Supporting Information

One-pot double [3+2] cycloaddition for diastereoselective synthesis of novel tetracyclic pyrrolidine compounds

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1. General experimental information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz Varian NMR spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz). LC-MS were performed on an Agilent 2100 system. A C_{18} column (5.0 μm, 6.0 x 50 mm) was used for the analysis. The mobile phases were methanol and water both containing 0.05% trifluoroacetic acid. A linear gradient was used to increase from 25:75 v/v methanol/water to 100% methanol over 5 min at a flow rate of 0.7 mL/min. The routine UV detections were at 210 nm, 254.4 nm and 365 nm. The mass spectra were recorded in APCI (atmospheric pressure chemical ionization). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer.

Sorbent silica gel XHL TLC plates (130815) were used for thin-layer chromatography (TLC). Flash chromatography separations were performed on YAMAZEN AI-580 Flash column system with Agela 12g or 20g (230-400μm) silica gel cartridges. The microwave experiments were performed in a Biotage initiator under optimized reaction conditions of power and pressure.

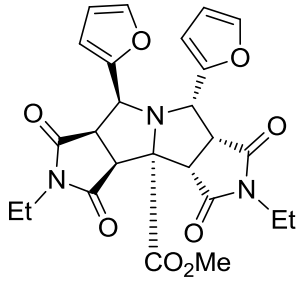
2. General experimental procedures and compound characterization

General procedure for the synthesis of symmetric double (3+2) cycloaddition of azomethine ylides 5(a-j)

A solution of furfural (0.038 g, 0.4 mmol), methyl 2-aminoacetate hydrochloride (0.025 g, 0.2 mmol), *N*-ethylmaleimide (0.05 g, 0.4 mmol, 2 equiv), and Et_3N (86 μL) in 0.5 mL of toluene was irradiated in a Biotage initiator microwave reactor at 180 ℃ for 30 min. The crude mixture was quenched with water and extracted with ethyl acetate. The combined extracts were concentrated and purified by flash chromatography (3:2 hexanes:EtOAc) to give product **5a** (63 mg, 65% yield).

General procedure for the synthesis of double [3+2] cycloaddition products 5(l-n)

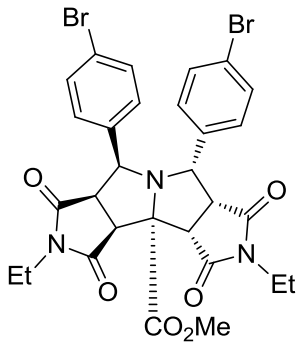
A solution of 4-nitrobenzaldhyde (0.030 g, 0.2 mmol), methyl 2-aminoacetate hydrochloride (0.025 g, 0.2 mmol), *N*-ethylmaleimide (0.025 g, 0.2 mmol), and Et_3N (86 μL) in 0.5 mL of toluene was irradiated in a Biotage initiator microwave reactor at 180 ℃ for 10 min. To reaction mixture was then added 2-thiazolecarboxaldehyde (0.022g, 0.2 mmol) and *N*-ethylmaleimide (0.025 g, 0.2 mmol), and Et_3N (86 μL, 3 equiv). The mixture was heated again at 180 ℃ for 30 min. The crude mixture was mixed with water and extracted ethyl acetate. The combined extracts were concentrated and purified on flash chromatography (3:2 hexanes:EtOAc) to give product **5m** (88 mg, 78% yield).



Dicycloaddition product **5a**

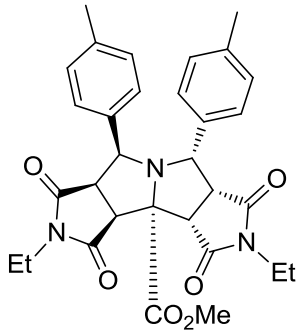
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.13 (d, *J* = 1.6 Hz,

1H), 6.25 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.11 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.04 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.84 (d, *J* = 3.2 Hz, 1H), 4.80 (dd, *J* = 14.3, 9.9 Hz, 2H), 4.63 (d, *J* = 8.6 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 3.67 – 3.57 (m, 2H), 3.56 – 3.51 (m, 2H), 3.42 (dd, *J* = 6.7, 2.9 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 176.3, 175.0, 174.9, 173.7, 170.1, 150.9, 145.9, 143.00, 141.8, 112.3, 110.3, 110.0, 107.1, 79.8, 60.4, 60.1, 53.5, 52.0, 49.2, 48.7, 47.8, 34.2, 34.0, 12.8, 11.9. MS (APCI) m/z: 496.2 (M^++1); HRMS (ESI-TOF) Calcd. for $C_{25}H_{26}N_3O_8$: 496.1720 ($[M+1]^+$), found: 496.1718 ($[M+1]^+$).



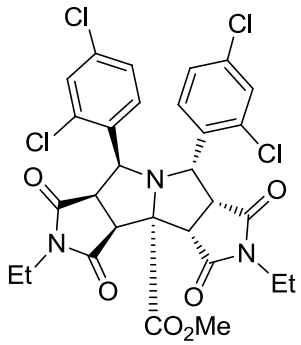
Dicycloaddition product **5b**

^{1}H NMR (300 MHz, CDCl3) δ 7.10 (t, J = 8.6 Hz, 4H), 6.94 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 4.68 (d, J = 8.8 Hz, 1H), 4.58 (d, J = 8.5 Hz, 1H), 4.38 (d, J = 10.4 Hz, 1H), 4.24 (d, J = 8.1 Hz, 1H), 3.95 (s, 3H), 3.70 (dd, J = 7.1, 4.5 Hz, 2H), 3.61 – 3.51 (m, 1H), 3.44 (dd, J = 10.4, 8.5 Hz, 1H), 3.29 (dd, J = 9.0, 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 176.0, 174.7, 173.1, 170.7, 137.3, 132.7, 131.0, 130.9, 130.1, 128.9, 123.1, 121.5, 80.3, 68.2, 65.0, 53.7, 52.8, 50.4, 49.5, 48.3, 34.5, 34.2, 13.0, 12.5; MS (APCI) m/z: 674.0 (M^++1).



Dicycloaddition product **5c**

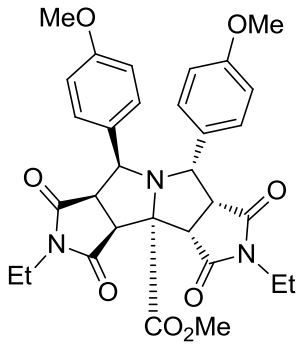
^{1}H NMR (300 MHz, CDCl3) δ 6.81 (d, J = 8.2 Hz, 2H), 6.65 (dd, J = 8.0, 4.8 Hz, 6H), 4.61 (d, J = 9.0 Hz, 1H), 4.51 (d, J = 8.5 Hz, 1H), 4.43 (d, J = 10.3 Hz, 1H), 4.15 (d, J = 8.1 Hz, 1H), 3.86 (s, 3H), 3.67 – 3.56 (m, 2H), 3.46 – 3.33 (m, 2H), 3.20 (dd, J = 12.3, 7.2 Hz, 2H), 2.06 (s, 3H), 2.01 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 176.3, 175.1, 173.7, 173.2, 138.2, 136.7, 135.3, 131.0, 128.3, 128.2, 127.1, 117.6, 80.4, 68.7, 65.3, 53.5, 52.7, 50.8, 50.0, 48.3, 34.3, 34.0, 21.2, 21.0, 13.0, 12.4. MS (APCI) m/z: 544.2 (M^{+}+1).



Dicycloaddition product **5d**

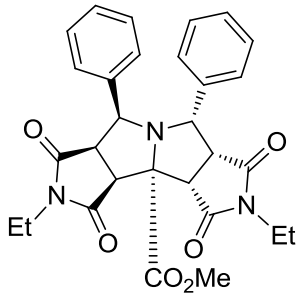
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 2.2 Hz, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 5.24 (d, *J* = 9.3 Hz, 1H), 4.67 (dd, *J* = 9.3, 4.2 Hz, 2H), 4.38 (d, *J* =

8.3 Hz, 1H), 3.93 (s, 3H), 3.72 (dd, *J* = 7.3, 4.8 Hz, 2H), 3.61 – 3.49 (m, 2H), 3.32 (dd, *J* = 7.2, 2.6 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 172.6, 172.4, 171.3, 171.1, 137.0, 135.7, 134.6, 131.5, 129.5, 128.8, 128.2, 127.8, 126.8, 126.2, 124.6, 117.4, 80.5, 62.3, 61.4, 53.7, 52.2, 48.7, 48.2, 47.6, 34.7, 34.2, 13.1, 13.0. MS (APCI) m/z: 654.0 (M^++1).



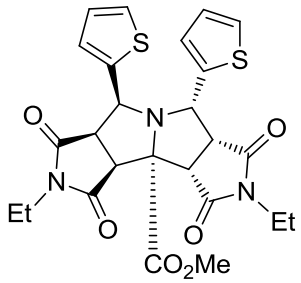
Dicycloaddition product **5e**

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.45 – 6.35 (m, 4H), 4.61 (d, *J* = 8.9 Hz, 1H), 4.49 (d, *J* = 8.5 Hz, 1H), 4.40 (d, *J* = 10.4 Hz, 1H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.65 – 3.58 (m, 2H), 3.57 (s, 3H), 3.54 (s, 3H), 3.44 – 3.33 (m, 2H), 3.20 (dd, *J* = 11.0, 7.3 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 176.4, 175.1, 173.6, 171.1, 159.4, 158.6, 132.4, 130.6, 128.3, 123.3, 117.5, 113.0, 80.2, 68.4, 65.0, 55.3, 55.2, 53.5, 52.8, 50.7, 49.9, 48.3, 34.3, 34.0, 13.0, 12.4.MS (APCI) m/z: 576.2 (M^++1).



Dicycloaddition product **5f**

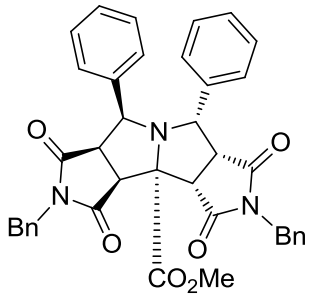
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, J = 1.9 Hz, 2H), 6.96 – 6.87 (m, 8H), 4.74 (d, J = 8.9 Hz, 1H), 4.58 (dd, J = 12.4, 9.5 Hz, 2H), 4.25 (d, J = 8.0 Hz, 1H), 3.95 (s, 3H), 3.70 (dd, J = 13.9, 7.1 Hz, 2H), 3.60 – 3.41 (m, 2H), 3.27 (dd, J = 9.7, 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 176.5, 176.1, 174.8, 173.3, 170.9, 138.2, 131.1, 130.9, 128.3, 128.2, 127.4, 127.4, 127.2, 127.0, 80.3, 77.4, 77.0, 76.6, 68.9, 65.3, 53.4, 52.6, 50.5, 49.8, 48.12, 34.19, 33.8, 12.7, 12.2. MS (APCI) m/z: 516.2 (M^{+}+1).



Dicycloaddition product **5g**

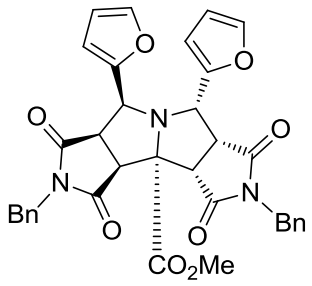
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.94 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.68 (ddd, *J* = 12.5, 5.1, 3.6 Hz, 2H), 6.55 (d, *J* = 3.5 Hz, 1H), 5.11 (d, *J* = 8.9 Hz, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 4.59 (d, *J* = 8.5 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.73 – 3.63 (m, 2H), 3.59 – 3.43 (m, 2H), 3.35-3.20 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 176.2, 175.5, 174.6, 173.1, 170.5, 143.7, 132.7, 130.7, 126.7,

126.6, 126.4, 125.2, 79.5, 63.3, 61.6, 53.6, 52.6, 50.4, 50.2, 48.7, 34.5, 34.2, 12.7, 12.5. MS (APCI) m/z: 528.1(M^++1).



Dicycloaddition product **5h**

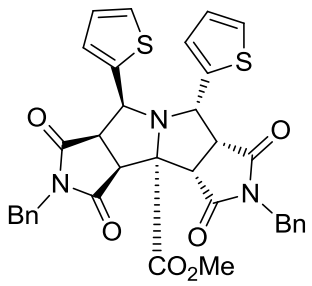
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2H), 7.54 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.25 – 7.19 (m, 3H), 7.18 – 7.11 (m, 2H), 6.90 – 6.63 (m, 6H), 6.63 – 6.56 (m, 2H), 6.37 – 6.29 (m, 2H), 4.78 (d, *J* = 6.0 Hz, 2H), 4.62 (d, *J* = 8.7 Hz, 1H), 4.51 (d, *J* = 9.3 Hz, 1H), 4.42-4.25 (m, 3H), 3.85 (d, *J* = 10.2 Hz, 1H), 3.69 (s, 3H), 3.46 (dd, *J* = 9.2, 8.0 Hz, 1H), 3.17 (dd, *J* = 10.2, 8.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 175.4, 174.8, 173.1, 170.9, 137.8, 135.2, 134.5, 131.2, 130.4, 129.9, 129.2, 129.0, 128.3, 128.1, 127.8, 127.1, 127.0, 126.8, 126.7, 80.6, 68.9, 65.0, 53.3, 52.0, 50.5, 50.2, 47.6, 42.8, 42.4, MS (APCI) m/z: 640.2 (M^++1).



Dicycloaddition product **5i**

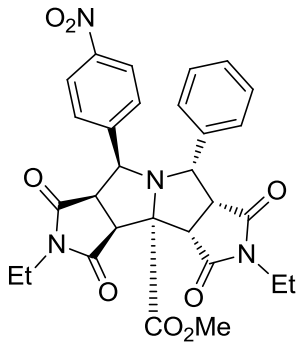
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.37 (m, 6H), 7.27 (t, *J* = 2.8 Hz, 4H), 6.88 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.77 (d, *J* = 1.3 Hz, 1H), 6.09 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.98

(dd, *J* = 3.3, 1.9 Hz, 1H), 5.86 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.34 (d, *J* = 3.2 Hz, 1H), 4.72 (s, 2H), 4.66 (d, *J* = 9.6 Hz, 1H), 4.60 (d, *J* = 8.7 Hz, 1H), 4.50 (d, *J* = 7.2 Hz, 2H), 4.21 (d, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 10.1 Hz, 1H), 3.68 (s, 3H), 3.39 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.19 (dd, *J* = 10.1, 8.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 174.5, 173.4, 172.5, 170.2, 145.5, 142.7, 141.5, 135.2, 134.3, 129.6, 128.9, 128.8, 128.6, 128.4, 127.7, 117.3, 112.0, 110.0, 109.6, 106.9, 79.8, 60.4, 59.7, 53.4, 51.7, 49.4, 48.6, 47.7, 43.0, 42.6. MS (APCI) m/z: 620.1 (M^++1).



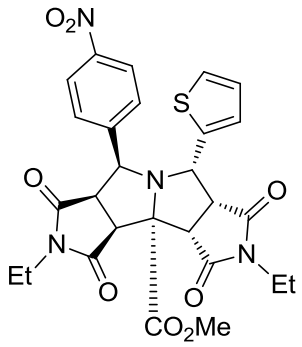
Dicycloaddition product **5j**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.36 (m, 6H), 7.17 – 7.04 (m, 4H), 6.88 (d, *J* = 5.1 Hz, 1H), 6.66 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.46 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.39 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.29 (d, *J* = 3.5 Hz, 1H), 5.96 (d, *J* = 2.9 Hz, 1H), 4.82 (d, *J* = 8.9 Hz, 1H), 4.67 (t, *J* = 8.8 Hz, 2H), 4.40 (d, *J* = 8.6 Hz, 1H), 4.32 (d, *J* = 13.9 Hz, 1H), 4.20-4.10 (m, 2H), 3.97 (d, *J* = 10.4 Hz, 1H), 3.73 (s, 3H), 3.41 (t, *J* = 8.4 Hz, 1H), 2.88 – 2.73 (m, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 174.9, 174.5, 172.5, 170.5, 143.2, 135.2, 134.5, 132.0, 130.7, 129.8, 129.5, 129.4, 129.3, 128.5, 127.8, 126.7, 126.1, 126.0, 124.7, 124.5, 79.8, 63.3, 61.4, 53.6, 52.2, 50.2, 49.9, 48.3, 43.1, 42.8. MS (APCI) m/z: 652.1 (M^++1).



Dicycloaddition product **5l**

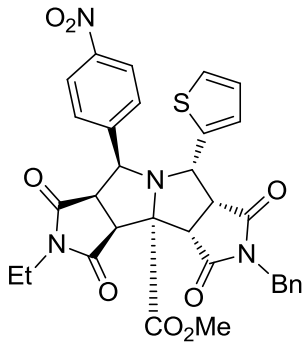
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 5H), 4.64 (d, *J* = 8.7 Hz, 2H), 4.56 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 3.70 – 3.60 (m, 2H), 3.52 – 3.42 (m, 2H), 3.21 (d, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 175.9, 173.1, 172.7, 170.6, 146.9, 146.1, 131.3, 130.8, 129.1, 128.1, 128.0, 122.8, 80.6, 68.7, 64.8, 53.8, 52.5, 50.5, 49.8, 48.1, 34.5, 34.2, 13.0, 12.5. MS (APCI) m/z: 561.2 (M^++1).



Dicycloaddition product **5m**

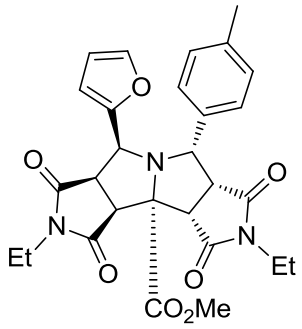
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.84 (dd, *J* = 5.2, 0.9 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 6.46 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.98 (d, *J* = 9.0 Hz, 1H), 4.60 (d, *J* = 8.5 Hz, 1H), 4.50 (d, *J* = 10.6 Hz, 1H), 4.18 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 3.70 – 3.60 (m, 2H), 3.51 – 3.39 (m, 2H), 3.20

(dd, *J* = 7.2, 4.8 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 175.5, 174.5, 173.0, 170.3, 147.0, 145.9, 132.5, 130.8, 128.0, 127.0, 126.9, 122.8, 80.1, 65.3, 63.0, 53.9, 52.6, 50.1, 49.7, 48.6, 34.6, 34.2, 13.0, 12.5. MS (APCI) m/z: 567.1(M^++1); HRMS (ESI-TOF) Calcd. for $C_{27}H_{27}N_4O_8S$: 567.1550 ($[M+1]^+$), found: 567.1556 ($[M+1]^+$).



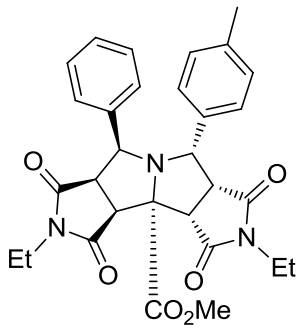
Dicycloaddition product **5n**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.51 (m, 7H), 6.85 – 6.78 (m, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.38 (dd, *J* = 5.2, 3.7 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 4.91 (d, *J* = 9.0 Hz, 1H), 4.81 (s, 2H), 4.57 (d, *J* = 8.5 Hz, 1H), 4.29 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.77 (d, *J* = 10.5 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.25-3.21(m, 2H), 3.05-2.99 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 175.0, 174.5, 172.8, 170.3, 146.7, 145.8, 134.7, 132.0, 130.8, 130.1, 129.5, 129.4, 127.7, 126.9, 126.6, 122.5, 80.2, 64.9, 62.9, 53.9, 52.3, 49.7, 49.6, 48.3, 43.2, 34.1, 13.0. MS (APCI) m/z: 629.2 (M^++1).



Dicycloaddition product **5o**

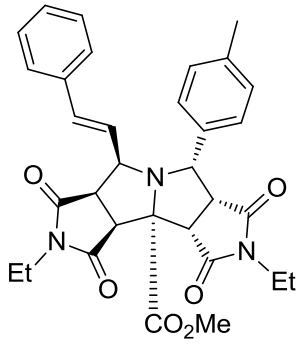
^{1}H NMR (300 MHz, CDCl3) δ 7.11 (d, J = 1.0 Hz, 1H), 6.94 (t, J = 5.6 Hz, 4H), 5.99 (dd, J = 3.3, 1.8 Hz, 1H), 5.70 (d, J = 3.3 Hz, 1H), 4.70 – 4.48 (m, 4H), 3.97 (d, J = 7.8 Hz, 1H), 3.78 (s, 3H), 3.68 – 3.52 (m, 5H), 2.24 (s, 3H), 1.23 (t, 3H), 1.07 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 177.4, 175.6, 174.0, 172.8, 164.7, 141.3, 129.7, 129.3, 128.9, 110.4, 108.7, 78.0, 65.5, 56.6, 53.2, 51.7, 51.0, 50.3, 47.3, 34.4, 34.1, 21.2, 12.9, 12.7. MS (APCI) m/z: 520.2 (M^{+}+1).



Dicycloaddition product **5p**

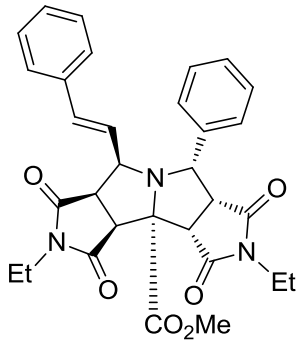
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 – 6.75 (m, 7H), 6.64 (d, *J* = 7.9 Hz, 2H), 4.63 (d, *J* = 8.9 Hz, 1H), 4.50 (dd, *J* = 16.3, 9.3 Hz, 2H), 4.17 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.72 – 3.52 (m, 3H), 3.41 (dd, *J* = 11.7, 7.2 Hz, 2H), 3.28 – 3.08 (m, 2H), 2.00 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 176.3, 175.1, 173.6, 172.6, 138.4, 131.1, 128.3, 127.6, 127.3, 80.5, 68.7, 65.4, 53.6, 52.8, 50.7, 50.0, 48.3, 34.3, 34.0, 21.0, 12.9, 12.4. MS (APCI) m/z: 530.2

(M^++1).



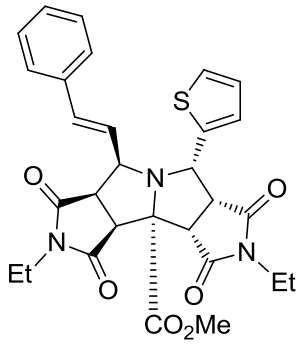
Dicycloaddition product **5q**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 9.8, 7.0 Hz, 3H), 7.06 – 6.95 (m, 4H), 6.88 (d, *J* = 8.1 Hz, 2H), 5.94 (dd, *J* = 15.7, 9.1 Hz, 1H), 5.64 (d, *J* = 15.7 Hz, 1H), 4.63 (d, *J* = 9.9 Hz, 1H), 4.25 (d, *J* = 9.0 Hz, 1H), 4.11 (t, *J* = 9.4 Hz, 1H), 3.85 (t, *J* = 9.7 Hz, 1H), 3.77 (d, *J* = 7.4 Hz, 1H), 3.70 (s, 3H), 3.65 – 3.56 (m, 2H), 3.54 – 3.44 (m, 3H), 2.23 (s, 3H), 1.15 – 1.06 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 175.5, 175.1, 174.9, 172.0, 138.7, 136.7, 134.6, 130.8, 129.4, 128.7, 128.5, 127.7, 126.6, 124.3, 61.1, 58.4, 53.9, 53.2, 51.9, 48.7, 46.7, 34.3, 34.2, 21.4, 13.0. MS (APCI) m/z: 556.2(M^++1).



Dicycloaddition product **5r**

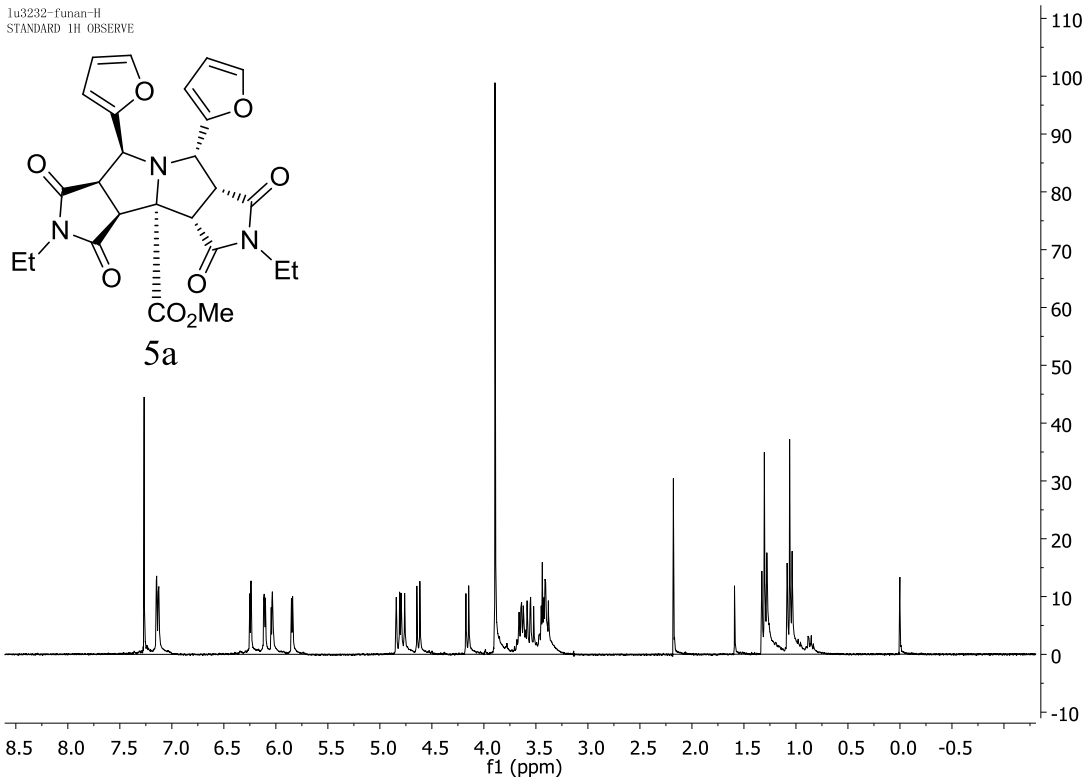
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 3H), 7.20 (dd, *J* = 8.5, 6.8 Hz, 3H), 7.07 (dd, *J* = 9.2, 5.0 Hz, 4H), 6.06 (dd, *J* = 15.7, 9.3 Hz, 1H), 6.06 (dd, *J* = 15.7, 9.3 Hz, 1H), 5.69 (d, *J* = 15.7 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.34 (d, *J* = 8.9 Hz, 1H), 4.22 (t, *J* = 9.4 Hz, 1H), 3.96 (t, *J* = 9.7 Hz, 1H), 3.90 – 3.68 (m, 6H), 3.59 (dd, *J* = 7.3, 1.8 Hz, 3H), 1.24 – 1.15 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 175.4, 174.9, 174.9, 172.1, 136.6, 134.9, 134.0, 129.0, 128.7, 128.6, 128.5, 127.8, 126.6, 124.1, 61.0, 58.3, 54.1, 53.2, 52.0, 48.5, 46.7, 34.3, 34.2, 13.1. MS (APCI) m/z: 542.2(M^++1)

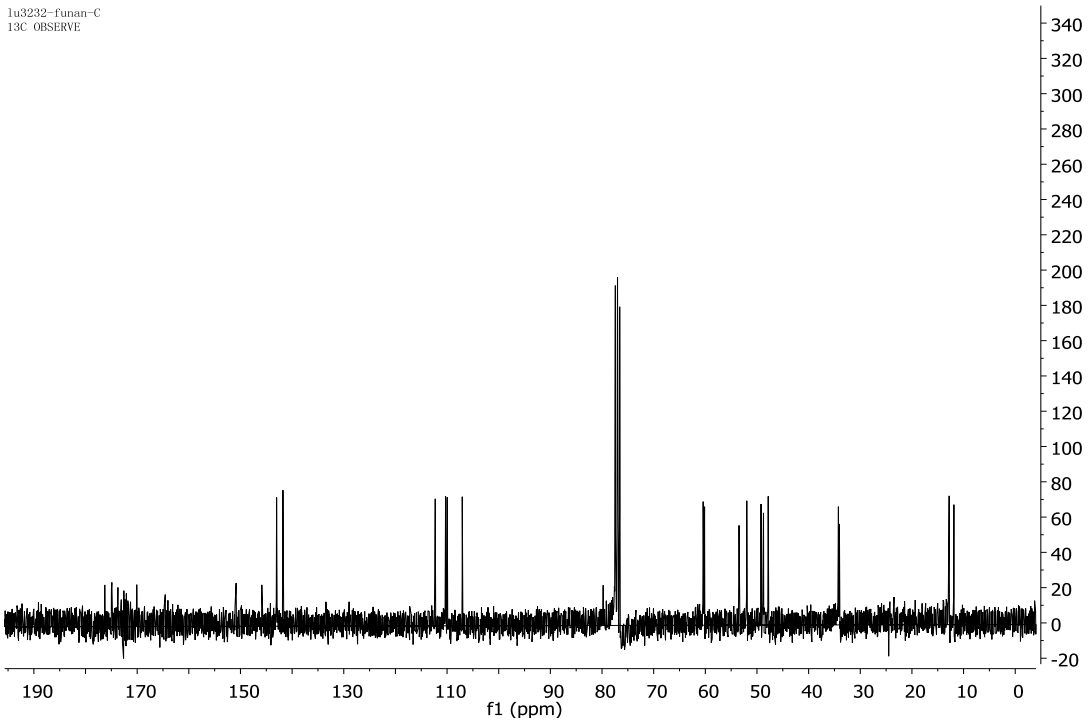


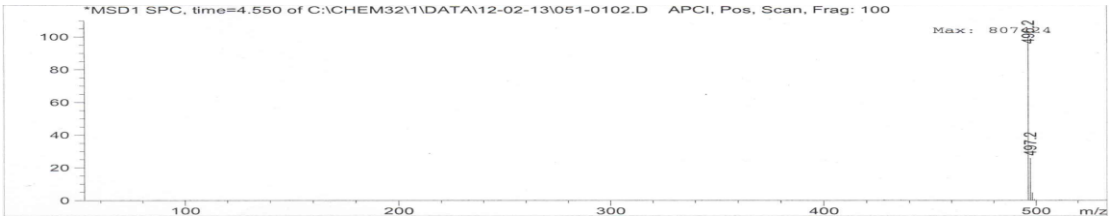
Dicycloaddition product **5s**

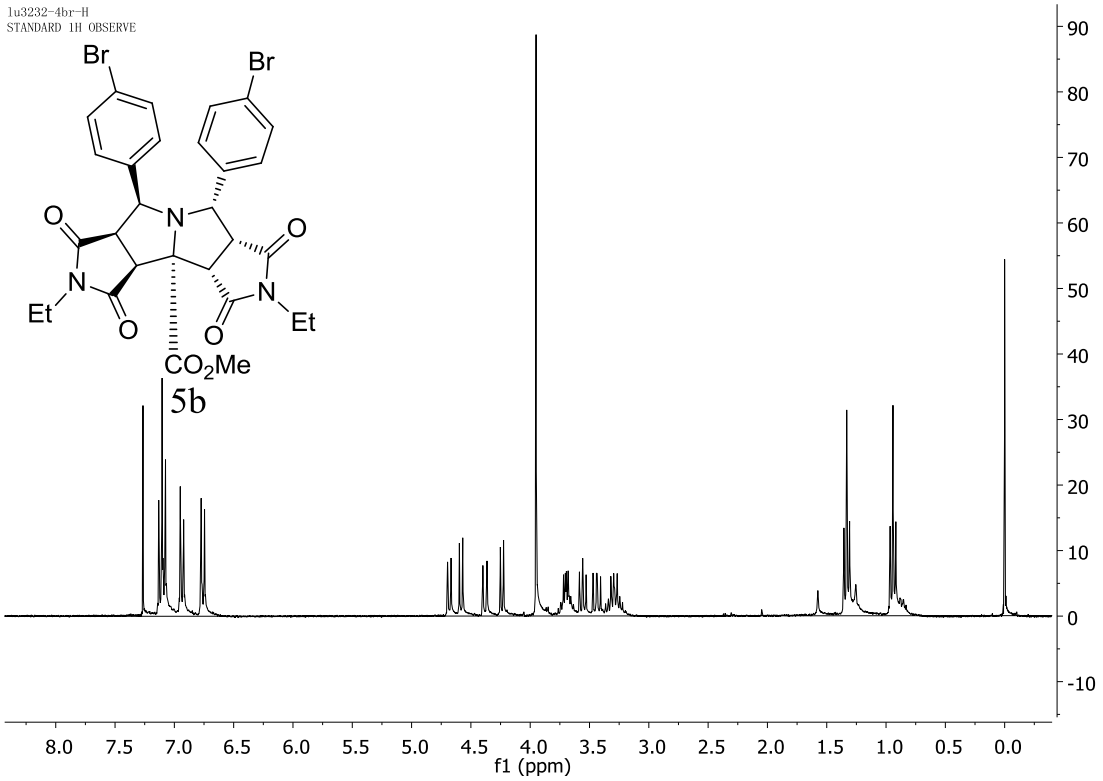
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.03 (m, 4H), 7.00 (d, *J* = 6.3 Hz, 2H), 6.94 (d, *J* = 3.7 Hz, 1H), 6.85 – 6.76 (m, 1H), 5.96 (d, *J* = 15.8 Hz, 1H), 5.77 (dd, *J* = 15.6, 7.6 Hz, 1H), 4.80 (d, *J* = 8.9 Hz, 1H), 4.53 (d, *J* = 9.3 Hz, 1H), 4.23 – 3.95 (m, 1H), 3.89 (d, *J* = 7.7 Hz, 1H), 3.76 (s, 3H), 3.63 – 3.45 (m, 6H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 175.2, 175.1, 174.5, 171.8, 136.7, 135.9, 132.8, 128.7, 128.5, 127.6, 127.0, 126.6, 125.1, 78.3, 60.5, 59.7, 53.4, 52.1, 50.7, 50.4, 47.5, 34.5, 34.2, 13.1, 12.8. MS (APCI) m/z: 548.2 (M^++1).

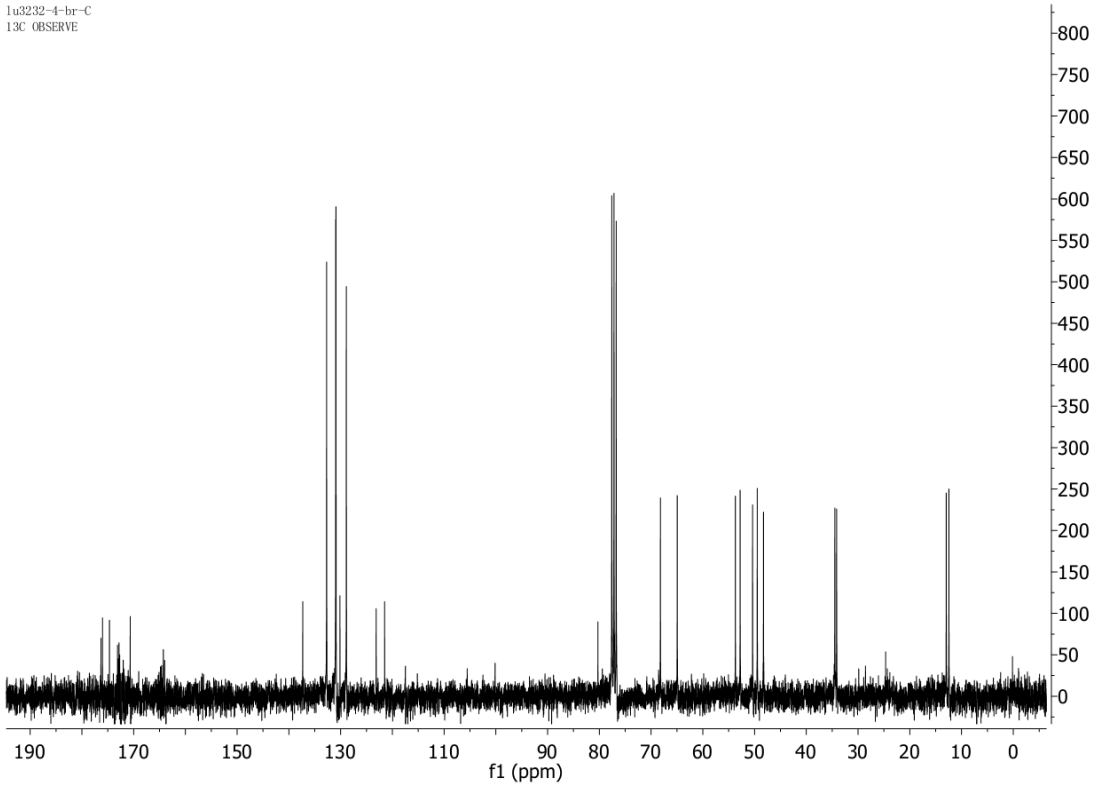
3. MS, ^{1}H and ^{13}C NMR spectra of compounds 5a-s

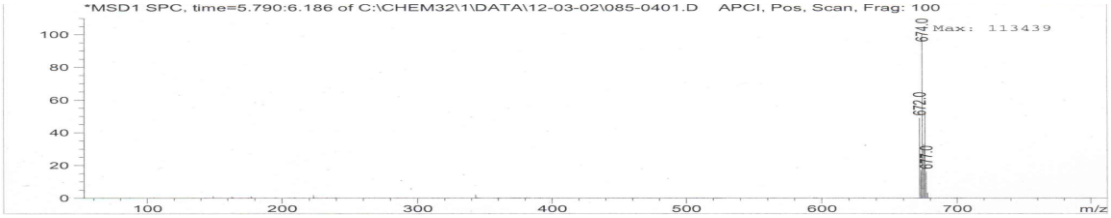


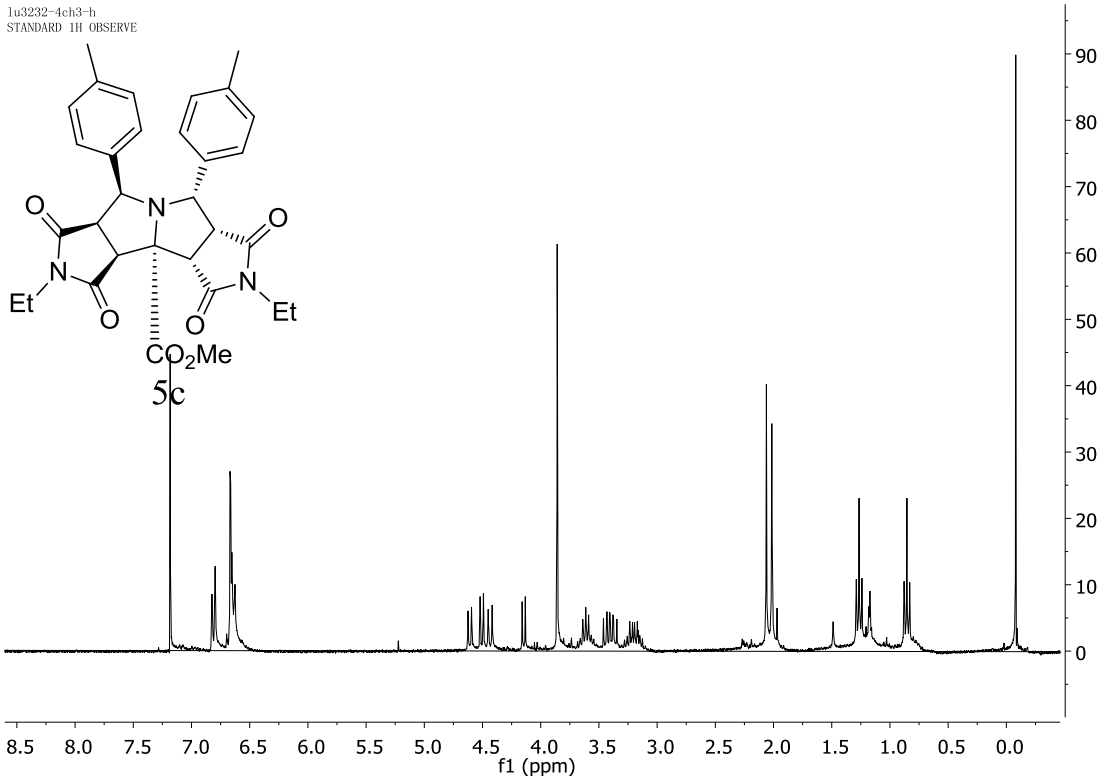


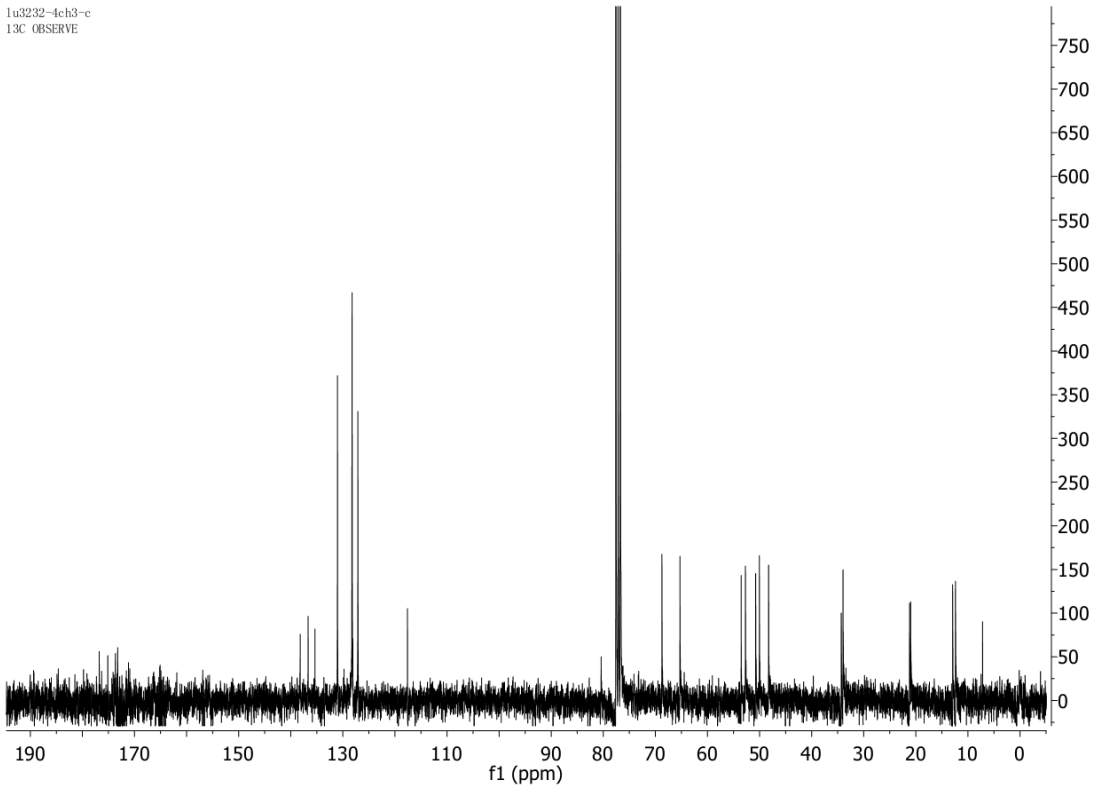


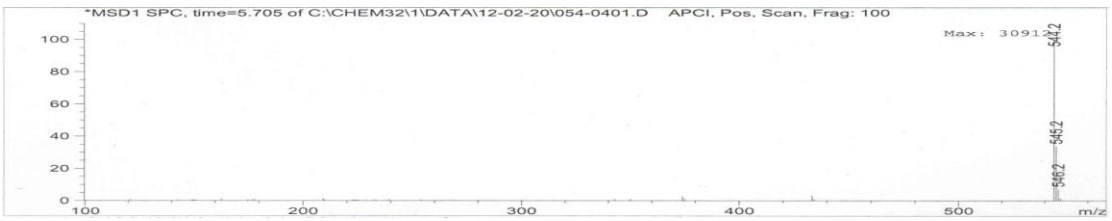


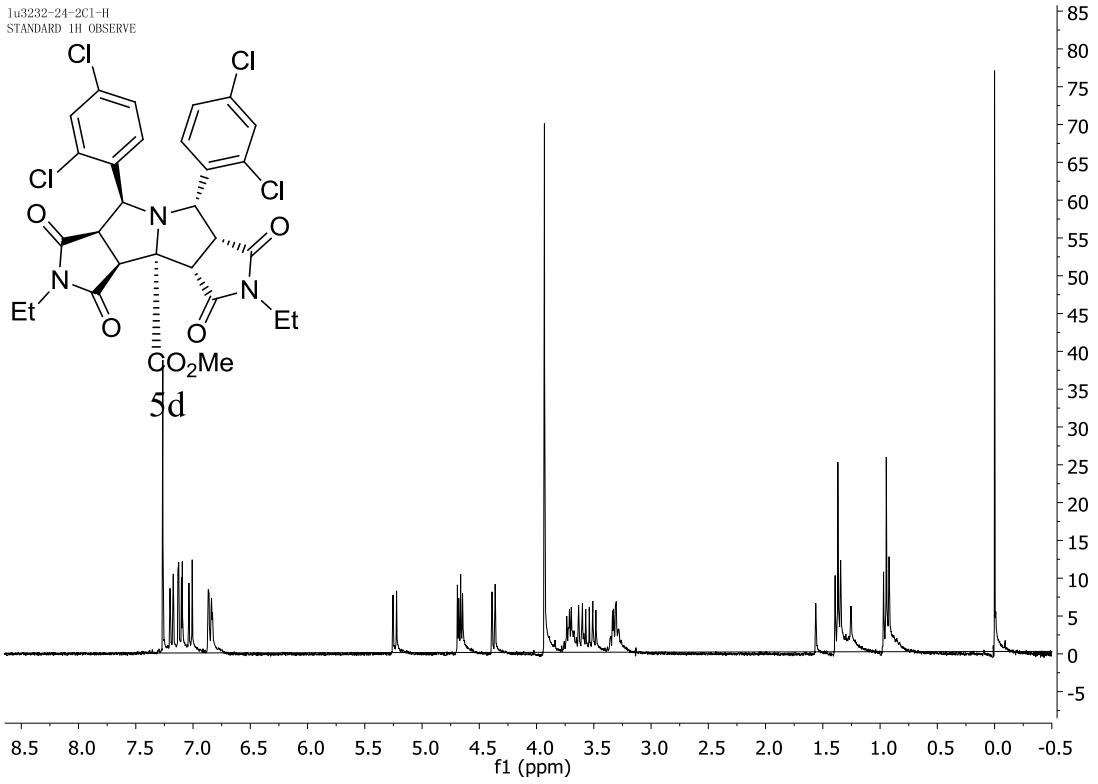












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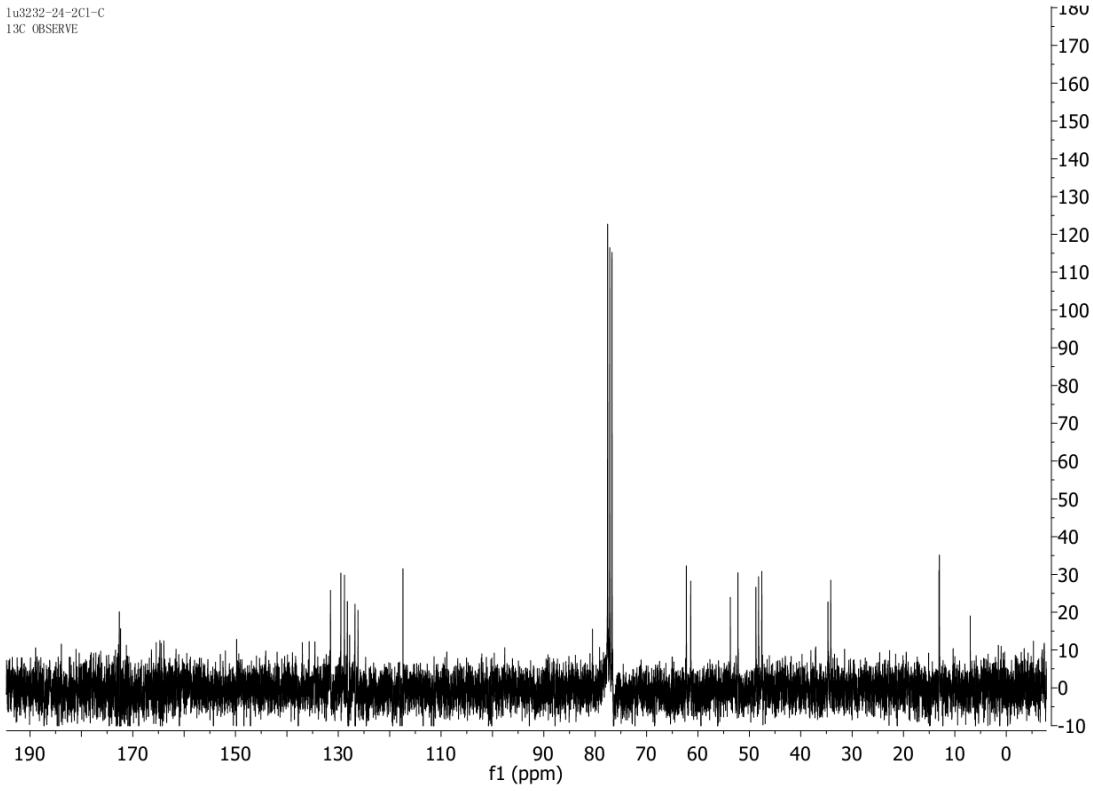

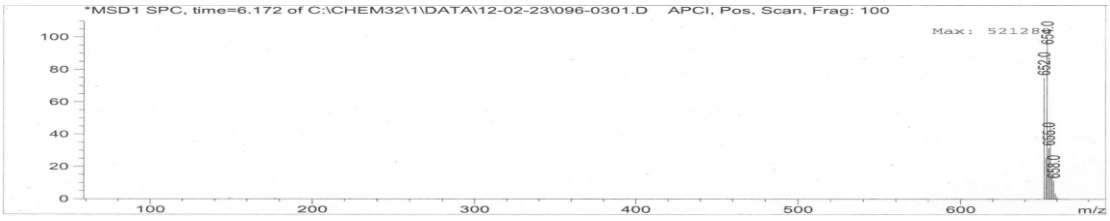

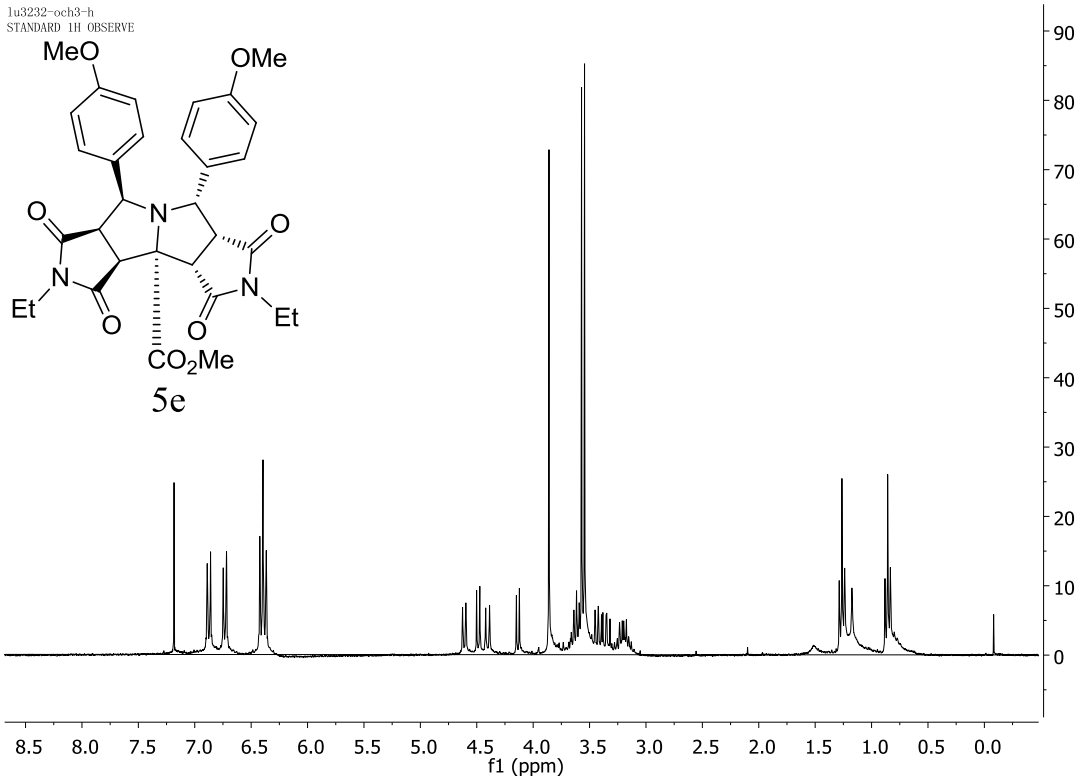

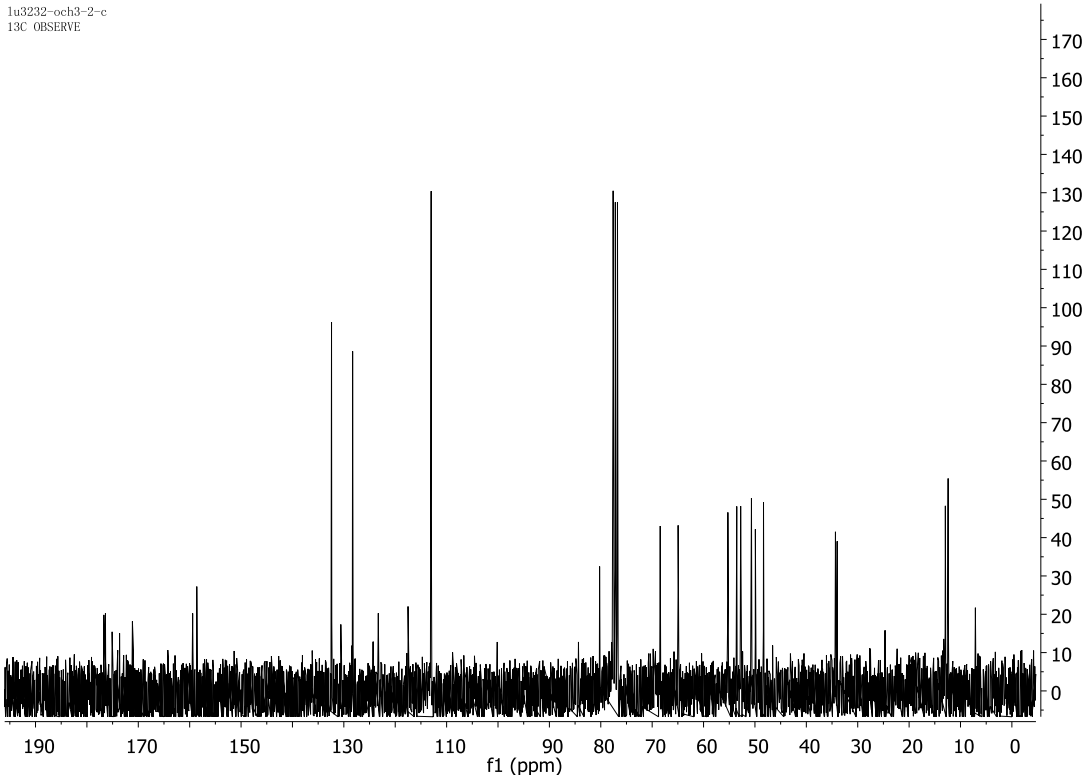

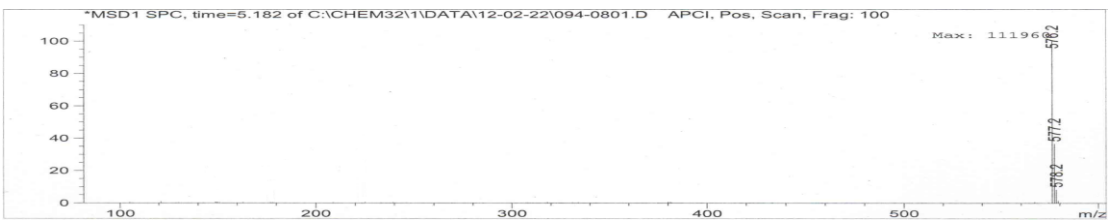

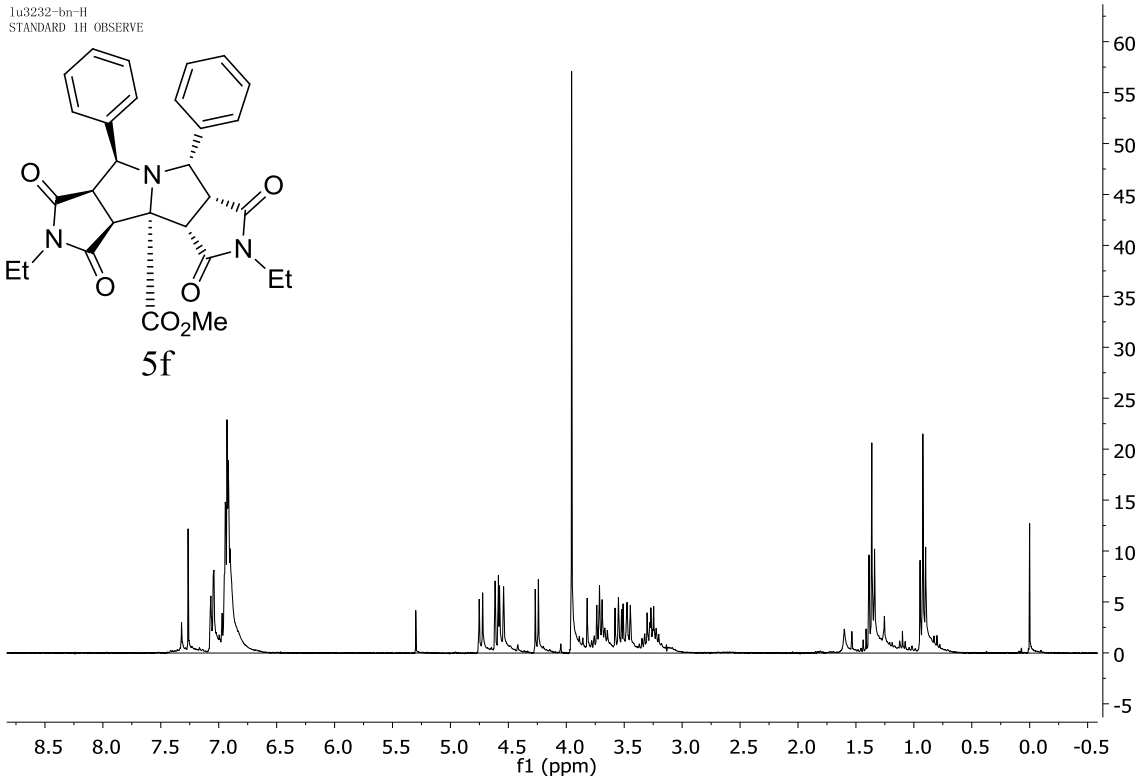
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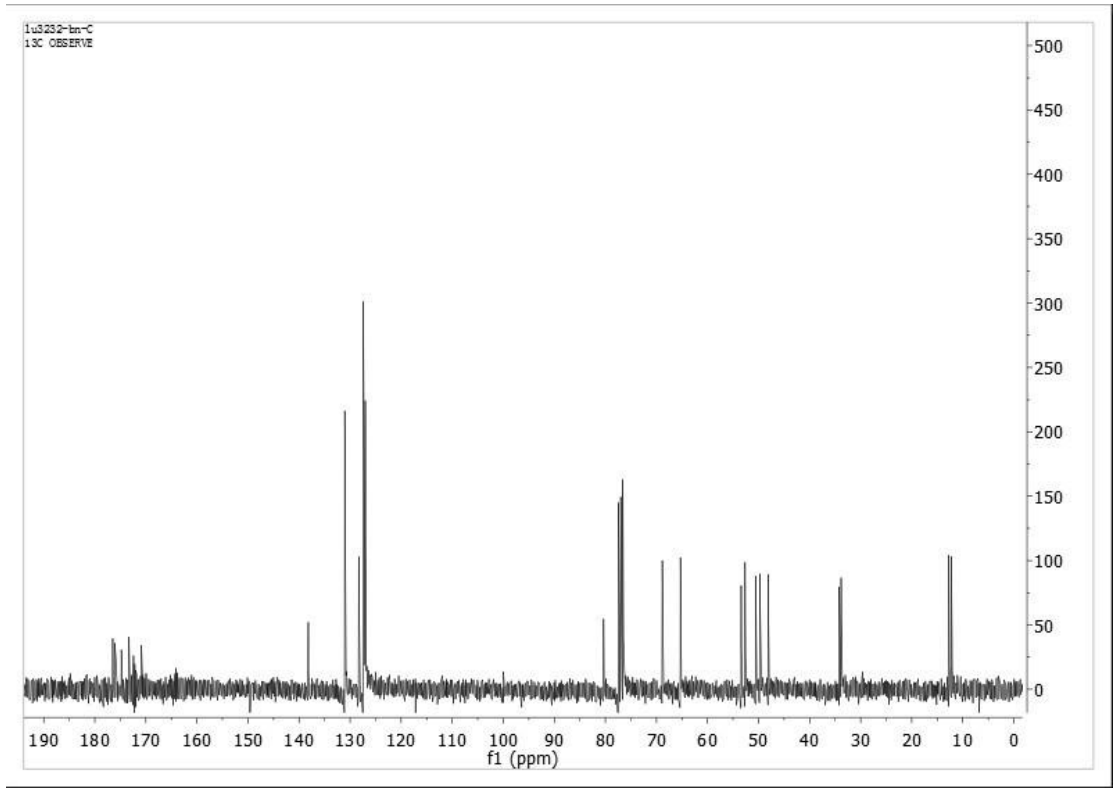
Et
N
O
O
N
Et
O
CO2Me
5f
f1 (ppm)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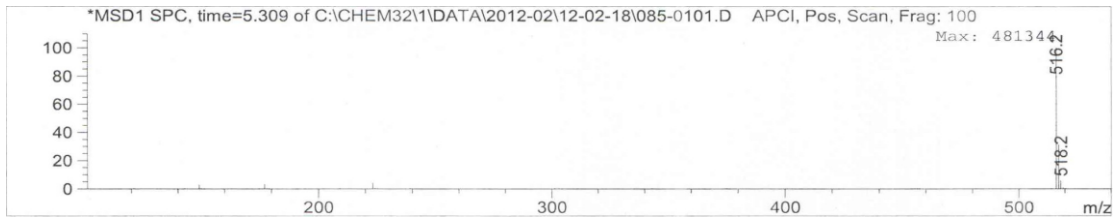
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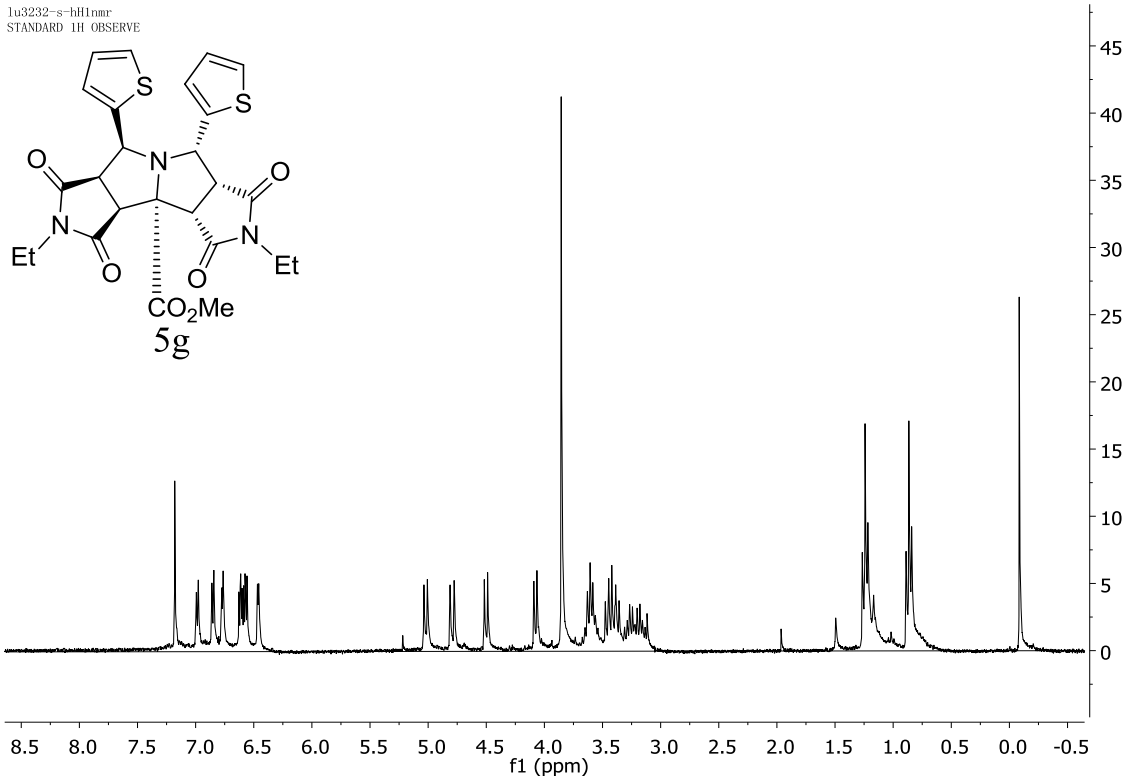
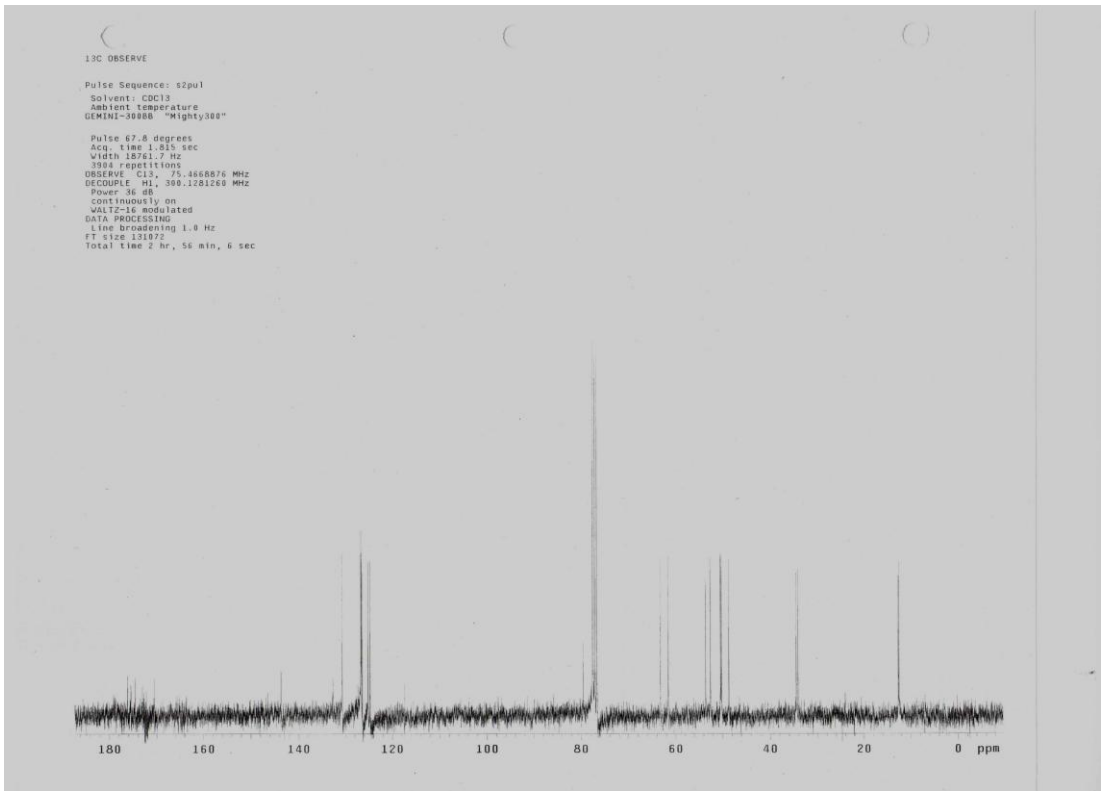
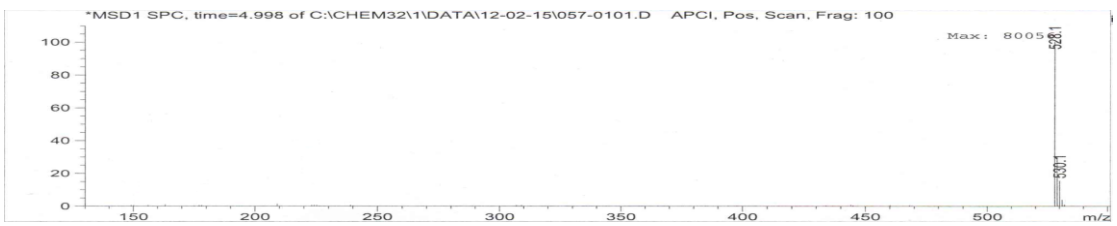
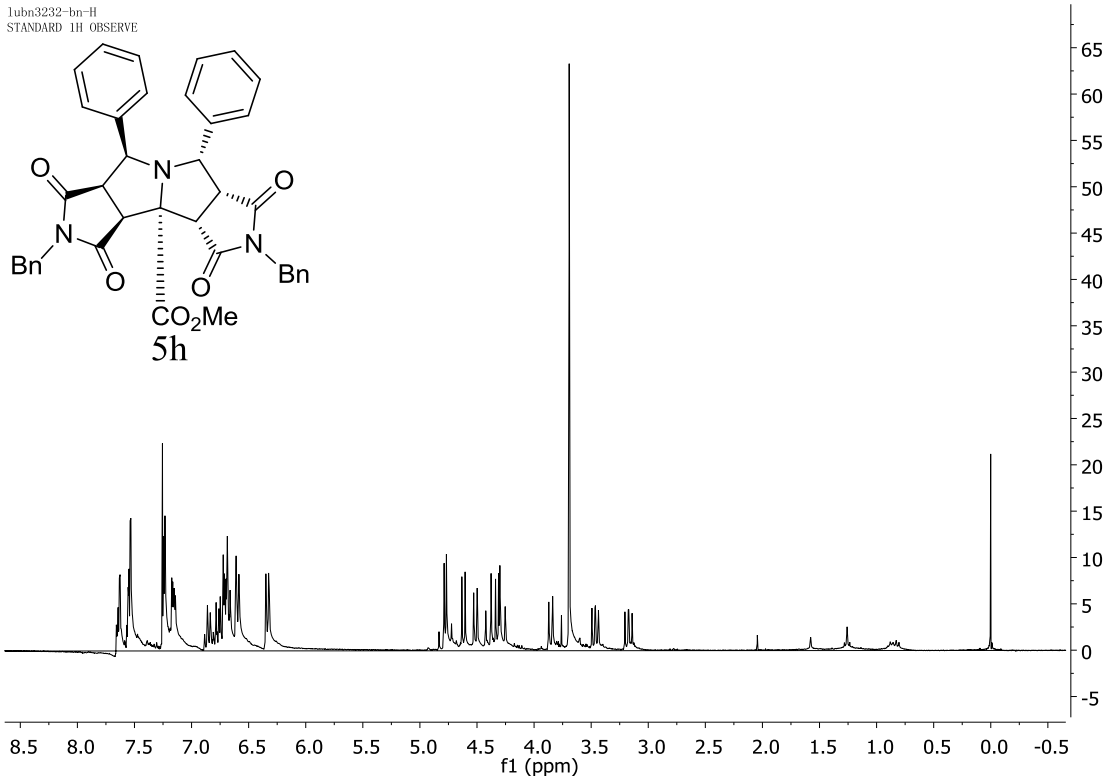
m/z





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Bn
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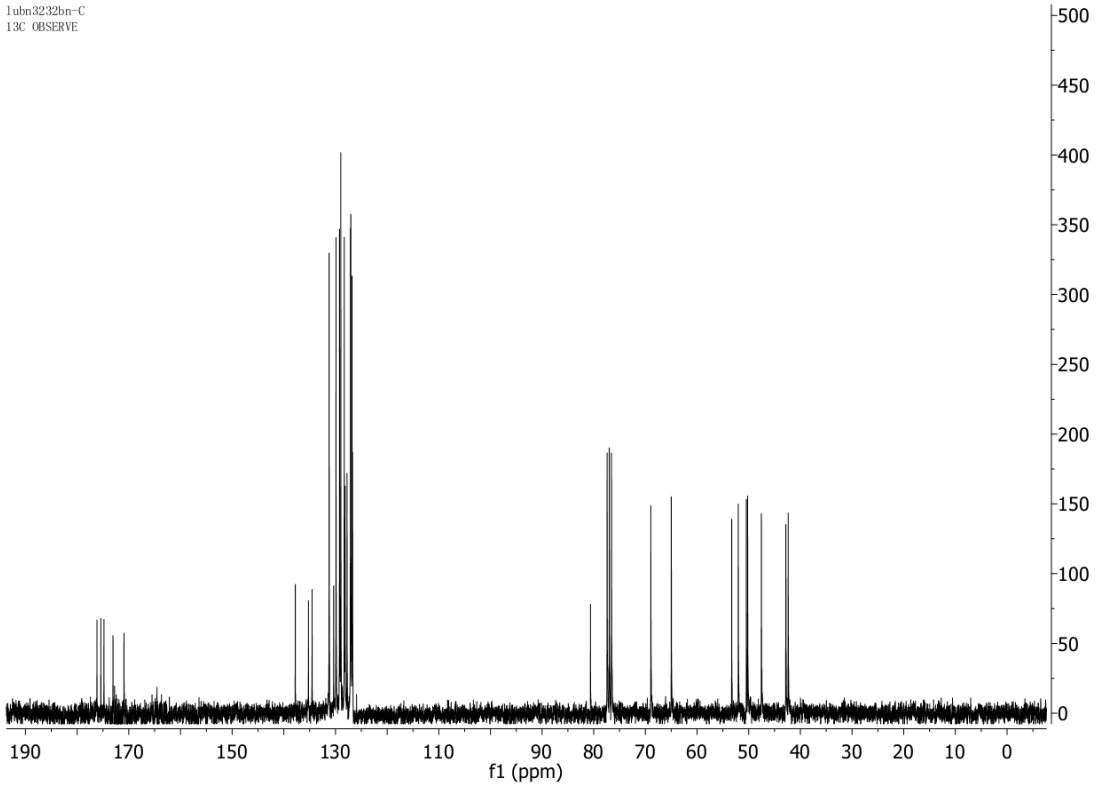
CO2Me
5h
f1 (ppm)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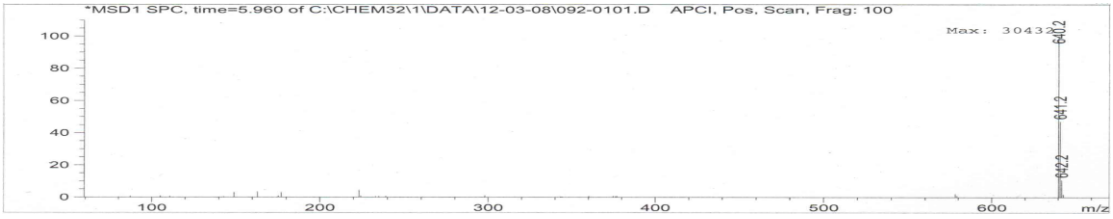
f1 (ppm)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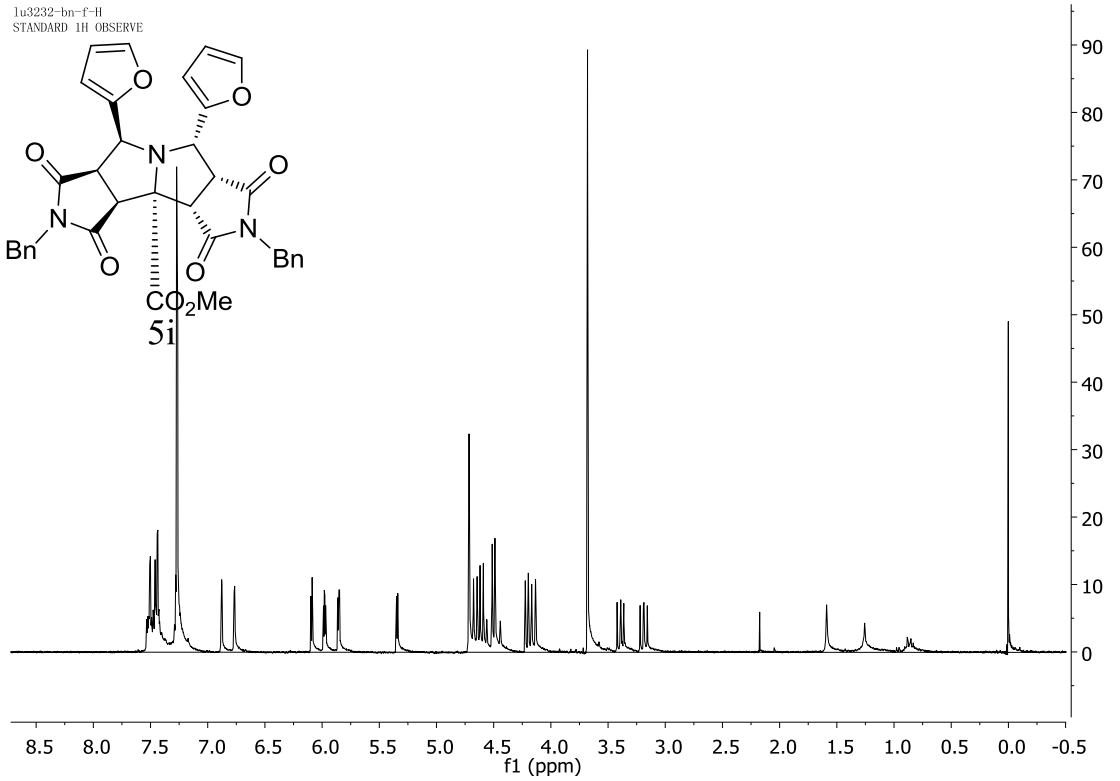
m/z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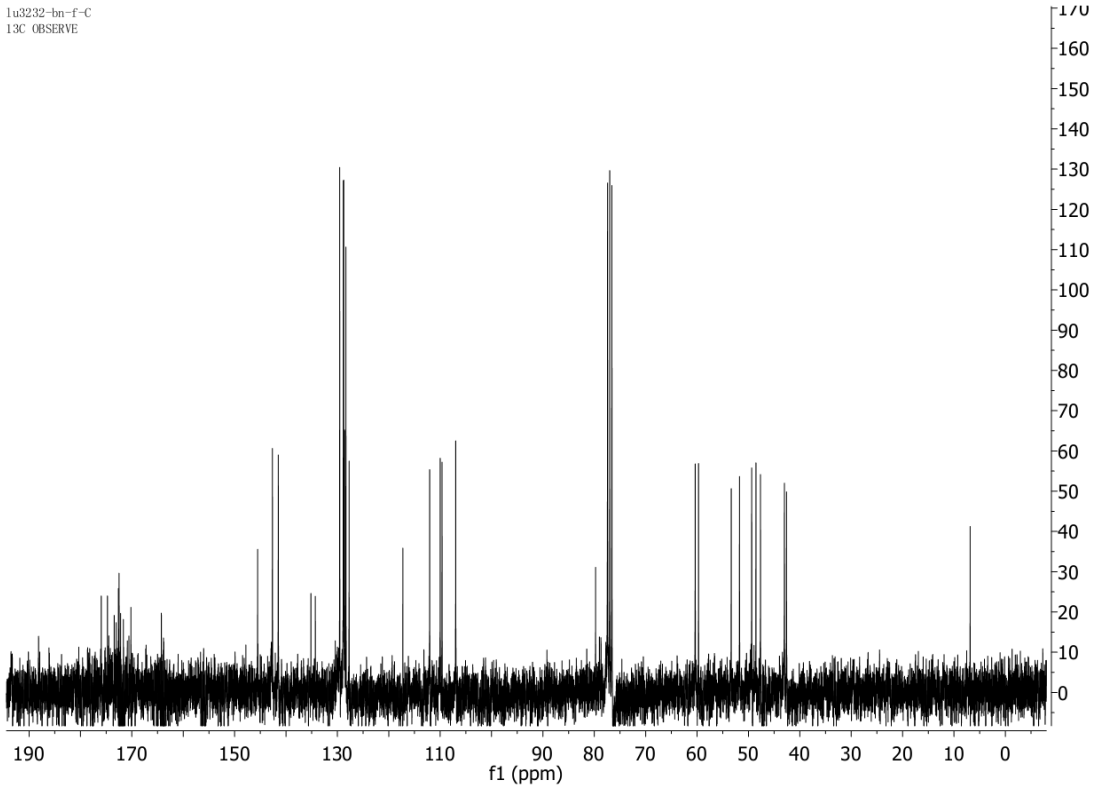
5i
f1 (ppm)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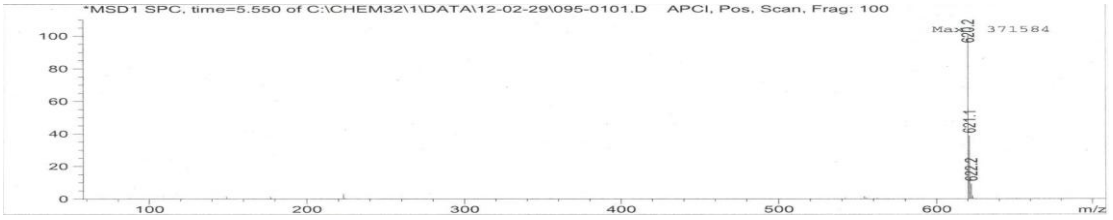
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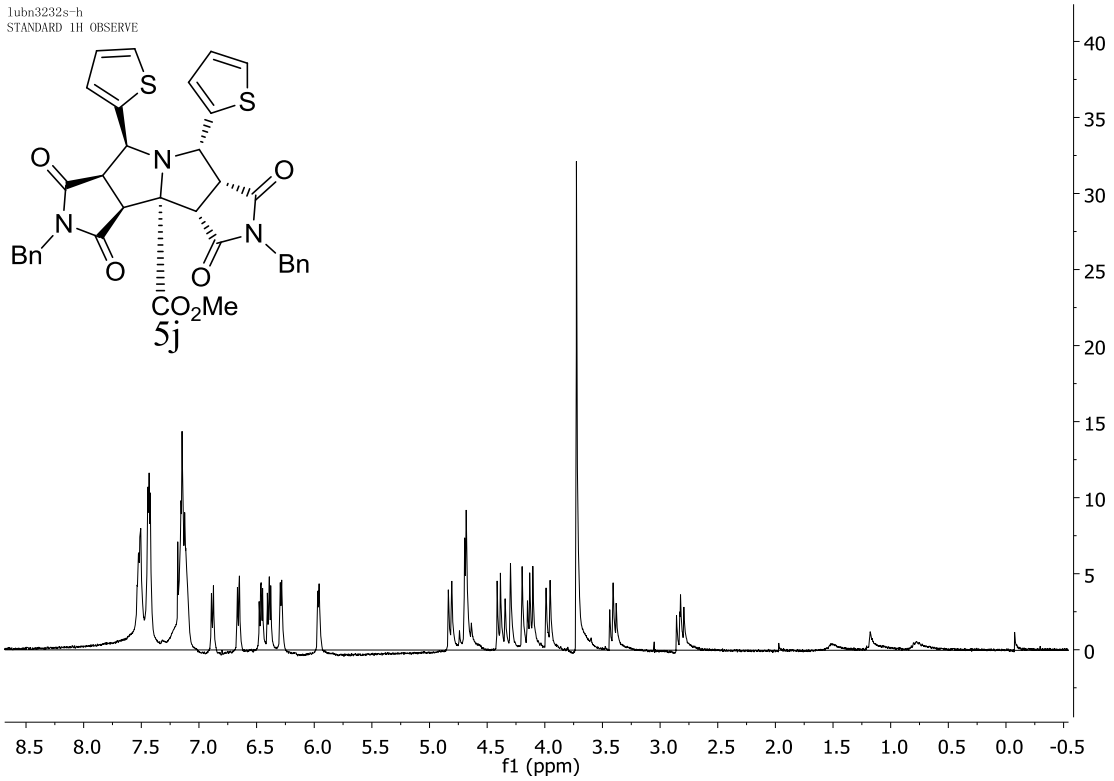
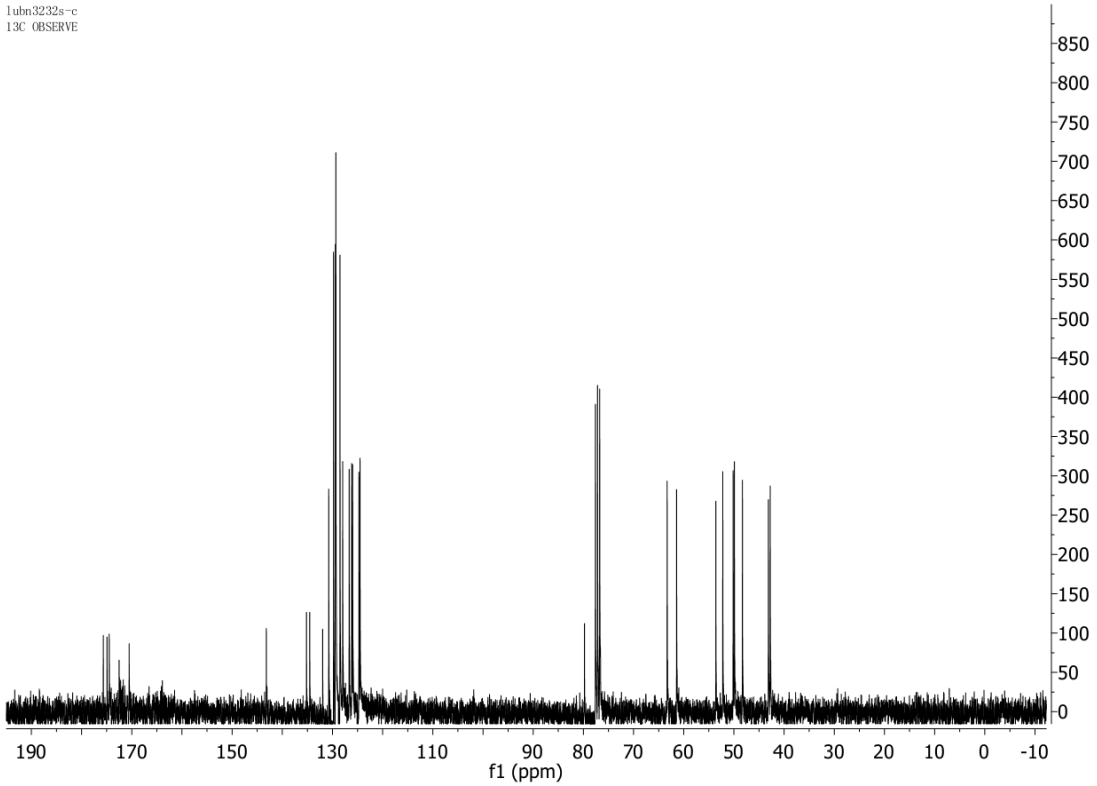
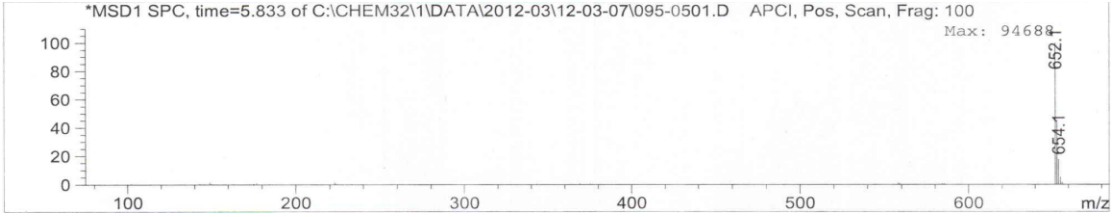
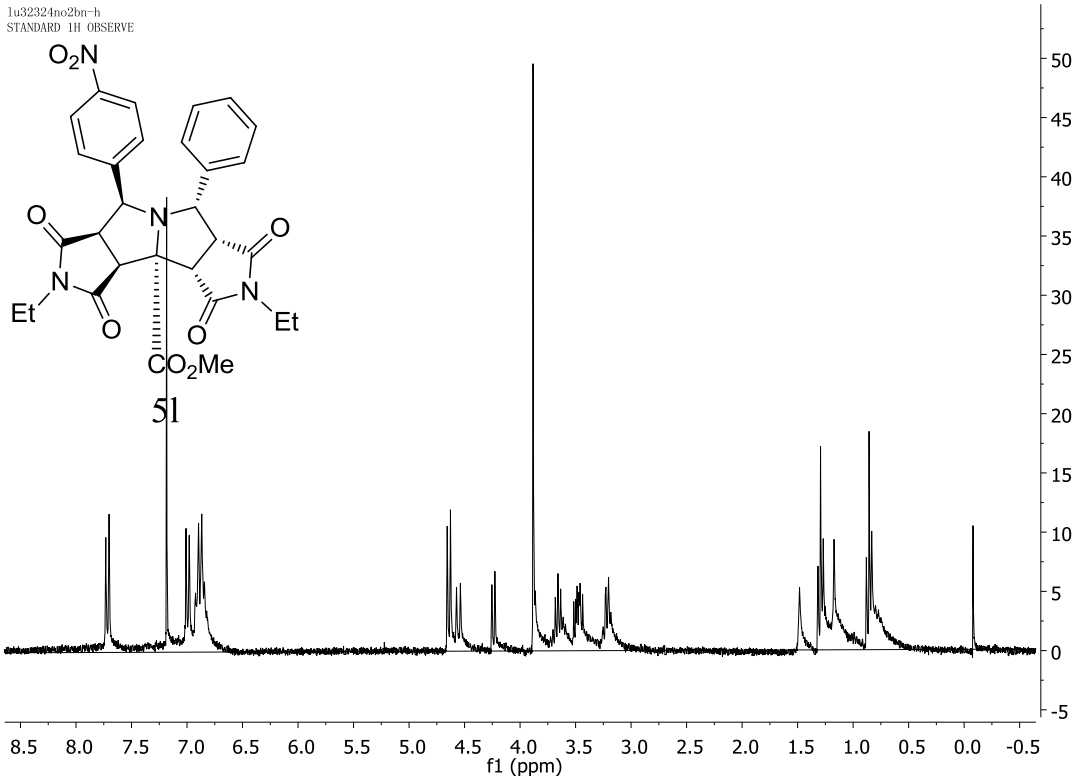
m/z





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Et
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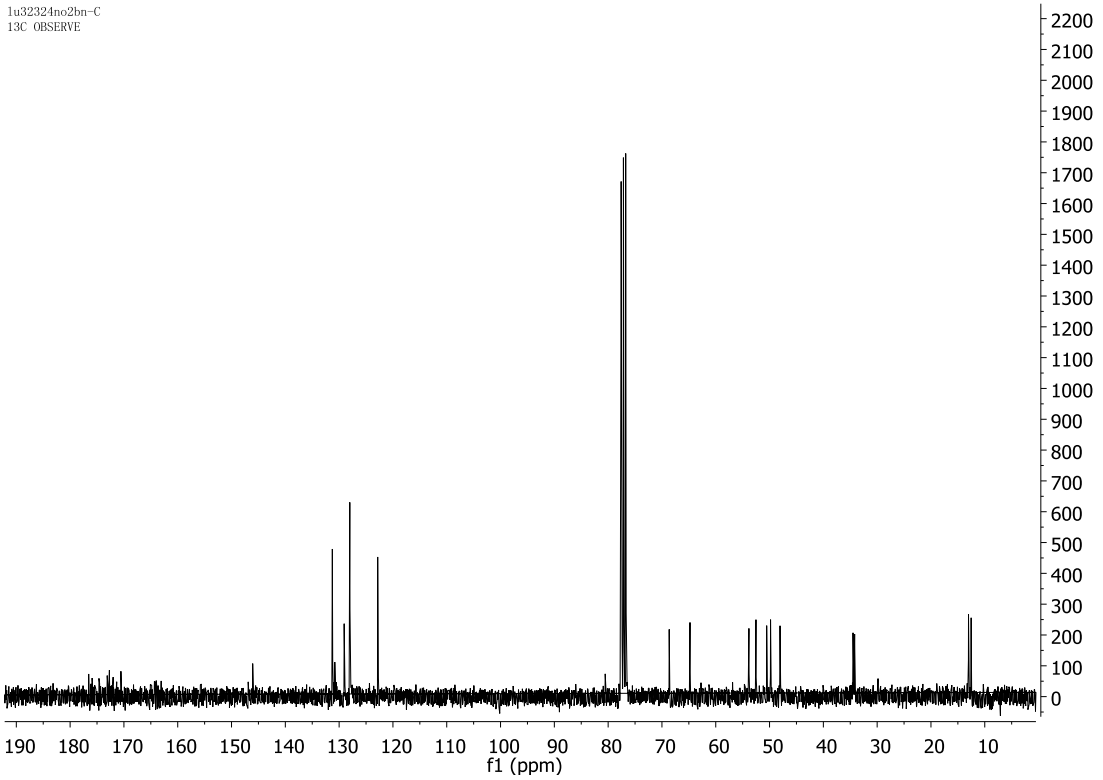
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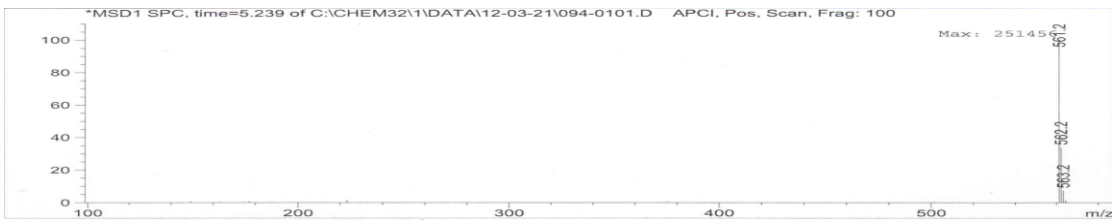
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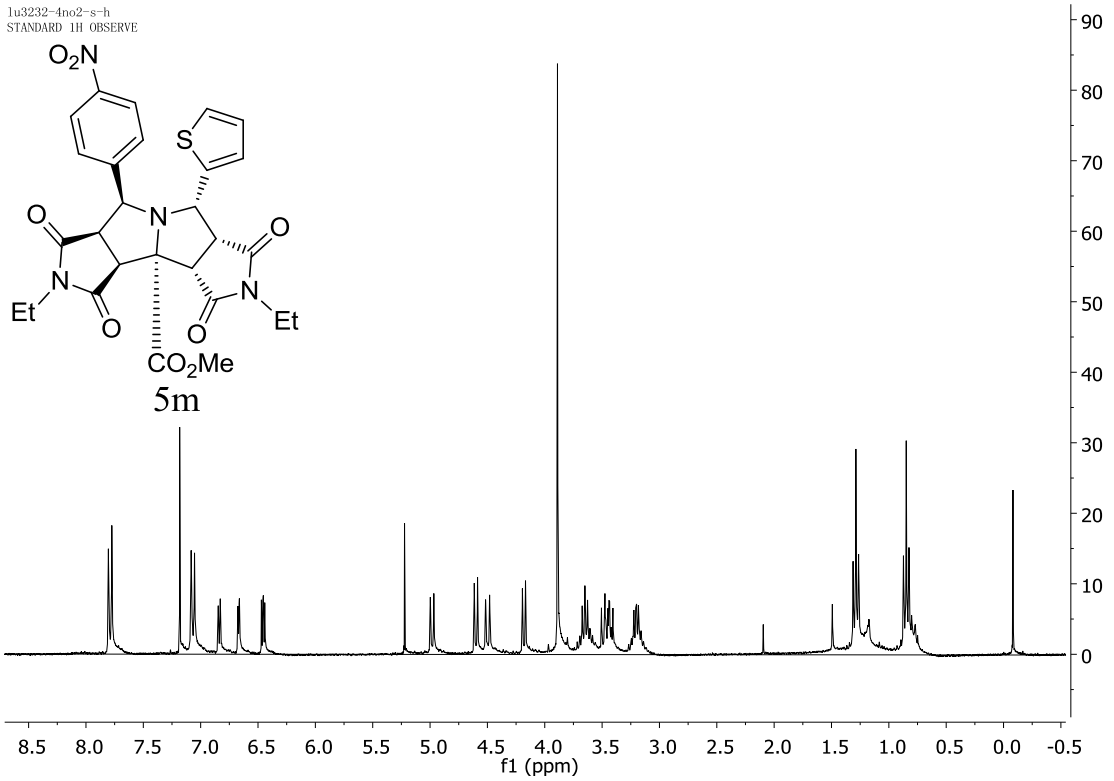
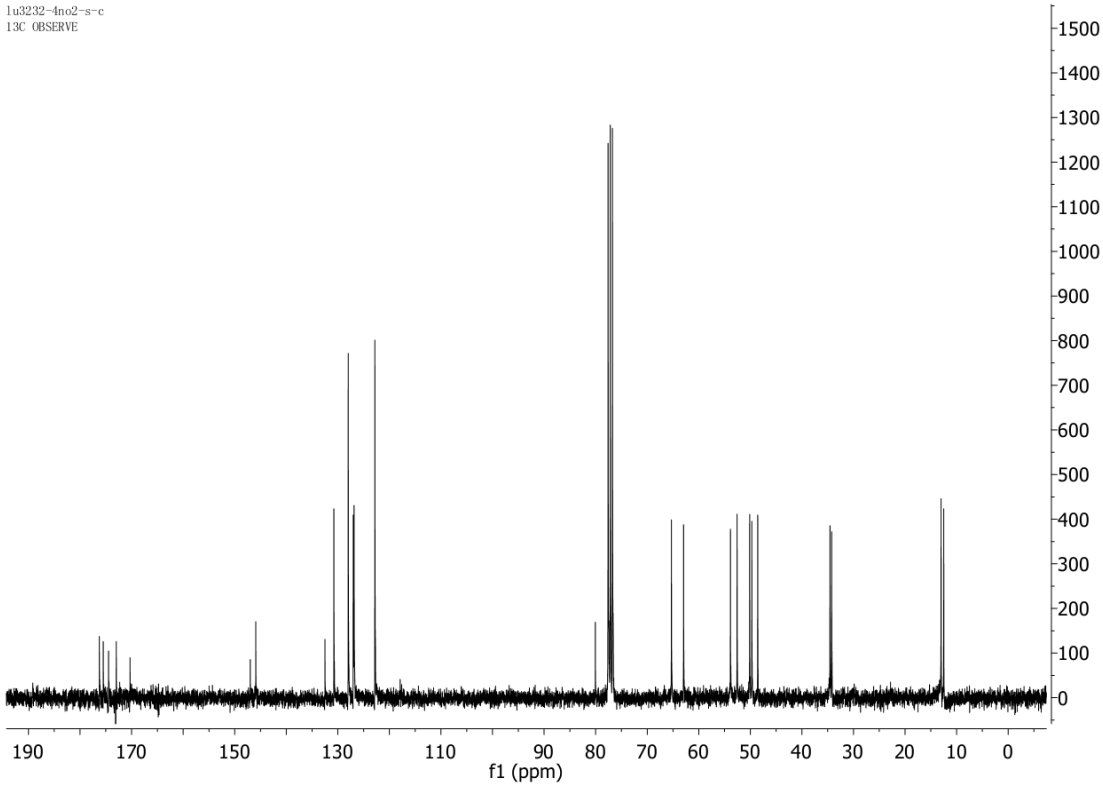
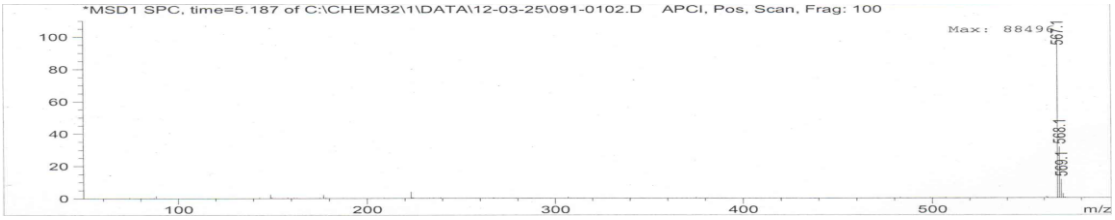
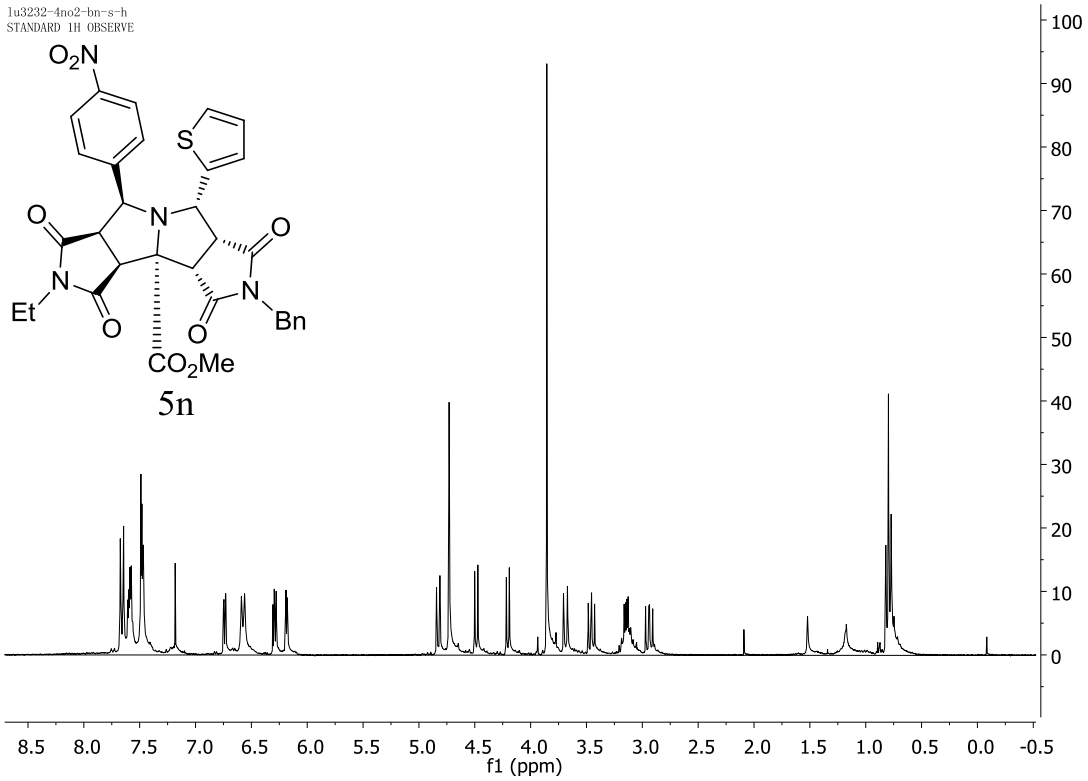
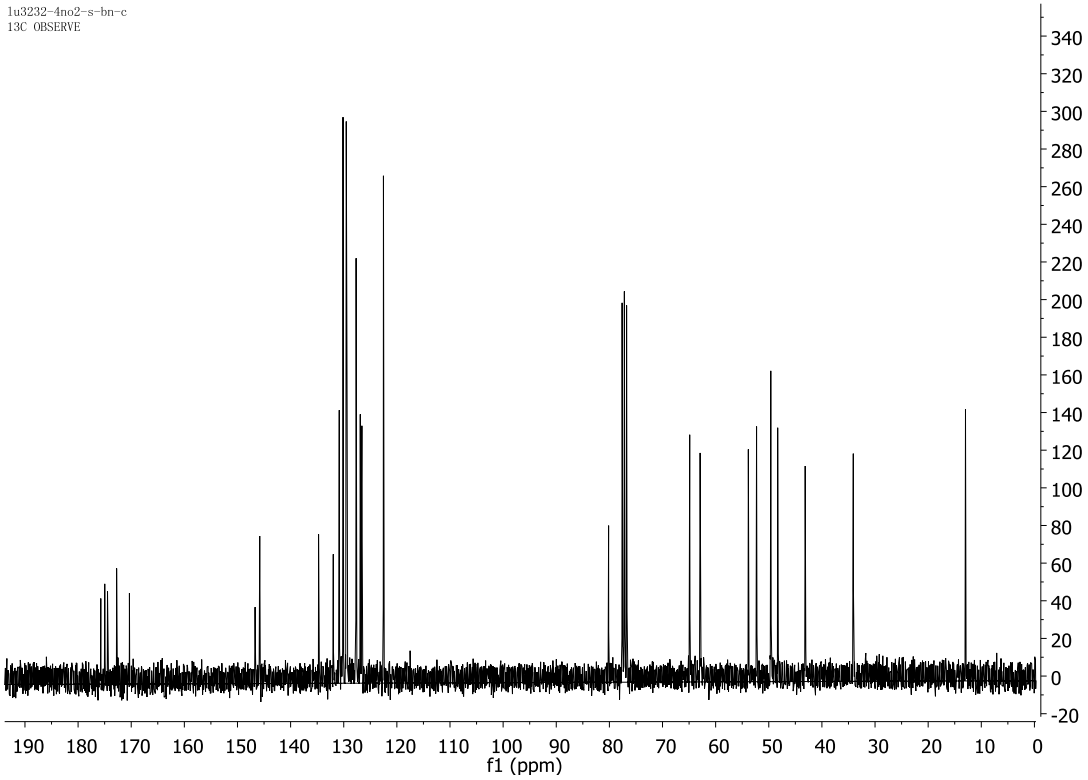
m/z








lu3232-4no2-bn-s-h
STANDARD 1H OBSERVE
O2N
S
O
N
O
N
Et
O
O
N
Bn
O
CO2Me
5n
f1 (ppm)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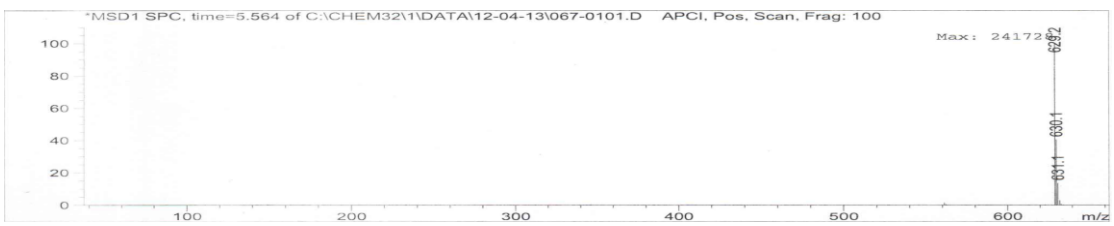
13C OBSERVE
f1 (ppm)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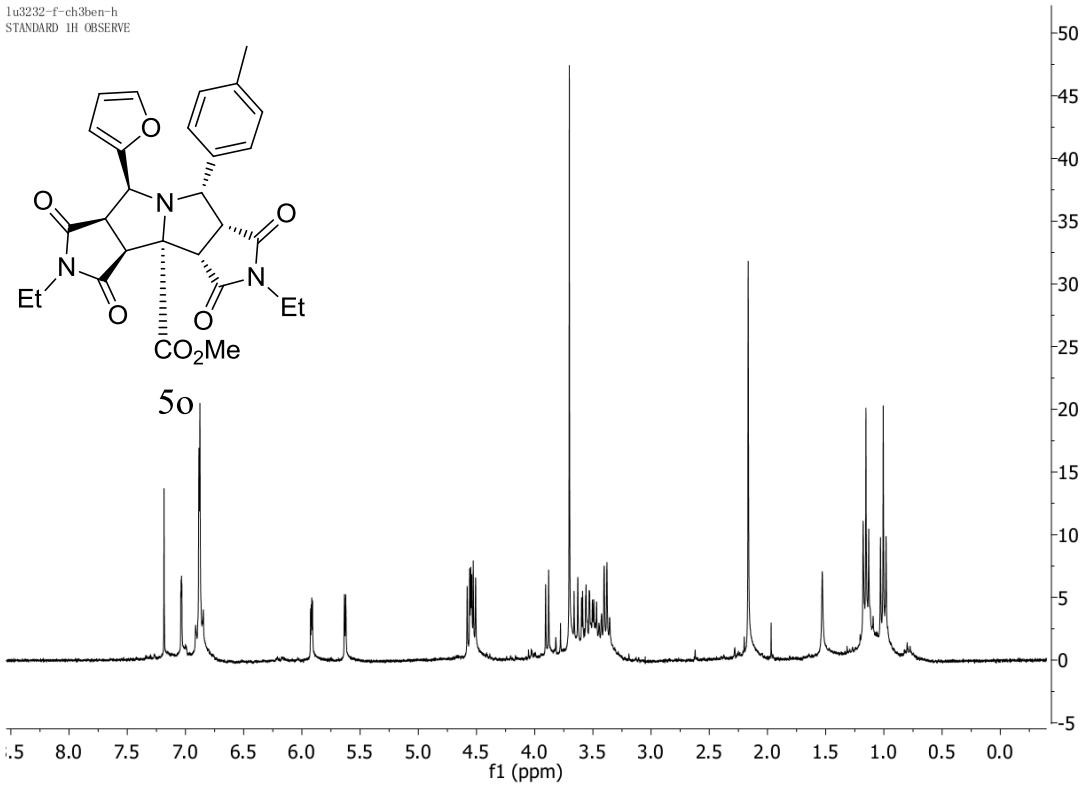
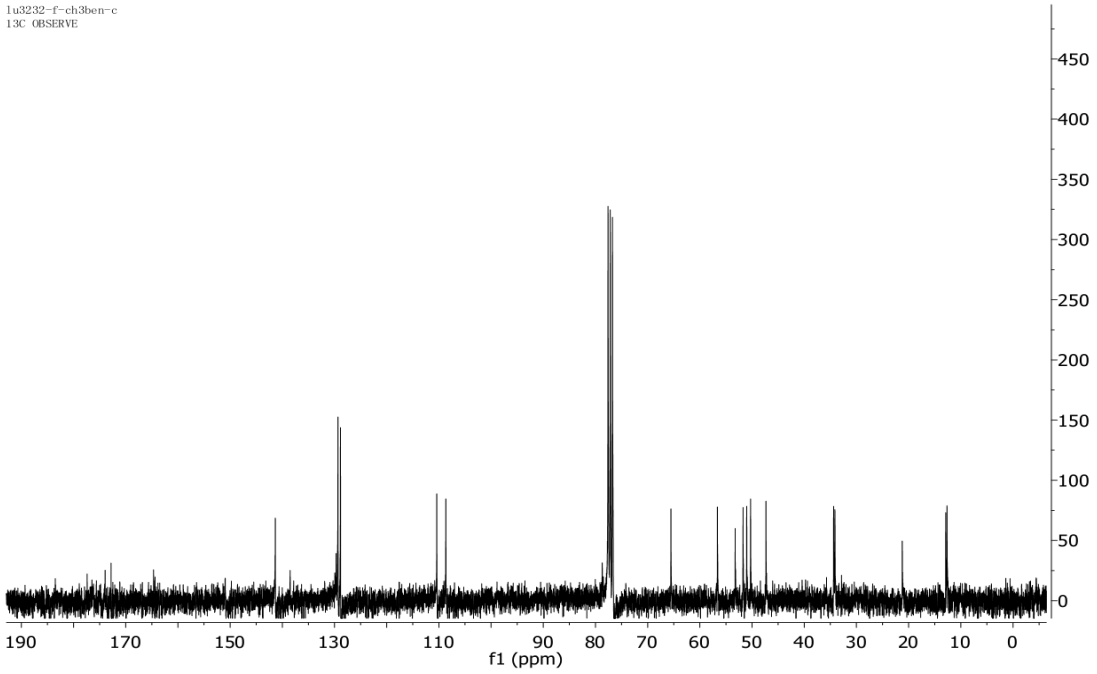
630.1
631.1
m/z


1u3232-f-ch3ben-h
STANDARD 1H OBSERVE
O
N
O
N
Et
O
O
N
Et
O
CO2Me
5o
f1 (ppm)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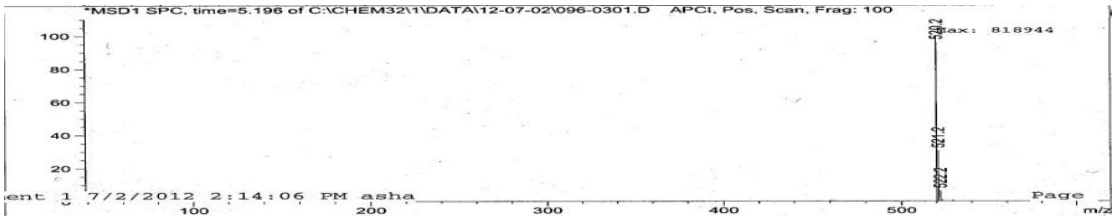
f1 (ppm)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7/2/2012 2:14:06 PM asha
Page
m/z