (30% EtOAc in hexanes) of crude residue provided naphthalene-1,4-diyl bis(benzylcarbonate) **21** (0.96 g, 70%) along with some naphthalenedione **S4** (0.27 g, 30%). **Analytical data for 21:** R_f = 0.52 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.48 – 7.36

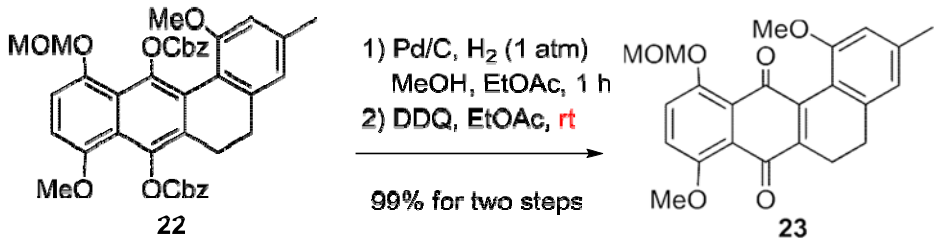
(m, 10H), 7.15 (s, 1H), 7.04 – 7.01 (d, J = 8.8 Hz, 1H), 6.73 – 6.71 (d, J = 8.8 Hz, 1H), 6.64 (d, J = 0.8 Hz, 1H), 6.49 (d, J = 1.6 Hz, 1H), 5.30 (m, 4H), 4.94 (bs, 2H), 3.87 (s, 3H), 3.58 (s, 3H), 3.39 (s, 3H), 3.03 – 2.94 (m, 4H), 2.27 (s, 3H); **δC (100 MHz, $CDCl_3$):** 158.0, 153.8, 150.3, 146.4, 145.3, 144.2, 142.5, 139.3, 135.1, 135.1, 131.2, 128.9, 128.8, 128.7, 128.7, 128.6, 123.2, 121.8, 121.6, 120.9, 112.3, 109.8, 107.4, 96.0, 88.3, 70.3, 70.2, 56.4, 56.2, 56.1, 41.4, 30.8, 21.2; **HRMS (ESI)**: calcd for $C_{39}H_{37}INaO_{10}^+$ $[M + Na]^+$ 815.1324, found m/z 815.1322.

2.20 1,8-Dimethoxy-11-(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl Bis(benzylcarbonate) (22)



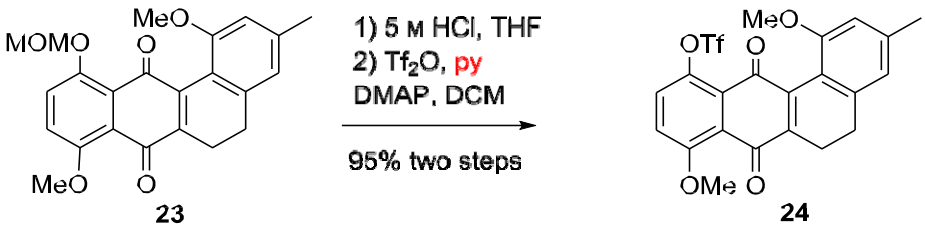
A sealed tube was charged with compound **21** (500 mg, 0.63 mmol) and sodium bicarbonate (317 mg, 3.78 mmol). Then, added anhydrous *N*,*N*-dimethylacetamide (52 mL) and stirred for 10 min at rt under N_2. A pre-mixed solution of $Pd(OAc)_2$ (70 mg, 0.31 mmol), $PCy_3 \cdot HBF_4$ (232 mg, 0.63 mmol) and pivalic acid (144 µL, 1.26 mmol) in anhydrous *N*,*N*-dimethylacetamide (18 mL) was added dropwise to the above solution. The reaction mixture was stirred for 10 h at 95 °C. Then, the reaction mixture was quenched with water (50 mL) and extracted with EtOAc (2 × 75 mL). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over Na_2SO_4. The crude residue was purified by flash silica-gel column chromatography (4/5.4/0.6, DCM/hexanes/EtOAc) to give dihydrobenz[*a*]anthracene-7,12-diyl bis(benzylcarbonate) **22** (300 mg, 72%) as a white foam. **Analytical data for 22:** R_f = 0.5 (4/5/1, DCM/hexanes/EtOAc); assignment of the NMR spectroscopic data (^1H and ^{13}C) of **22** was impossible due to the signal broadening (see ^1H and ^{13}C spectra for **22** in NMR spectra section); **HRMS (ESI)**: calcd for $C_{39}H_{36}NaO_{10}^+$ $[M + Na]^+$ 687.2201, found m/z 687.2198.

2.21 1,8-Dimethoxy-11-methoxymethoxy-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-dione (23)



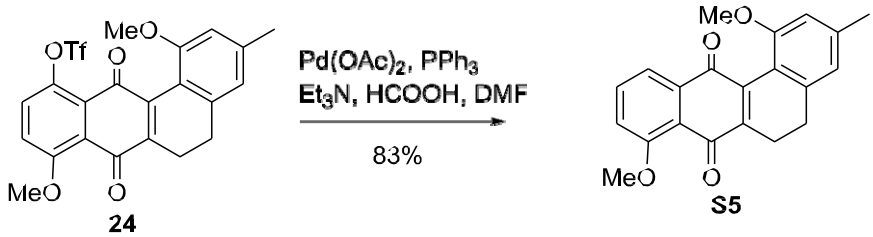
To a stirred solution of **22** (200 mg, 0.30 mmol) in EtOAc/MeOH (1:1, 60 mL, 5 mM) was added 10% Pd on charcoal (50 mg). After being treated with H_2 for 1 h, the mixture was filtered. The filtrate was concentrated under *vacuo* to give the residue, which was absorbed with EtOAc (60 mL) followed by addition of DDQ (75 mg, 0.33 mmol) at rt. After stirring for 1 h, quenched with satd. $NaHCO_3$ (50 mL) and separated organic layer. The aqueous layer was extracted with EtOAc (25 mL) and the combined organic layers were washed with water, brine and dried over Na_2SO_4. The residue was purified by flash silica-gel column chromatography with 50% ethyl acetate in hexanes to give dihydrobenz[*a*]anthracene-7,12-dione **23** (117 mg, 99%) as yellow solid. **Analytical data for 23**: R_f = 0.30 (40% EtOAc in hexanes); δ_H (400 MHz, $CDCl_3$): 7.42 – 7.40 (d, *J* = 9.6 Hz, 1H), 7.16 – 7.14 (d, *J* = 9.6 Hz, 1H), 6.70 (s, 1H), 6.66 (s, 1H), 5.26 (s, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H), 2.71 (m, 4H), 2.35 (s, 3H); δ_C (100 MHz, $CDCl_3$): 184.4, 182.9, 157.0, 154.5, 148.9, 143.5, 141.9, 141.0, 140.9, 126.6, 125.2, 121.4, 121.3, 117.7, 117.3, 111.6, 96.8, 56.7, 56.4, 56.0, 28.3, 21.9, 19.4; HRMS (ESI): calcd for $C_{23}H_{22}NaO_6^+$ $[M + Na]^+$ 417.1309, found *m*/*z* 417.1309.

2.22 11-Trifluoromethylsulfonyl-1,8-Dimethoxy-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-dione (24):



To a solution of **23** (90 mg, 0.22 mmol) in THF (7 mL) was added 5.0 M HCl solution (154 μL, 0.77 mmol) at 0 °C. The mixture was raised to rt and stirred for 10 h. Then, reaction was cooled to 0 °C, diluted with EtOAc (50 mL) and slowly quenched with satd. $NaHCO_3$ (25 mL). Layers were separated and aqueous layer was extracted with EtOAc (25 mL). The combined organic layers were washed with water (50 mL), brine (50 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo* to give MOM-deprotected product which was dissolved in 1:1 DCM:pyridine (5.0 mL). This solution was treated with 4-dimethylaminopyridine (DMAP) (5.3 mg, 0.04 mmol) and Tf_2O (370 μL, 2.20 mmol) at 0 °C. After stirring for 5 h at rt, the reaction was quenched with water (25 mL) and extracted with DCM (2 × 30 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$. The crude residue was purified by flash silica-gel column chromatography (5/4.5/0.5, DCM/hexanes/EtOAc) to furnish dihydrobenz[*a*]anthracene-7,12-dione **24** (104 mg, 95% for two steps) as a yellow glassy solid. **Analytical data for 24:** R_f = 0.48 (5/4.2/0.8, DCM/hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 7.49 – 7.47 (d, *J* = 9.2 Hz, 1H), 7.26 – 7.24 (d, *J* = 9.6 Hz, 1H), 6.69 (s, 2H), 4.00 (s, 3H), 3.82 (s, 3H), 2.71 (s, 4H), 2.35 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 181.4, 181.4, 158.5, 157.4, 142.6, 142.5, 142.4, 140.8, 139.2, 129.1, 128.2, 128.2, 123.5, 121.3, 121.1, 120.3, 117.4, 117.1, 116.5, 111.7, 56.9, 55.8, 28.2, 21.9, 19.7; **HRMS (ESI)**: calcd for $C_{22}H_{17}F_3NaO_7S^+$ $[M + Na]^+$ 505.0539, found *m*/*z* 505.0540.

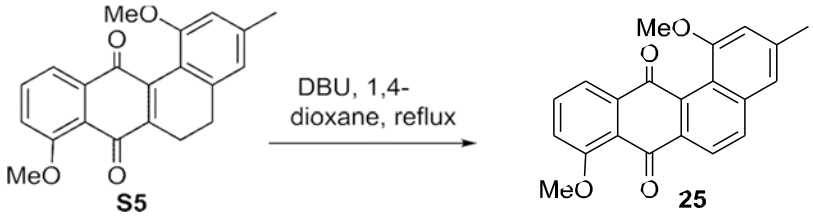
2.23 1,8-Dimethoxy-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-dione (S5):



A sealed tube was charged with benz[*a*]anthraquinone **24** (80 mg, 0.16 mmol), $Pd(OAc)_2$ (3.7 mg, 0.016 mmol), triphenylphosphine (13 mg, 0.049 mmol), triethylamine (137 μL, 0.99 mmol) and formic acid (1.2 mL) in *N*,*N*-dimethylformamide (16 mL). After stirring for 16 h at 80 °C, the reaction mixture was quenched with water (30 mL) and extracted with EtOAc (2 × 30 mL). The

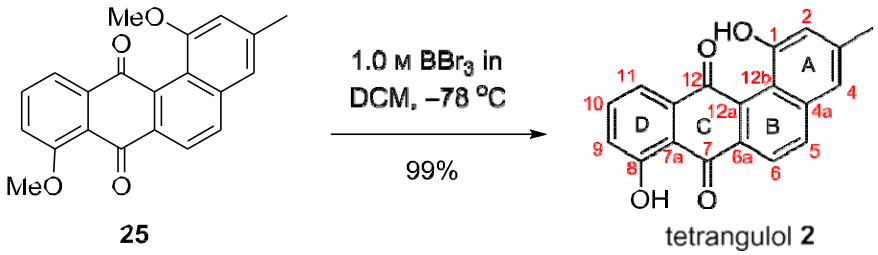
combined organic extracts were washed with water (50 mL), brine (50 mL), and dried over Na_2SO_4. The crude product was purified by flash silica-gel column chromatography with 80 to 100% DCM in hexanes to afford dihydrobenz[*a*]anthracenedione **S5** (46 mg, 83%) as thick yellow solid. **Analytical data for S5:** R_f = 0.55 (4/5/1, DCM/hexane/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 7.69 – 7.67 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.65 – 7.61 (dd, *J* = 7.6 Hz, *J* = 8.0 Hz, 1H), 7.26 – 7.23 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 6.72 (s, 1H), 6.69 (s, 1H), 4.00 (s, 3H), 3.79 (s, 3H), 2.71 (s, 4H), 2.36 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 183.8, 182.9, 159.2, 157.3, 144.4, 141.8, 141.6, 141.1, 136.7, 134.4, 121.1, 120.0, 118.9, 117.0, 116.8, 111.6, 56.5, 56.0, 28.4, 21.9, 20.5; **HRMS (ESI)**: calcd for $C_{21}H_{18}NaO_4^+$ $[M + Na]^+$ 357.1097, found *m*/*z* 357.1099.

2.24 1,8-Dimethoxy-3-methylbenz[*a*]anthracene-7,12-dione (25)



To a solution of **S5** (30 mg, 0.08 mmol) in 1,4-dioxane (4.5 mL) was added DBU (182 μL, 1.21 mmol) at rt. After being refluxed (120 ºC) for 16 h, the mixture was cooled to rt, quenched with water (25 mL), and extracted with EtOAc (2 × 25 mL). The combined organic extracts were washed with water (25 mL), brine (25 mL) and dried over Na_2SO_4. The crude residue was purified by flash silica-gel column chromatography with 25% EtOAc in hexanes to give benz[*a*]anthracene-7,12-dione **25** (26 mg, 89%) as orange solid. **Analytical data for 31:** R_f = 0.42 (5/4.4/0.6, DCM/hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 8.22 – 8.20 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.90 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.66 (dd, *J* = 7.6 Hz, *J* = 9.6 Hz, 1H), 7.67 (s, 1H), 7.26 – 7.22 (m, 2H), 6.88 (s, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 2.52 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 186.6, 182.2, 159.4, 157.0, 140.3, 139.4, 137.8, 135.2, 135.0, 133.9, 132.5, 122.7, 120.7, 120.1, 119.1, 118.5, 116.3, 111.2, 56.5, 56.1, 22.1; **HRMS (ESI)**: calcd for $C_{21}H_{16}NaO_4^+$ $[M + Na]^+$ 355.0941, found *m*/*z* 355.0943.

2.25 Tetrangulol (2)



To a stirred solution of **25** (20 mg, 0.06 mmol) in DCM (6 mL) was added BBr_3 (1 M solution in DCM, 150 µL, 0.15 mmol) at –78 °C. After stirring at –78 °C for 3 h, the reaction was diluted with DCM (50 mL) and quenched with water (10 mL). The organic layer was successively washed with water (25 mL), brine (25 mL), and dried over Mg_2SO_4. The crude residue was purified by flash silica-gel column chromatography (DCM/hexanes, 1/1) to provide tetrangulol **2** (18 mg, 99%) as a brown solid. **Analytical data for 2:** R_f = 0.56 (50% DCM in Hexane); **δ_H (600 MHz, $CDCl_3$):** 12.22 (s, 1H, OH at C8, correlate with C8, C9, and C11a in HMBC), 11.26 (s, 1H, OH at C1, correlate with C1 and C2 in HMBC), 8.28 (d, *J* = 8.4 Hz, 1H, H6, correlate with C12a, C7, and C6a in HMBC), 8.10 (d, *J* = 9.0 Hz, 1H, H5, correlation with C2, C4, C6, C6a, and C7a in HMBC), 7.83 (d, *J* = 7.8 Hz, 1H, H11, correlation with C11a, C9, and C10 in HMBC), 7.67 (t, *J* = 7.8 Hz, 1H, H10, correlation with C11, C7a, and C8 in HMBC), 7.31 (d, *J* = 8.4 Hz, 1H, H9, correlation with C11a, C11, and C8 in HMBC), 7.22 (s, 1H, H4, correlation with C2, C5, and C6a in HMBC), 7.11 (s, 1H, H2, correlation with C1 and C2 in HMBC), 2.48 (s, 3H, CH_3 at C3); **δ_C (150 MHz, $CDCl_3$):** 189.6 (C12, correlation with H11 in HMBC), 187.8 (C7, correlation with H6 in HMBC and with H7 in HSQC), 161.7 (C8, correlation with C9 and C10 in HMBC and with H8 in HSQC), 155.3 (C1, correlation with OH at C1), 142.0 (C3, correlation with C*H*$_3$ at C3 in HMBC), 139.1 (C6a, correlation with H4, H5, and H6 in HMBC), 137.7 (C5, correlation with H4 in HMBC and with H5 in HSQC), 136.9 (C10, correlation with H11 in HMBC and with H10 in HSQC), 134.723 (C11a/C12b, correlation with H5/H10 in HMBC), 134.717 (C11a/C12b, correlation with H5/H10 in HMBC), 132.3 (C12a, correlation with H6 in HMBC), 124.8 (C9, correlation with OH at C8, H11 in HMBC and H9 in HSQC), 121.9 (C6, correlation with H5 in HMBC and H6 in HSQC), 121.22 (C11, correlation with H10, H9 in HMBC and H11 in HSQC), 121.18 (C4, correlation with

H5, C<u>*H*</u>$_3$ in HMBC and H4 in HSQC), 120.2 (C2, correlation with OH at C1 and H4 in HMBC), 120.0 (C4a, correlation with H5 and H4 in HMBC), 114.7 (C7a, correlation with OH at C8, H11, and H9 in HMBC), 21.3 (<u>*C*</u>H$_3$ at C3); **HRMS (ESI)**: calcd for $C_{19}H_{12}NaO_4^+$ $[M + Na]^+$ 327.0628, found *m*/*z* 327.0622.

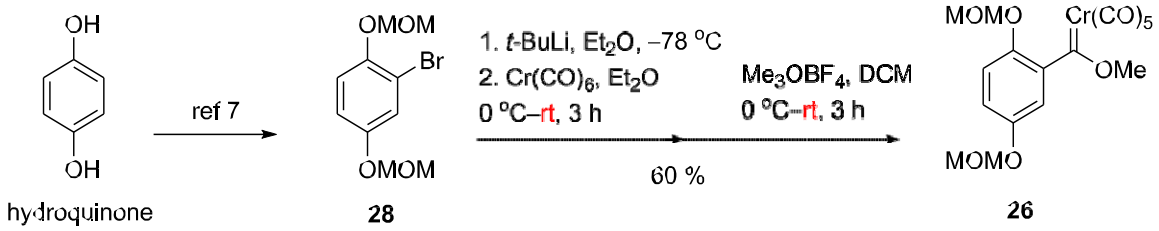
2.26 Table S3: Comparison of proton NMR data of tetrangulol 2 with the literature

^{1}H identity	δ_H data (ppm) from present study (600 MHz, $CDCl_3$)[a]	δ_H data (ppm) from Kaliappan (400 MHz, $CDCl_3$) [5a]	δH data (ppm) from Hsu (400 MHz, $CDCl_3$)[5b]
H-2	7.11 (s)	7.14 (d, *J* = 1.8)	7.13 (d, *J* = 1.6)
CH_3 at C3	2.48 (s)	2.49 (s)	2.49 (s)
H-4	7.22 (s)	7.26 (s)	7.25 (d, *J* = 1.6)
H-5	8.10 (d, *J* = 9.0)	8.13 (d, *J* = 8.6)	8.12 (d, *J* = 8.6)
H-6	8.28 (d, *J* = 8.4)	8.31 (d, *J* = 8.6)	8.30 (d, *J* = 8.6)
H-9	7.31 (d, *J* = 7.8)	7.33 (d, *J* = 7.6)	7.33 (d, *J* = 8.0)
H-10	7.67 (t, *J* = 7.8)	7.69 (t, *J* = 7.6)	7.68 (dd, *J* = 8.0, 7.2)
H-11	7.83 (d, *J* = 7.8)	7.85 (d, *J* = 7.36)	7.85 (d, *J* = 7.2)
OH at C1	11.26 (s)	11.27 (s)	11.27 (s)
OH at C8	12.22 (s)	12.25 (s)	12.24 (s)

2.27 Table S4: Comparison of ^{13}C NMR data of tetrangulol 2 with the literature

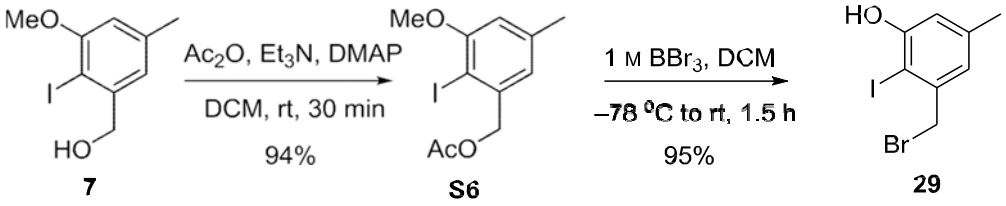
^{13}C identity	δ_C data (ppm) from present study (150 MHz, $CDCl_3$)	δ_C data (ppm) of from Kaliappan (100.2 MHz, $CDCl_3$)[5a]	δC data (ppm) of from Hsu (125 MHz, $CDCl_3$)[5b]
C1 (at A ring)	155.3	155.4	155.2
C2 (at A ring)	120.2	120.4	120.1
C3 (at A ring)	142.0	142.2	142.2
C4 (at A ring)	121.18	121.5	121.2
C4a (at A/B ring)	120.0	120.4	120.0
C5 (at B ring)	137.7	137.9	137.7
C6 (at B ring)	121.9	122.0	121.8
C6a (at B/C ring)	139.1	139.3	139.1
C7 (at C ring)	187.8	188.0	187.8
C7a (at C/D ring)	114.7	114.8	114.6
C8 (at D ring)	161.7	161.8	161.6
C9 (at D ring)	124.8	124.9	124.7
C10 (at D ring)	136.9	137.0	136.9
C11 (at D ring)	121.22	121.5	121.3
C11a (at C/D ring)	134.72 (overlapped with C12b)	135.0	134.78
C12 (at C ring)	189.2	189.9	189.6
C12a (at B/C ring)	132.3	132.6	132.3
C12b (at A/B ring)	134.72 (overlapped with C11a)	135.0	134.77

2.28 [2,4-Bis(methoxymethoxy)phenyl]methoxymethylene]pentacarbonylchromium (26).



To a solution of **28** (5 g, 18.9 mmol) in Et_2O (38 mL), *tert*-butyl lithium solution (*t*-BuLi) (1.6 M in pentane, 20.8 mL, 20.8 mmol) was added dropwise at –78 °C.[7] After stirring at –78 °C for 20 min, it was transferred to another cooled (0 °C) solution containing chromium (0) hexacarbonyl ($Cr(CO)_6$, 5.00 g, 22.72 mmol) in Et_2O (38 mL) *via* cannula. The resulting mixture was stirred at rt for 3 h. Then, the solvent was removed under *vacuo* and the residue was dissolved in DCM (76 mL). To this DCM suspension, trimethyloxonium tetrafluoroborate (4.20 g, 28.40 mmol) was added at 0 °C. Then, the reaction mixture was stirred at rt for 3 h. The dark red solution was concentrated under *vacuo* to give the residue for purification with flash silica-gel column chromatography (10% to 15% EtOAc in hexanes) furnishing the titled chromium complex **26** (6.7 g, 81%) as dark red solid. R_f = 0.25 (10% EtOAc in hexanes), which was stored at < –20 °C before the Dötz benzannulation.

2.29 3-Bromo-2-iodo-5-methylphenol (29)

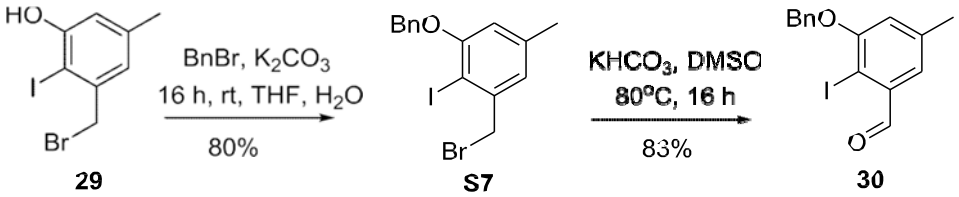


To a solution of **7** (2.0 g, 7.19 mmol) in dry DCM (14 mL) was added Et_3N (1.2 mL, 8.63 mmol), DMAP (20 mg) and Ac_2O (0.82 mL, 8.63 mmol) at rt. After stirring at rt for 30 min, the reaction mixture was diluted with DCM (30 mL), and washed with 1 N $HCl_{(aq)}$ (20 mL), H_2O (20 mL), brine (20 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography (15% EtOAc in hexanes) to give product **S6** (2.17 g, 94%) as orange solid. **Analytical data for S6:** R_f = 0.73 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 6.813 (s, 1H), 6.60 (d, *J* = 0.8 Hz, 1H), 5.11 (s, 2H), 3.85 (s,

3H), 2.33 (s, 3H), 2.13 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 170.4. 157.9. 139.44. 139.41. 122.5. 111.5. 86.4. 70.2. 56.4. 21.3. 20.8; **HRMS (ESI)**: calcd for $C_{11}H_{13}INaO_3^+$ $[M + Na]^+$ 342.9802, found *m*/*z* 342.9804.

To a solution of **S6** (1.66 g, 5.19 mmol) in dry DCM (26 mL), boron tribromide (BBr_3) (1 M solution in dry DCM, 10.4 mL, 10.4 mmol) was added dropwise at –78 °C. Then, the reaction was allowed to reach rt slowly and stirred for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (25 mL) and separated organic layer. The aqueous layer was extracted with DCM (15 mL × 2) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by silica-gel chromatography (17% EtOAc in hexanes) to get product **29** (1.64 g, 95%) as a white solid. **Analytical data for 29:** R_f = 0.43 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 6.87 (d, *J* = 1.2 Hz, 1H), 6.74 (s, *J* = 1.6 Hz, 1H), 5.56 (s, 1H), 5.54 (s, 2H), 2.27 (s 3H); **δ_C (100 MHz, $CDCl_3$):** 155.3, 140.5, 140.4, 123.9, 115.8, 88.0, 39.2, 20.8; **HRMS (ESI)**: calcd for $C_8H_9BrIO^+$ $[M + H]^+$ 326.8876, found *m*/*z* 326.8874.

2.30 3-(Benzyloxy)-2-iodo-5-methylbenzaldehyde (30)

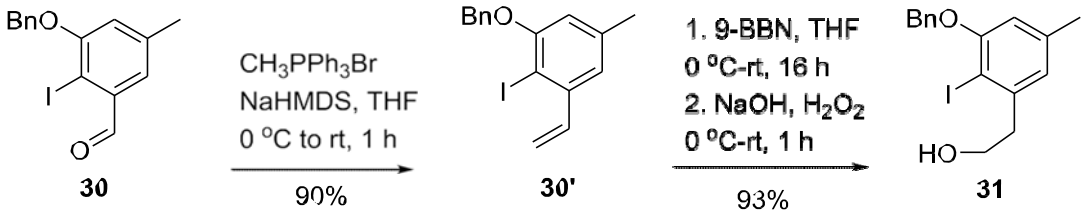


To a solution of **29** (3.86 g, 11.81 mmol) in acetone (110 mL) was added benzyl bromide (5.6 mL, 47.22 mmol) and K_2CO_3 (13.0 g, 94.45 mmol). After stirring for 16 h, the reaction mixture was quenched with H_2O (150 mL). The aqueous phase was extracted with EtOAc (75 mL × 2) and the pooled organic phases was washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by silica-gel chromatography (Elution: 4% gradient to 10% DCM in hexanes) to get product **S7** (4.11 g, 80%) as a white solid. **Analytical data for S7:** R_f = 0.52 (20% DCM in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.52 – 7.23 (m, 5H), 6.93 (d, *J* = 0.8 Hz, 1H), 6.57 (d, *J* = 1.2 Hz, 1H), 5.08 (s, 2H), 4.61 (s, 2H), 2.27 (s, 3H); **δ_C (100 MHz,**

$CDCl_3$): 157.6, 141.5, 139.8, 136.4, 128.6, 127.9, 127.0, 124.0, 113.4, 89.3, 71.1, 39.6, 21.3; **HRMS (ESI)**: calcd for $C_{15}H_{14}BrINaO^+$ $[M + H]^+$ 438.9165, found *m*/*z* 438.9168

To a solution of **S7** (5.26 g, 12.61 mmol) in dry dimethyl sulfoxide (140 mL) was added potassium bicarbonate (6.4 g, 64.32 mmol). The reaction mixture was heated under N_2 at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature and then diluted with EtOAc/H_2O and extracted with EtOAc (70 mL × 2). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by silica-gel chromatography (10% EtOAc in hexanes) to get methylbenzaldehyde **30** (3.67 g, 83%) as a white glassy solid. **Analytical data for 30:** R_f = 0.6 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 10.13 (s, 1H), 7.52 – 7.27 (m, 6H), 6.87 (s, 1H), 5.12 (s, 2H), 2.31 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 196.5, 157.3, 139.9, 136.3, 136.0, 128.6, 128.0, 127.0, 123.2, 118.9, 90.9, 71.3, 21.1; **HRMS (ESI)**: calcd for $C_{15}H_{13}INaO_2^+$ $[M + Na]^+$ 374.9852, found *m*/*z* 374.9853.

2.31 2-(3-(Benzyloxy)-2-iodo-5-methylphenyl)ethanol (31)

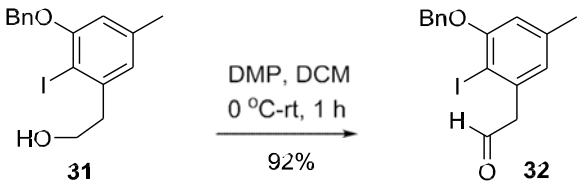


To a solution of methyltriphenylphosphonium bromide (3.8 g, 10.73 mmol) in dry THF (13 mL), sodium bis(trimethylsilyl)amide (2 M solution in THF, 4 mL, 8.05 mmol) was added dropwise at 0 °C. After 30 min of stirring at 0 °C, the solution of **30** (1.9 g, 5.37 mmol) in dry THF (13 mL) was added to the mixture. Then, the reaction mixture was stirred for 0.5 h at room temperature and quenched with satd. NH_4Cl (40 mL). The aqueous layer was extracted with ether (20 mL × 2) and the combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by silica-gel chromatography (Elution: 10% gradient to 15% DCM in hexanes,) to get vinylbenzene **30′** (1.66 g, 90%) as a colorless oil. **Analytical data for 30′:** R_f = 0.65 (20% DCM in hexanes); **δ_H (400**

MHz, $CDCl_3$): 7.53 – 7.26 (m, 5H), 7.04 – 6.94 (m, 2H), 6.57 (s, 1H), 5.58 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 5.08 (s, 2H), 2.28 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 157.1, 142.3, 141.1, 139.1, 136.7, 128.5, 127.0, 120.2, 116.7, 112.7, 89.0, 71.1, 21.4; **HRMS (ESI)**: calcd for $C_{16}H_{15}INaO^+$ $[M + Na]^+$ 373.0060, found *m*/*z* 373.0065.

To a solution of vinylbenzene **30′** (1.27 g, 3.64 mmol) in dry THF (15 mL), 9-borabicyclo[3.3.1]nonane (0.5 M solution in THF, 8.7 mL, 4.36 mmol) was added dropwise at 0 °C. Then, the reaction mixture was raised to rt and stirred for 16 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of MeOH (6.2 mL). $NaOH_{(aq)}$ (2 M, 15.1 mL) and 30% H_2O_2 (3.0 mL) were poured into the stirred mixture. Stirring was continued for 2 h, and the mixture was quenched with H_2O. The aqueous layer was extracted with Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by silica-gel chromatography (Elution: 12% gradient to 20% EtOAc in hexanes) to get phenylethanol **31** (1.25 g, 93%) as a white glassy solid. **Analytical data for 31:** R_f = 0.20 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.54 – 7.27 (m, 5H), 6.73 (s, 1H), 6.55 (s, 1H), 5.09 (s, 1H), 3.84 (t, *J* = 6.8 Hz, 1H), 3.04 (t, *J* = 6.8 Hz, 1H), 2.28 (s, 3H), 1.72 (bs, 1H); **δ_C (100 MHz, $CDCl_3$):** 157.3, 142.6, 139.2, 136.7, 128.5, 127.8, 127.0, 124.1, 111.8, 89.8, 71.0, 62.3, 43.9, 21.3; **HRMS (ESI)**: calcd for $C_{16}H_{17}INaO_2^+$ $[M + Na]^+$ 391.0165, found *m*/*z* 391.0170.

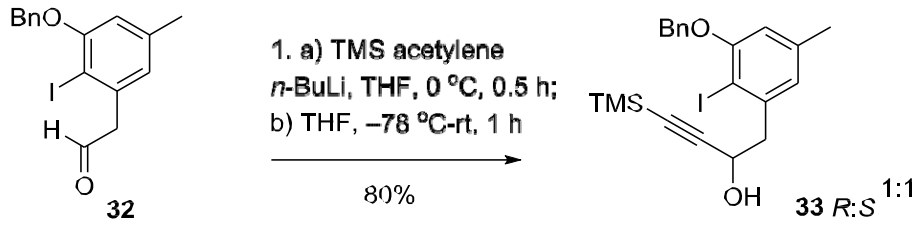
2.32 2-(3-(Benzyloxy)-2-iodo-5-methylphenyl)acetaldehyde (32)



To a solution of **31** (1.01 g, 2.74 mmol) in dry DCM (27 mL), Dess-Martin periodinane (DMP) (1.40 g, 3.29 mmol), was added at 0 °C. Then, the reaction mixture was raised to rt and stirred for 1 h then quenched with 10% $Na_2S_2O_3$ solution. The aqueous layer was extracted with DCM. The combined organic extracts were washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by silica-gel chromatography

(Elution: 4% gradient to 8% EtOAc in hexanes) to get phenylacetaldehyde **32** (1.25 g, 92%) as a colorless oil. **Analytical data for 32:** R_f = 0.65 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 9.76 (s, 1H), 7.54 – 7.29 (m, 5H), 6.70 (s, 1H), 6.63 (s, 1H), 5.13 (s, 2H), 3.90 (d, *J* = 1.6 Hz, 2H), 2.30(s, 3H); **δ_C (100 MHz, $CDCl_3$):** 199.0, 157.7, 139.8, 137.8, 136.5, 128.6, 127.9, 127.1, 124.6, 112.6, 90.1, 71.1, 54.9, 21.3; **HRMS (ESI)**: calcd for $C_{16}H_{15}INaO_2^+$ $[M + Na]^+$ 389.0009, found *m*/*z* 389.0013.

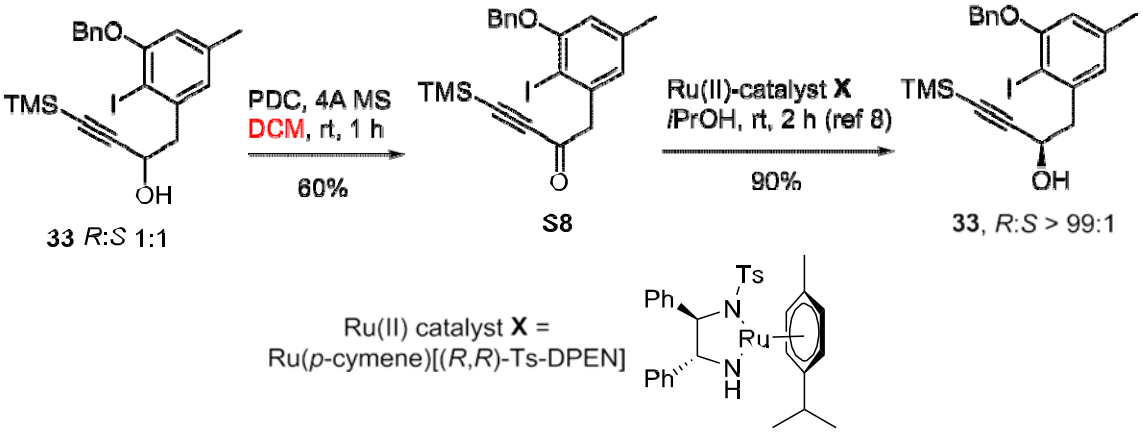
2.33 (*R*/*S*)-1-(3-(Benzyloxy)-2-iodo-5-methylphenyl)-4-(trimethylsilyl)but-3-yn-2-ol (33)



A solution of TMS-acetylene (1.5 mL, 10.81 mmol) in dry THF (19 mL) was treated dropwise with *n*-BuLi (1.6 M solution in hexane, 5.7 mL, 9.190 mmol) at 0 ºC. The solution was stirred for 30 min, and transferred via cannula to a solution of **32** (1.98 g, 5.41 mmol) in THF (7 mL) while maintaining at –78 ºC. After stirring at –78 ºC for 1 h, the reaction was allowed to reach rt and stirred for 1 h. The reaction was quenched with 5% HCl and the volatiles were removed under *vacuo*. The reaction was extracted with ether (30 mL × 3) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by silica-gel chromatography (Elution: DCM/hexanes/EtOAc, 4/5.95/0.05 gradient to 4/5.9/0.1) to give but-3-yn-2-ol **33** (1.99 g, 80%) as a racemic mixture. **Analytical data for 33:** R_f = 0.55 (4/5.8/0.2, DCM/hexanes/EtOAc); **δ_H (400 MHz, $CDCl_3$):** 7.54 – 7.28 (m, 5H), 6.81 (s, 1H), 6.58 (s, 1H) 5.10 (s, 1H), 4.68 (t, *J* = 6.8 Hz, 1H), 3.19 (ddd, *J* = 13.6 Hz, *J* = 13.2 Hz, *J* = 10.8 Hz, 2H), 2.29(s, 3H), 2.02 (bs, 1H), 0.17 (s, 9H); **δ_C (100 MHz, $CDCl_3$):** 157.2, 140.9, 138.9, 136.7, 128.6, 127.8, 125.3, 112.2, 105.8, 90.4, 90.3, 71.1, 62.4, 48.6, 21.3, 0.1; **HRMS (ESI)**: calcd for $C_{21}H_{25}INaO_2Si^+$ $[M + Na]^+$ 487.0561, found *m*/*z* 487.0560. The *R*:*S* ratio was determined by HPLC with CHIRALPAK IC column (250 mm × 4.6 mm). Elution- 97:3 hexanes:isopropanol over 0.8 $mLmin^{-1}$. UV detector at 286 nm was

used. The retention times of *R* and *S* enantiomers are 11.0 min and 16.74 min, respectively (See HPLC chromatogram).

2.34 (2*R*)-1-(3-Benzyloxy-2-iodo-5-methylphenyl)-4-trimethylsilylbut-3-yn-2-ol (33)



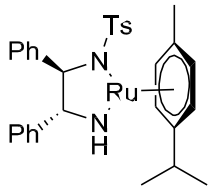
To a solution of 1:1 (*R*/*S*)-enantiomers of but-3-yn-2-ol **33** (126 mg, 0.32 mmol) in dry DCM (2 mL) was added dropwise to a suspension of freshly activated 4 Å molecular sieves (540 mg) and pyridinium dichromate (PDC) (163 mg, 0.35 mmol) in dry DCM (4.4 mL) at room temperature. After stirring for 1 h at room temperature, the reaction mixture was diluted with Et_2O and filtered over celite. The filtrate was concentrated under *vacuo*. The filtrate was concentrated under *vacuo*. The crude product was purified by flash silica-gel chromatography with 6% Et_2O in hexanes to obtain ketone intermediate **S8** (81 mg, 66%) as a colorless oil. Noted excessive amount of PDC should be avoided due to the poor stability of **S8. Analytical data for S8:** R_f = 0.63 (20% Et_2O in hexane); **δ_H (400 MHz, $CDCl_3$):** 7.51 (d, *J* = 7.2 Hz, 2H, Ar*H* of Bn), 7.39 (t, *J* = 7.2 Hz, 2H, Ar*H* of Bn), 7.31 (t, *J* = 7.6 Hz, 1H, Ar*H* of Bn), 6.72 (s, 1H, Ar*H*), 6.61 (s, 1H, Ar*H*), 5.11 (s, 2H, OCH_2 of Bn), 4.05 (s, 1H, CH_2), 2.29 (s, 3H, CH_3), 0.18 (s, 9H, TMS*H*). ; **δ_C (100 MHz, $CDCl_3$):** 183.8,157.5, 139.3, 138.5, 136.6, 128.6, 127.9, 127.0, 124.8, 112.5, 101.8, 99.9, 90.7, 71.1, 56.6, 21.3, 0.8. **S6** was too unstable for mass spectrometry analysis.

To a solution of aldehyde **S8** (25 mg, 0.05 mmol) in *i*PrOH (1.0 mL) under N_2 was added [Ru(*p*-cymene)[(*R*,*R*)-Ts-DPEN] (0.17 M in DCM, 16 µL, 0.003 mmol) in one portion (see next paragraph for preparation).[8] The reaction mixture was stirred at rt for 2 h then concentrated. The crude mixture was purified by silica-gel chromatography (Elution: 6% gradient to 10% EtOAc in

hexanes) to get desired *R*-enantiomer of but-3-yn-2-ol **33** (24 mg, 93%, *R*:*S* > 99:1) as a colorless oil. The *R*:*S* ratio was determined by HPLC with CHIRALPAK IC column (250 mm × 4.6 mm). Elution- 97:3 hexanes:isopropanol over 0.8 $mLmin^{-1}$. UV detector at 286 nm was used. The retention times of *R* and *S* enantiomers are 10.93 min and 17.97 min, respectively (See HPLC chromatogram).

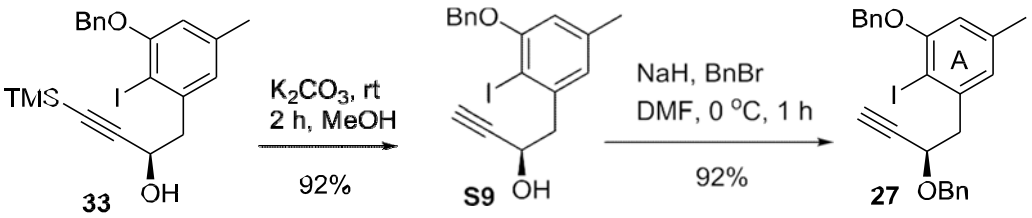
2.35 Preparation of Ru(*p*-cymene)[(1*R*,2*R*)-*N*-tosyl-1,2-diphenylethylenediamine] catalyst

Ru(II) catalyst **X** = Ru(*p*-cymene)[(*R*,*R*)-Ts-DPEN]



[Ru(*p*-cymene)[(*R*,*R*)-Ts-DPEN] was freshly prepared according to literature procedure.[8] Thus, a flame-dried single neck round bottom flask equipped with a stirrer bar and under Ar was charged with (1*R*,2*R*)-(−)-*N*-*p*-toluenesulfonyl-1,2-diphenylethylenediamine (92 mg, 0.25 mmol), dichloro(*p*-cymene)ruthenium(II) dimer (77 mg, 0.125 mmol) finely powdered KOH (100 mg, 1.78 mmol,) and distilled DCM (1.8 mL). The reaction mixture was stirred at rt for 5 min then distilled H_2O (1.8 mL) was added and the reaction mixture was stirred for 15 min during which time the organic phase turns dark purple. The reaction mixture was diluted with distilled DCM (1.8 mL) and transferred to a separating funnel. The phases were separated and the aqueous phase was extracted with distilled DCM (2 × 3.5 mL). The combined organic phases were washed with distilled H_2O (9 mL), and the organic phase was dried by careful addition of CaH_2, then filtered on cotton wool to remove the salts. The filtrate was concentrated under reduced pressure to give [Ru(*p*-cymene)[(*R*,*R*)-Ts-DPEN] as a dark purple solid (156 mg, quantitative yield). The ruthenium catalyst was used as a solution form in distilled DCM (0.17 M), which was kept in fridge before use.

2.36 1-(Benzyloxy)-3-{[(*R*)-2-benzyloxy]but-3-yn-1-yl)}-2-iodo-5-methylbenzene (27)

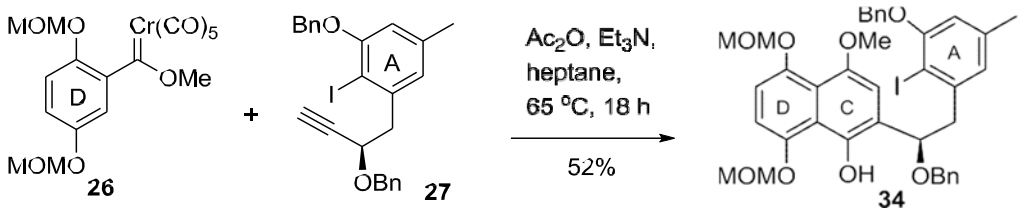


A solution of (2*R*)-but-3-yn-2-ol **33** (106 mg, 0.23 mmol) in MeOH (3.3 mL) was treated with K_2CO_3 (38 mg, 0.28 mmol) and stirred at room temperature for 2 h. The reaction mixture was quenched with water (15 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude product was purified by flash silica-gel chromatography with (Elution: 15% EtOAc in hexanes) to obtain alcohol intermediate **S9** (83 mg, 95%) as a white solid. **Analytical data for S9:** R_f = 0.45 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.54 – 7.28 (m, 5H), 6.80 (d, *J* = 0.8 Hz, 1H), 6.59 (d, *J* = 1.2 Hz, 1H), 5.11 (s, 2H), 4.70 (m, 1H), 3.22 (d, *J* = 2.8 Hz, 1H), 3.20 (d, *J* = 4.4 Hz, 1H), 2.50 (d, *J* = 2.0 Hz, 1H), 2.30 (s, 3H), 2.05 (d, *J* = 5.5 Hz, 1H); **δ_C (100 MHz, $CDCl_3$):** 157.3, 140.8, 139.1, 136.7, 128.6, 127.9, 127.1, 125.1, 112.3, 90.1, 84.1, 73.8, 71.1, 61.9, 48.6, 21.3; **HRMS (ESI)**: calcd for $C_{18}H_{17}INaO_2^+$ $[M + Na]^+$ 415.0165, found *m*/*z* 415.0164.

To a solution of **S9** (774 mg, 1.97 mmol) in dry DMF (33 mL) at 0 °C was added benzyl bromide (0.94 mL, 7.89 mmol) followed by tetra-*n*-butylammonium iodide (TBAI) (30 mg), After stirring at 0 °C for 20 min, 60% NaH (237 mg, 5.92 mmol) was added. The reaction mixture was stirred at 0 °C for 30 min and quenched with satd NH_4Cl (20 mL). The mixture was extracted with Et_2O (40 mL × 3) and the combined organic layers were pooled and then washed with water, brine, dried over Na_2SO_4, filtered, and concentrated for purification with silica-gel chromatography (Elution: 8% gradient to 12% EtOAc in hexanes) to get A-ring alkyne **27** (880 mg, 93%) as a colorless oil. **Analytical data for 27:** R_f = 0.63 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.54 – 7.21 (m, 10H, Ar*H* of Bn), 6.81 (s, 1H, Ar*H*), 6.57 (s, 1H, Ar*H*) 5.10 (s, 1H, OCH_2 ofBn), 4.80 (d, *J* = 11.6 Hz, 1H, OCH_2 of Bn), 4.50 (d, *J* = 12.0 Hz, 1H, OCH_2 of Bn), 4.41 (t, *J* = 7.2 Hz, 1H, -C*H*(OBn)), 3.30 (dd, *J* = 13.6 Hz, *J* = 7.2 Hz, 1H, -CH_2-), 3.18 (dd, *J* = 13.6 Hz, *J* = 6.8 Hz,

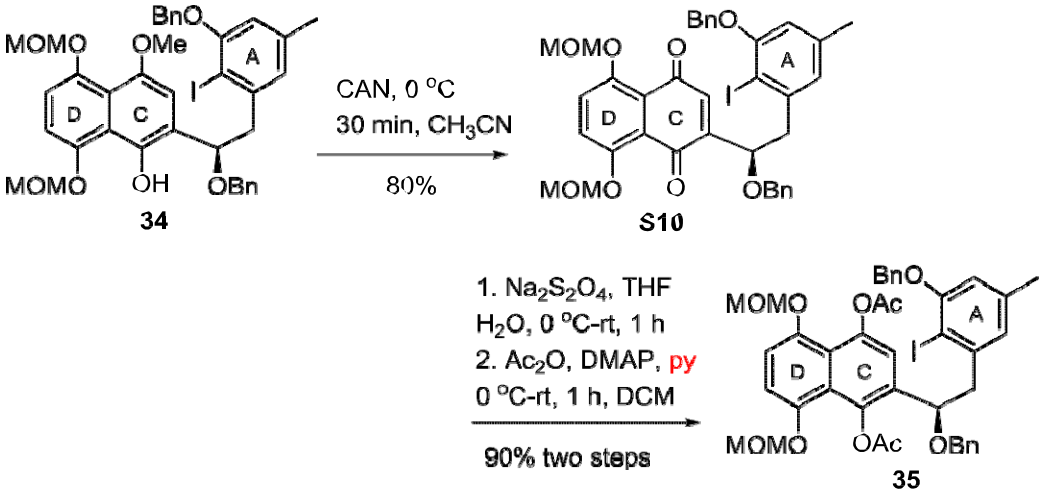
1H, -CH_2-), 2.48 (t, J = 1.2 Hz, 1H, C*sp*-H), 2.28 (s, 3H, CH_3); **δ_C (100 MHz, $CDCl_3$):** 157.1, 141.1, 138.7, 137.7, 136.8, 128.6, 128.3, 127.9, 127.8, 127.7, 127.1, 125.5, 112.1, 90.1, 82.2, 74.6, 71.1, 70.8, 68.0, 46.7, 21.3; **HRMS (ESI)**: calcd for $C_{25}H_{23}INaO_2^+$ $[M + Na]^+$ 505.0635, found *m*/*z* 505.0625.

2.37 2-{1-Benzyloxy-2-[3-(benzyloxy)-2-iodo-5-methylphenyl]ethyl}-4-methoxy-5,8-bis-(methoxymethoxy)naphthalenetetrol (34)



To a stirred solution of D-ring carbene **26** (958 mg, 2.22 mmol) and A-ring alkyne **27** (415 mg, 0.86 mmol) in anhydrous heptane (17 mL) was added Ac_2O (0.12 mL, 1.29 mmol) and Et_3N (0.18 mL, 1.29 mmol) at rt. After being stirred at 65 °C for 0.5 h, the reaction mixture was concentrated and purified by flash silica-gel column chromatography (Elution: 15% EtOAc in hexanes) to afford naphthalenetetrol **34** (337 mg, 52%) as a light yellow oil. **Analytical data for 34:** R_f = 0.22 (20% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 9.53 (s, 1H, O*H* at C ring), 7.54 (d, J = 7.2 Hz, 2H, ArH of Bn), 7.39 (t, J = 7.2 Hz, Ar*H* of Bn), 7.30 (d, J = 6.8 Hz, 1H, ArH of Bn), 7.22 – 7.13 (m, 6H including Ar*H* from Bn and a quinone-C*H* at C ring), 7.02 (d, J = 8.4 Hz, 1H, ArH at D ring), 6.97 (d, J = 8.4 Hz, 1H, ArH at D ring), 5.40 (dd, J = 4.4, 8.4 Hz, 1H, OC*H*(OBn)), 5.35 (s, 2H, OCH_2), 5.16 (s, 2H, OCH_2), 5.12 (s, 2H, OCH_2), 4.46 (d, J = 12.0, 1H, OCH_2), 4.30 (d, J = 12.0 Hz, 1H, OCH_2), 3.88 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3) 3.36 – 3.22 (m, 2H, -CH_2-), 2.22 (s, 3H, CH_3 at A ring); **δ_C (100 MHz, $CDCl_3$):** 156.9, 149.6, 149.3, 149.1, 145.8, 143.3, 138.8, 138.2, 137.0, 128.5, 128.1, 127.7, 127.2, 127.0, 125.0, 122.7, 120.8, 117.8, 115.2, 111.5, 109.4, 108.5, 97.9, 96.5, 90.8, 74.4, 71.1, 70.8, 57.7, 56.8, 56.4, 47.3, 21.2. Some atypical splitting pattern was observed in the ^1H and ^{13}C spectra of naphthalenetetrol **34**. As **34** would gradually be oxidized at rt, the compound was converted to **S8** without mass spectrometry analysis.

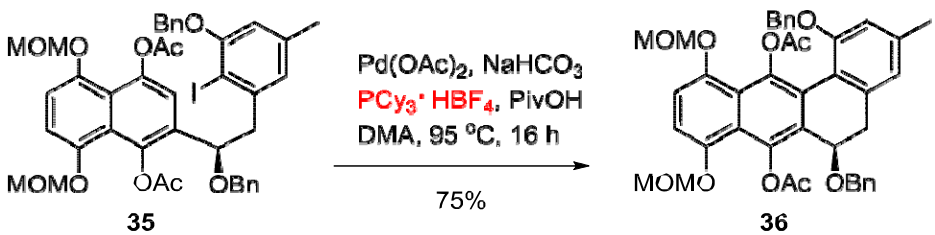
2.38 2-{1-Benzyloxy-2-[3-(benzyloxy)-2-iodo-5-methylphenyl]ethyl}-4-methyl-5,8-bis-(methoxymethoxy)naphthalene-1,4-diyl diacetate (35)



A solution of naphthalene-1-ol **34** (486 mg, 0.65 mmol) in CH_3CN (14 mL) was treated with cooled (0 °C) solution of CAN (887 mg, 1.62 mmol) in H_2O (14 mL) at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was extracted with EtOAc (30 mL × 2). The combined organic layers were washed with satd. $NaHCO_3$ (40 mL), water (40 mL), brine (20 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography (Elution: 22% gradient to 30% EtOAc in hexanes) to give naphthalene-1,4-dione **S10** (393 mg, 80%) as an orange oily substance. **Analytical data for S10:** R_f = 0.30 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.55 – 7.10 (m, 12H including Ar*H* from D ring and two Bn groups), 6.87 (s, 1H, quinone C*H* at C ring), 6.78 (s, 1H, Ar*H* at A ring), 6.54 (s, 1H, Ar*H* at A ring), 5.26 (s, 2H, OCH_2), 5.23 (d, *J* = 6.8 Hz, 1H, OCH_2), 5.19 (d, *J* = 7.2 Hz, 1H, OCH_2), 5.10 (s, 2H, OCH_2), 5.03 (t, *J* = 6.4 Hz, 1H, OC*H*(OBn)), 4.50 (d, *J* = 12.0 Hz, 1H, OCH_2), 4.28 (d, *J* = 12.0 Hz, 1H, OCH_2), 3.533 (s, 3H, OCH_3), 3.525 (s, 3H, OCH_3), 3.23 – 3.19 (m, 2H, -CH_2), 2.20 (s, 3H, CH_3 at A ring); **δ_C (100 MHz, $CDCl_3$):** 184.6 (C=O), 184.2 (C=O), 157.1, 152.2, 152.0, 149.8, 141.9, 138.6, 137.7, 136.8, 134.3, 128.5, 128.2, 127.8, 127.7, 127.6, 127.0, 125.14, 125.12, 125.0, 122.9, 122.4, 111.9, 96.2 (OCH_2 of MOM), 96.1 (OCH_2 of MOM), 91.0, 74.4, 71.8, 71.1, 56.6, 46.4, 21.2 (CH_3 at A ring); **HRMS (ESI)**: calcd for $C_{37}H_{35}INaO_8^+$ $[M + Na]^+$ 757.1269, found *m*/*z* 757.1259.

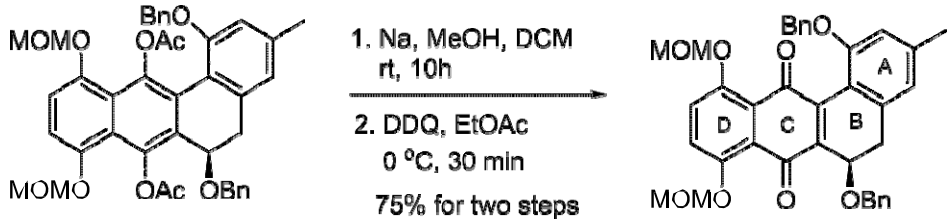
A solution of naphthalene-1,4-dione **S10** (304 mg, 0.41 mmol) in THF (17 mL) was treated with the solution of sodium dithionite (288 mg, 1.66 mmol) in H_2O (17 mL) at 0 °C. Then, the reaction was raised to room temperature and stirred for 1 h. The reaction mixture was extracted with EtOAc (30 mL × 2). The combined organic layers were washed with H_2O (40 mL), brine (20 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo* to give the crude naphthalene hydroquinone derivative, which was used for next step without purification. The solution of crude residue in dry DCM (6.2 mL) and pyridine (2.1 mL) was treated with acetic anhydride (0.3 mL, 3.31 mmol) at 0 °C. Then, the reaction was allowed to reach room temperature and stirred for 1 h. The reaction was quenched with 5% HCl and extracted with DCM (20 mL × 2). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography (Elution: 25% gradient to 30% EtOAc in hexanes) to afford naphthalene-1,4-diyl diacetate **35** (309 mg, 90%) as light yellow oil. **Analytical data for 35:** R_f = 0.20 (30% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 7.55 – 7.10 (m, 12H), 6.87 (s, 1H), 6.78 (s, 1H), 6.54 (s, 1H), 5.26 (s, 2H), 5.23 (d, *J* = 6.8 Hz, 1H), 5.19 (d, *J* = 7.2 Hz, 1H), 5.10 (s, 2H), 5.03 (t, *J* = 6.4 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 3.53 (s, 3H), 3.53 (s, 3H), 3.23 – 3.19 (m, 2H), 2.20 (s, 3H); **δ_C (100 MHz, $CDCl_3$):** 184.6 (C=O), 184.2 (C=O), 157.1, 152.2, 152.0, 149.8, 141.9, 138.6, 137.7, 136.8, 134.3, 128.5, 128.2, 127.8, 127.7, 127.6, 127.0, 125.14, 125.12, 125.0, 122.9, 122.4, 111.9, 96.2, 96.1, 91.0, 74.4, 71.8, 71.1, 56.6, 46.4, 21.2. Peak assignment of the ^1H and ^{13}C NMR spectra of **35** was difficult due to the broadening of NMR signals and atypical splitting. **HRMS (ESI)**: calcd for $C_{41}H_{41}INaO_{10}^+$ $[M + Na]^+$ 843.1637, found *m*/*z* 843.1625.

2.39 1,6-Dibenzyloxy-8,11-bis(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-diyl diacetate (36)



The thick glass reaction vessel was charged with naphthalene-1,4-diyl diacetate **35** (264 mg, 0.32 mmol) and satd. $NaHCO_3$ (162 mg, 1.93 mmol). Then, added anhydrous DMA (27 mL) and stirred at rt under N_2 for 10 min. The premade solution of $Pd(OAc)_2$ (36 mg, 0.16 mmol), $PCy_3.HBF_4$ (119 mg, 0.32 mmol) and PivOH (72 µL, 0.64 mmol) in anhydrous DMA (9.0 mL) was added dropwise to the above solution. The reaction mixture was stirred for 14 h at 95°C. Then, the reaction mixture was quenched with water (30 mL) and extracted with EtOAc (55 × 2 mL). The combined organic layers were washed with water (30 mL), brine (30 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by flash silica-gel column chromatography (Elution: 20% gradient to 40% EtOAc in hexanes) to give dihydrobenz[*a*]anthracene-7,12-diyl diacetate **36** (168 mg, 75%) as light brown solid. **Analytical data for 36:** R_f = 0.35 (40% EtOAc in hexanes). Peak assignment of the ^1H and ^{13}C NMR spectra of **36** was difficult due to the broadening of NMR signals and atypical splitting. **HRMS (ESI)** calcd for $C_{41}H_{40}NaO_{10}^+$ $[M + Na]^+$ 715.2514, found *m/z* 715.2473.

2.40 1,6-Bis(benzyloxy)-8,11-bis(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*] anthracene-7,12-dione (37)

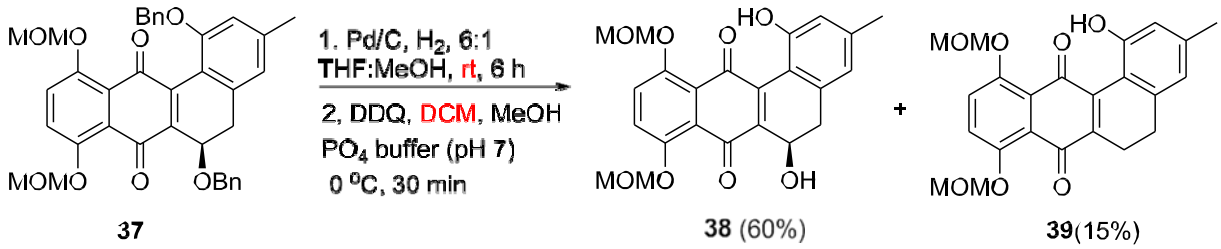


36 **37**

A solution of dihydrobenz[*a*]anthracene-7,12-diyl diacetate **36** (114 mg, 0.16 mmol) in dry DCM (4 mL) was treated with $Na_{(s)}$ (~70 mg) in MeOH (4 mL) at rt. After stirring for 14 h, the reaction was quenched with satd. NH_4Cl (20 mL). The aqueous layer was extracted with DCM (20 mL × 2) and the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo* to give the crude hydroquinone derivative which was used for next step without purification. To the solution of above crude residue in EtOAc (3 mL) was added DDQ (41 mg, 0.18 mmol) at 0 °C. After stirring for 30 min, the reaction mixture was quenched with satd. $NaHCO_3$ (20 mL) and separated organic layer. The aqueous layer was

extracted with EtOAc (10 mL × 2) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The residue was purified by flash silica-gel column chromatography (Elution: DCM/hexanes/EtOAc, 6/3.6/0.4 gradient to 6/3.3/0.7) to give dihydrobenz[*a*]anthracene-7,12-dione **37** (75 mg, 75%) as a yellow amorphous solid. **Analytical data for 37:** R_f = 0.50 (6/3.2/0.8, DCM/hexanes/EtOAc); **δ_H (600 MHz, $CDCl_3$):** 7.43 (d, *J* = 7.8 Hz, 2H, Ar*H* of Bn), 7.37 (d, *J* = 9.6 Hz, ArH at D ring), 7.35 (d, *J* = 9.6 Hz, ArH at D ring), 7.32 (t, *J* = 7.2 Hz, 2H, Ar*H* of Bn), 7.28 – 7.26 (m, 2H, Ar*H* of Bn), 7.19 – 7.15 (m. 4H, Ar*H* of Bn), 6.75 (s, 1H, Ar*H* at C4 of A ring), 6.67 (s, 1H, Ar*H* at C2 of A ring), 5.30 (dd, *J* = 7.2, 12.0 Hz, 2H, OCH_2 of MOM at D ring), 5.19 (d, *J* = 13.2 Hz, 1H, OCH_2 of Bn at C1 of A ring), 5.13 (1H, -OC*H*- at C6 of B ring; overlapped by the signal at 5.12 ppm), 5.12 (d, *J* = 13.2 Hz, 1H, OCH_2 of Bn at C1 of A ring), 5.01 (d, *J* = 7.2 Hz, 1H, OCH_2 of MOM at D ring), 4.93 (d, *J* = 13.2 Hz, 1H, OCH_2 of MOM at D ring), 4.57 (d, *J* = 12.6 Hz, 1H, OCH_2 of Bn at C6), 4.50 (d, *J* = 12.6 Hz, 1H, OCH_2 of Bn at C6), 3.56 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.13 (d, *J* = 15.6 Hz, 1H, -CH_2 at C5), 2.82 (dd, *J* = 3.6, 16.8 Hz, 1H, -CH_2 at C5), 2.31 (s, 3H, CH_3 at C3); **δ_C (150 MHz, $CDCl_3$):** 185.0 (C=O), 182.8 (C=O), 157.0 (C1), 151.6, 150.2, 145.1, 142.7, 138.8, 138.0, 137.7, 136.5, 128.5, 128.1, 127.8, 127.6, 127.4, 126.8, 126.1, 124.1, 123.4, 123.0 (C4), 122.9, 116.5 (C4a), 113.4 (C2), 96.2, 96.1, 71.5 (OCH_2 of Bn at C6), 71.2 (OCH_2 of Bn at A ring), 65.3 (C6), 56.6, OCH_3 of MOM), 56.3 (OCH_3 of MOM), 35.0 (C5), 22.1 (CH_3 at C3); **HRMS (ESI)** calcd for $C_{37}H_{34}NaO_8^+$ [M + Na]$^+$ 629.2146, found *m*/*z* 629.2144.

2.41 1,6-Dihydroxy-8,11-bis(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*]anthracene-7,12-dione (38) and 1-hydroxy-8,11-bis(methoxymethoxy)-3-methyl-5,6-dihydrobenz[*a*] anthracene-7,12-dione (39)

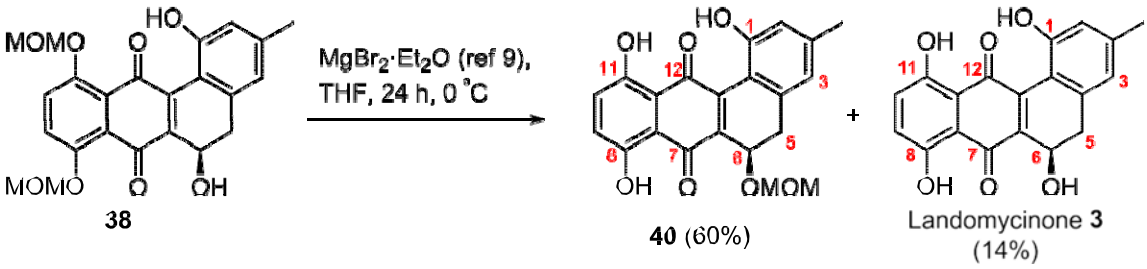


37 **38** (60%) **39**(15%)

To a stirred solution of dihydrobenz[*a*]anthracene-7,12-dione **37** (60 mg, 0.10 mmol) in 6:1 THF:MeOH (20 mL, 5 mM) was added 10% Pd on charcoal (40 mg). After being treated with hydrogen for 5 h, the mixture was filtered and washed with DCM (10 mL). To the filtrate was added MeOH (15 mL) and buffer solution (5 mL, pH = 7). To the above solution was added DDQ (50 mg, 0.22 mmol) at 0 °C. After stirring for 30 at 0 °C, the reaction mixture was quenched with satd. $NaHCO_3$ (25 mL) and separated organic layer. The aqueous layer was extracted with DCM (25 mL × 2) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The residue was purified by flash silica-gel column chromatography (Elution: 30% gradient to 70% EtOAc in hexanes) to give dihydrobenz[*a*]anthracenedione **38** (27 mg, 70%) as an orange glassy solid together with 6-deoxy dihydrobenz[*a*]anthracenedione **39** (6.0 mg, 15%). **Analytical data for 38:** R_f = 0.20 (60% EtOAc in hexanes); **δ_H (600 MHz, $CDCl_3$):** 8.94 (s, 1H, O*H* at C1), 7.51 (d, *J* = 6.0 Hz, 1H, Ar*H* at D ring), 7.48 (d, *J* = 6.0 Hz, 1H, Ar*H* at D ring), 6.76 (s, 1H, Ar*H* at A ring), 6.72 (s, 1H, Ar*H* at A ring), 5.30 (dd, *J* = 6.6, 9.0 Hz, 2H, OCH_2 of MOM), 5.28 (dd, *J* = 6.6, 12.0 Hz, 2H, OCH_2 of MOM), 5.14 (dd, *J* = 6.4 Hz, *J* = 3.2 Hz, 1H, -OC*H*- at C6), 3.55 (s, 3H, OCH_3 of MOM), 3.54 (s, 3H, OCH_3 of MOM), 3.07 (dd, *J* = 10.4 Hz, *J* = 3.6 Hz, 1H, -CH_2- at C5), 2.95 (dd, *J* = 10.4 Hz, *J* = 3.2 Hz, 1H, -CH_2- at C5), 2.88 (d, *J* = 2.4 Hz, 1H, O*H* at C6), 2.31 (s, 3H, CH_3 at C3); **δ_C (150 MHz, $CDCl_3$):** 189.6 (C=O at C ring), 183.9 (C=O at C ring), 155.6 (C1), 152.2, 151.7, 143.6, 142.2, 140.8, 136.8 (C6a), 125.3, 124.7, 123.9, 123.5 (C4), 121.5, 119.7 (C2), 113.3 (C4a), 96.0 (OCH_2 of MOM), 95.9 (OCH_2 of MOM), 61.9 (OCH_3 of MOM), 56.8 (OCH_3 of MOM), 36.7 (C5), 21.3 (CH_3 at C3); **HRMS (ESI)**: calcd for $C_{23}H_{22}NaO_8^+$ $[M + Na]^+$ 449.1207, found *m*/*z* 449.1209.

Analytical data for 39: R_f = 0.38 (60% EtOAc in hexanes); **δ_H (400 MHz, $CDCl_3$):** 8.69 (s, 1H, O*H* at C1), 7.49 (d, *J* = 9.2 Hz, 1H, Ar*H* at D ring), 7.46 (d, *J* = 9.6 Hz, 1H, Ar*H* at D ring), 6.75 (s, 1H, Ar*H* at A ring), 6.65 (s, 1H, Ar*H* at A ring), 5.30 (s, 2H, OCH_2 of MOM), 5.28 (s, 2H, OCH_2 of MOM), 3.56 (s, 3H, OCH_3 of MOM), 3.55 (s, 3H, OCH_3 of MOM), 2.76 (dd, *J* = 4.4 Hz, *J* = 4.4 Hz, 2H, -CH_2 at B ring), 2.71 (dd, *J* = 4.8 Hz, *J* = 4.4 Hz, 2H, -CH_2 at B ring), 2.30 (s, 3H, -CH_3 at A ring)**; HRMS (ESI)**: calcd for $C_{23}H_{22}NaO_7^+$ $[M + Na]^+$ 433.1258, found *m*/*z* 433.1261.

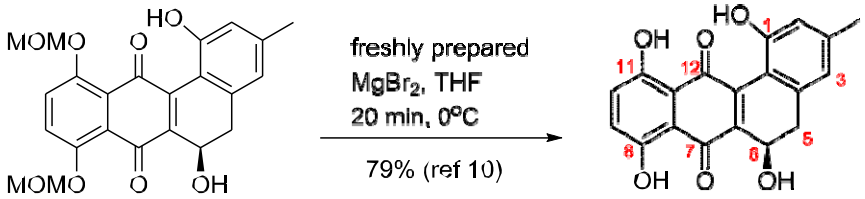
2.42 MOM-migration product 40 from deprotection of 38 with commercial $MgBr_2 \cdot Et_2O$



To a solution of dihydrobenz[*a*]anthracene-7,12-dione **38** (18 mg, 0.042 mmol) in dry THF (1.1 mL) was added available $MgBr_2 \cdot Et_2O$ (21.8 mg, 0.084 mmol) at 0 °C.[9] After stirring at 0 °C for 24 h, the reaction was quenched with satd. $NaHCO_3$ (5 mL). The resulting mixture was extracted with DCM (3 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by purified by using preparative TLC plate with a 5% MeOH in DCM developing solution to give landomycinone **3** (2.0 mg, 14%) along with MOM-migration product **40** (9 mg, 60%) as purple solid both. **Analytical data for 40:** R_f = 0.85 (5% MeOH in DCM); **δ_H (600 MHz, $CDCl_3$):** 13.02 (s, 1H, O*H* at C8, correlation with C7, C7a, C8, and C10 in HMBC), 12.82 (s, 1H, O*H* at C11, correlation with C11, C9, and C11a in HMBC), 9.11 (s, 1H, O*H* at C1, correlation with C1, C2, and C12b in HMBC), 7.35 (d, *J* = 9.6 Hz, 1H, H10, correlation with C11 and C11a in HMBC), 7.29 (d, *J* = 9.6 Hz, 1H, H9, correlation with C11a and C8 in HMBC), 6.83 (s, 1H, H2, correlation with C12b, C4, and C1 in HMBC), 6.76 (s, 1H, H4, correlation with C12b and C2 in HMBC), 5.25 (t, *J* = 3.2 Hz, 1H, H6, correlation with C4a in HMBC), 4.71 and 4.68 (d, *J* = 6.8 Hz, 1H, $OC\underline{H_2}OCH_3$, correlation with C6 and $OCH_2O\underline{C}H_3$ in HMBC), 3.24 (s, 3H, $OCH_2OC\underline{H_3}$, correlation with $O\underline{C}H_2OCH_3$ in HMBC), 3.19 (dd, *J* = 16.4 Hz, *J* = 2.4 Hz, 1H, $5H_\beta$, correlation with C12b, C4, C4a, and C6 in HMBC), 2.84 (dd, *J* = 16.4 Hz, *J* = 3.2 Hz, 1H, $5H_\alpha$, correlation with $H5_\beta$ in COSY), 2.34 (s, 3H, C*H*$_3$ at C3); **δ_C (150 MHz, $CDCl_3$):** 186.7 (C12 from HMBC), 182.8 (C7, correlation with OH at C8 and H6), 162.8 (C11, correlation with OH at C11 and H10), 161.2 (C8, correlation with OH at C8 and H9), 155.7 (C1, correlation with OH at C1 and H2), 143.9 (C3, correlation with C*H*$_3$), 142.9 (C6a, correlation with H6 and H5), 141.3 (C12a, correlation with H6 and H5), 137.5 (C4a, correlation with H5), 132.6 (C9, based on HSQC), 130.9 (C10, based on

HSQC), 123.6 (C4, correlation with H2 and H5), 120.3 (C2, correlation with H4), 114.4 (C12b, correlation with OH at C1, H2 and H4), 112.7 (C11a, correlation with OH at C11 and H9), 111.0 (C7a, correlation with OH at C8 and H10), 95.6 (O*C*H$_2$ of MOM), 63.8 (C6), 55.7 O*C*H$_3$ of MOM, 35.4 (C5), 21.4 (*C*H$_3$ at C3); **HRMS (ESI)**: calcd for $C_{21}H_{18}NaO_7^+$ $[M + Na]^+$ 405.0945, found *m*/*z* 405.0949. Peak assignment of **40** was based on 2D COSY, HSQC, and HMBC NMR analysis. The assigned ^{1}H and ^{13}C NMR signals of **40** could be used as references in the assignment of the NMR spectra of landomycinone **3**.

2.43 Landomycinone 3 from deprotection of 38 with freshly prepared $MgBr_2$



To a solution of dihydrobenz[*a*]anthracene-7,12-dione **38** (12 mg, 0.028 mmol) in dry THF (2.2 mL) was added 0.22 M $MgBr_2$ in THF (2.2 mL) (prepared freshly using Vedejs protocol[11]) at 0 °C. After stirring at 0 °C for 20 min, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with DCM (4 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo*. The crude residue was purified by using preparative TLC method with a 5% MeOH in DCM developing solution to give landomycinone **3** (8.0 mg, 79%) as a purple solid. **Analytical data for 3:** R_f = 0.37 (5% MeOH in DCM); **δ_H (600 MHz, $CDCl_3$):** 12.87 (s, 1H, O*H* at C11, correlation with C10 in HMBC), 12.76 (s, 1H, O*H* at C8), 9.01 (s, 1H, O*H* at C1, correlation with C2 and C1 in HMBC), 7.35 (d, *J* = 9.6 Hz, 1H, H10, referring to the ^{1}H assignment of the migration product **40**), 7.30 (d, *J* = 9.6 Hz, 1H, H9, referring to the ^{1}H assignment of the migration product **40**), 6.82 (s, 1H, H2, correlation with C4a, C4, and C1 in HMBC), 6.78 (s, 1H, H4, correlation with C12b, C4a, and C2 in HMBC), 5.23 (s, 1H, H6, correlation with C4a and C12a in HMBC), 3.11 (dd, *J* = 15.6, 4.8 Hz, 1H, H5$_\alpha$, correlation with C12b, C6a, C5, C4, and C4a in HMBC), 2.94 (dd, *J* = 15.6, 4.2 Hz, 1H, H5$_\beta$, correlation with C12b, C6a, C5, C4, and C4a in HMBC), 2.68 (s, 1H, O*H*

at C6, correlation with H6 in COSY), 2.34 (s, 3H, CH_3 at C3);**δ_C (150 MHz, $CDCl_3$):** 187.0 (C12, referring to the assignment of the migration product **40**), 183.7 (C7, referring to the assignment of the migration product **40**), 162.5 (C11, correlation with H10), 160.9 (C8 correlation with H9), 155.7 (C1, correlation with OH at C1 and H2), 144.3 (C3, correlation with C$\underline{H}_3$), 144.2 (C6a, correlation with H5), 141.2 (12a, correlate with H6), 136.6 (C12b, correlation with H4 and H5), 132.6 (C10, correlation with OH at C11 in HMBC and with H10 in HSQC), 131.1 (C9, correlation with H9 in HSQC), 124.0 (C4, correlation with H2 and H5 in HMBC), 120.6 (C2, correlation with OH at C1 and H4 in HMBC), 114.0 (C4a, correlation with OH at C1, H2, H4, and C$\underline{H}_3$ at C3), 112.5 (C7a, correlation with H9), 111.0 (C11a, correlation with H10), 61.2 (C6, correlation with H5), 36.7 (C5, correlation with H5 in HSQC), 21.3 (*C*H_3 at C3, correlation with CH_3 in HSQC and with C3 in HMBC); **HRMS (ESI)**: calcd for $C_{19}H_{14}NaO_6^+$ $[M + Na]^+$ 361.0683, found *m*/*z* 361.0681.

2.44 Table S5: Comparison of proton NMR data of landomycinone 3 with the literature

^{1}H identity	δ data (ppm) from present study (600 MHz, $CDCl_3$)	δ data (ppm) from literature (500 MHz, $CDCl_3$)[10]
H2	6.82 (s)	6.81 (s)
CH_3 at C3	2.34 (s)	2.32 (s)
H4	6.78 (s)	6.76 (s)
$H5_{eq}$	2.94 (dd, *J* = 15.6, 4.2)	2.92 (dd, *J* = 15.6, 4.1)
$H5_{ax}$	3.11 (dd, *J* = 15.6, 4.8)	3.10 (dd, *J* = 15.6, 4.6)
H6	5.23 (s)	5.21 (d, *J* = 4.1)
H9	7.30 (d, *J* = 9.6)	7.29 (d, *J* = 9.3)
H10	7.35 (d, *J* = 9.6)	7.34 (d, *J* = 9.3)
OH at C1	9.01 (s)	9.00 (s)
OH at C8	12.87 (s)	12.86 (s)
OH at C11	12.76 (s)	12.76 (s)

2.45 Table S6: Comparison of ^{13}C NMR data of landomycinone 3 with the literature

^{13}C identity	δ_C data (ppm) from present study (150 MHz, $CDCl_3$)	Partial δ_C data (ppm) from literature (125 MHz, $CDCl_3$)[10]
C1 (at A ring)	155.7	-
C2 (at A ring)	120.0	120.5
C3 (at A ring)	144.3	-
C4 (at A ring)	124.0	123.9
C4a (at A/B ring)	136.6	-
C5 (at B ring)	36.7	61.1[a]
C6 (at B ring)	61.2	36.6[a]
C6a (at B/C ring)	144.2	-
C7 (at C ring)	183.7	-
C7a (at C/D ring)	112.5	112.4
C8 (at D ring)	160.9	-
C9 (at D ring)	131.1	131.0
C10 (at D ring)	132.6	-
C11 (at D ring)	162.5	-
C11a (at C/D ring)	111.0	110.9
C12 (at C ring)	187.0	-
C12a (at B/C ring)	141.2	-
C12b (at A/B ring)	114.0	-

[a] The initial assignment for C5 and C6 based on ^{1}H and UV spectroscopic data (by Roush) was amended by Rohr based on the ^{18}O isotopic labelling experiment.[12] The amended assignments are 36.6 ppm for C5 and 61.1 ppm for C6.

3. References

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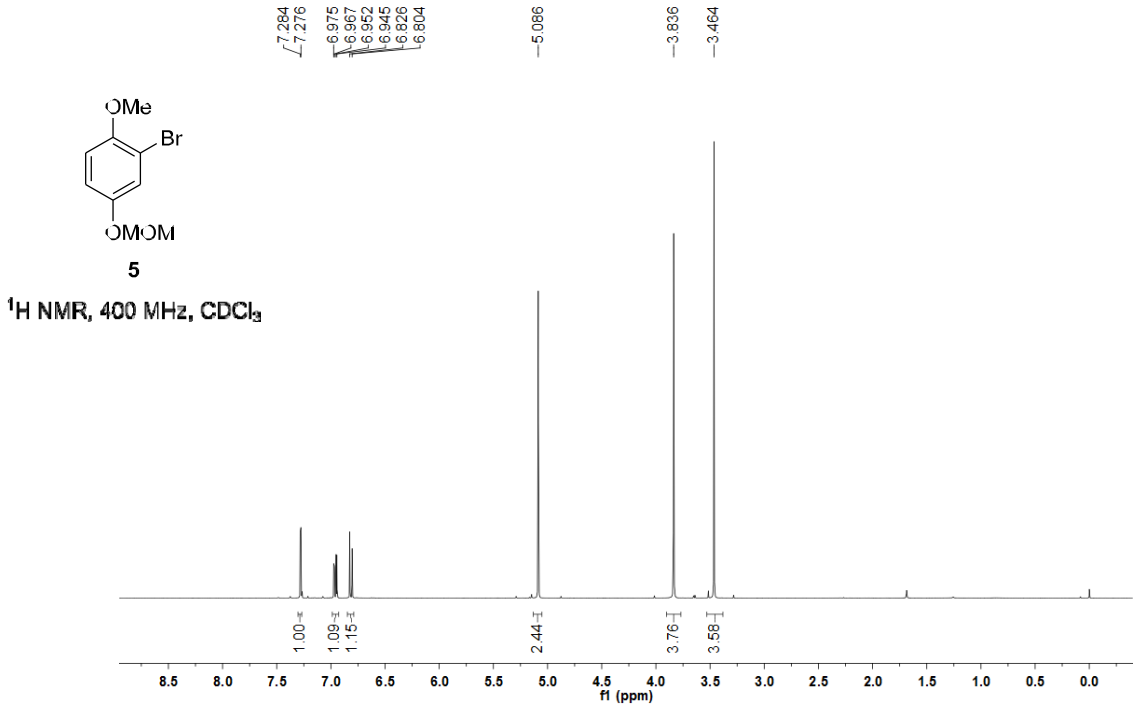
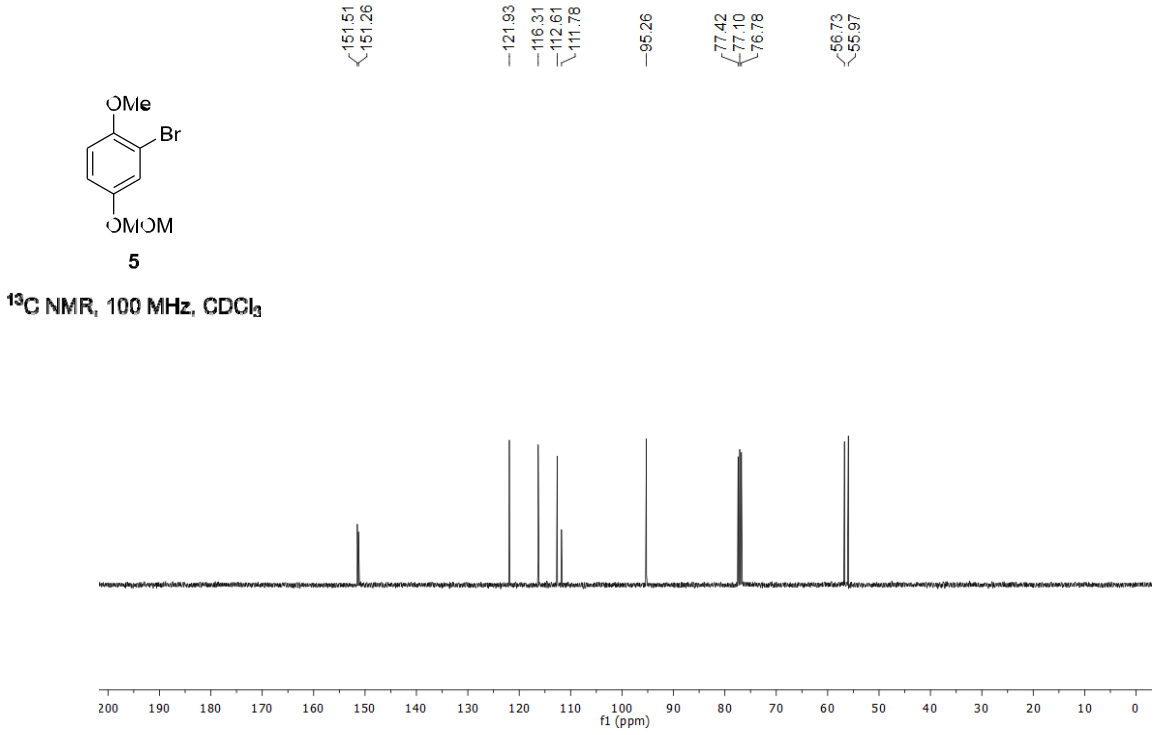
4. NMR spectra and HPLC chromatograms

4.1 NMR spectra of compound 5

^{1}H NMR spectrum

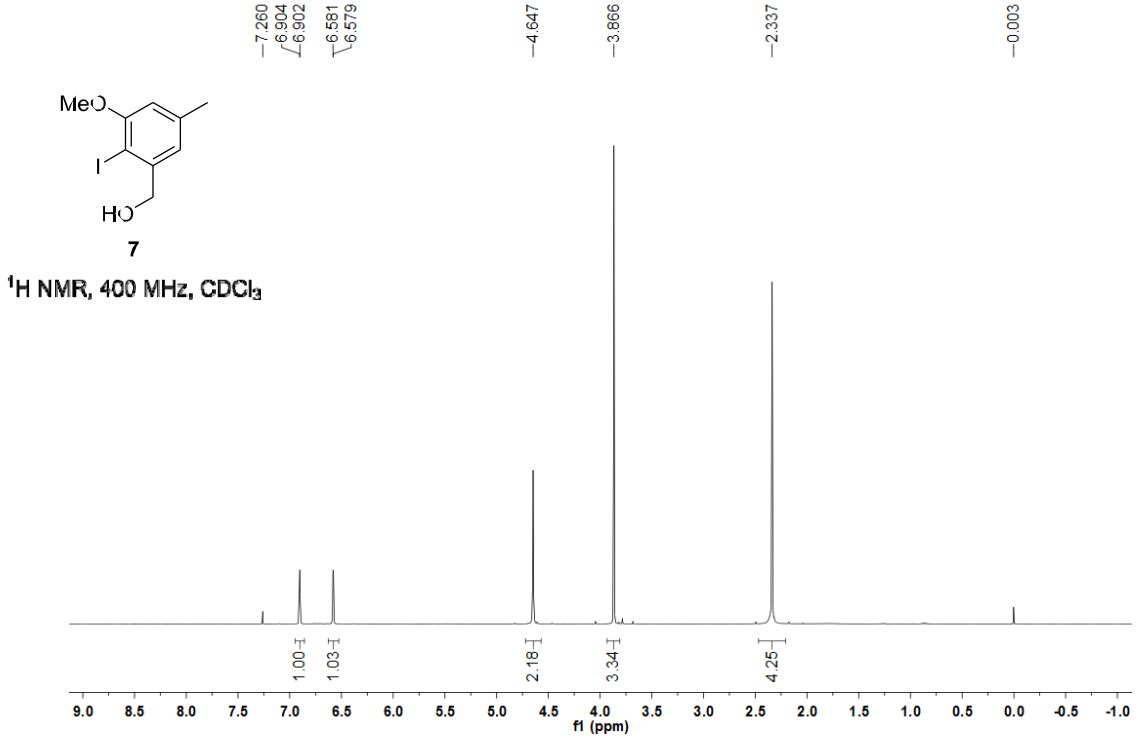


^{13}C NMR spectrum

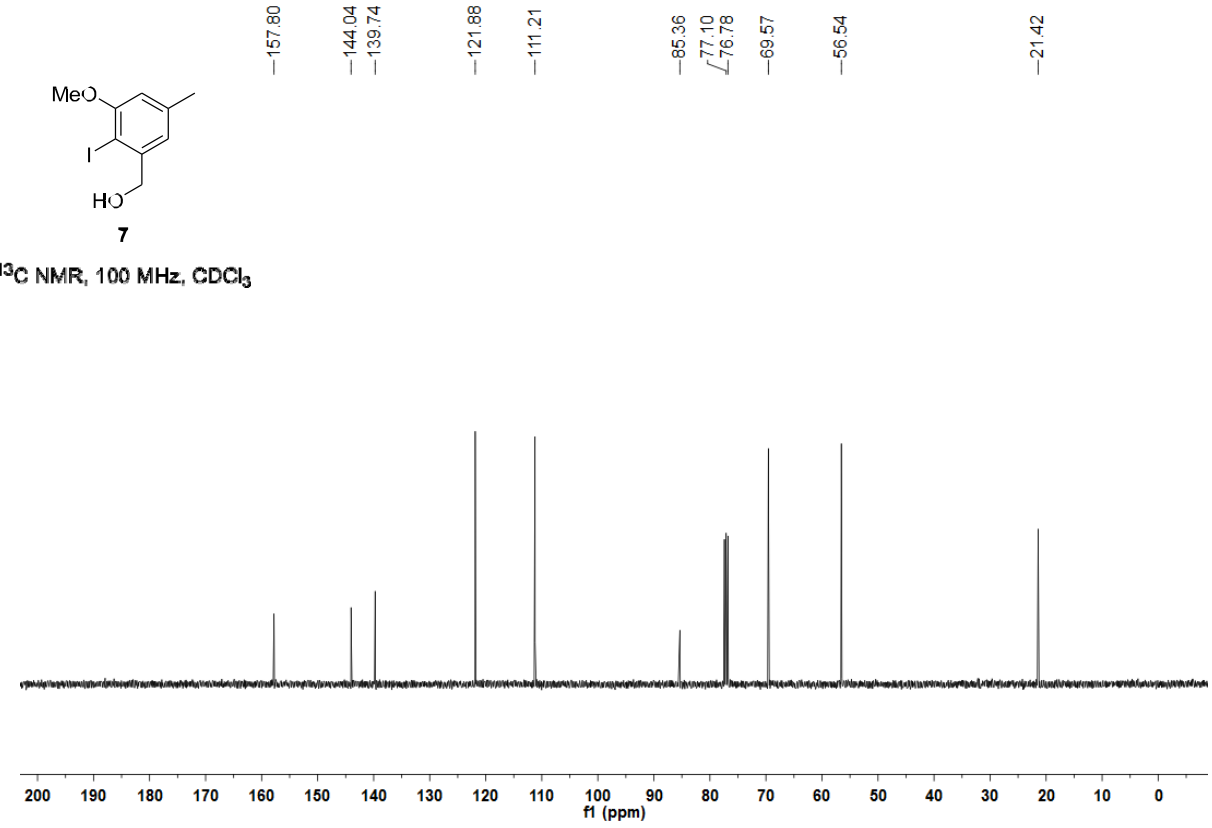


4.2 NMR spectra of compound 7

^{1}H NMR spectrum

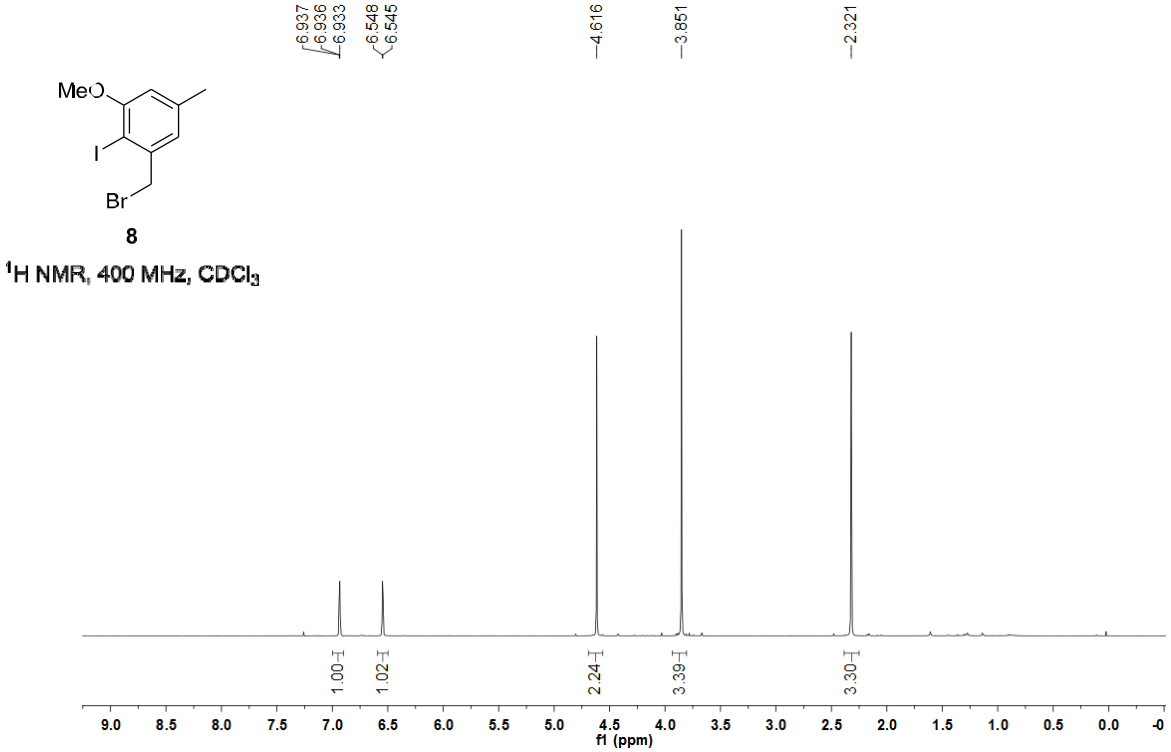


^{13}C NMR spectrum

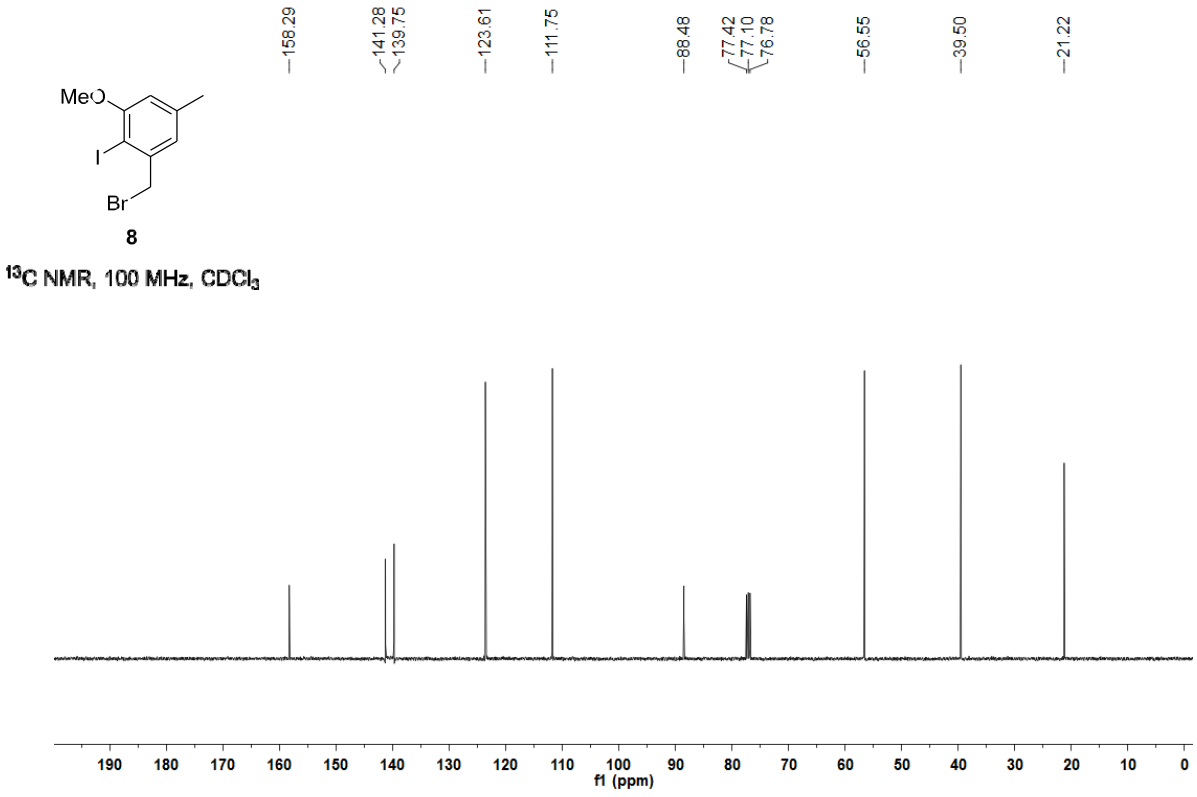


4.3 NMR spectra of compound 8

^{1}H NMR spectrum

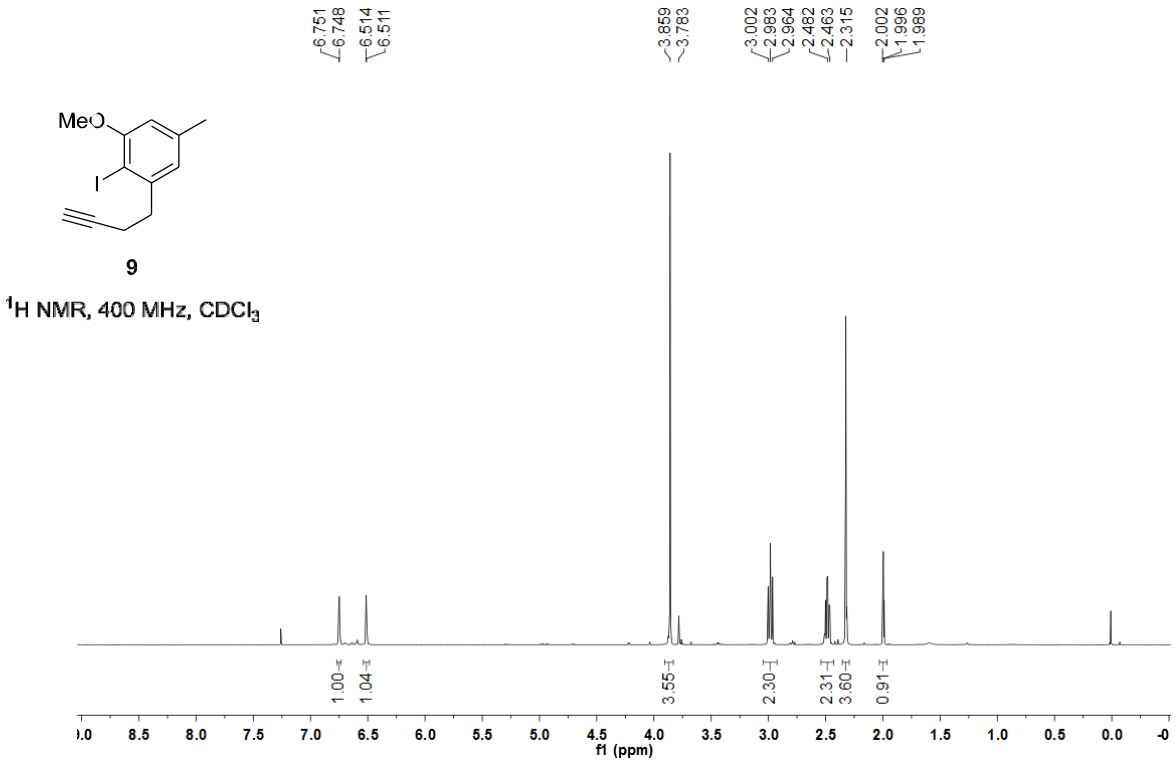


^{13}C NMR spectrum

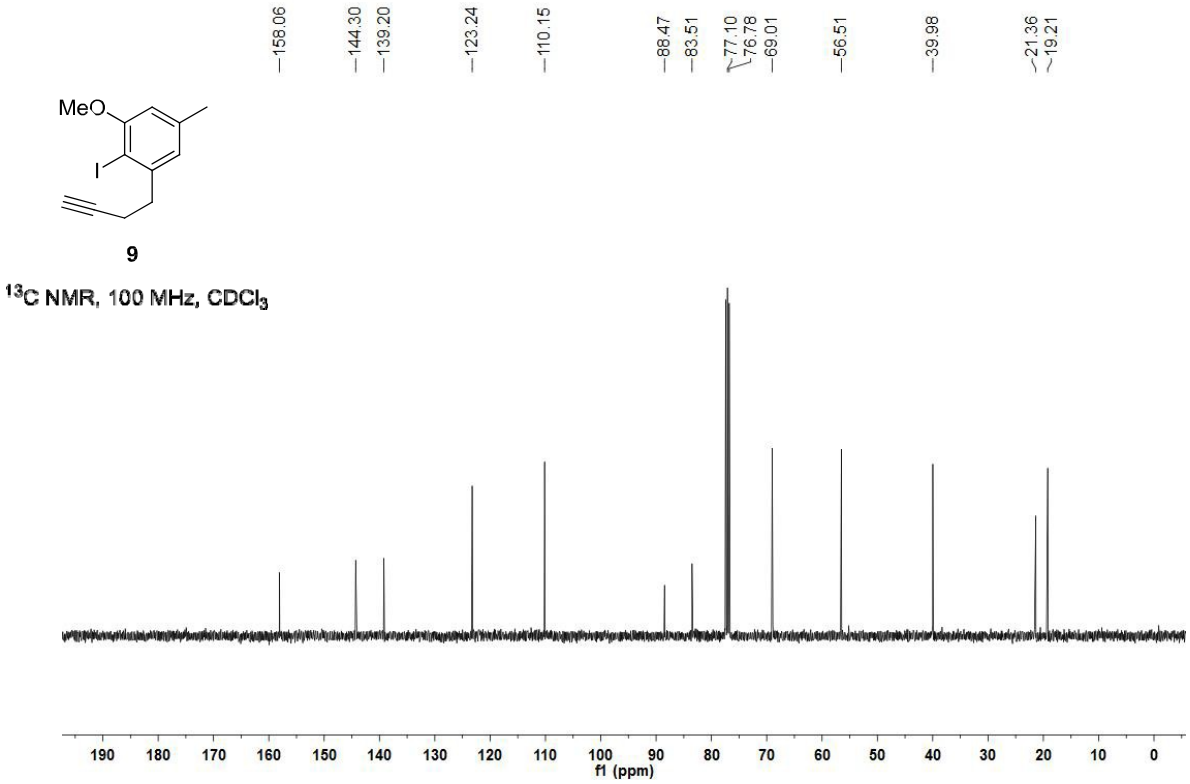


4.4 NMR spectra of compound 9

^{1}H NMR spectrum

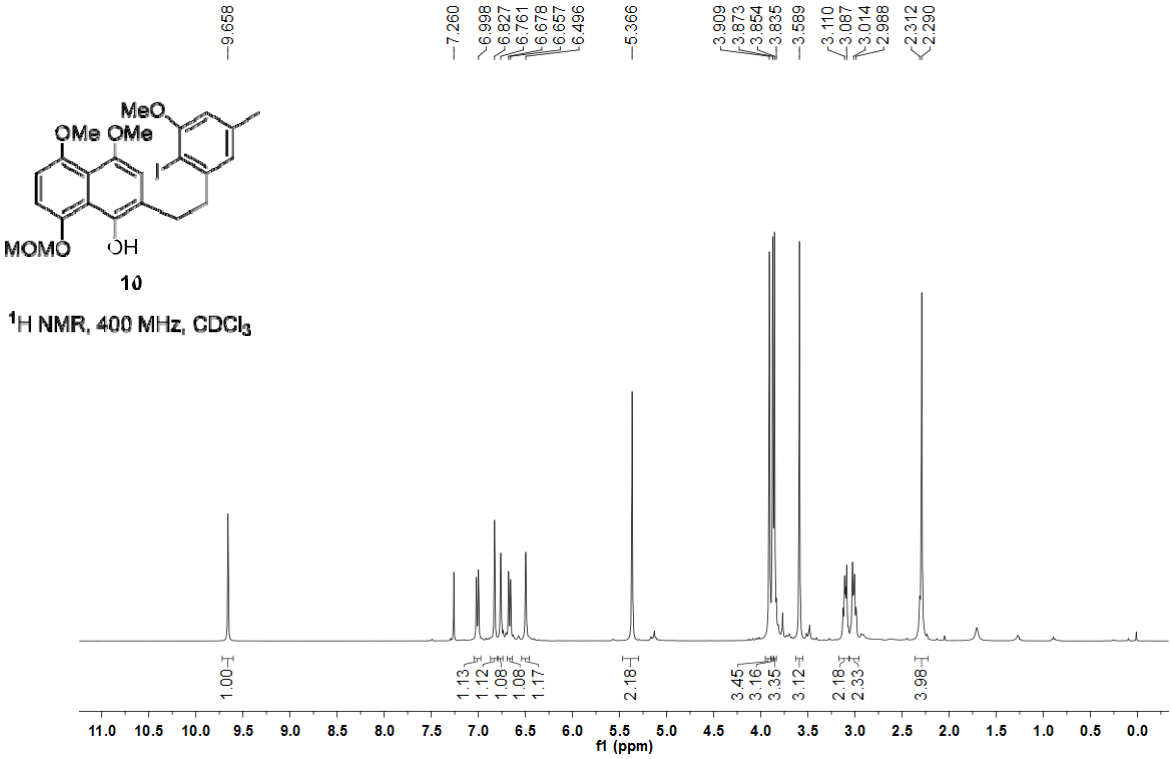


^{13}C NMR spectrum

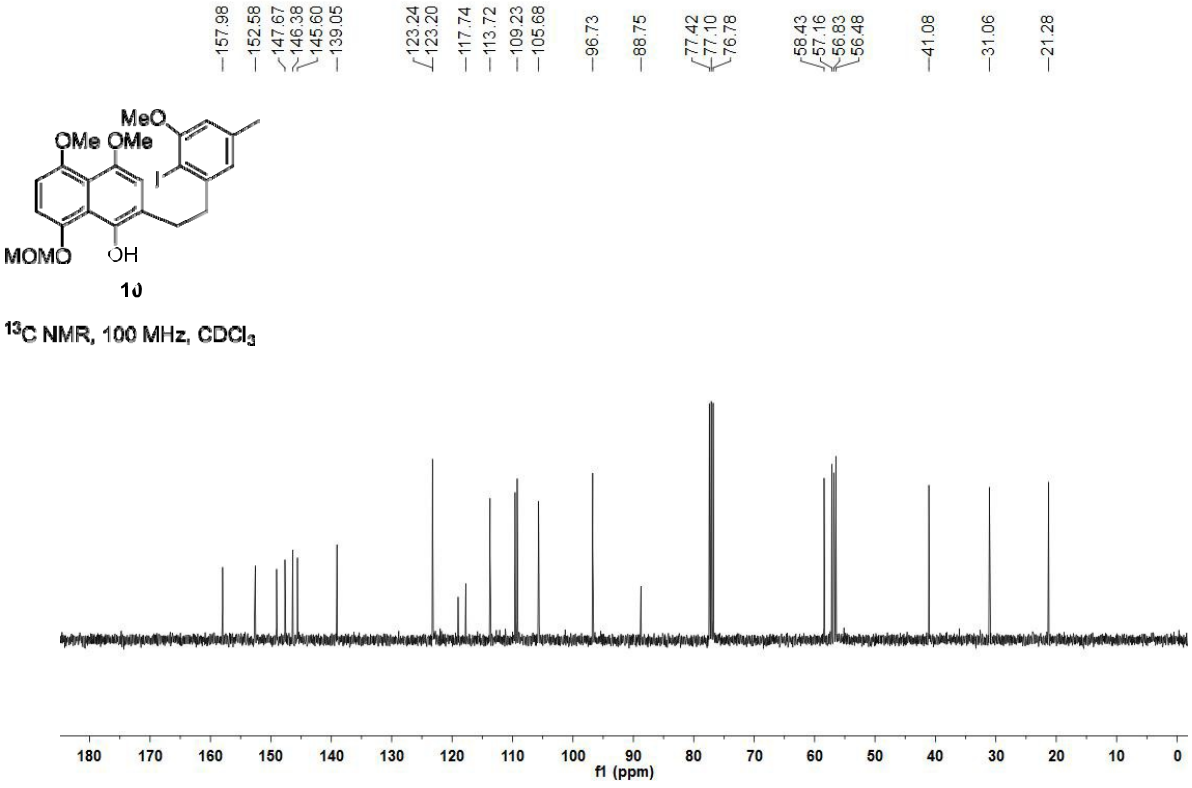


4.5 NMR spectra of compound 10

^{1}H NMR spectrum

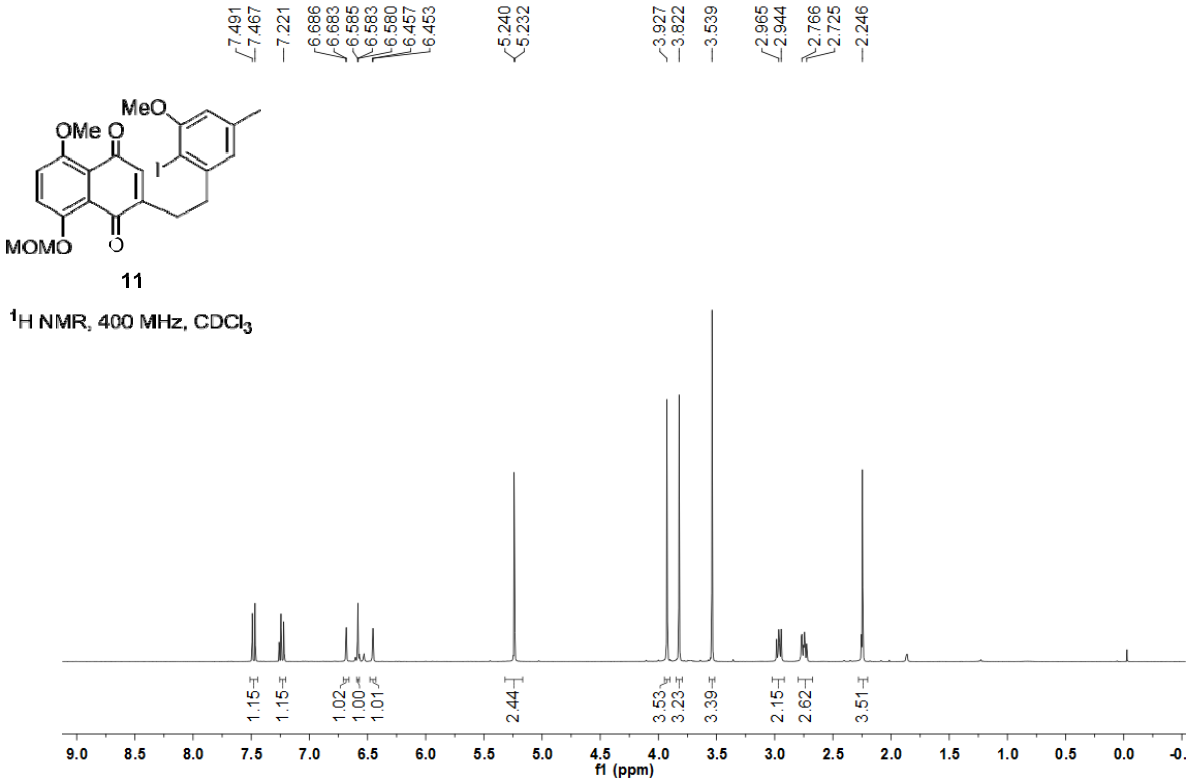


^{13}C NMR spectrum

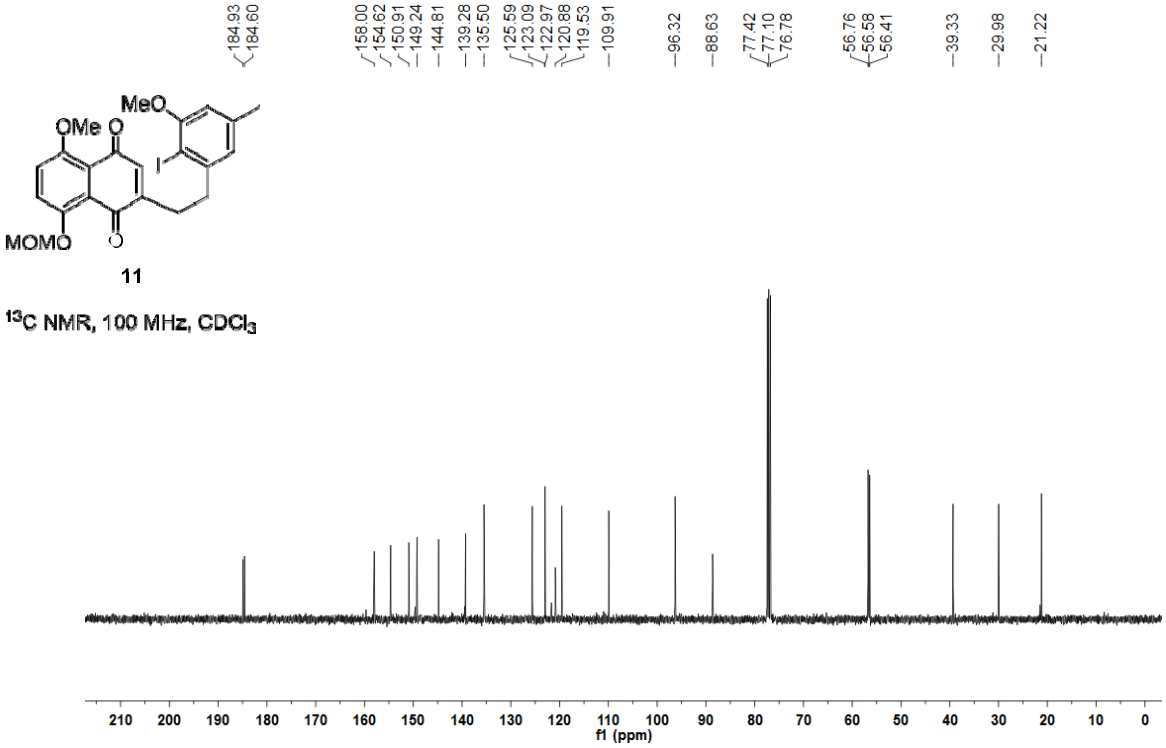


4.6 NMR spectra of compound 11

^{1}H NMR spectrum

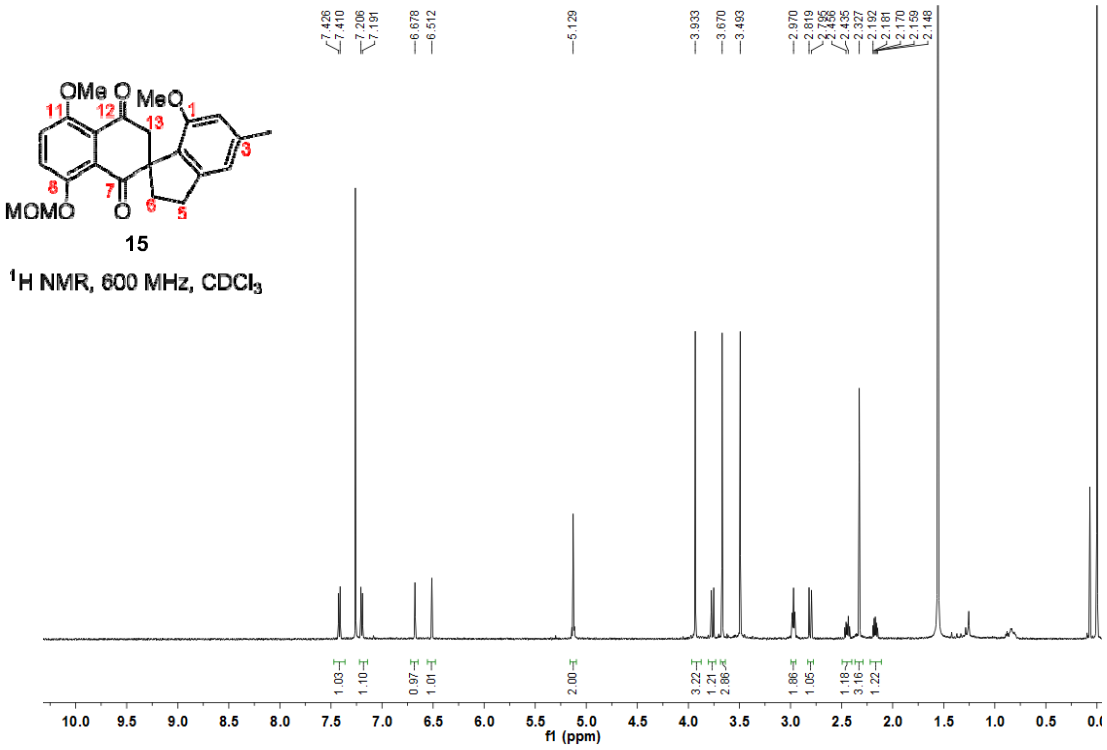


^{13}C NMR spectrum

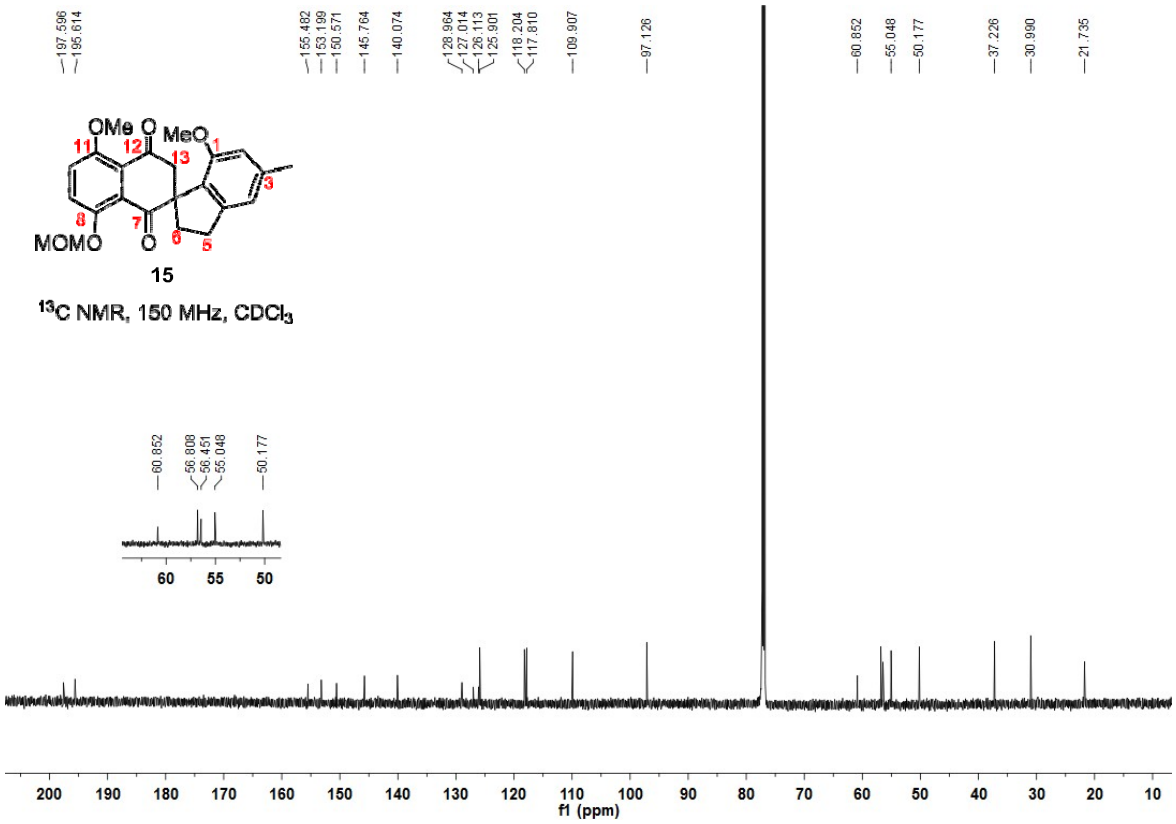


4.7 NMR spectra of compound 15

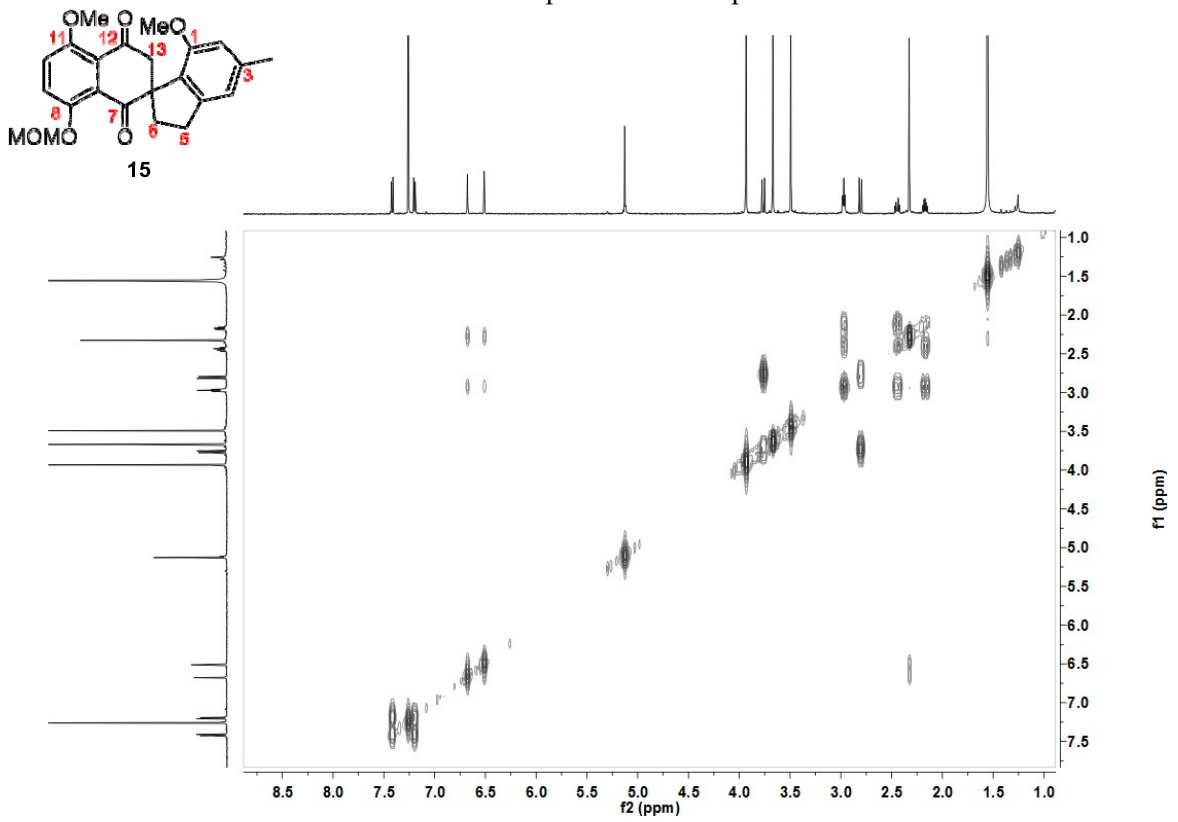
^{1}H NMR spectrum



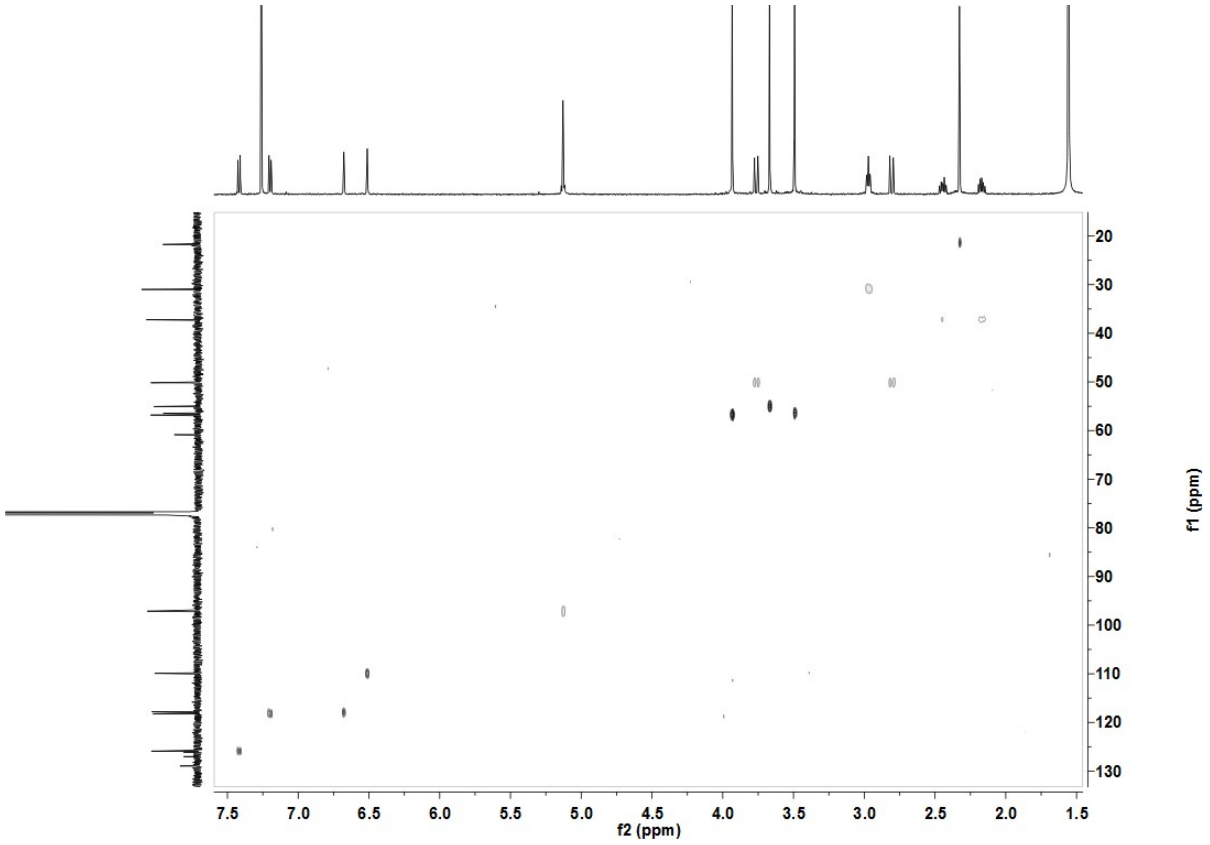
^{13}C NMR spectrum



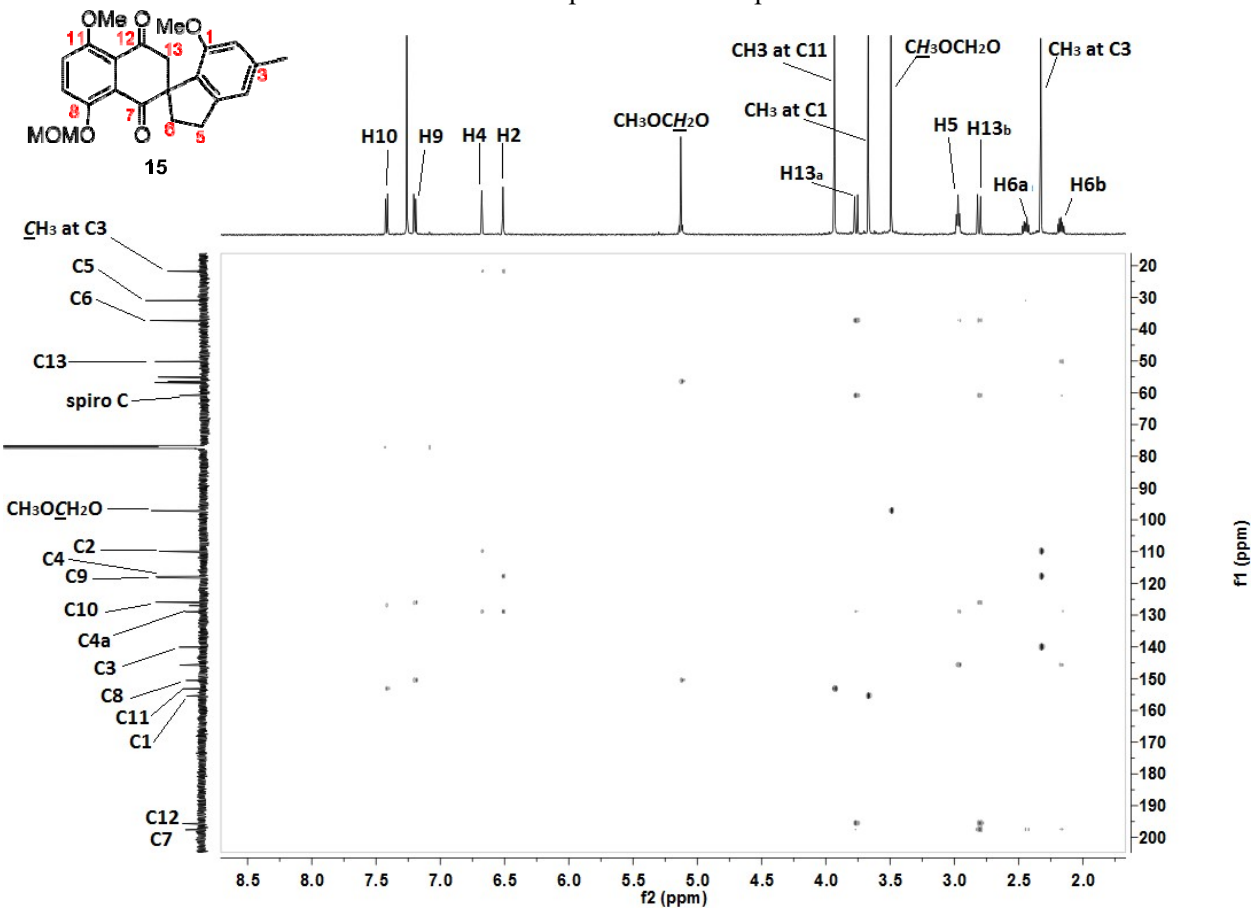
COSY NMR spectrum of compound **15**



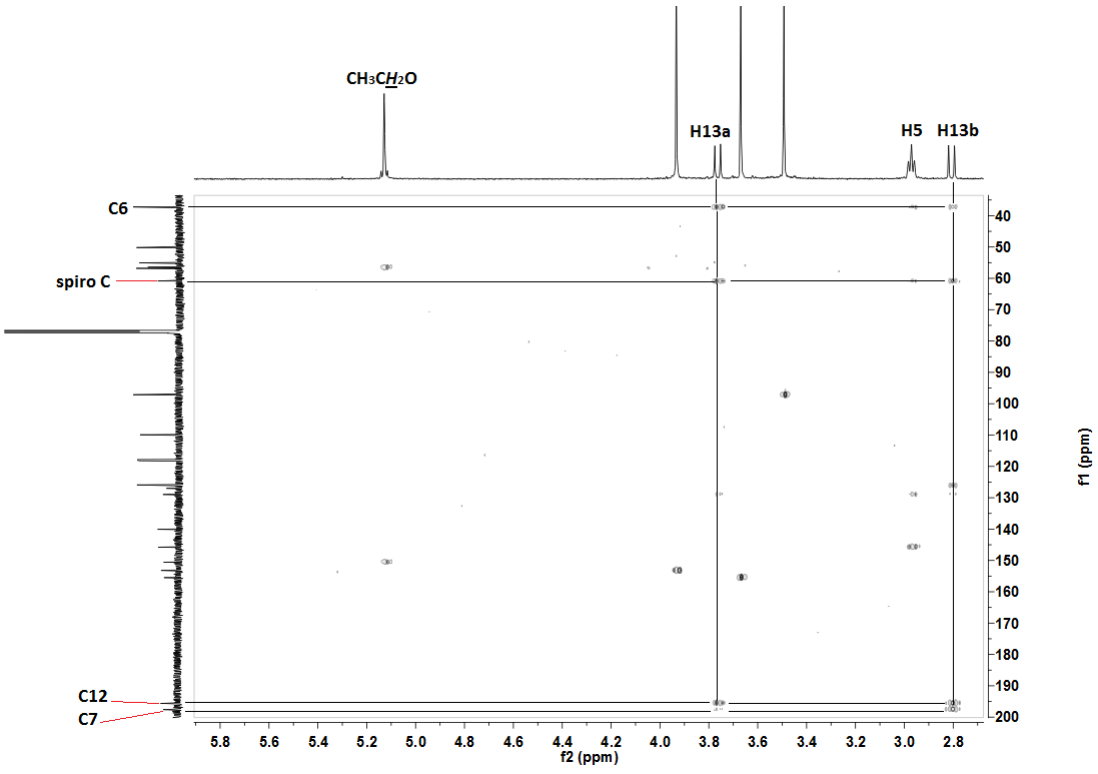
HSQC NMR spectrum



HMBC NMR spectrum of compound **15**

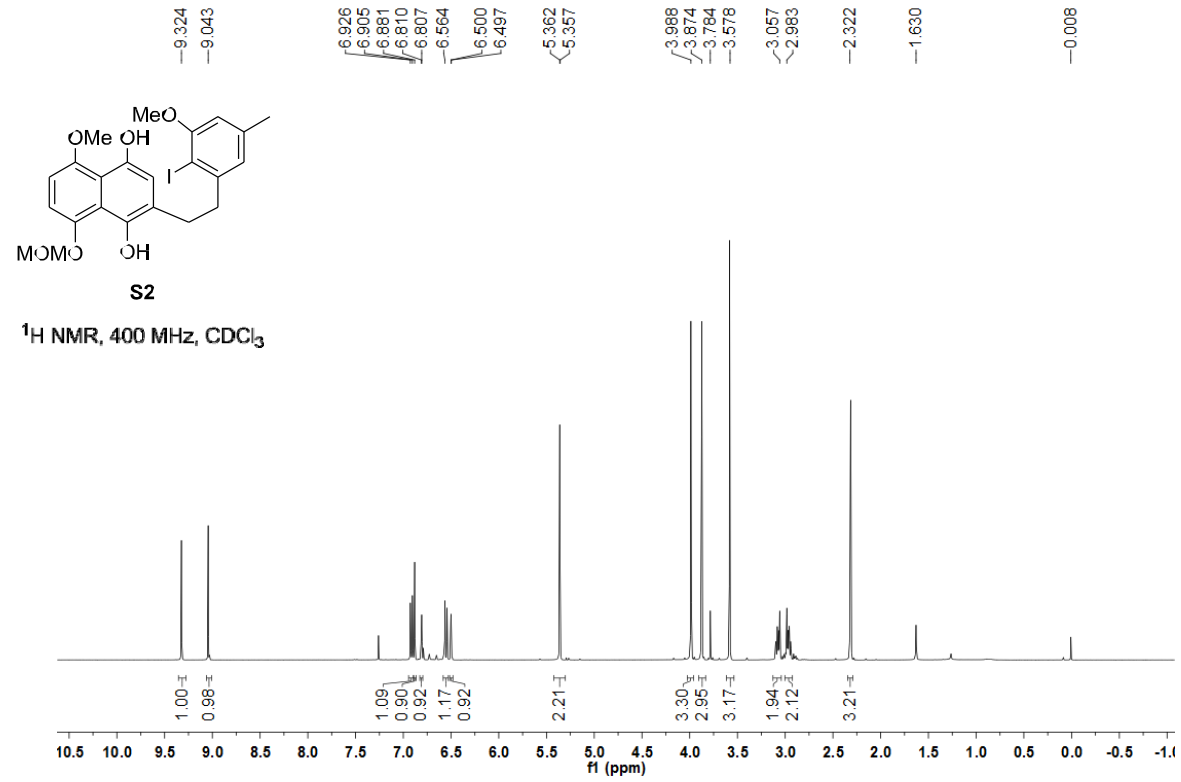


Expanded HMBC NMR spectrum

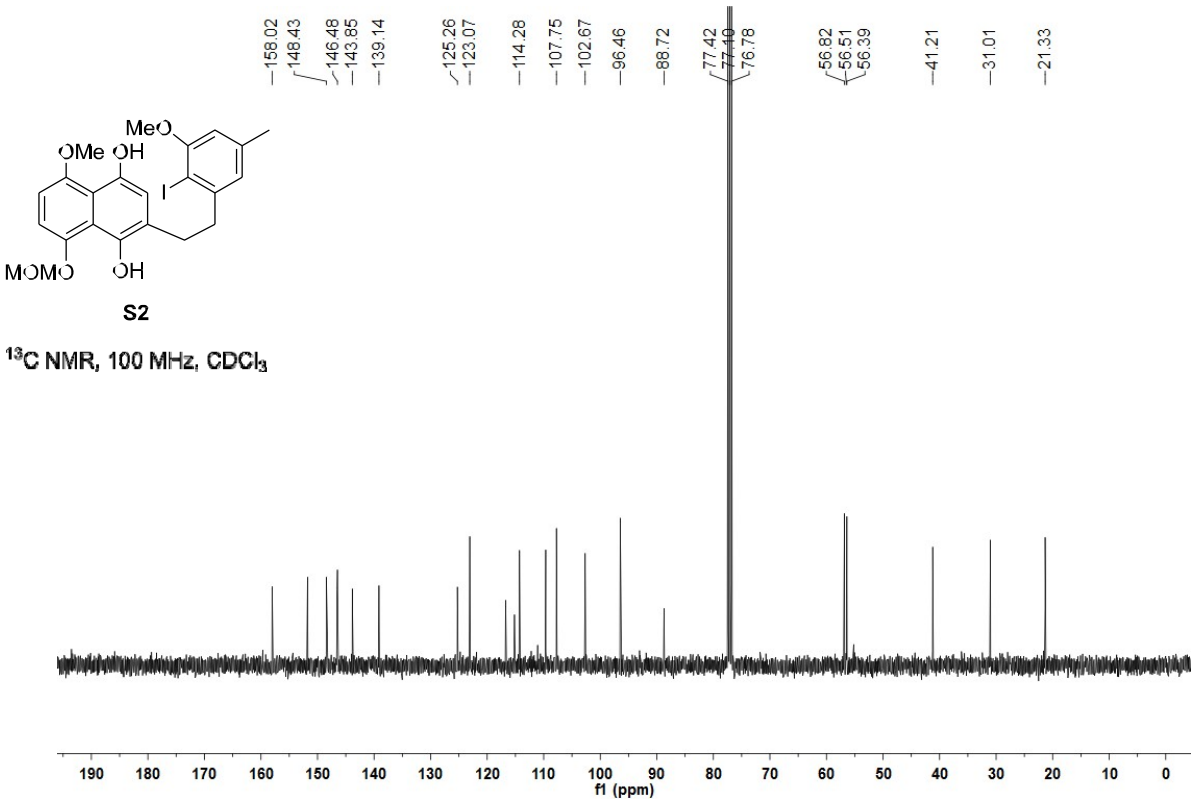


4.8 NMR spectra of compound S2

^{1}H NMR spectrum

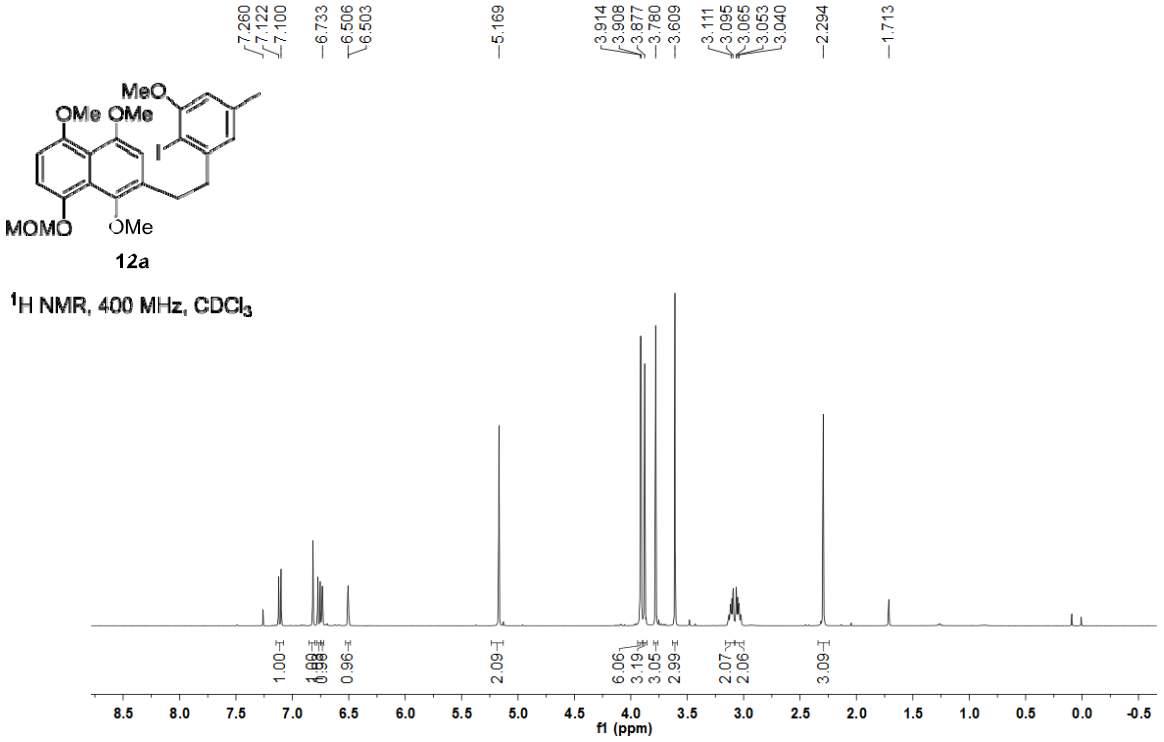


^{13}C NMR spectrum

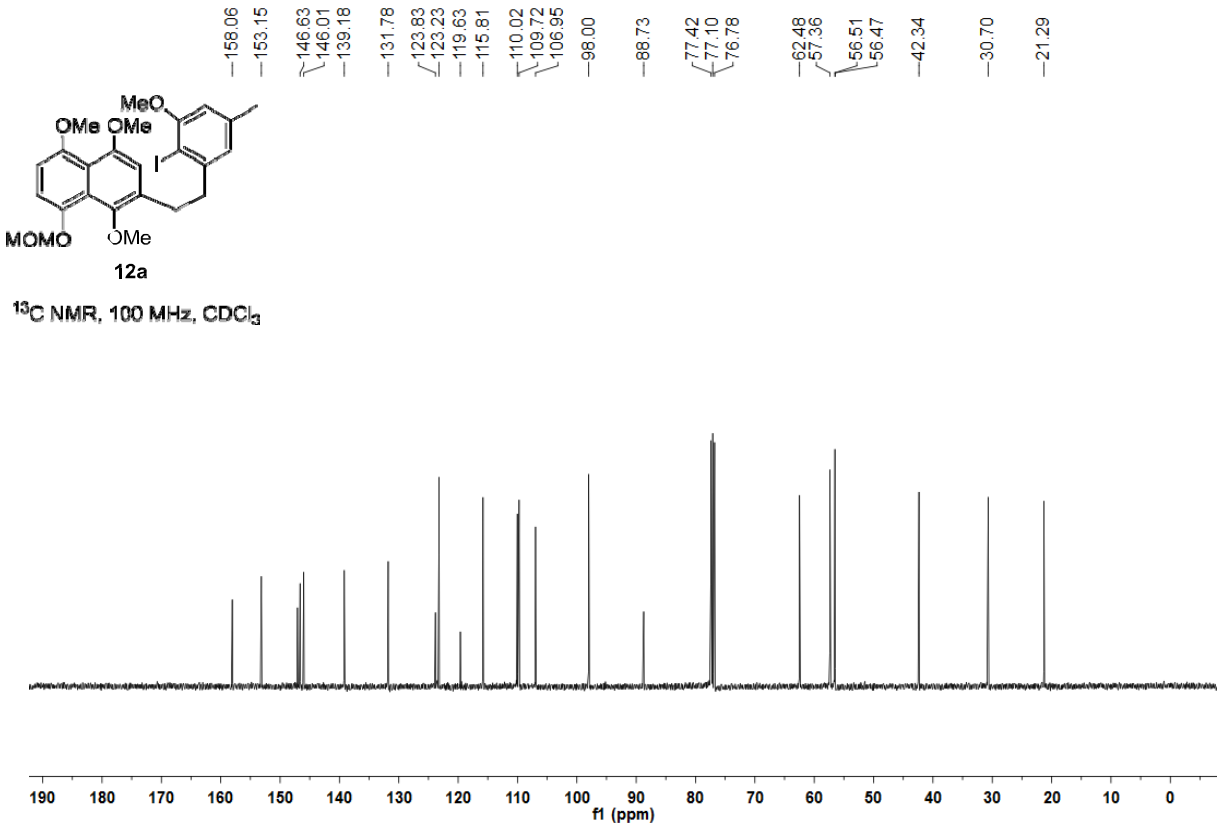


4.9 NMR spectra of compound 12a

^{1}H NMR spectrum

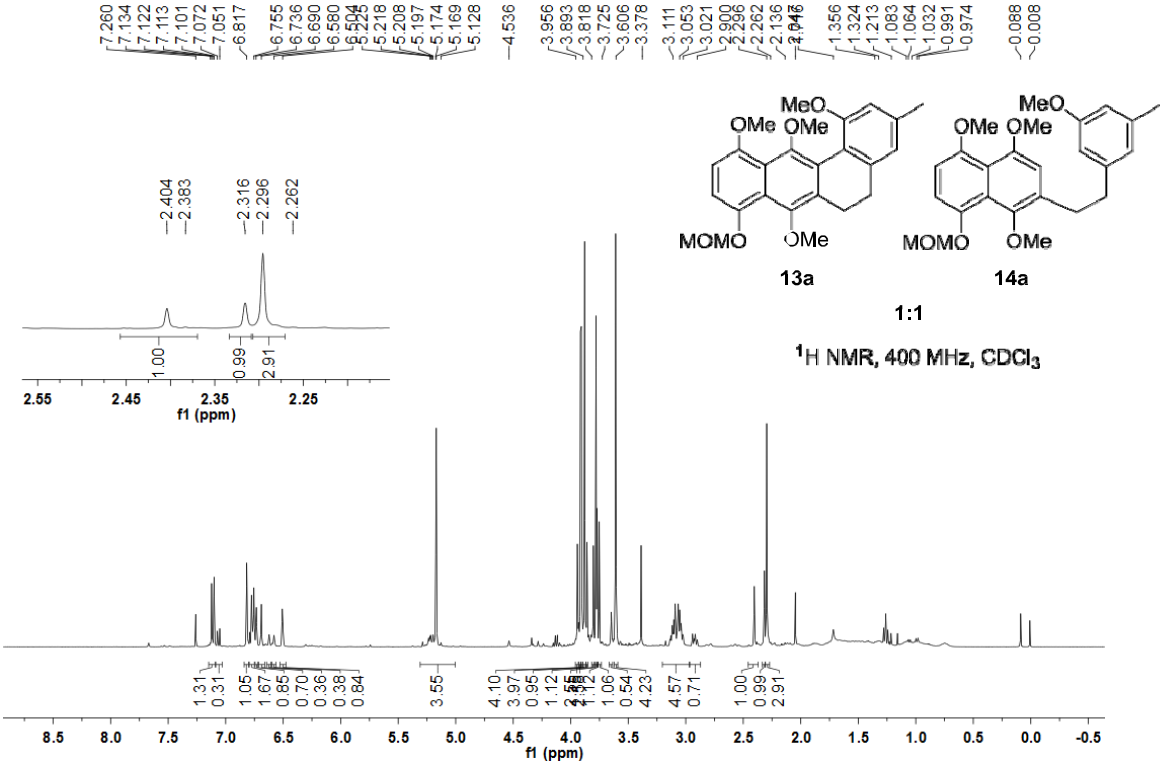


^{13}C NMR spectrum



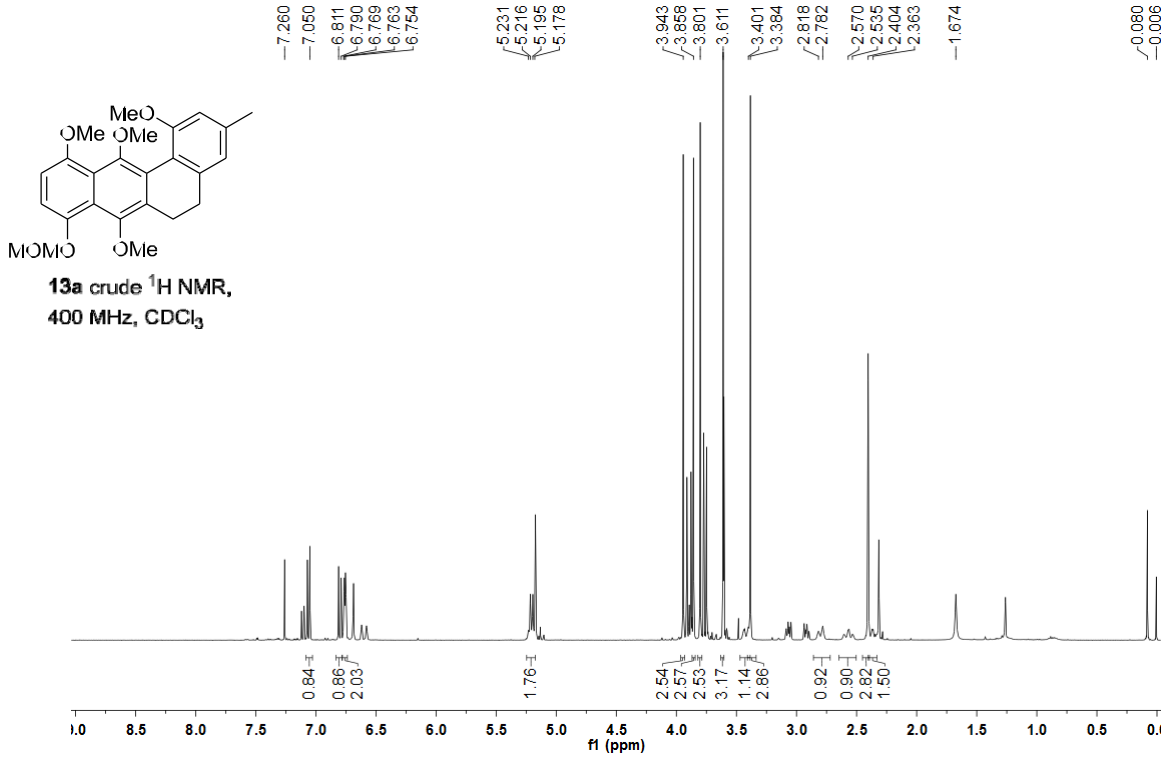
4.10 Crude NMR spectra of compound 13a and 14a (Table 1, entry 1)

Crude ^{1}H NMR spectrum



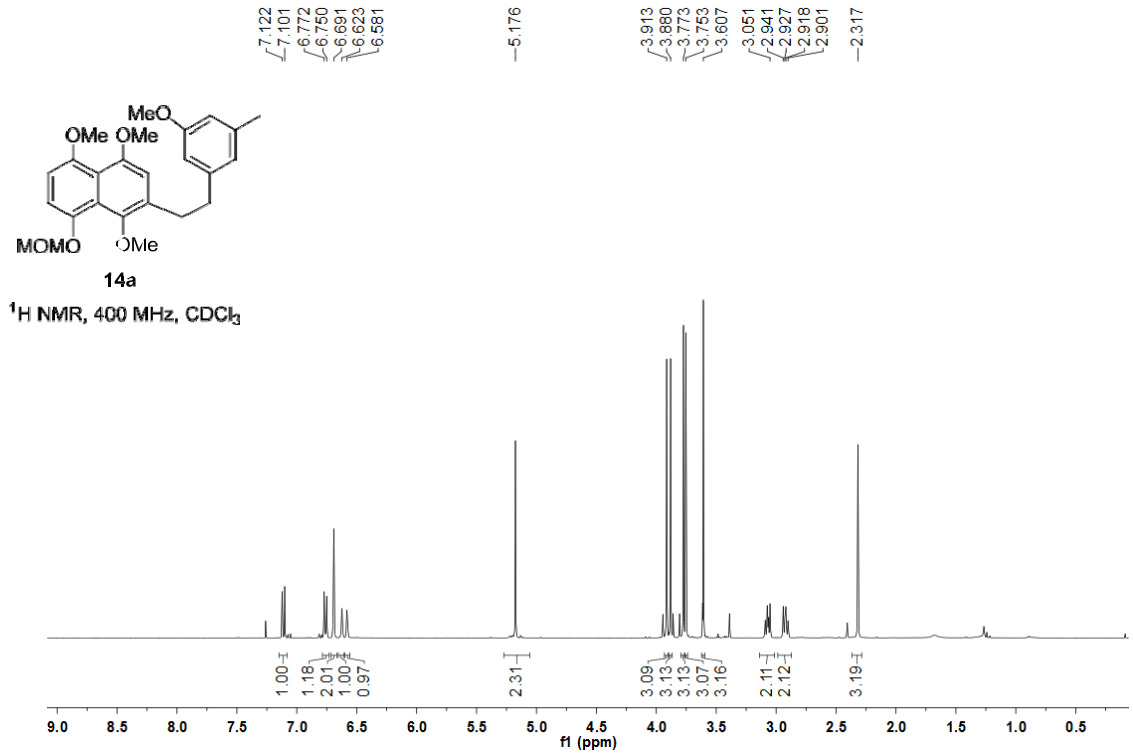
4.11 NMR spectra of compound 13a after deletion of signals from 14a

^{1}H NMR spectrum

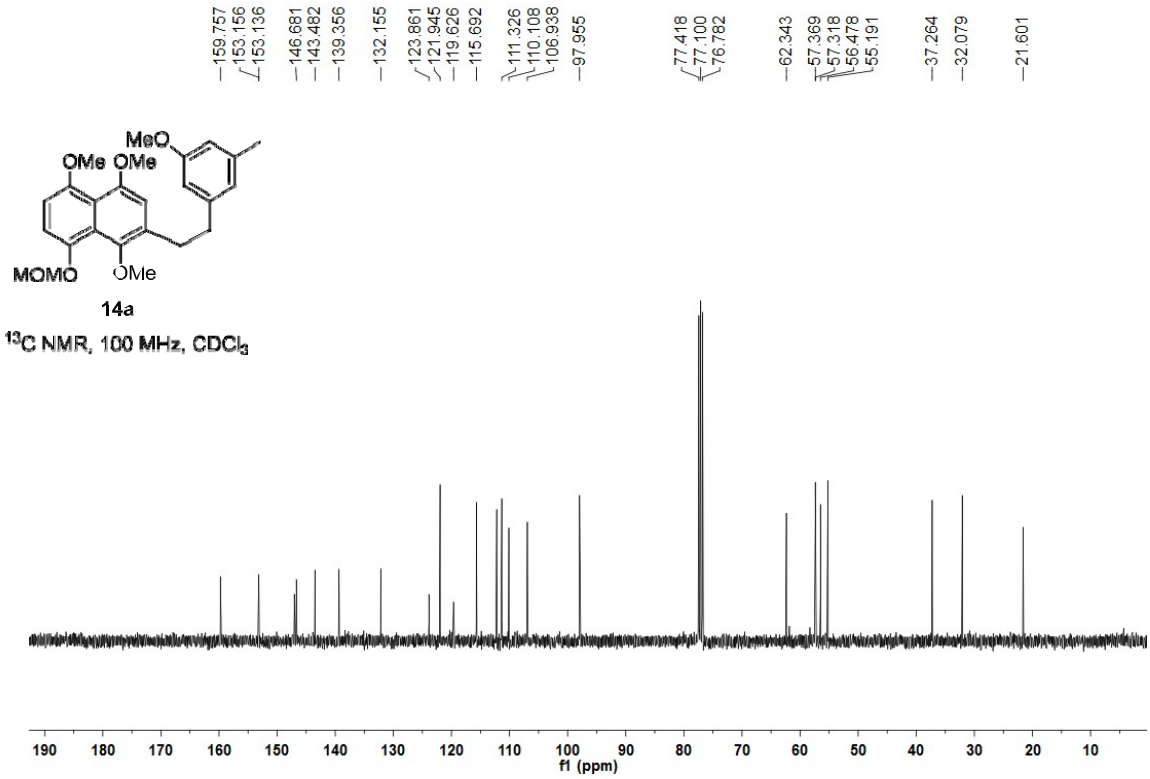


4.12 NMR spectra of compound 14a

^{1}H NMR spectrum

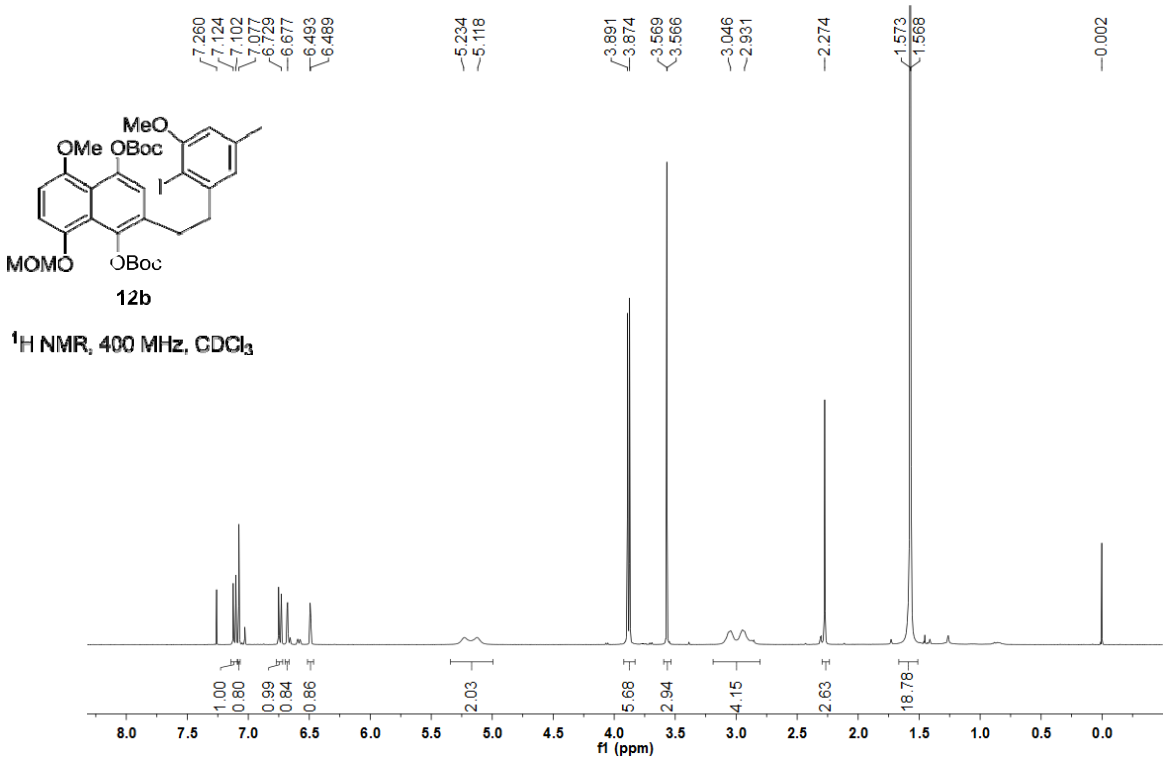


^{13}C NMR spectrum

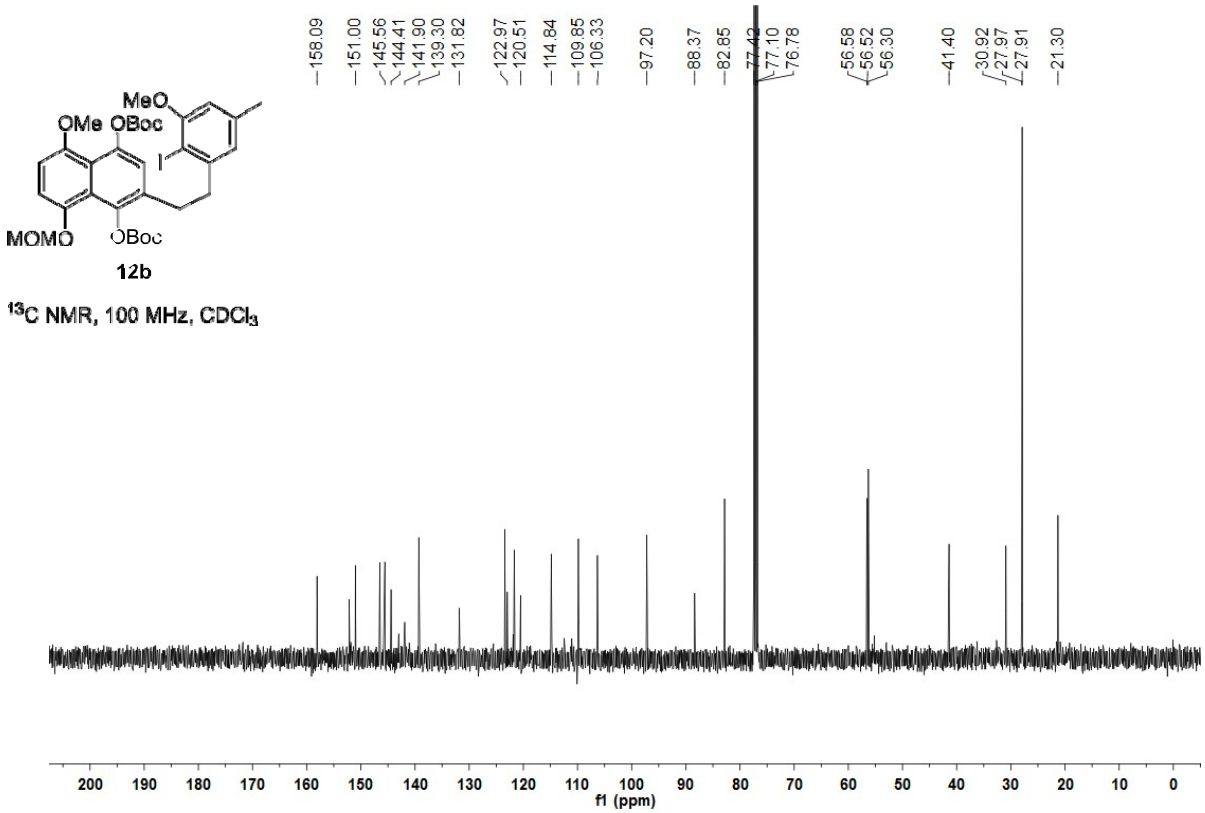


4.13 NMR spectra of compound 12b

^{1}H NMR spectrum

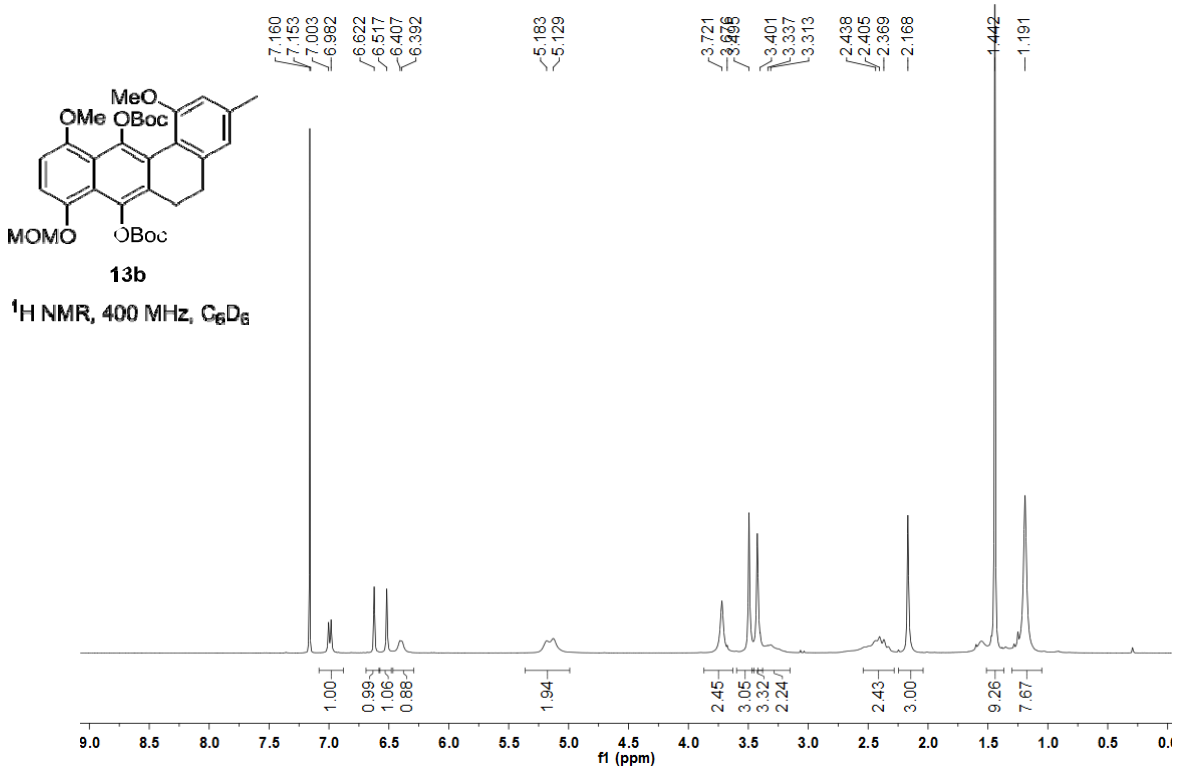


^{13}C NMR spectrum

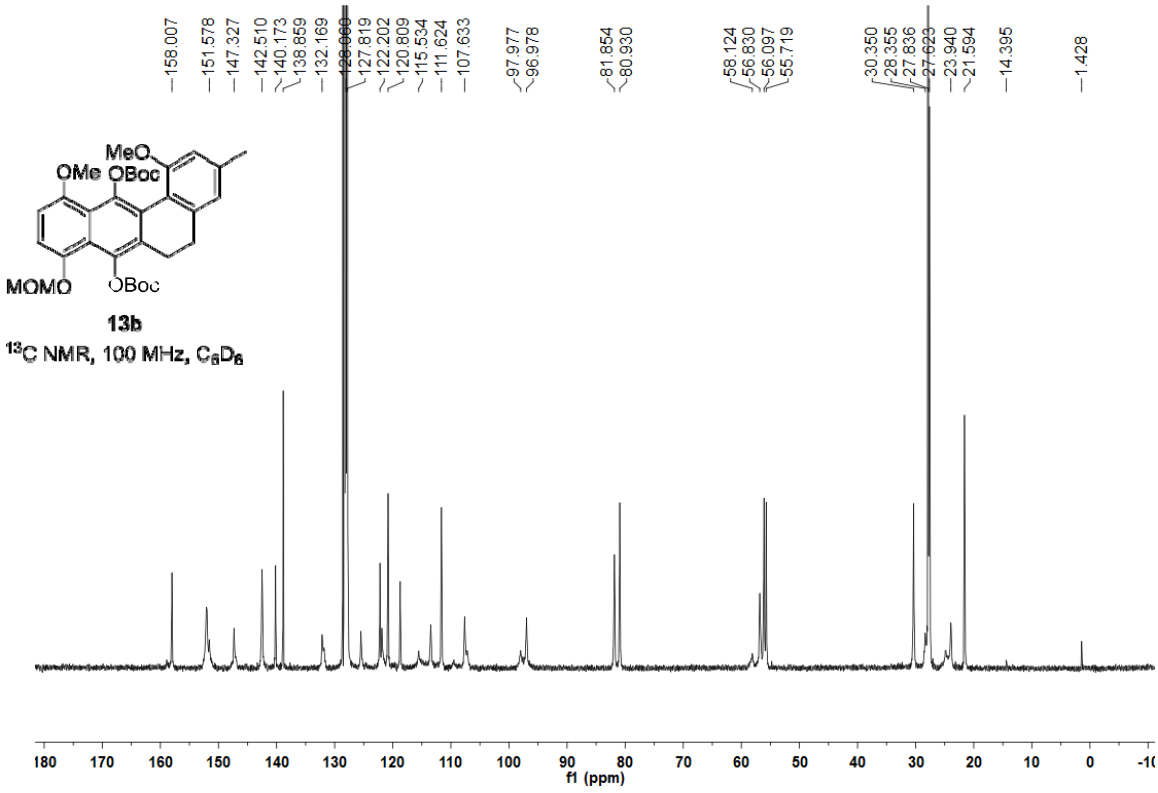


4.14 NMR spectra of compound 13b

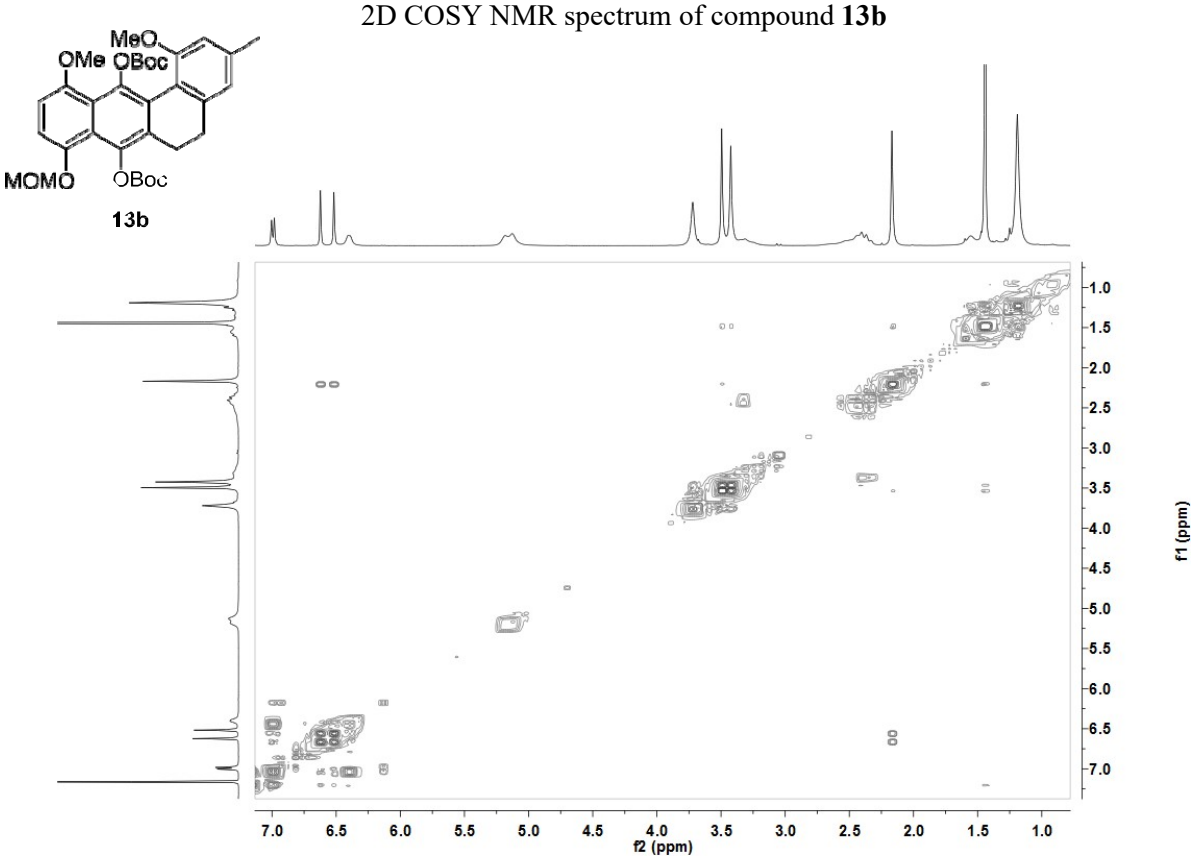
^{1}H NMR spectrum



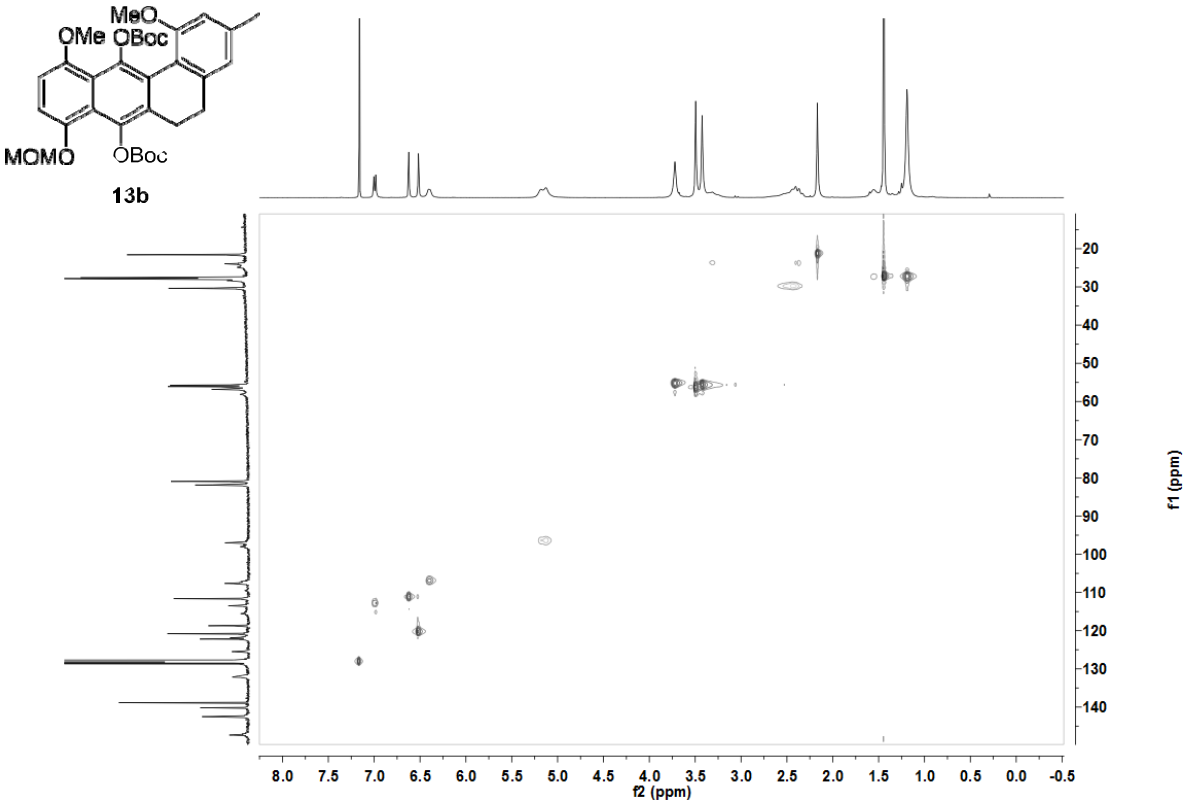
^{13}C NMR spectrum



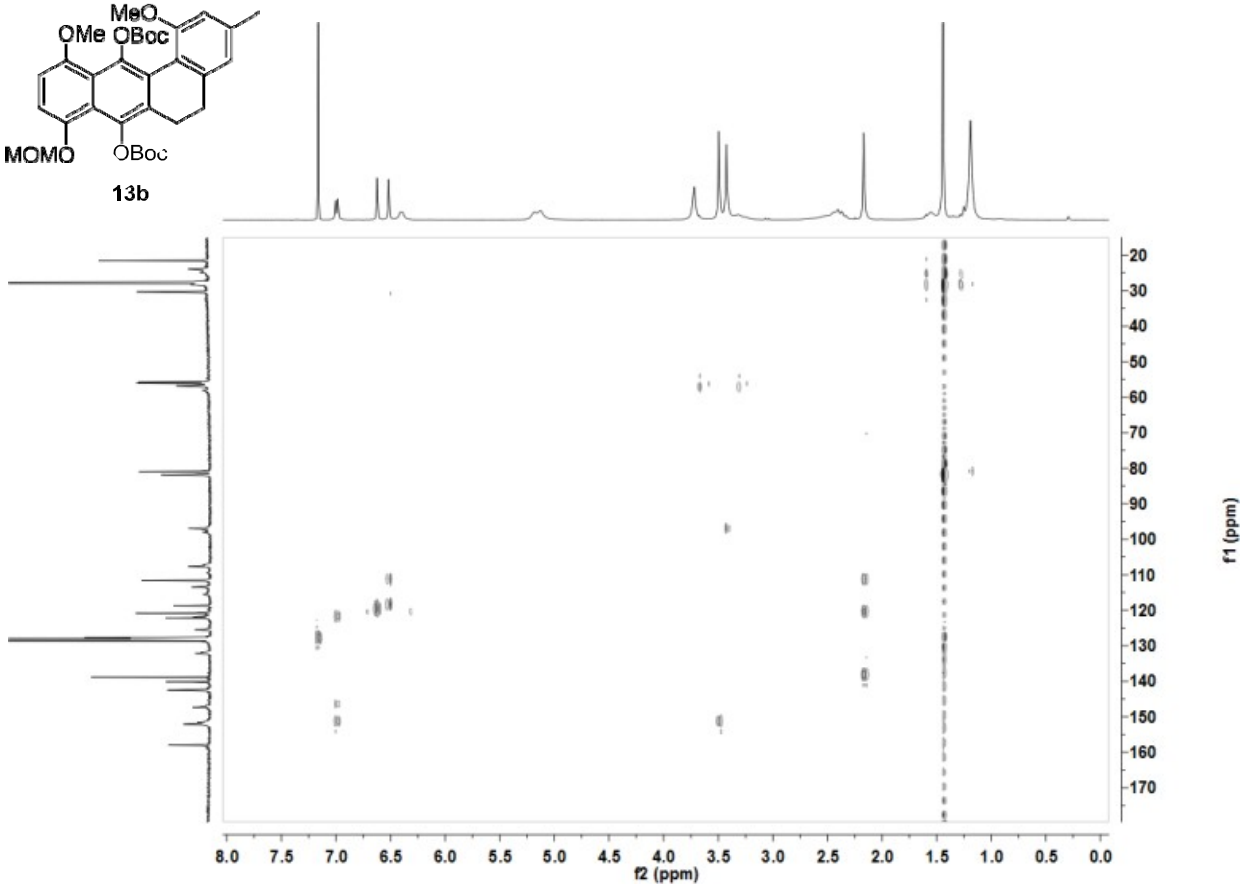
2D COSY NMR spectrum of compound **13b**



2D HSQC NMR spectrum

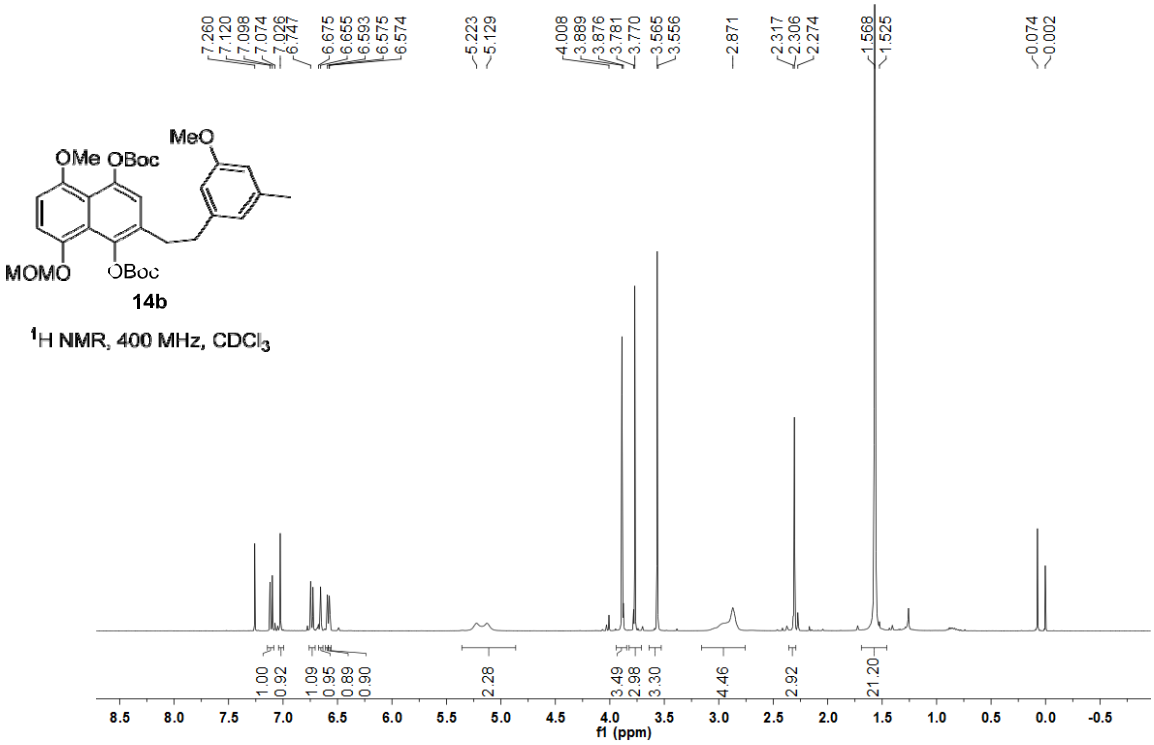


2D HMBC NMR spectrum of compound **13b**

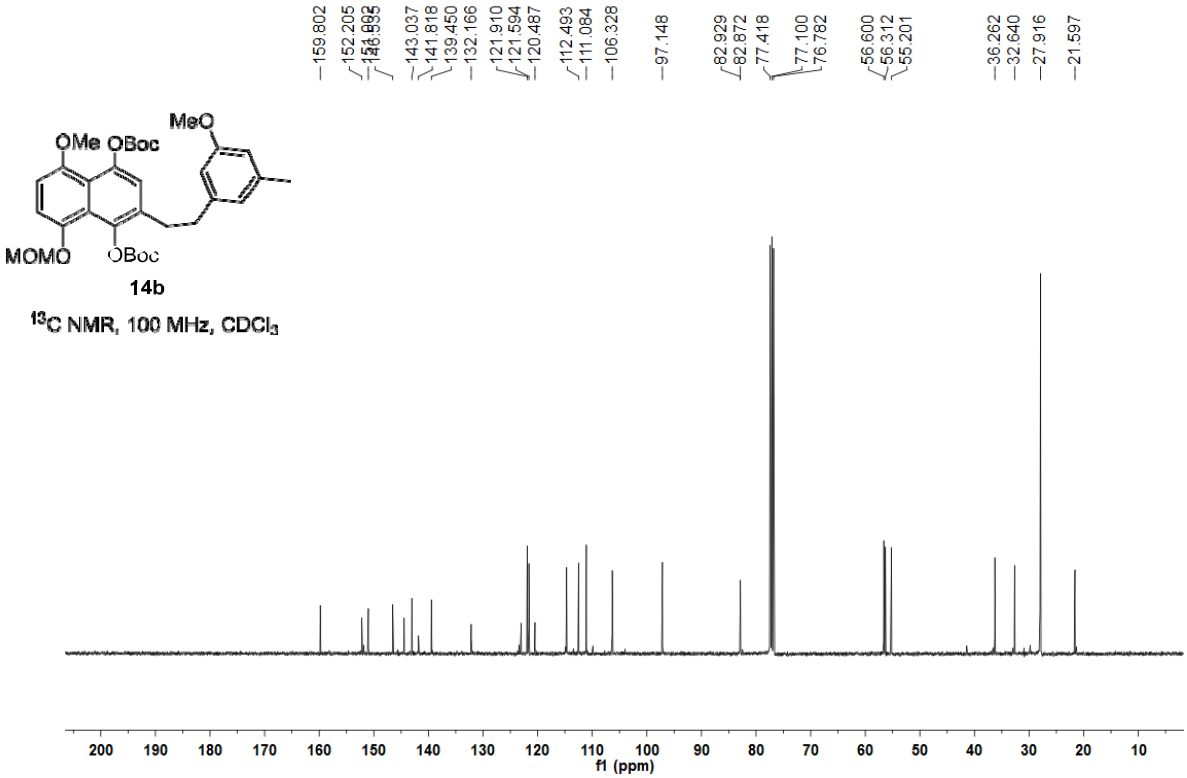


4.15 NMR spectra of compound 14b

^{1}H NMR spectrum

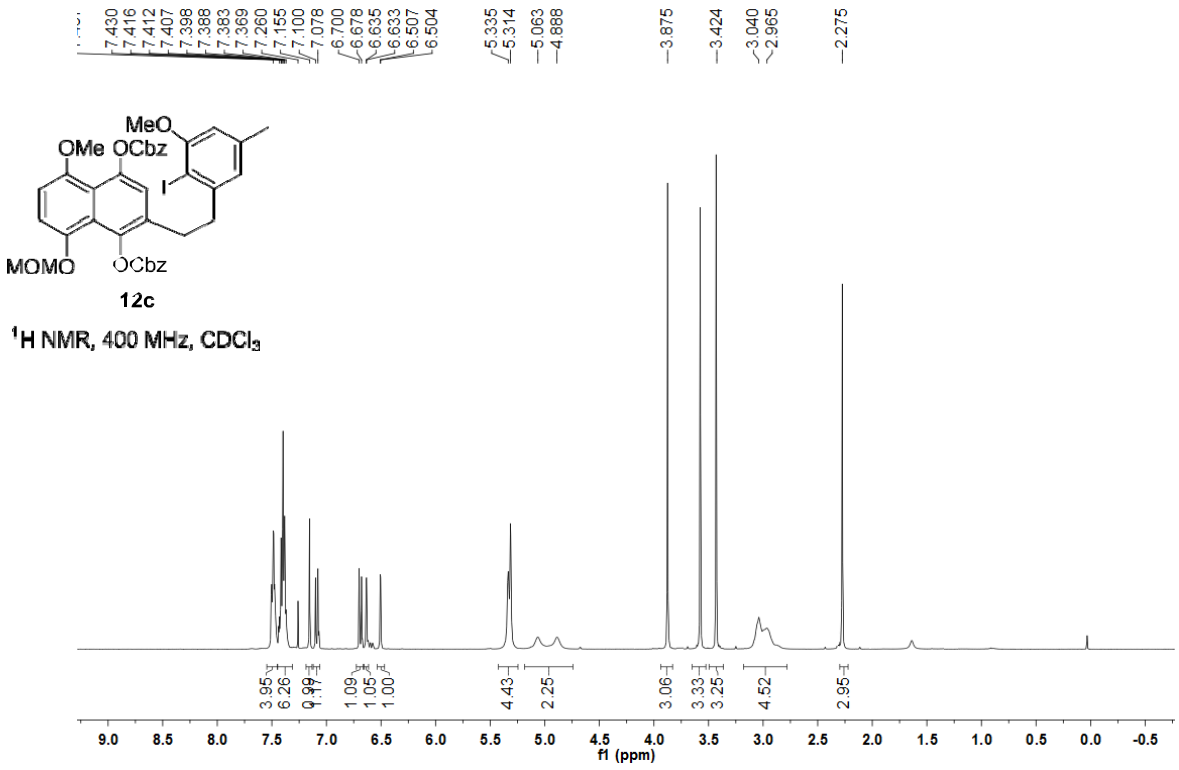


^{13}C NMR spectrum

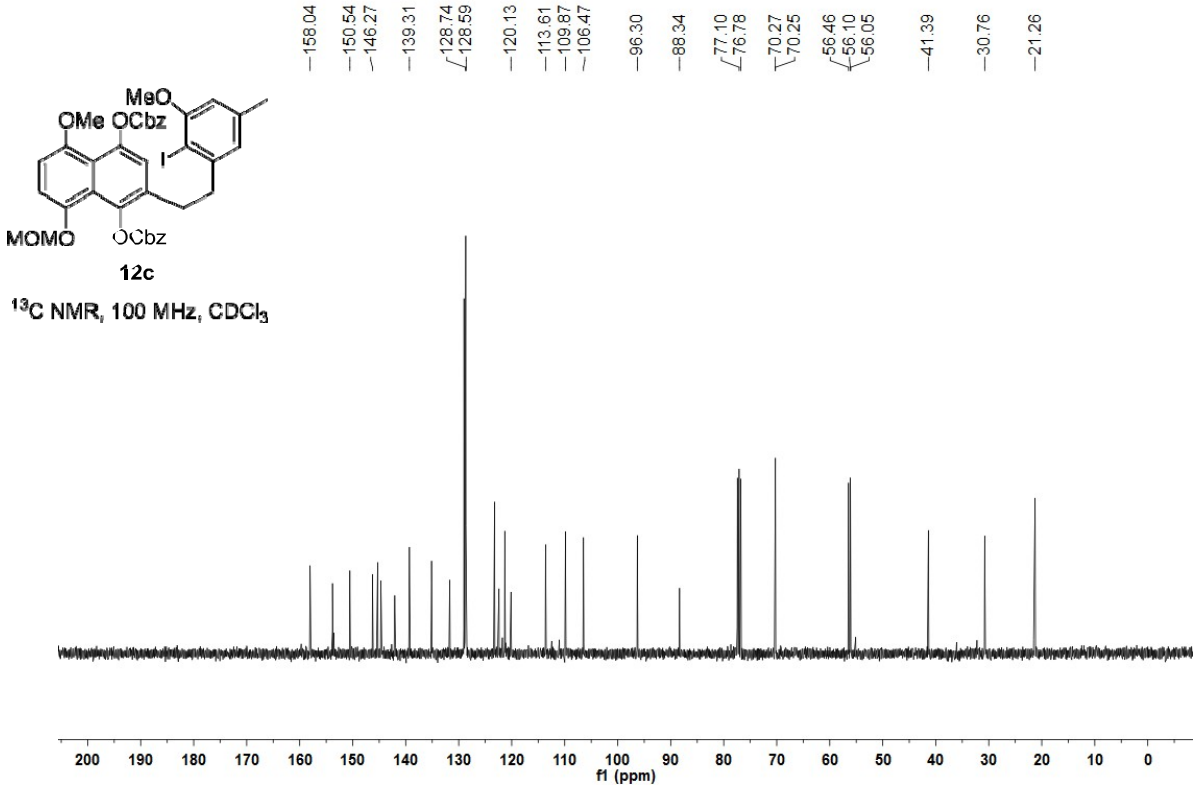


4.16 NMR spectra of compound 12c

^{1}H NMR spectrum

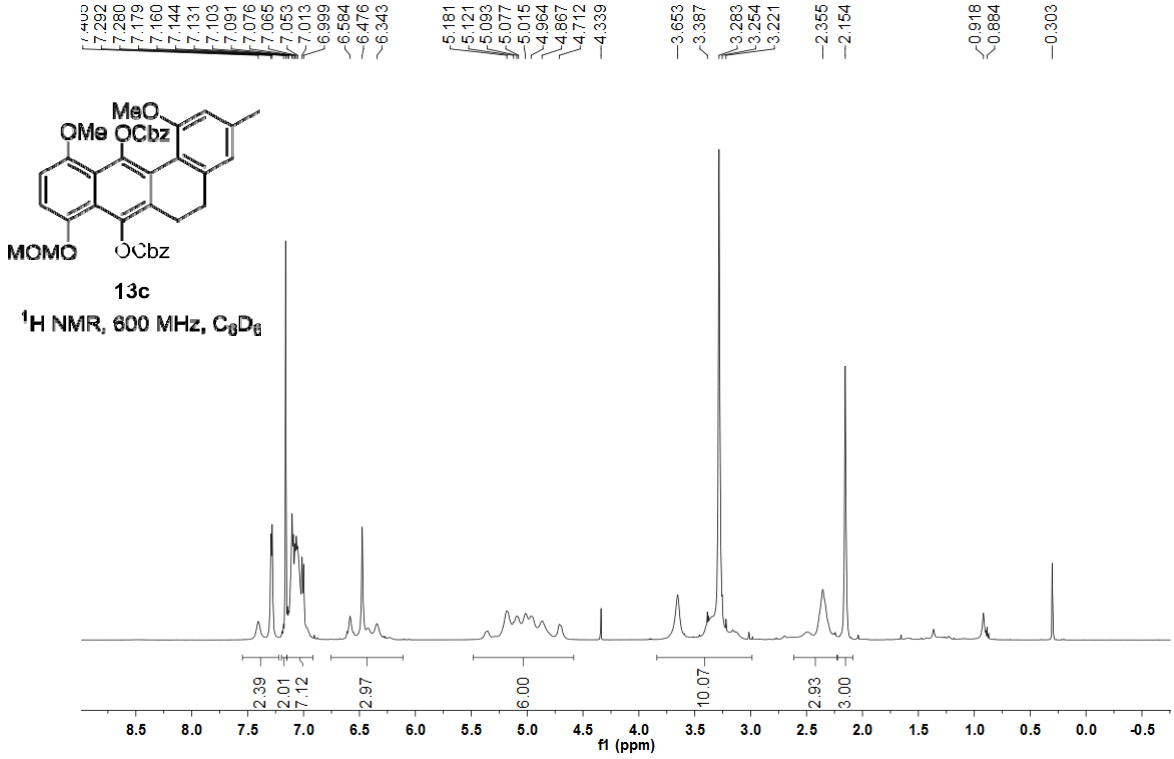


^{13}C NMR spectrum

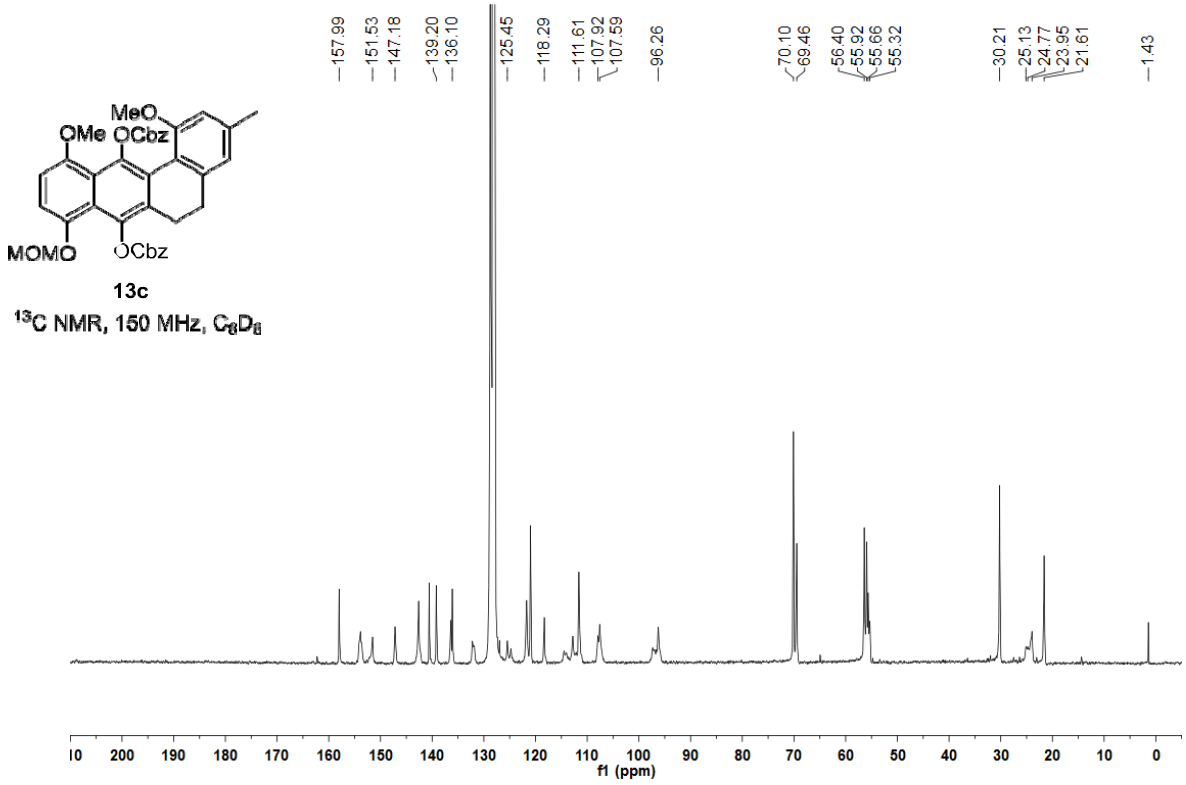


4.17 NMR spectra of compound 13c

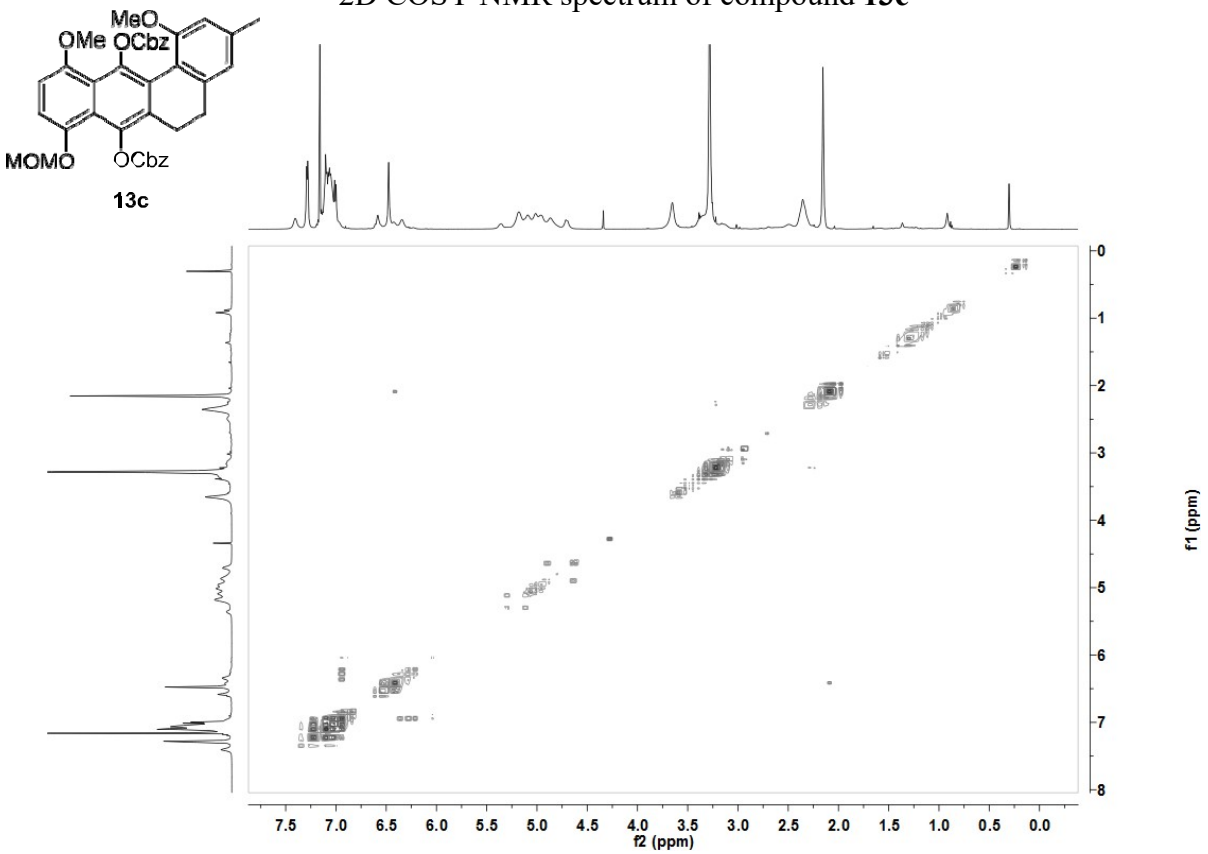
^{1}H NMR spectrum



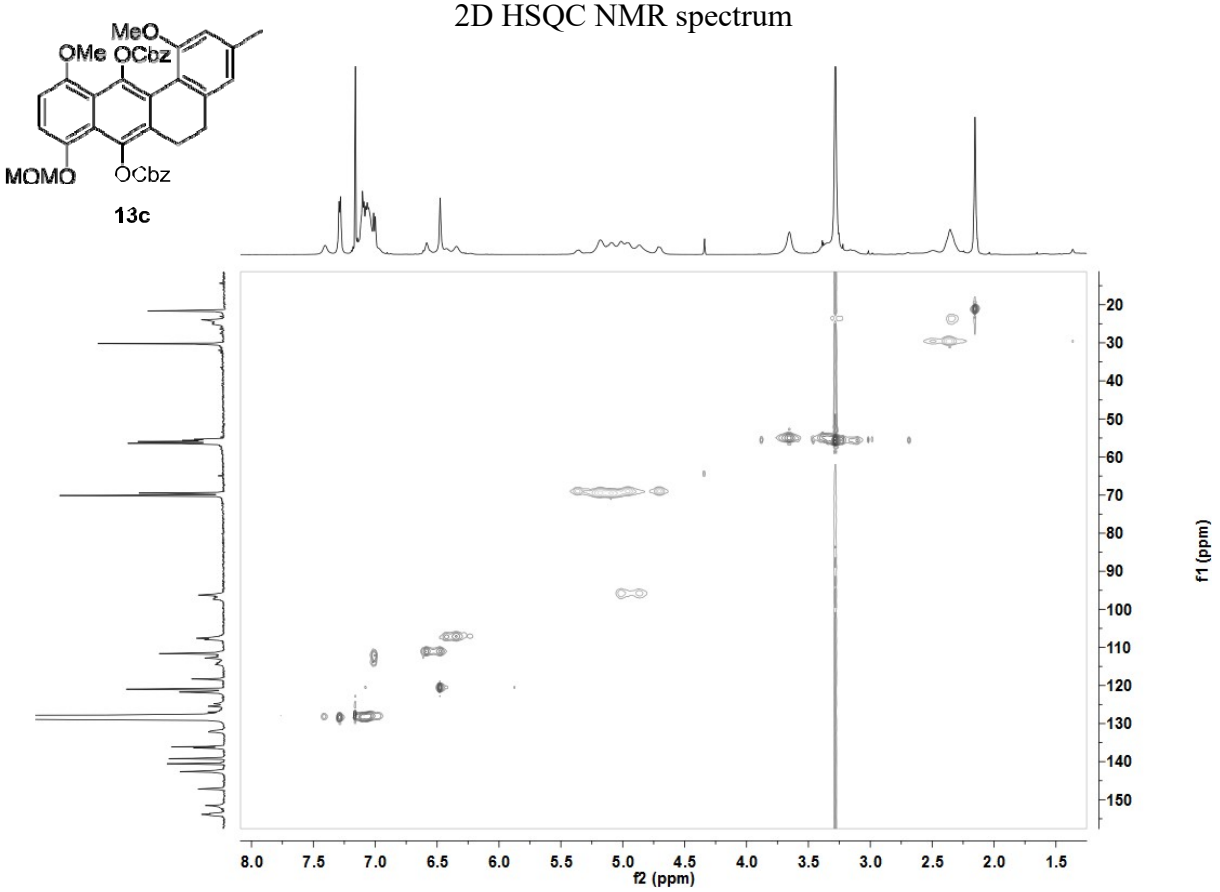
^{13}C NMR spectrum



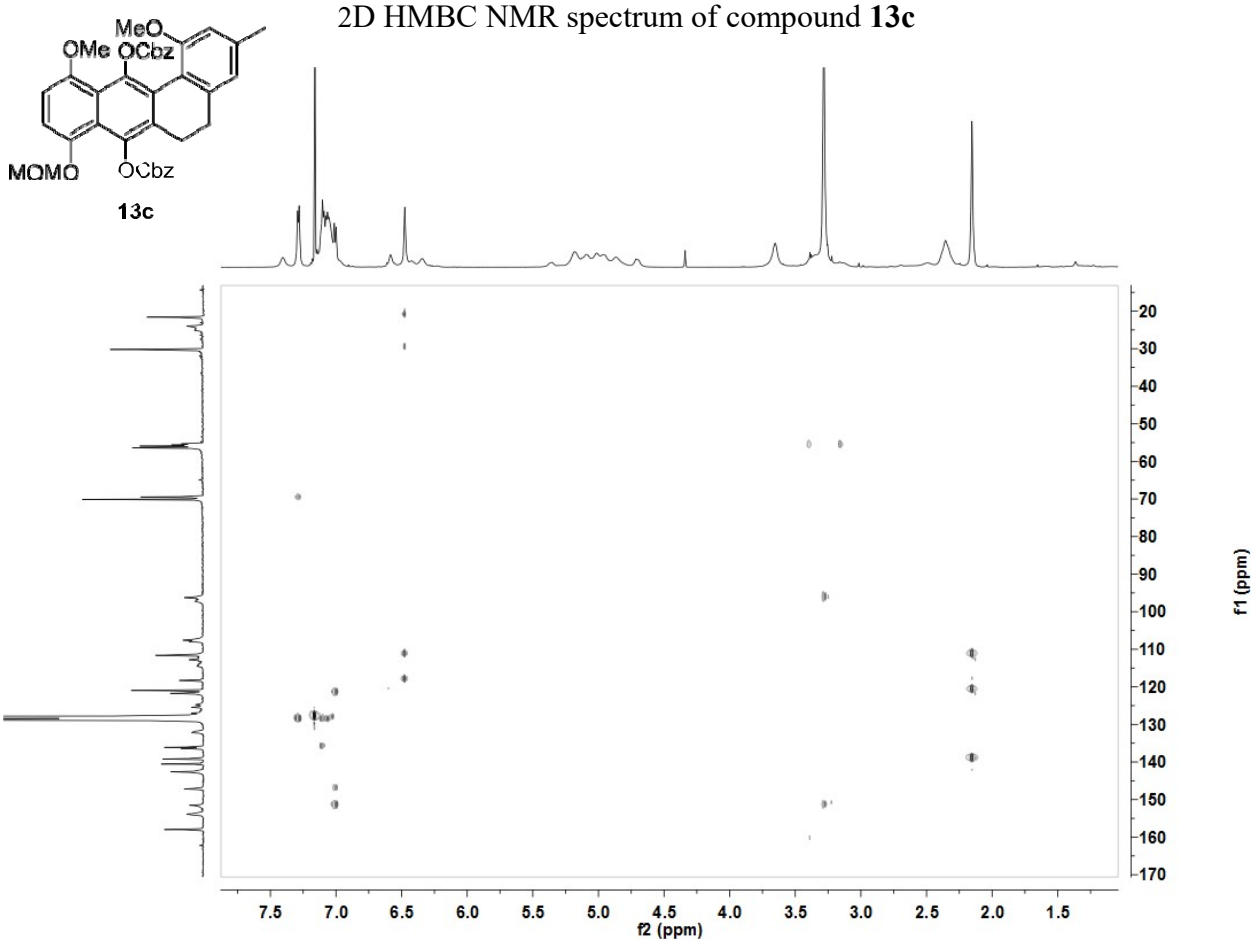
2D COSY NMR spectrum of compound **13c**



2D HSQC NMR spectrum

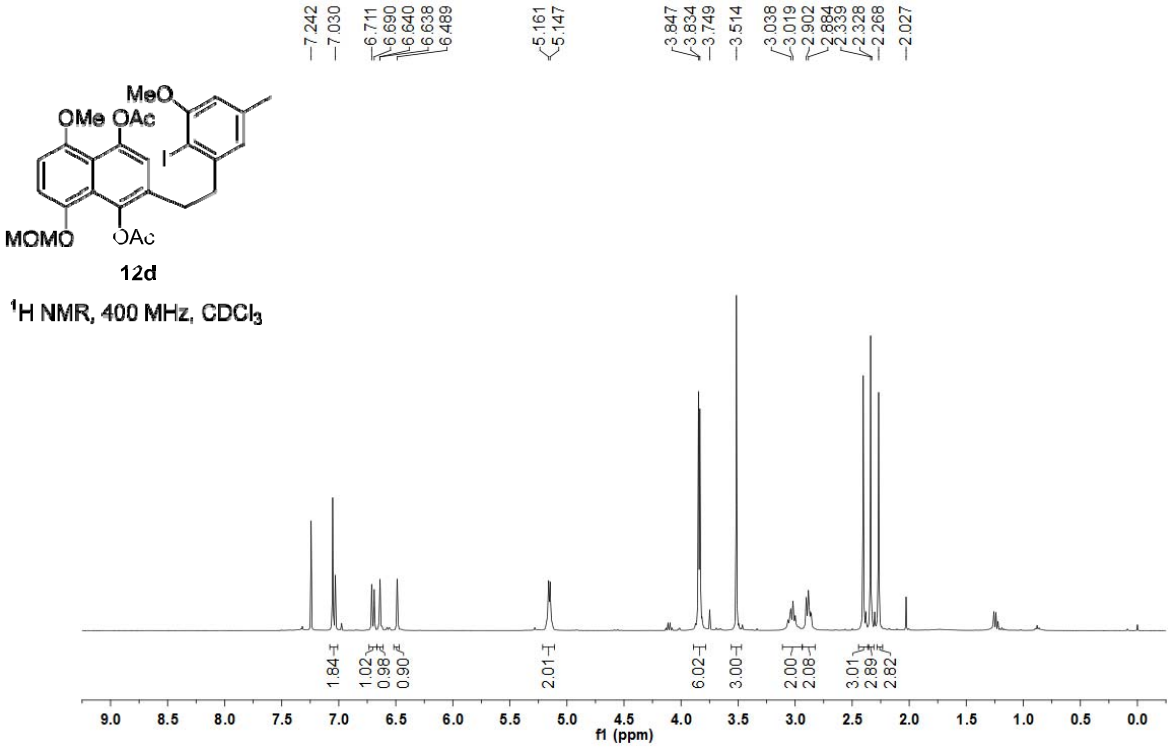


2D HMBC NMR spectrum of compound **13c**

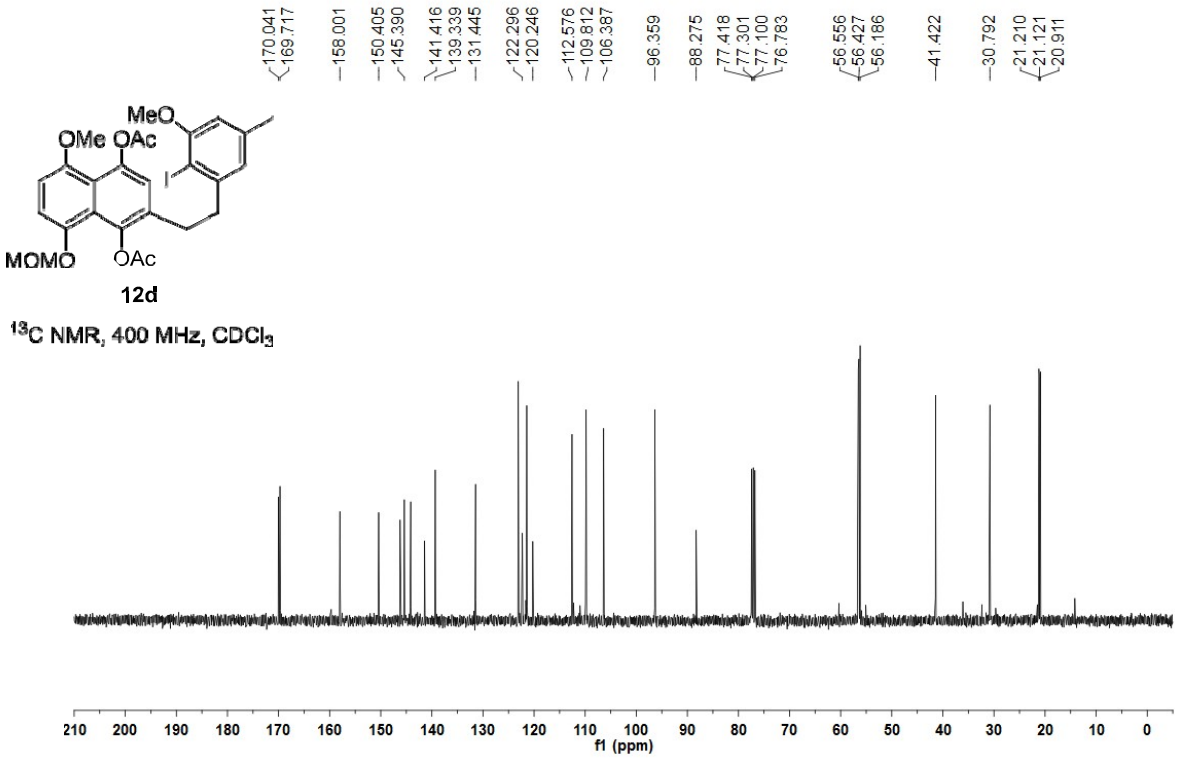


4.18 NMR spectra of compound 12d

^{1}H NMR spectrum

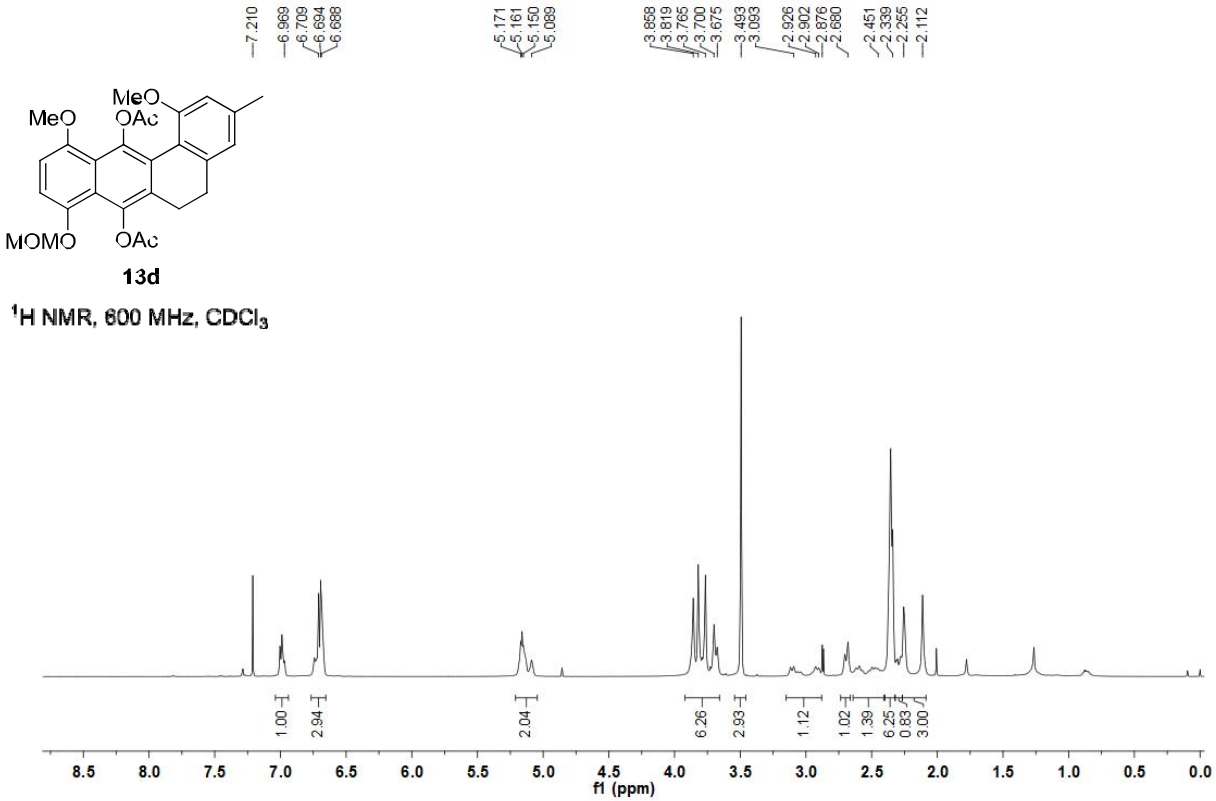


^{13}C NMR spectrum

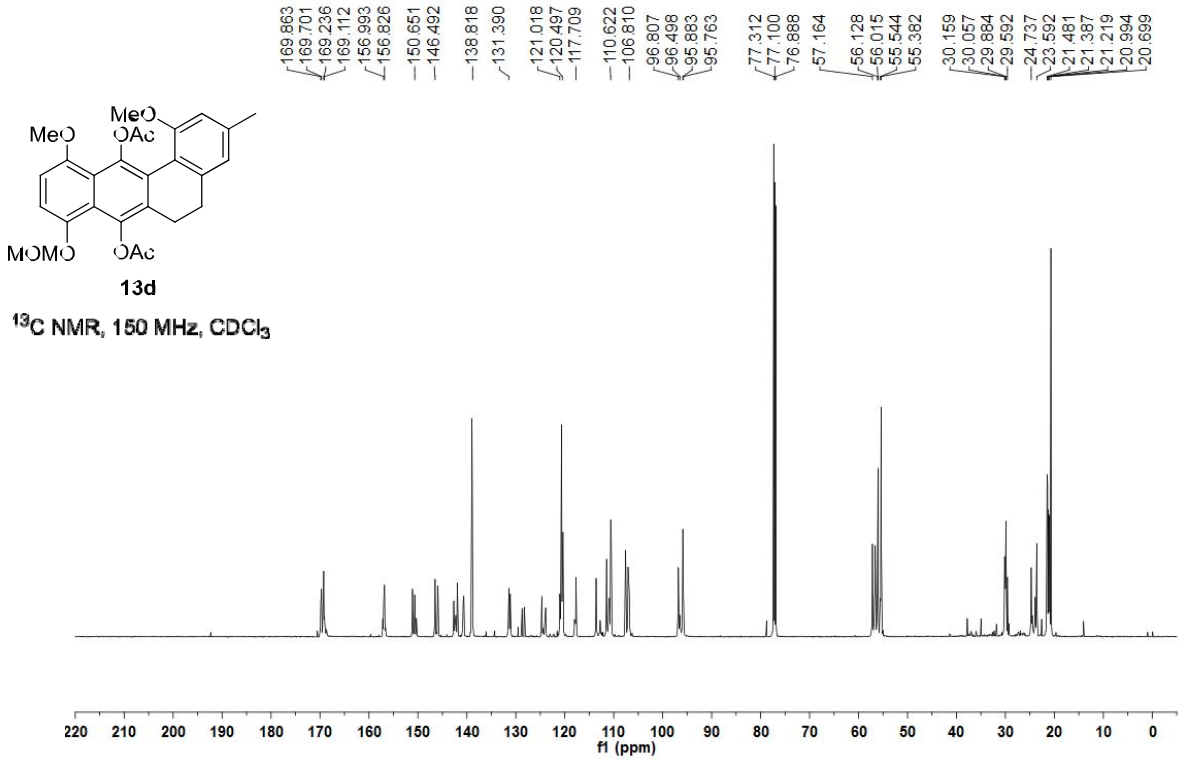


4.19 NMR spectraof compound 13d

^{1}H NMR spectrum

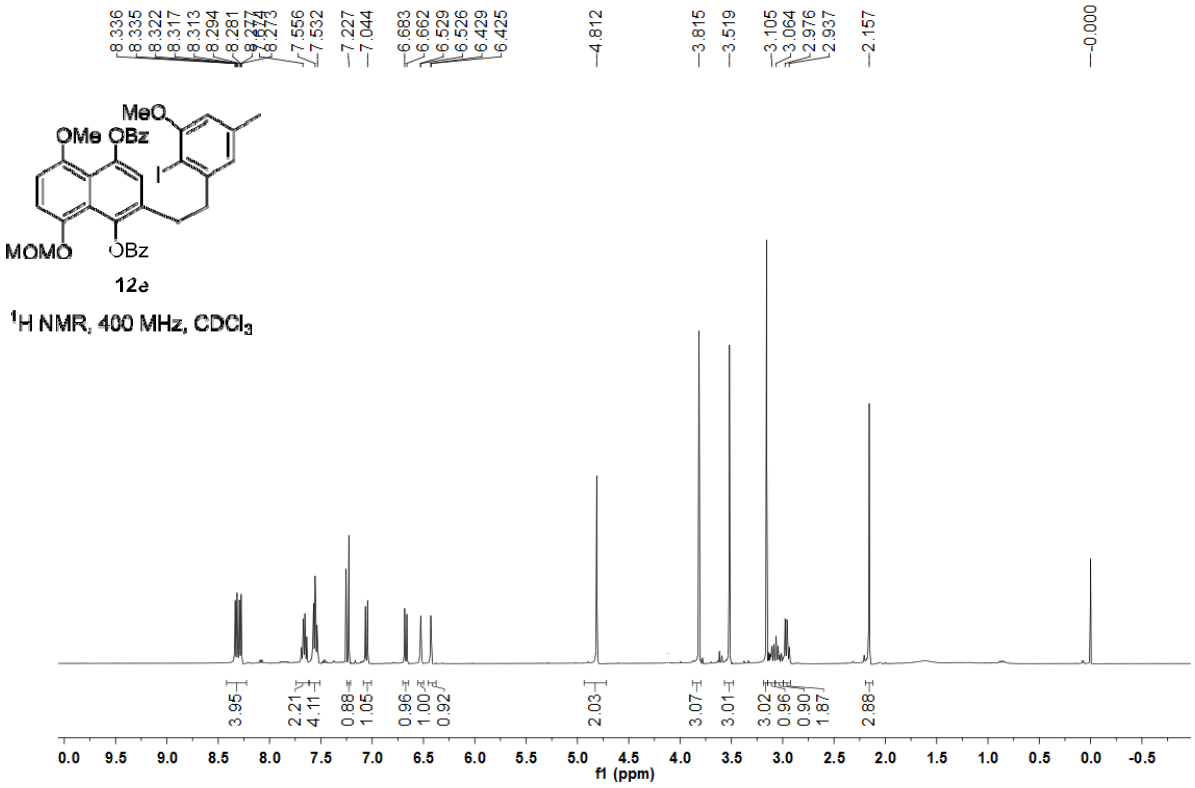


^{13}C NMR spectrum

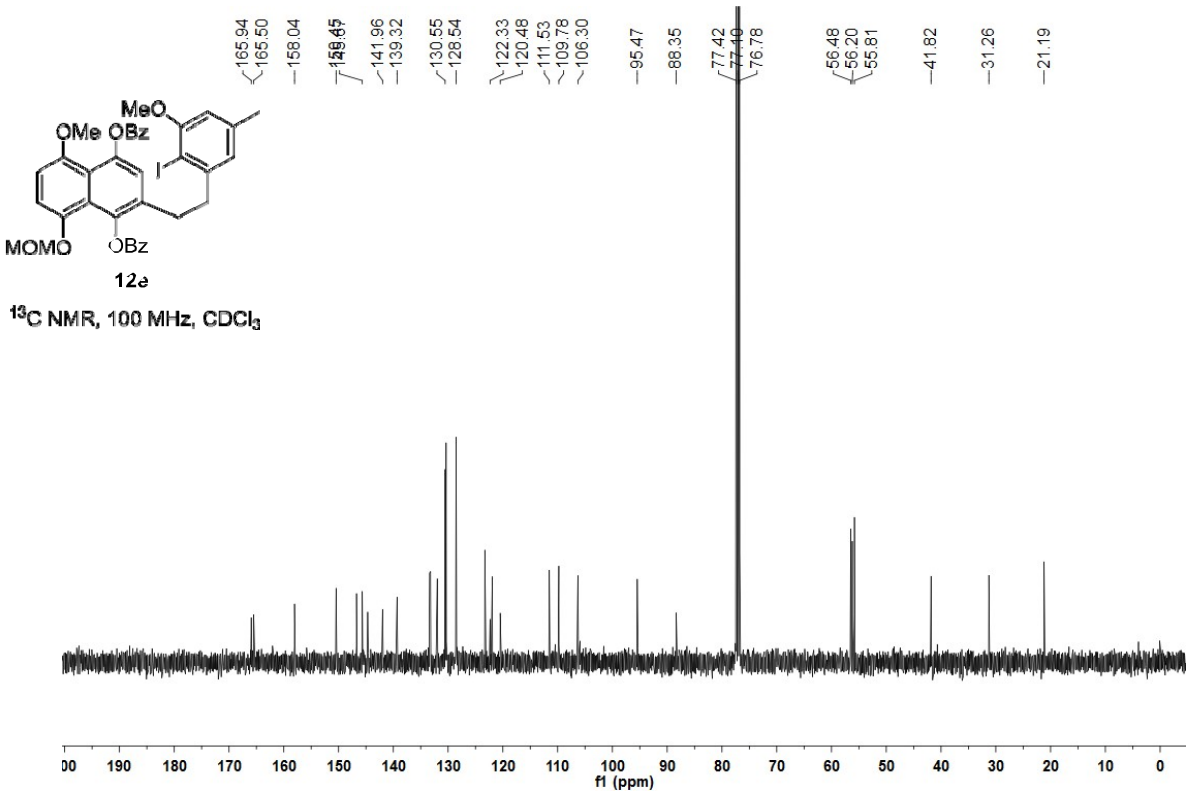


4.20 NMR spectra of compound 12e

^{1}H NMR spectrum

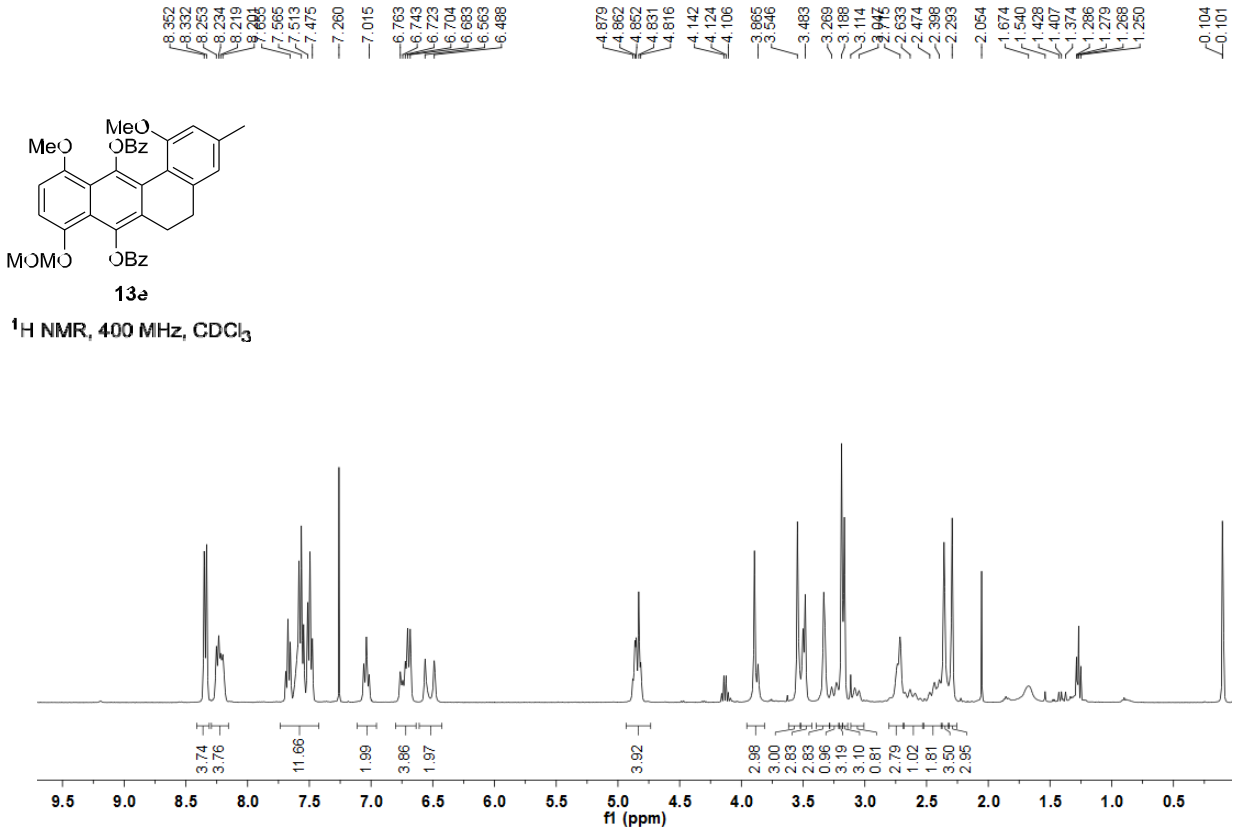


^{12}C NMR spectrum

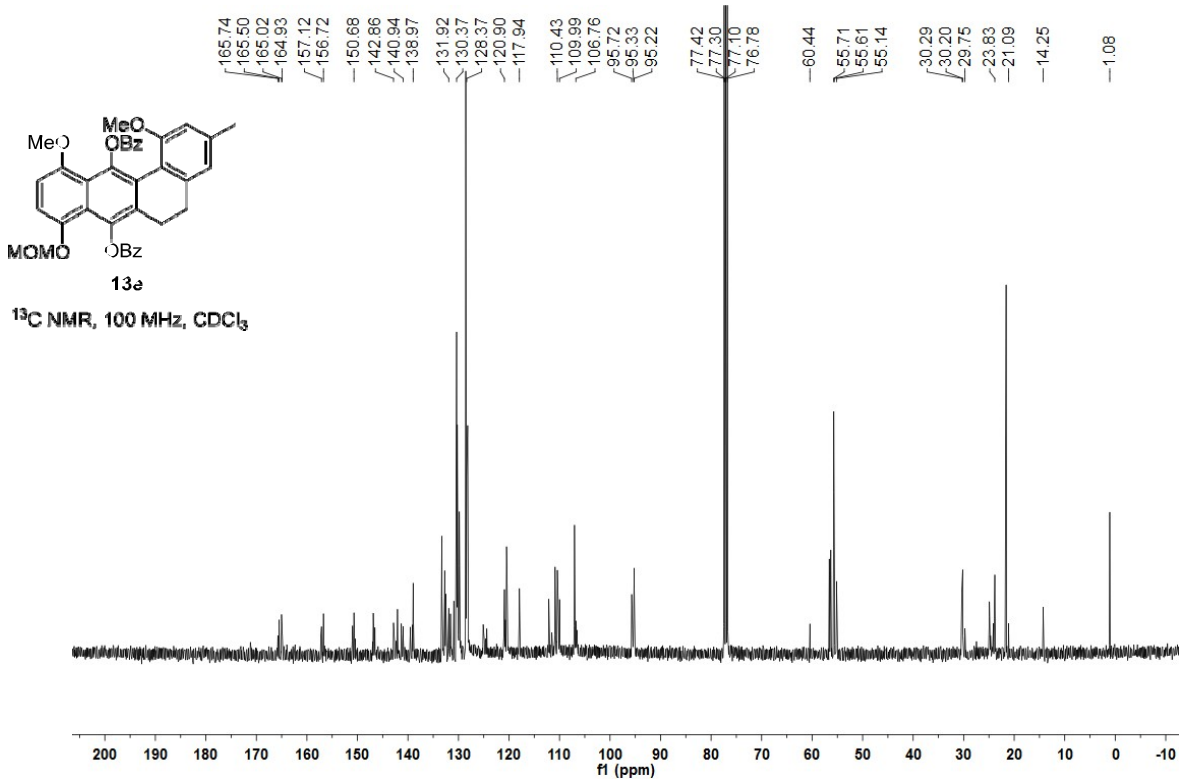


4.21 Crude ^{1}H NMR Spectra of compound 13e

Crude ^{1}H NMR spectrum

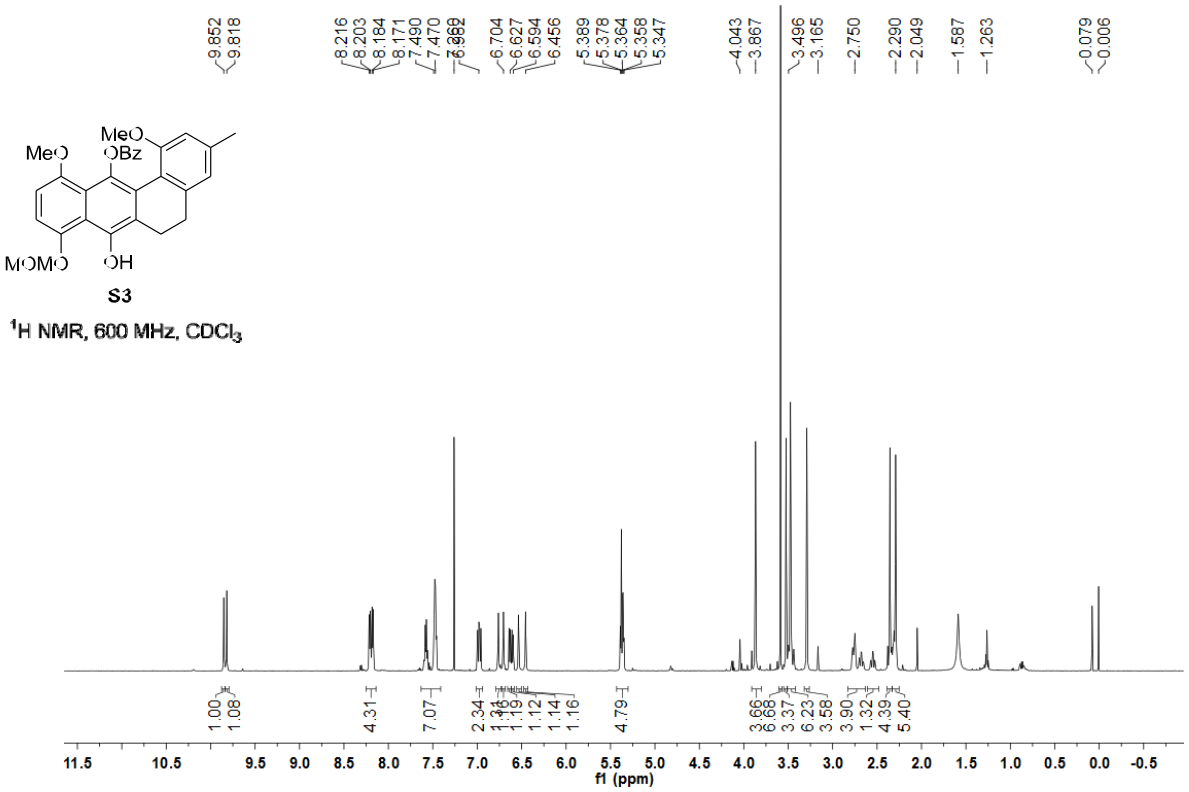


^{13}C NMR spectrum

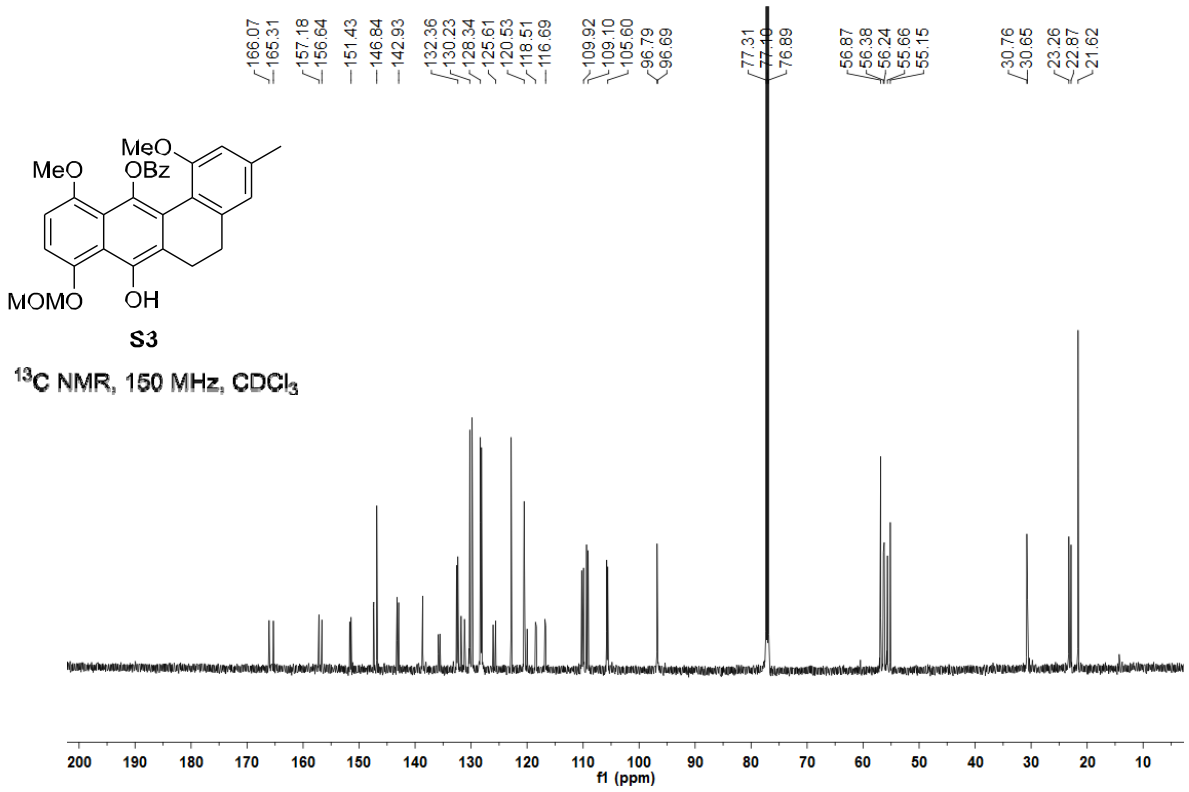


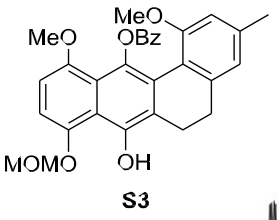
4.22 NMR spectra of compound S3

^{1}H NMR spectrum



^{13}C NMR spectrum

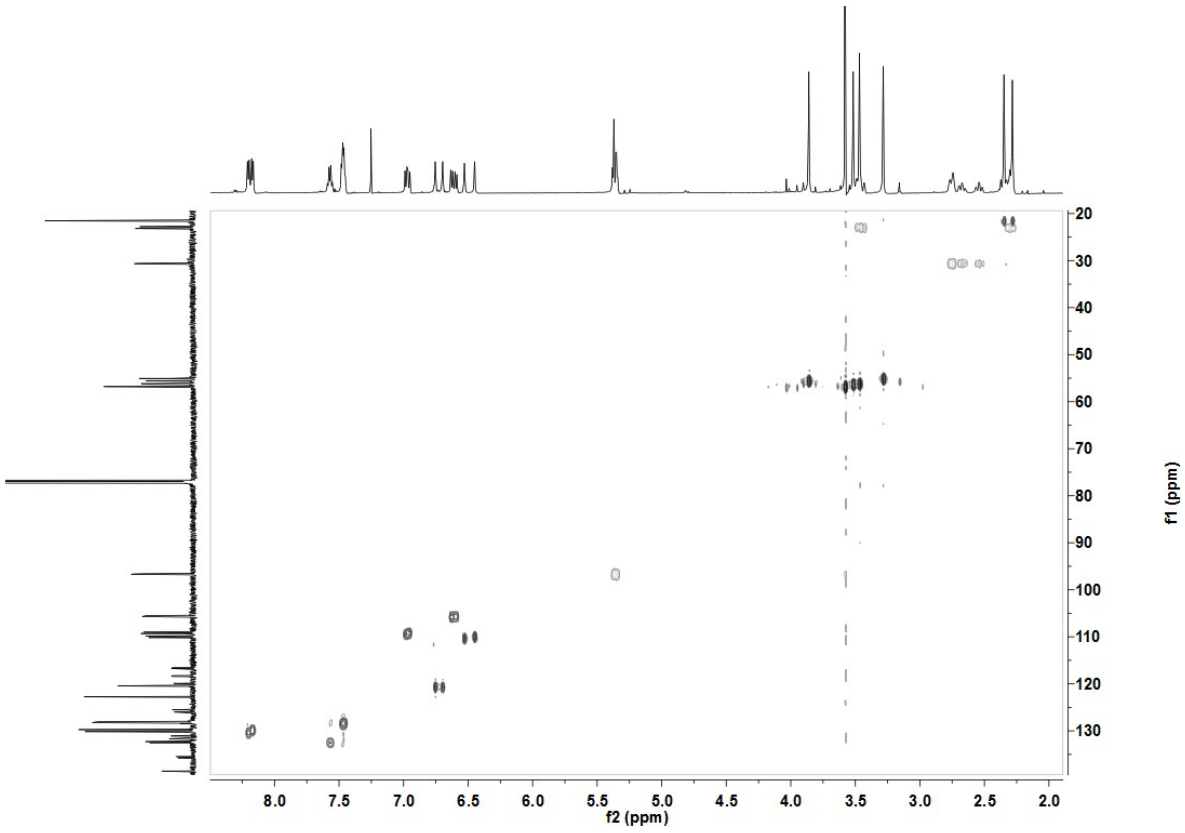




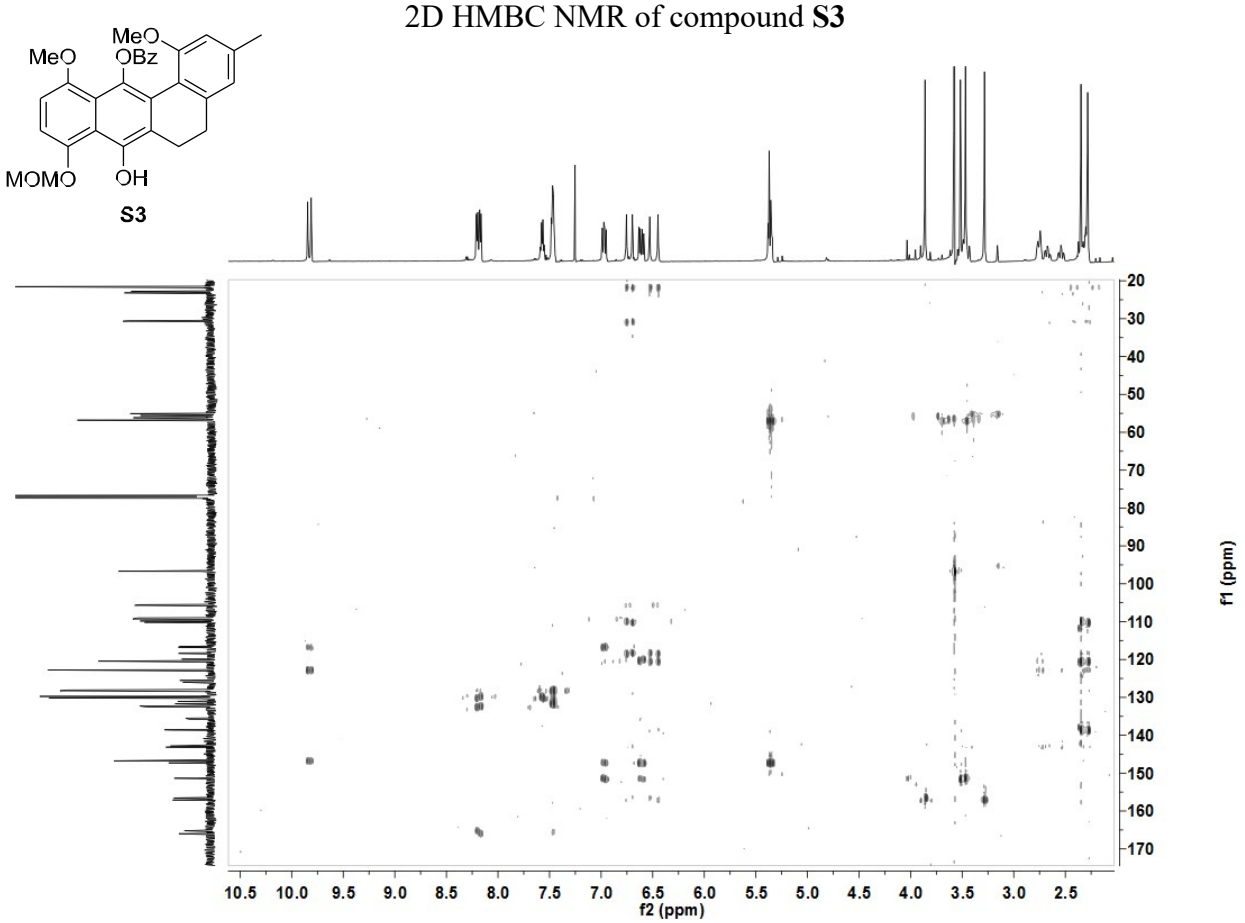
S3

2D COSY NMR of compound **S3**

2D HSQC NMR of compound **S3**

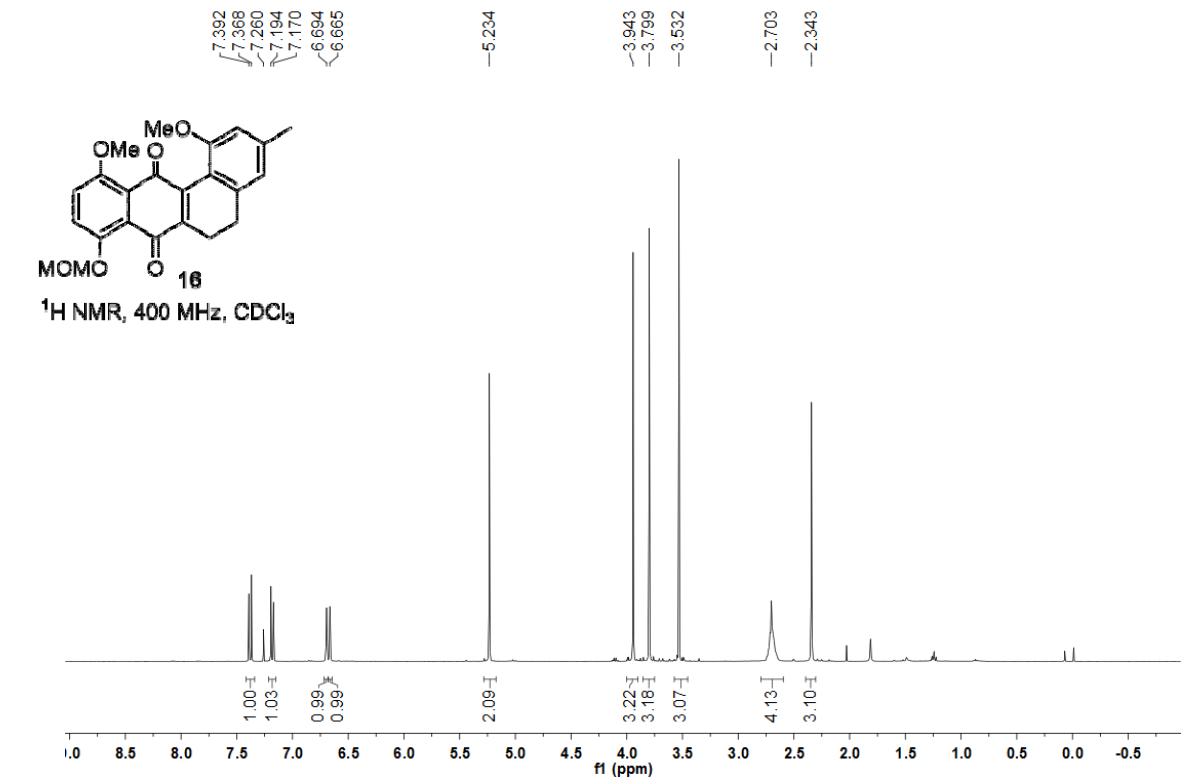


2D HMBC NMR of compound **S3**

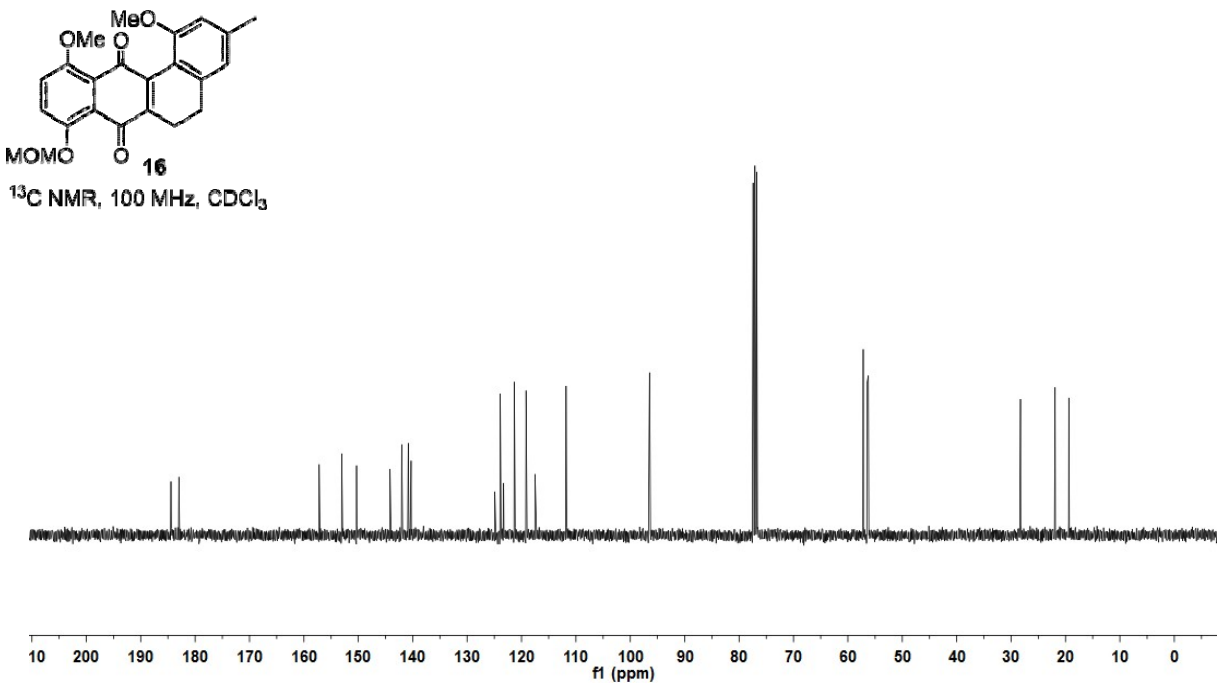


4.23 NMR spectra of compound 16

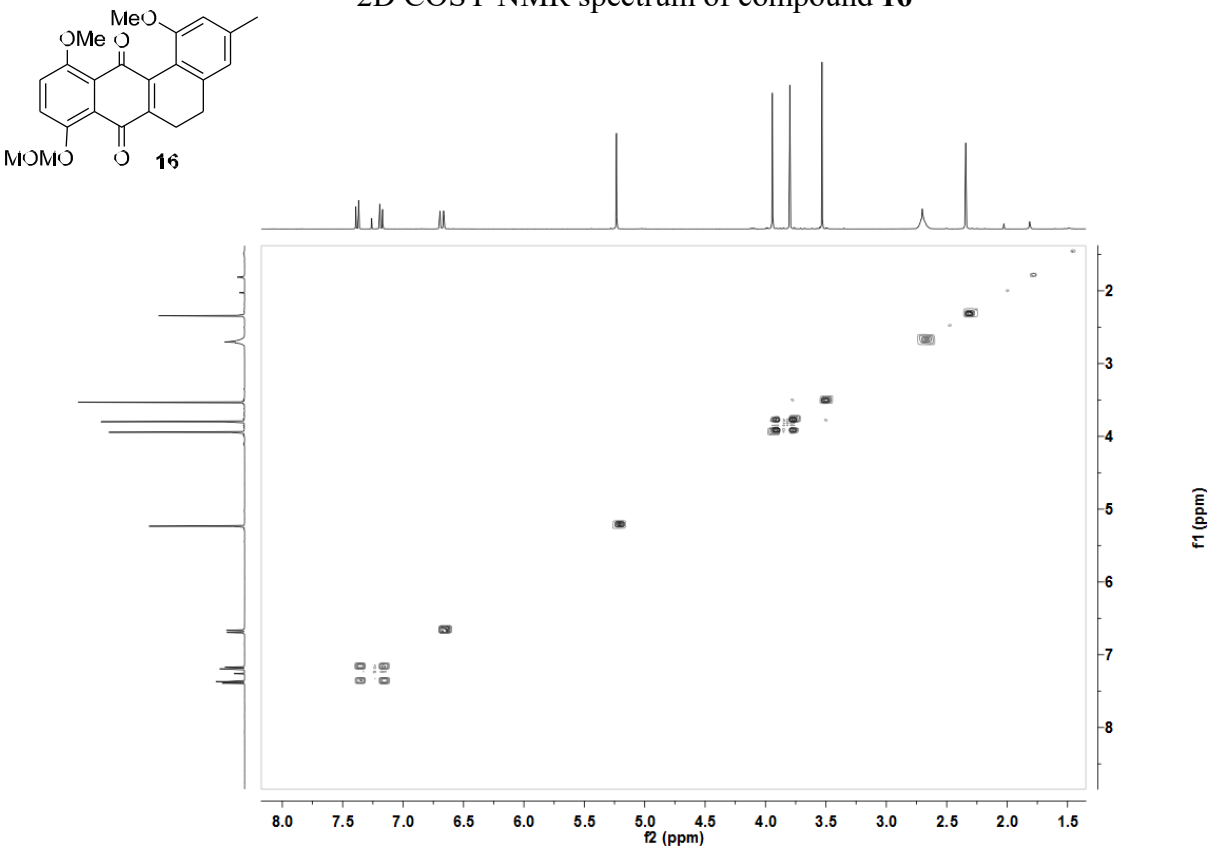
^{1}H NMR spectrum



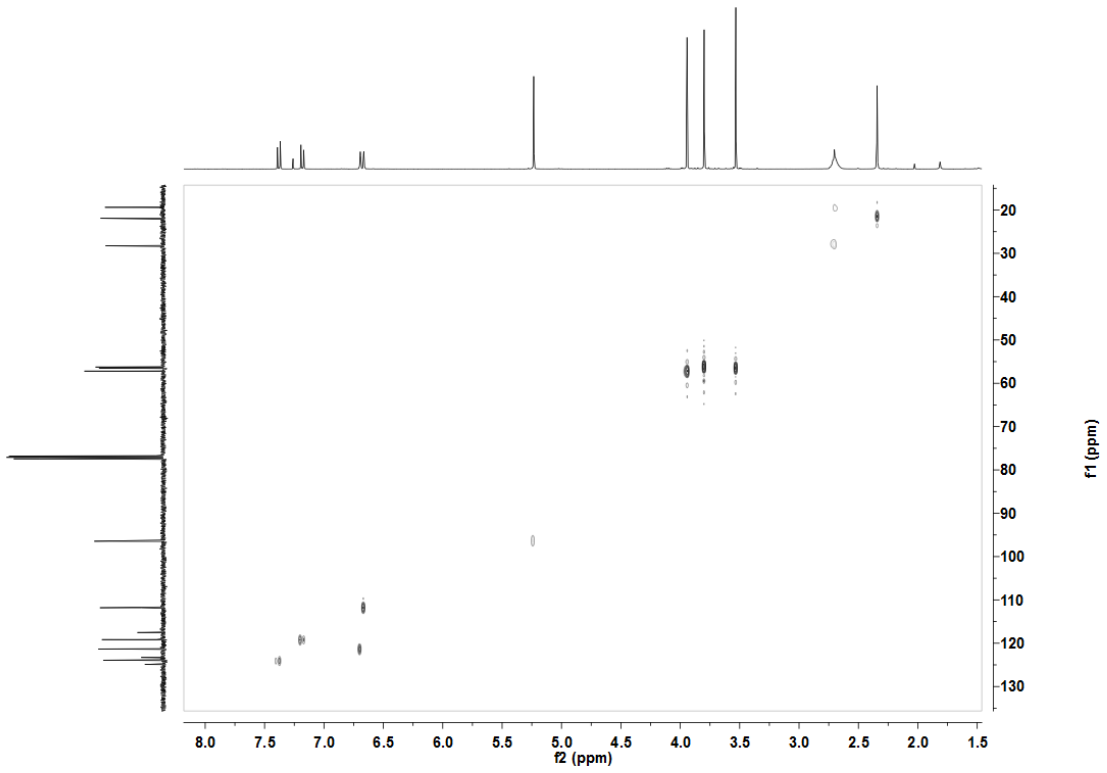
^{13}C NMR spectrum



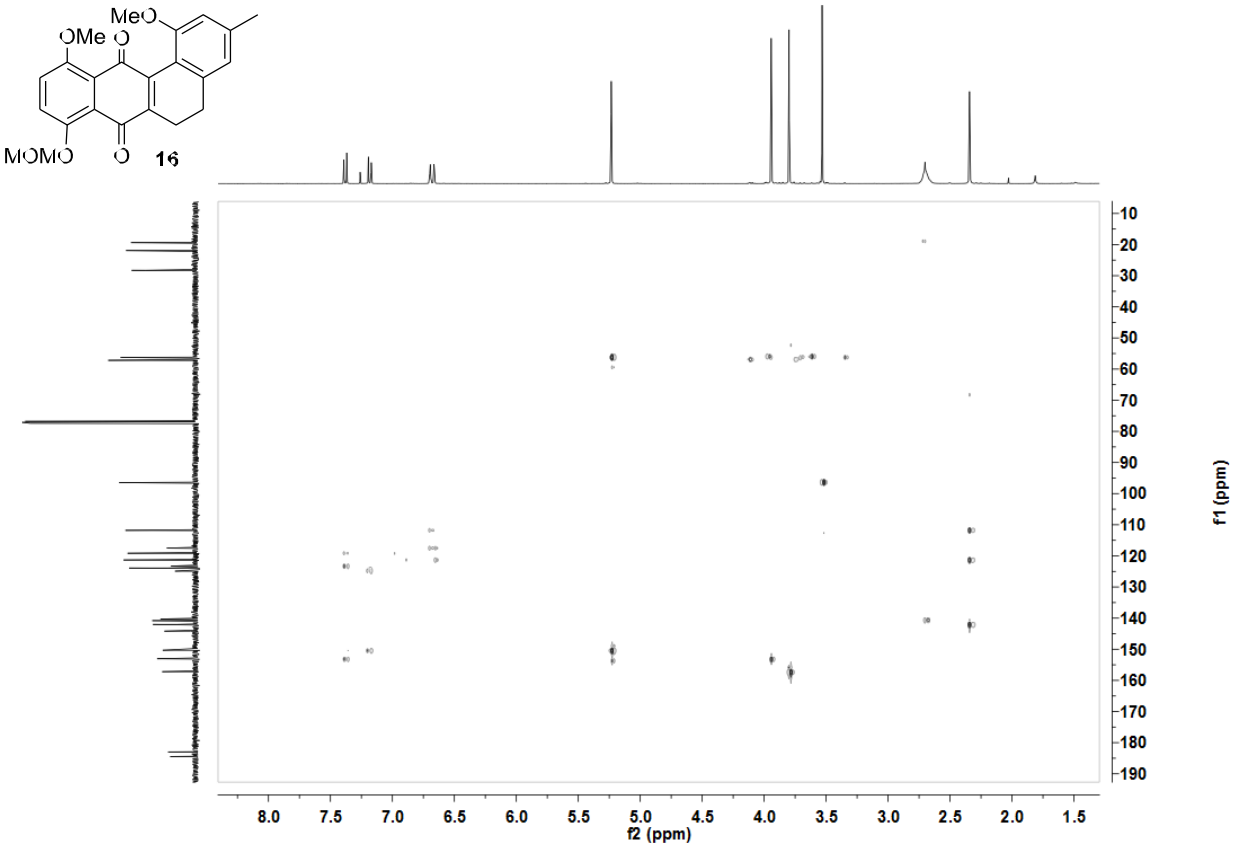
2D COSY NMR spectrum of compound **16**



2D HSQC NMR spectrum of compound **16**

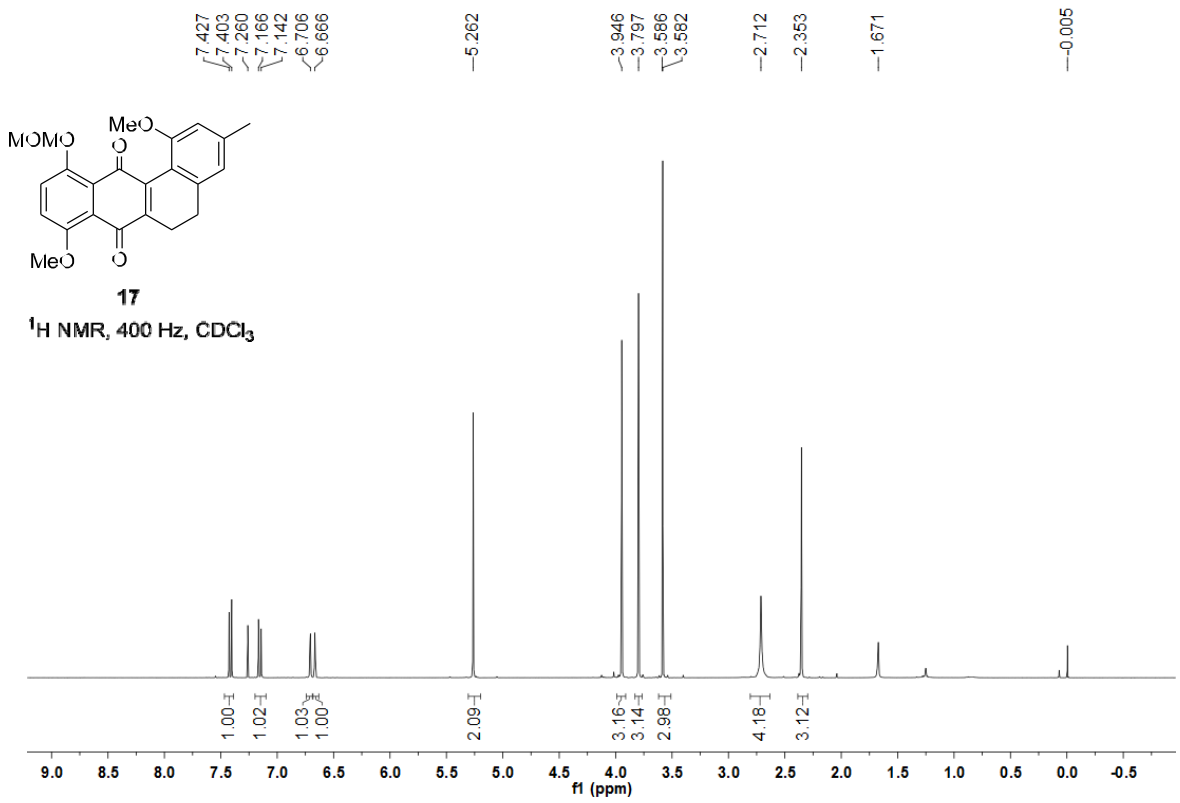


2D HMBC NMR spectrum of compound **16**

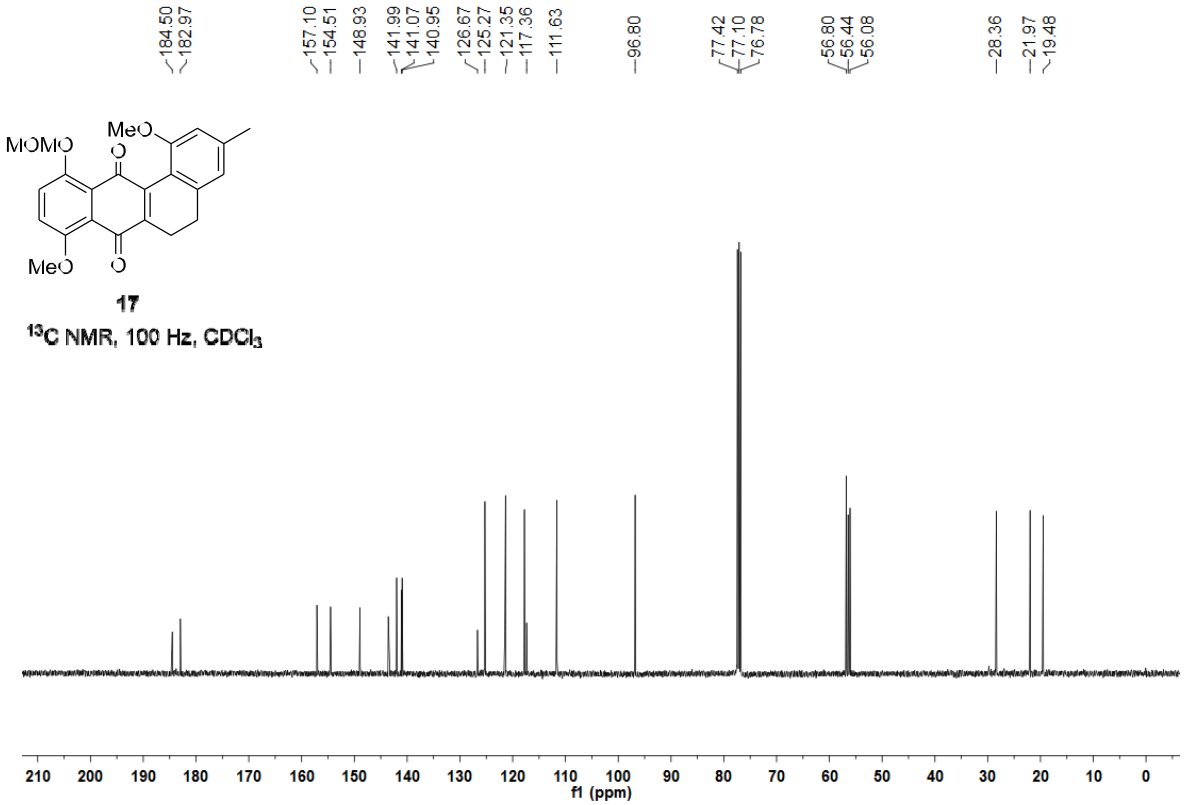


4.24 NMR spectra of compound 17

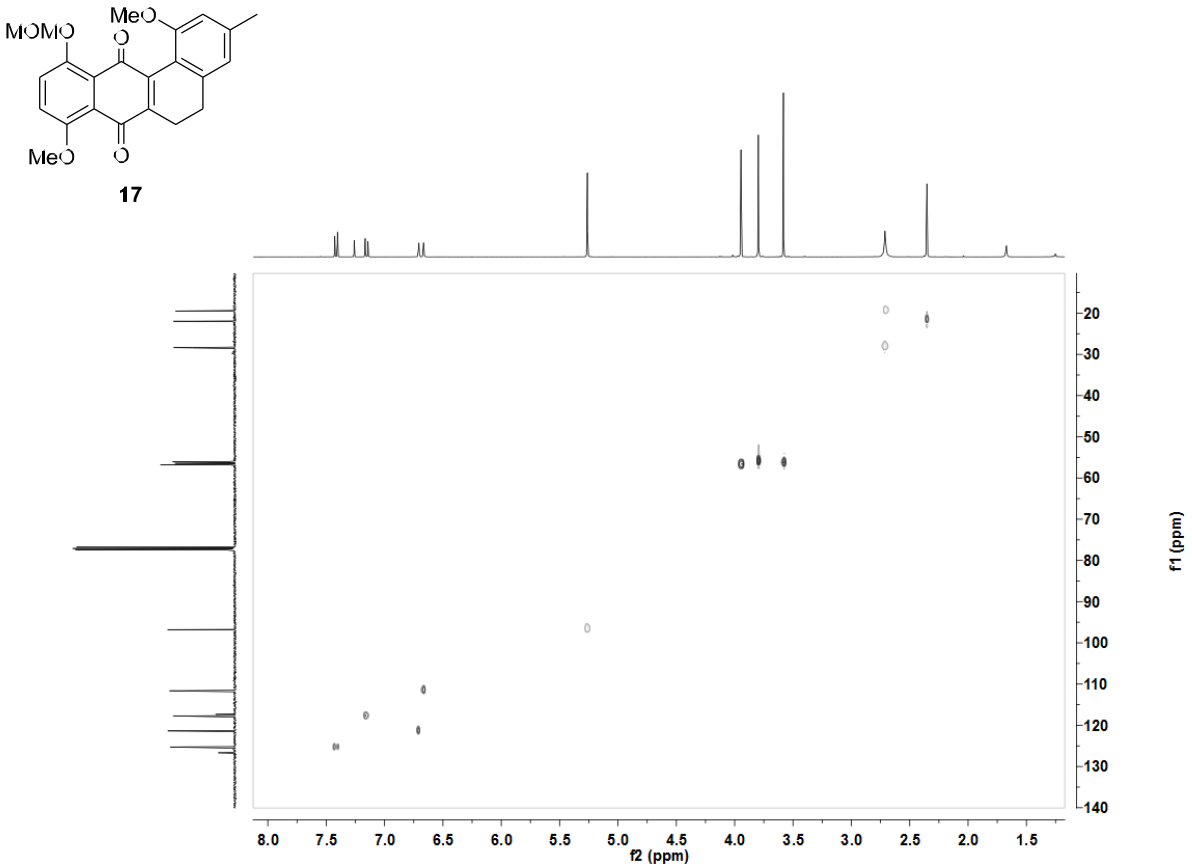
^{1}H NMR spectrum



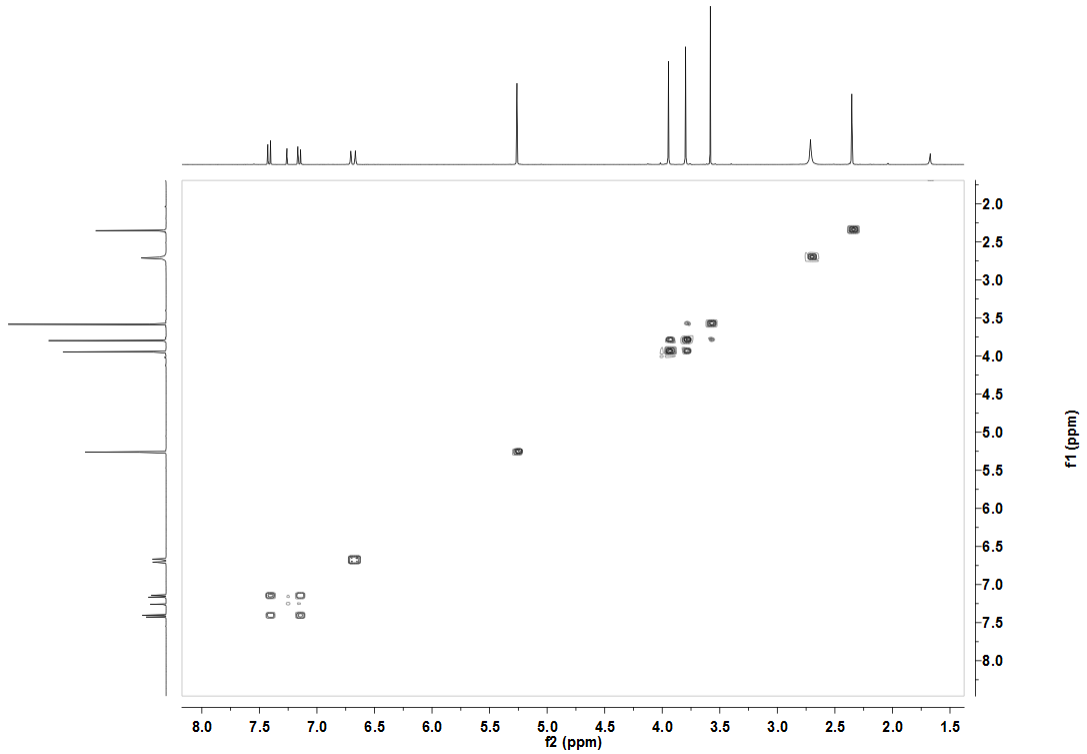
^{13}C NMR spectrum



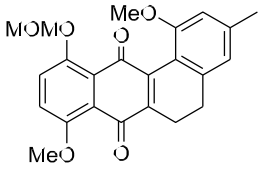
2D COSY NMR spectrum of compound **17**



2D HSQC NMR spectrum of compound **17**



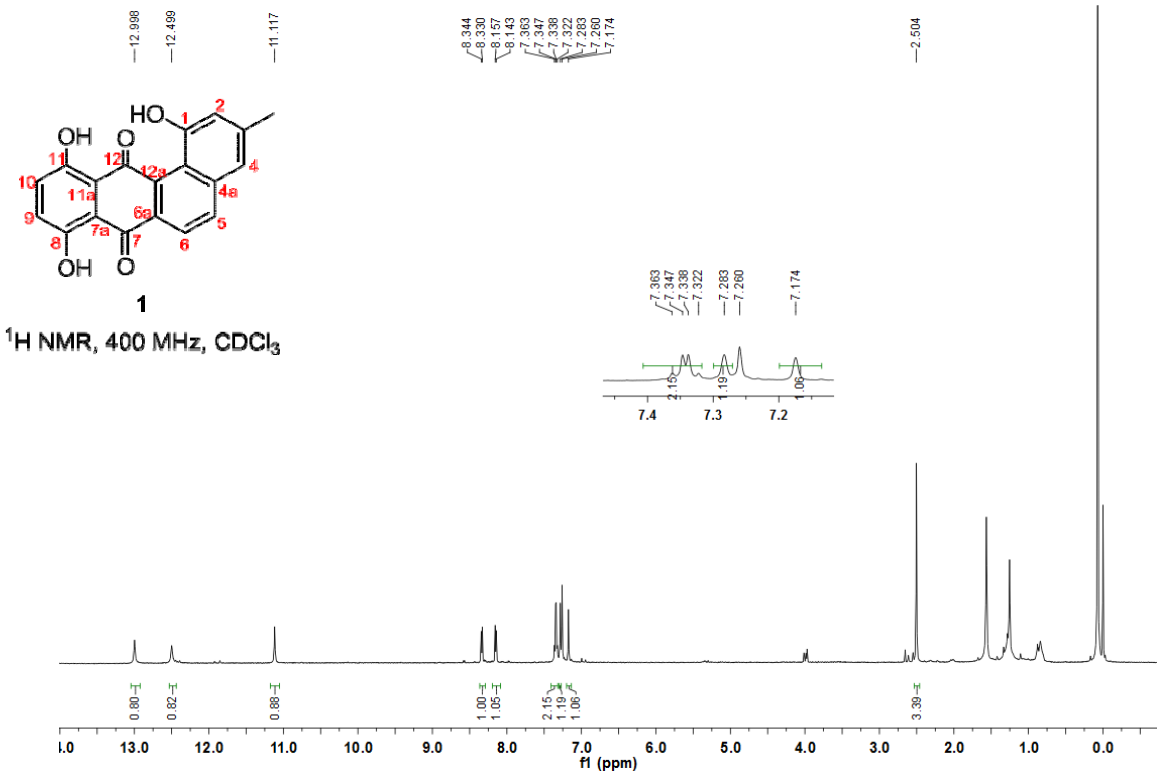
2D HBMC NMR spectrum of compound **17**



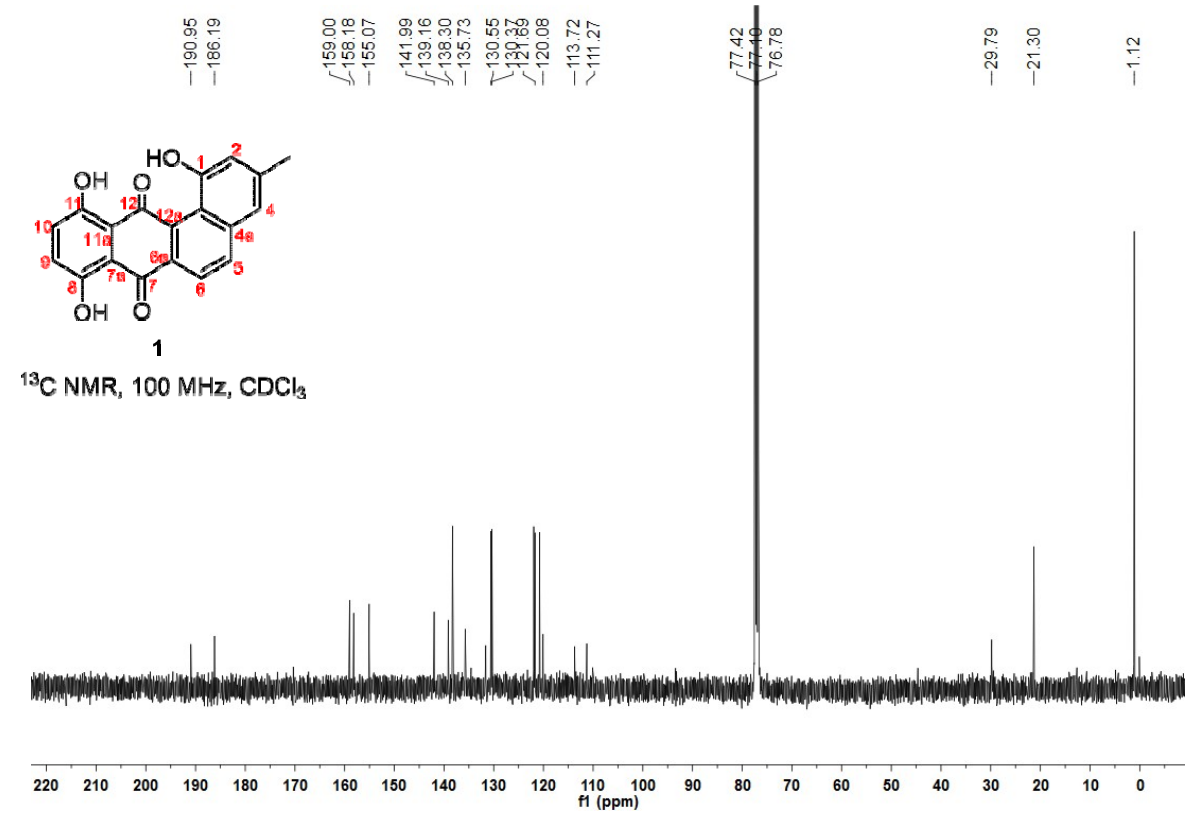
17

4.25 NMR spectrum of 5,6-anhydrolandomycinone 1

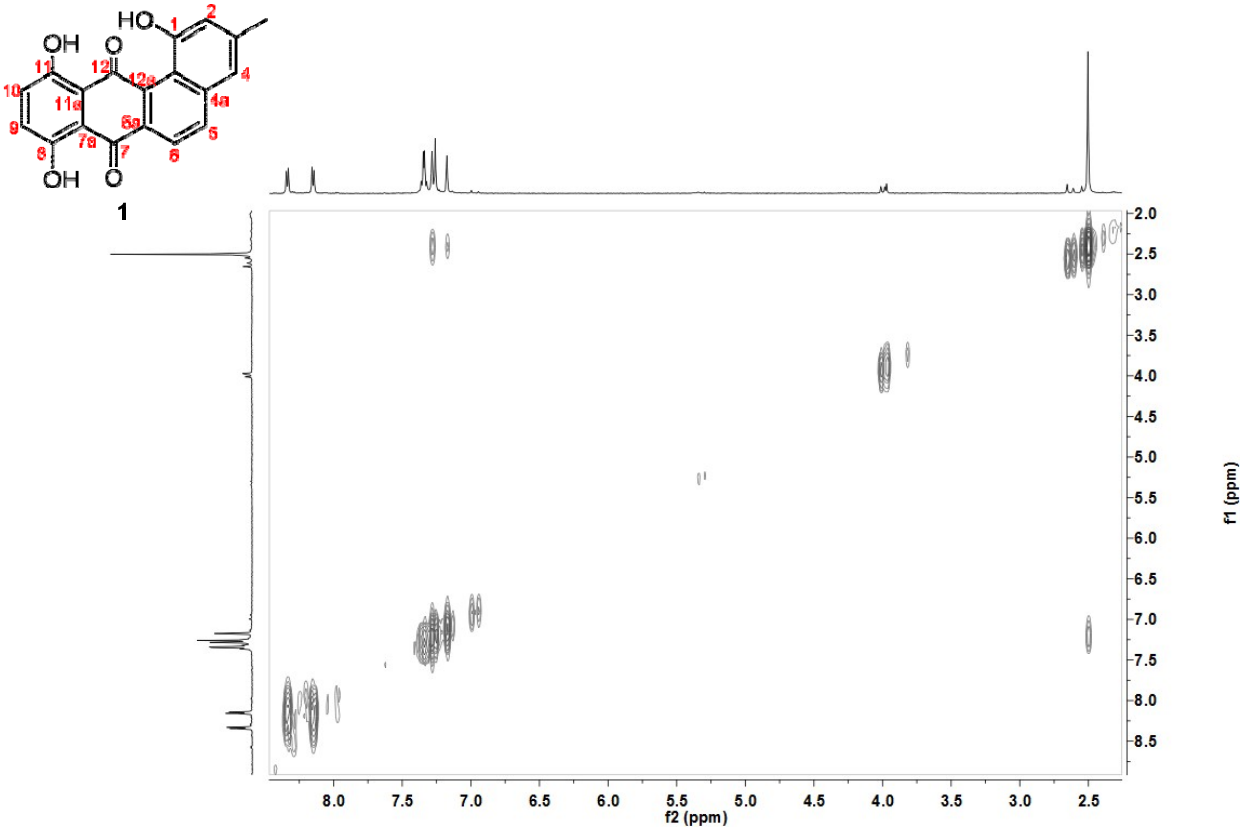
^{1}HNMR spectrum



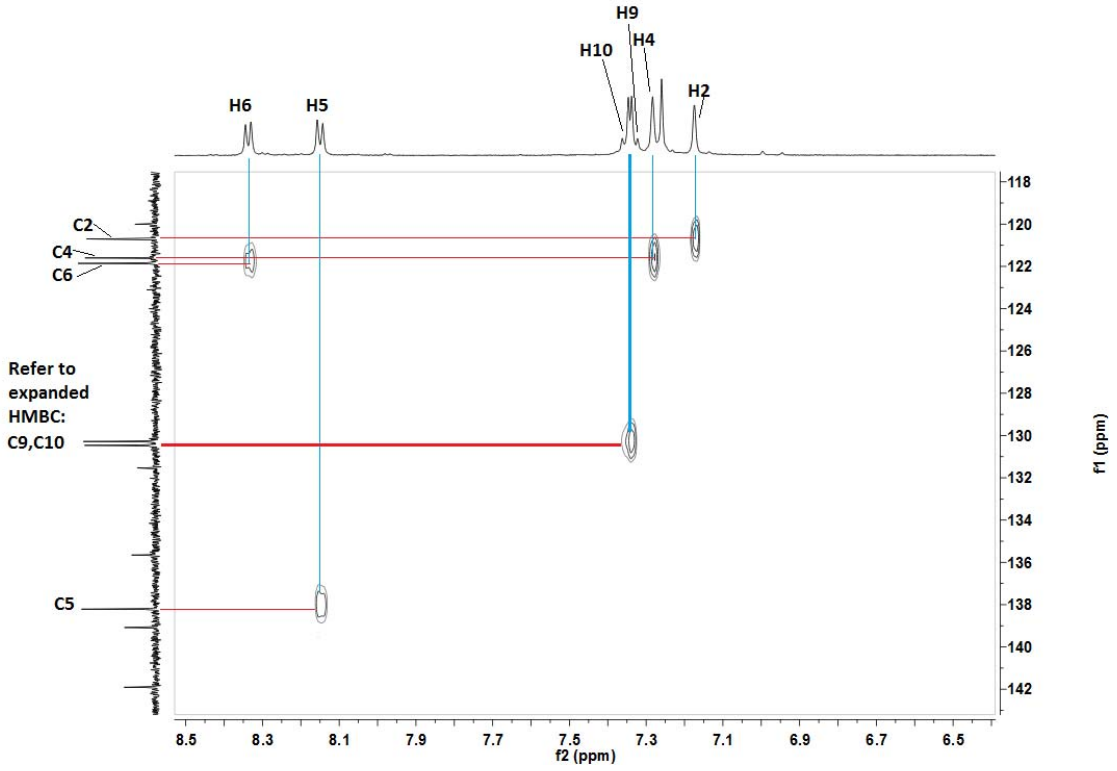
^{13}C NMR spectrum



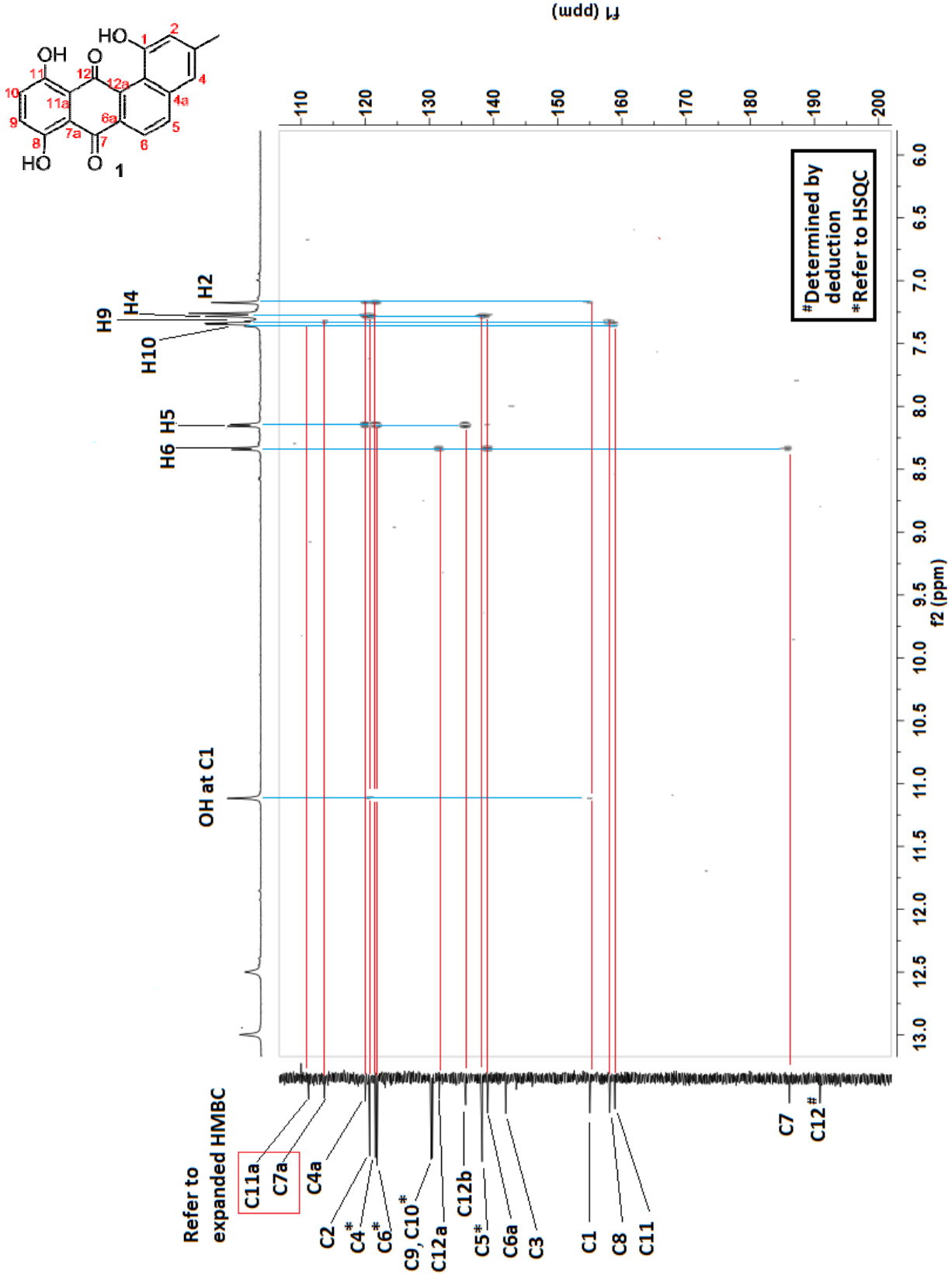
2D COSY NMR spectrum of 5,6-anhydrolandomycinone **1**



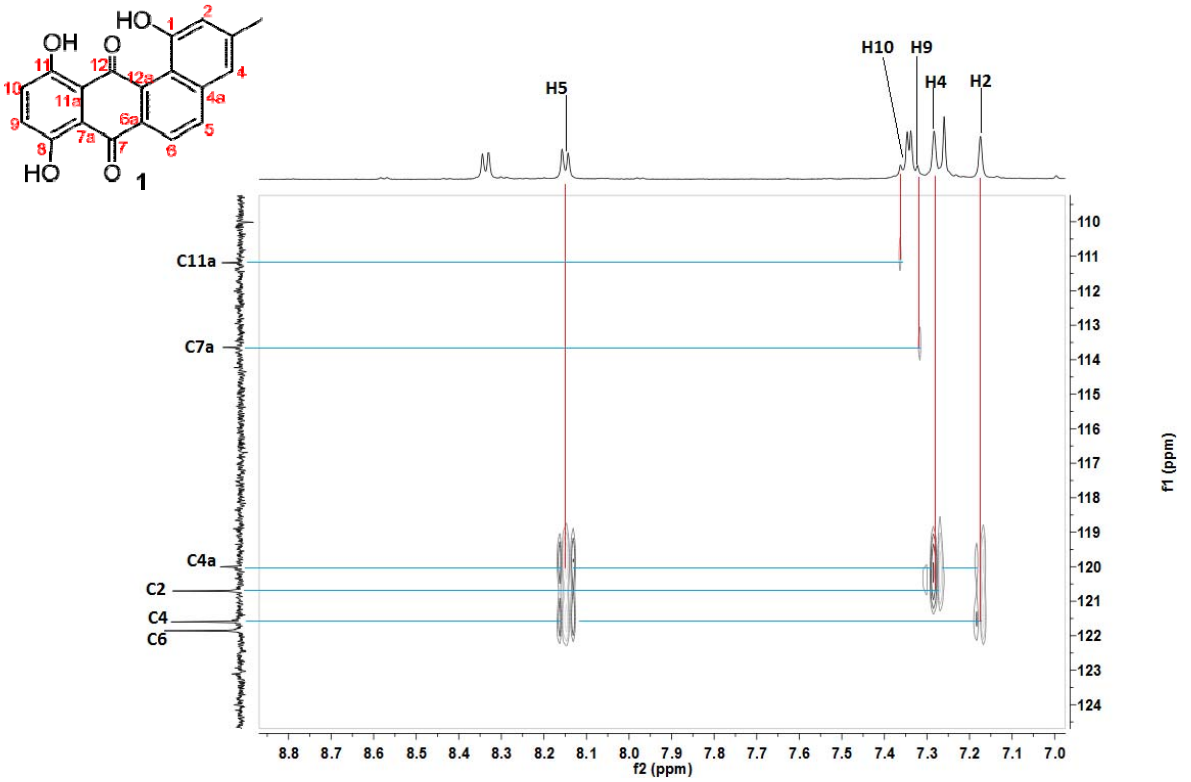
2D HSQC NMR spectrum of 5,6-anhydrolandomycinone **1**



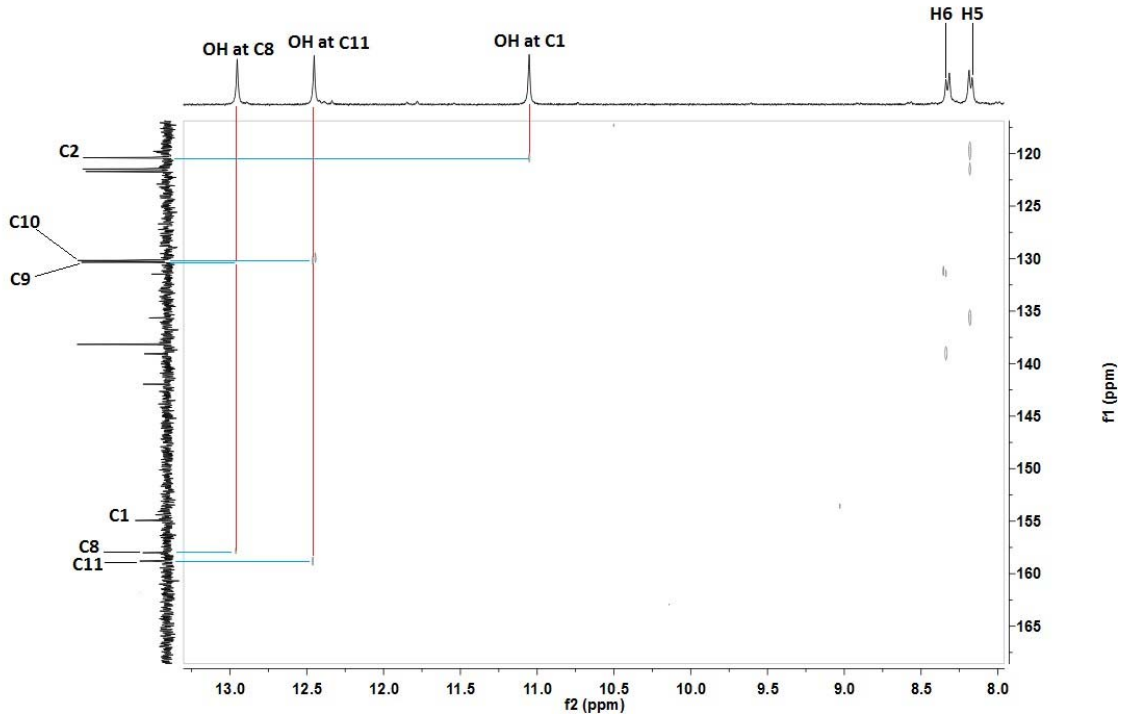
2D HMBC NMR spectrum of 5,6-anhydrolandomycinone **1**



Expanded 2D HMBC spectrum of 5,6-anhydrolandomycinone **1**

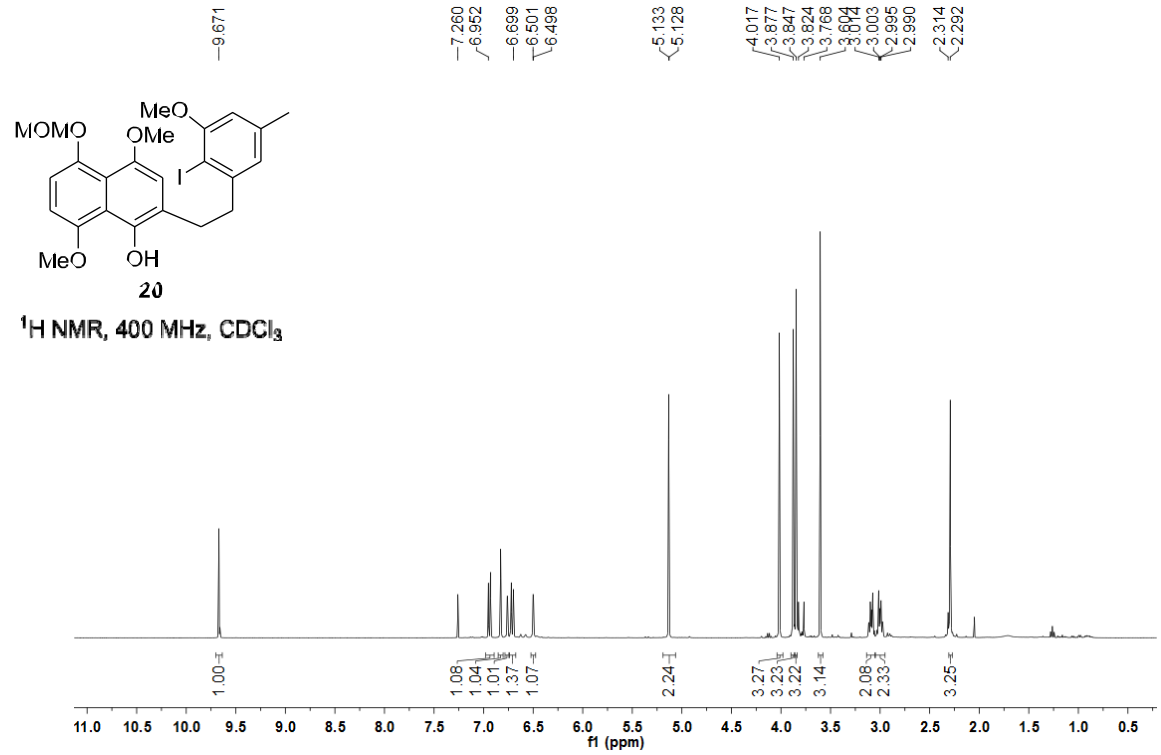


Expanded 2D HMBC of 5,6-anhydrolandomycinone **1** (from a repeated NMR experiment)

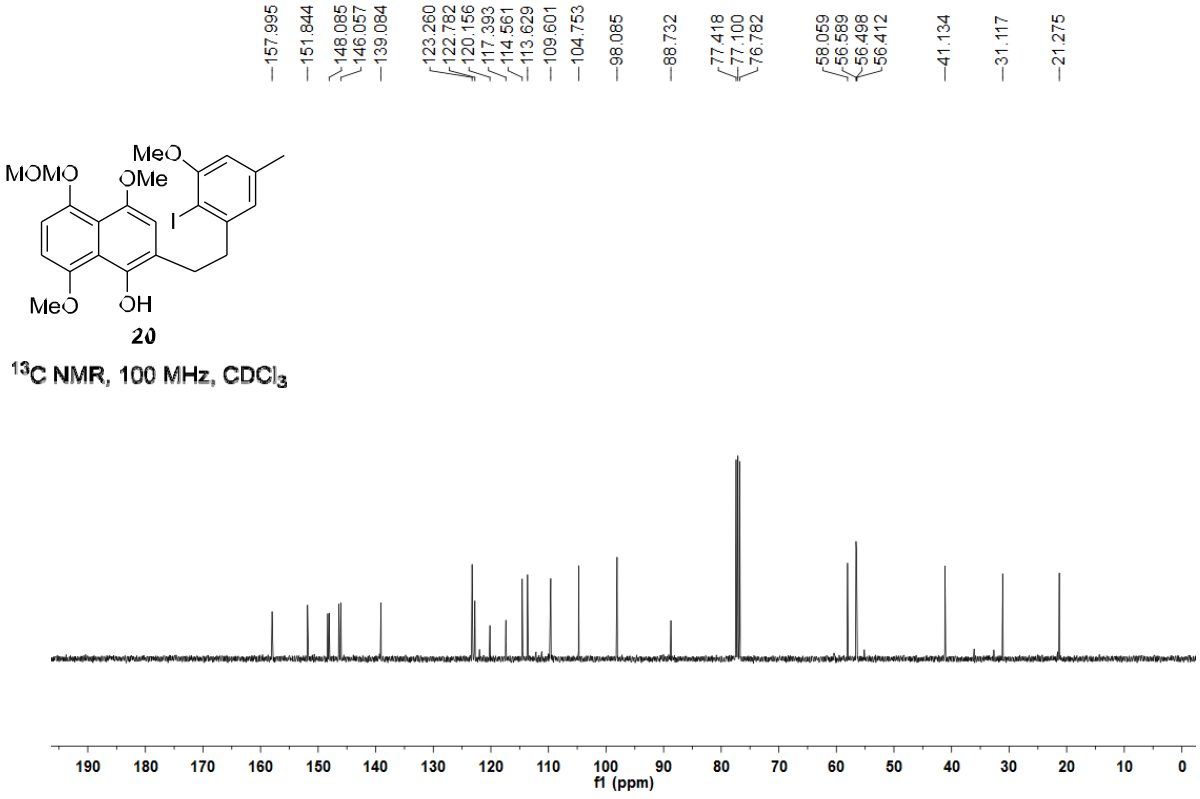


4.26 NMR spectra of compound 20

^{1}H NMR spectrum

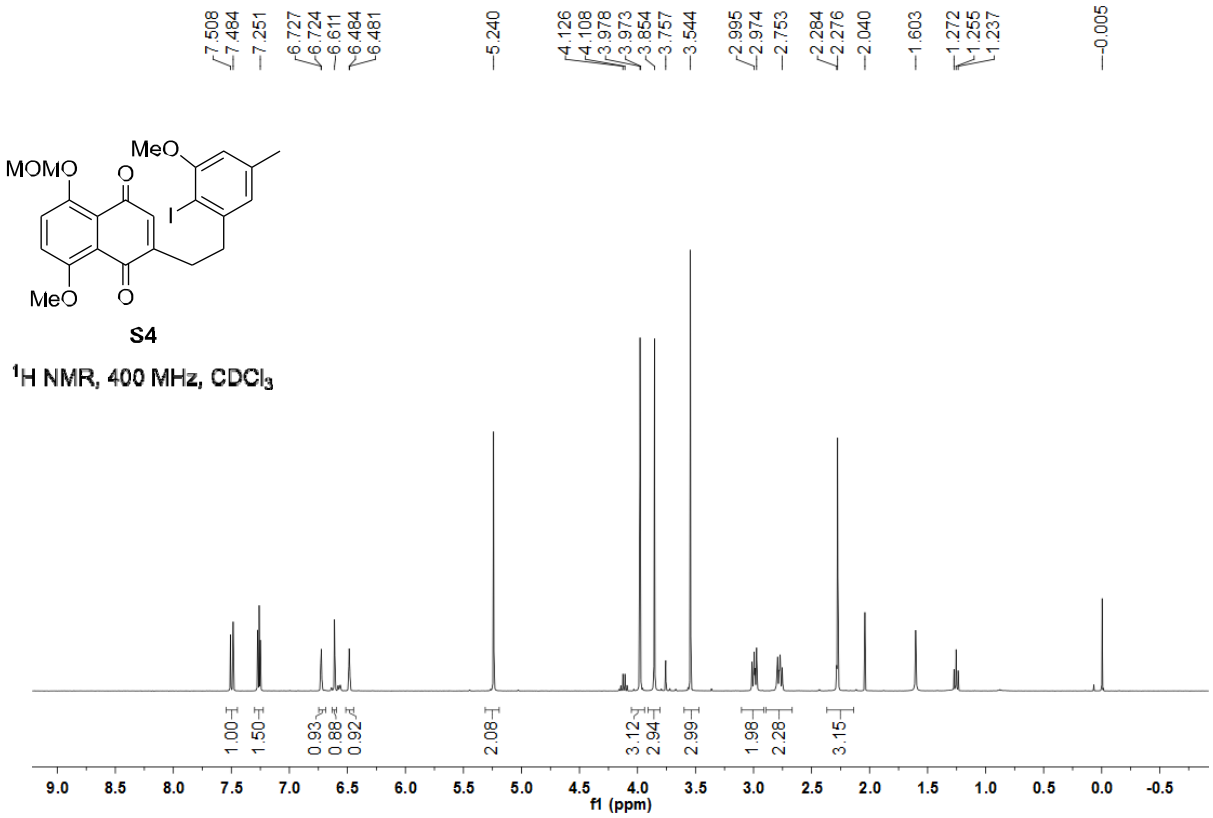


^{13}C NMR spectrum

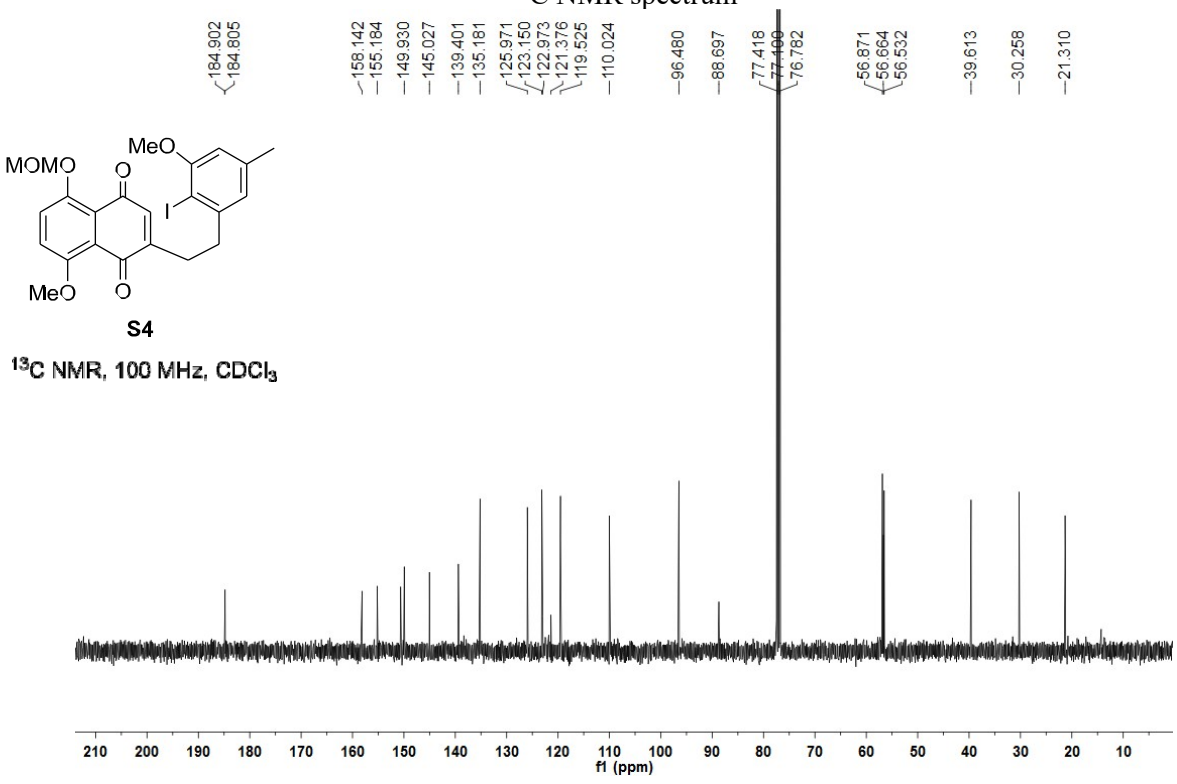


4.27 NMR spectra of compound S4

^{1}H NMR spectrum

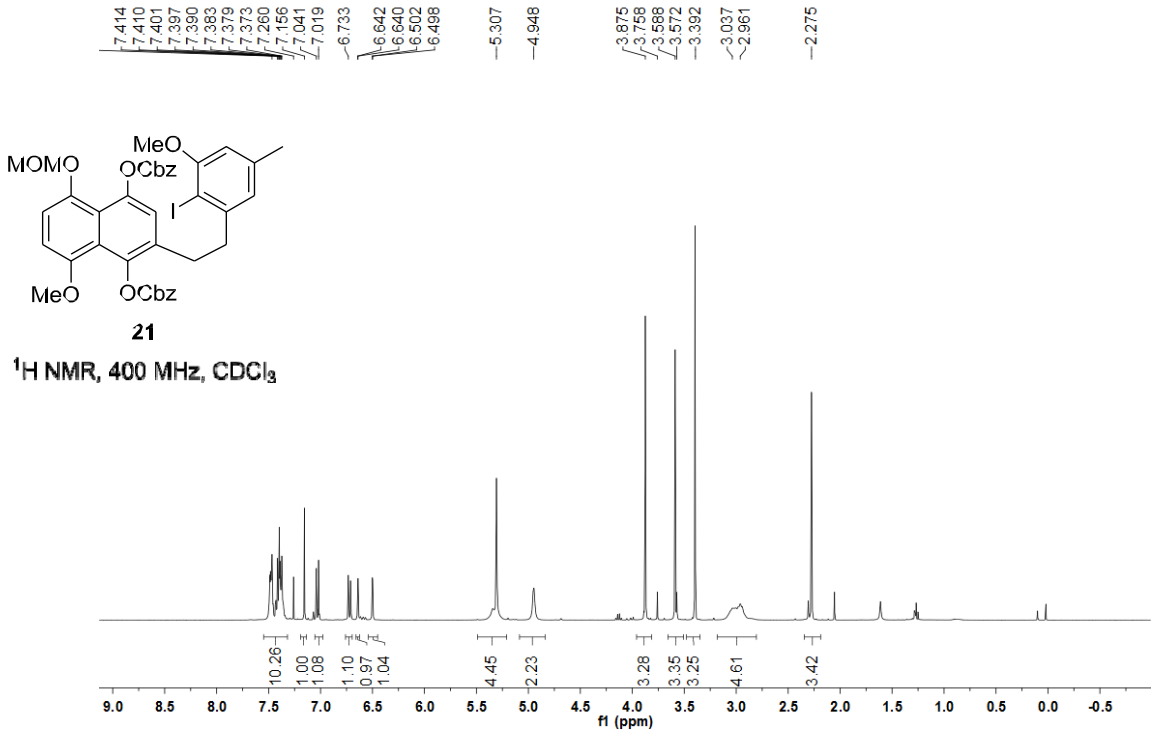


^{13}C NMR spectrum

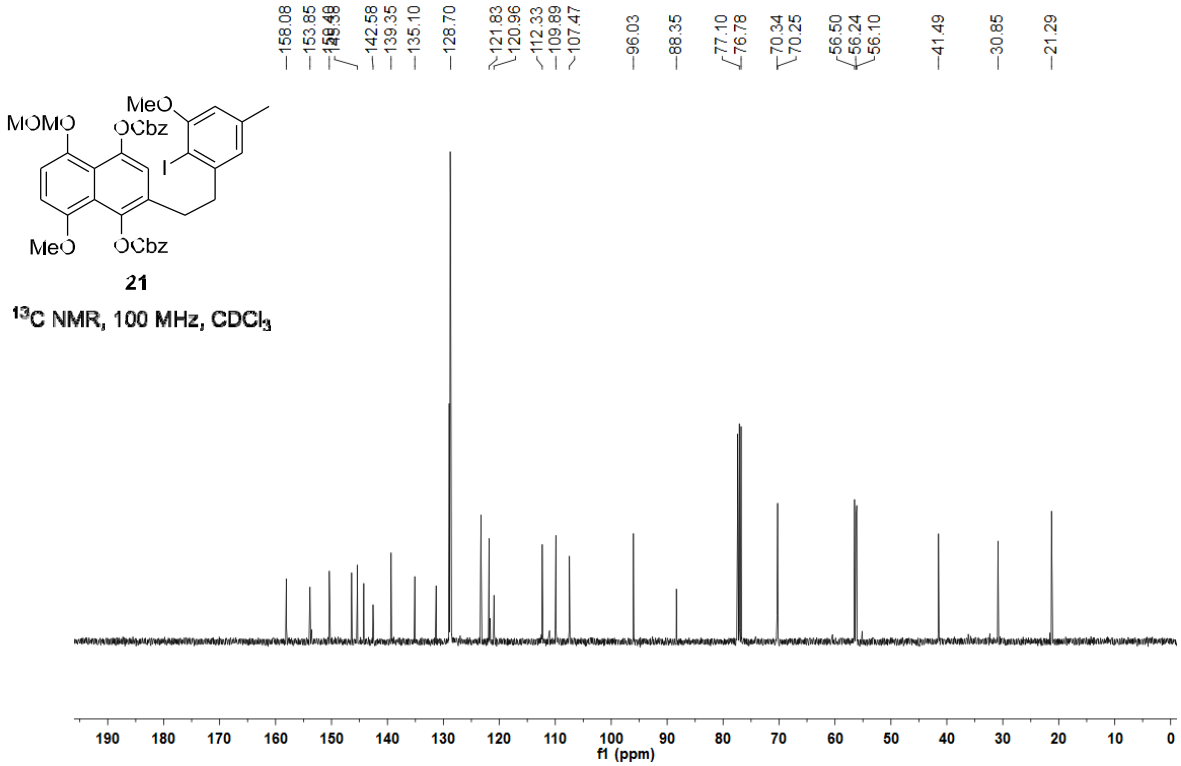


4.28 NMR spectra of compound 21

^{1}H NMR spectrum

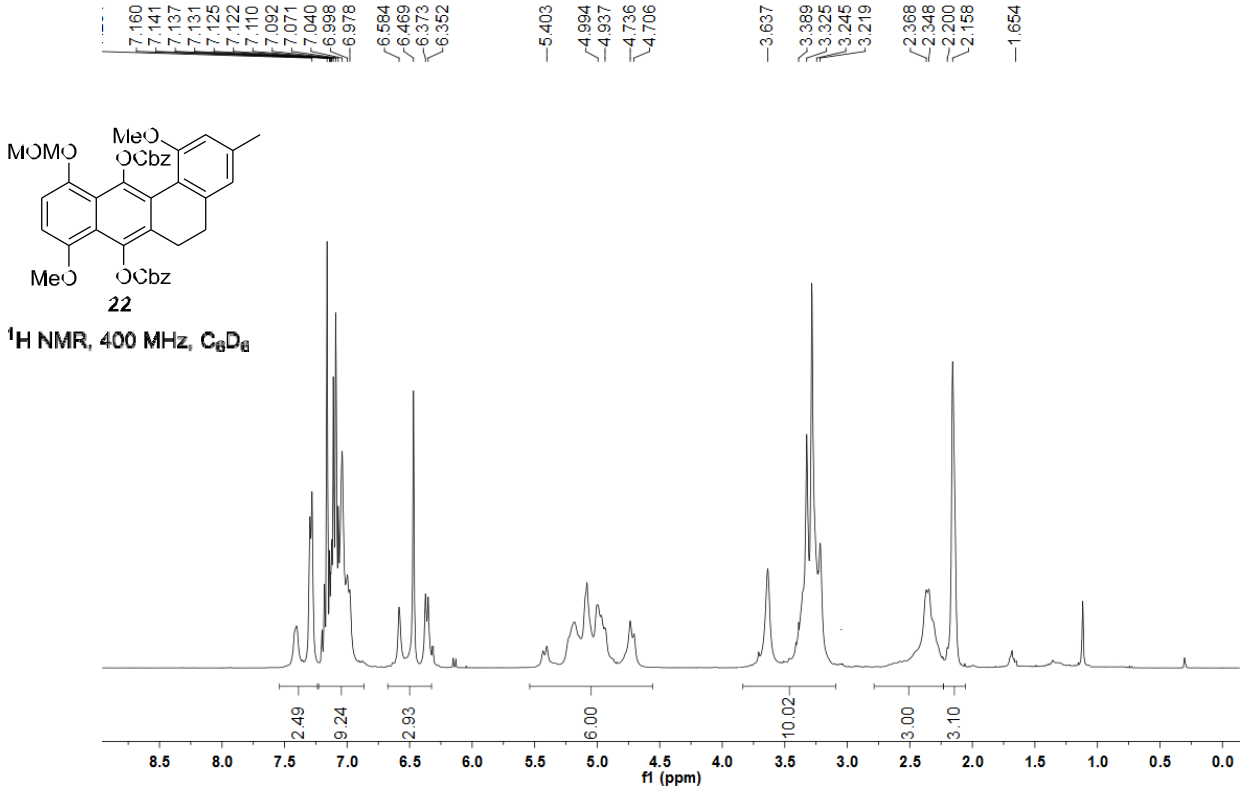


^{13}C NMR spectrum

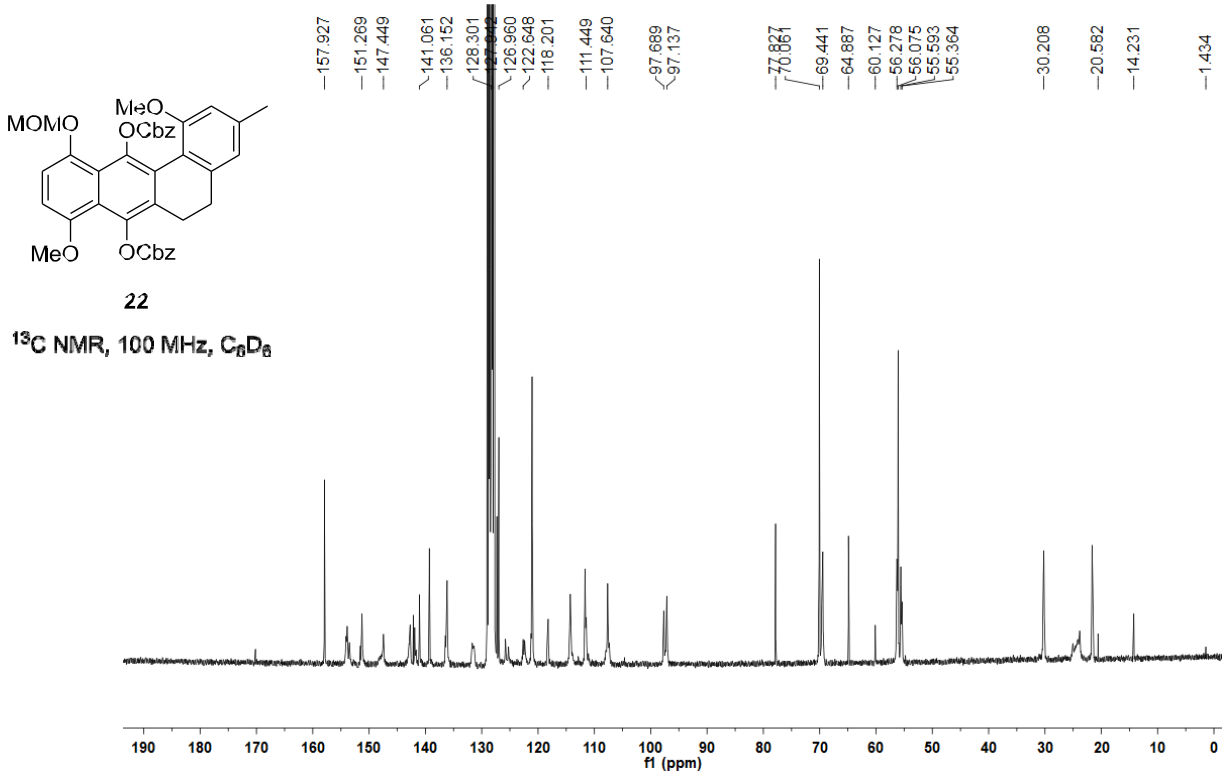


4.29 NMR spectra of compound 22

^{1}H NMR spectrum

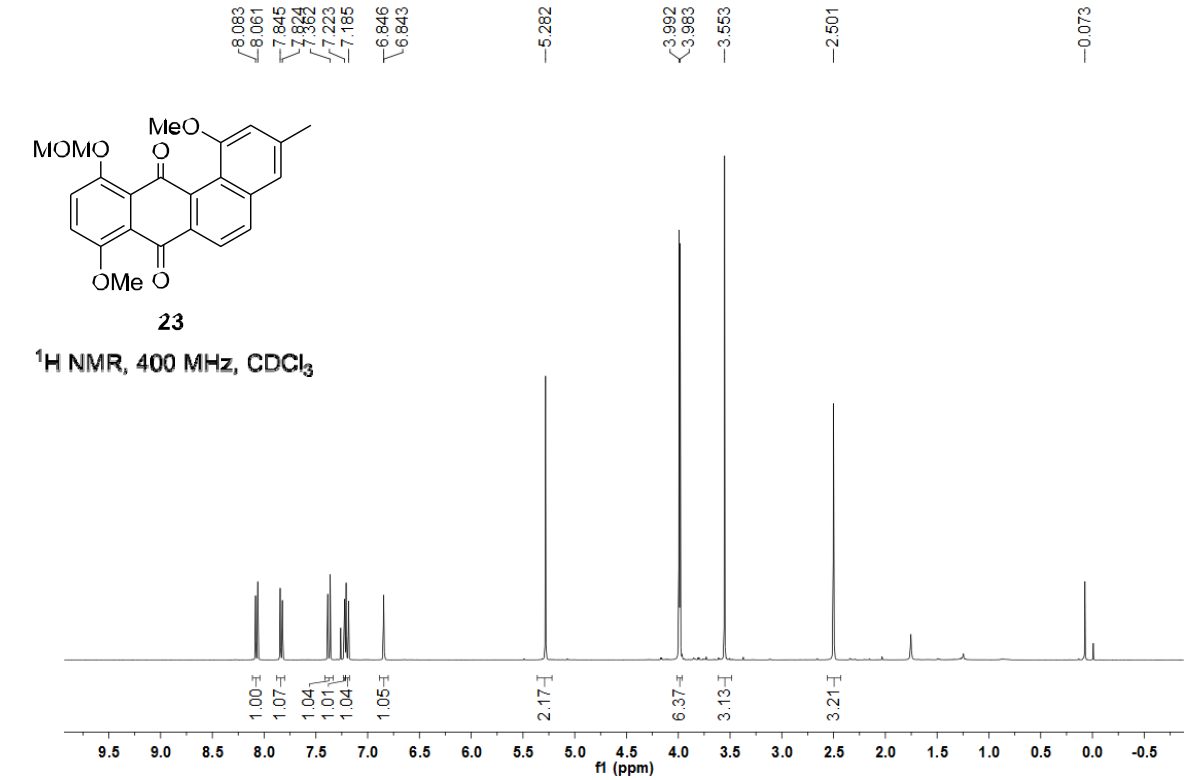


^{13}C NMR spectrum

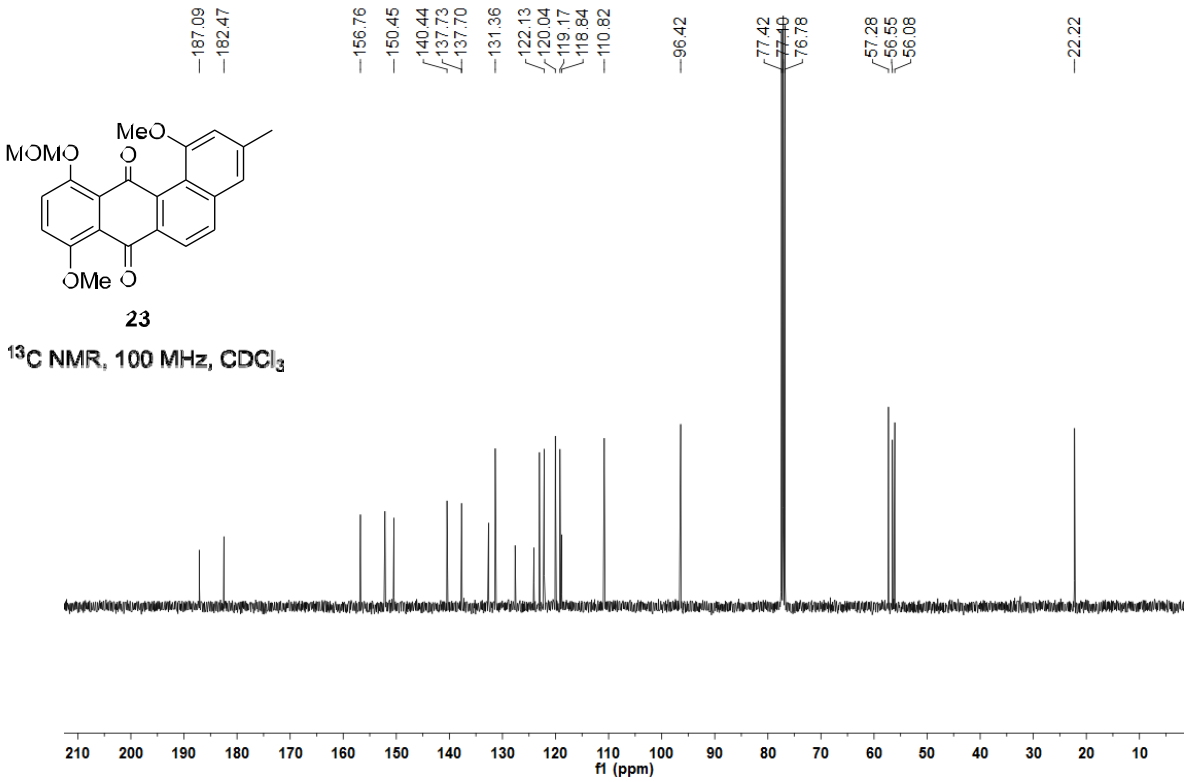


4.30 NMR spectra of compound 23

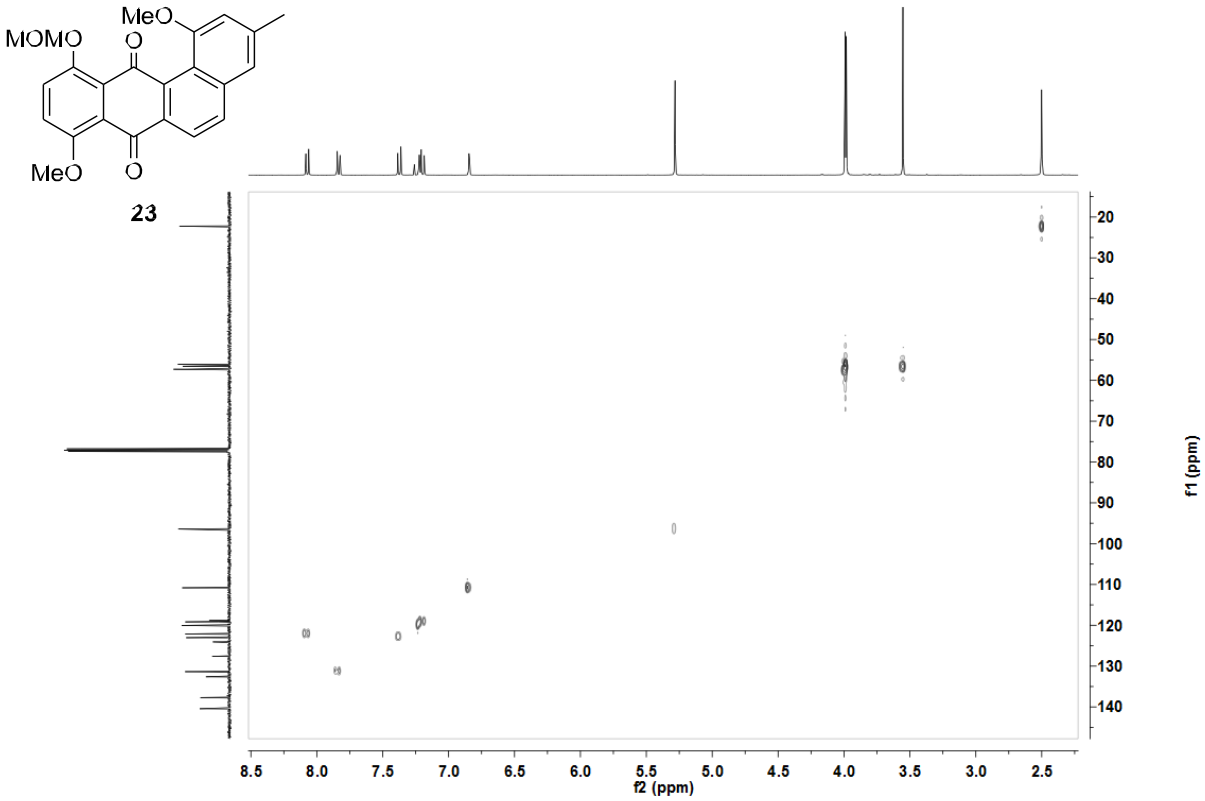
^{1}H NMR spectrum



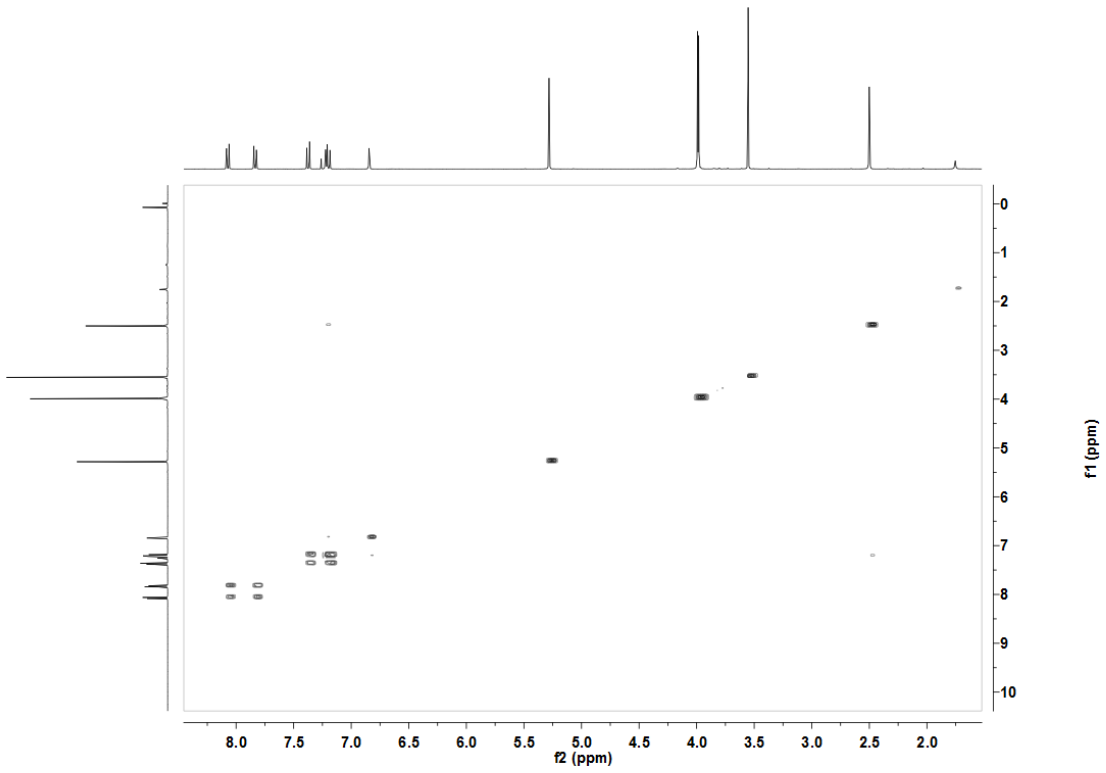
^{13}C NMR spectrum



2D COSY NMR spectrum of compound **23**

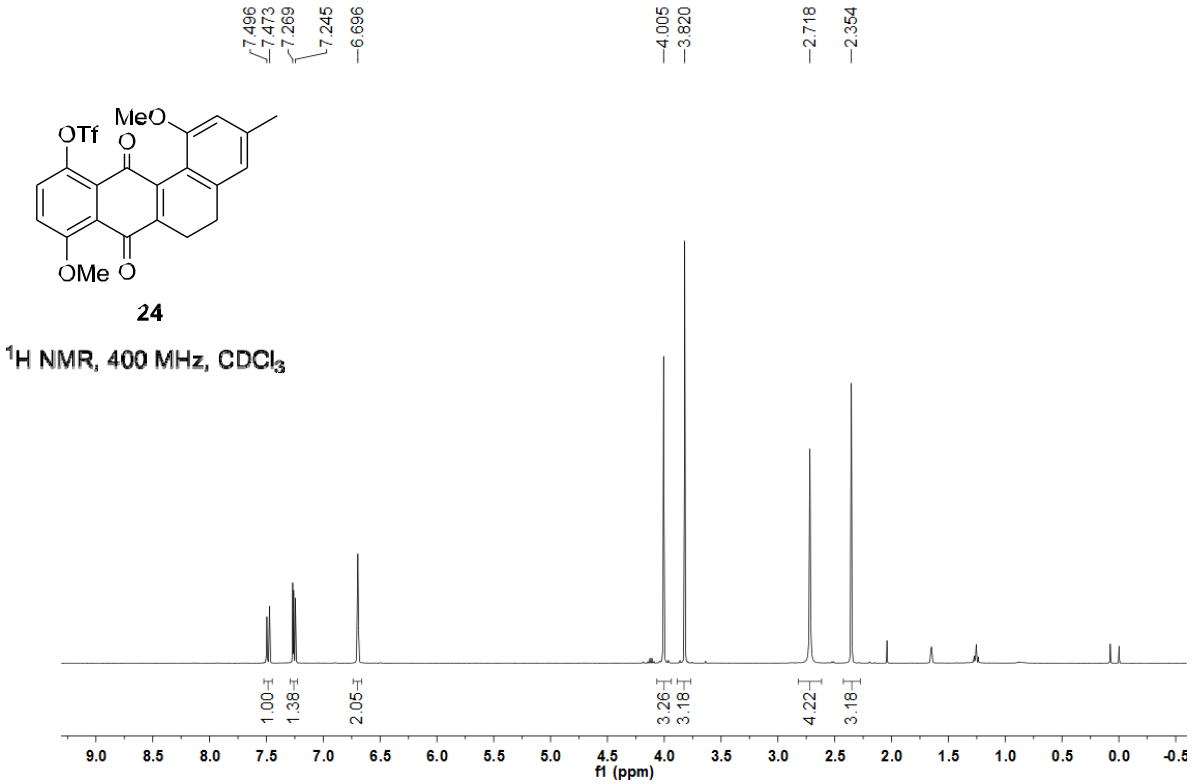


2D HSQC NMR spectrum of compound **23**

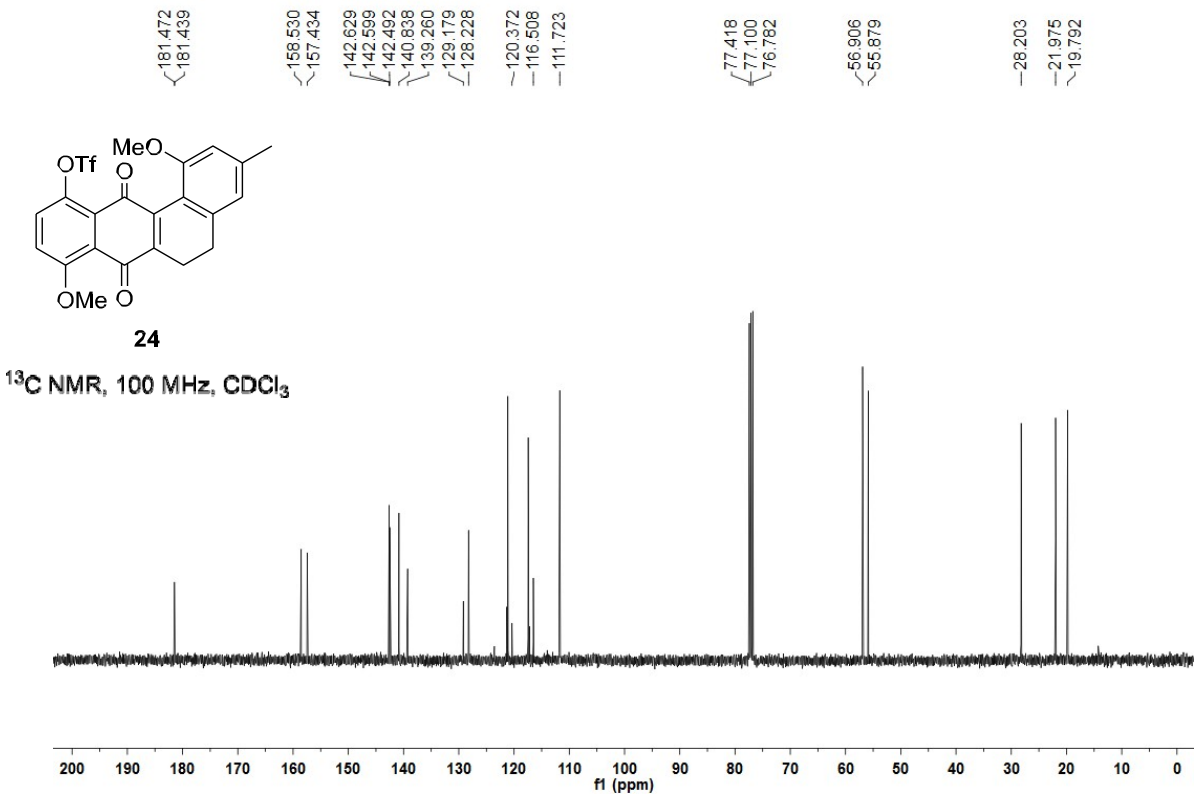


4.31 NMR spectra of compound 24

^{1}H NMR spectrum

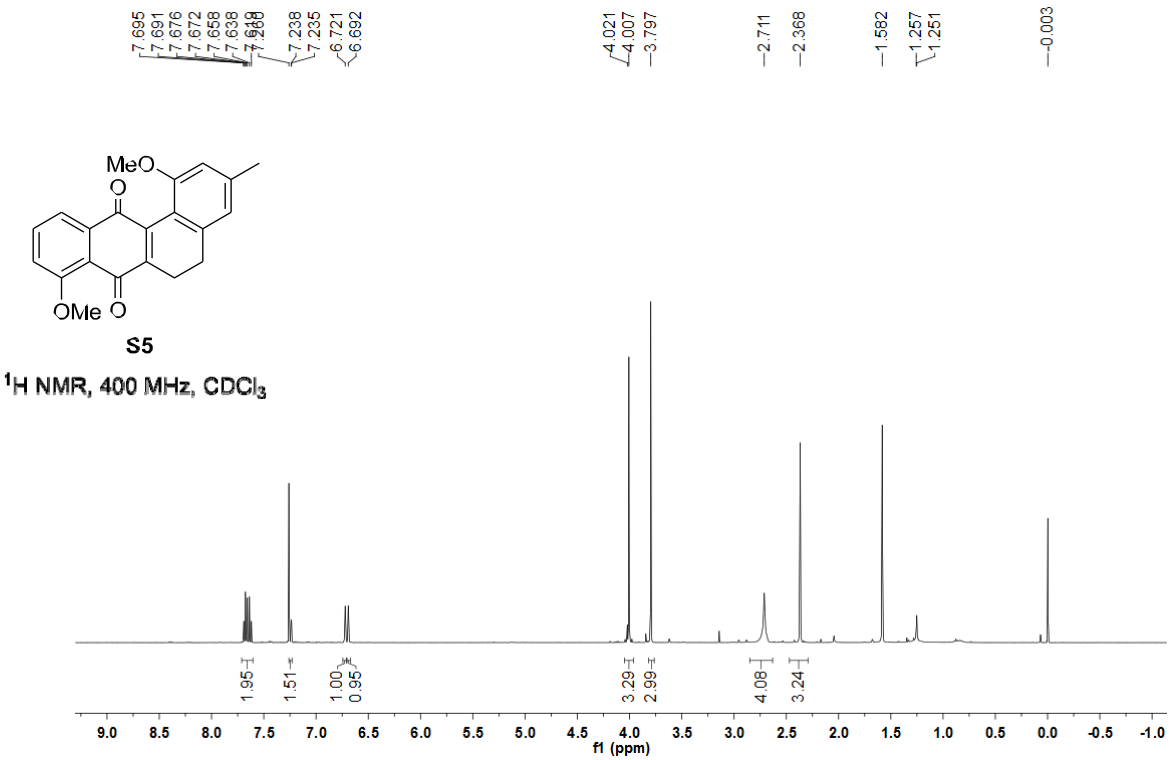


^{13}C NMR spectrum

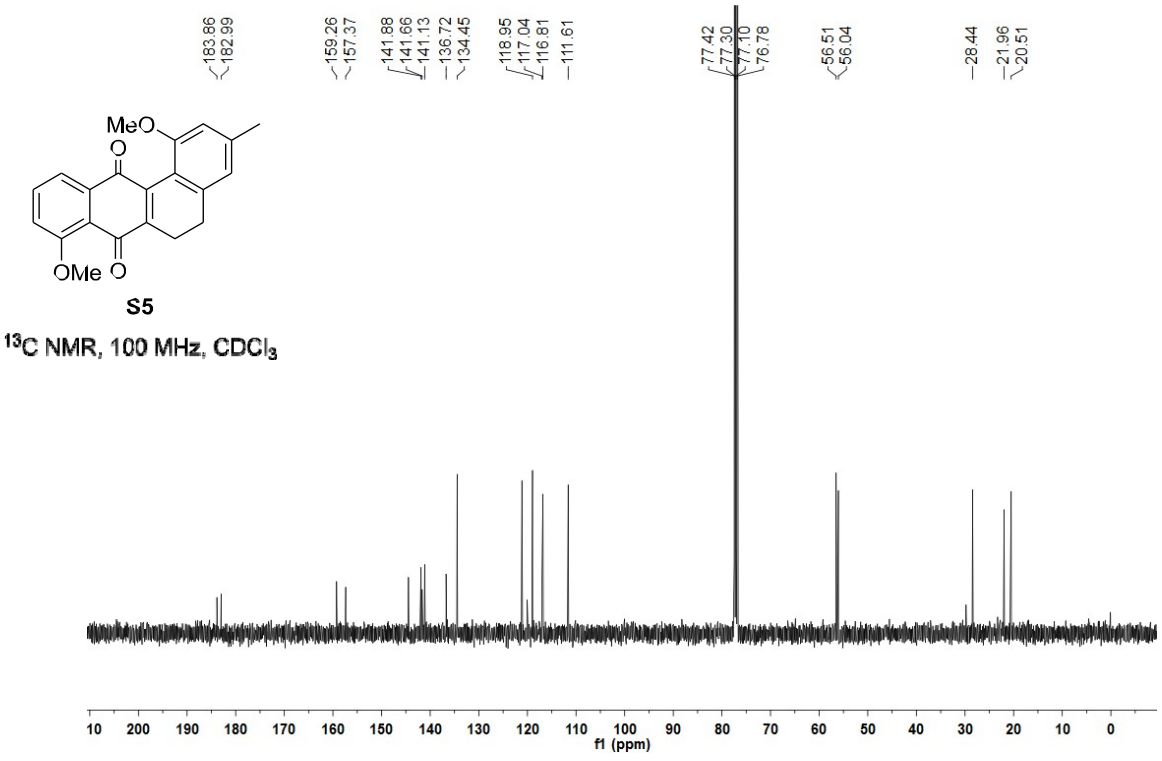


4.32 NMR spectra of compound S5

^{1}H NMR spectrum

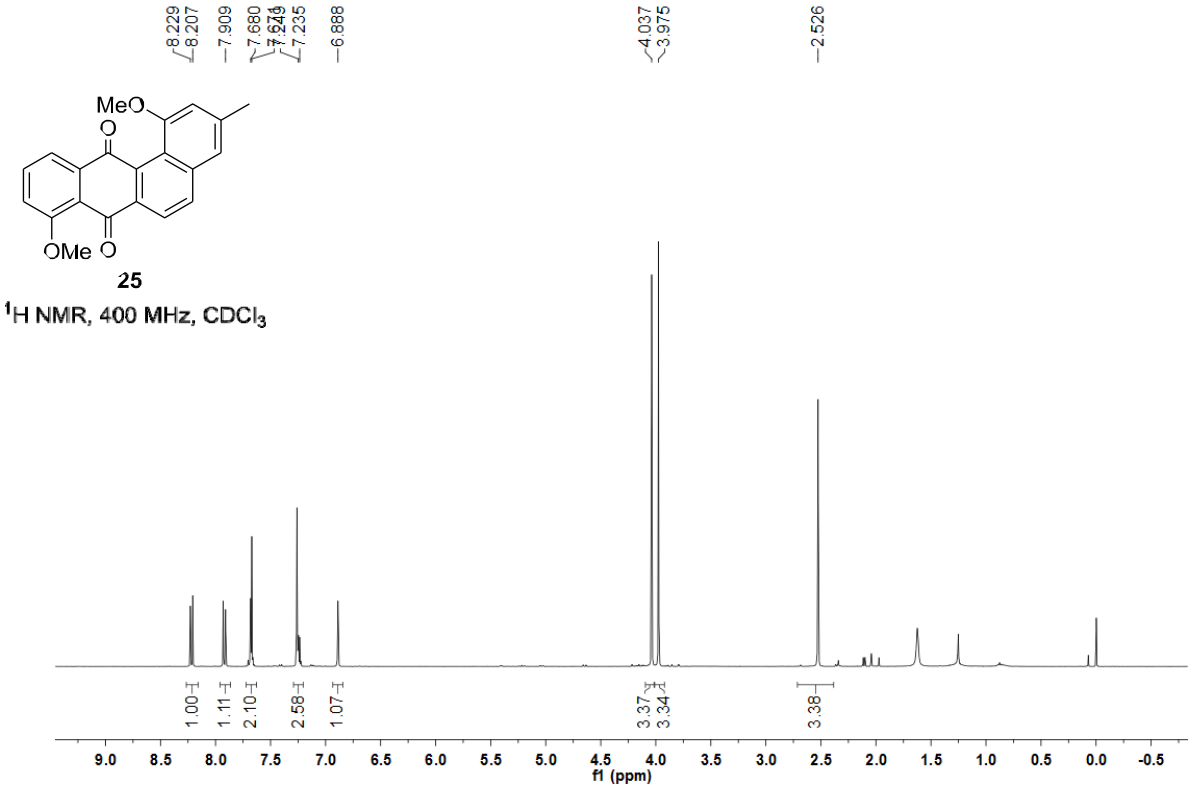


^{13}C NMR spectrum

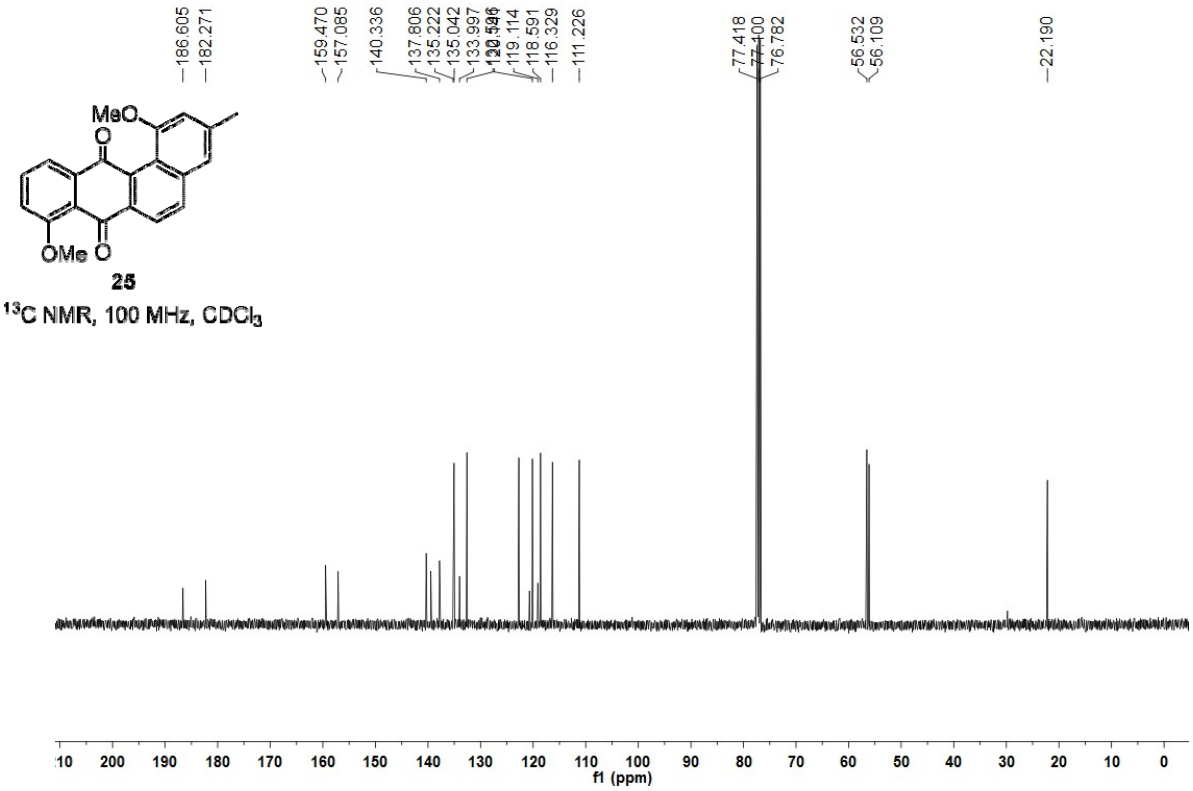


4.33 NMR spectra of compound 25

^{1}H NMR spectrum

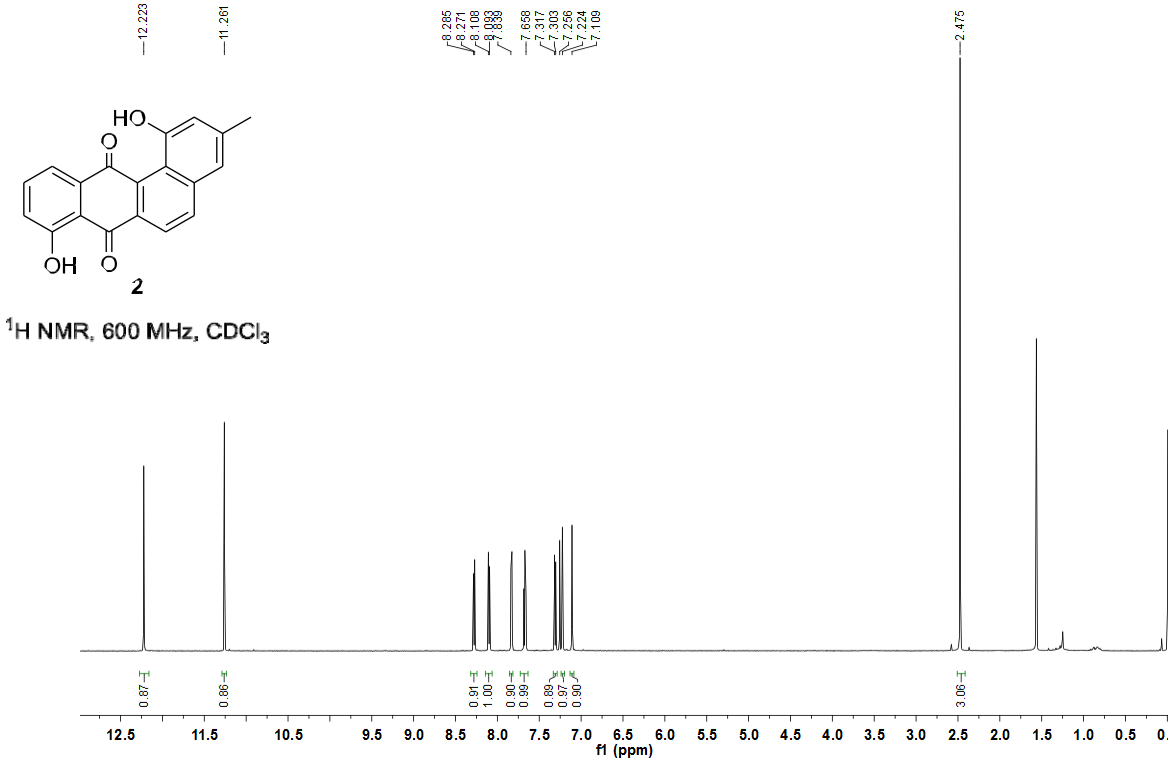


^{13}C NMR spectrum

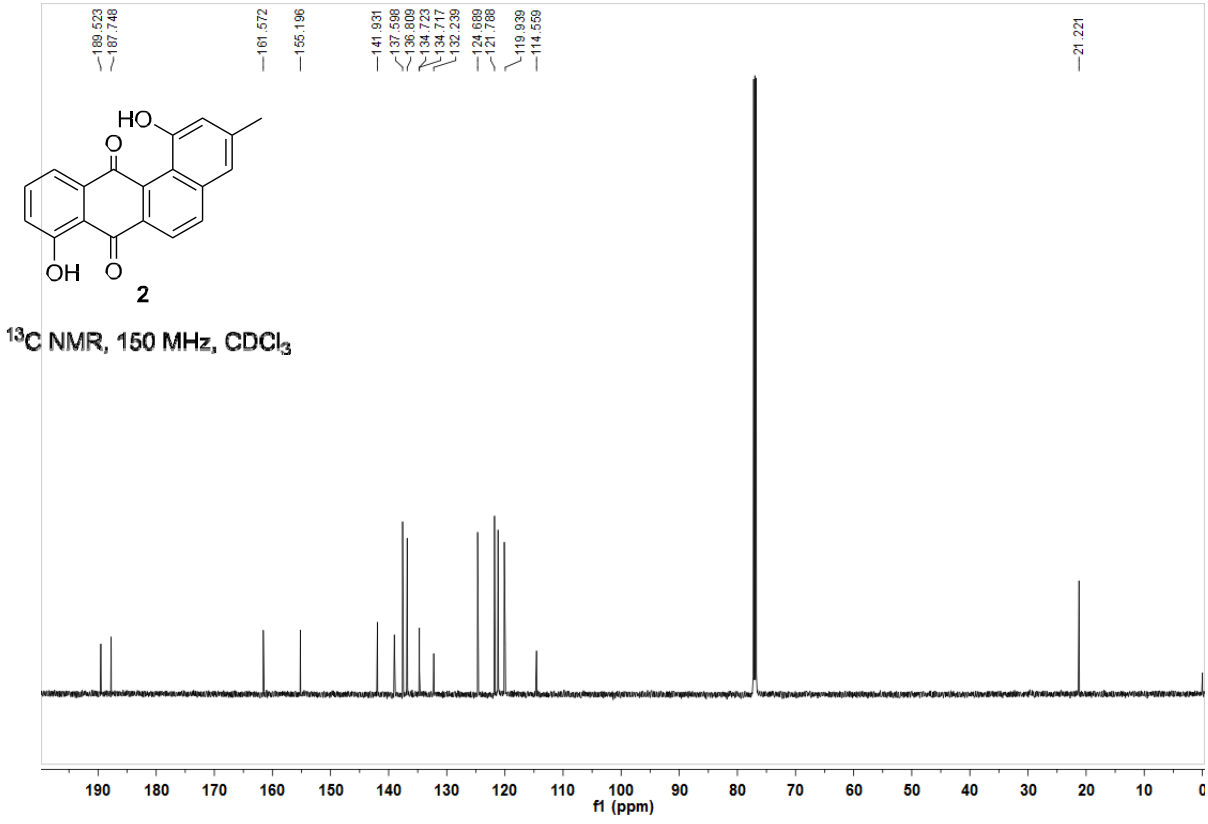


4.34 NMR spectra of tetrangulol 2

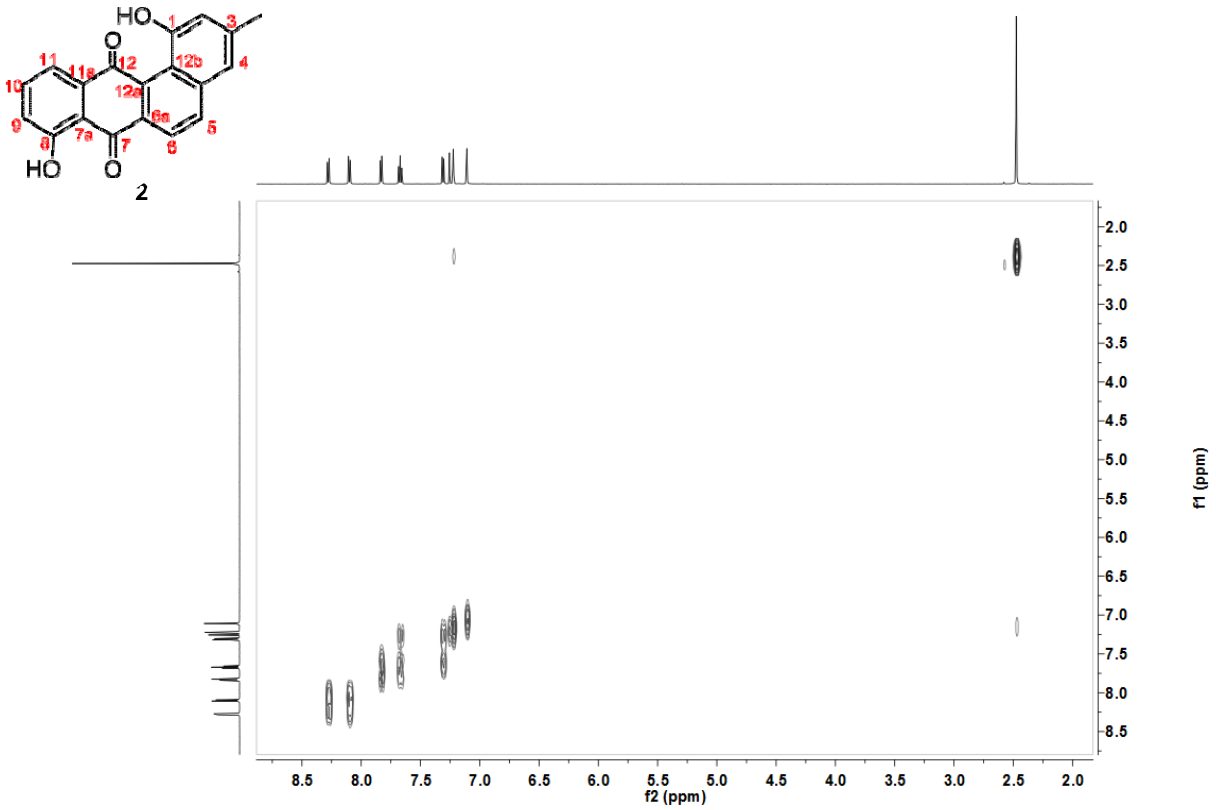
^{1}H NMR spectrum



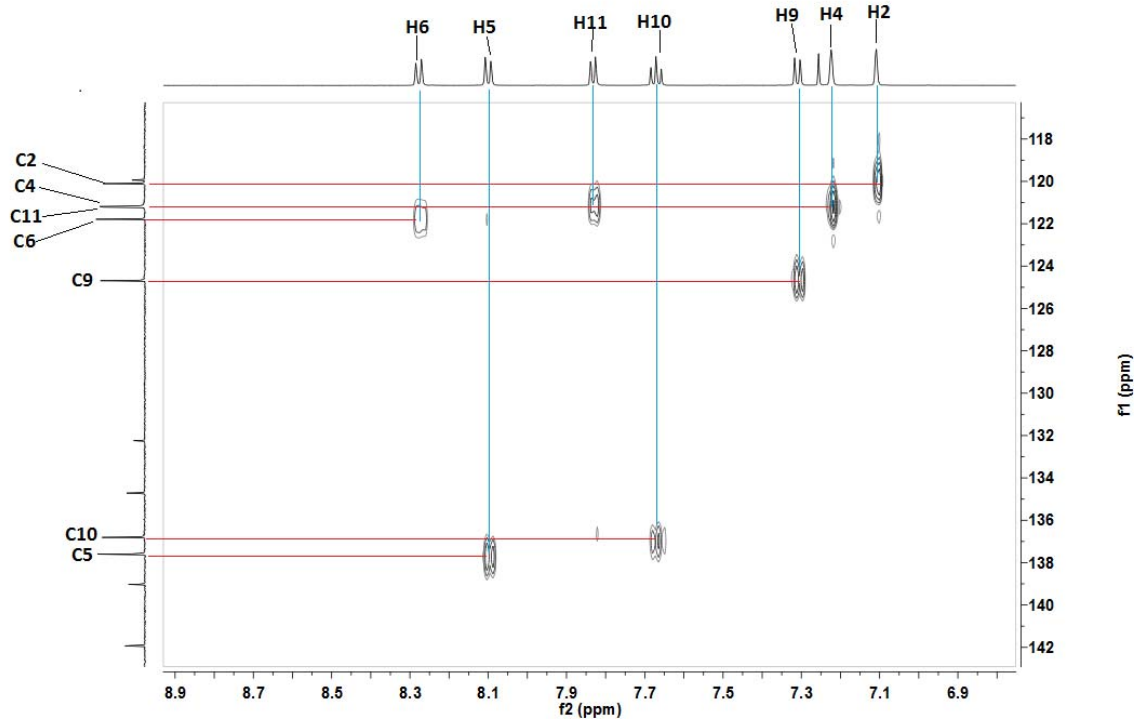
^{13}C NMR spectrum



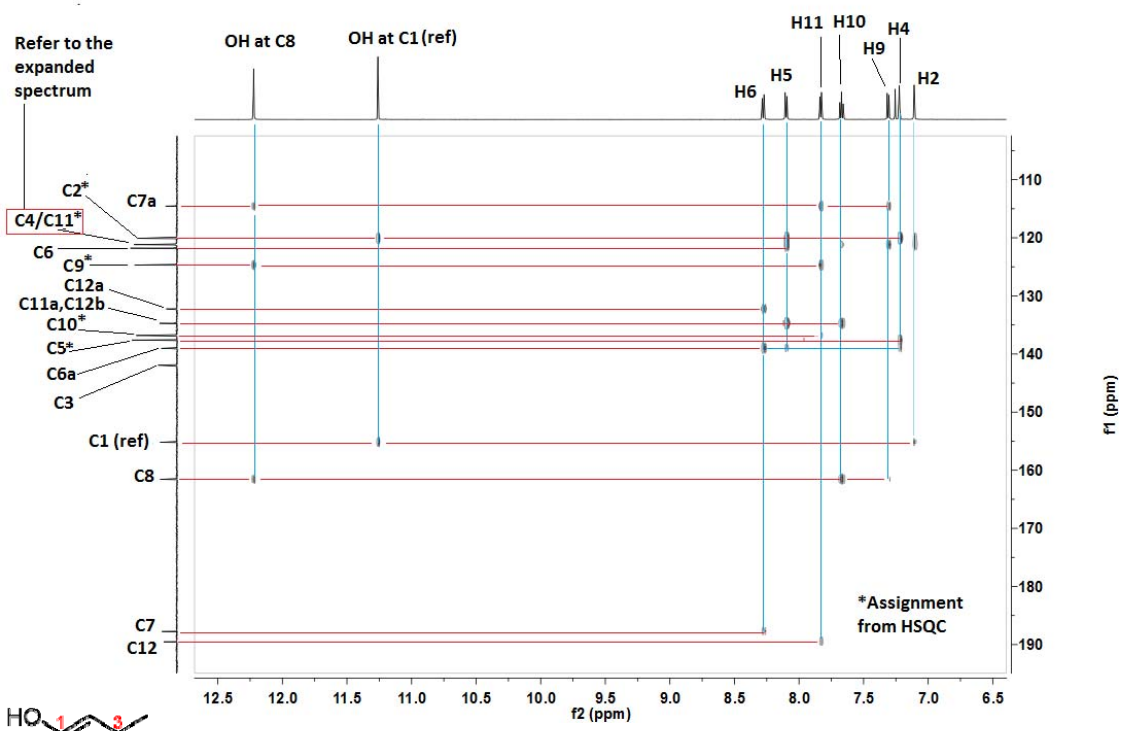
2D COSY NMR spectrum of tetrangulol **2**

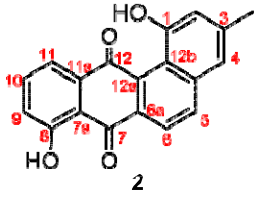


2D HSQC NMR spectrum of tetrangulol **2**

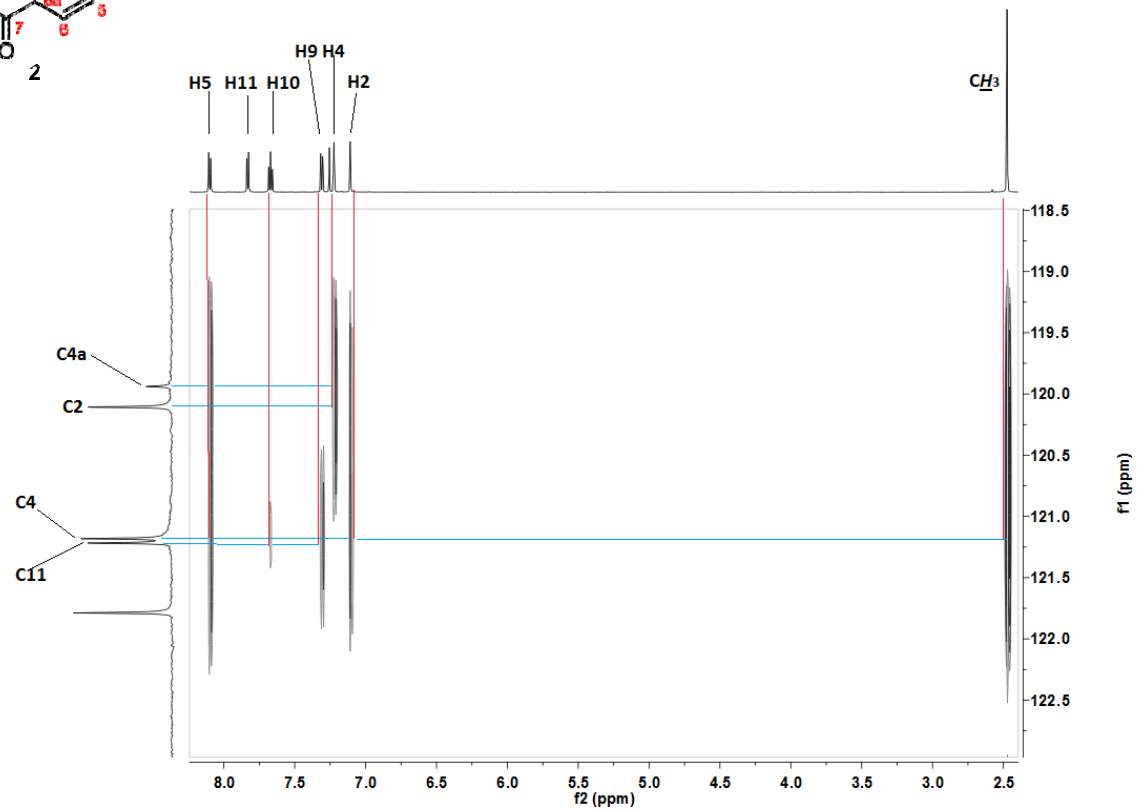


2D HMBC NMR spectrum of tetrangulol **2**



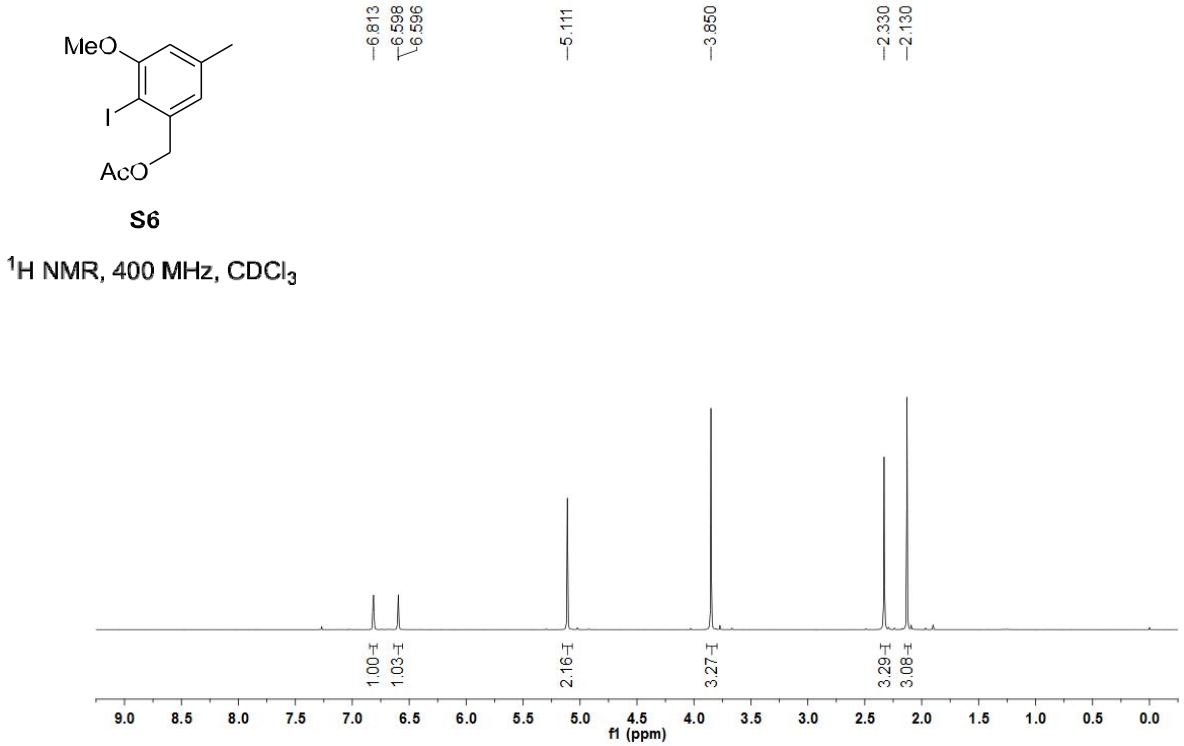


Expanded 2D HMBC NMR spectrum of tetrangulol **2**



4.35 NMR spectrum of compound S6

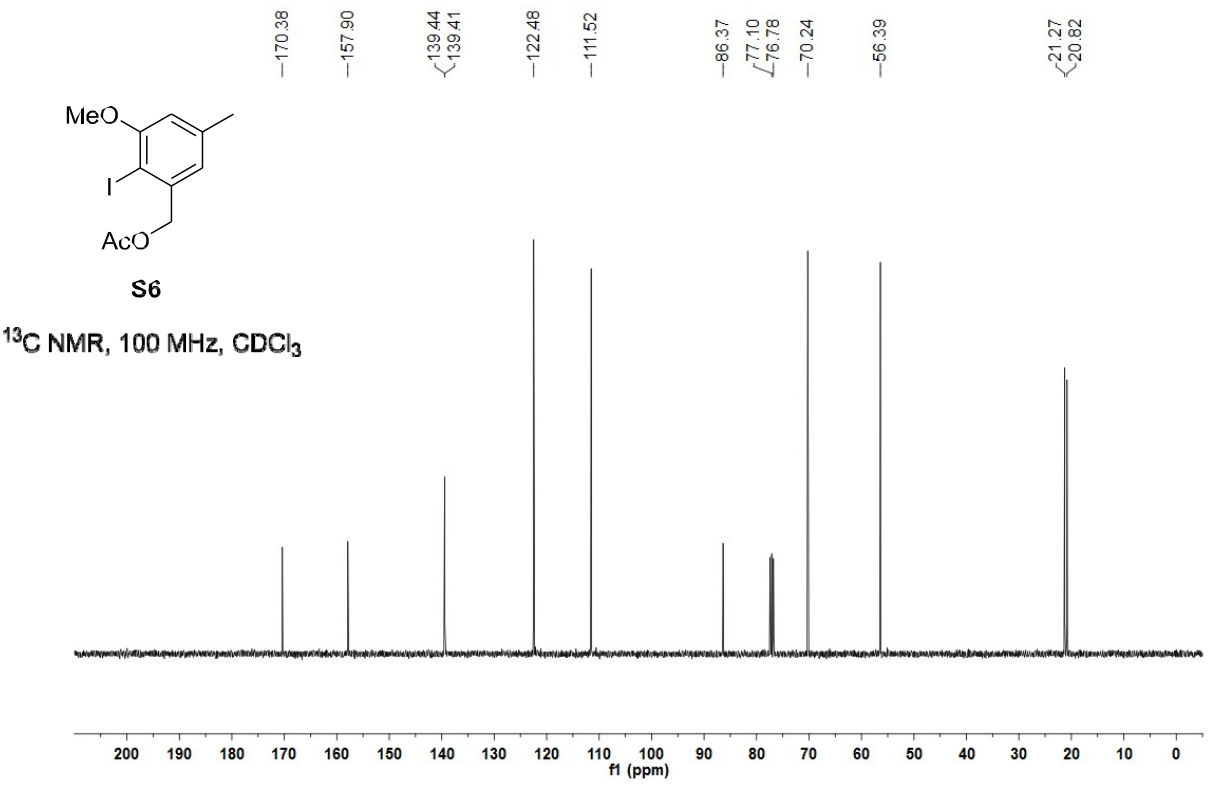
^{1}H NMR spectrum



S6

^{1}H NMR, 400 MHz, $CDCl_3$

^{13}C NMR spectrum

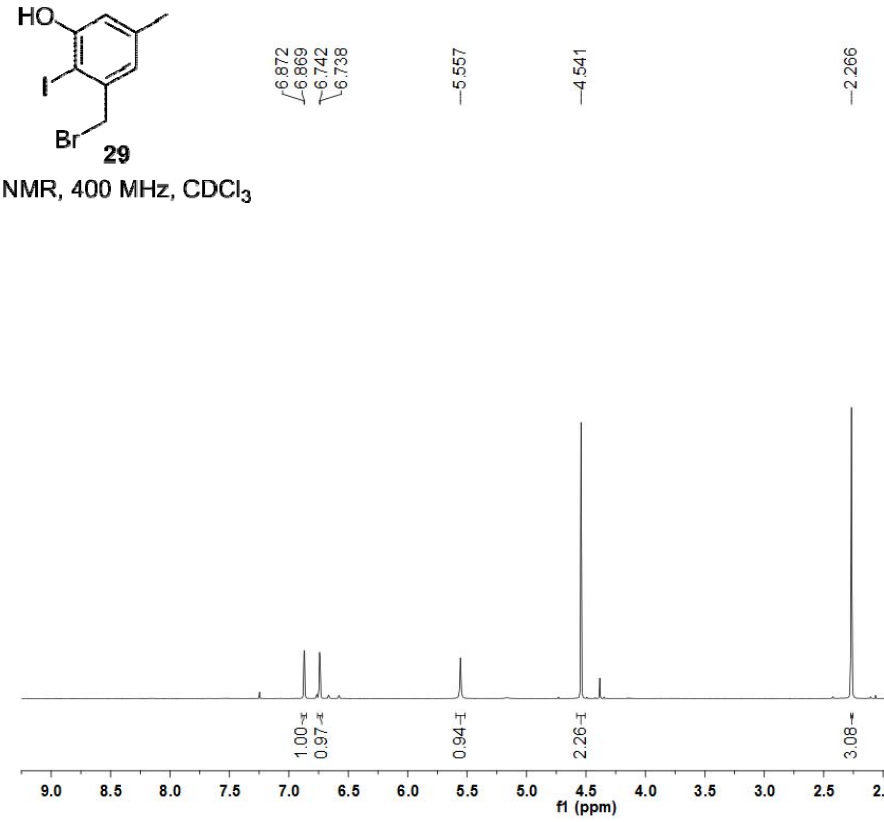


S6

^{13}C NMR, 100 MHz, $CDCl_3$

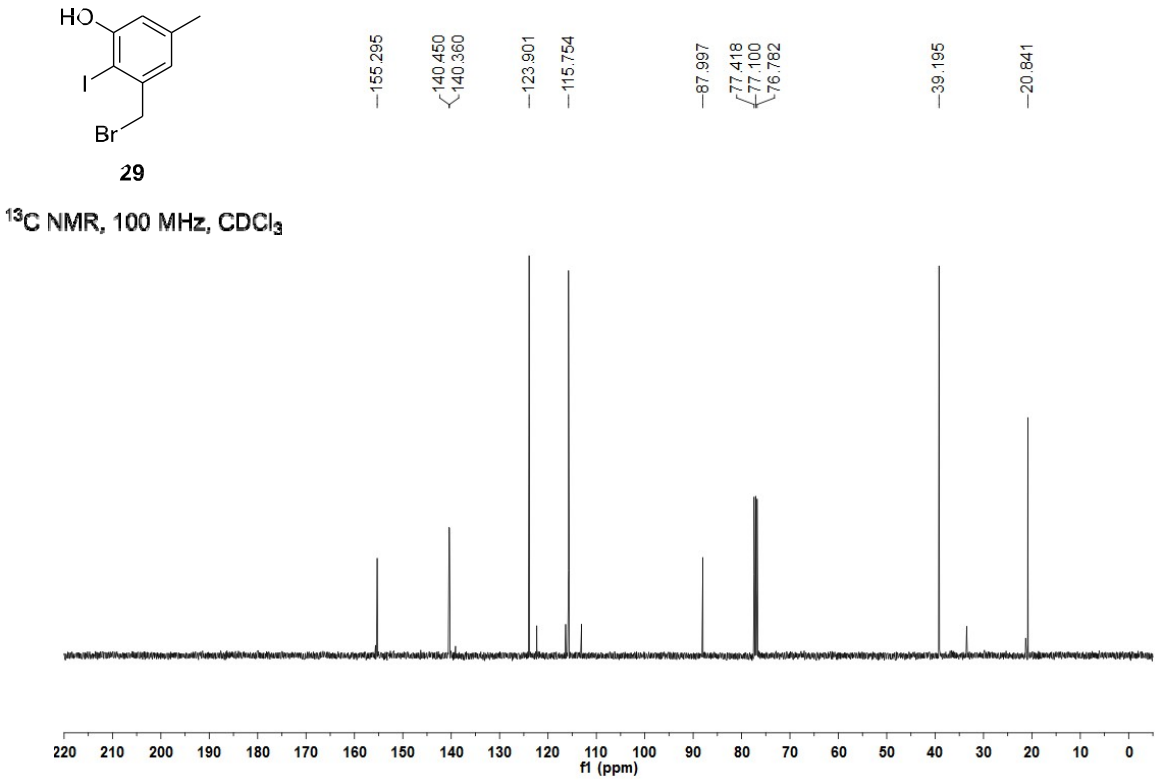
4.36 NMR spectra of compound 29

^{1}H NMR spectrum



^{1}H NMR, 400 MHz, $CDCl_3$

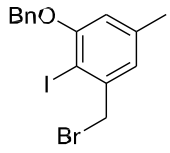
^{13}C NMR spectrum



^{13}C NMR, 100 MHz, $CDCl_3$

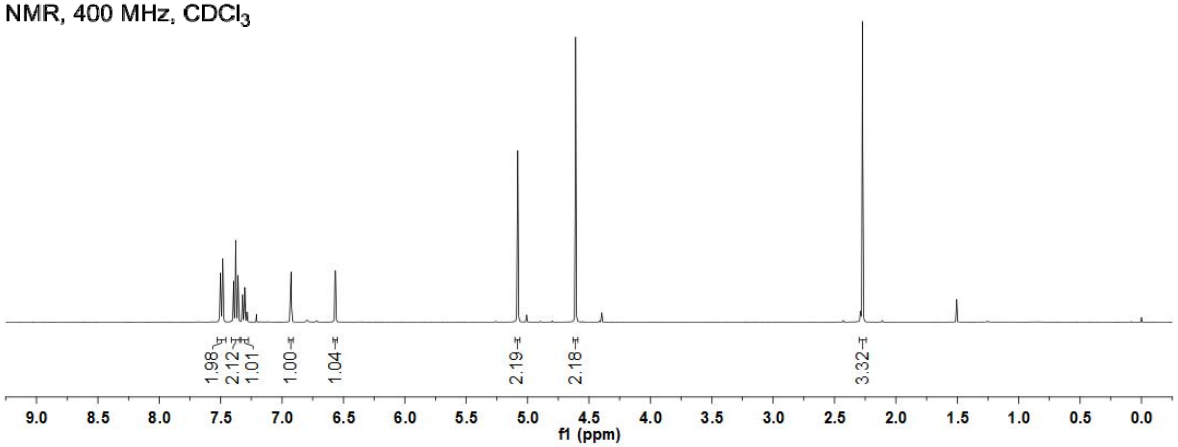
4.37 NMR spectra of compound S7

^{1}H NMR spectrum

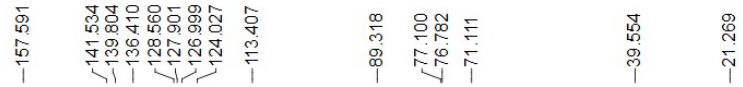


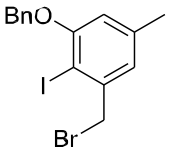
S7

^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR spectrum



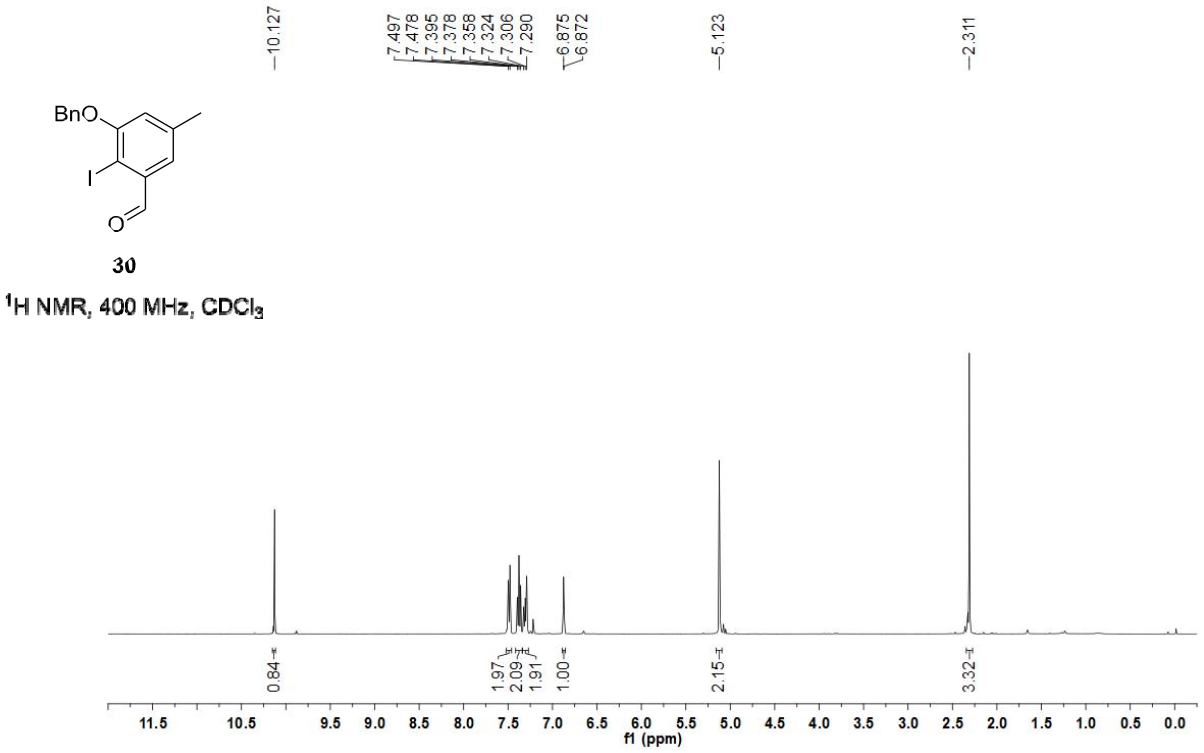


S7

^{13}C NMR, 100 MHz, $CDCl_3$

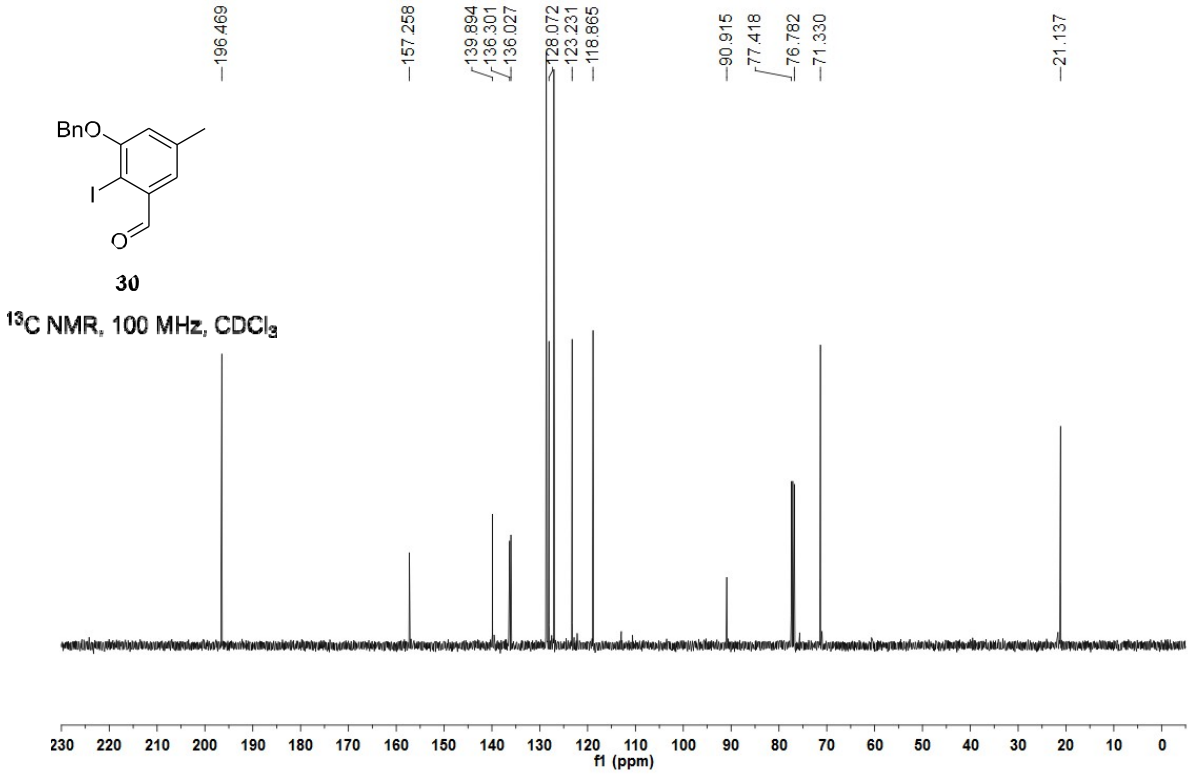
4.38 NMR spectra of compound 30

^{1}H NMR spectrum



^{1}H NMR, 400 MHz, $CDCl_3$

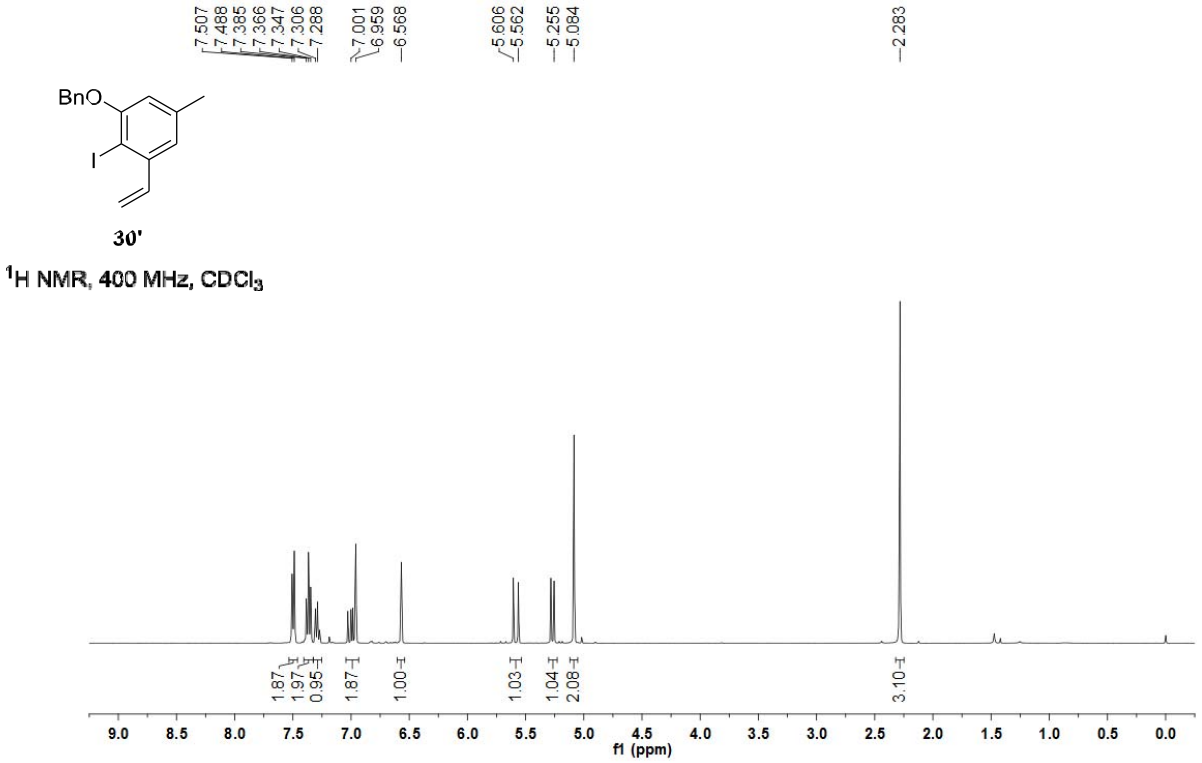
^{13}C NMR spectrum



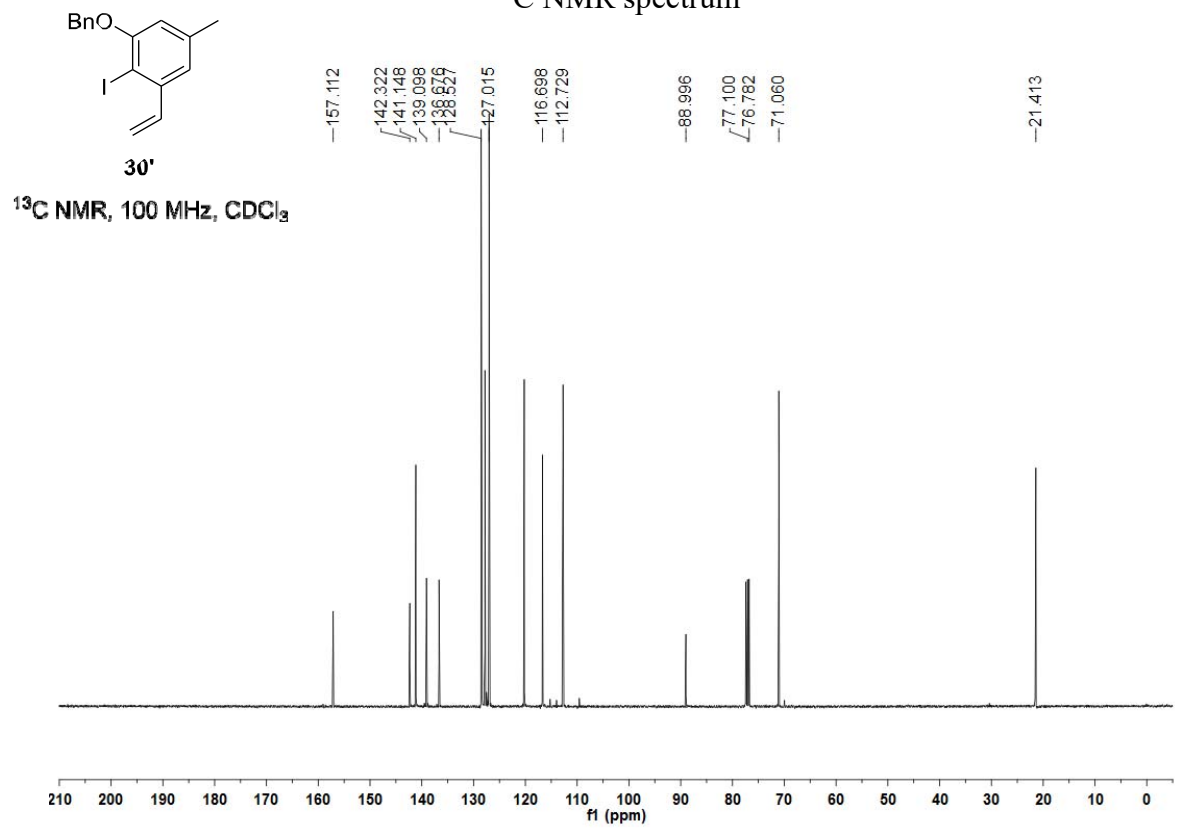
^{13}C NMR, 100 MHz, $CDCl_3$

4.39 NMR spectra of compound 30′

^{1}H NMR spectrum

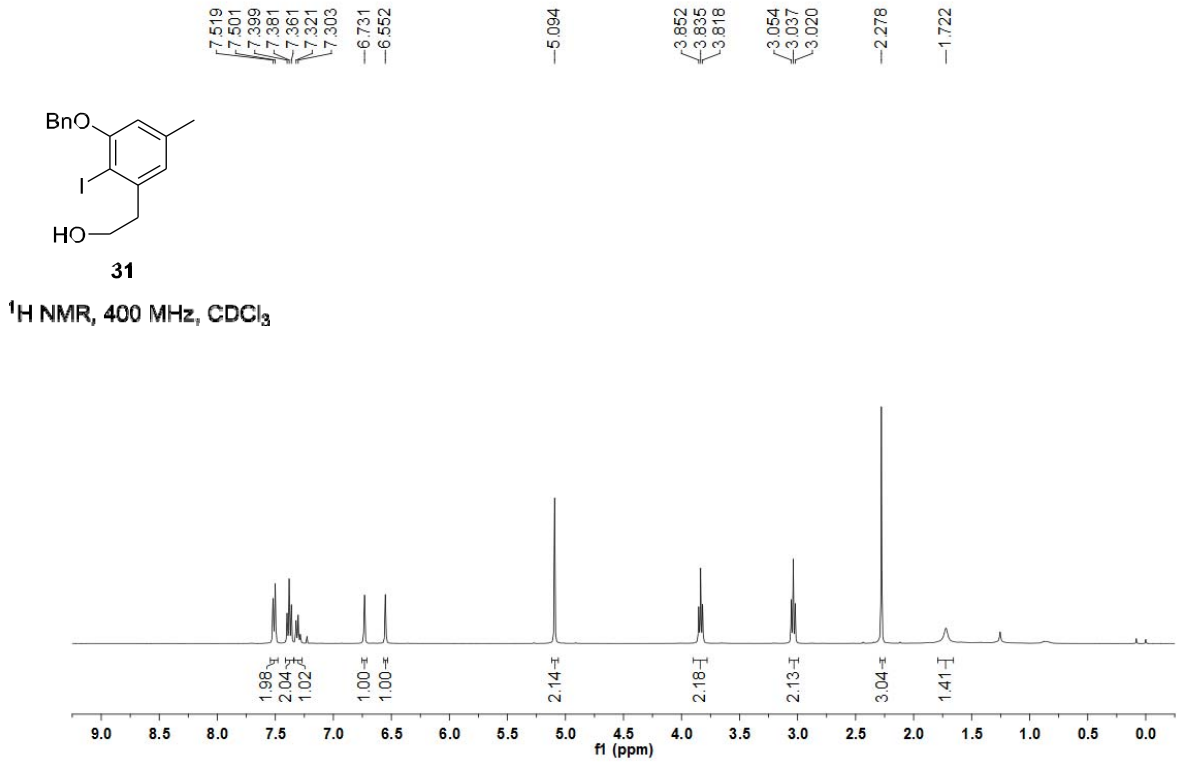


^{13}C NMR spectrum

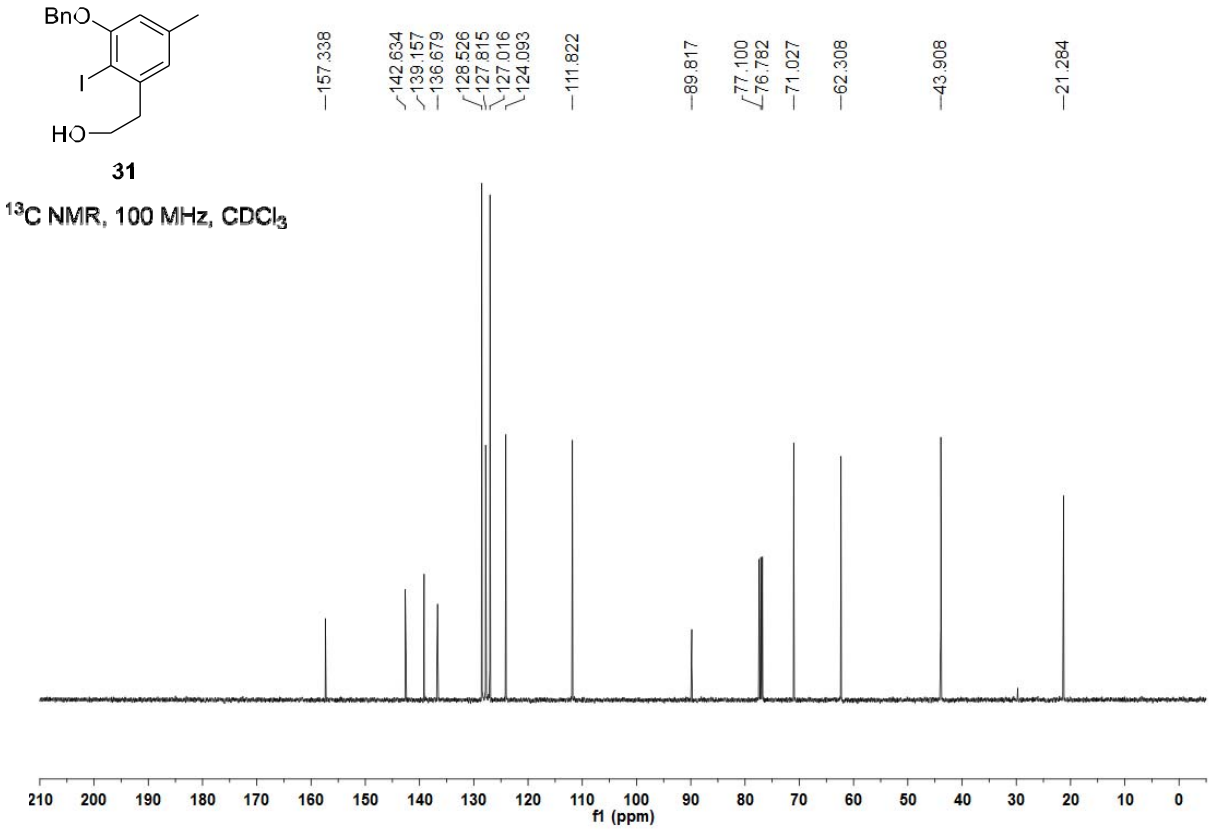


4.41 NMR spectra of compound 31

^{1}H NMR spectrum

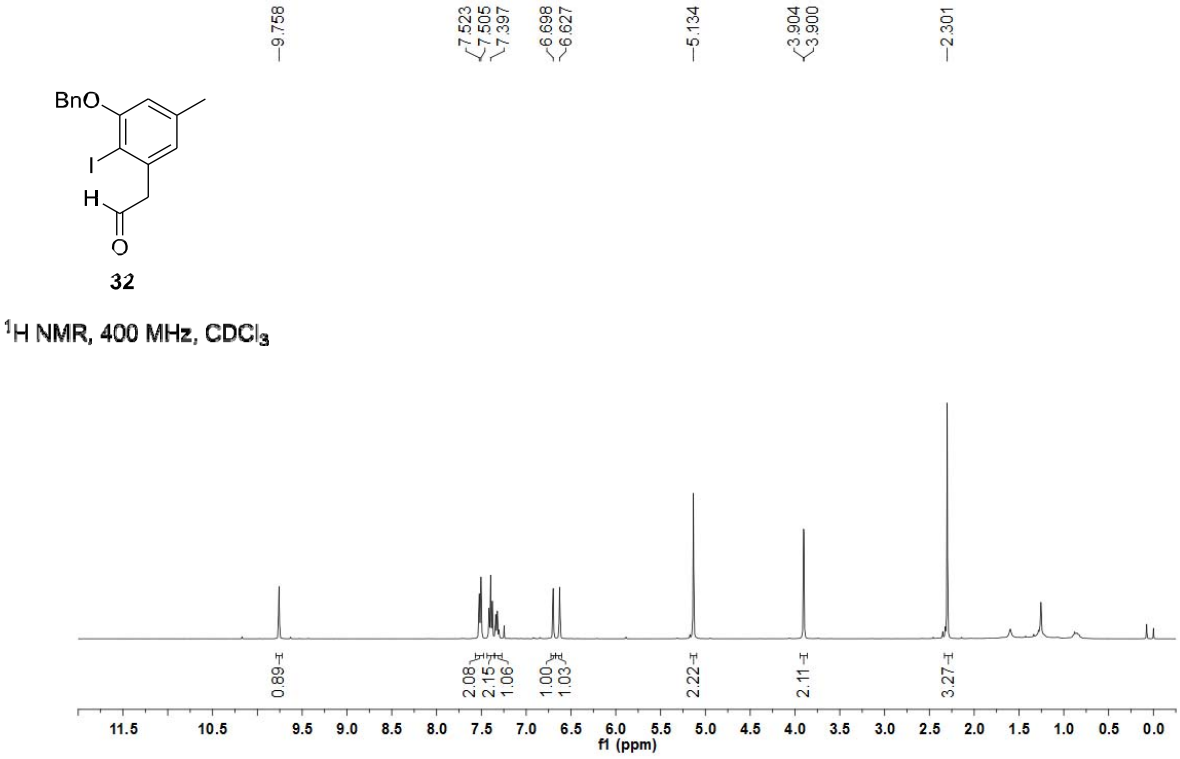


^{13}C NMR spectrum



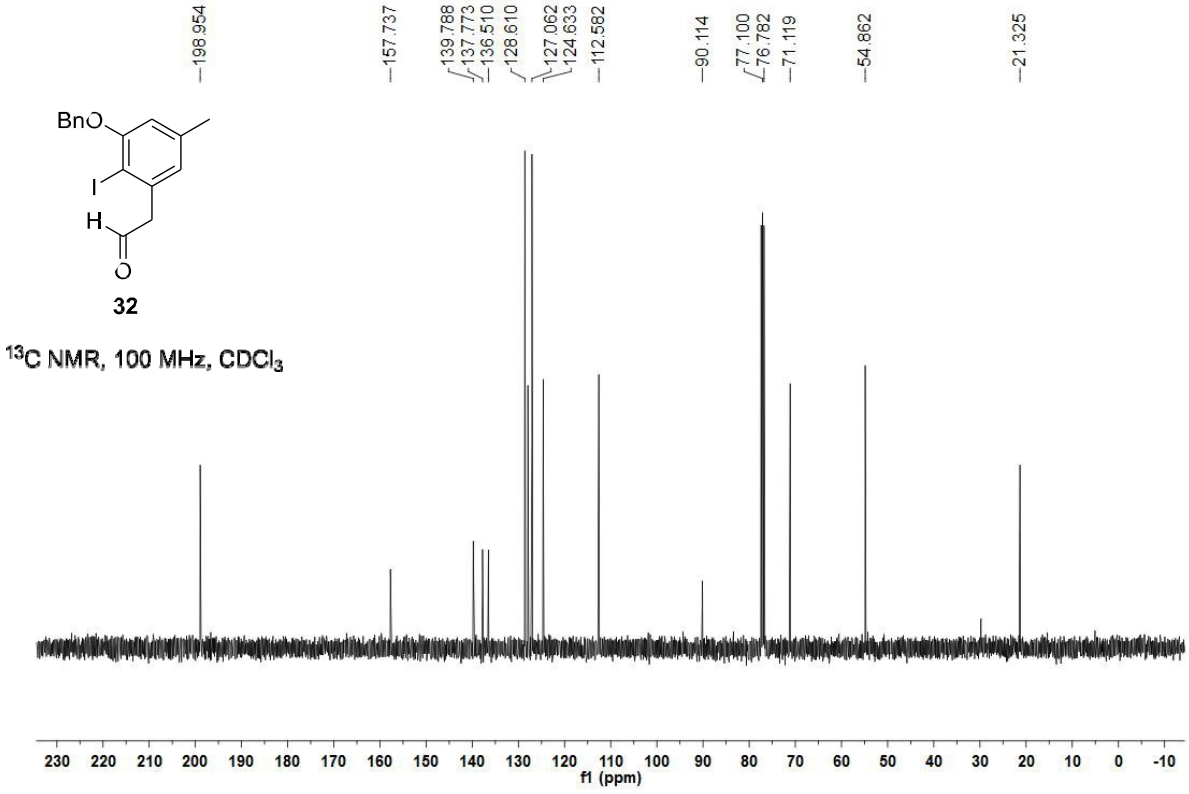
4.42 NMR spectra of compound 32

^{1}H NMR spectrum



^{1}H NMR, 400 MHz, $CDCl_3$

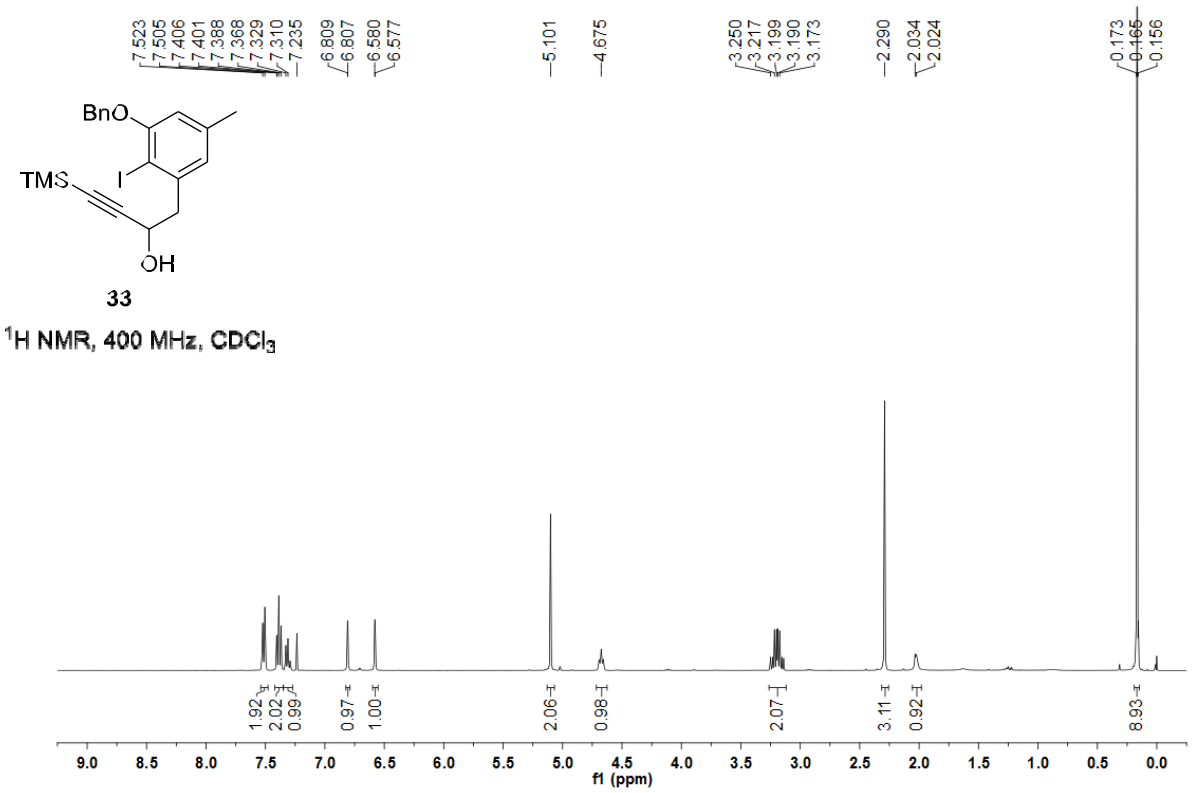
^{13}C NMR spectrum



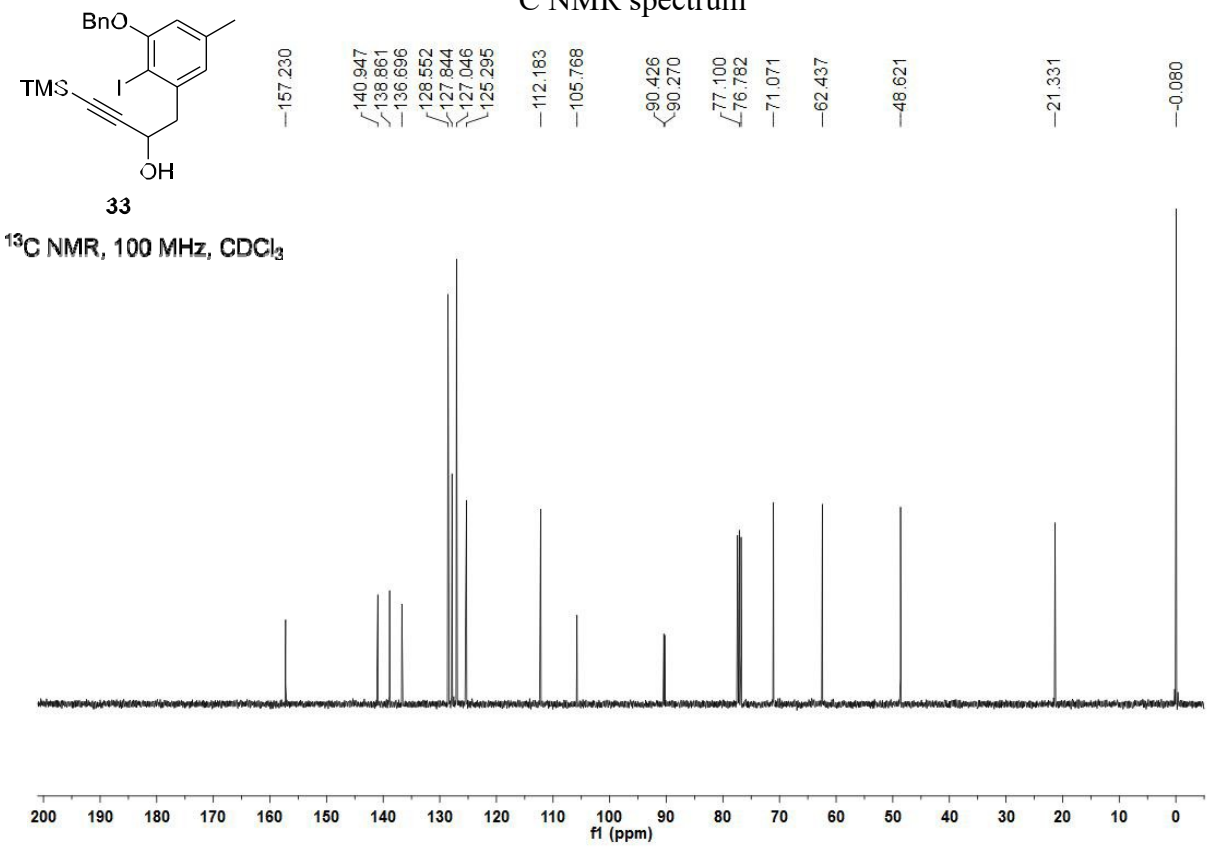
^{13}C NMR, 100 MHz, $CDCl_3$

4.43 NMR spectra of compound 33

^{1}H NMR spectrum

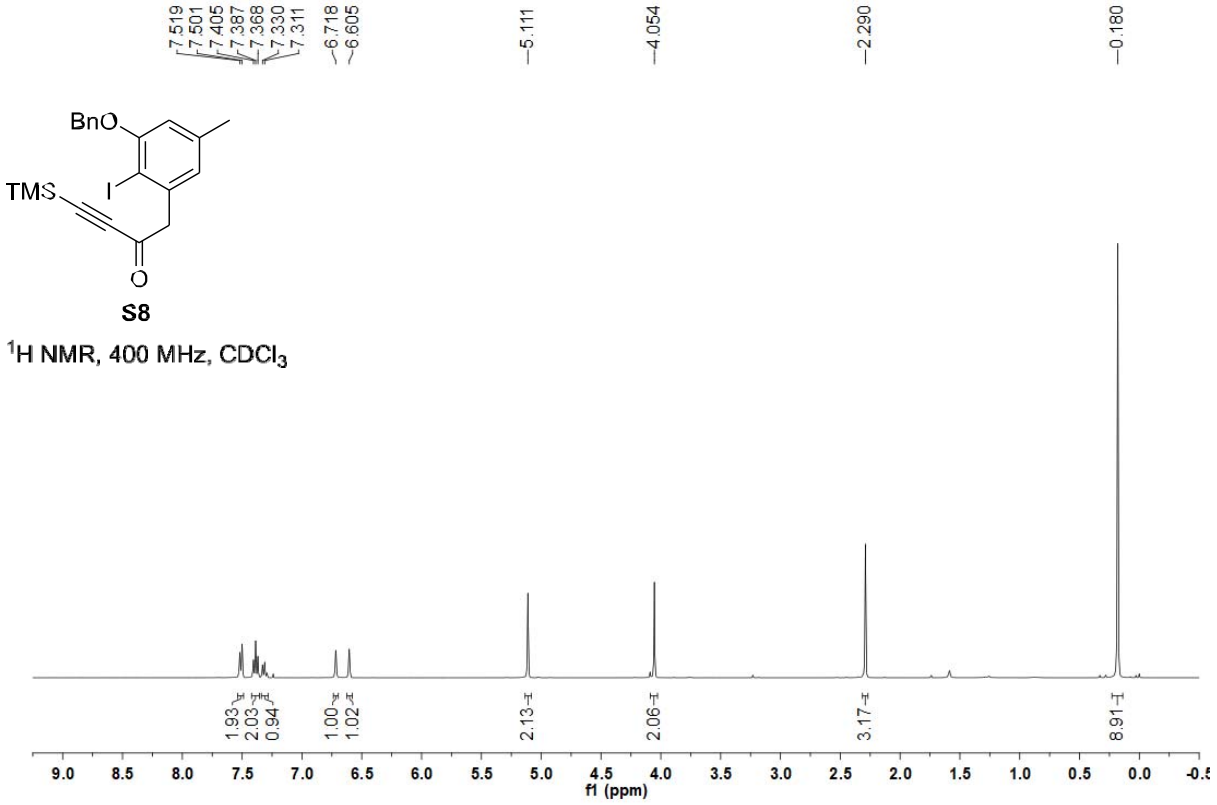


^{13}C NMR spectrum

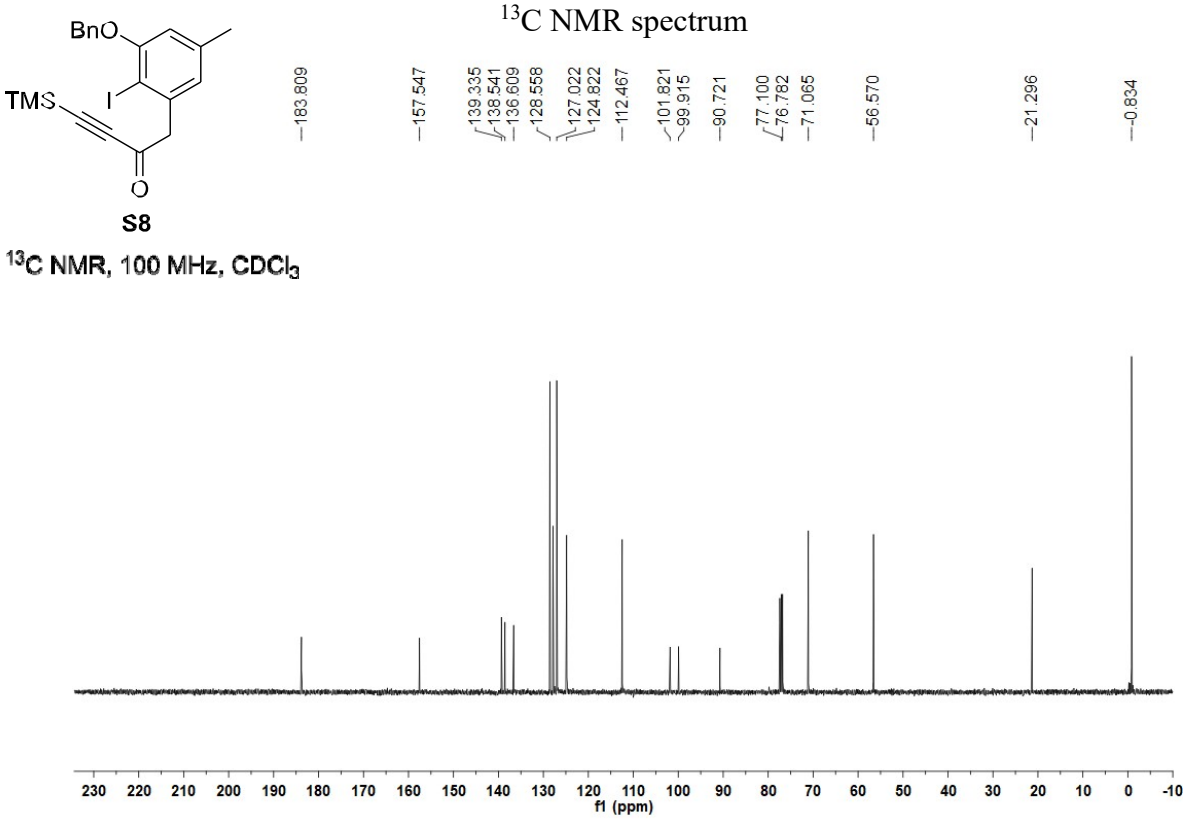


4.44 NMR spectra of compound S8

^{1}H NMR spectrum

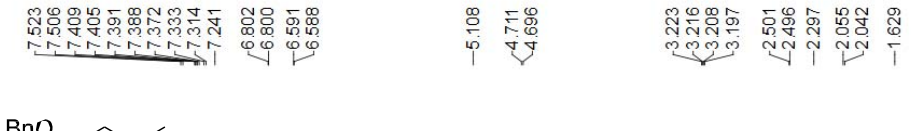


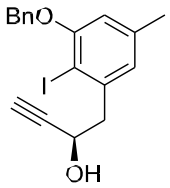
^{13}C NMR spectrum



4.45 NMR spectra of compound S9

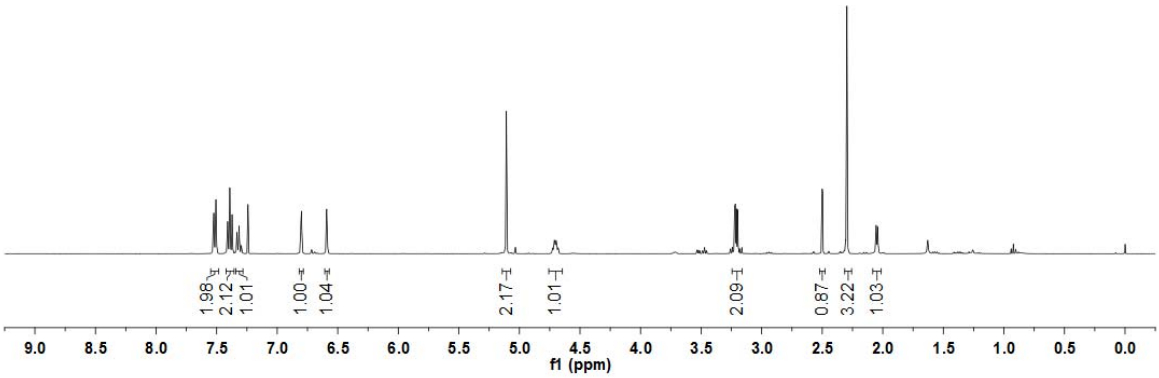
^{1}H NMR spectrum



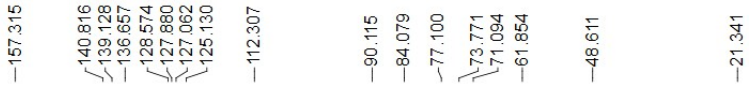


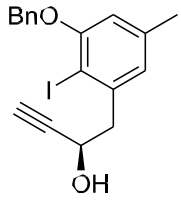
S9

^{1}H NMR, 400 MHz, $CDCl_3$



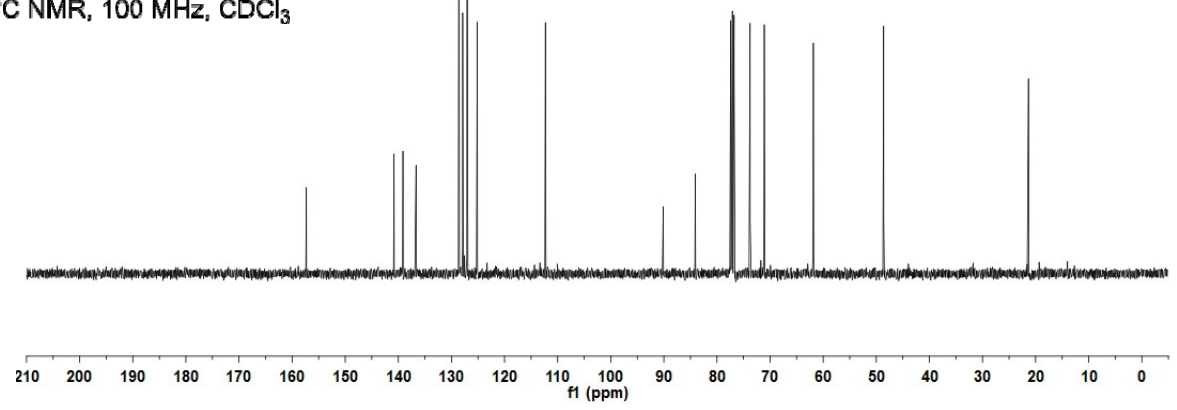
^{13}C NMR spectrum





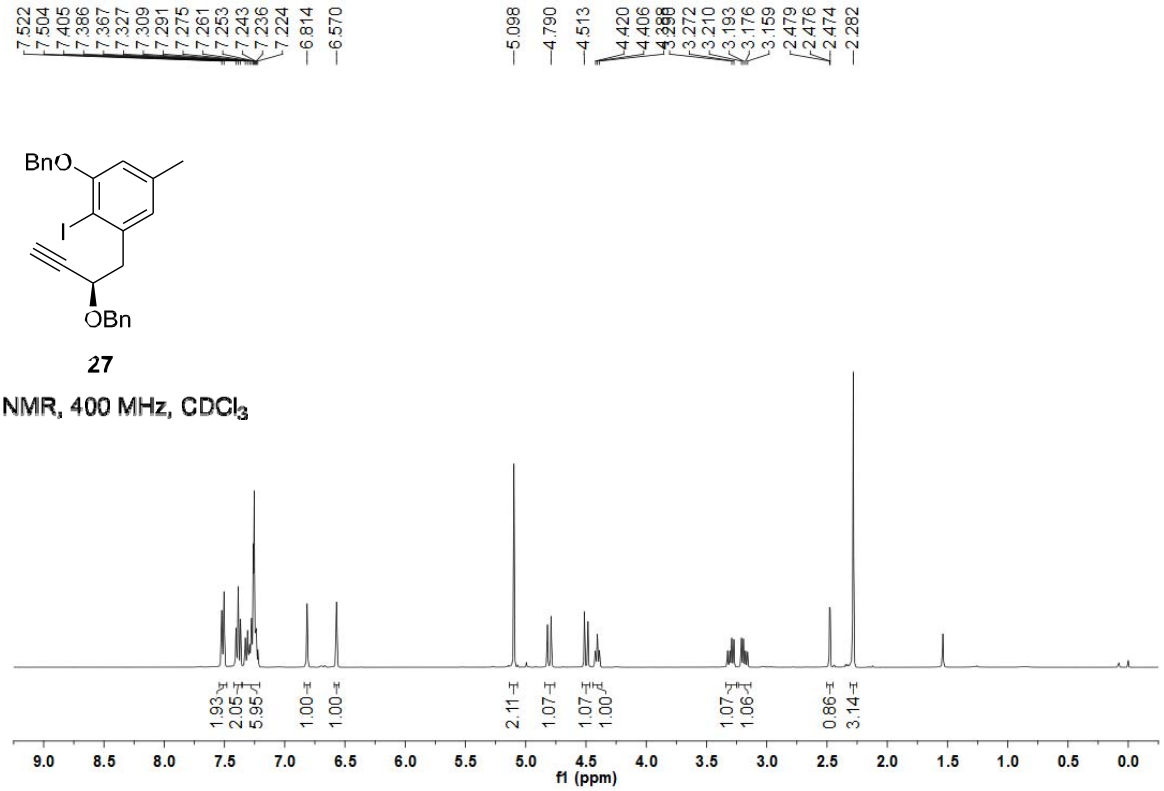
S9

^{13}C NMR, 100 MHz, $CDCl_3$

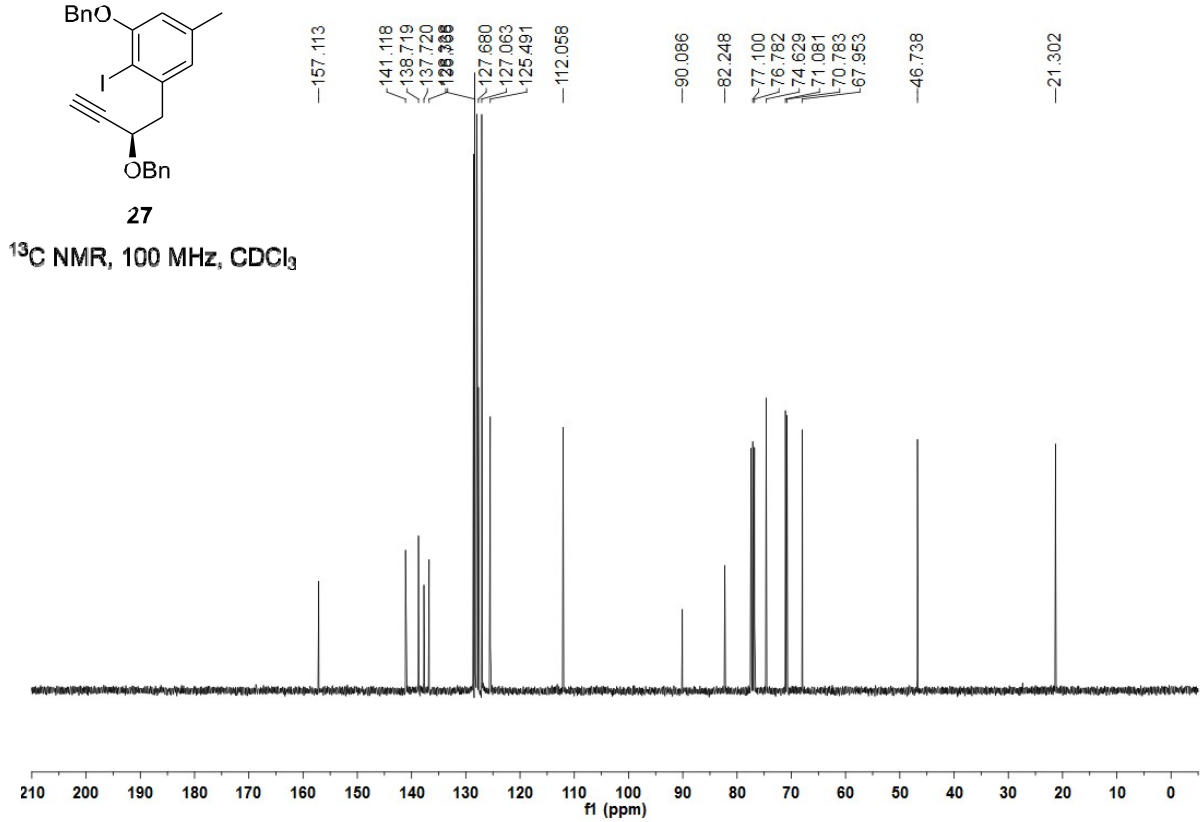


4.46 NMR spectra of compound 27

^{1}H NMR spectrum

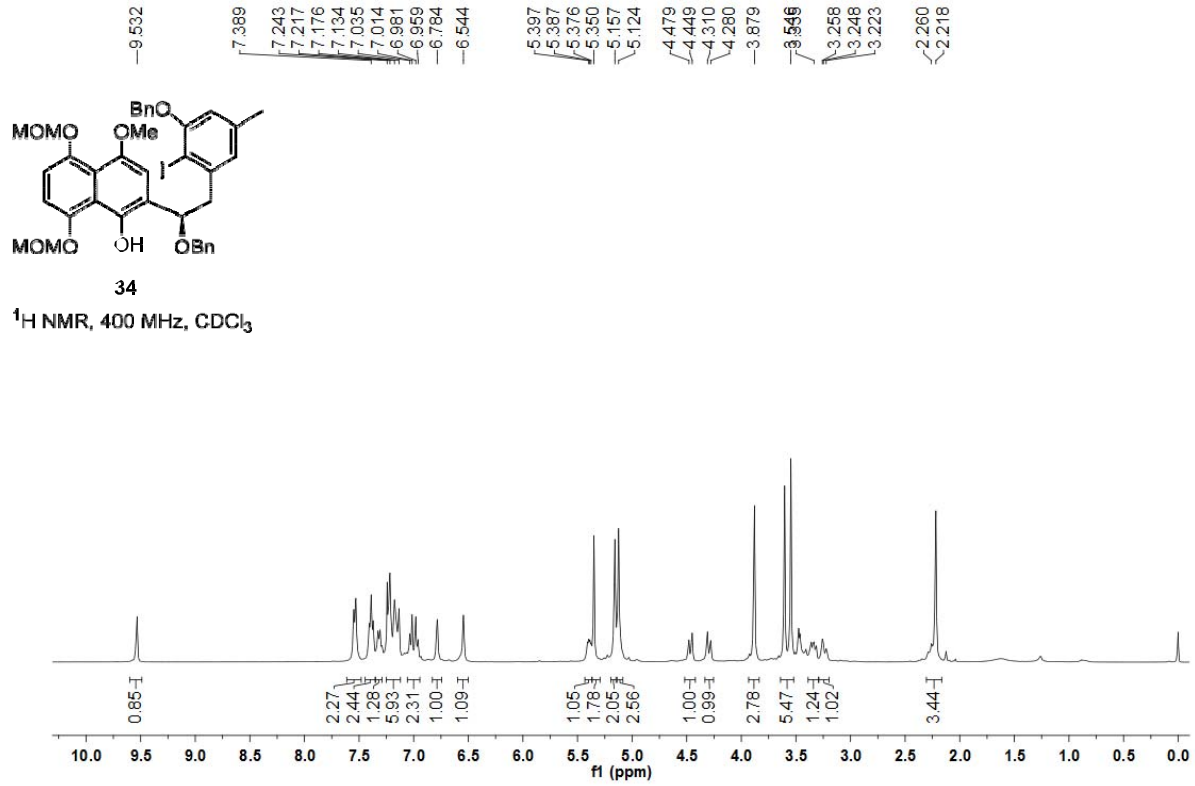


^{13}C NMR spectrum

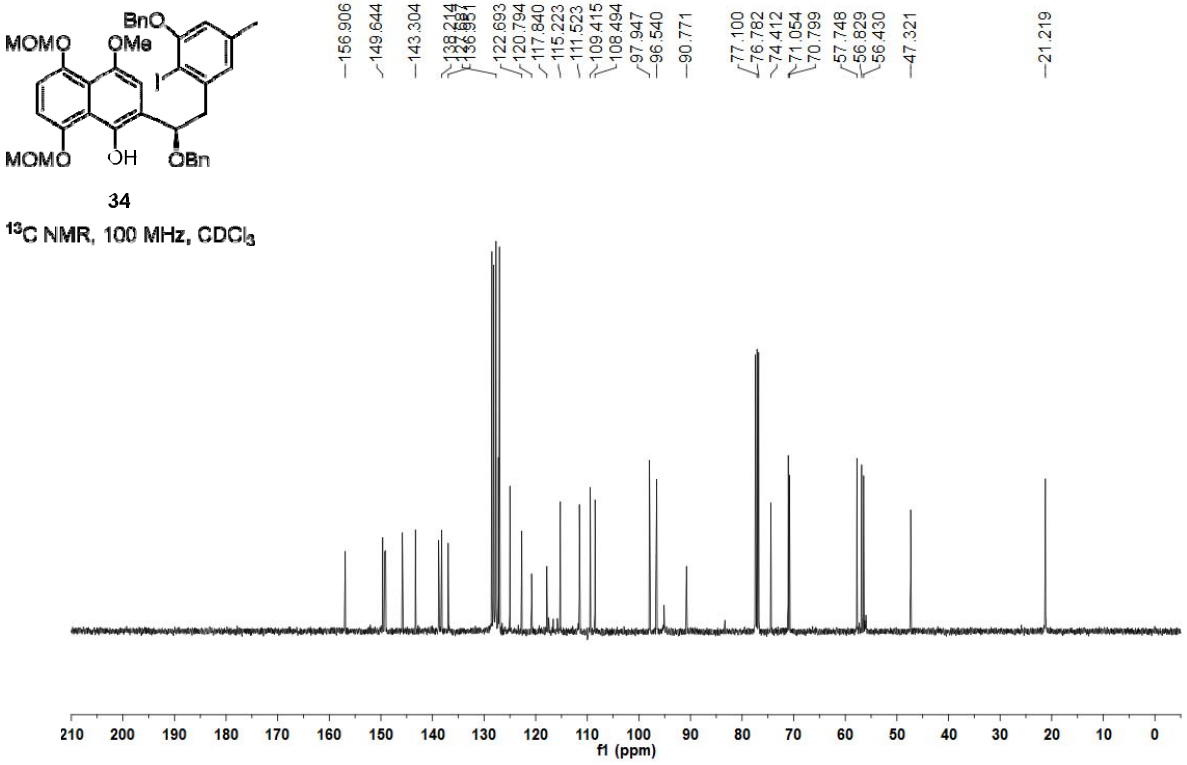


4.47 NMR spectra of compound 34

^{1}H NMR spectrum

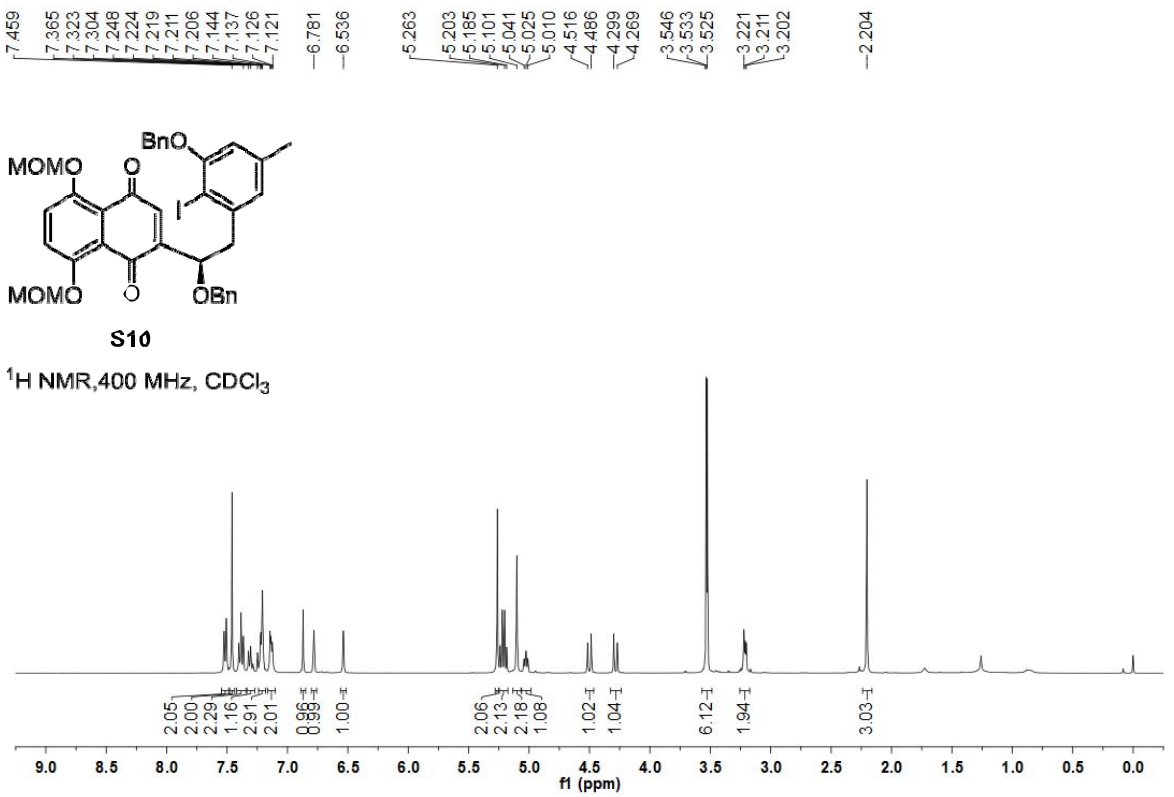


^{13}C NMR spectrum

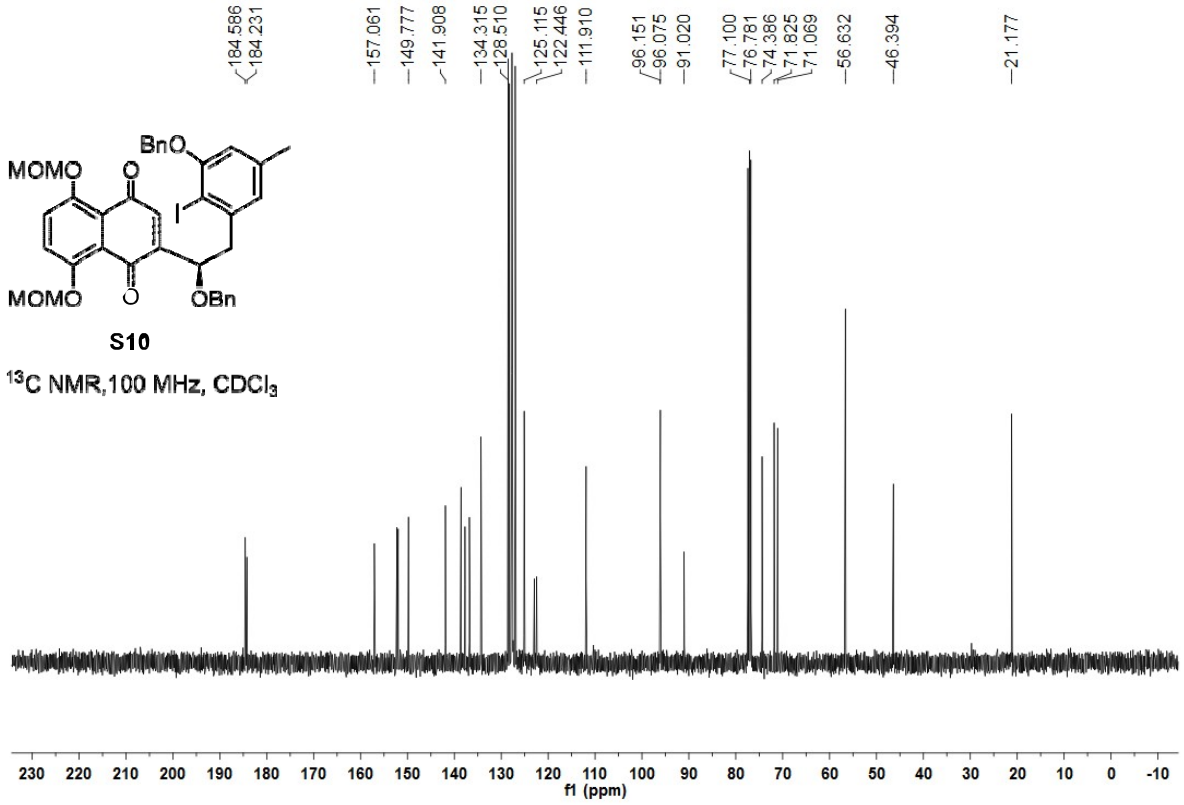


4.48 NMR spectraof compound S10

^{1}H NMR spectrum

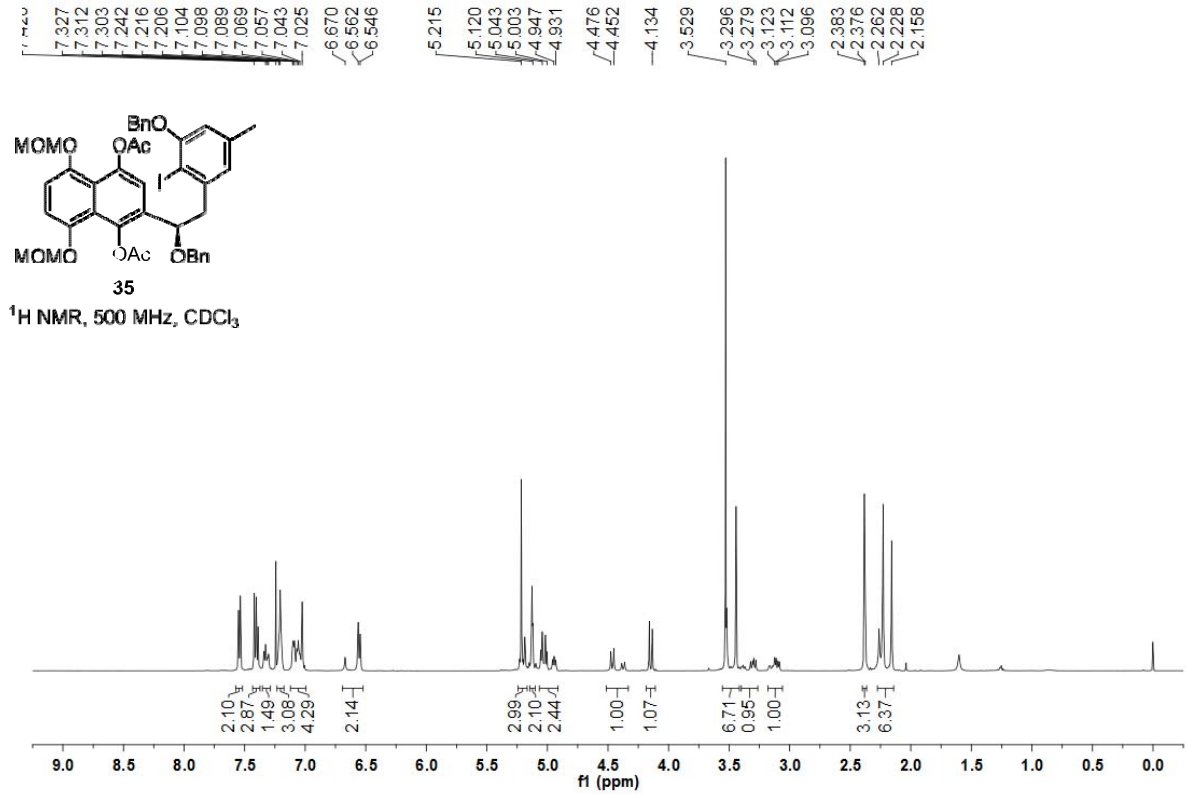


^{13}C NMR spectrum

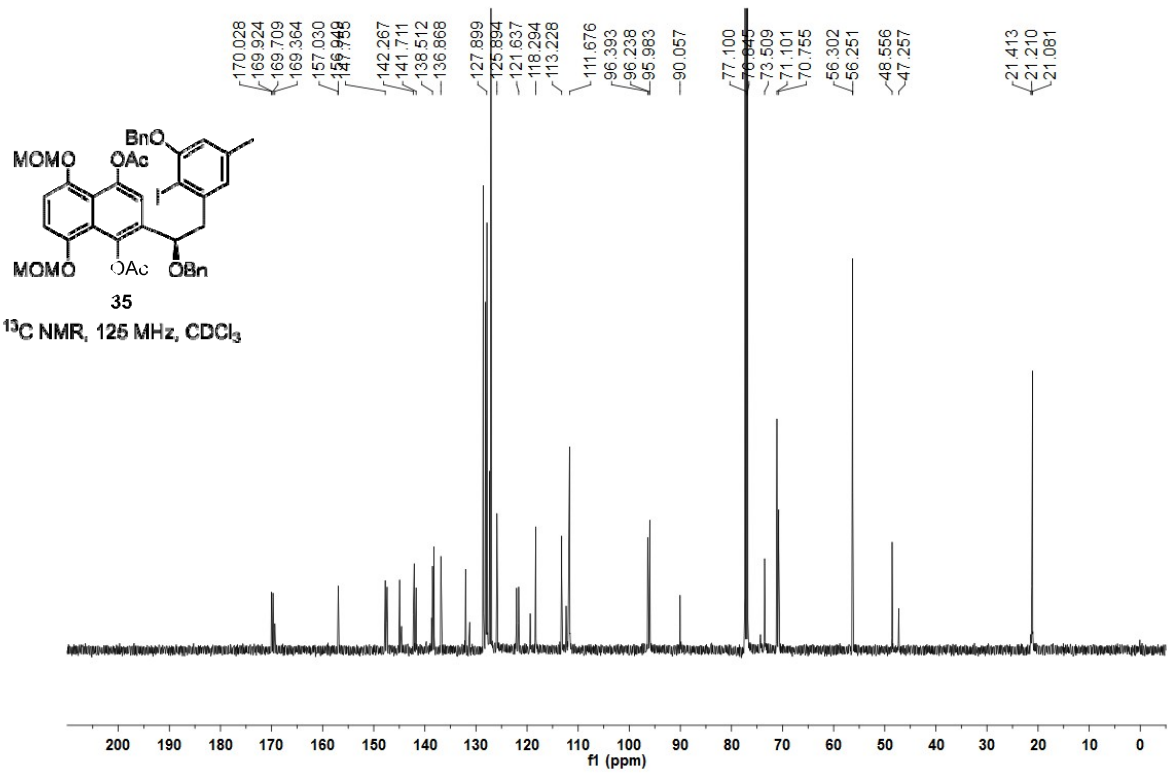


4.49 NMR spectra of compound 35

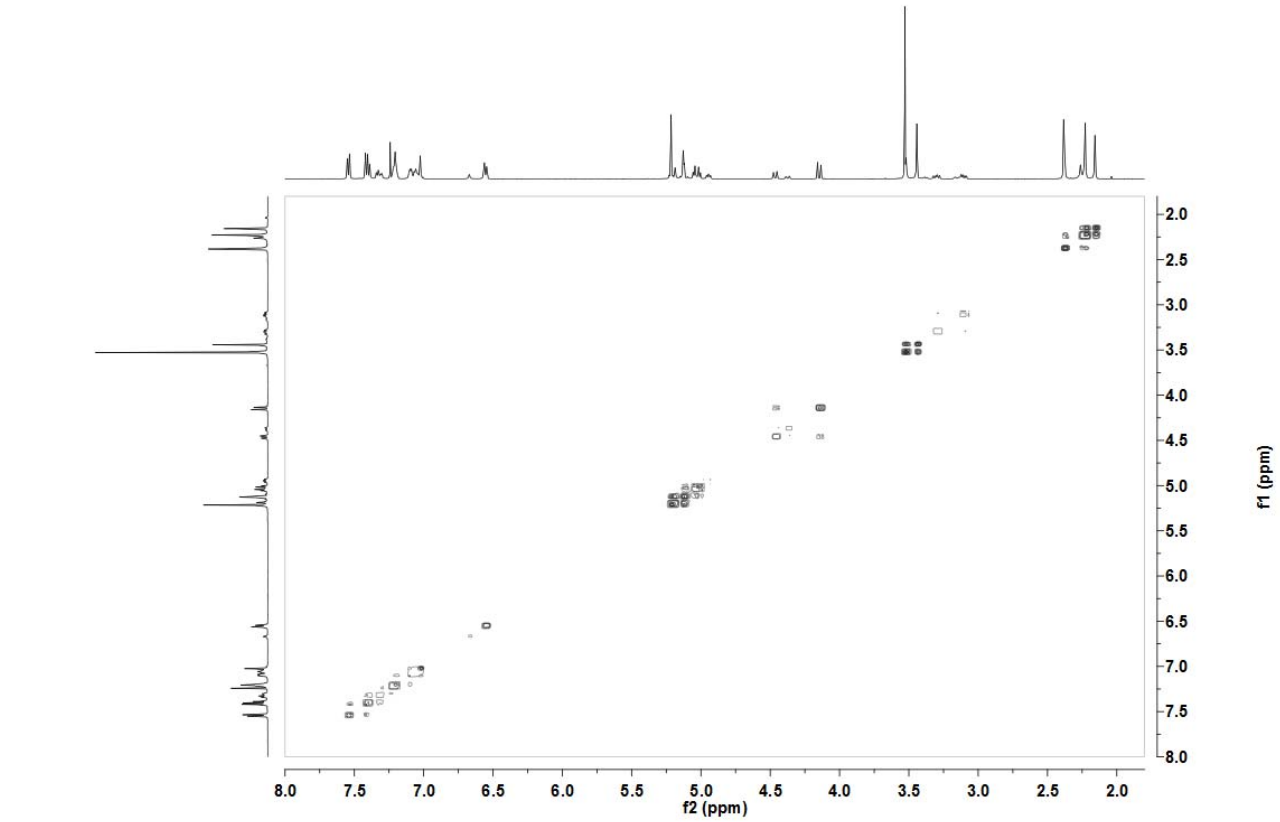
^{1}H NMR spectrum

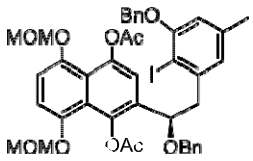


^{13}C NMR spectrum



2D COSY NMR spectrum of compound **35**



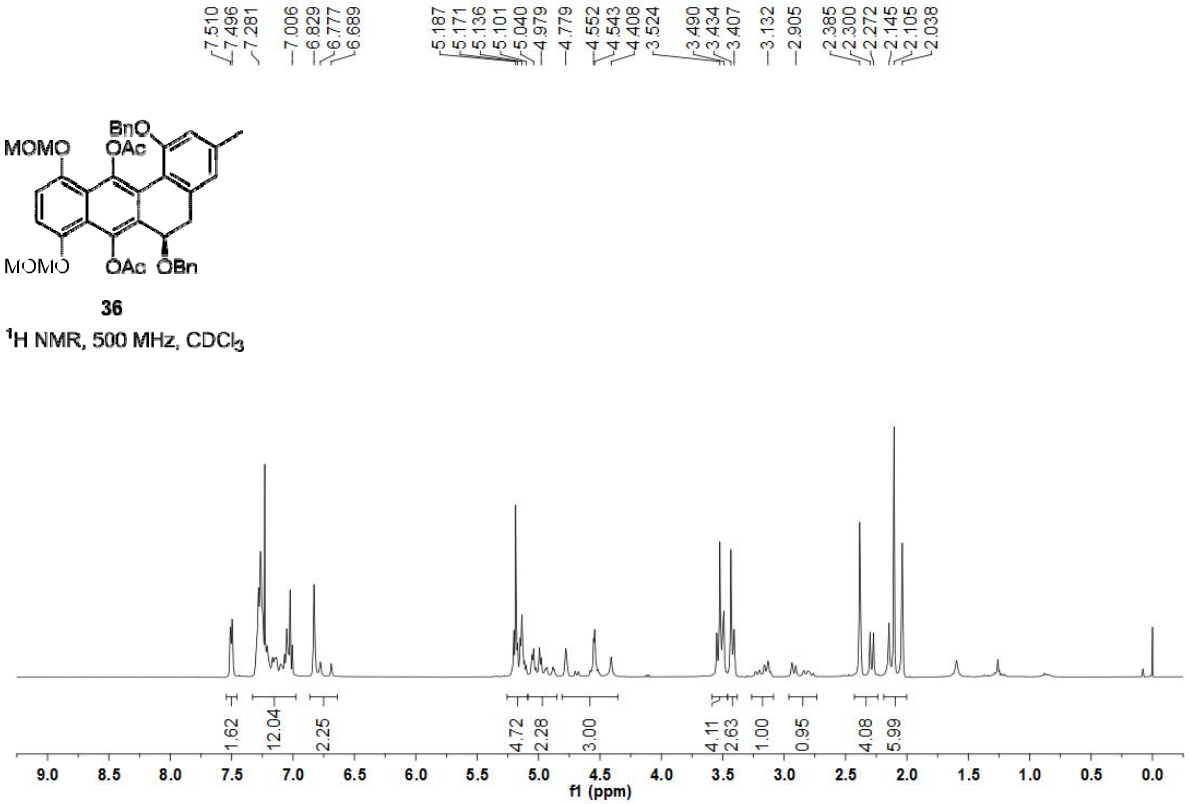


35

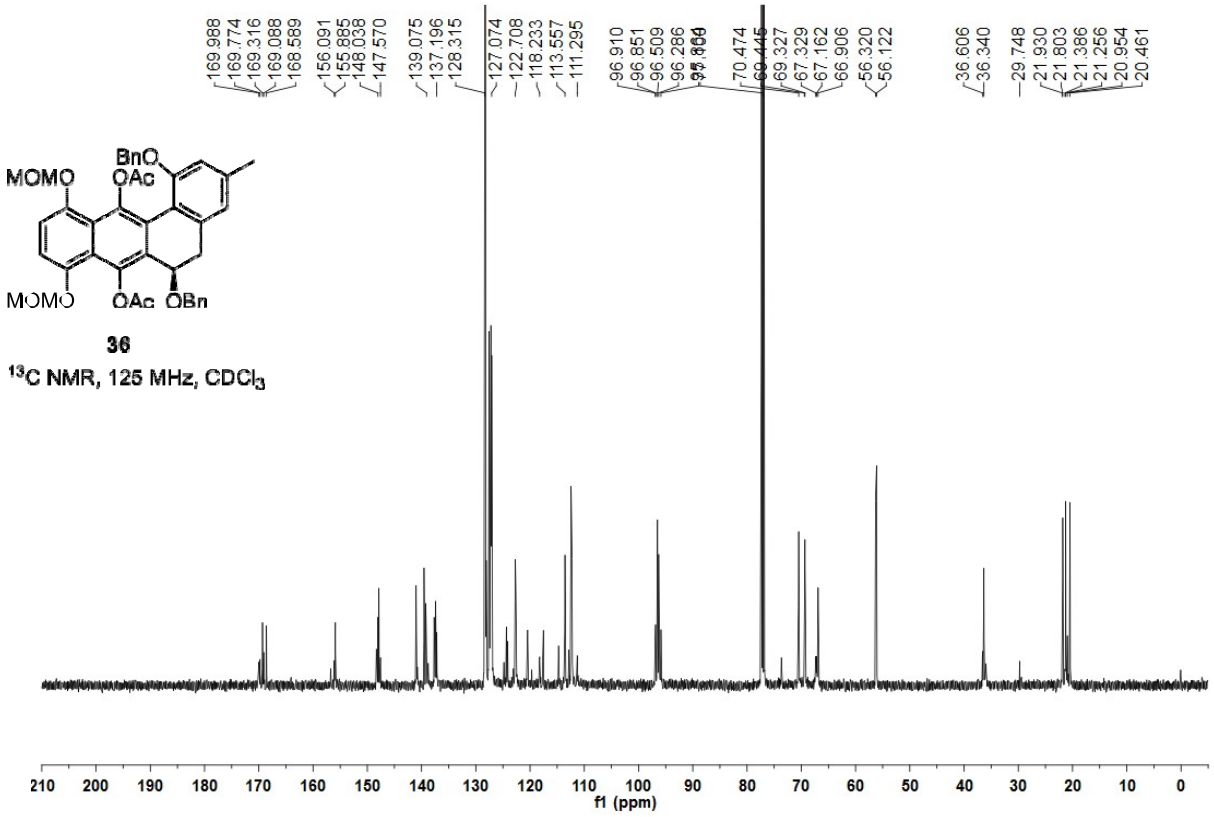
2D HSQC NMR spectrum of compound **35**

4.50 NMR spectra of compound 36

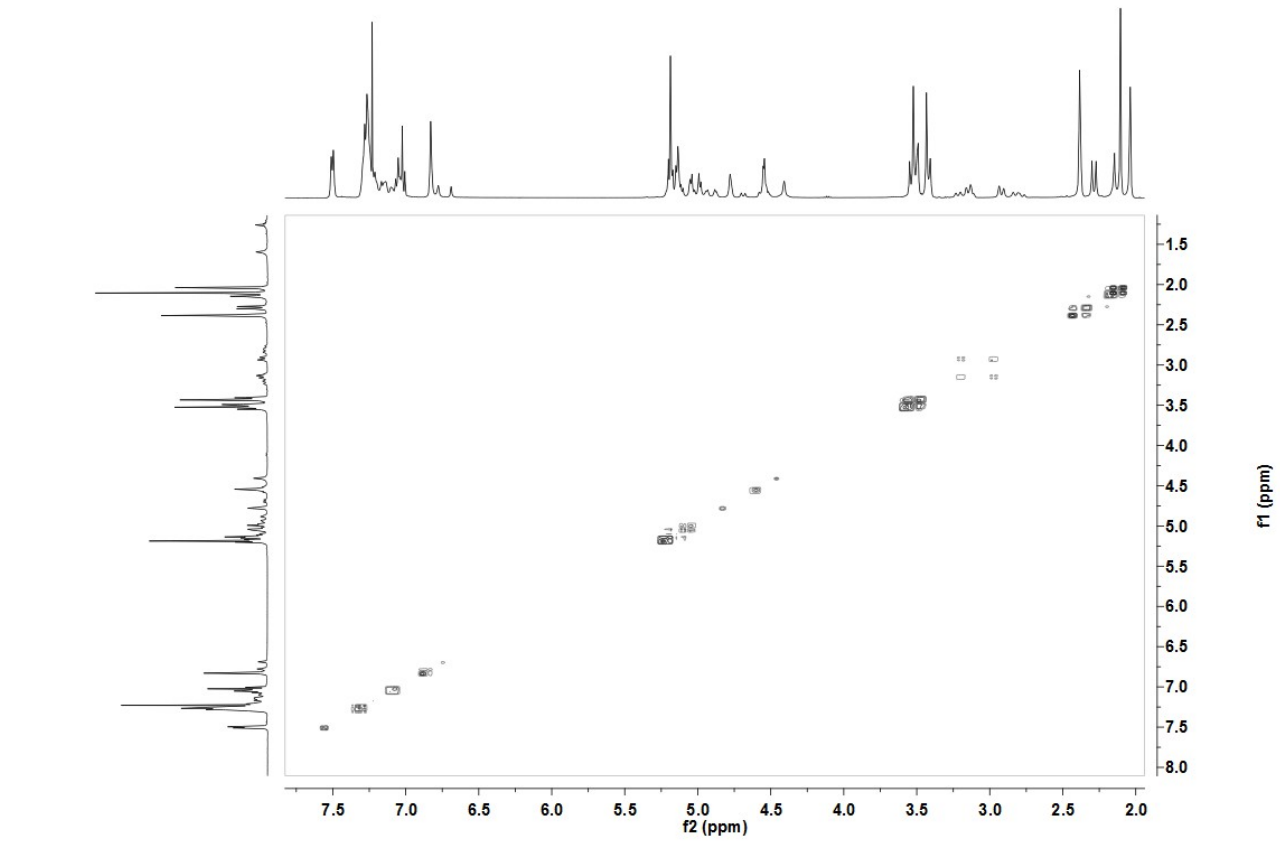
^{1}H NMR spectrum

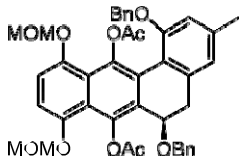


^{13}C NMR spectrum



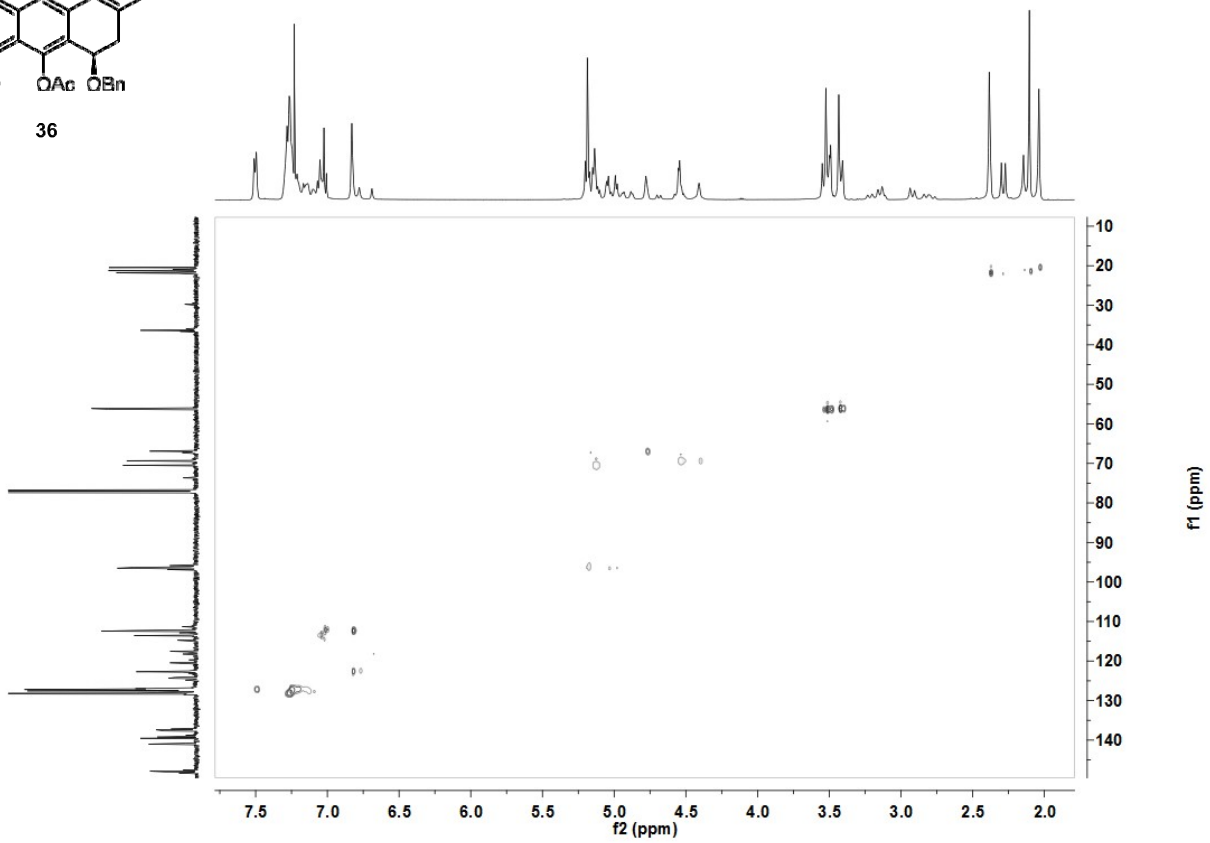
2D COSY NMR spectrum of compound **36**





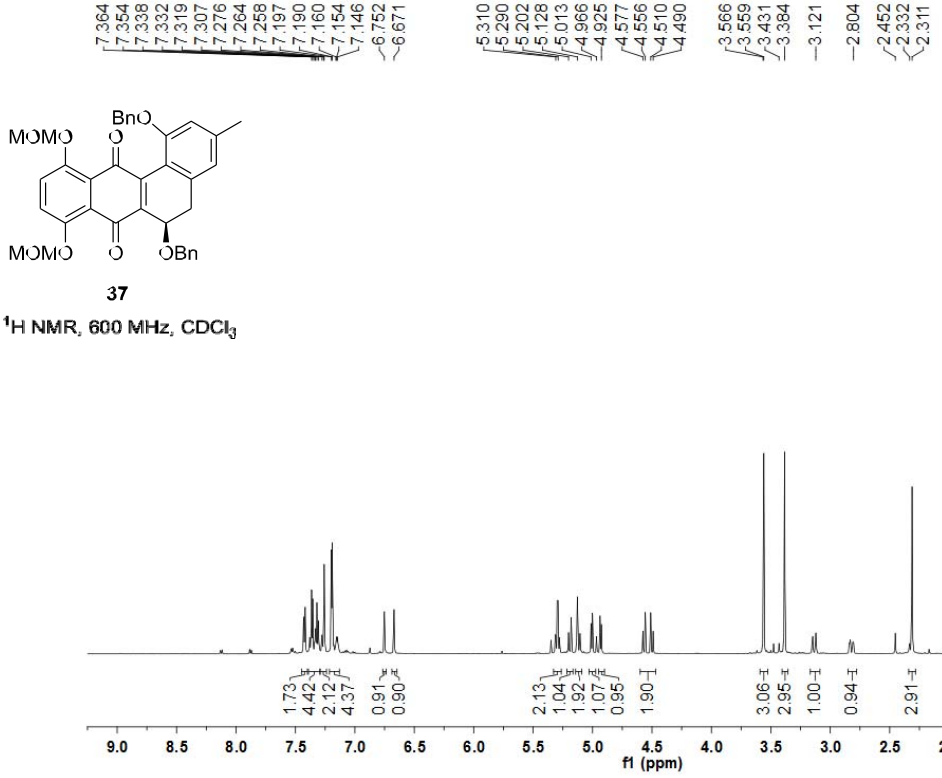
36

2D HSQC NMR spectrum of compound **36**

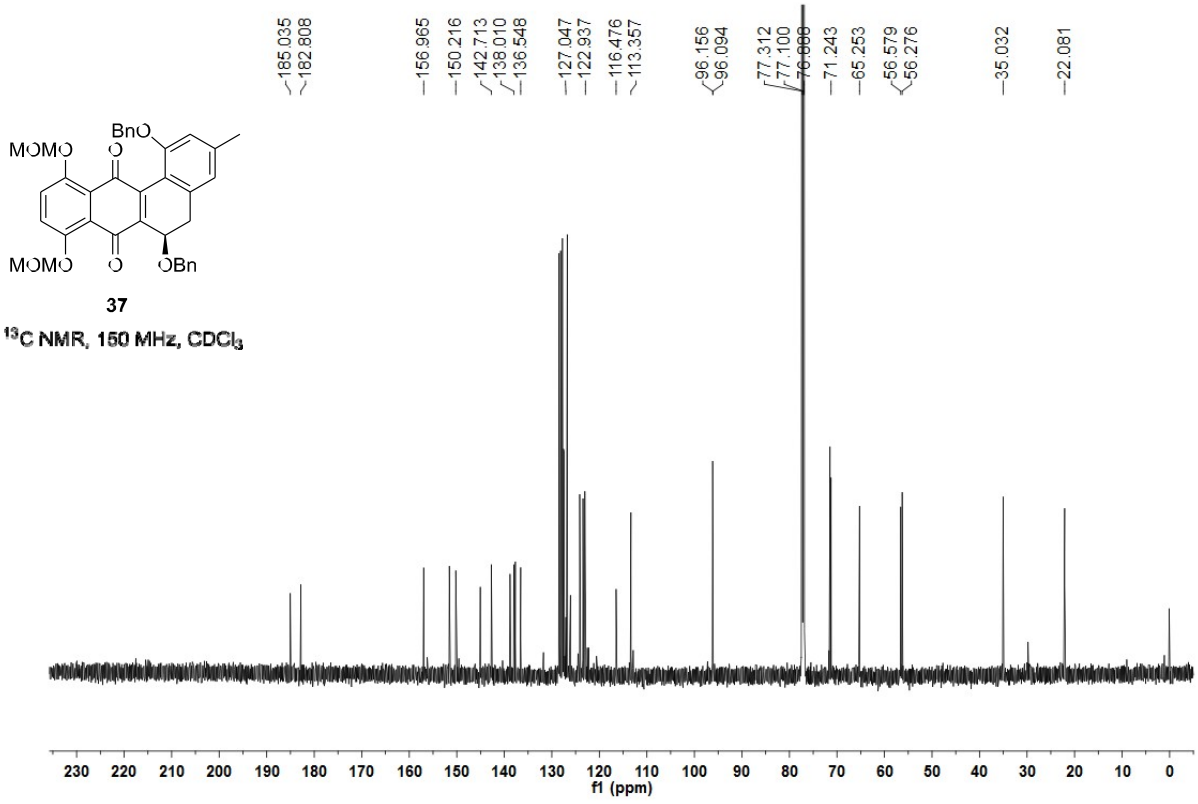


4.51 NMR spectra of compound 37

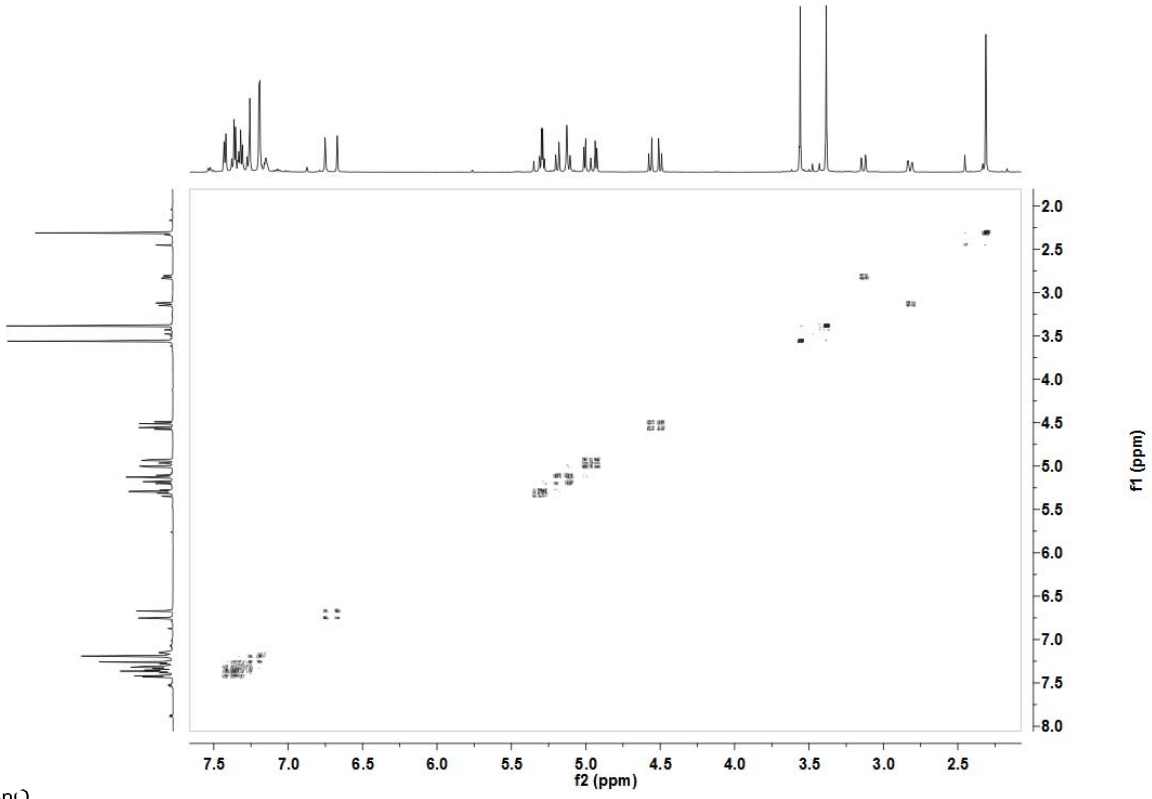
^{1}H NMR spectrum

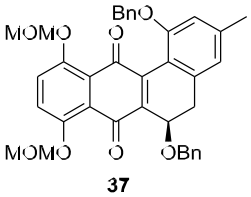


^{13}C NMR spectrum



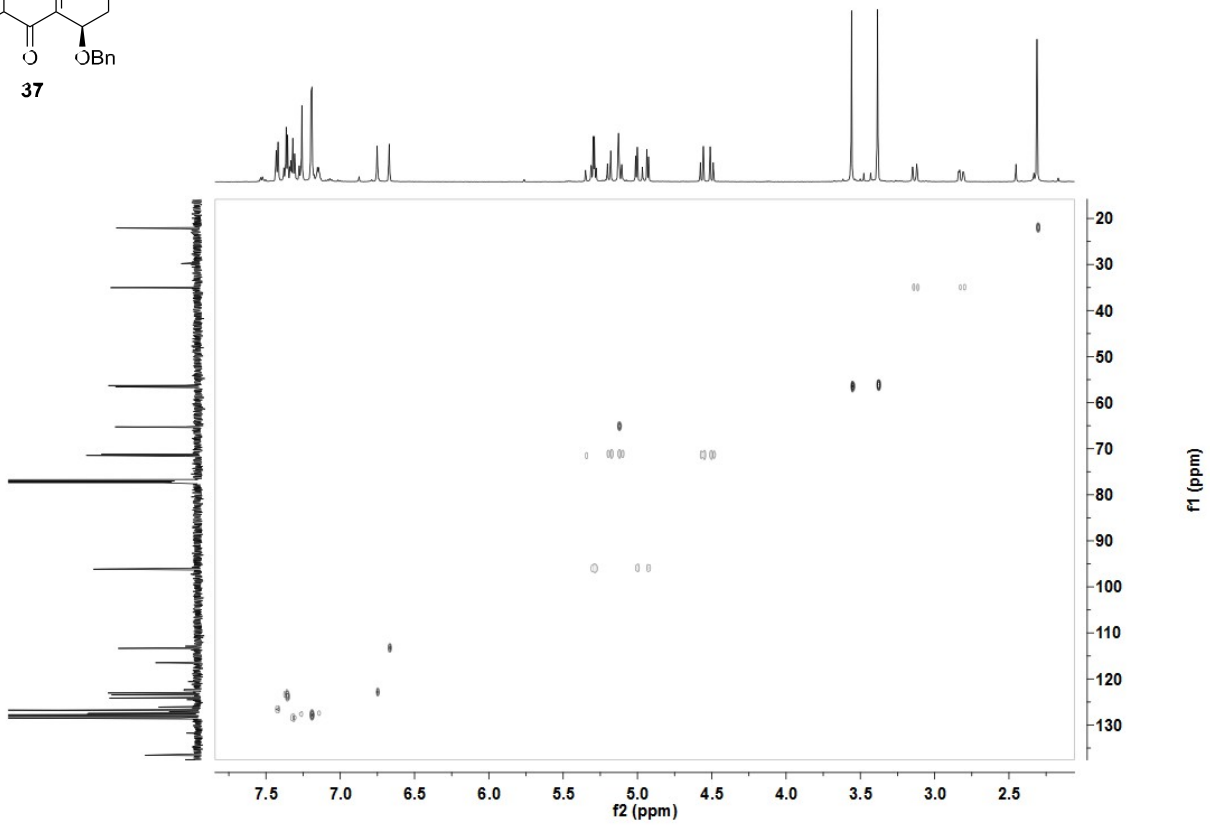
2D COSY NMR spectrum of compound **37**



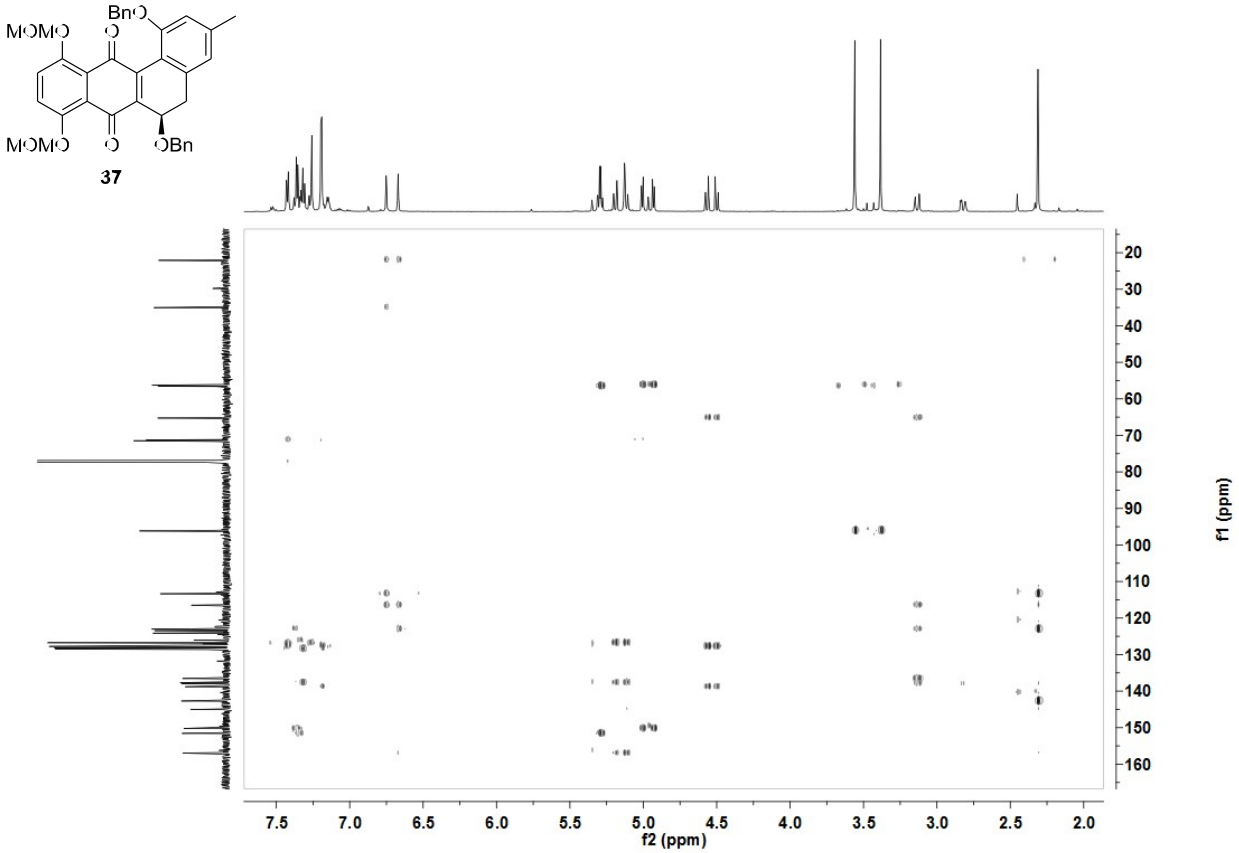


37

2D HSQC NMR spectrum of compound **37**

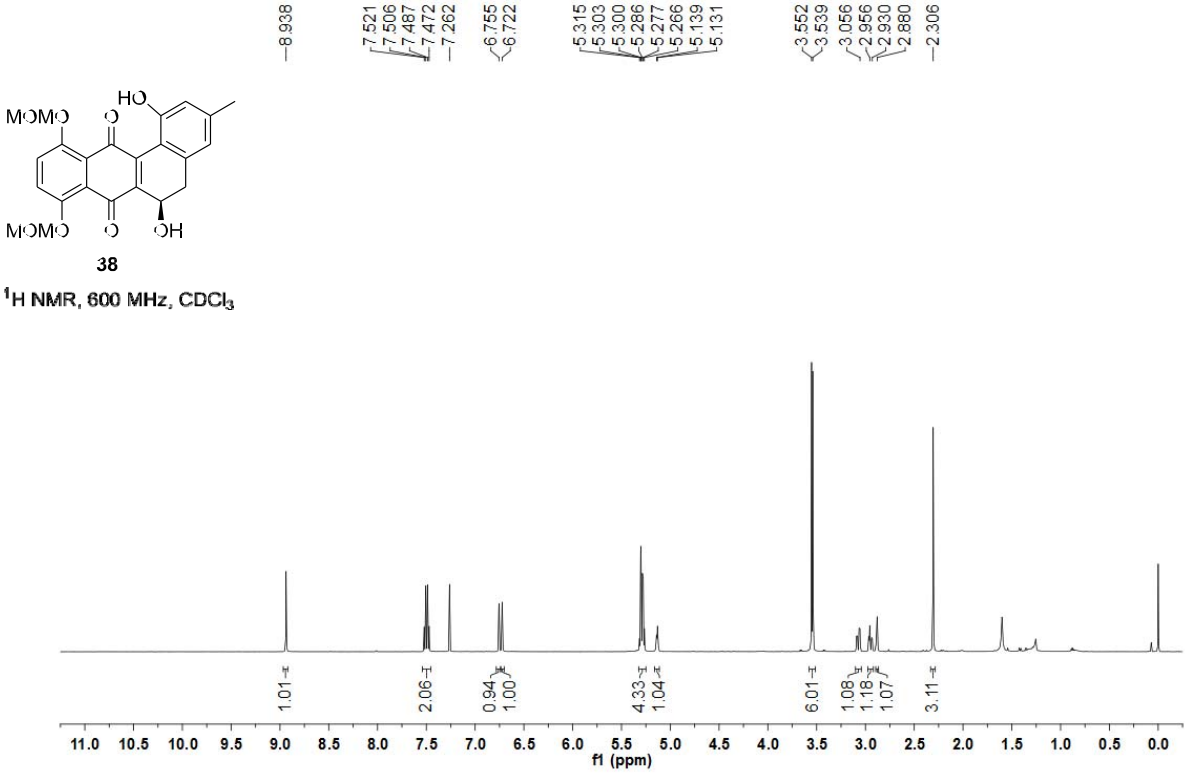


2D HMBC NMR spectrum of compound **37**

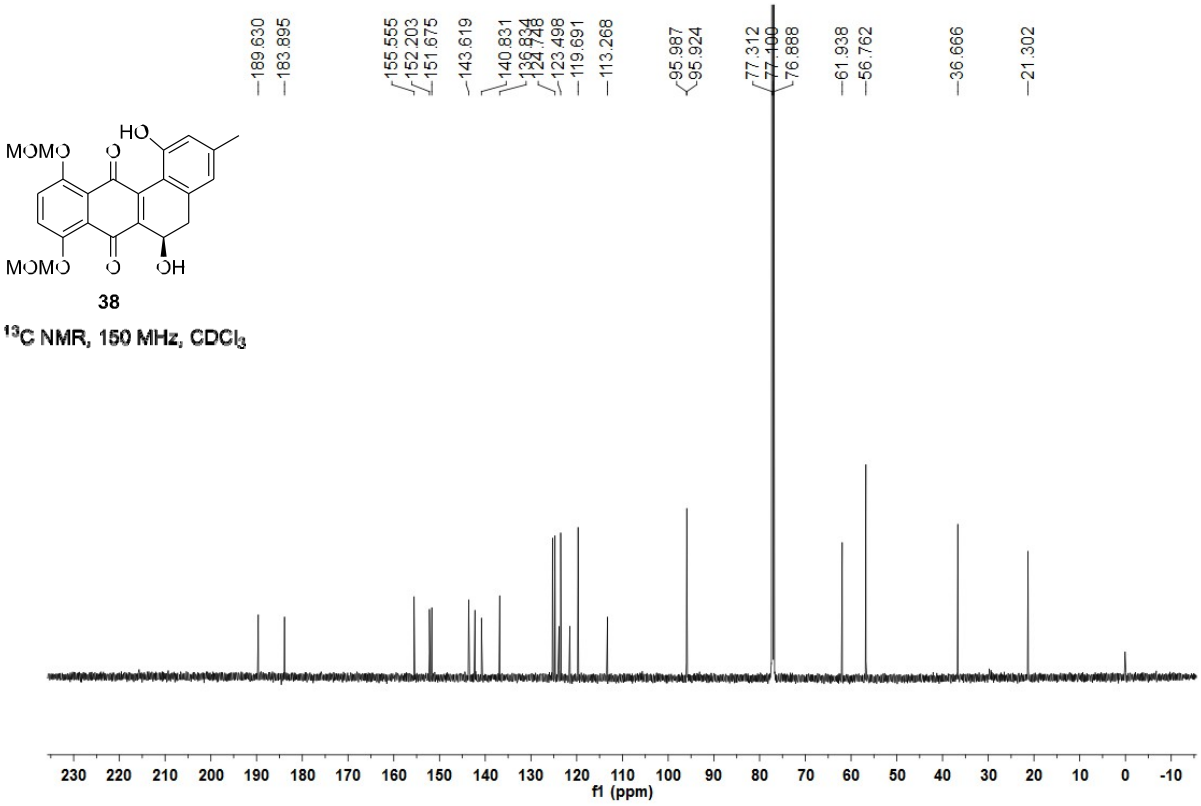


4.52 NMR spectra of compound 38

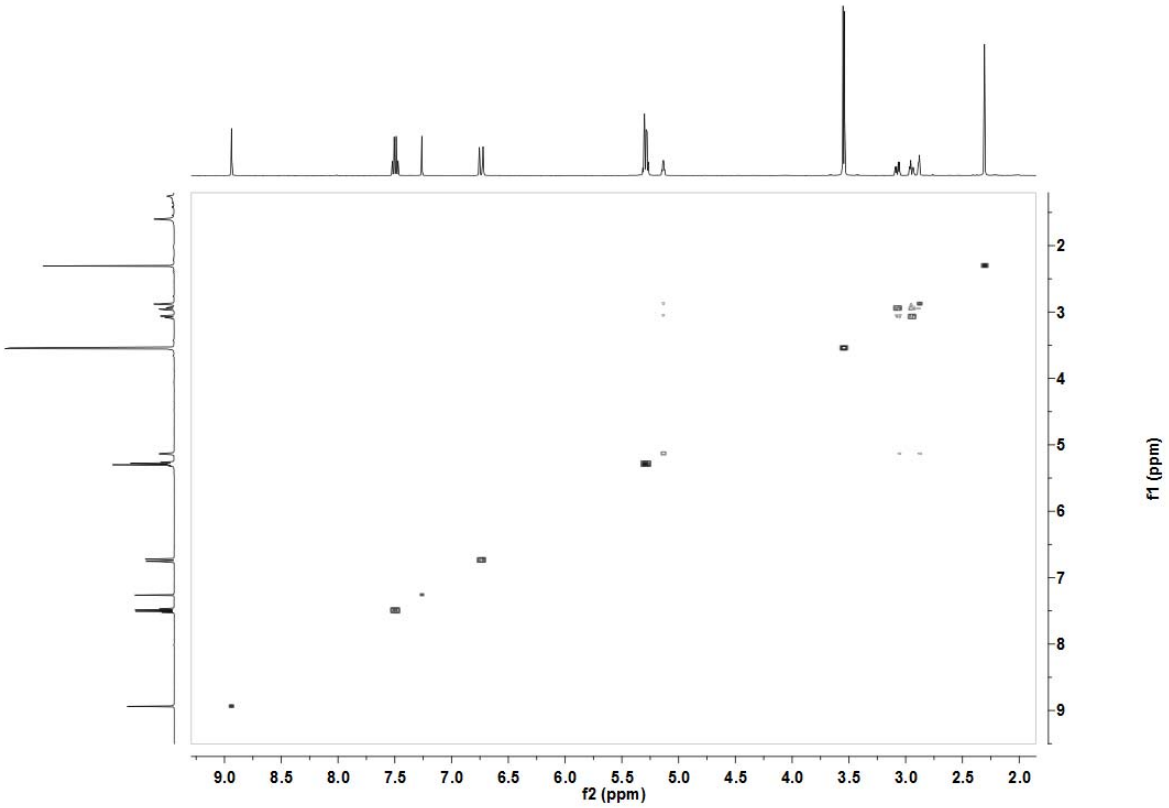
^{1}H NMR spectrum

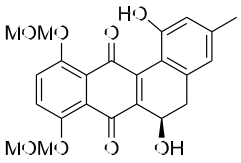


^{13}C NMR spectrum



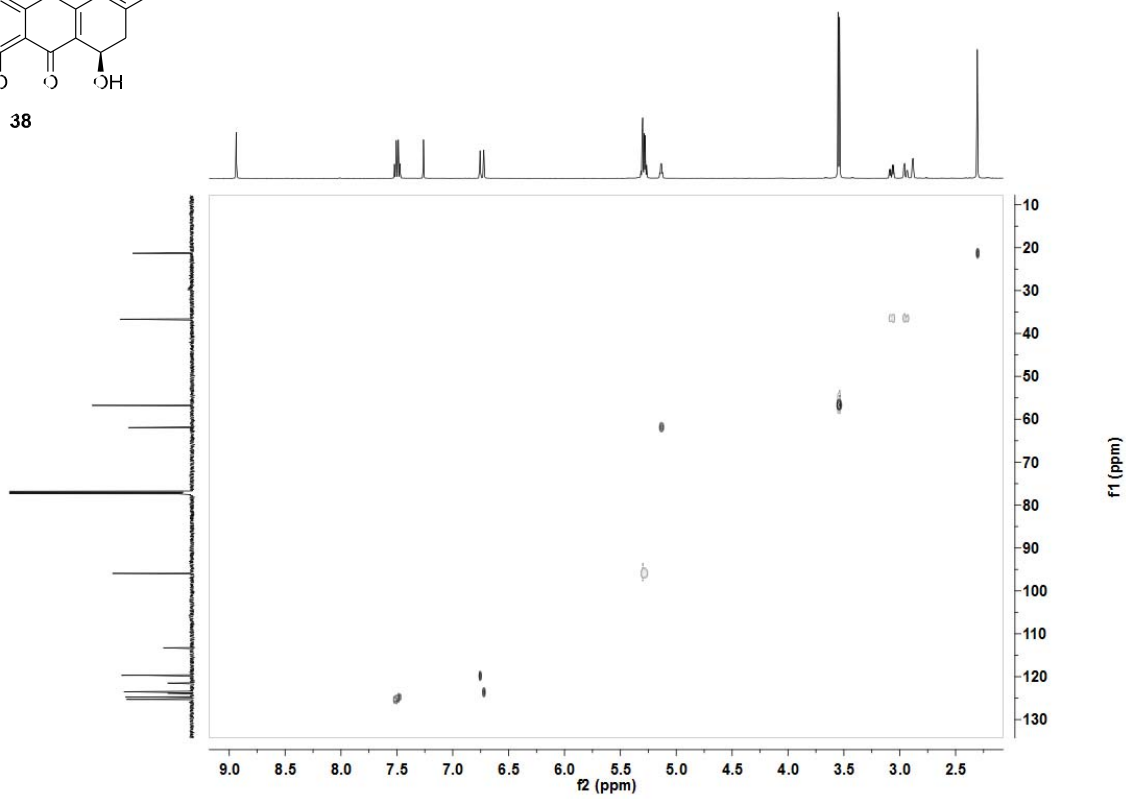
2D COSY NMR spectrum of compound **38**



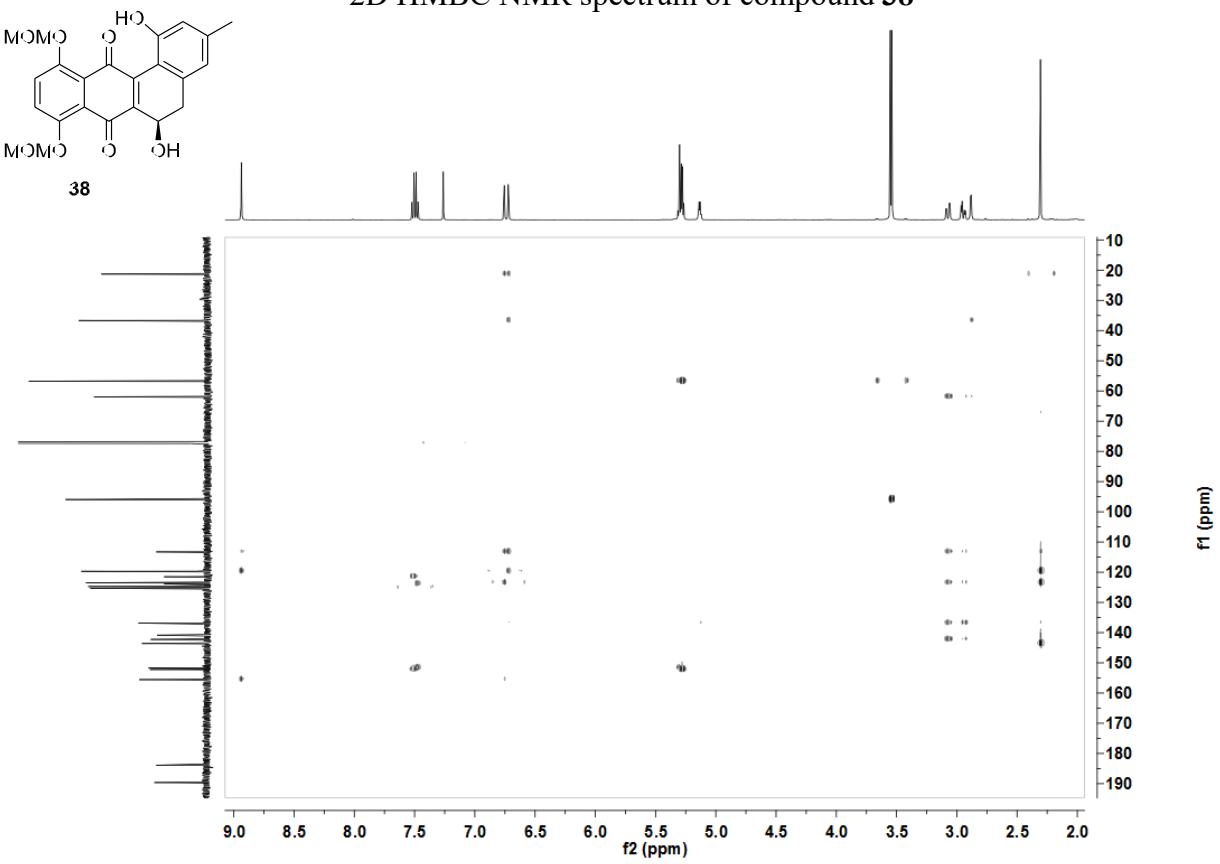


38

2D HSQC NMR spectrum of compound **38**

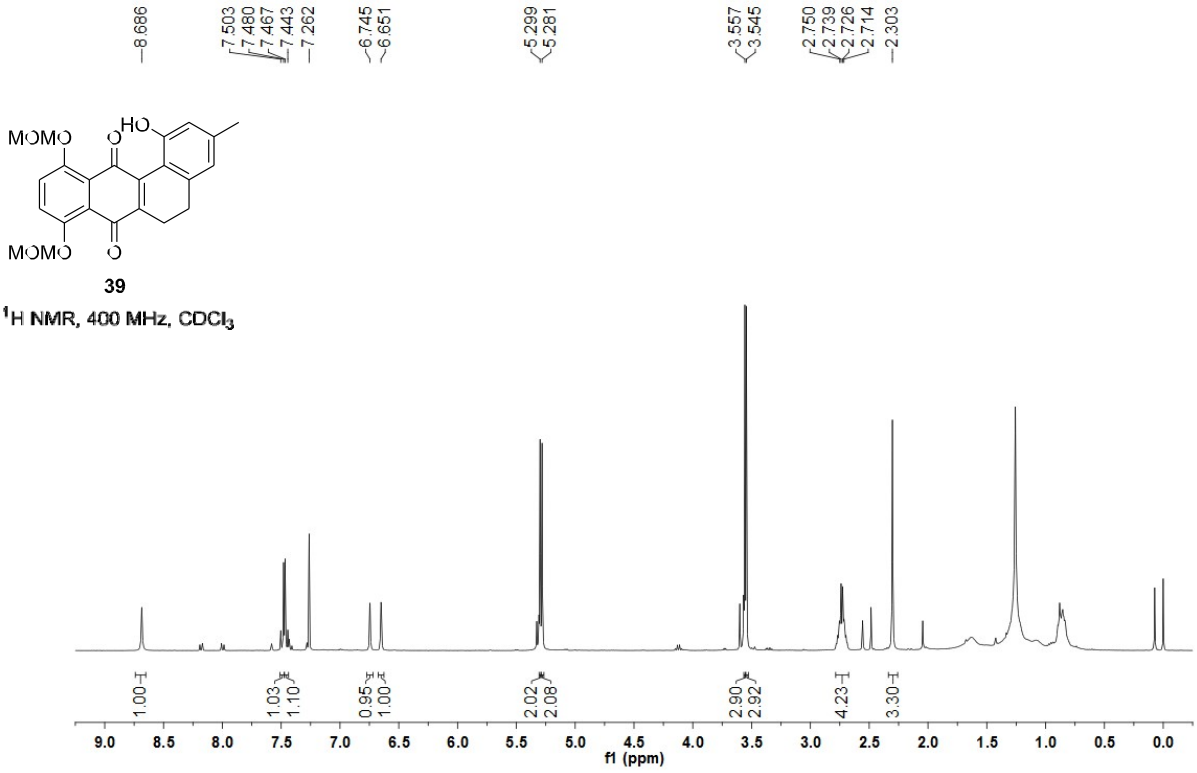


2D HMBC NMR spectrum of compound **38**



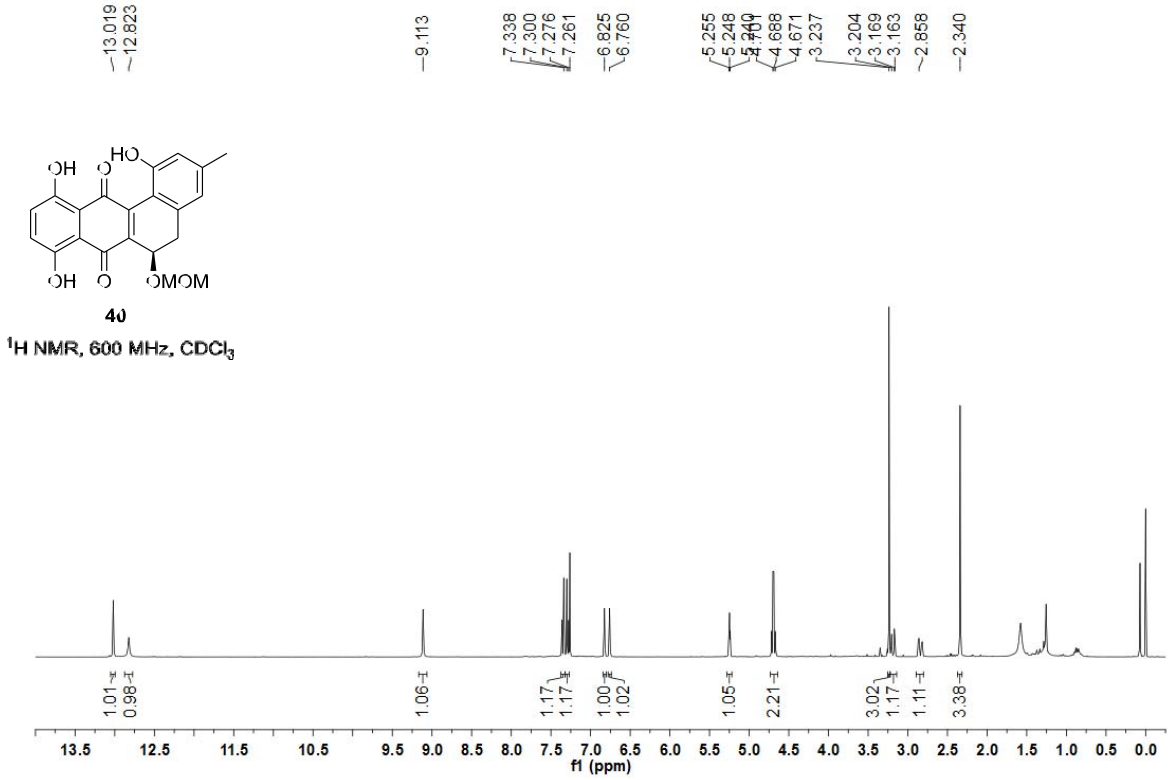
4.53 NMR spectrum of compound 39

^{1}H NMR spectrum

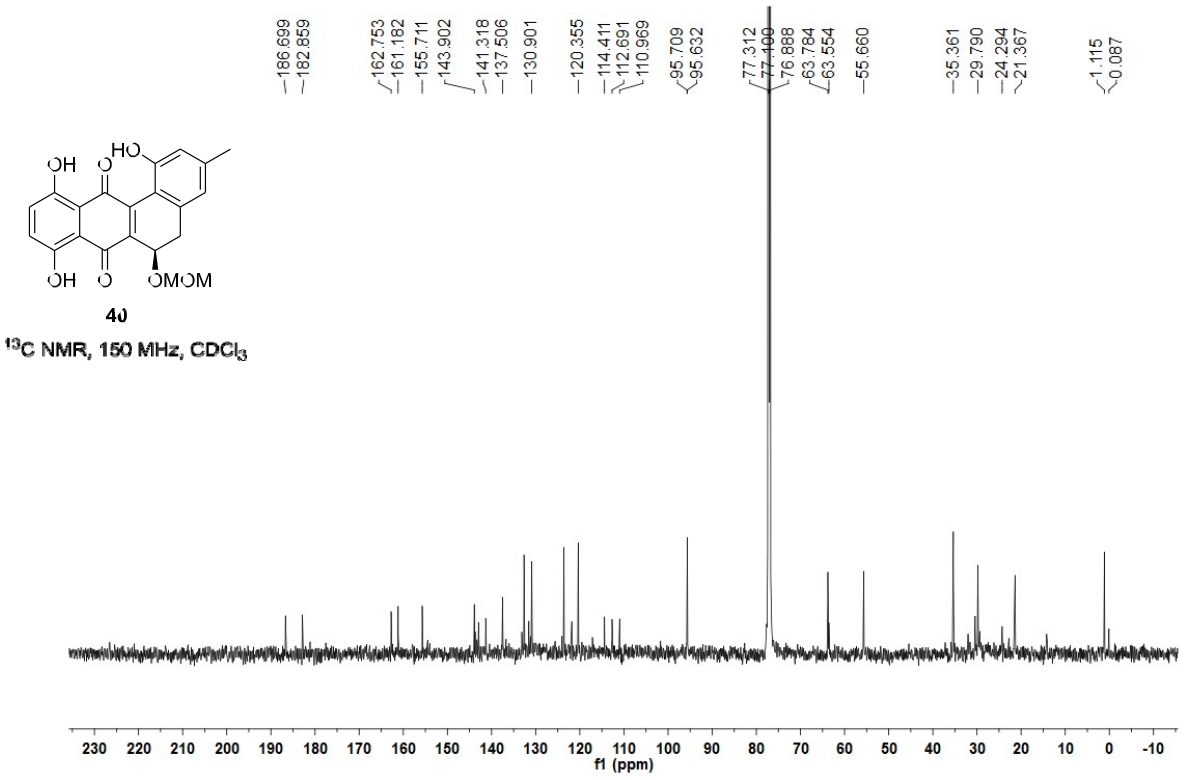


4.54 NMR spectra of compound 40

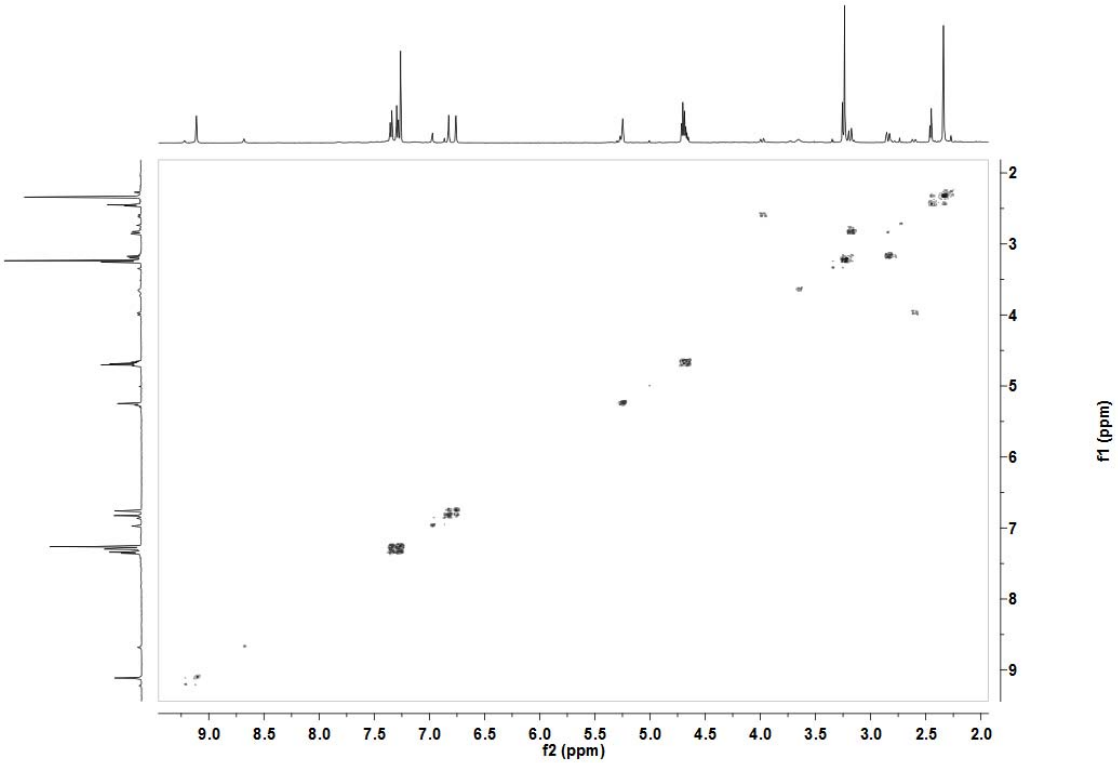
^{1}H NMR spectrum



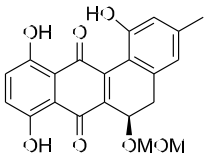
^{13}C NMR spectrum



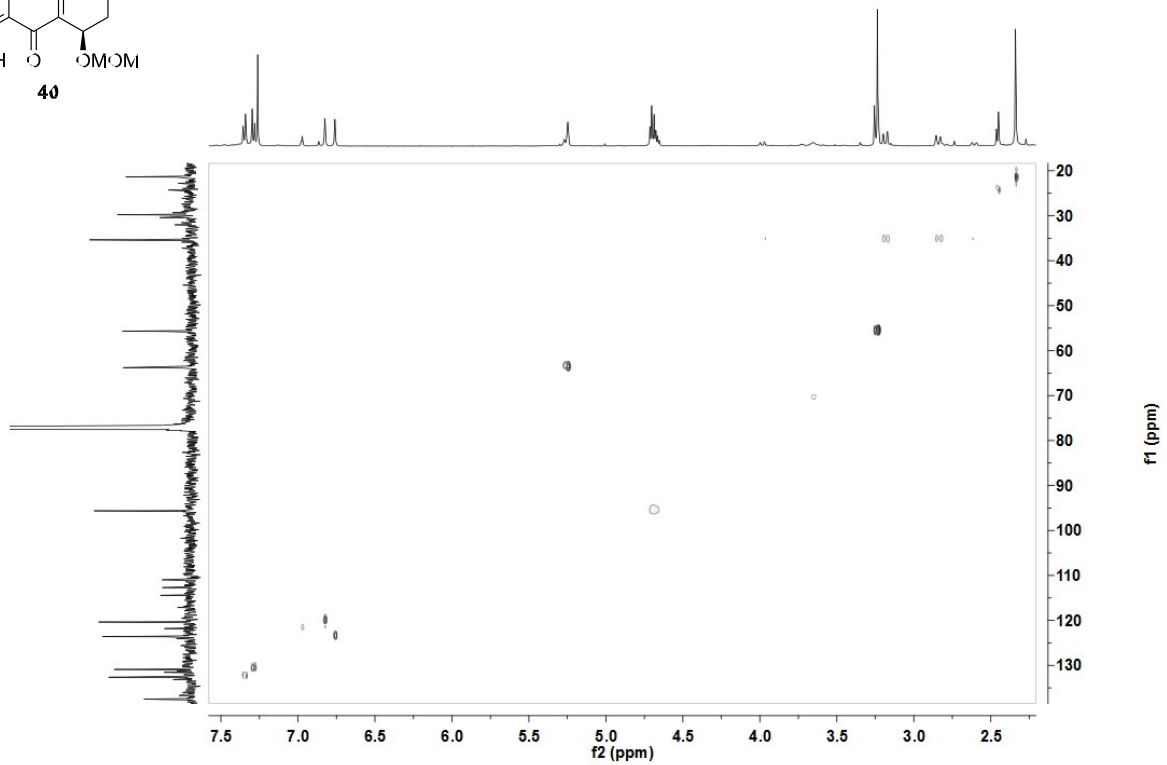
2D COSY NMR spectrum of compound **40**



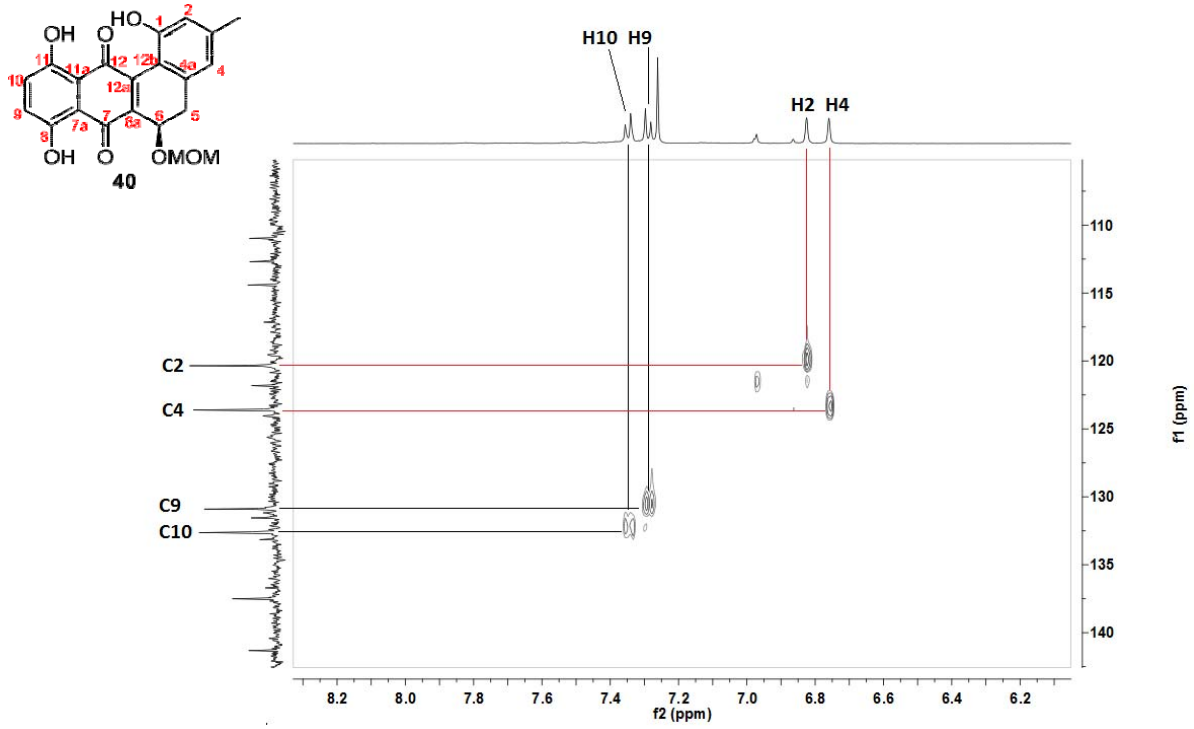
2D HSQC NMR spectrum of compound **40**



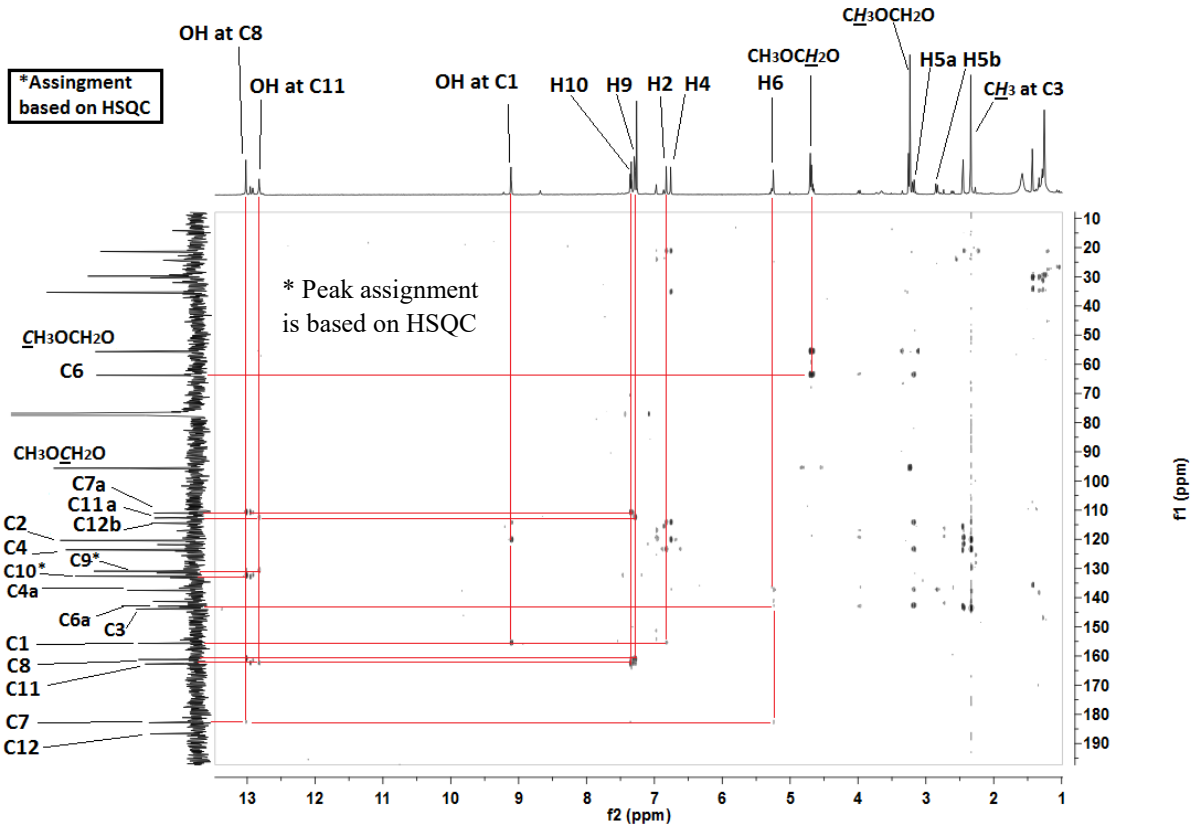
40



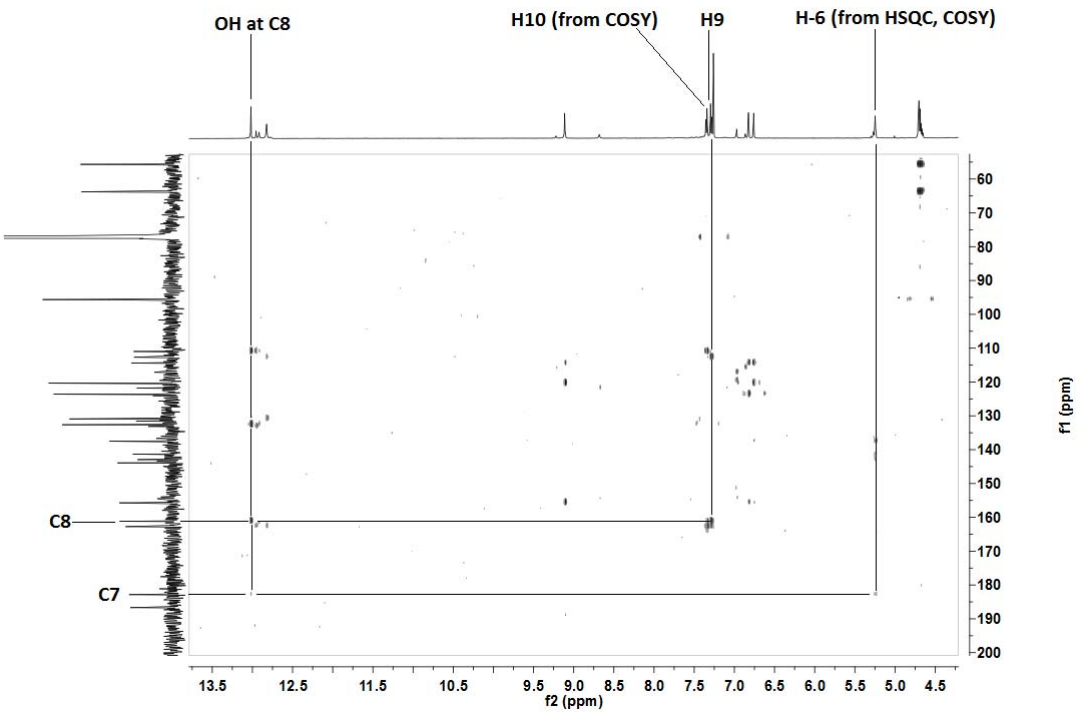
Expanded HSQC NMR spectrum of compound **40**for H2, C2, H4, C4, H9, C9, H10, C10



2D HMBC NMR spectrum of compound **40**

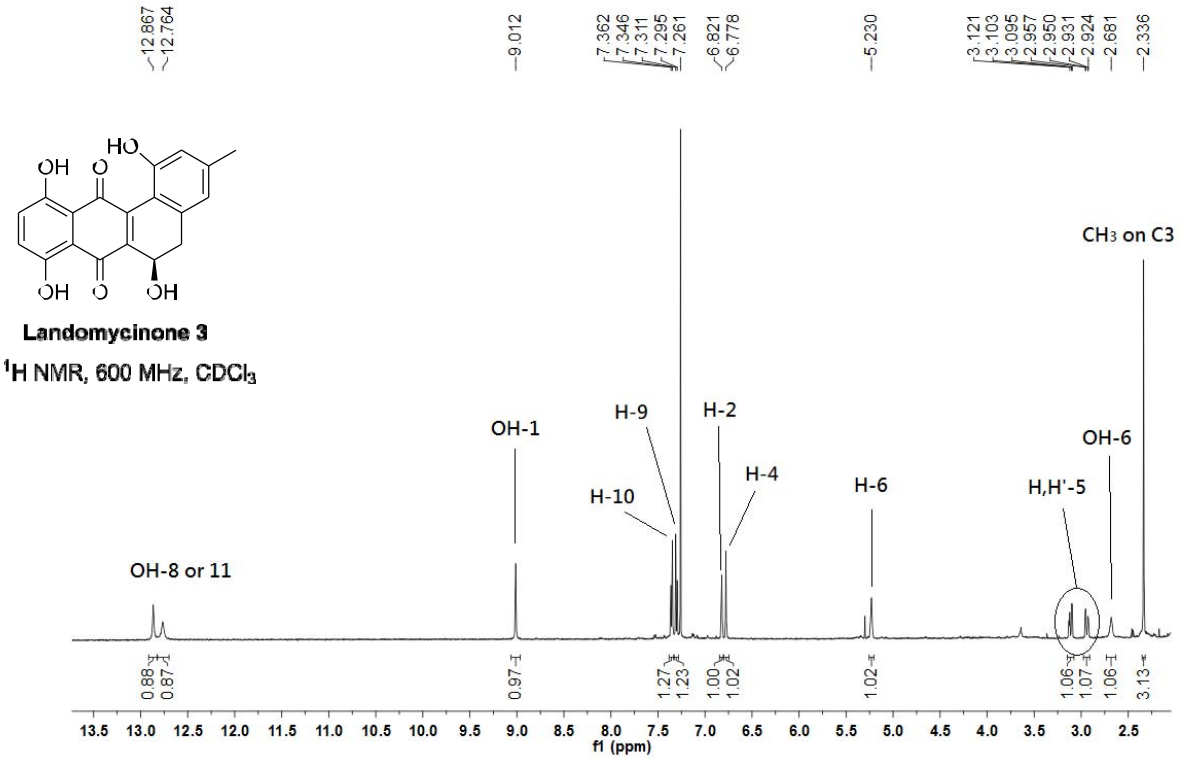


Expanded HMBC NMR spectrum of compound **40** for H9 and H10

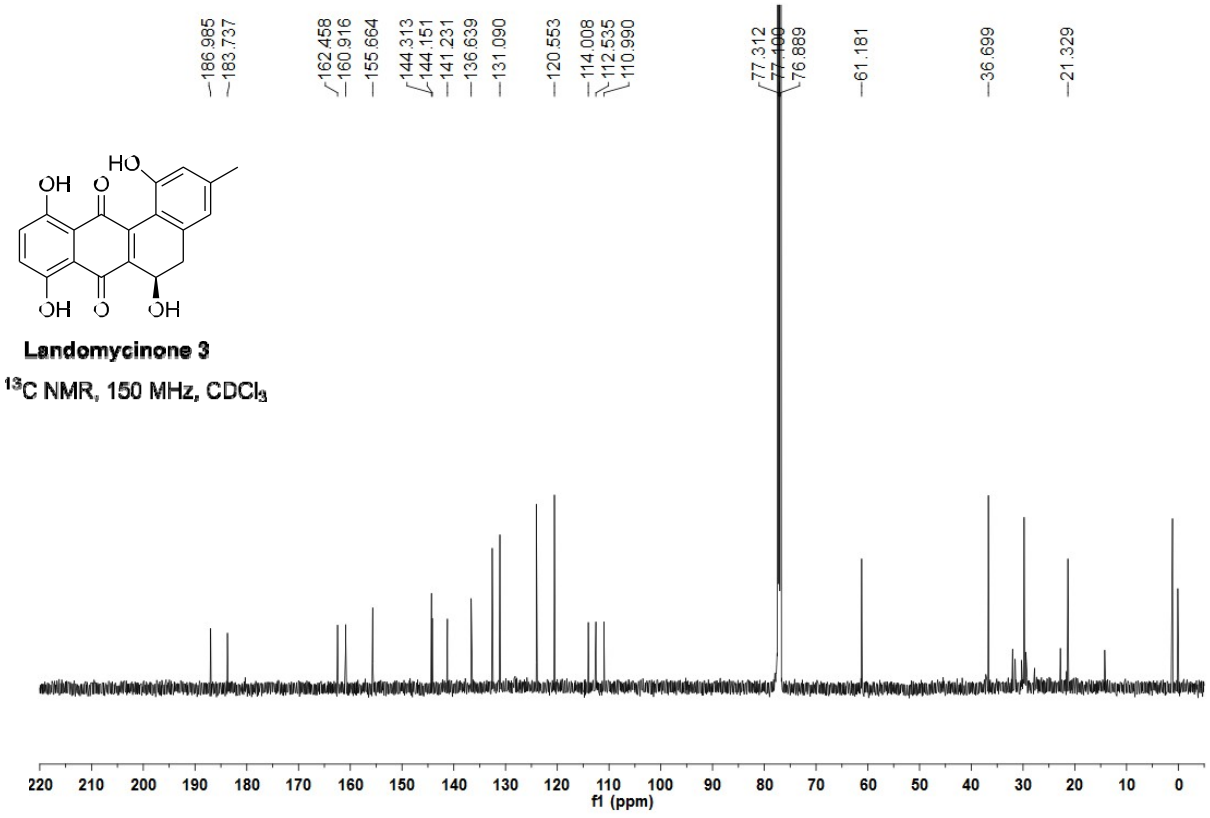


4.55 NMR spectra of landomycinone 3

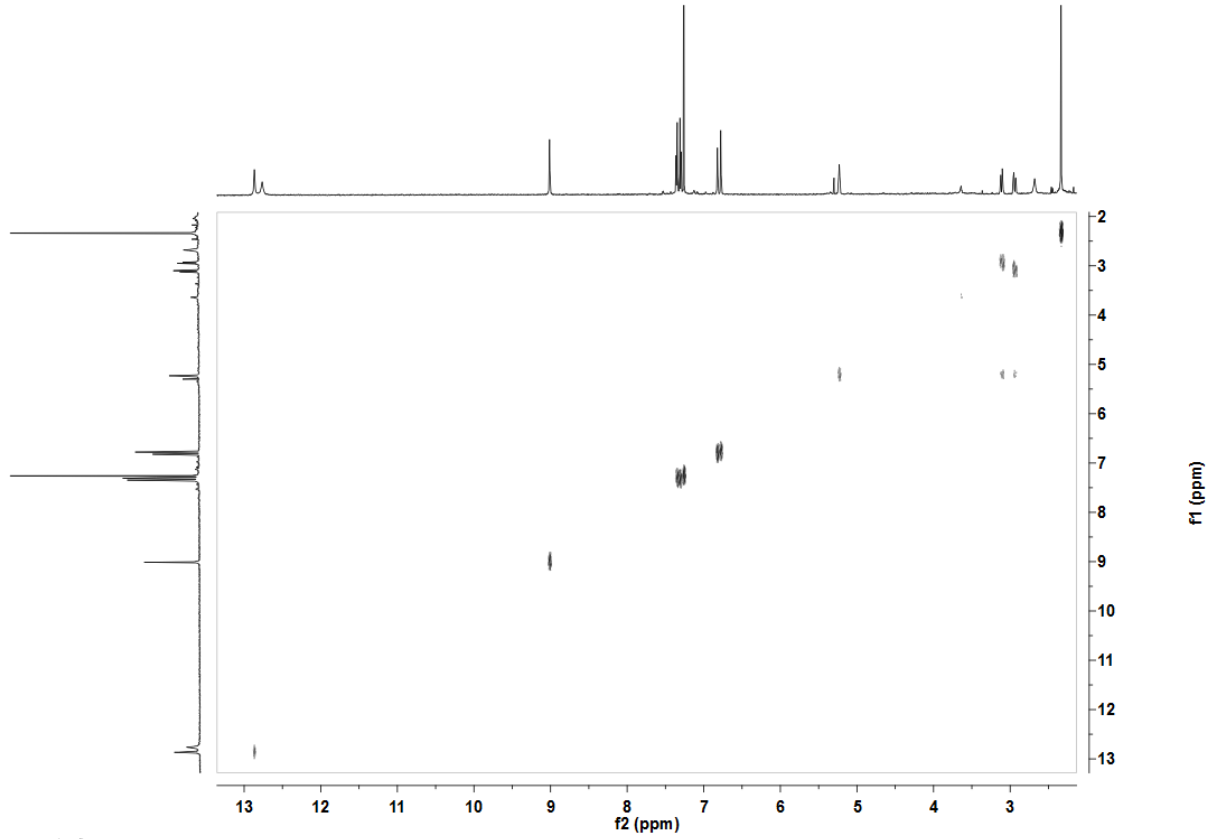
^{1}H NMR spectrum

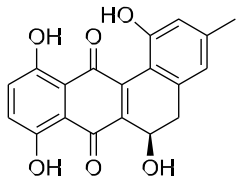


^{13}C NMR spectrum



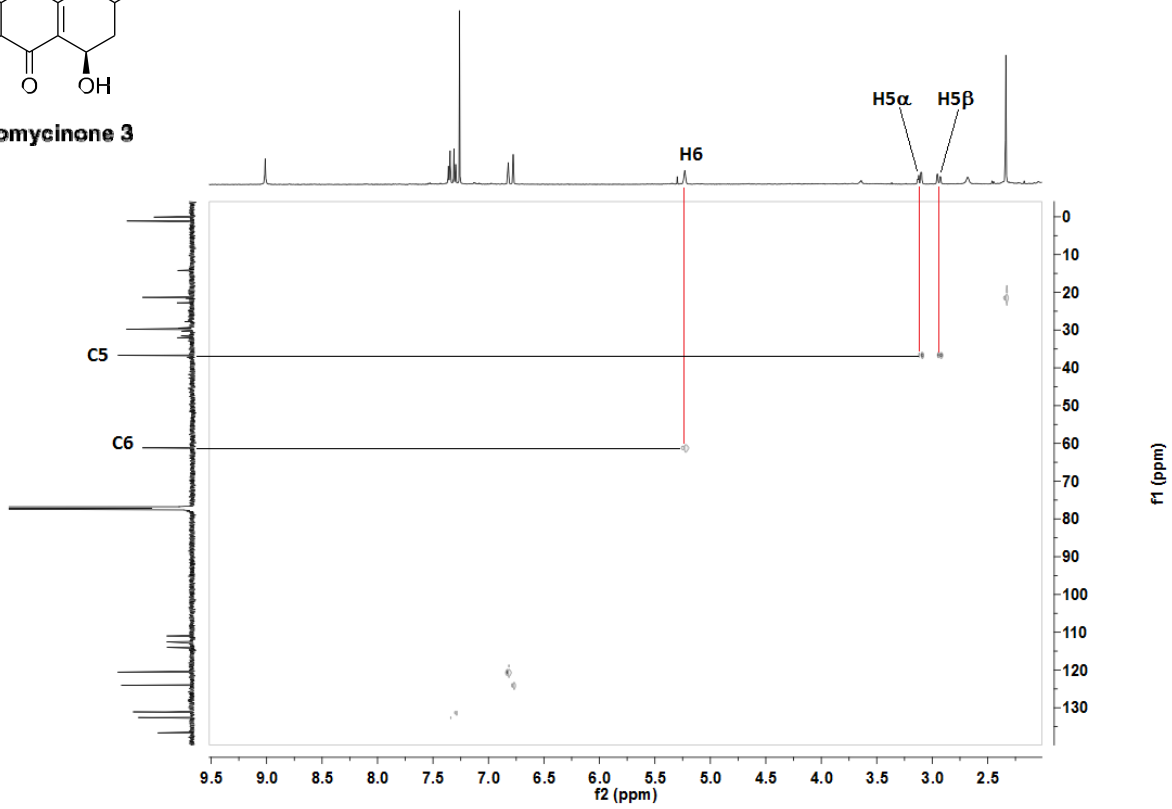
2D COSY NMR spectrum of landomycinone **3**



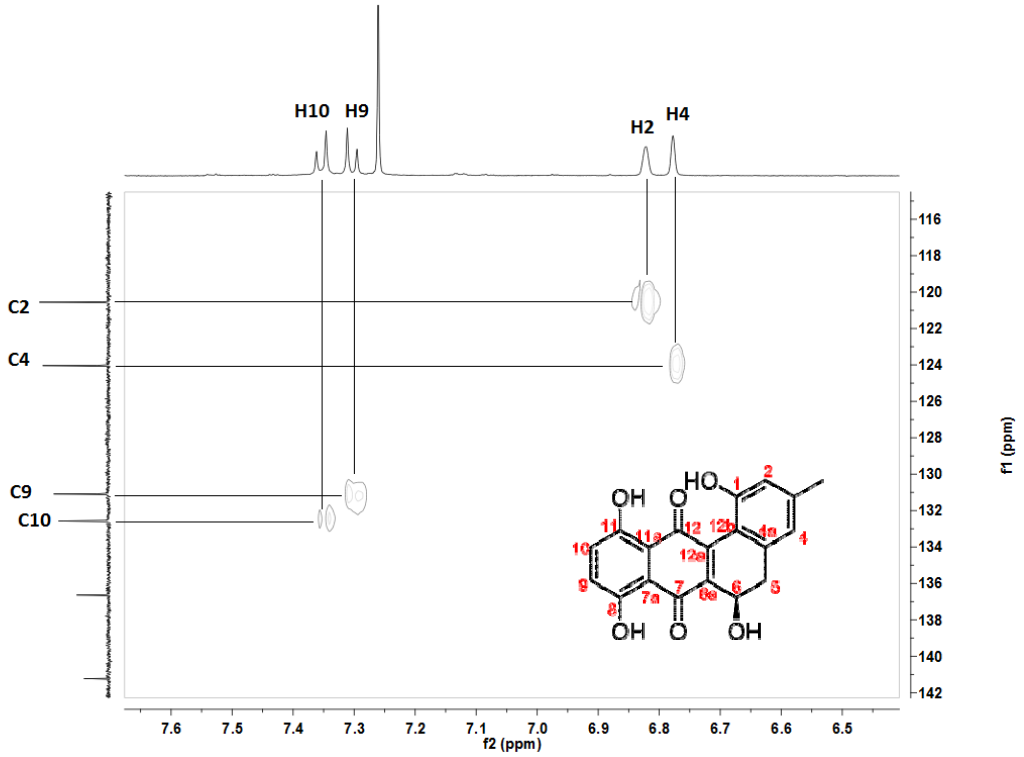


Landomycinone 3

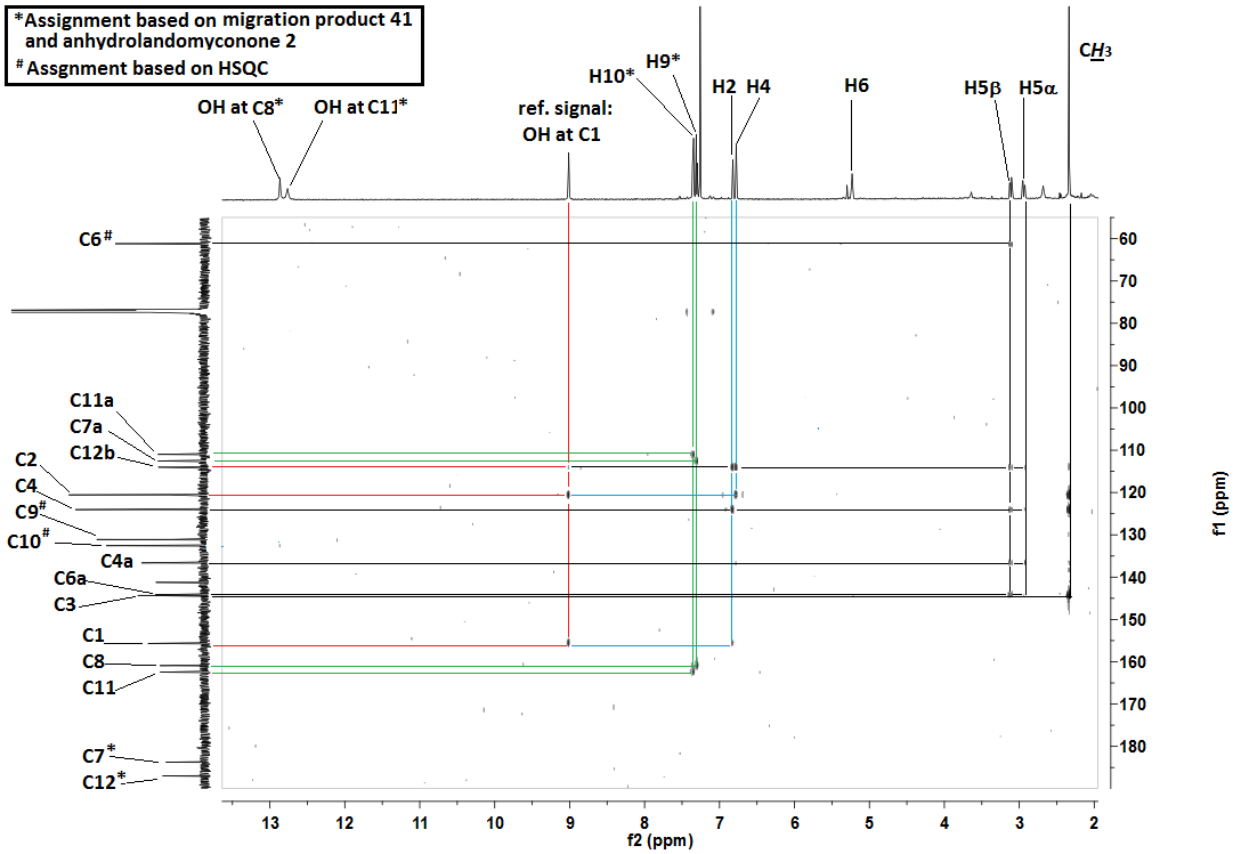
2D HSQC NMR spectrum of landomycinone **3**



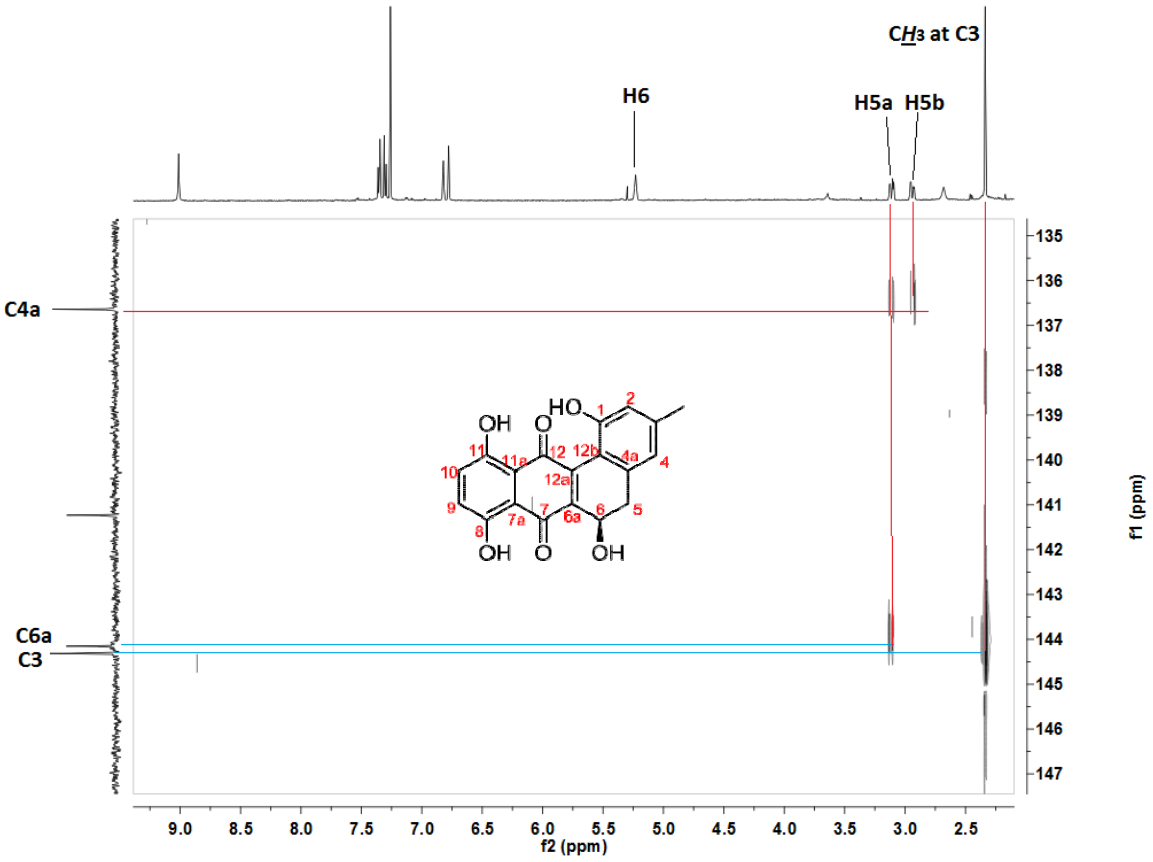
Partial Expanded HSQC NMR spectrum of landomycinone **3**



2D HMBC NMR spectrum of landomycinone **3**



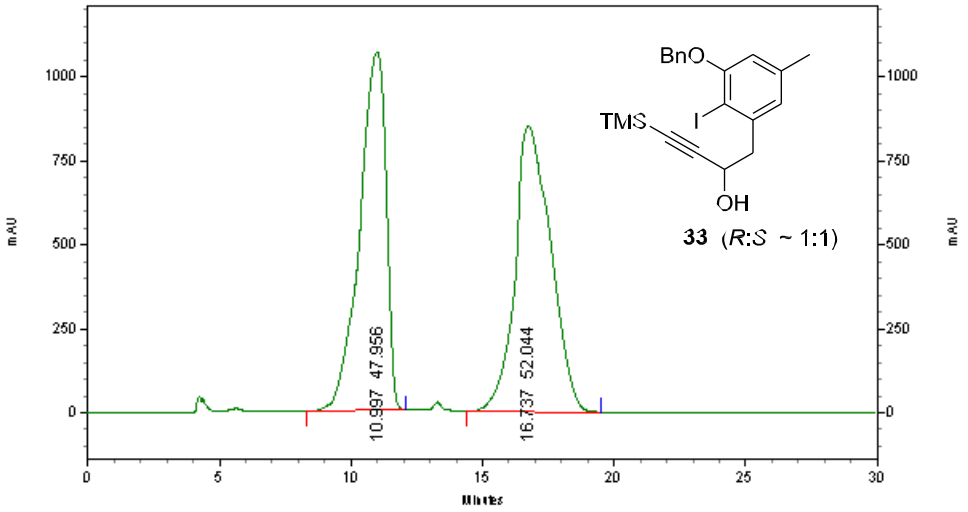
Expanded HMBC NMR spectrum of landomycinone **3**



4.56 HPLC spectra for but-3-yn-2-ol 33

1:1 mixture of (*R*/*S*)-but-3-yn-2-ol **33** from alkynlation of ketone **32** (See section 2.33)

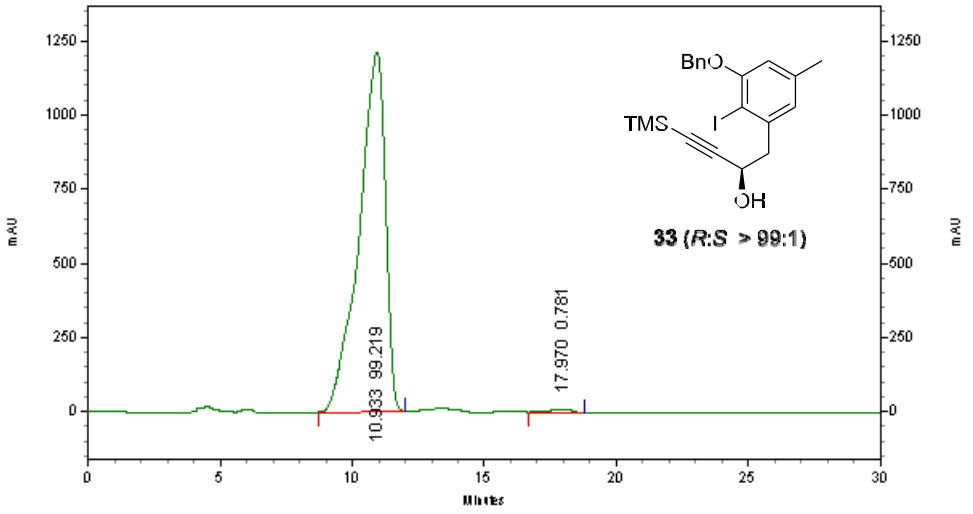
CHIRALPAK IC column (250 mm x 4.6 mm), hexanes:*i*PrOH 97:3, 0.8 cm^3/min, T = 25 °C.



UV Results

Retention Time	Area Percent
10.997	47.956
16.737	52.044
Totals	100.000

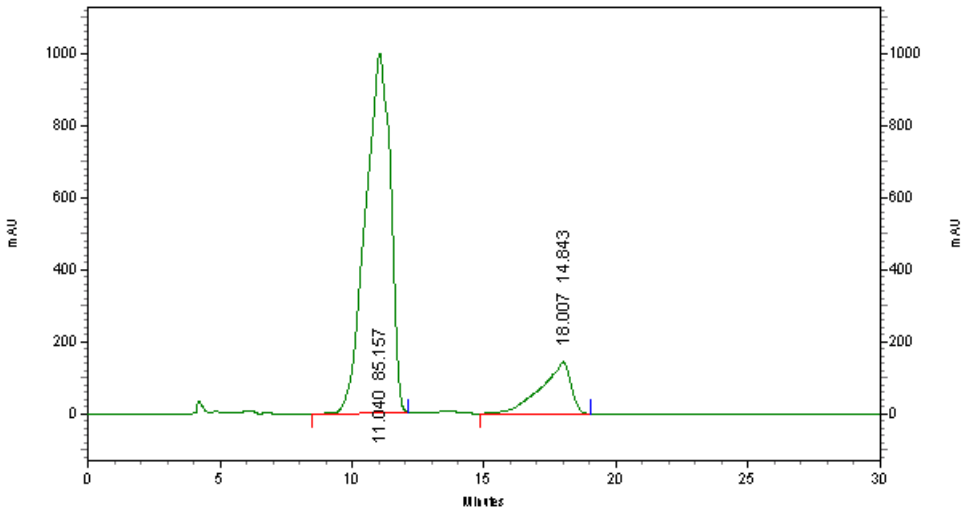
(*R*)- But-3-yn-2-ol **33** obtained by Ru-catalyzed asymmetric hydrogen transfer reduction of ketone **S8** catalyzed by *in-situ* prepared [Ru(*p*-cymene)[(*R*,*R*)-Ts-DPEN]) (see section 2.34).



UV Results

Retention Time	Area Percent
10.933	99.219
17.970	0.781
Totals	100.000

(*R/S*)-**34** spiked with (*R*)-**34** obtained asymmetric reduction.



UV Results

Retention Time	Area Percent
11.040	85.157
18.007	14.843
Totals	100.000