Selective synthesis and reactivity expansion of α, β-unsaturated geminal diazides

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Supplementary Information

1. General Information

General remarks. Commercially available materials were purchased from Energy Chemical (Shanghai, China), Bidepharm (Shanghai, China), Titan (Shanghai, China), and were used as received without further purification. Solvents were purchased from Titan. Dichloromethane, THF, toluene, $CHCl_3$ and CH_3OH were distilled after the treatment with P_2O_5 or metal sodium. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (Yantai Jiangyou Silica gel Development Co.,LTD, Yantai, China) using UV light as a visualizing agent. Commercial silica gel (Qingdao Haiyang Chemical Co.,LTD, Qingdao, China) was used for column chromatography. ^{1}H- and ^{13}C-NMR spectra were recorded on 400 MHz or 600 MHz spectrometers (Agilent Tech., Palo Alto, USA). ^{1}H-NMR spectra were referenced to Chloroform-*d* (7.26 ppm) or DMSO-d_6 (2.50 ppm), and reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet). Chemical shifts of the ^{13}C-NMR spectra were measured relative to chloroform-*d* (77.23 ppm) or DMSO-d_6 (39.51 ppm). Mass spectral data were obtained from Bruker Daltonics Data analysis 3.2 mass spectrometer (Bruker, Beijing, China).

Caution! Geminal diazides are potentially hazardous and should be handled with appropriate care and safety equipment.

2. General procedures

General procedures A for the synthesis of 2-phenyl-2H-chromene-3-carbaldehyde derivatives 1a-1f. According to the previous report,[1–3] salicylaldehyde derivatives (4 mmol) and unsaturated aldehydes (4.4 mmol) were taken in a round bottom flask and 5 ml of DMF was added to it followed by pyrrolidine (1.6 mmol). Then it was stirred at room temperature. The progress of the reaction was monitored by TLC and was found to be completed after 12 h. 30 ml of water was added and extracted with ethyl acetate. The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and concentrated in rotavapor. Column chromatography on silica gel (petroleum ether/EtOAc =10/1) was performed with hexane-ethyl acetate as eluent to afford the corresponding 2-phenyl-2*H*-chromene-3-carbaldehyde derivatives **1a-1f**.

General procedures B for the synthesis of cinnamaldehyde derivatives 1g-1w. According to the previous report,[4–6] benzaldehyde derivatives (1 mmol) and propanal (1.5 mmol) were added successively at room temperature to a stirred suspension of powdery KOH (1 mmol) in the EtOH (5 mL). Until the condensation was complete (TLC monitoring), 30 ml of water was added and extracted with ethyl acetate (3× 10 mL). The combined organic layers were washed with water (2× 5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc =30/1) to

afford the corresponding products cinnamaldehyde derivatives **1g-1w**.

General procedures C for the synthesis of α, β-unsaturated geminal diazides 2a-2f. To an over-dried reaction tube were added $Yb(TfO)_3$ (0.02 mmol) and compounds **1a-1d** (0.2 mmol) under N_2. Then redistilled dichloromethane (1 mL) and $TMSN_3$ (0.8 mmol) were added successively by syringe. The mixture was stirred at room temperature for 24 h. The reaction solution was condensed and purified by column chromatography on neutral aluminum oxide with hexane-ethyl acetate (30:1) as eluent to afford the corresponding α, β-unsaturated geminal diazides **2a-2f**.

General procedures D for the synthesis of α, β-unsaturated bistriazoles 5b-5t. To an over-dried reaction tube were added $Yb(TfO)_3$ (0.05 mmol) and compounds **1g-1w** (0.5 mmol) under N_2. Then redistilled dichloromethane (2 mL) and $TMSN_3$ (2 mmol) were added successively by syringe. After stirring for 24 h in room temperature, the reaction solution was condensed and purified by column chromatography on neutral aluminum oxide (hexane/EtOAc=30/1). The crude diazides, 4-ethynylanisole (1.5 mmol), sodium L-ascorbate (0.5 mmol), $CuSO_4 \cdot 5H_2O$ (0.05 mmol), DMF (2 mL) was added to a round-bottom flask. The mixture was stirred for 12 h at room temperature and was monitored by TLC. Upon completion, ethyl acetate was added, and the mixture was washed with saturated aqueous NaCl and dried with Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with hexane-ethyl acetate (2:1) as eluent to afford compound α, β-unsaturated bistriazoles **5b-5t**.

General procedures for the synthesis of 6a. To a round-bottom flask were added diazide **2a** (0.2 mmol), sodium L-ascorbate (0.2 mmol), $CuSO_4 \cdot 5H_2O$ (0.02 mmol) and DCM (20 mL). The mixture was stirred for 12 h at room temperature and was monitored by TLC. Upon completion, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with hexane-ethyl acetate (5:1) as eluent to afford compound **6a**.

General procedures for the synthesis of 5a and 6b. To a round-bottom flask were added diazide **2a** (0.2 mmol), 4-ethynylanisole (**4a**, 0.8 mmol) or 1,7-octadiyne (**7**, 0.44 mmol), sodium L-ascorbate (0.2 mmol), $CuSO_4 \cdot 5H_2O$ (0.02 mmol) and DMF (5 mL). The mixture was stirred for 12 h at room temperature and was monitored by TLC. Upon completion, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with hexane-ethyl acetate (2:1) as eluent to afford compound **5a** or **6b**.

General procedures E for the synthesis of α, β-unsaturated bis(heterocyclyl)methane 9a-9k. To an over-dried reaction tube were added $Cu(TfO)_2$ (0.02 mmol), diazides **2a** or **2g** (0.2 mmol) and heterocycle **8a-8j** (0.8 mmol) under N_2. Then redistilled dichloromethane (1 mL) was added by syringe. The mixture was stirred at room temperature for 5 h. The reaction solution was condensed and purified by column chromatography on silica gel with hexane-ethyl acetate (2:1) as eluent to afford the corresponding α, β-unsaturated bis(heterocyclyl)methane **9a-9k**.

General procedures F for the synthesis of (2-phenyl-2H-chromen-3-yl)methanimine derivatives 11a-11c. To an over-dried reaction tube were added $Cu(TfO)_2$ (0.02 mmol), diazides **2a** (0.2 mmol) and amino linked to strong electron-withdrawing group **10a-10c** (0.4 mmol) under

N_2. Then redistilled dichloromethane (1 mL) was added by syringe. The mixture was stirred at room temperature for 5 h. The reaction solution was condensed and purified by column chromatography on silica gel with hexane-ethyl acetate (2:1) as eluent to afford the corresponding α, β-unsaturated bis(heterocyclyl)methane **11a-11c**.

3. Experimental data

3-(diazidomethyl)-2-phenyl-2H-chromene (**2a**). According to the general procedure C using (0.05 g, 0.21 mmol, 1.0 equiv) 2-phenyl-2*H*-chromene-3-carbaldehyde **1a**, 3-(diazidomethyl)-2-phenyl-2*H*-chromene (0.045 g, 0.15 mmol, 70%) (**2a**) was obtained and chromatography (PE:EA=30:1) as yellow solid. TLC: R_f = 0.8 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 – 7.29 (m, 6H), 7.15 (td, *J* = 7.8, 1.7 Hz, 1H), 7.05 (s, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.1, 138.2, 131.1, 129.5, 129.2, 129.1, 128.3, 128.0, 123.9, 122.1, 121.0, 116.5, 76.6, 75.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}N_6O$: 305.1145; found 305.1147. For gram scale reaction, using (1.18 g, 5 mmol, 1.0 equiv) 2-phenyl-2*H*-chromene-3-carbaldehyde **1a**, 3-(diazidomethyl)-2-phenyl-2*H*-chromene (0.924 g, 3.04 mmol, 61%) (**2a**) was obtained.

2-phenyl-2H-chromene-3-carbonitrile (**3**). According to the general procedure C, when using other catalyst, such as $Cu(TfO)_2$, the Schmidt product *2-phenyl-2H-chromene-3-carbonitrile* (**3**) was obtained and chromatography (PE:EA=20:1) as yellow solid. TLC: R_f = 0.6 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 (s, 1H), 7.45 (m, 5H), 7.33 (m, 2H), 7.02 (td, *J* = 7.8, 1.7 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.19 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.1, 139.2, 138.0, 133.7, 129.9, 129.4, 129.3, 127.7, 122.7, 119.7, 117.4, 116.9, 106.7, 75.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{12}NO$: 234.0913; found 234.0912.

3-(diazidomethyl)-2-phenyl-2H-chromen-7-yl acetate (**2b**). According to the general procedure C using (0.06 g, 0.2 mmol, 1.0 equiv) 3-formyl-2-phenyl-2*H*-chromen-7-yl acetate **1b**, 3-(diazidomethyl)-2-phenyl-2*H*-chromen-7-yl acetate (0.038 g, 0.1 mmol, 52%) (**2b**) was obtained and chromatography (PE:EA=20:1) as colorless oil. TLC: R_f = 0.5 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 5H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.43 (dd, *J* = 10.1, 2.0 Hz, 1H), 5.94 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.88 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.71 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 155.1, 144.1, 139.6, 128.9, 127.4, 127.3, 126.4, 119.7, 117.6, 115.6, 114.1, 77.5, 74.7, 20.6. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ calcd for $C_{18}H_{18}N_7O_3$: 380.1466; found 380.1461.

3-(diazidomethyl)-7-methoxy-2-phenyl-2H-chromene (**2c**). According to the general procedure C using (0.057 g, 0.2 mmol, 1.0 equiv) 7-methoxy-2-phenyl-2*H*-chromene-3-carbaldehyde **1c**, 3-(diazidomethyl)-7-methoxy-2-phenyl-2*H*-chromene (0.02 g, 0.059 mmol, 30%) (**2c**) was obtained and chromatography (PE:EA=30:1) as yellow oil. TLC: R_f = 0.7 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.33 (m, 5H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.78 (dt, *J* = 9.2, 1.1 Hz, 1H), 6.67 (dd, *J* = 8.6, 0.8 Hz, 1H), 6.04 (s, 1H), 5.94 – 5.86 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 153.8, 140.1, 128.8, 128.7, 127.3, 127.1, 125.1, 120.7, 118.5, 115.1, 112.5,

77.01, 73.9, 63.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{14}N_6O_2Na$: 357.1070; found 357.1069.

3-(diazidomethyl)-8-methoxy-2-phenyl-2H-chromene (**2d**). According to the general procedure C using (0.057 g, 0.2 mmol, 1.0 equiv) 8-methoxy-2-phenyl-2*H*-chromene-3-carbaldehyde **1d**, 3-(diazidomethyl)-8-methoxy-2-phenyl-2*H*-chromene (0.041 g, 0.123 mmol, 61%) (**2d**) was obtained and chromatography (PE:EA=30:1) as yellow oil. TLC: R_f = 0.8 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.30 (m, 3H), 6.88 (s, 1H), 6.86 – 6.83 (m, 1H), 6.79 (m, 2H), 5.91 (s, 1H), 4.94 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 141.4, 137.8, 129.3, 128.9, 128.3, 127.7, 123.4, 121.3, 120.8, 119.9, 113.9, 77.2, 76.7, 56.2. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ calcd for $C_{17}H_{18}N_7O_2$: 352.1516; found 352.1513.

3-(diazidomethyl)-2H-chromene (**2e**). According to the general procedure C using (0.032 g, 0.2 mmol, 1.0 equiv) 2*H*-chromene-3-carbaldehyde **1e**, *3-(diazidomethyl)-2H-chromene* (0.035 g, 0.152 mmol, 76%) (**2e**) was obtained and chromatography (PE:EA=30:1) as yellowy solid. TLC: R_f = 0.8 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.24 – 7.16 (m, 2H), 6.93 (td, *J* = 7.5, 1.2 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 6.08 (s, 1H), 4.73 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 153.7, 130.7, 128.3, 127.8, 123.3, 122.2, 121.4, 116.0, 77.1, 64.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_9ON_6$: 229.0832; found: 229.0834.

3-(diazidomethyl)-2-methyl-2H-chromene (**2f**). According to the general procedure C using (0.035 g, 0.2 mmol, 1.0 equiv) 2-methyl-2H-chromene-3-carbaldehyde **1f**, *3-(diazidomethyl)-2-methyl-2H-chromene* (0.02 g, 0.084 mmol, 42%) (**2f**) was obtained and chromatography (PE:EA=30:1) as yellow oil (it is red in Chloroform-*d*). TLC: R_f = 0.8 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.98 (td, *J* = 7.7, 1.7 Hz, 1H), 6.88 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.70 (td, *J* = 7.5, 1.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 5.03 (s, 1H), 4.72 (q, *J* = 6.6 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 130.3, 130.1, 127.4, 122.9, 121.3, 120.4, 116.4, 77.0, 70.7, 19.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_9ON_6$: 241.0832; found 241.0831. (two hydrogens were lost under the HRMS condition)

1,1'-((2-phenyl-2H-chromen-3-yl)methylene)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5a**, 0.108 g, 0.191 mmol, 95%) (**2a**) was obtained and chromatography (PE:EA=2:1) as white solid. TLC: R_f = 0.2 (PE:EA 2:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.86 (s, 1H), 8.70 (s, 1H), 8.08 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.14 (m, 6H), 7.06 – 6.98 (m, 4H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.78 – 6.70 (m, 2H), 5.99 (s, 1H), 3.86 – 3.71 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 159.8, 152.1, 147.6, 147.3, 137.2, 131.6, 129.6, 129.0, 128.7, 128.0, 127.7, 127.4, 127.3, 126.1, 122.9, 122.2, 121.1, 120.9, 120.9, 116.5, 114.8, 114.7, 76.6, 72.5, 55.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{34}H_{28}N_6O_3Na$: 591.2115; found 591.2110.

(E)-1,1'-(2-methyl-3-phenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5b**). According to the general procedure D using (0.07 mL, 0.5 mmol, 1.0 equiv) (*E*)-2-methyl-3-phenylacrylaldehyde **1g**, (*E*)-1,1'-(2-methyl-3-phenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.101 g, 0.21 mmol, 42%) (**5b**) was obtained and chromatography (PE:EA=10:3) as white solid. TLC: R_f = 0.2 (PE:EA 10:2) [UV]. ^{1}H NMR (400

MHz, DMSO-d_6) δ 8.81 (s, 2H), 8.29 (s, 1H), 7.87 (d, J = 8.8 Hz, 4H), 7.49 – 7.24 (m, 5H), 7.03 (d, J = 8.8 Hz, 4H), 6.38 (s, 1H), 3.80 (s, 6H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.4, 135.7, 131.1, 129.7, 128.9, 128.3, 127.4, 123.1, 120.9, 114.8, 76.9, 55.7, 15.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{28}H_{26}N_6O_2Na$: 501.2009; found 501.2006.

(E)-1,1'-(2-benzylideneheptane-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5c**). According to the general procedure D using (0.104 mL, 0.5 mmol, 1.0 equiv) (*E*)-2-methyl-3-phenylacrylaldehyde **1h**, (*E*)-1,1'-(2-benzylideneheptane-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.09 g, 0.168 mmol, 34%) (**5c**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 2H), 8.27 (s, 1H), 7.87 (d, J = 8.7, 4H), 7.44 – 7.28 (m, 5H), 7.03 (d, J = 8.7, 4H), 6.32 (s, 1H), 3.79 (s, 6H), 2.32 (t, J = 7.4, 2H), 1.32 (p, J = 7.3 Hz, 2H), 1.19 – 1.07 (m, 4H), 0.73 (t, J = 6.9, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.4, 135.7, 131.2, 129.2, 129.0, 128.3, 127.4, 123.0, 121.1, 114.8, 75.3, 55.7, 31.5, 29.0, 27.2, 22.0, 14.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{36}H_{34}N_6O_2Na$: 557.2635; found 557.2613.

(E)-1,1'-(3-(2-chlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5d**). According to the general procedure D using (0.1 g, 0.607 mmol, 1.0 equiv) (*E*)-3-(2-chlorophenyl)-2-methylacrylaldehyde **1i**, (*E*)-1,1'-(3-(2-chlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.128 g, 0.249 mmol, 41%) (**5d**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (s, 2H), 8.39 (s, 1H), 7.87 (d, J = 8.7 Hz, 4H), 7.58 (dd, J = 7.5, 1.9 Hz, 1H), 7.51 (dd, J = 7.7, 1.7 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.04 (d, J = 8.7 Hz, 4H), 6.32 (s, 1H), 3.80 (s, 6H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.4, 133.8, 133.5, 133.2, 131.5, 130.2, 129.8, 127.9, 127.6, 127.4, 123.0, 120.9, 114.8, 76.2, 55.7, 15.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{28}H_{25}ClN_6O_2Na$: 535.1620; found 535.1613.

(E)-1,1'-(3-(3-chlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5e**). According to the general procedure D using (0.142 g, 0.86 mmol, 1.0 equiv) (*E*)-3-(3-chlorophenyl)-2-methylacrylaldehyde **1j**, (*E*)-1,1'-(3-(3-chlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.126 g, 0.242 mmol, 28%) (**5e**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (s, 2H), 8.30 (s, 1H), 7.87 (d, J = 8.8 Hz, 4H), 7.48 (s, 1H), 7.44 – 7.33 (m, 3H), 7.03 (d, J = 8.8 Hz,4H), 6.36 (s, 1H), 3.79 (s, 6H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.4, 137.9, 133.6, 132.7, 130.7, 129.8, 129.3, 128.3, 128.1, 127.4, 127.2, 123.1, 121.0, 114.8, 76.6, 55.7, 15.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{26}ClN_6O_2$: 513.1800; found 513.1804.

(E)-1,1'-(3-(4-chlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5f**). According to the general procedure D using (0.1 g, 0.607 mmol, 1.0 equiv) (*E*)-3-(4-chlorophenyl)-2-methylacrylaldehyde **1k**, (*E*)-1,1'-(3-(4-chlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.150 g, 0.293 mmol, 48%) (**5f**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 2H), 8.29 (s, 1H), 7.87 (d, J = 8.8 Hz, 4H), 7.49 – 7.40 (m, 4H), 7.03 (d, J

= 8.8 Hz, 4H), 6.35 (s, 1H), 3.79 (s, 6H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.4, 134.6, 132.8, 132.0, 131.5, 129.9, 128.9, 127.4, 127.2, 123.0, 121.0, 114.8, 76.7, 55.7, 15.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{26}ClN_6O_2$: 513.1800; found 513.1801.

(E)-1,1'-(2-methyl-3-(3-nitrophenyl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5g**). According to the general procedure D using (0.144 g, 0.754 mmol, 1.0 equiv) (*E*)-2-methyl-3-(3-nitrophenyl)acrylaldehyde **1l**, (*E*)-1,1'-(2-methyl-3-(3-nitrophenyl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.14 g, 0.268 mmol, 36%) (**5g**) was obtained and chromatography (PE:EA=10:3) as white solid. TLC: R_f = 0.2 (PE:EA 2:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 2H), 8.35 (s, 1H), 8.24 (t, *J* = 2.0 Hz, 1H), 8.18 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.91 – 7.83 (m, 5H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 4H), 6.50 (s, 1H), 3.79 (s, 6H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 148.3, 147.5, 137.5, 136.1, 133.8, 130.4, 129.1, 127.4, 124.2, 123.1, 122.9, 121.0, 114.8, 76.4, 55.7, 15.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{28}H_{25}N_7O_4Na$: 546.1860; found 546.1867.

(E)-1,1'-(2-methyl-3-(4-nitrophenyl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5h**). According to the general procedure D using (0.31 g, 1.62 mmol, 1.0 equiv) (E)-2-methyl-3-(4-nitrophenyl)acrylaldehyde **1m**, (*E*)-1,1'-(2-methyl-3-(4-nitrophenyl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.442 g, 0.84 mmol, 52%) (**5h**) was obtained and chromatography (PE:EA=10:3) as white solid. TLC: R_f = 0.2 (PE:EA 2:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 2H), 8.37 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 4H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 4H), 6.47 (s, 1H), 3.80 (s, 6H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.5, 146.9, 142.7, 134.9, 131.0, 129.3, 127.4, 123.9, 123.0, 121.0, 114.8, 76.4, 55.7, 16.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{26}N_7O_4$: 524.2041; found 524.2036.

(E)-1,1'-(3-(2-methoxyphenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5i**). According to the general procedure D using (0.14 g, 0.794 mmol, 1.0 equiv) (*E*)-3-(2-methoxyphenyl)-2-methylacrylaldehyde **1n**, (*E*)-1,1'-(3-(2-methoxyphenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.251 g, 0.494 mmol, 62%) (**5i**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 2H), 8.32 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 4H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.09 – 6.95 (m, 6H), 6.41 (s, 1H), 3.80 (s, 6H), 3.72 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 157.3, 147.4, 130.7, 130.6, 130.0, 127.4, 127.0, 124.1, 123.1, 120.9, 120.5, 114.8, 111.5, 76.8, 55.9, 55.7, 15.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{29}H_{28}N_6O_3Na$: 531.2115; found 531.2122.

(E)-1,1'-(3-(3-methoxyphenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5j**). According to the general procedure D using (0.158 g, 0.9 mmol, 1.0 equiv) (*E*)-3-(3-methoxyphenyl)-2-methylacrylaldehyde **1o**, (*E*)-1,1'-(3-(3-methoxyphenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.166 g, 0.327 mmol, 36%) (**5j**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 2H), 8.28 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 4H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 4H), 6.98 – 6.86 (m, 3H), 6.36 (s, 1H), 3.79 (s, 6H), 3.76 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 159.6, 147.4, 137.1, 131.6, 131.0, 129.9, 127.3, 123.0, 122.0,

120.9, 114.9, 114.8, 114.0, 76.8, 55.6, 15.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{29}H_{28}N_6O_3Na$: 531.2115; found 531.2119.

(E)-1,1'-(2,3-diphenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5k**). According to the general procedure D using (0.104 g, 0.5 mmol, 1.0 equiv) (*E*)-2,3-diphenylacrylaldehyde **1p**, (*E*)-1,1'-(2,3-diphenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.082 g, 0.152 mmol, 30%) (**5k**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (s, 2H), 8.71 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.24 (m, 4H), 7.19 – 7.11 (m, 2H), 7.03 (d, *J* = 8.6, 4H), 6.97 – 6.90 (m, 2H), 6.32 (s, 1H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.3, 135.9, 135.3, 134.9, 131.4, 129.9, 129.7, 129.4, 129.0, 128.6, 127.3, 123.0, 121.4, 114.8, 75.8, 55.67. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{33}H_{28}N_6O_2Na$: 563.2166; found 563.2165.

(E)-1,1'-(2-(4-methoxyphenyl)-3-phenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5l**). According to the general procedure D using (0.1g, 0.42 mmol, 1.0 equiv) (*E*)-2-(4-methoxyphenyl)-3-phenylacrylaldehyde **1q**, (*E*)-1,1'-(2-(4-methoxyphenyl)-3-phenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.125 g, 0.218 mmol, 52%) (**5l**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (s, 2H), 8.66 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 4H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.02 (d, *J* = 8.7 Hz, 4H), 6.99 – 6.93 (m, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.25 (s, 1H), 3.79 (s, 6H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.7, 158.5, 146.1, 134.1, 133.9, 129.9, 128.7, 127.6, 127.4, 126.6, 126.2, 121.9, 120.2, 113.7, 74.7, 54.6, 54.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{34}H_{30}N_6O_3Na$: 593.2272; found 593.2262.

(E)-1,1'-(3-(furan-2-yl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5m**). According to the general procedure D using (0.1 mL, 0.8 mmol, 1.0 equiv) (*E*)-3-(furan-2-yl)-2-methylacrylaldehyde **1r**, (*E*)-1,1'-(3-(furan-2-yl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.138 g, 0.294 mmol, 37%) (**5m**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 2H), 8.30 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 4H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 4H), 6.69 (d, *J* = 3.4 Hz, 1H), 6.60 (dd, *J* = 3.5, 1.9 Hz, 1H), 6.14 (s, 1H), 3.80 (s, 6H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 151.1, 147.4, 144.1, 128.4, 127.4, 123.0, 120.9, 119.3, 114.8, 113.0, 112.5, 76.7, 55.7, 16.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{26}H_{24}N_6O_3Na$: 491.1802; found 491.1786.

(E)-1,1'-(2-methyl-3-(thiophen-2-yl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5n**). According to the general procedure D using (0.105 g, 0.69 mmol, 1.0 equiv) (*E*)-2-methyl-3-(thiophen-2-yl)acrylaldehyde **1s**, (*E*)-1,1'-(2-methyl-3-(thiophen-2-yl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.109 g, 0.227 mmol, 33%) (**5n**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 2H), 8.29 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 4H), 7.71 (d, *J* = 5.1 Hz, 1H), 7.26 (d, *J* = 3.6 Hz, 1H), 7.14 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 4H), 6.63 (s, 1H), 3.79 (s, 6H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.4, 138.4, 130.8, 128.7, 128.0, 127.4,

124.8, 123.1, 120.9, 114.8, 77.0, 55.7, 16.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{26}H_{24}N_6O_2SNa$: 507.1574; found 507.1586.

(E)-1,1'-(2-methyl-3-(naphthalen-1-yl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5o**). According to the general procedure D using (0.06 g, 0.31 mmol, 1.0 equiv) (*E*)-2-methyl-3-(naphthalen-1-yl)acrylaldehyde **1t**, (*E*)-1,1'-(2-methyl-3-(naphthalen-1-yl)prop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.068 g, 0.129 mmol, 42%) (**5o**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (s, 2H), 8.46 (s, 1H), 8.00 – 7.86 (m, 6H), 7.86 – 7.80 (m, 1H), 7.60 – 7.52 (m, 4H), 7.04 (d, *J* = 8.5 Hz, 4H), 6.81 (s, 1H), 3.80 (s, 6H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.5, 133.6, 133.3, 132.7, 131.5, 129.2, 129.0, 128.6, 127.4, 127.4, 127.0, 126.6, 125.9, 124.7, 123.0, 121.0, 114.8, 76.5, 55.7, 15.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}N_6O_2Na$:551.2166; found 551.2163.

(E)-1,1'-(3-(6-methoxynaphthalen-1-yl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5p**). According to the general procedure D using (0.03 g, 0.13 mmol, 1.0 equiv) (*E*)-3-(6-methoxynaphthalen-1-yl)-2-methylacrylaldehyde **1u**, (*E*)-1,1'-(3-(6-methoxynaphthalen-1-yl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.046 g, 0.083 mmol, 64%) (**5p**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 2H), 8.33 (s, 1H), 7.91 – 7.80 (m, 7H), 7.50 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 4H), 6.46 (s, 1H), 3.88 (s, 3H), 3.79 (s, 6H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.7, 157.2, 146.3, 133.0, 130.1, 129.8, 129.5, 129.0, 127.7, 127.6, 126.9, 126.3, 126.1, 122.0, 119.9, 118.4, 113.7, 105.2, 76.0, 54.6, 54.6, 15.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{33}H_{30}N_6O_3Na$: 581.2272; found 581.2275.

(E)-1,1'-(3-(anthracen-9-yl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5q**). According to the general procedure D using (0.044 mg, 0.18 mmol, 1.0 equiv) (*E*)-3-(anthracen-9-yl)-2-methylacrylaldehyde **1v**, (*E*)-1,1'-(3-(anthracen-9-yl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.045 g, 0.077 mmol, 43%) (**5q**) was obtained and chromatography (PE:EA=10:2) as yellow solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97 (s, 2H), 8.64 (d, *J* = 5.3 Hz, 2H), 8.18 – 8.07 (m, 4H), 7.92 (d, *J* = 8.5 Hz, 4H), 7.64 – 7.53 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 4H), 6.93 (s, 1H), 3.80 (s, 6H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.6, 135.9, 131.3, 129.7, 129.3, 129.1, 127.8, 127.4, 126.8, 126.0, 125.9, 123.0, 121.2, 114.8, 76.1, 55.7, 15.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{31}N_6O_2$:579.2503; found 579.2508.

(E)-1,1'-(3-(2,6-dichlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5r**). According to the general procedure D using (0.4 g, 1.4 mmol, 1.0 equiv) (*E*)-3-(2,6-dichlorophenyl)-2-methylacrylaldehyde **1w**, (*E*)-1,1'-(3-(2,6-dichlorophenyl)-2-methylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1*H*-1,2,3-triazole) (0.395 g, 0.722 mmol, 52%) (**5r**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.75 (s, 2H), 8.48 (s, 1H), 7.87 (d, *J* = 8.7 Hz, 4H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 4H), 6.21 (s, 1H), 3.80 (s, 6H), 1.63 (s, 3H). ^{13}C NMR (101

MHz, DMSO-d_6) δ 159.9, 147.5, 136.1, 134.2, 133.2, 131.0, 128.8, 127.4, 126.3, 122.9, 120.7, 114.9, 75.5, 55.7, 15.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{28}H_{24}N_6O_2Cl_2Na$:569.1230; found 569.1216.

(E)-1,1'-(3-phenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5s**). According to the general procedure D using (0.185 g, 1.4 mmol, 1.0 equiv) cinnamaldehyde **1x**, *(E)-1,1'-(3-phenylprop-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole)* (0.332 g, 0.714 mmol, 51%) (**5s**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.2 (PE:EA 10:5) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 2H), 8.30 (d, J = 7.7 Hz, 1H), 7.84 (d, J = 11.4 Hz, 4H), 7.65 (d, J = 7.5 Hz, 2H), 7.47 – 7.32 (m, 4H), 7.11 (d, J = 15.7 Hz, 1H), 7.03 (d, J = 8.5 Hz, 4H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 159.8, 147.5, 137.7, 135.1, 129.7, 129.3, 127.9, 127.3, 123.1, 121.3, 120.0, 114.8, 73.0, 55.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_6O_2$:465.2034; found 465.2035.

(E)-1,1'-(but-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole) (**5t**). According to the general procedure D using (0.1 g, 1.4 mmol, 1.0 equiv) crotonaldehyde **1x**, *(E)-1,1'-(but-2-ene-1,1-diyl)bis(4-(4-methoxyphenyl)-1H-1,2,3-triazole)* (0.248 g, 0.616 mmol, 44%) (**5t**) was obtained and chromatography (PE:EA=10:2) as white solid. TLC: R_f = 0.1 (PE:EA 10:5) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 1H), 8.65 (s, 1H), 7.87 – 7.75 (m, 4H), 7.67 (d, J = 14.3 Hz, 1H), 7.09 – 6.98 (m, 4H), 6.75 (dd, J = 14.3, 7.5 Hz, 1H), 5.67 (p, J = 6.9 Hz, 1H), 3.80 (s, 6H), 1.81 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 159.5, 147.3, 127.3, 127.0, 123.8, 123.0, 121.2, 119.5, 118.3, 114.8, 76.7, 55.6, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_6O_2$:403.1877; found 403.1876.

1-(azido(2-phenyl-2H-chromen-3-yl)methyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazole (**6a**). According to General procedures for the synthesis of 6a, **6a** (0.03 g, 0.069 mmol, 34%) was obtained and chromatography (PE:EA=10:1) as white solid. TLC: R_f = 0.5 (PE:EA 10:2) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (s, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.37 (dd, J = 7.5, 1.6 Hz, 1H), 7.34 – 7.23 (m, 5H), 7.23 – 7.14 (m, 2H), 7.05 – 6.91 (m, 4H), 6.72 (d, J = 8.0 Hz, 1H), 5.67 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 152.1, 147.6, 137.5, 131.3, 129.6, 129.1, 128.5, 128.1, 127.9, 127.3, 124.9, 123.1, 122.2, 121.0, 119.7, 116.4, 114.8, 75.9, 73.6, 55.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{20}N_6O_2Na$:459.1540; found 459.1535.

1,1'-((2-phenyl-2H-chromen-3-yl)methylene)bis(4-(hex-5-yn-1-yl)-1H-1,2,3-triazole) (**6b**). According to the general procedure for the synthesis of 5a and 6b, (0.045 g, 0. 088 mmol, 44%) (**6b**) was obtained and chromatography (PE:EA=10:1) as white solid. TLC: R_f = 0.4 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (s, 1H), 8.04 (s, 1H), 7.98 (s, 1H), 7.33 – 7.21 (m, 4H), 7.20 – 7.12 (m, 3H), 6.91 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.53 (s, 1H), 5.85 (s, 1H), 2.76 (t, J = 2.6 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 2.17 (tt, J = 6.9, 3.1 Hz, 4H), 1.69 – 1.55 (m, 4H), 1.44 (h, J = 7.3 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.9, 148.0, 147.7, 137.1, 131.5, 129.6, 129.0, 128.5, 128.3, 127.9, 125.5, 122.7, 122.4, 122.2, 120.9, 116.5, 84.9, 76.6, 71.9, 71.8, 28.2, 28.1, 27.9, 27.9, 24.8, 24.7, 17.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{32}N_6ONa$:539.2530; found 539.2525.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-pyrrole) (**9a**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-pyrrole)* (0.040 g, 0.11 mmol, 71%) (**5p**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.67 (d, *J* = 3.0 Hz, 1H), 10.47 (d, *J* = 3.0 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.06 – 6.99 (m, 2H), 6.84 – 6.78 (m, 1H), 6.69 – 6.59 (m, 3H), 6.27 (s, 1H), 5.99 – 5.88 (m, 3H), 5.75 (s, 1H), 5.58 (s, 1H), 4.55 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.4, 138.7, 138.3, 130.6, 130.2, 129.3, 129.0, 128.2, 126.9, 122.6, 121.7, 120.2, 117.8, 117.6, 116.0, 107.7, 107.6, 107.2, 106.6, 78.4, 41.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{21}N_2O$: 353.1648; found 353.1646.

1,1'-(((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-pyrrole-4,2-diyl))bis(propan-1-one) (**9b**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *1,1'-(((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-pyrrole-4,2-diyl))bis(propan-1-one)* (0.035 g, 0.084 mmol, 53%) (**9b**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.80 (s, 1H), 11.66 (s, 1H), 7.24 (s, 5H), 7.11 – 7.01 (m, 2H), 6.89 (dd, *J* = 3.7, 2.3 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 6.06 (dd, *J* = 3.7, 2.3 Hz, 1H), 6.03 (dd, *J* = 3.7, 2.3 Hz, 1H), 5.64 (s, 1H), 4.90 (s, 1H), 2.70 (dq, *J* = 11.5, 7.4 Hz, 4H), 1.05 (td, *J* = 7.4, 1.8 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 190.4, 151.5, 138.2, 138.0, 137.2, 135.6, 131.9, 131.6, 129.7, 128.9, 128.7, 128.2, 127.1, 122.4, 121.8, 121.6, 117.0, 116.9, 116.1, 110.2, 109.8, 78.6, 41.2, 30.7, 9.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{29}N_2O_3$: 465.2173; found 465.2169.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole) (**9c**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole)* (0.032 g, 0.071 mmol, 44%) (**9b**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.03 (d, *J* = 2.5 Hz, 1H), 10.82 (d, *J* = 2.5 Hz, 1H), 7.45 – 7.27 (m, 10H), 7.09 – 6.92 (m, 6H), 6.91 – 6.82 (m, 2H), 6.81 – 6.74 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.27 (s, 1H), 5.78 (s, 1H), 4.90 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.5, 139.6, 139.6, 137.3, 136.9, 129.4, 129.2, 129.1, 128.0, 127.2, 126.9, 126.8, 125.1, 124.0, 122.4, 121.5, 121.5, 121.4, 119.3, 118.9, 118.8, 115.8, 115.2, 115.2, 112.1, 112.1, 79.5, 36.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{25}N_2O$: 453.1961; found 453.1959.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(4-methyl-1H-indole) (**9d**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole)* (0.050 g, 0.104 mmol, 63%) (**9d**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (d, *J* = 2.5 Hz, 1H), 10.78 (d, *J* = 2.6 Hz, 1H), 7.35 – 7.26 (m, 1H), 7.26 – 7.20 (m, 3H), 7.19 – 7.05 (m, 5H), 6.98 – 6.75 (m, 5H), 6.57 (d, *J* = 7.1 Hz, 2H), 6.41 (d, *J* = 2.5 Hz, 1H), 6.01 (s, 1H), 5.89 (s, 1H), 5.44 (s, 1H), 2.13 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 152.7, 142.1, 140.4, 137.6, 129.8, 129.8, 129.3, 129.0, 128.6, 127.3, 127.0, 126.8, 125.4, 124.9, 123.8, 122.4, 121.6, 121.6, 121.3, 120.5, 119.9, 117.1, 117.0, 115.6, 110.1, 110.1, 80.6, 38.9, 19.9, 19.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{29}N_2O$: 481.2274; found 481.2272.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(5-methoxy-1H-indole) (**9e**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(5-methoxy-1H-indole)* (0.068 g, 0.133 mmol, 81%) (**9e**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (d, *J* = 2.5 Hz, 1H), 10.68 (d, *J* = 2.5 Hz, 1H), 7.47 – 7.38 (m, 5H), 7.31 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.02 (td, *J* = 7.7, 1.6 Hz, 1H), 6.97 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.82 – 6.72 (m, 4H), 6.69 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 6.23 (s, 1H), 5.74 (s, 1H), 4.80 (s, 1H), 3.56 (d, *J* = 3.4 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 153.4, 153.3, 151.5, 140.0, 139.3, 132.5, 132.0, 129.4, 129.2, 127.8, 127.6, 127.0, 126.9, 125.8, 124.9, 122.3, 121.6, 118.8, 115.8, 114.8, 114.6, 112.8, 111.8, 111.2, 101.5, 100.2, 79.5, 55.7, 36.9, 31.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{29}N_2O_3Na$: 513.2173; found 513.2169.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(2-methyl-1H-indole) (**9f**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(2-methyl-1H-indole)* (0.019 g, 0.040 mmol, 25%) (**9f**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 10.81 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.29 – 7.19 (m, 4H), 7.04 (td, *J* = 7.7, 1.7 Hz, 1H), 7.00 – 6.83 (m, 5H), 6.78 (td, *J* = 7.5, 1.1 Hz, 1H), 6.67 (dt, *J* = 7.6, 3.5 Hz, 2H), 6.20 (d, *J* = 1.9 Hz, 1H), 5.78 (s, 1H), 4.81 (d, *J* = 1.9 Hz, 1H), 2.16 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 151.6, 139.5, 139.4, 135.6, 135.5, 133.4, 132.5, 129.4, 129.3, 129.1, 128.9, 128.4, 127.9, 126.9, 122.2, 121.6, 120.3, 120.2, 120.2, 119.0, 118.6, 118.4, 115.9, 111.1, 111.0, 110.3, 108.6, 79.6, 36.5, 12.3, 12.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{29}N_2O$: 481.2274; found 481.2272.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole-5-carbonitrile) (**9g**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole-5-carbonitrile)* (0.022 g, 0.044 mmol, 27%) (**9g**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.65 (d, *J* = 2.4 Hz, 1H), 11.47 (d, *J* = 2.4 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.45 – 7.31 (m, 7H), 7.29 (d, *J* = 1.5 Hz, 1H), 7.11 (d, *J* = 2.3 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.80 (td, *J* = 7.4, 1.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H), 5.83 (s, 1H), 5.14 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.6, 139.4, 139.0, 138.9, 138.7, 129.5, 129.5, 129.0, 128.0, 127.6, 127.1, 127.0, 127.0, 126.4, 125.0, 124.7, 124.4, 124.2, 122.3, 121.6, 121.2, 121.0, 120.0, 116.2, 116.1, 116.0, 113.4, 100.9, 79.2, 36.2, 31.2. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ calcd for $C_{34}H_{26}N_5O$: 520.2132; found 520.2133.

3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(5-chloro-1H-indole) (**9h**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(5-chloro-1H-indole)* (0.055 g, 0.103 mmol, 64%) (**9h**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (d, *J* = 2.5 Hz, 1H), 11.07 (d, *J* = 2.5 Hz, 1H), 7.47 – 7.35 (m, 8H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.11 – 6.97 (m, 4H), 6.88 (dd, *J* = 14.9, 2.3 Hz, 2H), 6.79 (td, *J*

= 7.4, 1.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.26 (s, 1H), 5.80 (s, 1H), 4.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.6, 139.5, 139.1, 135.8, 135.5, 129.5, 129.4, 129.1, 128.3, 128.0, 127.8, 127.0, 126.8, 126.0, 123.6, 123.6, 122.3, 121.6, 121.6, 121.5, 119.5, 118.4, 118.2, 115.9, 114.9, 114.7, 113.8, 113.6, 79.3, 36.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{23}N_2OCl_2$: 521.1182; found 521.1178.

dimethyl 3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole-6-carboxylate) (**9i**). According to the general procedure E using (0.035 g, 0.115 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *dimethyl 3,3'-((2-phenyl-2H-chromen-3-yl)methylene)bis(1H-indole-6-carboxylate)* (0.050 g, 0.088 mmol, 77%) (**9i**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (d, *J* = 2.6 Hz, 1H), 11.30 (d, *J* = 2.6 Hz, 1H), 8.07 (d, *J* = 1.5 Hz, 1H), 8.02 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.41 – 7.34 (m, 6H), 7.10 – 7.00 (m, 3H), 6.97 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.27 (s, 1H), 5.79 (s, 1H), 4.99 (s, 1H), 3.84 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 167.7, 151.6, 139.4, 139.0, 136.5, 136.2, 130.6, 130.1, 129.4, 129.1, 129.0, 128.3, 128.0, 127.0, 122.7, 122.5, 122.3, 121.6, 119.8, 119.7, 119.6, 119.0, 118.6, 115.9, 115.7, 115.5, 114.2, 79.4, 52.3, 36.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{36}H_{28}N_2O_5Na$: 591.1890; found 591.1894.

(E)-3,3'-(2-methyl-3-phenylprop-2-ene-1,1-diyl)bis(1H-pyrrole) (**9j**). According to the general procedure E using (0.1 g, 0.47 mmol, 1.0 equiv) (E)-(3,3-diazido-2-methylprop-1-en-1-yl)benzene **2g**, *(E)-3,3'-(2-methyl-3-phenylprop-2-ene-1,1-diyl)bis(1H-pyrrole)* (0.050 g, 0.19 mmol, 41%) (**9j**) was obtained and chromatography (PE:EA=10:5) as brown solid. TLC: R_f = 0.2 (PE:EA 10:3) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.70 (s, 1H), 10.56 (s, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 6.70 – 6.61 (m, 2H), 6.11 – 5.99 (m, 3H), 5.93 (d, *J* = 2.7 Hz, 1H), 5.63 (d, *J* = 2.2 Hz, 1H), 4.80 (s, 1H), 1.83 (s, 3H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 147.8, 139.6, 137.4, 134.8, 133.8, 133.3, 131.4, 123.3, 123.2, 122.4, 122.1, 113.8, 112.6, 112.2, 111.7, 58.9, 24.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}N_2$: 263.1543; found 263.1541.

3-(di(furan-3-yl)methyl)-2-phenyl-2H-chromene (**9k**). According to the general procedure E using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *3-(di(furan-3-yl)methyl)-2-phenyl-2H-chromene* (0.036 g, 0.10 mmol, 64%) (**9k**) was obtained and chromatography (PE:EA=20:1) as colorless oil. TLC: R_f = 0.7 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.58 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.33 – 7.25 (m, 5H), 7.11 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.06 (td, *J* = 7.8, 1.7 Hz, 1H), 6.84 (td, *J* = 7.5, 1.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.44 – 6.37 (m, 3H), 6.31 (d, *J* = 3.2 Hz, 1H), 6.12 (d, *J* = 3.3 Hz, 1H), 5.72 (s, 1H), 4.82 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.9, 151.6, 151.4, 143.3, 143.1, 138.2, 134.3, 129.9, 129.2, 129.0, 128.1, 127.3, 122.1, 121.9, 121.8, 116.2, 111.1, 111.0, 108.6, 78.0, 42.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{19}O_3$: 355.1329; found 355.1326.

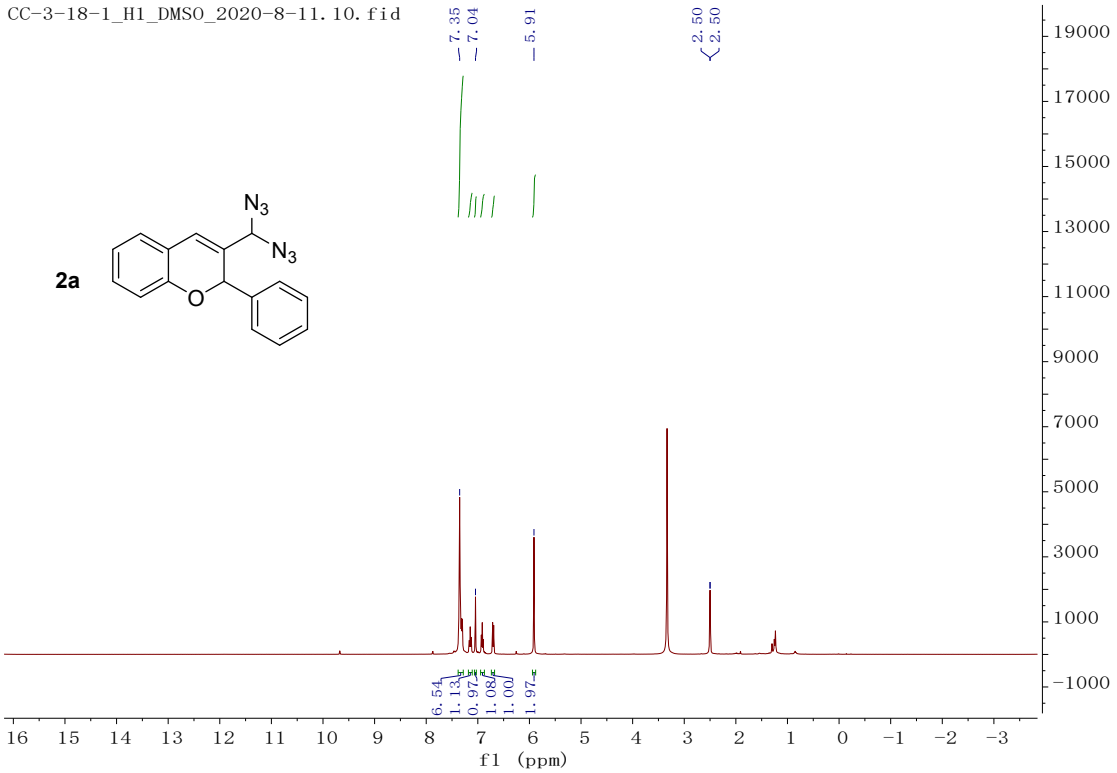
(E)-N-((2-phenyl-2H-chromen-3-yl)methylene)cyanamide (**11a**). According to the general procedure F using (0.09 g, 0.3 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *(E)-N-((2-phenyl-2H-chromen-3-yl)methylene)cyanamide* (0.040 g, 0.154 mmol, 51%) (**11a**) was obtained and chromatography (PE:EA=10:3) as yellow soild. TLC: R_f = 0.2 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.97 (s, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.41 – 7.29 (m, 6H), 7.01 (td, *J* =

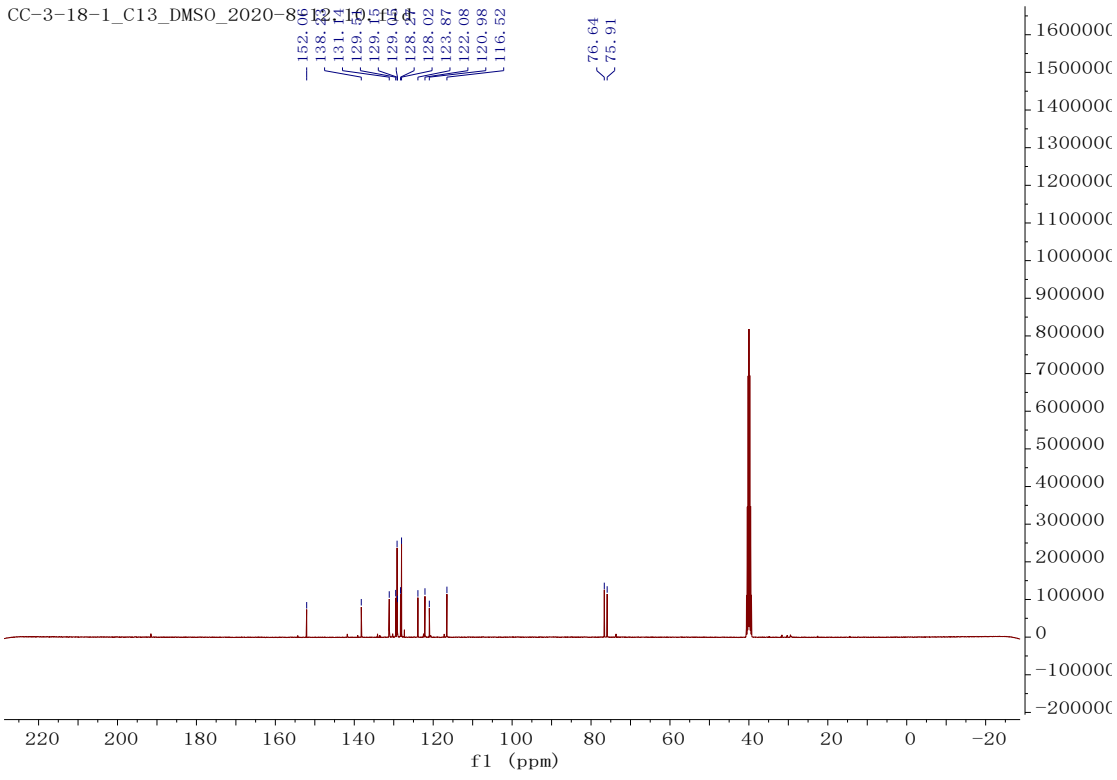
7.4, 1.1 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.34 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 182.7, 154.8, 145.4, 138.3, 135.1, 130.8, 129.4, 129.1, 127.6, 122.7, 121.0, 117.5, 116.5, 73.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}N_2O$: 261.1022; found 261.1019.

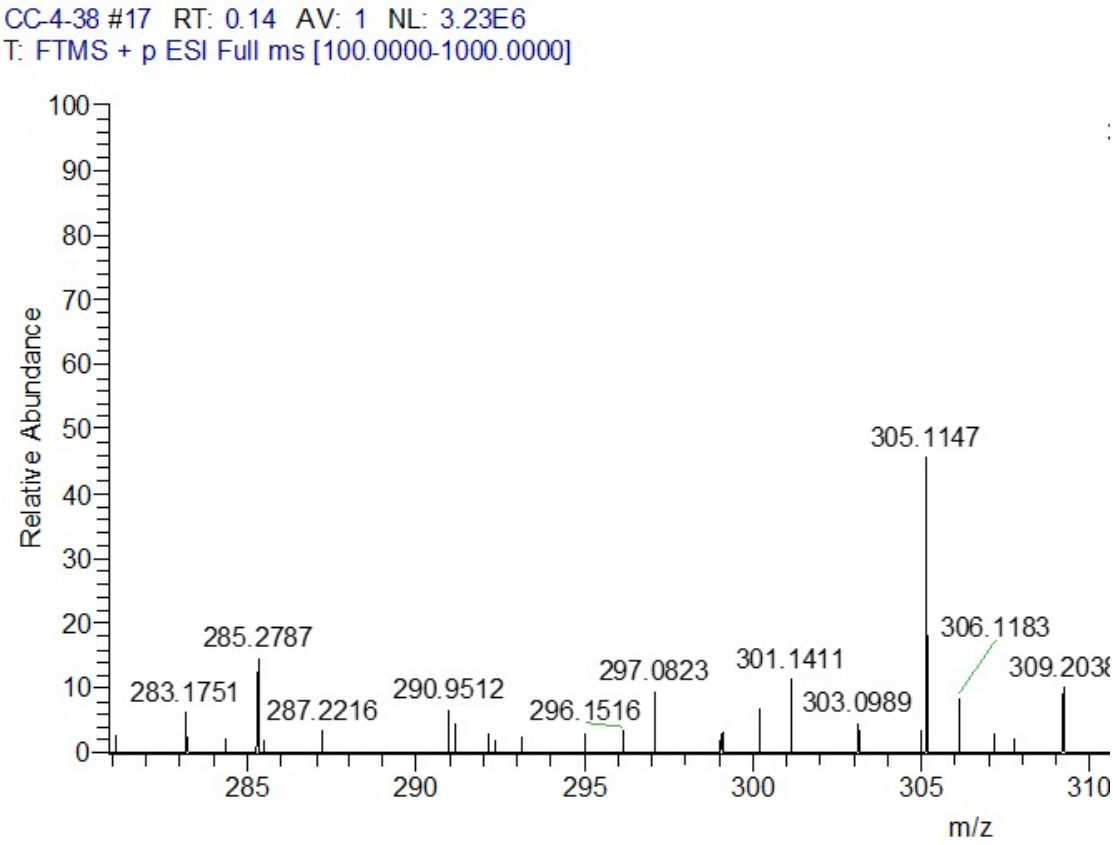
(E)-N-((2-phenyl-2H-chromen-3-yl)methylene)methanesulfonamide (**11b**). According to the general procedure F using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *(E)-N-((2-phenyl-2H-chromen-3-yl)methylene)methanesulfonamide* (0.03 g, 0.115 mmol, 70%) (**11b**) was obtained and chromatography (PE:EA=10:3) as yellow soild. TLC: R_f = 0.2 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 1H), 8.07 (s, 1H), 7.42 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.36 (s, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 155.1, 143.3, 138.5, 134.4, 129.6, 129.4, 128.8, 128.5, 127.0, 122.0, 120.3, 117.4, 74.9, 40.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}NO_3SNa$: 336.0665; found 336.0670.

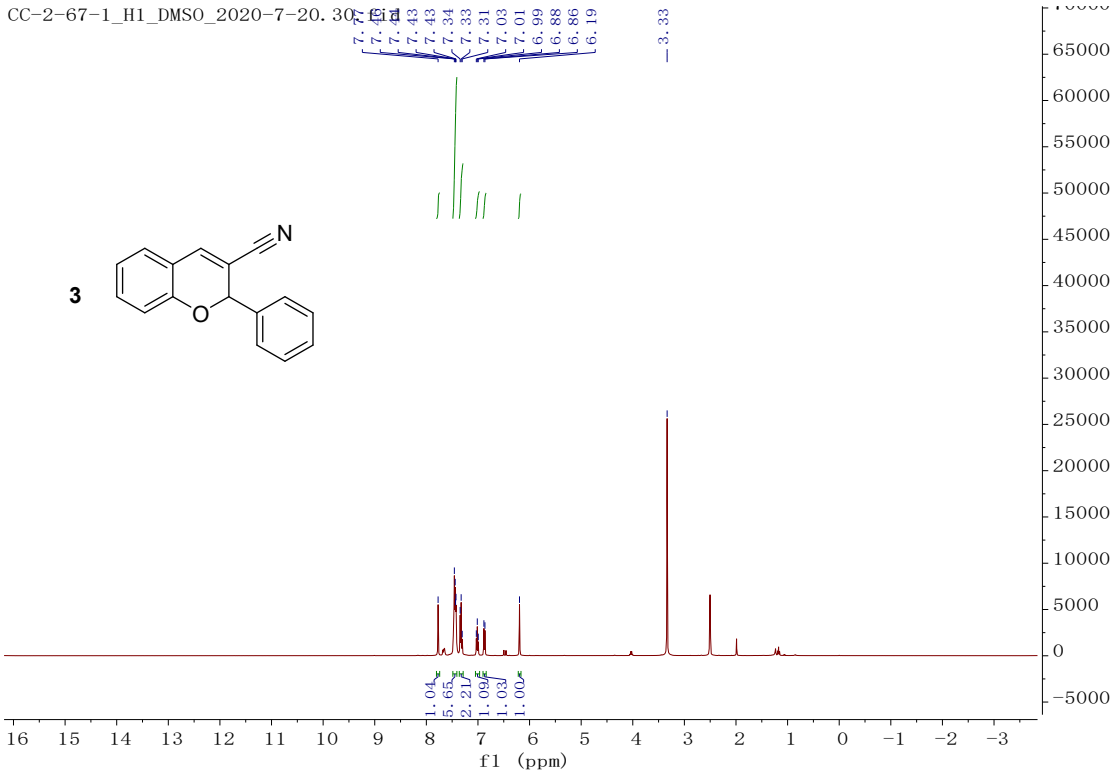
(E)-N-((2-phenyl-2H-chromen-3-yl)methylene)-4-(trifluoromethyl)benzenesulfonamide (**11c**). According to the general procedure F using (0.05 g, 0.16 mmol, 1.0 equiv) 3-(diazidomethyl)-2-phenyl-2H-chromene **2a**, *(E)-N-((2-phenyl-2H-chromen-3-yl)methylene)-4-(trifluoromethyl)benzenesulfonamide* (0.028 g, 062 mmol, 39%) (**11c**) was obtained and chromatography (PE:EA=10:3) as yellow soild. TLC: R_f = 0.2 (PE:EA 10:1) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (s, 1H), 8.14 (s, 1H), 8.01 – 7.91 (m, 4H), 7.43 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.36 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.01 (td, *J* = 7.6, 1.1 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.32 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.4, 154.8, 146.0, 142.6, 138.7, 135.1, 130.7, 129.4, 129.1, 128.9, 128.7, 127.1 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 274.1 Hz), 122.7, 120.9, 117.4, 74.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{17}NO_3F_3S$: 444.0876; found 444.0875.

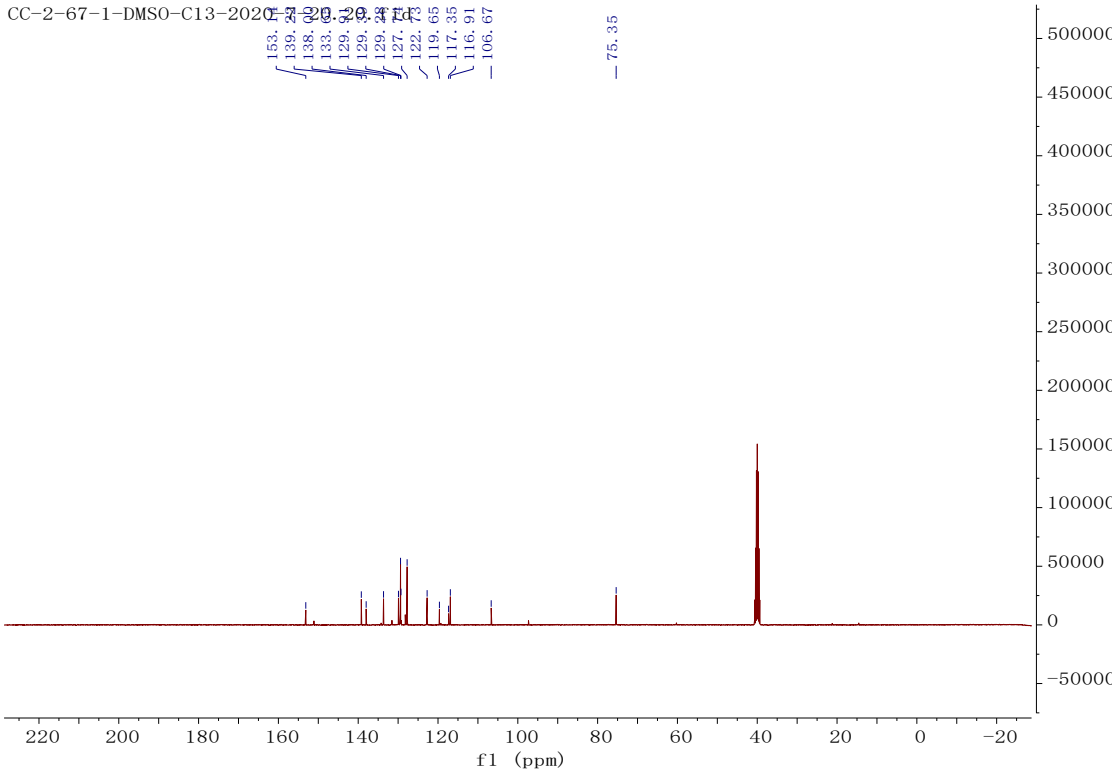
4. ^{1}H-, ^{13}C- NMR and HRMS spectra of new compounds

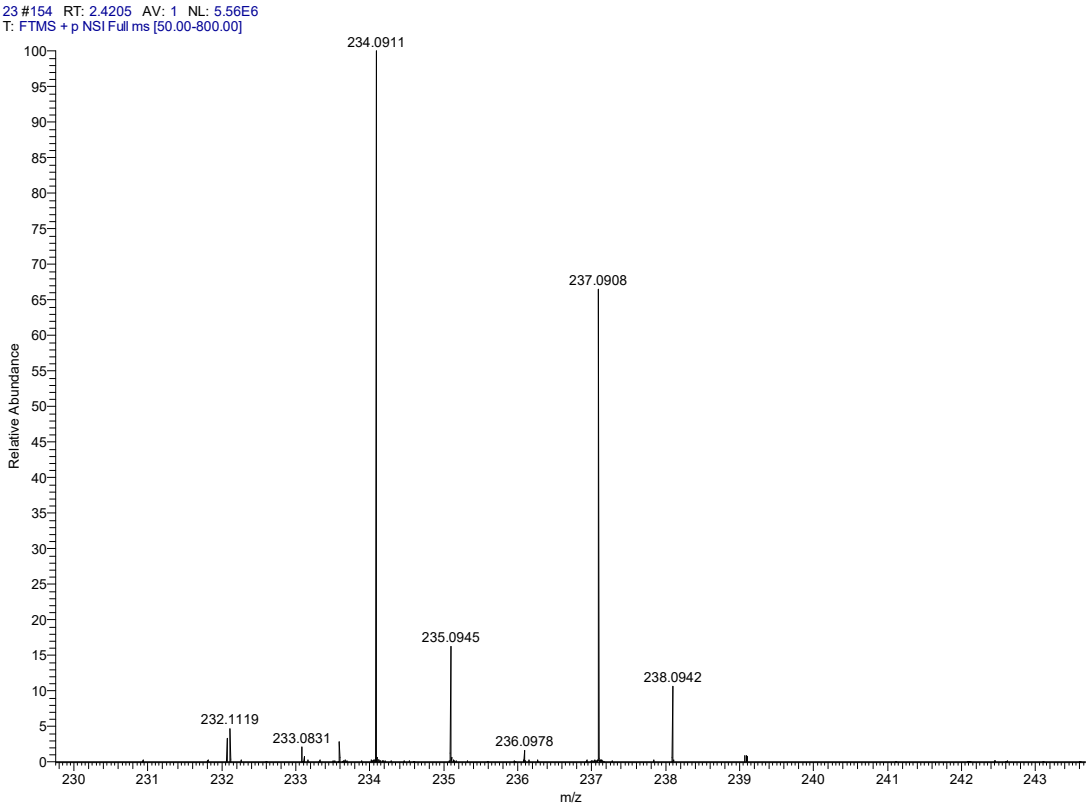


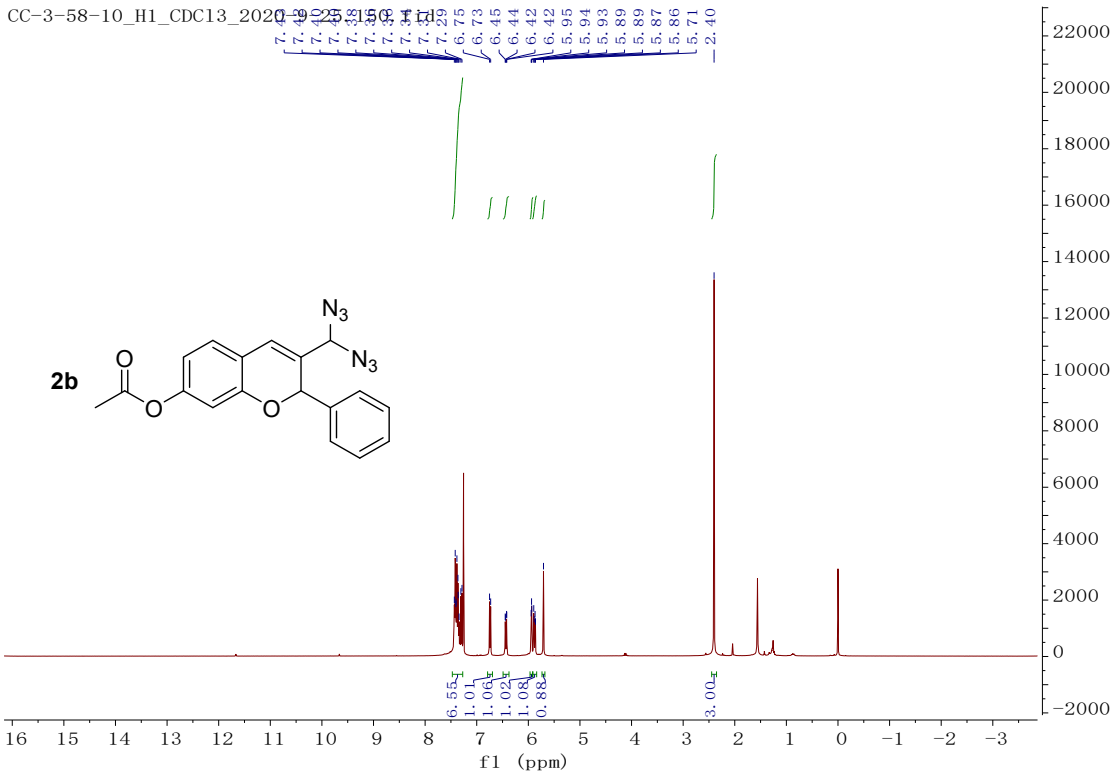


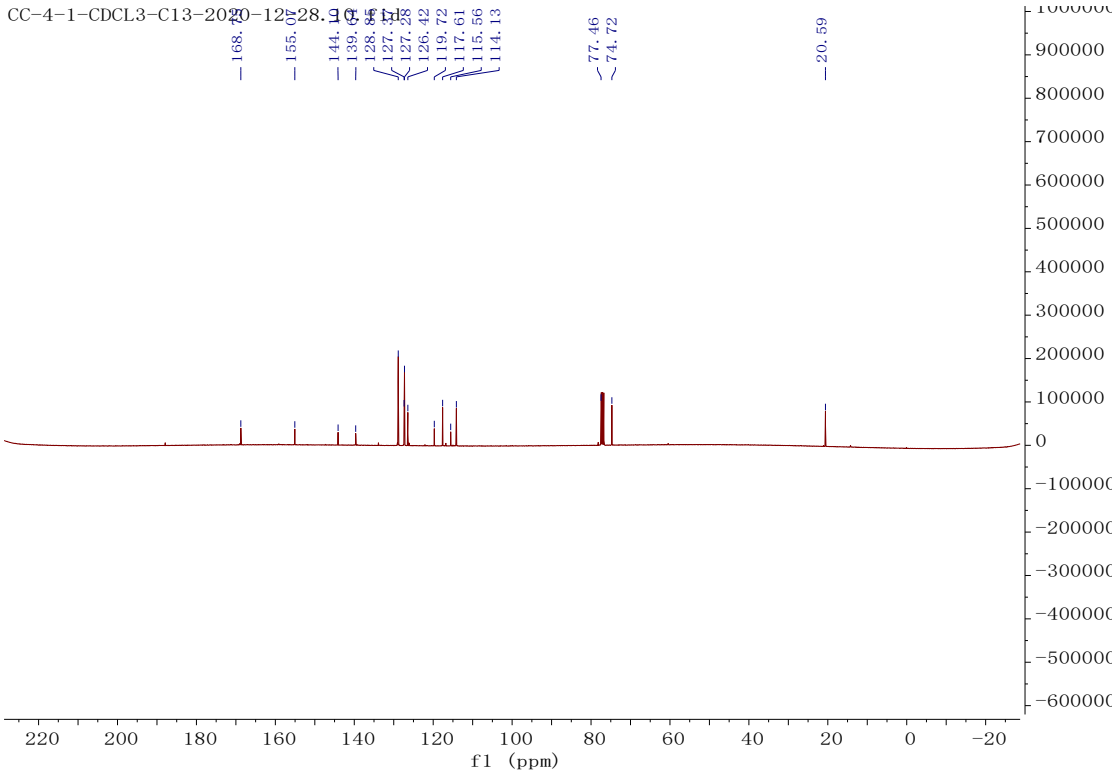

CC-4-38 #17 RT: 0.14 AV: 1 NL: 3.23E6
T: FTMS + p ESI Full ms [100.0000-1000.0000]
Relative Abundance
m/z
305.1147
306.1183
285.2787
283.1751
287.2216
290.9512
296.1516
297.0823
301.1411
303.0989

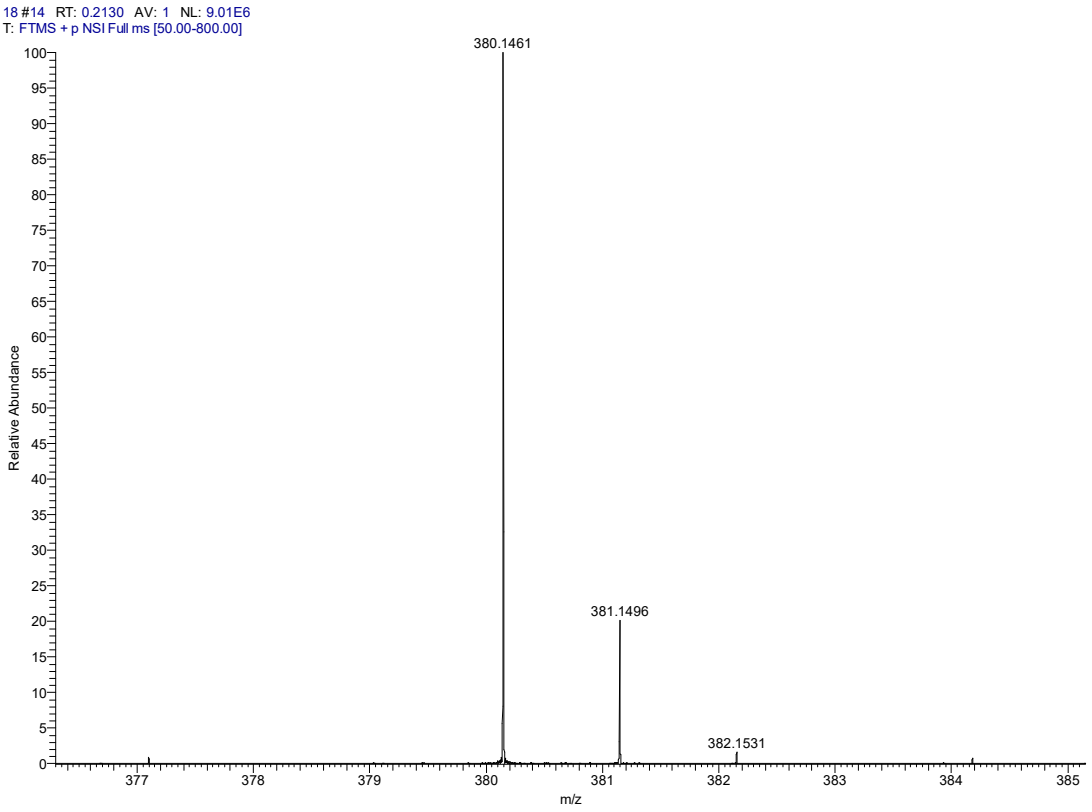

CC-2-67-1_H1_DMSO_2020-7-20.30.fid
3
N
O
f1 (ppm)

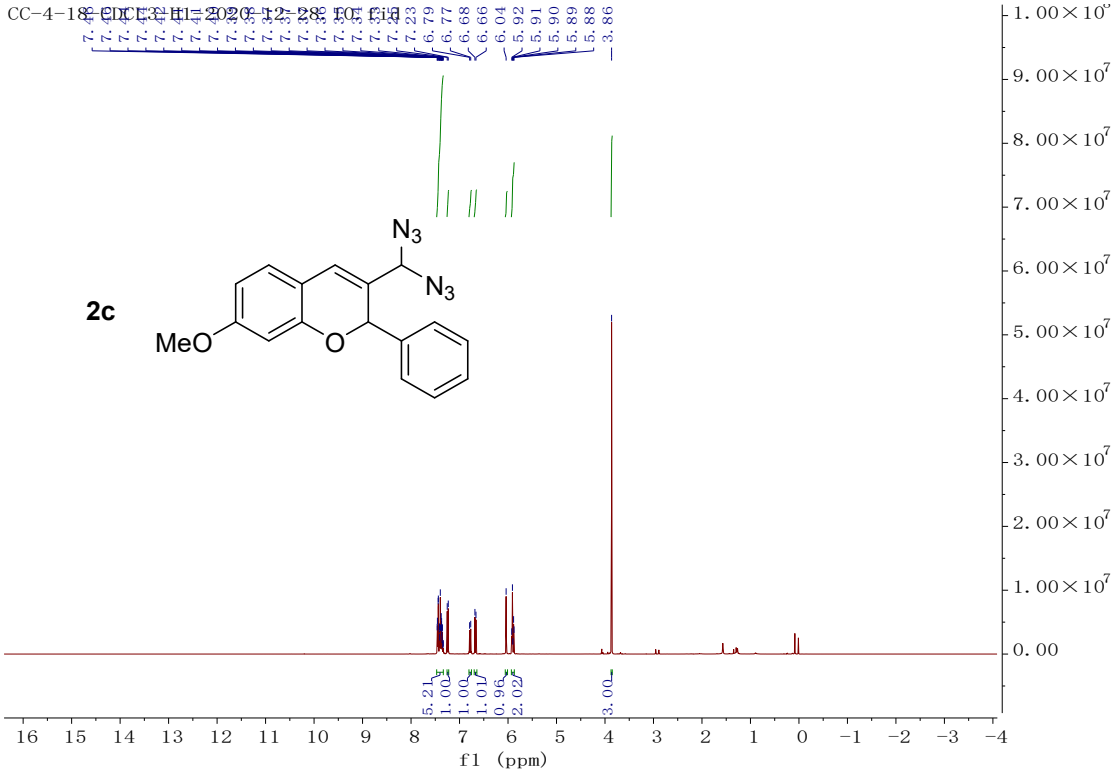

CC-2-67-1-DMSO-C13-2020-5-20.29.ft.fid
153.
139.
138.
133.
129.
129.
129.
127.
122.
119.65
117.35
116.91
106.67
75.35
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
220
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)

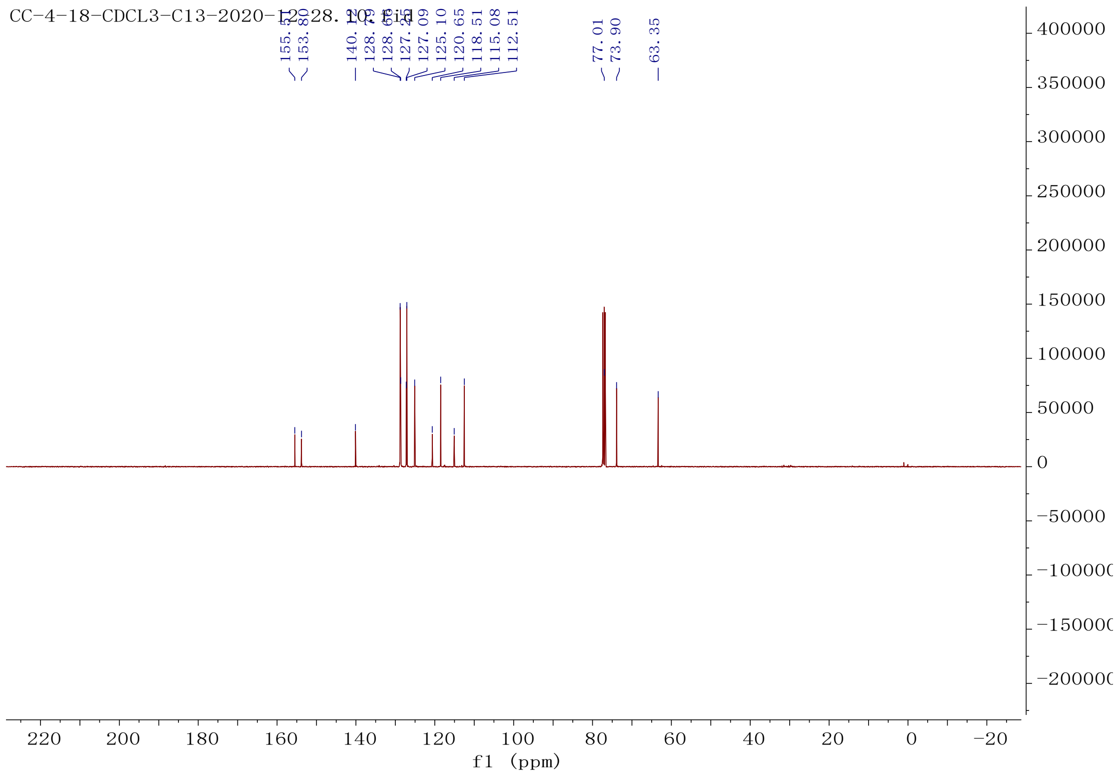

23 #154 RT: 2.4205 AV: 1 NL: 5.56E6
T: FTMS + p NSI Full ms [50.00-800.00]
234.0911
237.0908
235.0945
238.0942
232.1119
233.0831
236.0978
Relative Abundance
m/z


CC-3-58-10_H1_CDC13_2020-9-25 15:02:41.fid
2b
N3
N3
O
O
O
f1 (ppm)

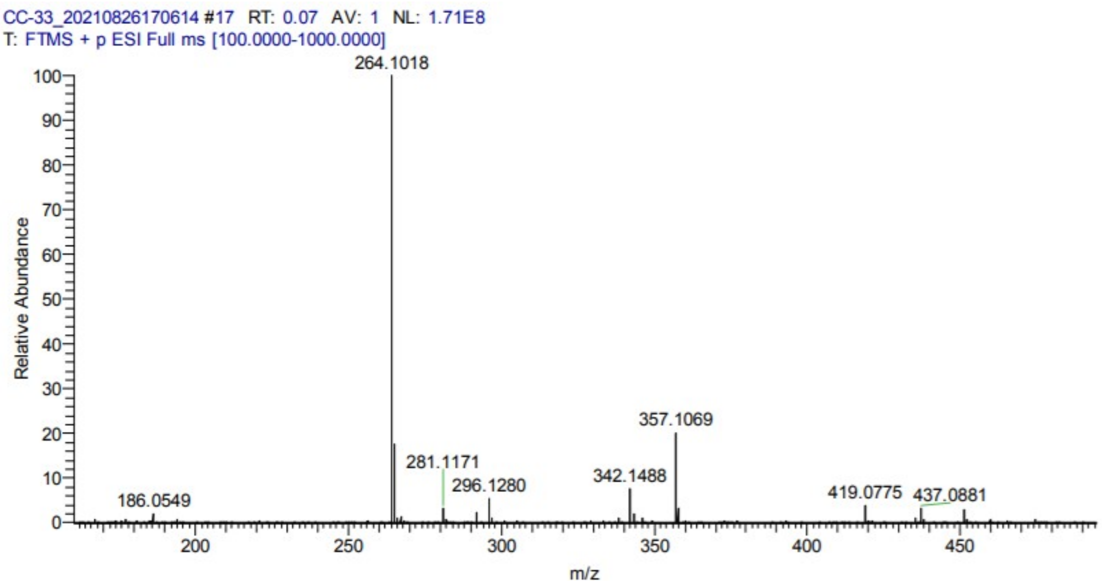

CC-4-1-CDCL3-C13-2020-12-28 10:41:18.fid
f1 (ppm)


18 #14 RT: 0.2130 AV: 1 NL: 9.01E6
T: FTMS + p NSI Full ms [50.00-800.00]
380.1461
381.1496
382.1531
Relative Abundance
m/z


2c
N3
N3
MeO
O
f1 (ppm)

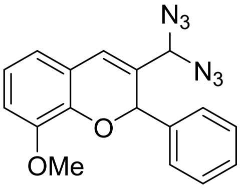


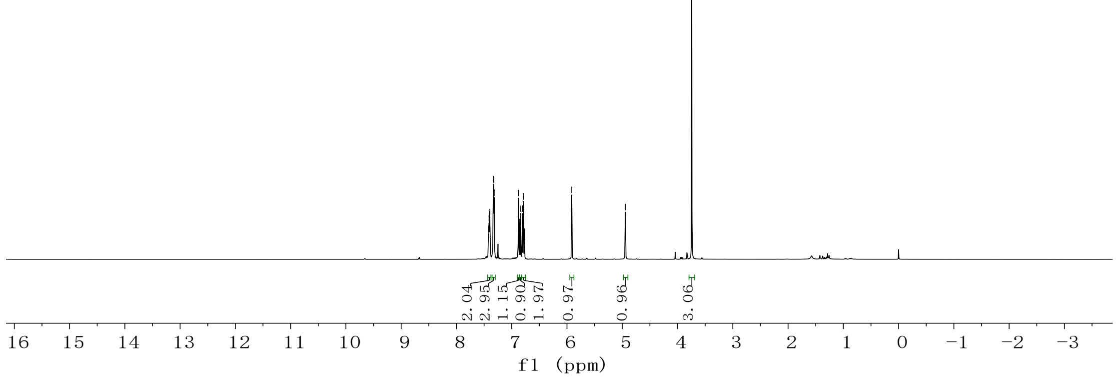
CC-4-18-CDCL3-C13-2020-12-28.10.fid
155.51
153.80
140.
128.
128.
127.
127.09
125.10
120.65
118.51
115.08
112.51
77.01
73.90
63.35
f1 (ppm)

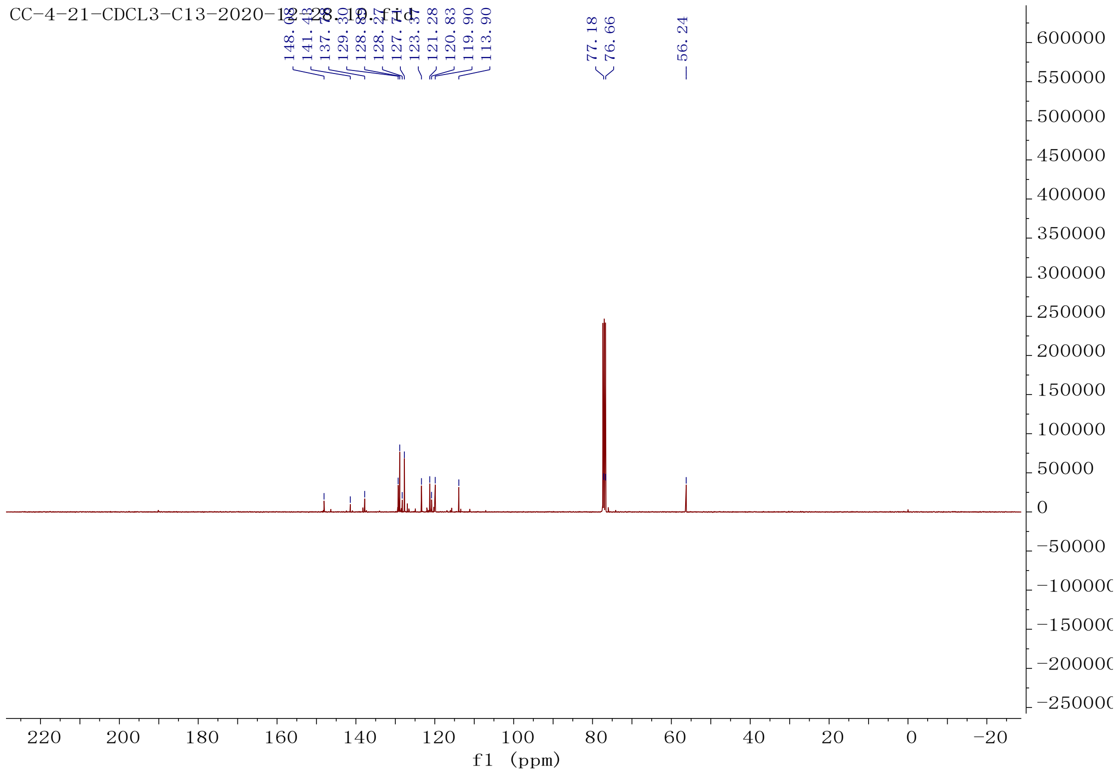


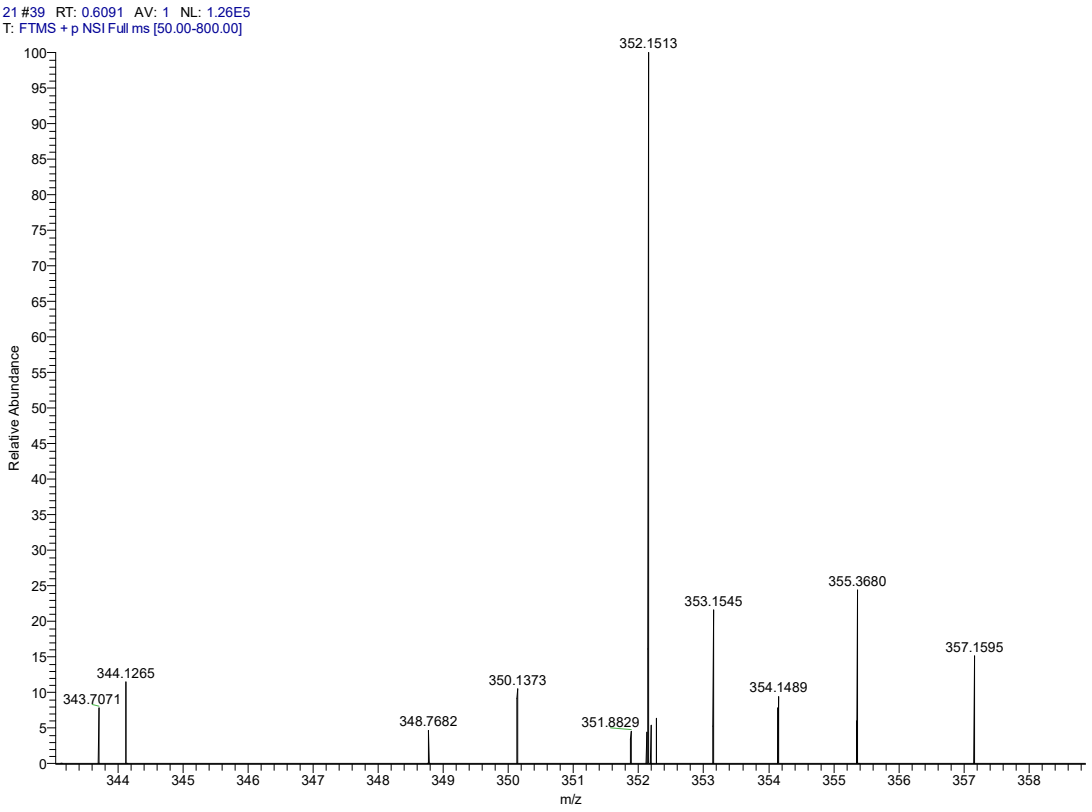
CC-33_20210826170614 #17 RT: 0.07 AV: 1 NL: 1.71E8
T: FTMS + p ESI Full ms [100.0000-1000.0000]
264.1018
357.1069
281.1171
296.1280
342.1488
186.0549
419.0775
437.0881
Relative Abundance
m/z

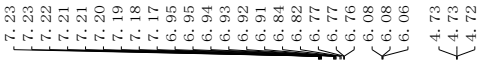
2d


N3
N3
O
OMe

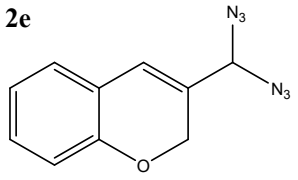

7.42
7.41
7.41
7.40
7.40
7.33
7.32
7.32
6.88
6.86
6.85
6.84
6.81
6.81
6.79
6.79
6.77
6.77
5.91
4.94
3.74
2.04
2.95
1.15
0.90
1.97
0.97
0.96
3.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

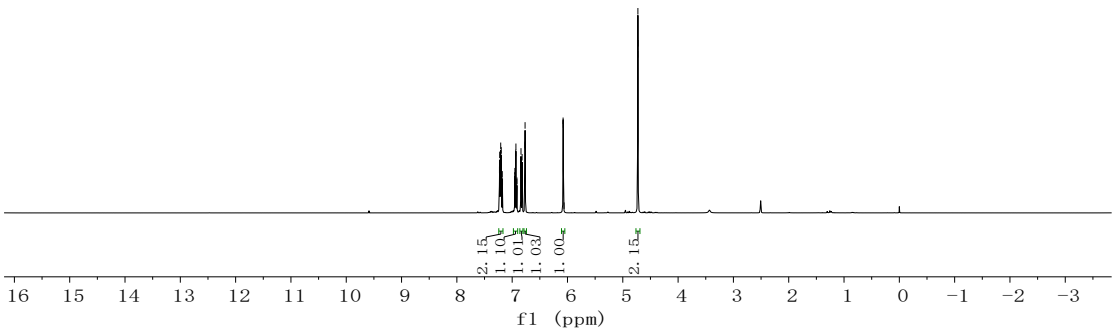

121.28
120.83
119.90
113.90
77.18
76.66
56.24
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
220 200 180 160 140 120 100 80 60 40 20 0 −20
f1 (ppm)

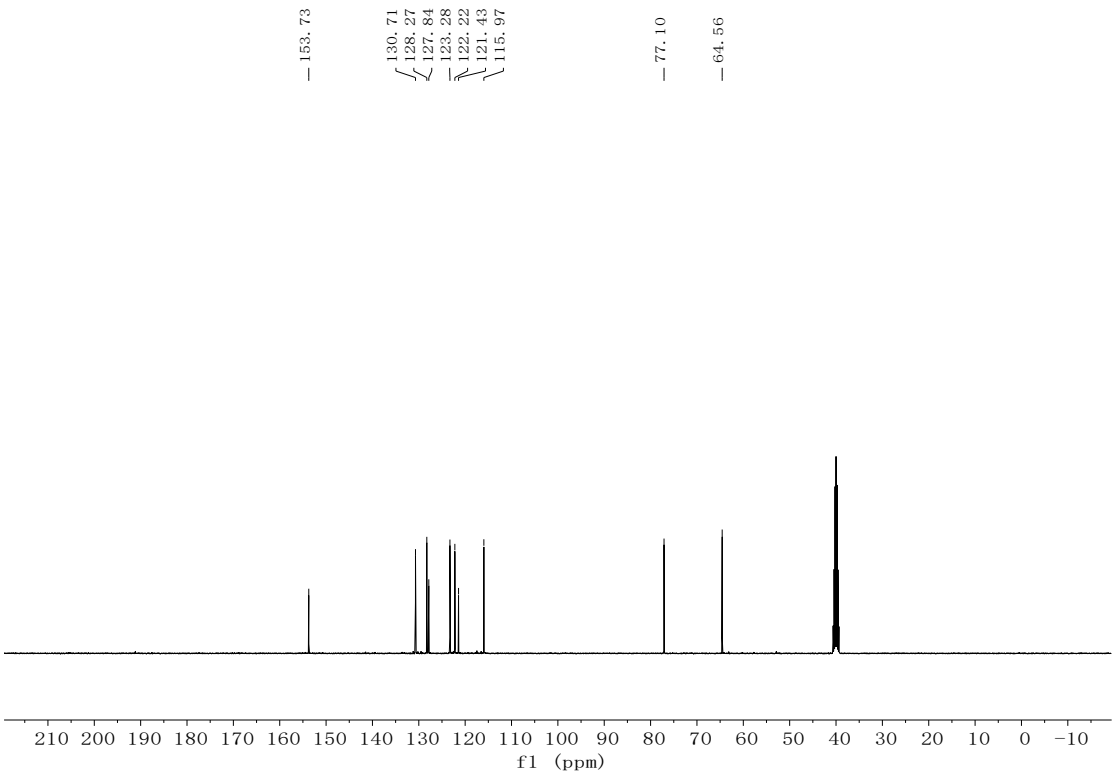

21 #39 RT: 0.6091 AV: 1 NL: 1.26E5
T: FTMS + p NSI Full ms [50.00-800.00]
Relative Abundance
m/z
352.1513
355.3680
353.1545
357.1595
354.1489
344.1265
350.1373
343.7071
348.7682
351.8829

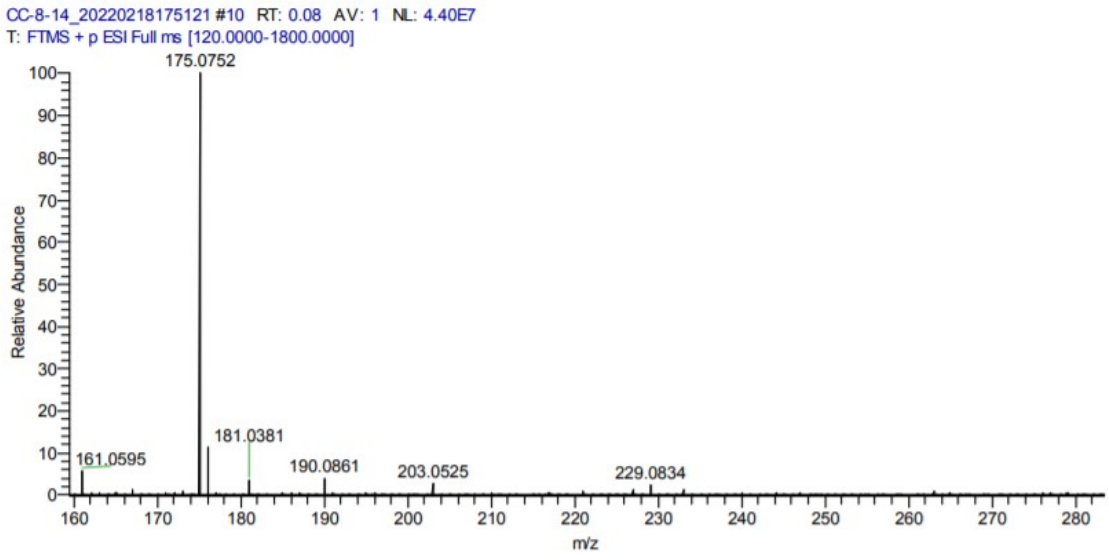

7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.17
6.95
6.94
6.93
6.92
6.91
6.84
6.82
6.77
6.77
6.76
6.08
6.06
4.73
4.73
4.72

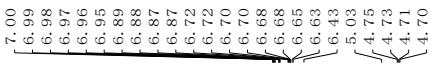
2e


N3
N3
O

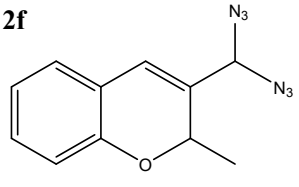

2.15
1.10
1.01
1.03
1.00
2.15
f1 (ppm)

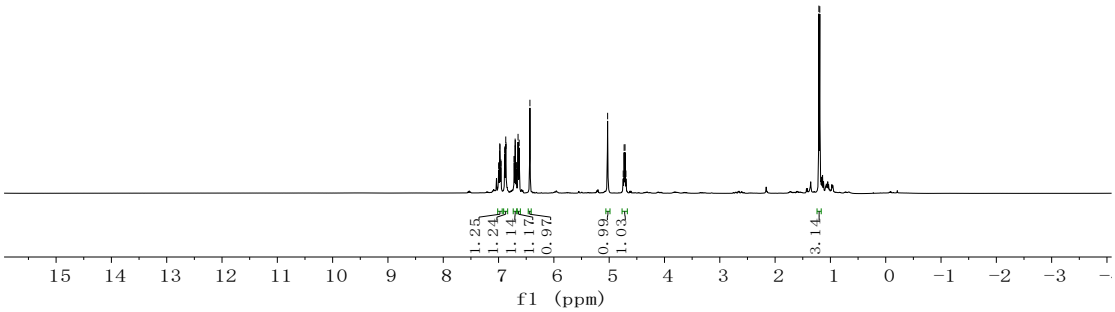

153.73
130.71
128.27
127.84
123.28
122.22
121.43
115.97
77.10
64.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CC-8-14_20220218175121 #10 RT: 0.08 AV: 1 NL: 4.40E7
T: FTMS + p ESI Full ms [120.0000-1800.0000]
175.0752
181.0381
161.0595
190.0861
203.0525
229.0834
Relative Abundance
m/z

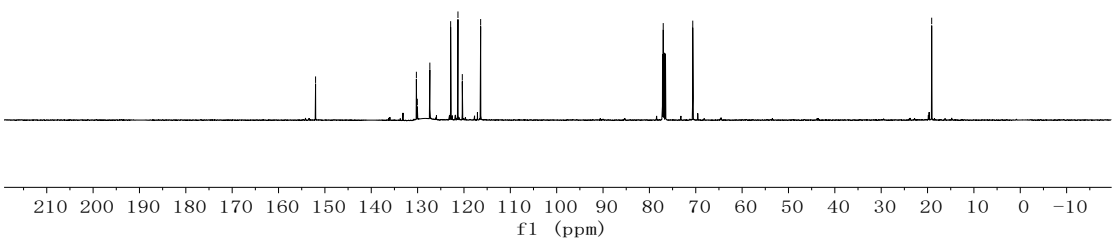

7.00
6.99
6.98
6.97
6.96
6.95
6.89
6.88
6.87
6.87
6.72
6.72
6.70
6.70
6.68
6.68
6.65
6.63
6.43
5.03
4.75
4.73
4.71
4.70
1.21
1.19

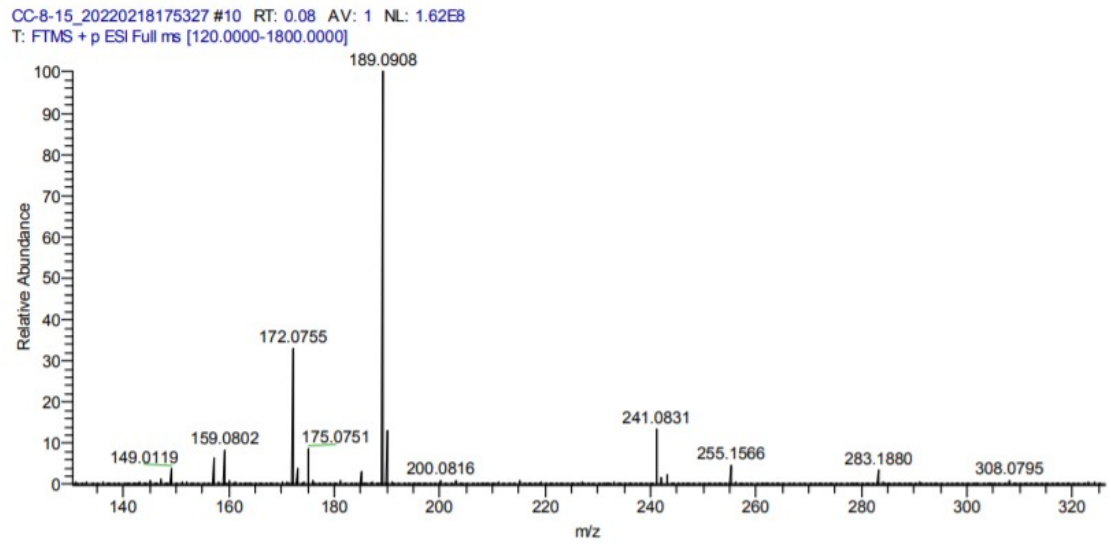
2f

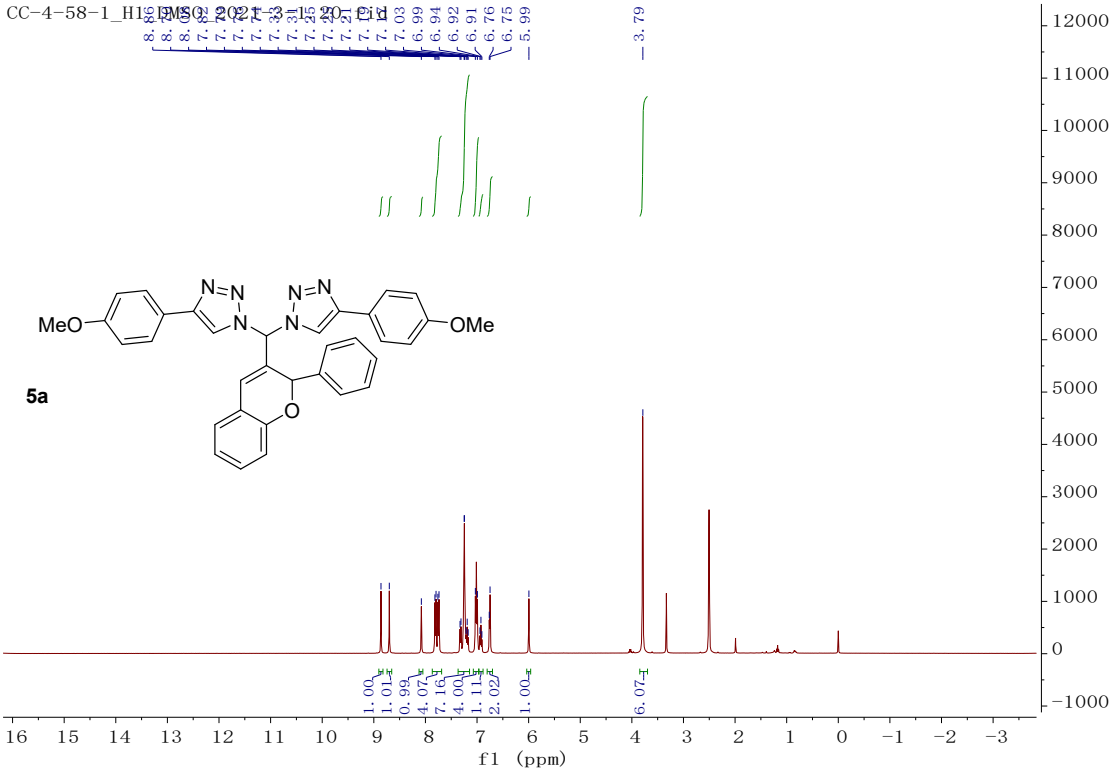

N3
N3
O

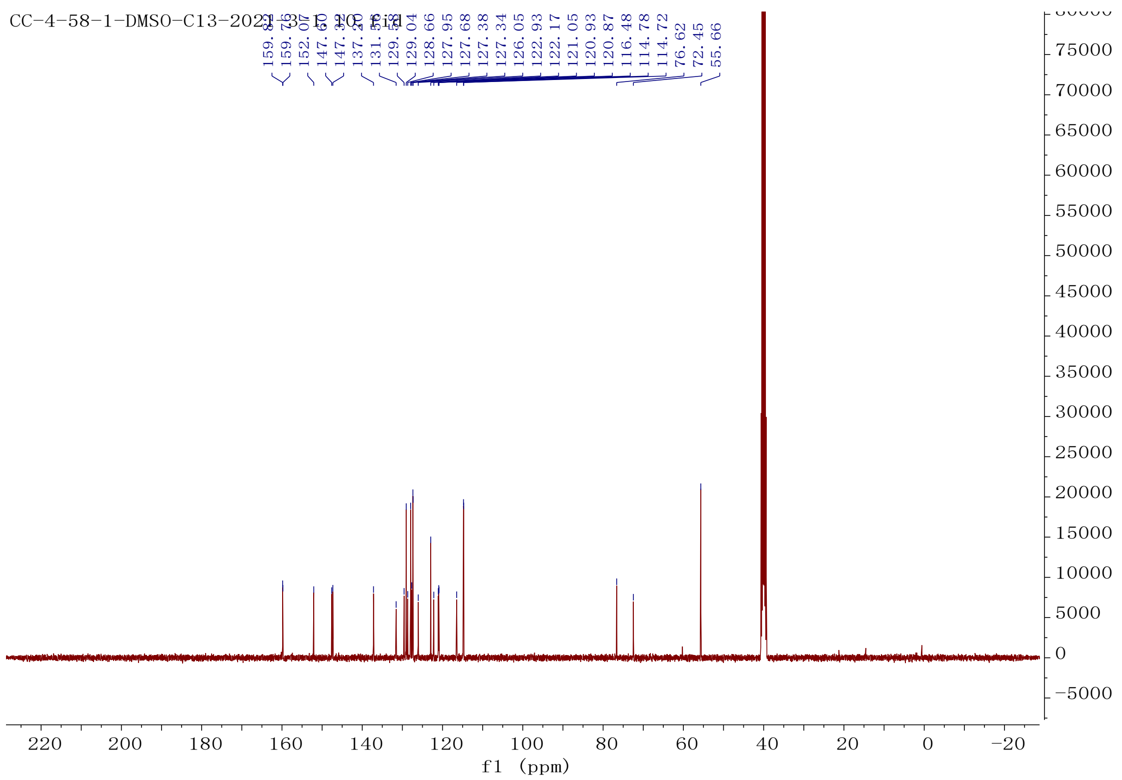

1.25
1.24
1.14
1.17
0.97
0.99
1.03
3.14
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

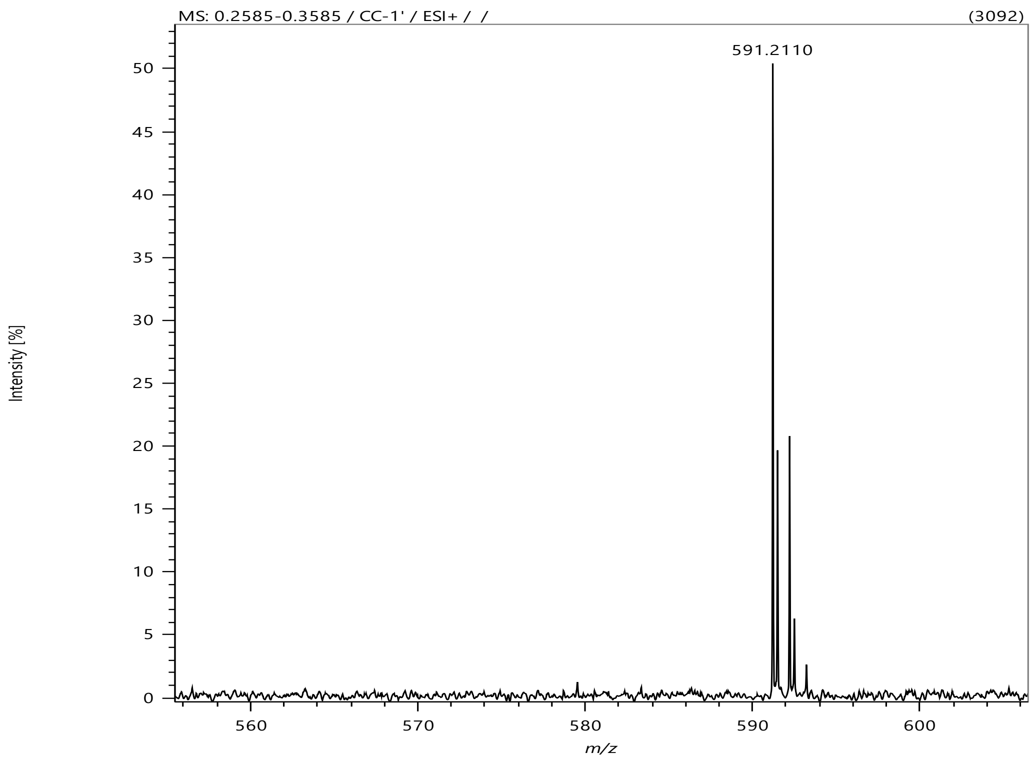

152.01
130.26
130.06
127.36
122.87
121.30
120.36
116.40
77.02
70.65
19.11

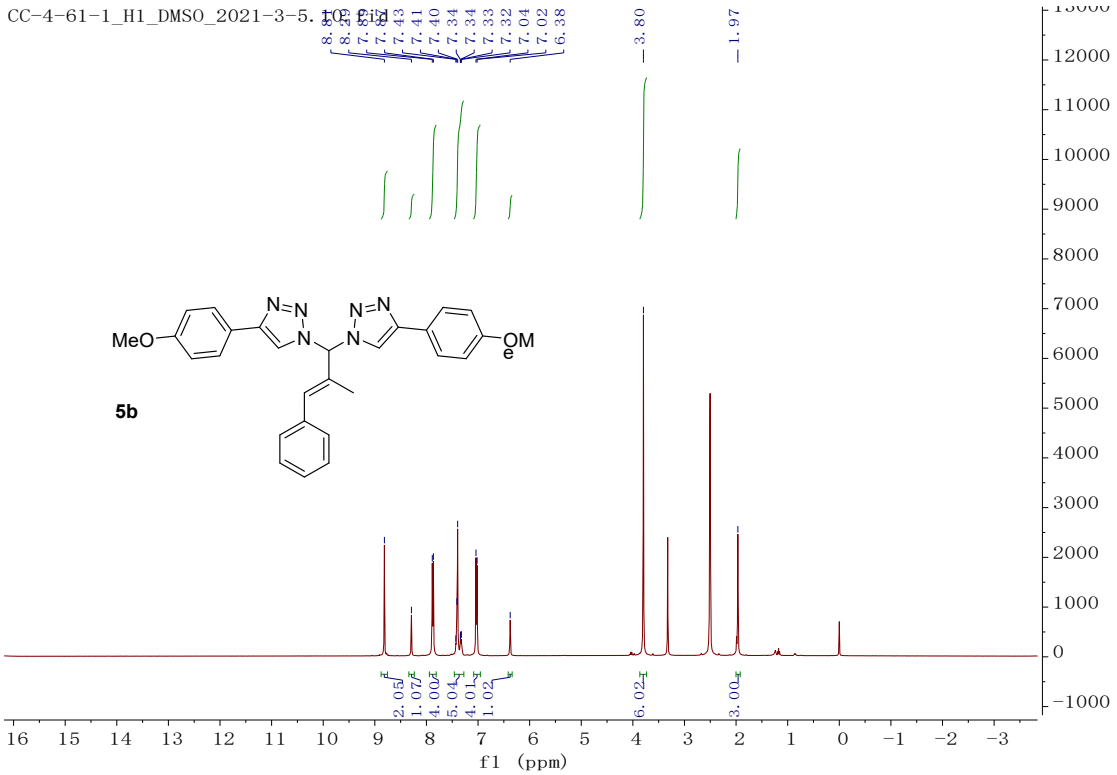

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

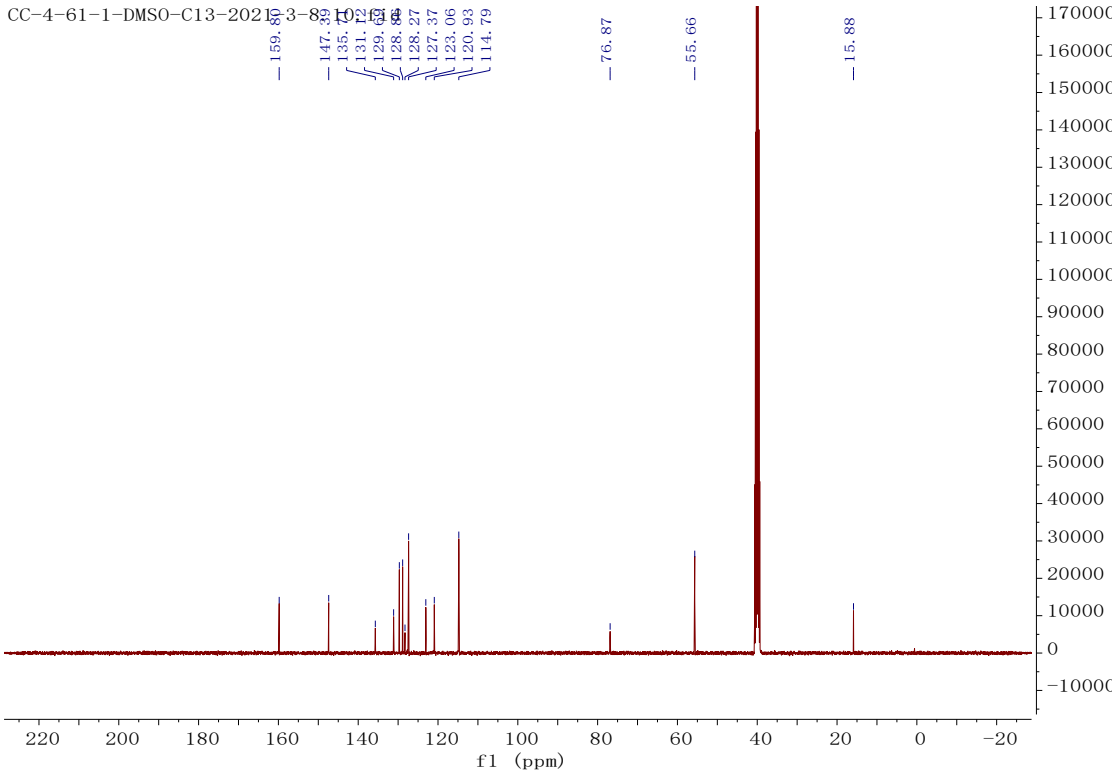

CC-8-15_20220218175327 #10 RT: 0.08 AV: 1 NL: 1.62E8
T: FTMS + p ESI Full ms [120.0000-1800.0000]
189.0908
172.0755
241.0831
159.0802
175.0751
149.0119
200.0816
255.1566
283.1880
308.0795
Relative Abundance
m/z

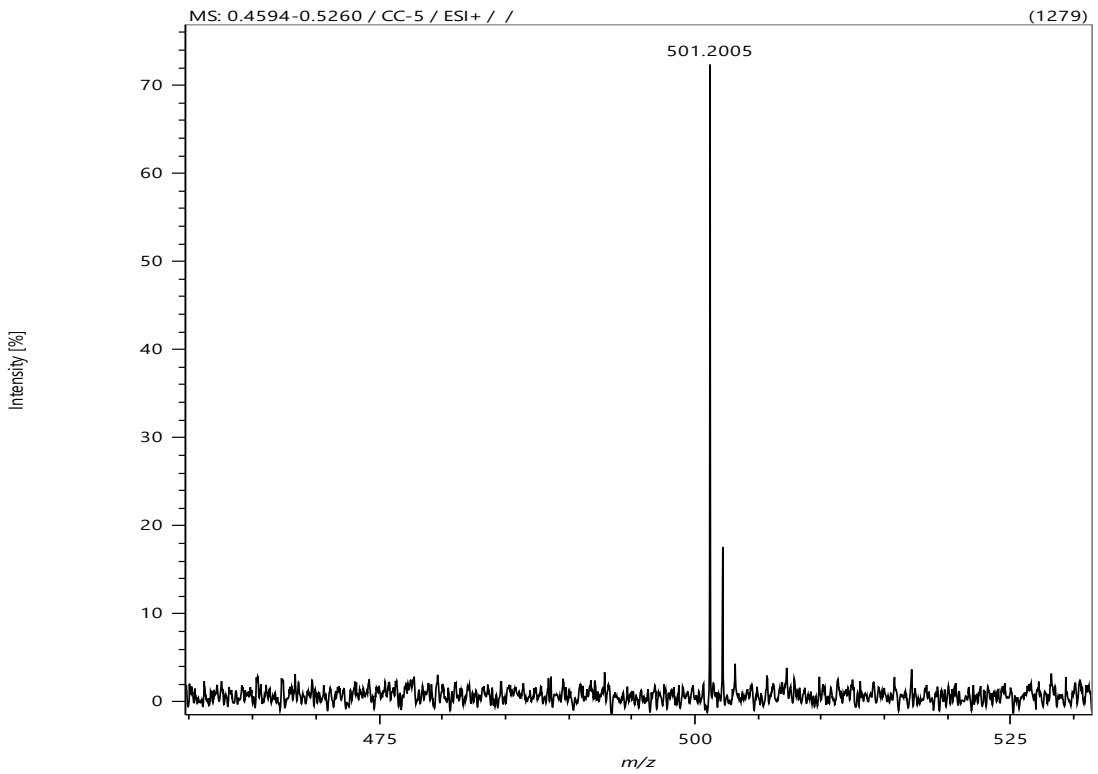

MeO
OMe
5a
f1 (ppm)

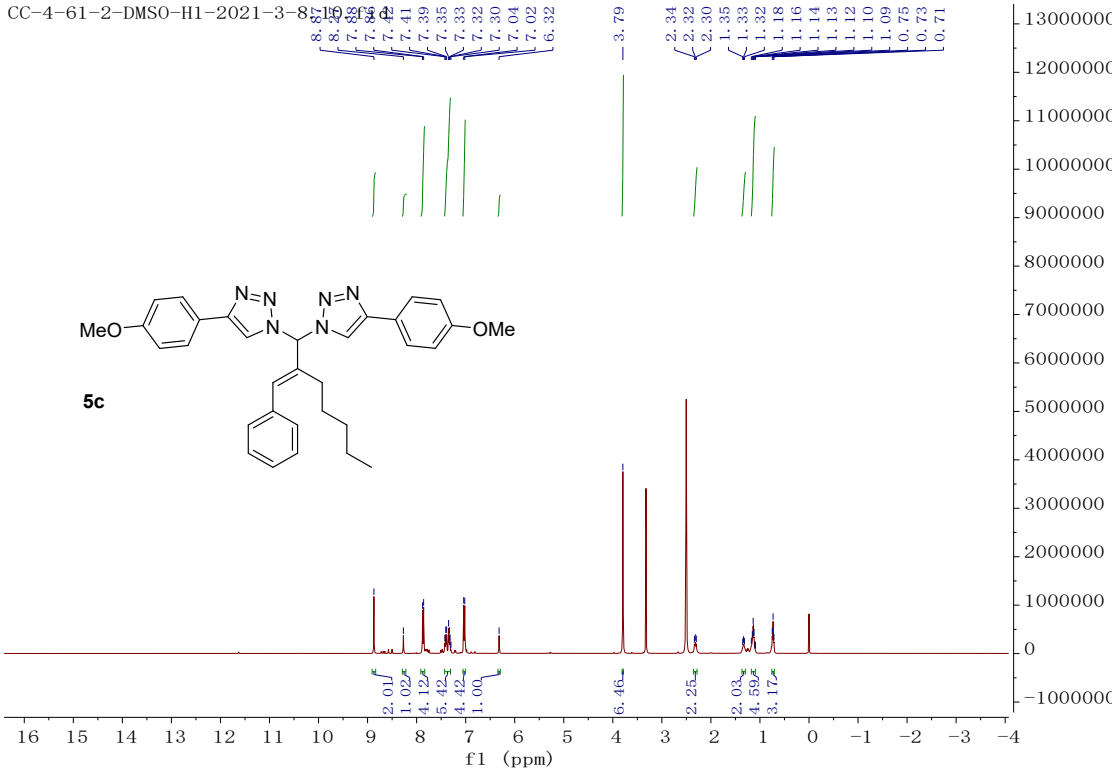

CC-4-58-1-DMSO-C13-2021-3-1-10C.fid
159.75
152.07
147.70
147.30
137.20
131.54
129.54
129.04
128.66
127.95
127.68
127.38
127.34
126.05
122.93
122.17
121.05
120.93
120.87
116.48
114.78
114.72
76.62
72.45
55.66
f1 (ppm)

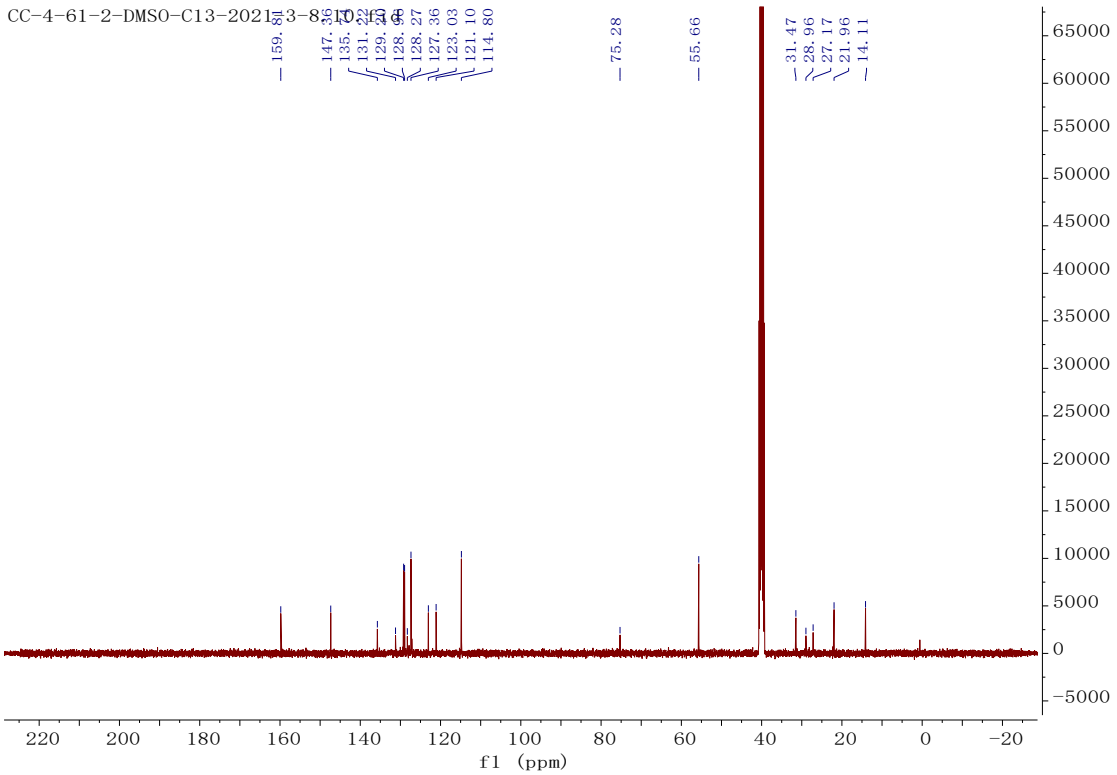

MS: 0.2585-0.3585 / CC-1' / ESI+ / /
(3092)
591.2110
Intensity [%]
m/z

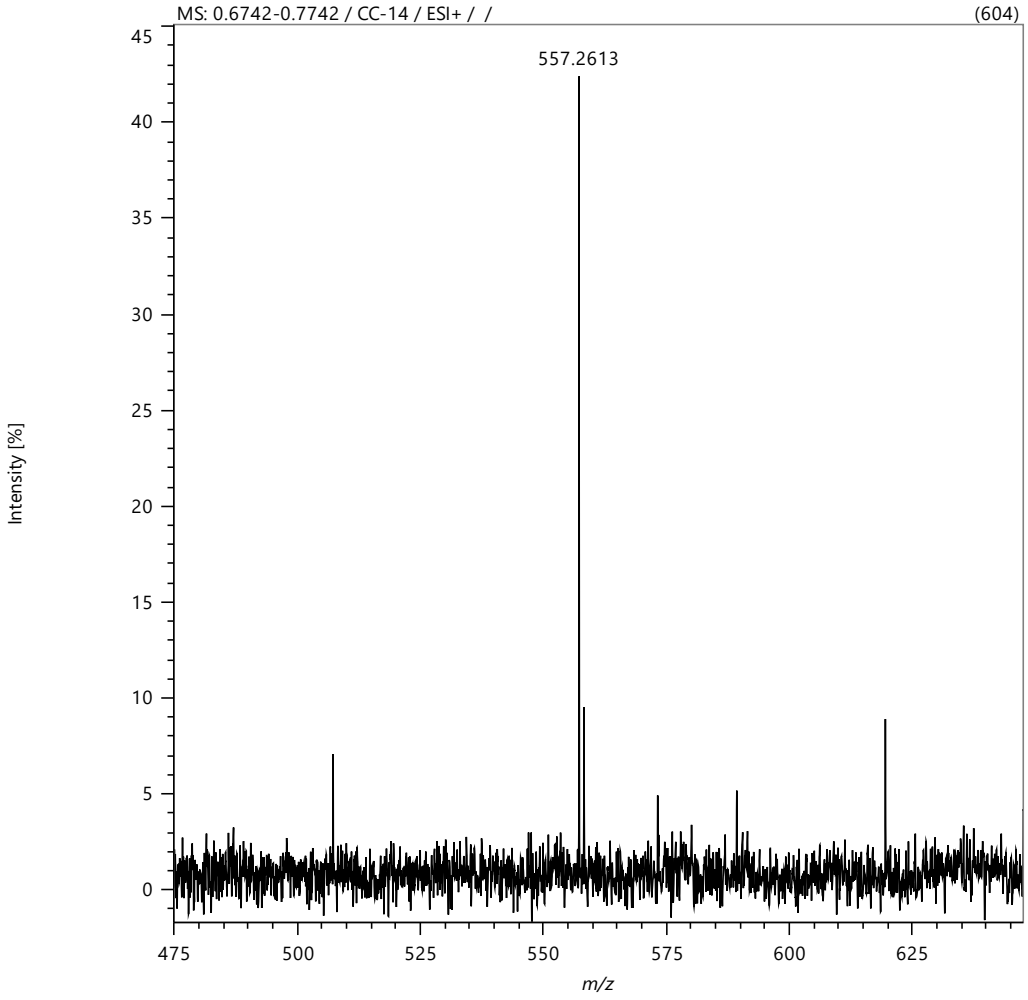

CC-4-61-1_H1_DMSO_2021-3-5.10.2.fid
8.29
8.27
7.84
7.82
7.43
7.41
7.40
7.34
7.34
7.33
7.32
7.04
7.02
6.38
3.80
1.97
MeO
OMe
5b
2.05
1.07
4.00
5.04
4.01
1.02
6.02
3.00
f1 (ppm)

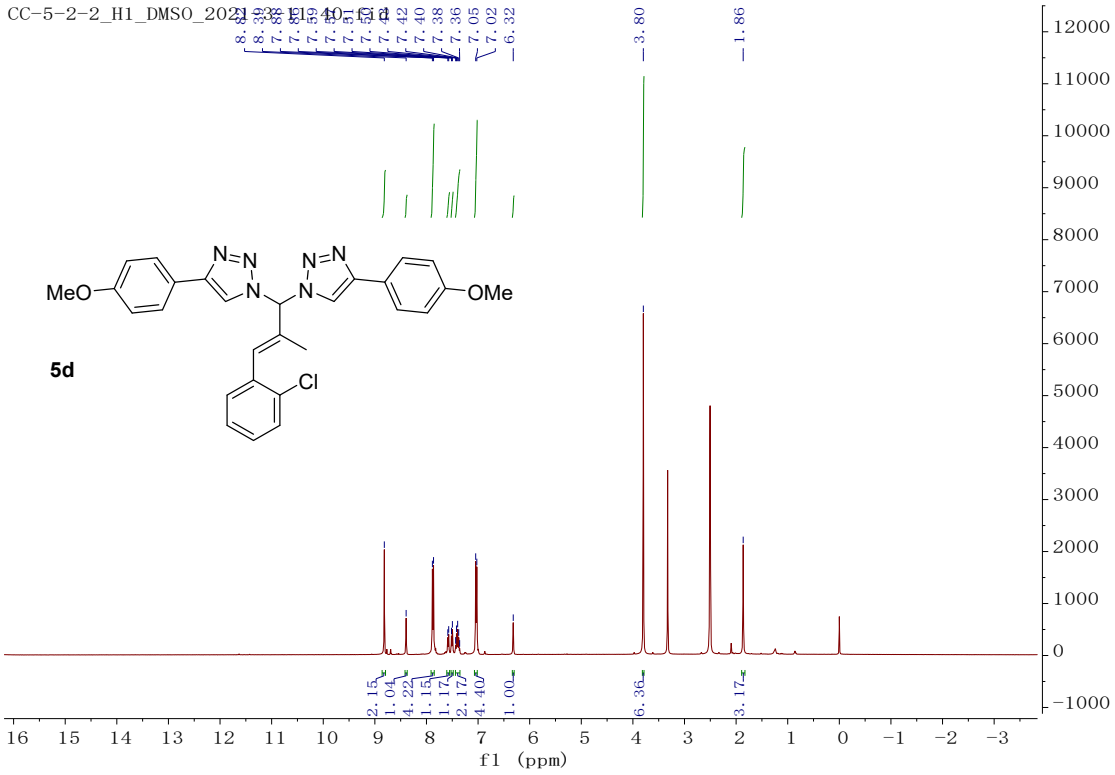

CC-4-61-1-DMSO-C13-2021-3-8.1.0.fid
159.80
147.39
135.12
131.12
129.64
128.84
128.27
127.37
123.06
120.93
114.79
76.87
55.66
39.15
f1 (ppm)

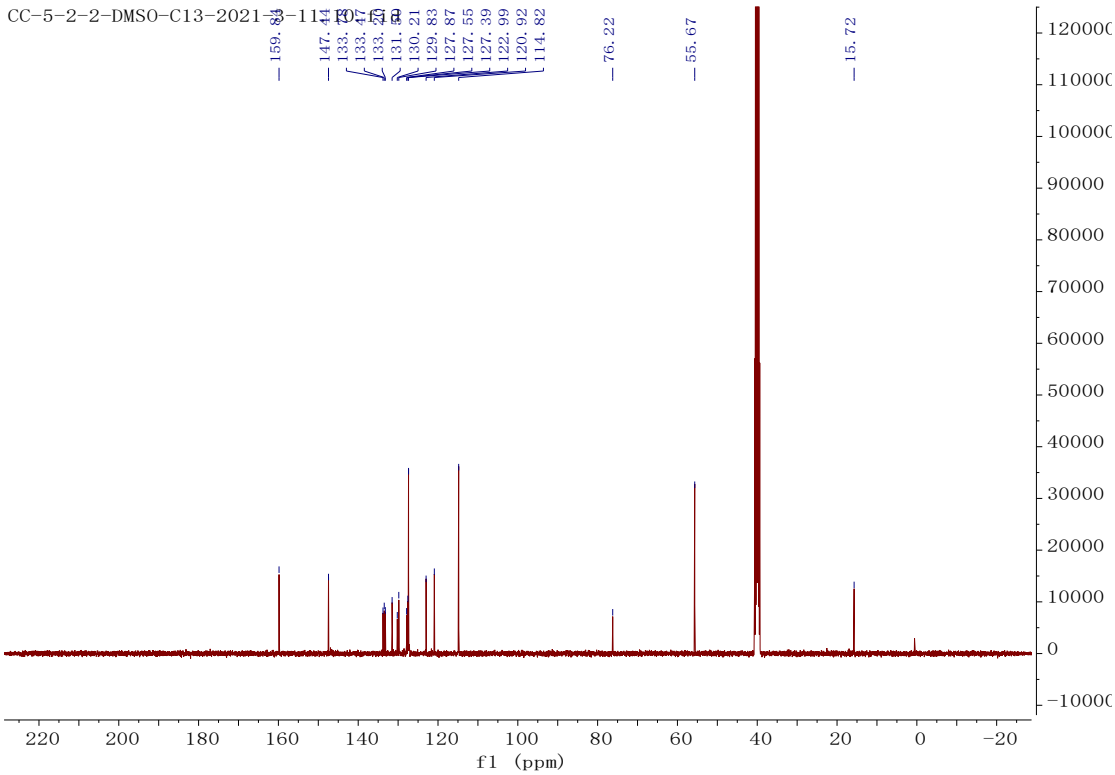

MS: 0.4594-0.5260 / CC-5 / ESI+ / /
(1279)
501.2005
Intensity [%]
m/z

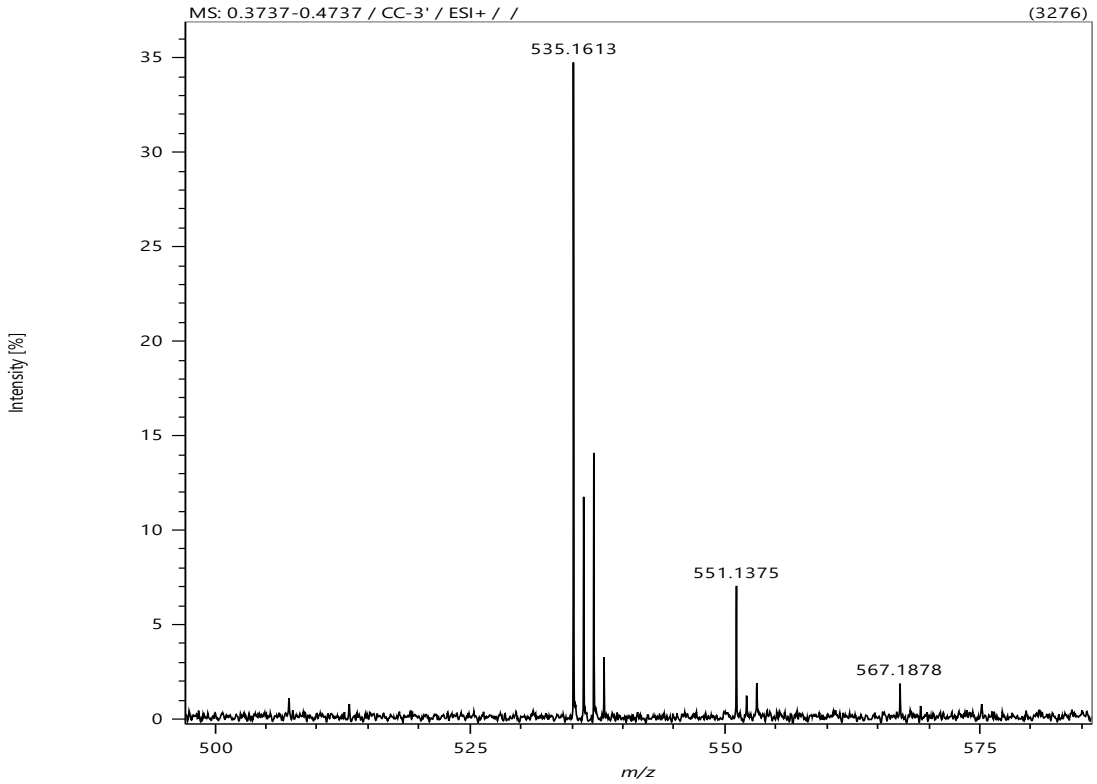

MeO
OMe
5c
f1 (ppm)

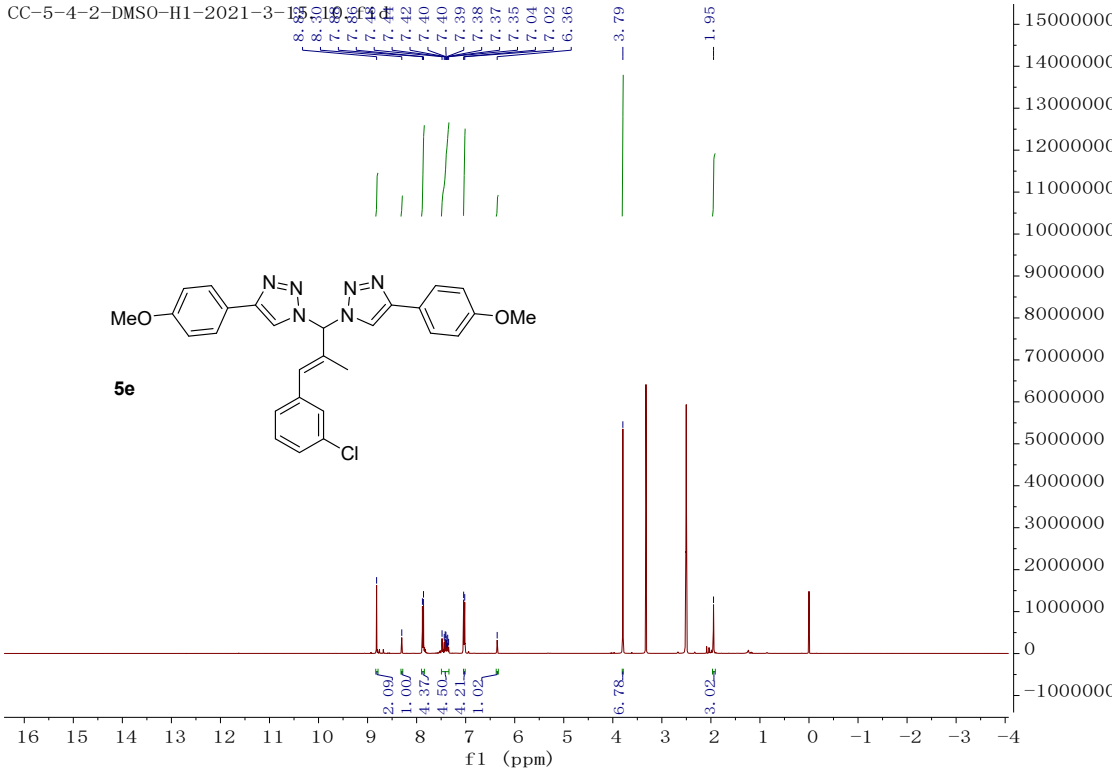

CC-4-61-2-DMSO-C13-2021-3-8-10-45-8
159.81
147.36
135.42
131.22
129.46
128.99
128.27
127.36
123.03
121.10
114.80
75.28
55.66
31.47
28.96
27.17
21.96
14.11
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
220
200
180
160
140
120
100
80
60
40
20
0
−20
f1 (ppm)

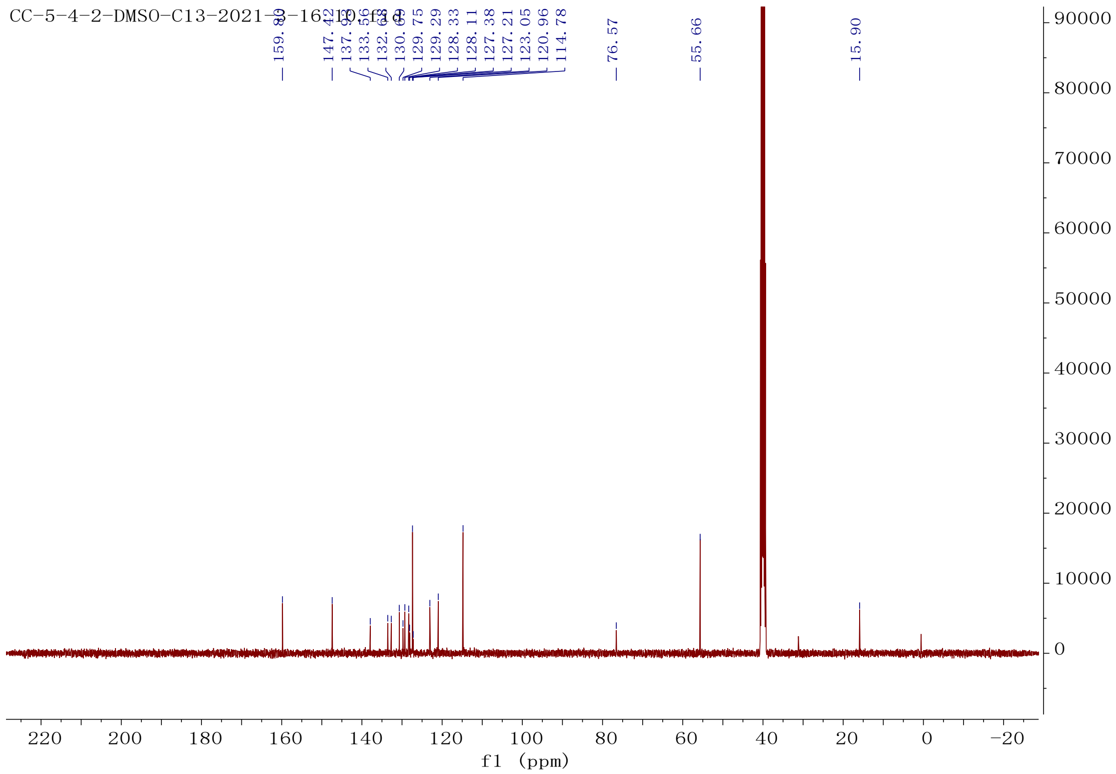

MS: 0.6742-0.7742 / CC-14 / ESI+ / /
(604)
557.2613
Intensity [%]
45
40
35
30
25
20
15
10
5
0
475
500
525
550
575
600
625
m/z


MeO
OMe
Cl
5d
f1 (ppm)

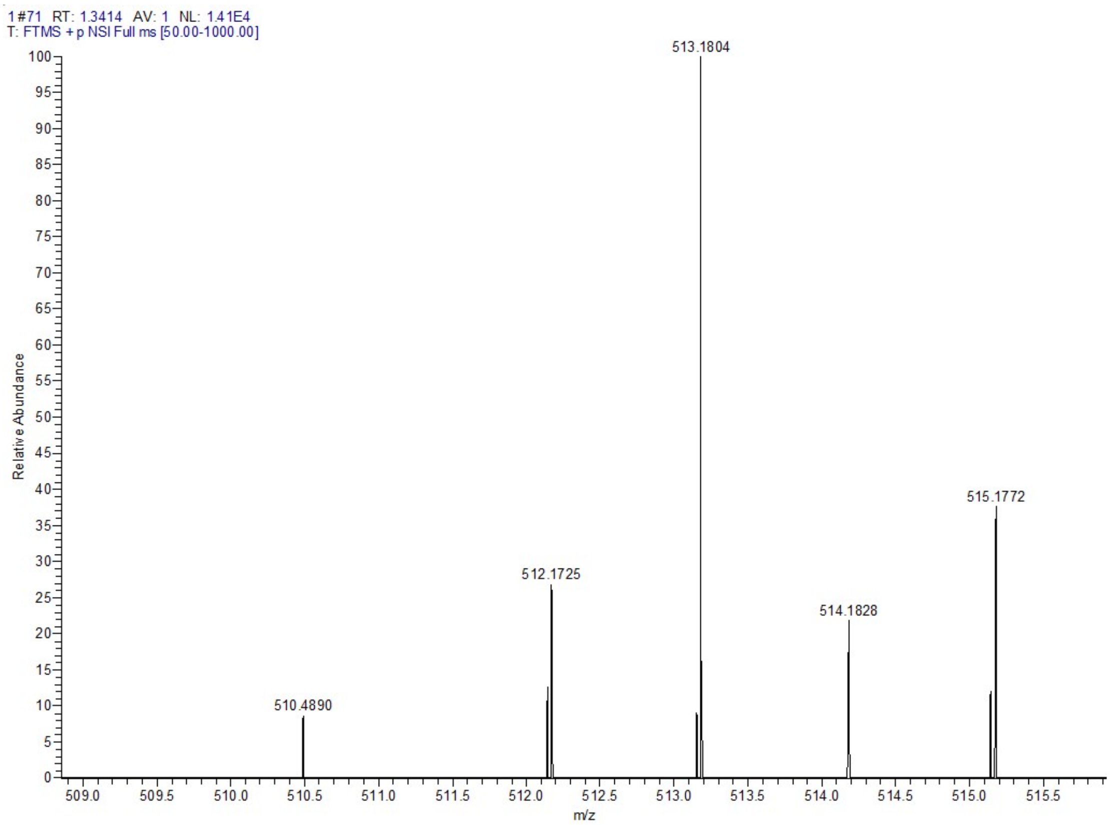

f1 (ppm)


MS: 0.3737-0.4737 / CC-3' / ESI+ / /
(3276)
535.1613
551.1375
567.1878
Intensity [%]
m/z

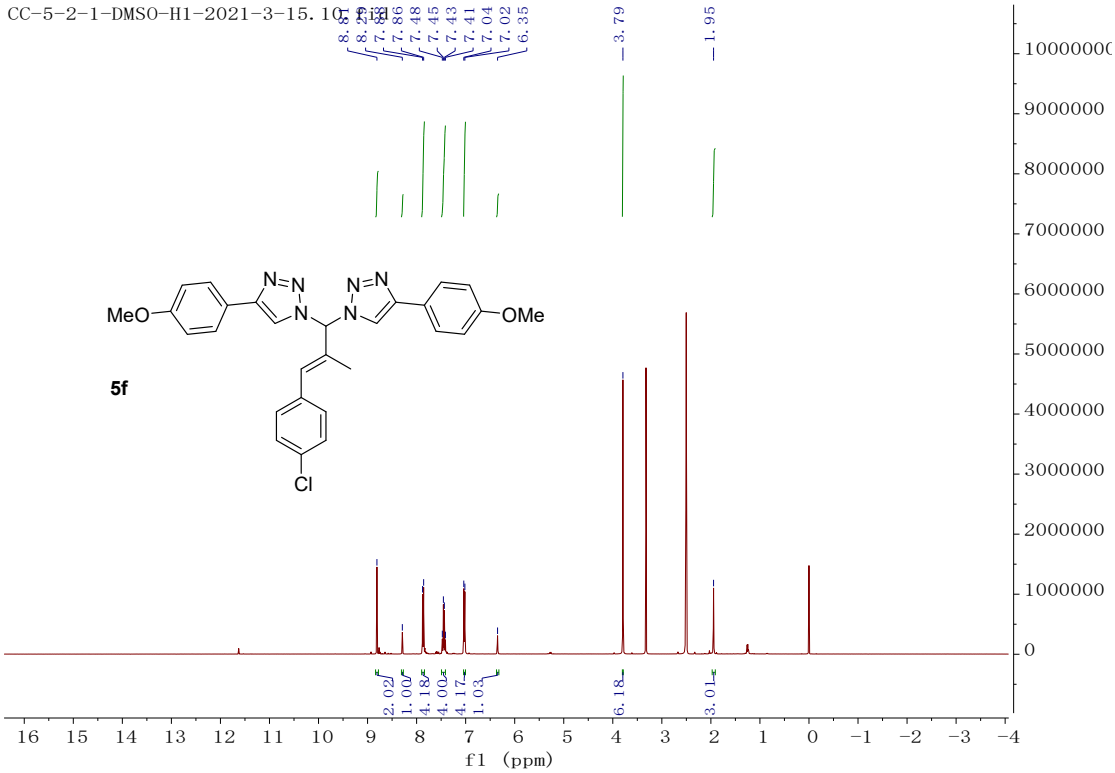

MeO
OMe
Cl
5e
f1 (ppm)

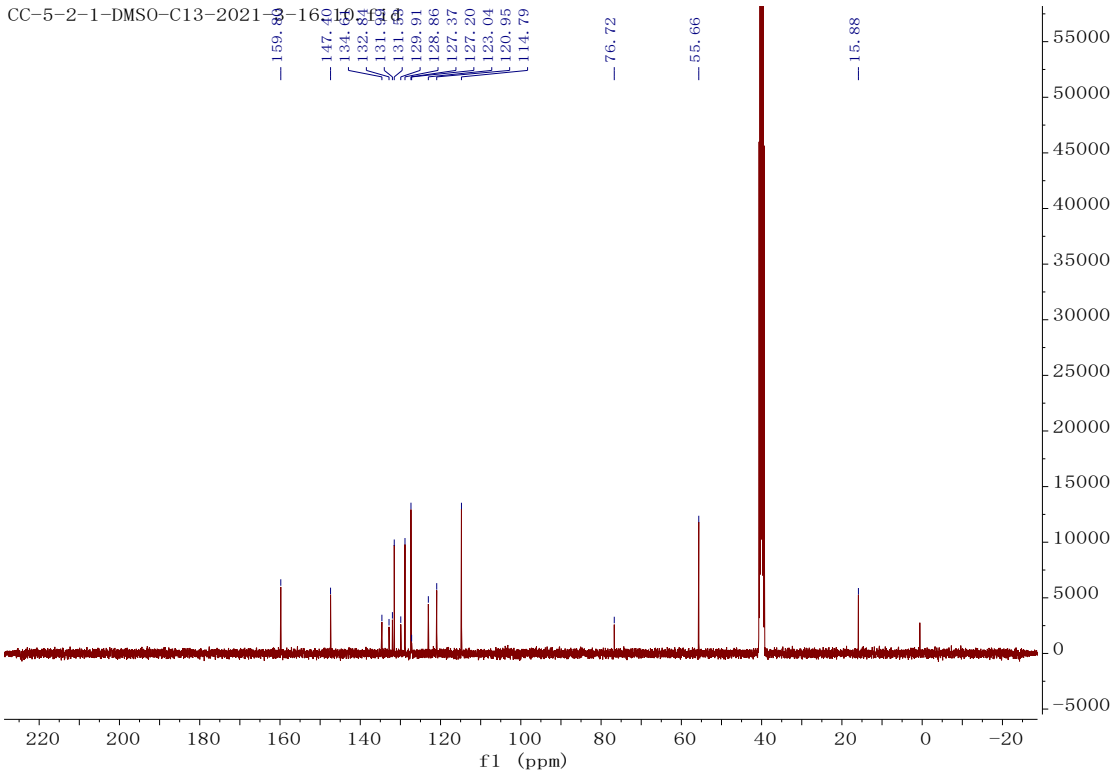


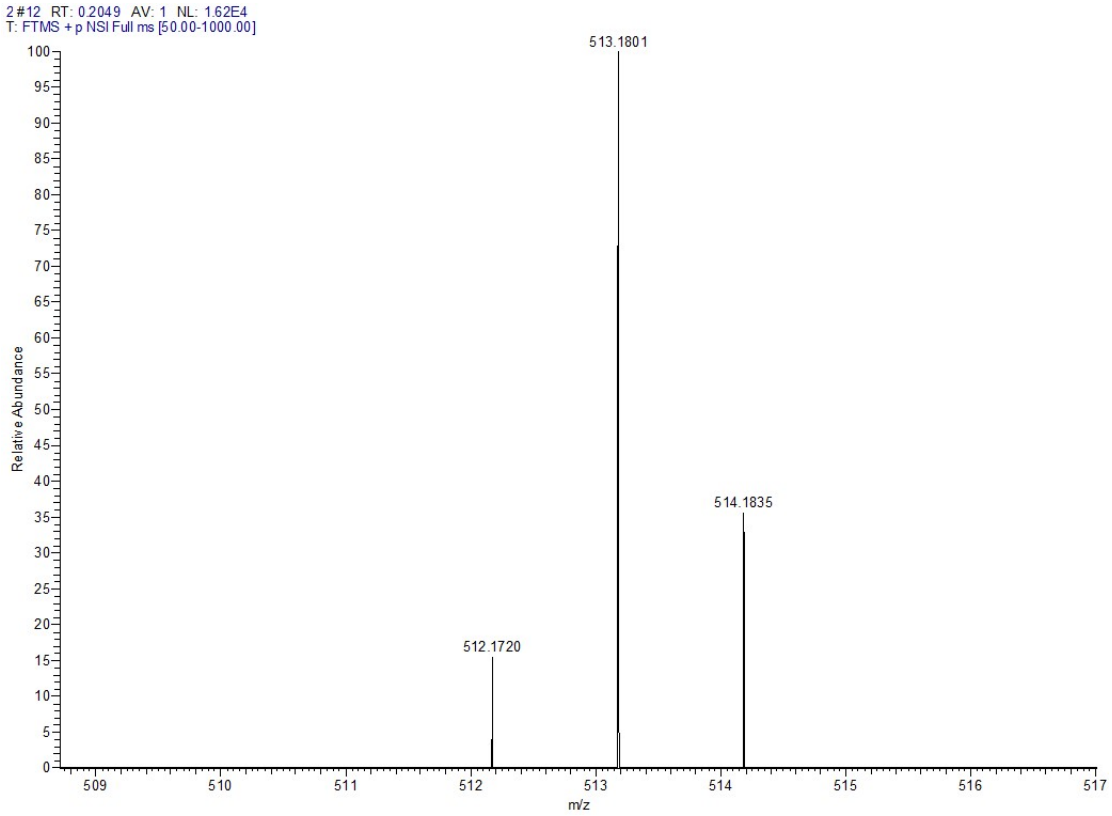
CC-5-4-2-DMSO-C13-2021-9-16.10.fid
159.80
147.42
137.95
133.56
132.63
130.69
129.75
129.29
128.33
128.11
127.38
127.21
123.05
120.96
114.78
76.57
55.66
15.90
f1 (ppm)

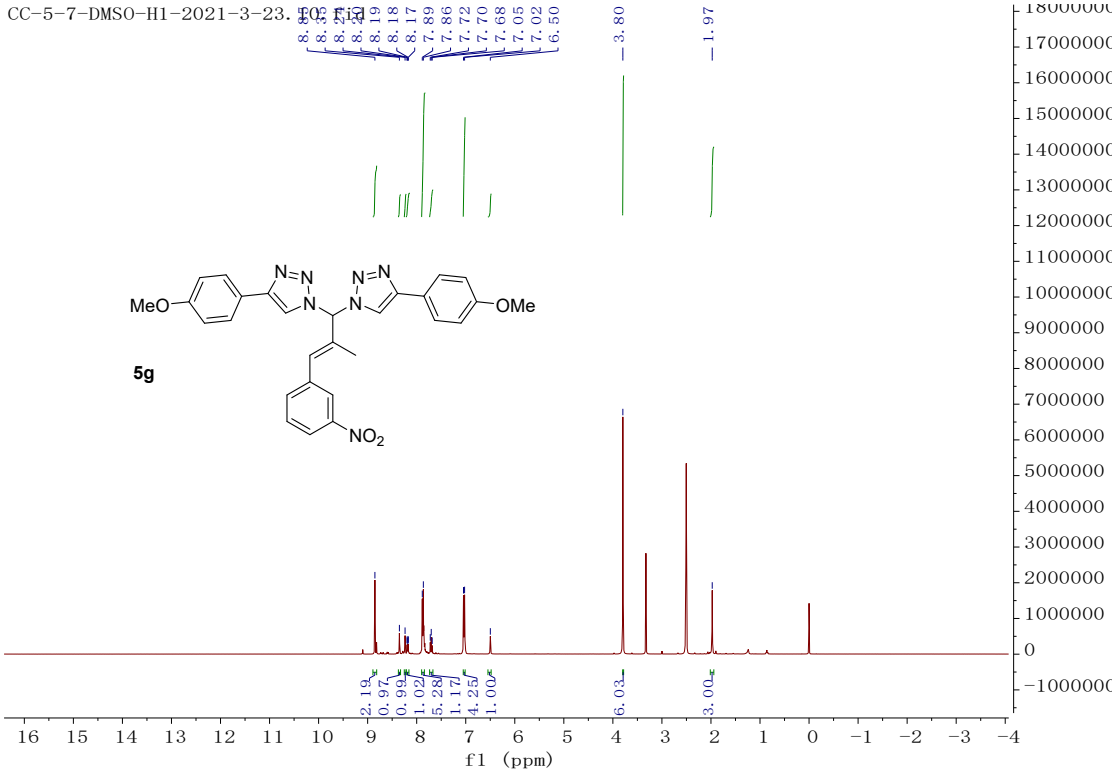


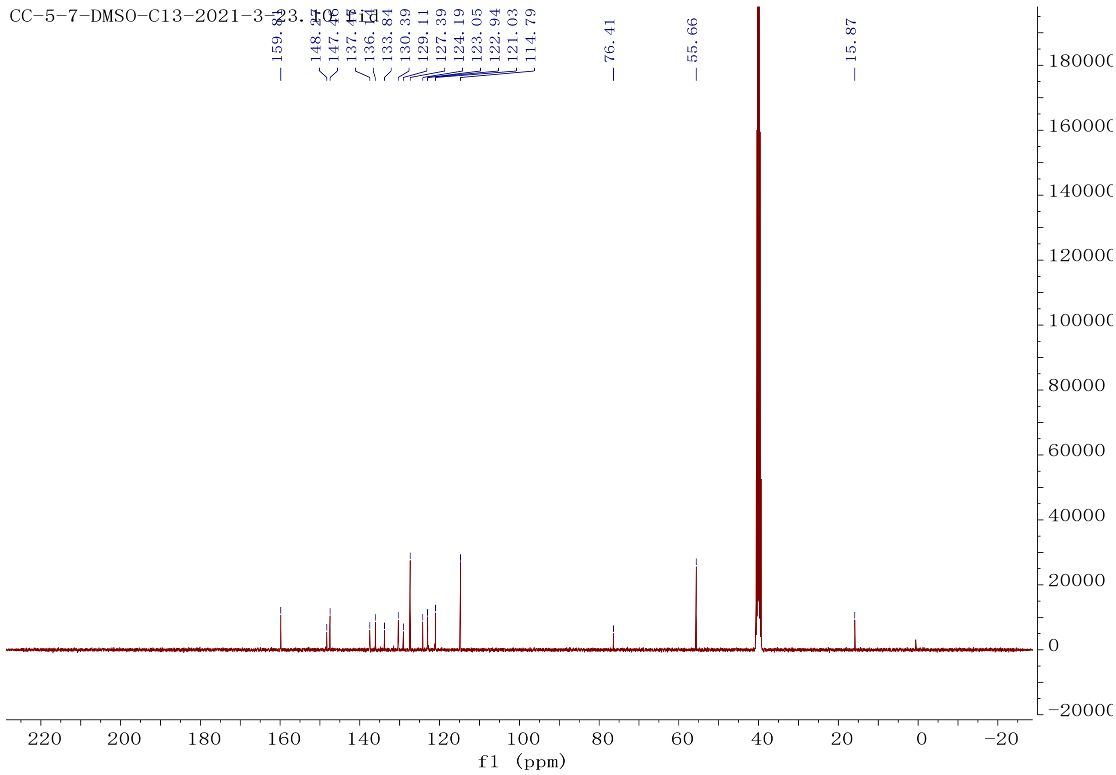
1#71 RT: 1.3414 AV: 1 NL: 1.41E4
T: FTMS + p NSI Full ms [50.00-1000.00]
513.1804
515.1772
512.1725
514.1828
510.4890
Relative Abundance
m/z

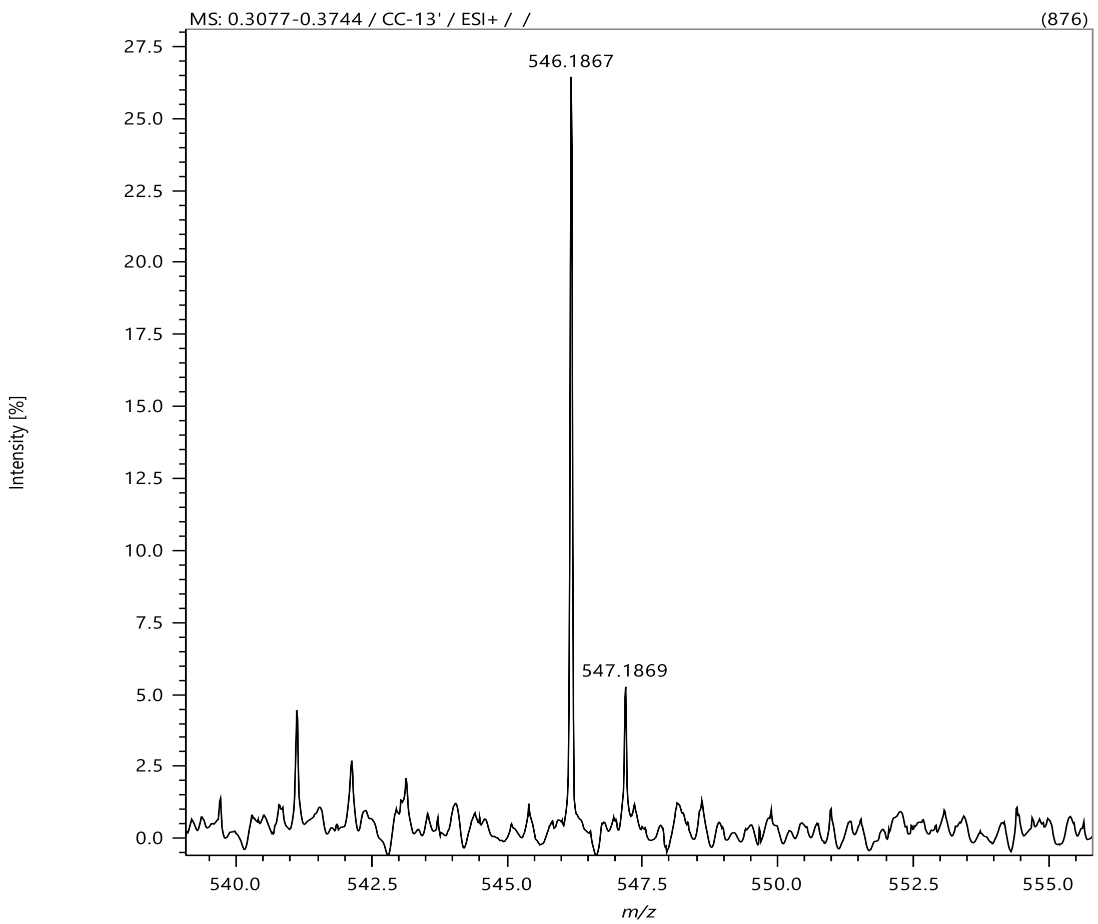

CC-5-2-1-DMSO-H1-2021-3-15.10.fid
8.44
8.43
7.88
7.86
7.48
7.45
7.43
7.41
7.04
7.02
6.35
3.79
1.95
MeO
OMe
Cl
5f
2.02
1.00
4.18
4.00
4.17
1.03
6.18
3.01
f1 (ppm)

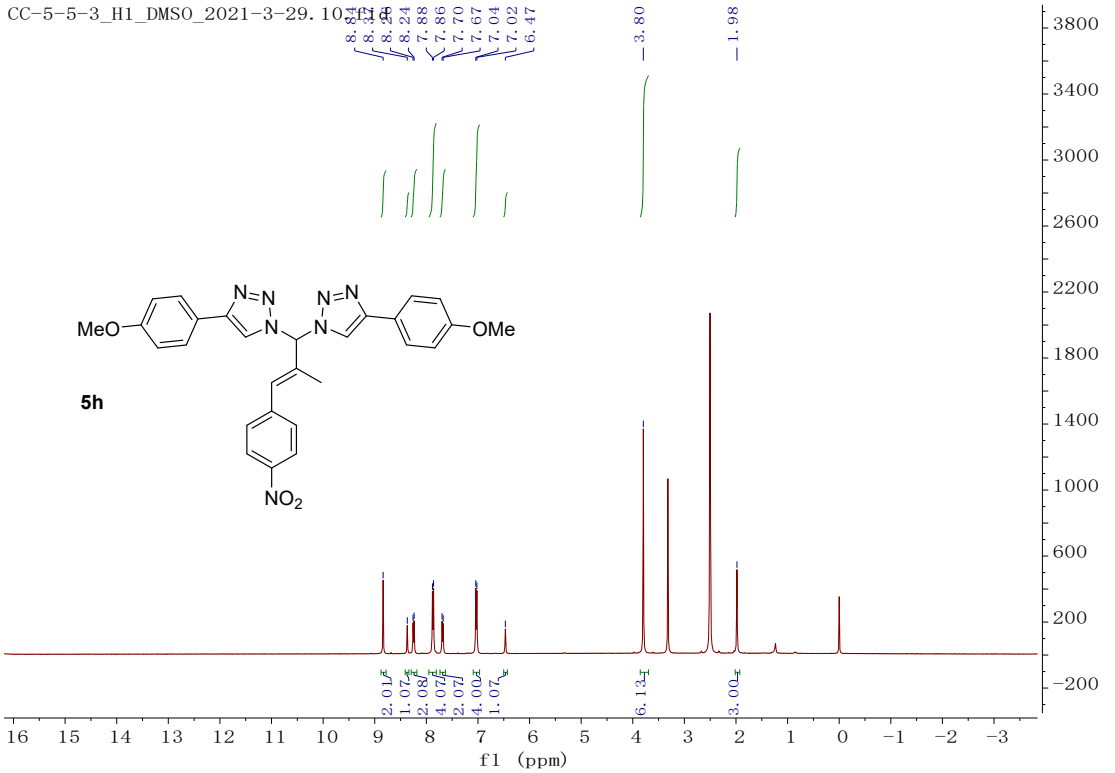

CC-5-2-1-DMSO-C13-2021-3-16.10.fid
159.80
147.40
134.66
132.84
131.94
131.58
129.91
128.86
127.37
127.20
123.04
120.95
114.79
76.72
55.66
15.88
f1 (ppm)

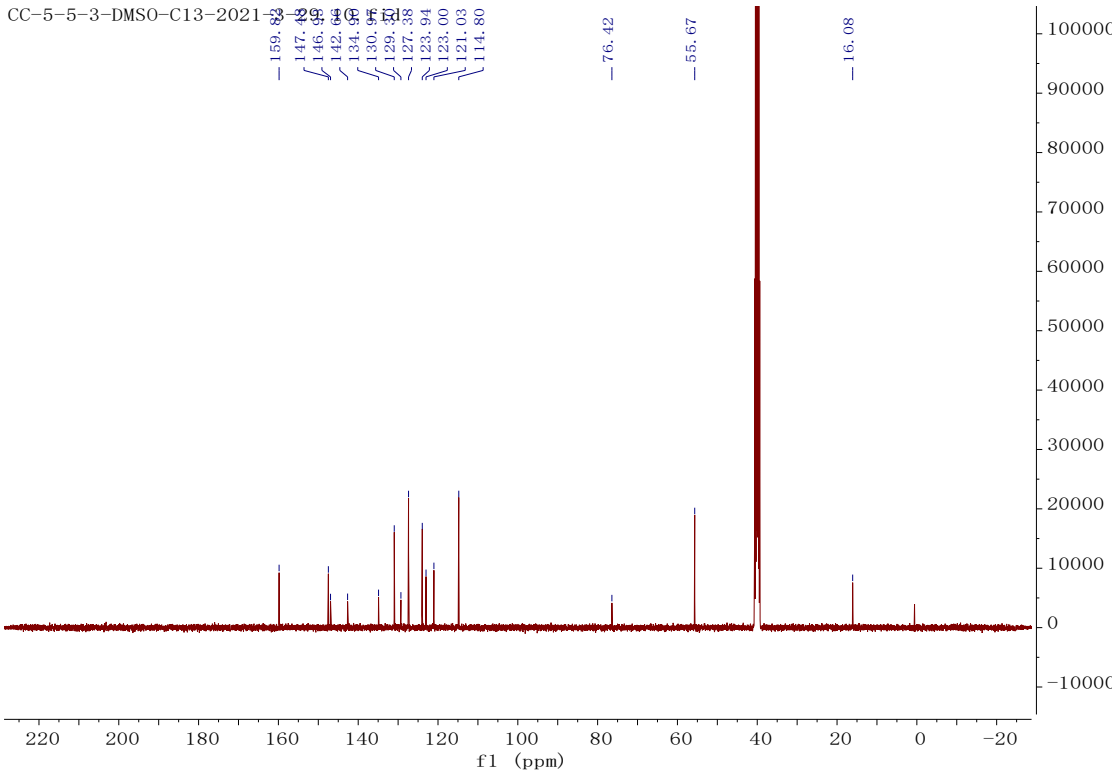

2 #12 RT: 0.2049 AV: 1 NL: 1.62E4
T: FTMS + p NSI Full ms [50.00-1000.00]
513.1801
514.1835
512.1720
Relative Abundance
m/z

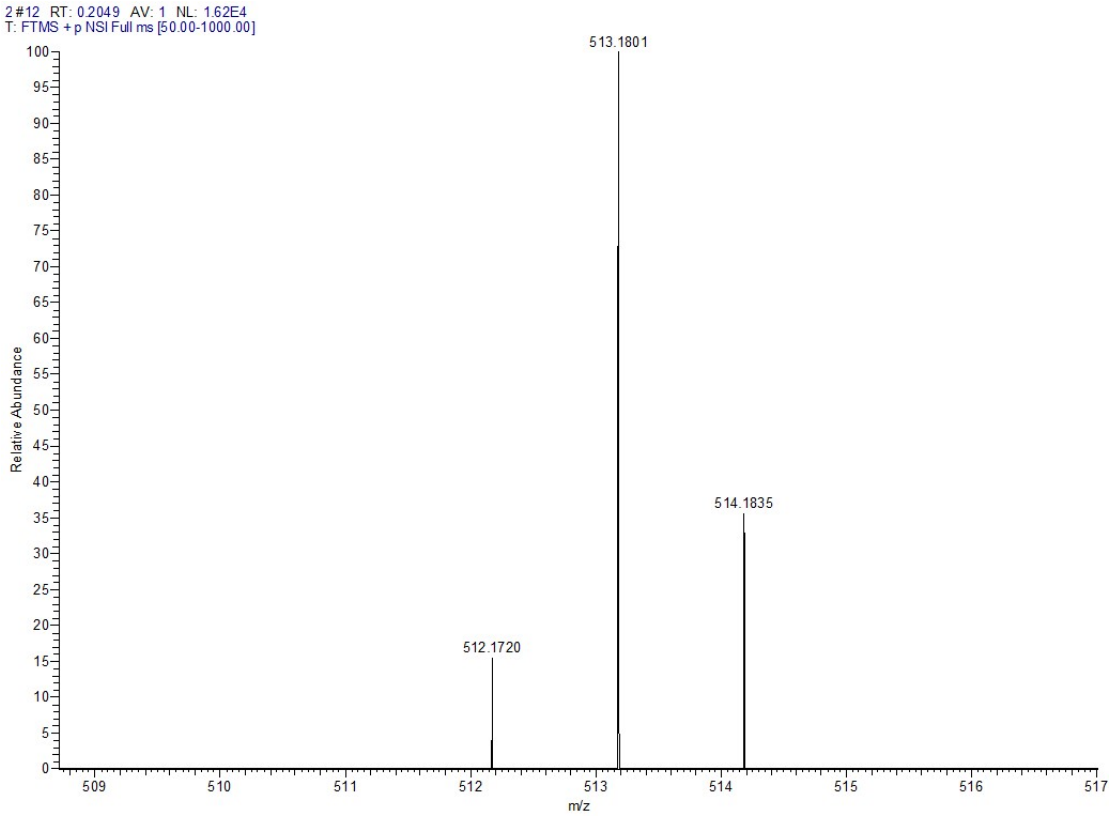

CC-5-7-DMSO-H1-2021-3-23.10.1.1
8.53
8.51
8.24
8.19
8.18
8.17
7.89
7.86
7.72
7.70
7.68
7.05
7.02
6.50
3.80
1.97
MeO
OMe
NO2
5g
2.19
0.97
0.99
1.02
5.28
1.17
4.25
1.00
6.03
3.00
f1 (ppm)

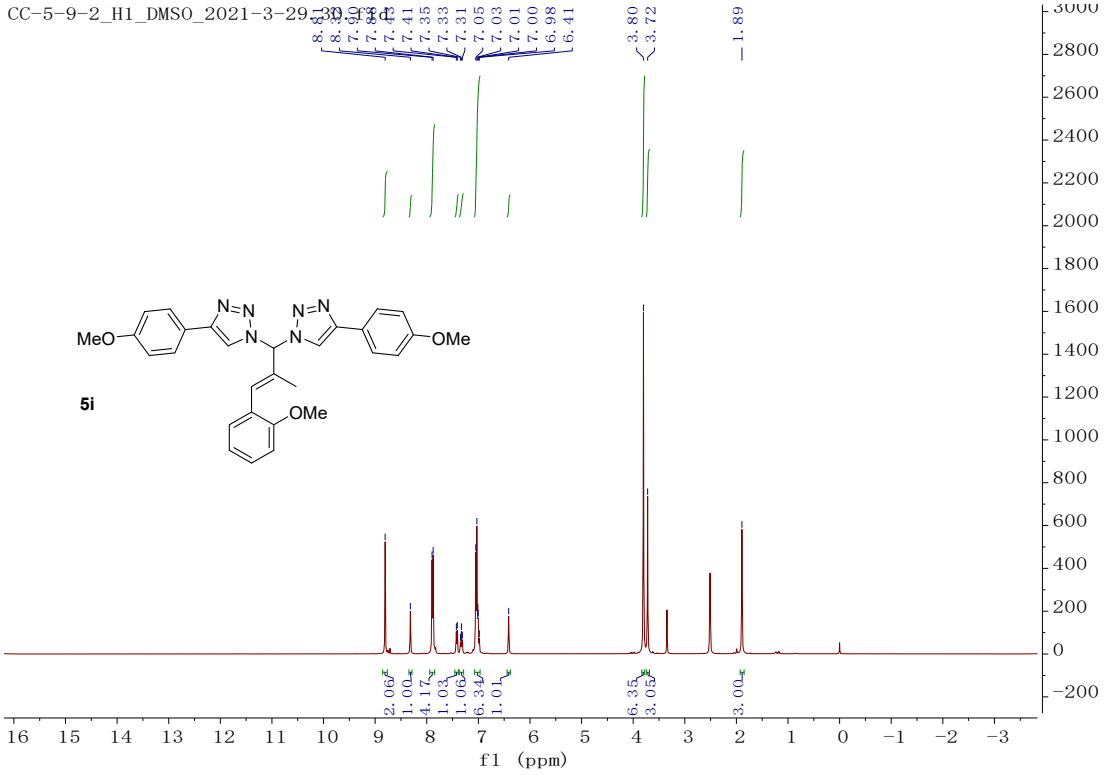

CC-5-7-DMSO-C13-2021-3-23.10.fid
159.81
148.27
147.45
137.45
136.11
133.84
130.39
129.11
127.39
124.19
123.05
122.94
121.03
114.79
76.41
55.66
15.87
f1 (ppm)

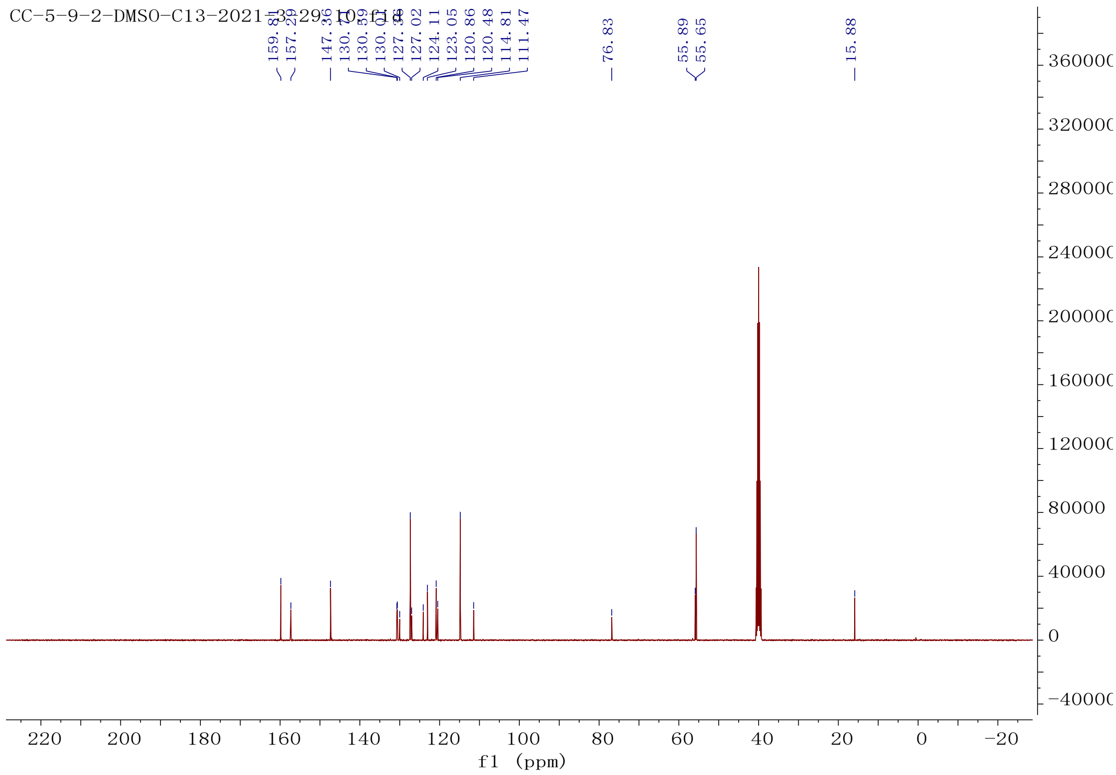

MS: 0.3077-0.3744 / CC-13' / ESI+ / /
(876)
546.1867
547.1869
Intensity [%]
m/z

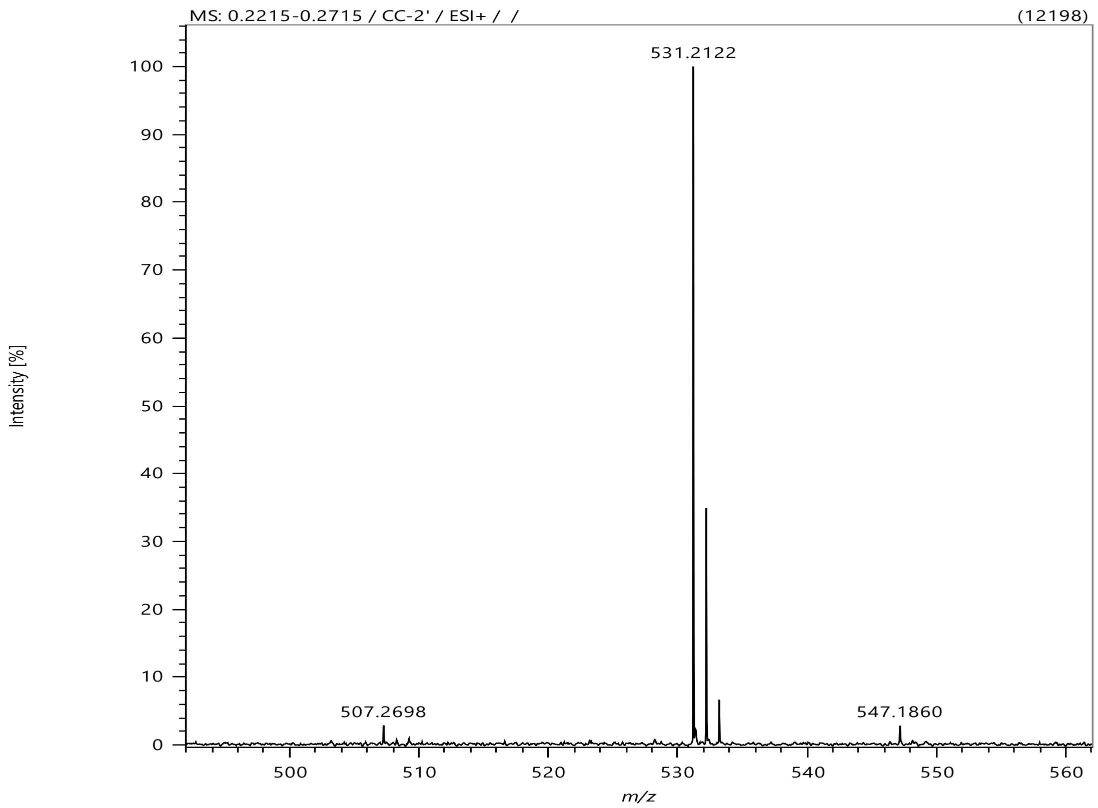

CC-5-5-3_H1_DMSO_2021-3-29.10.fid
8.44
8.34
8.24
7.88
7.86
7.70
7.67
7.04
7.02
6.47
3.80
1.98
MeO
OMe
N=N
N=N
N
N
NO2
5h
2.01
1.07
2.05
4.07
2.07
4.00
1.07
6.13
3.00
f1 (ppm)

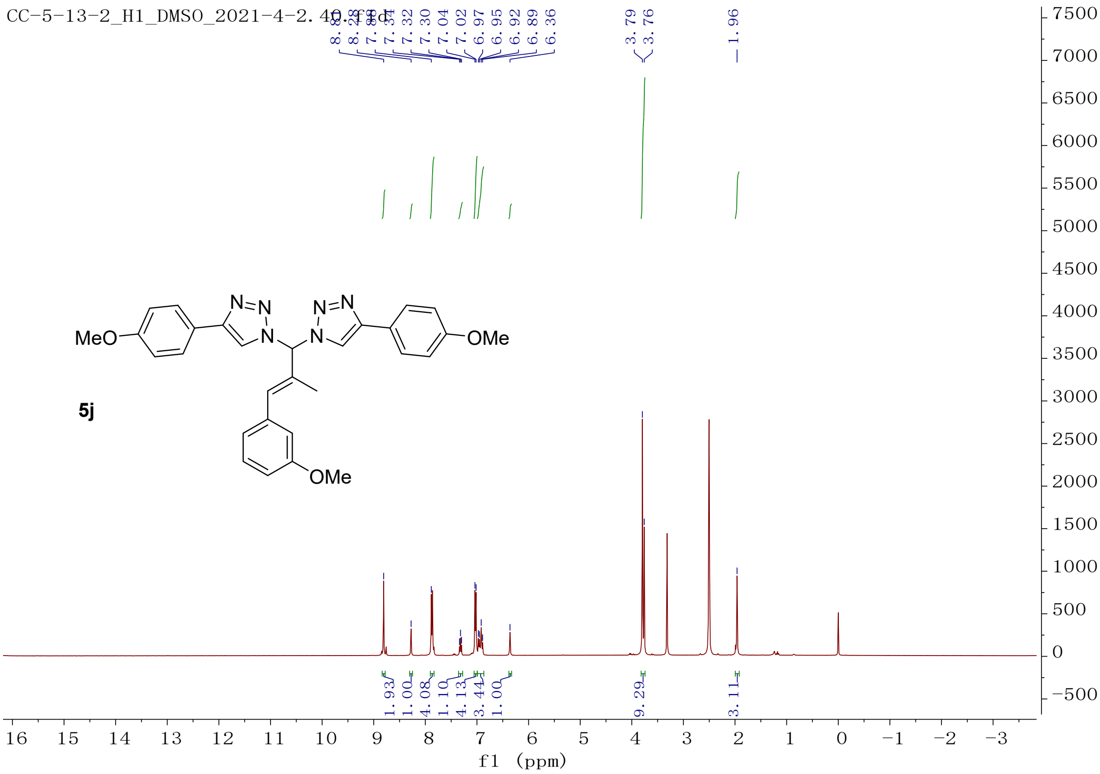

CC-5-5-3-DMSO-C13-2021-3-29.10.fid
159.83
147.42
146.94
142.66
134.94
130.94
129.32
127.38
123.94
123.00
121.03
114.80
76.42
55.67
16.08
f1 (ppm)


2#12 RT: 0.2049 AV: 1 NL: 1.62E4
T: FTMS + p NSI Full ms [50.00-1000.00]
513.1801
514.1835
512.1720
Relative Abundance
m/z

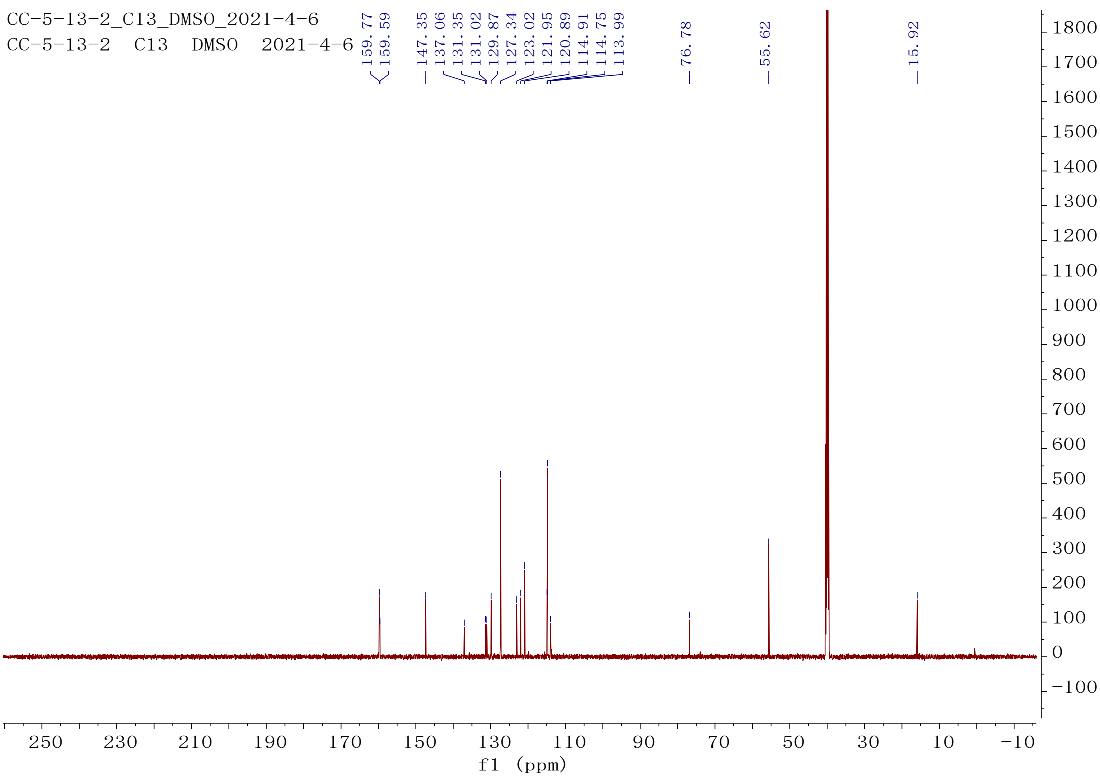

CC-5-9-2_H1_DMSO_2021-3-29 20:23:41
8.41
8.39
7.84
7.82
7.42
7.41
7.35
7.33
7.31
7.05
7.03
7.01
7.00
6.98
6.41
3.80
3.72
1.89
MeO
OMe
OMe
5i
2.06
1.00
4.17
1.03
1.06
6.34
1.01
6.35
3.05
3.00
f1 (ppm)


CC-5-9-2-DMSO-C13-2021-3-29-10-f14
159.81
157.29
147.36
130.17
130.59
130.01
127.34
127.02
124.11
123.05
120.86
120.48
114.81
111.47
76.83
55.89
55.65
15.88
f1 (ppm)

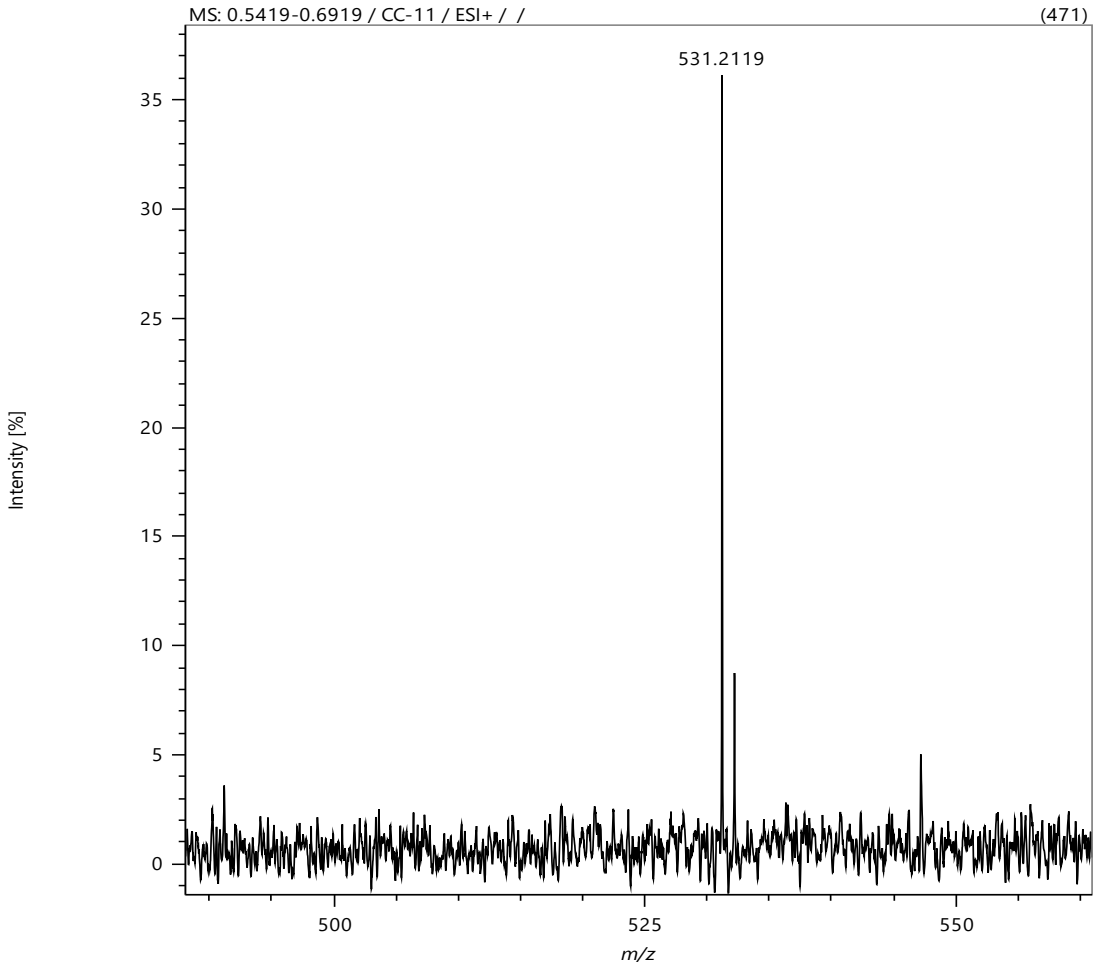

MS: 0.2215-0.2715 / CC-2' / ESI+ / /
(12198)
531.2122
507.2698
547.1860
Intensity [%]
m/z

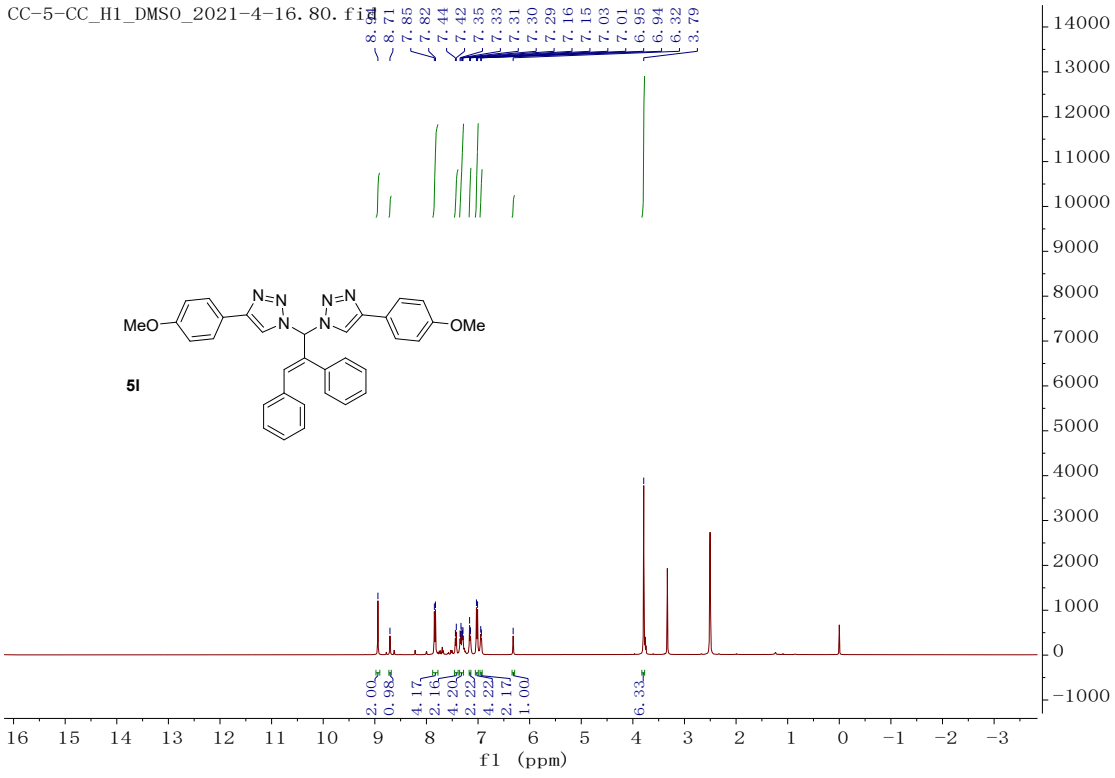


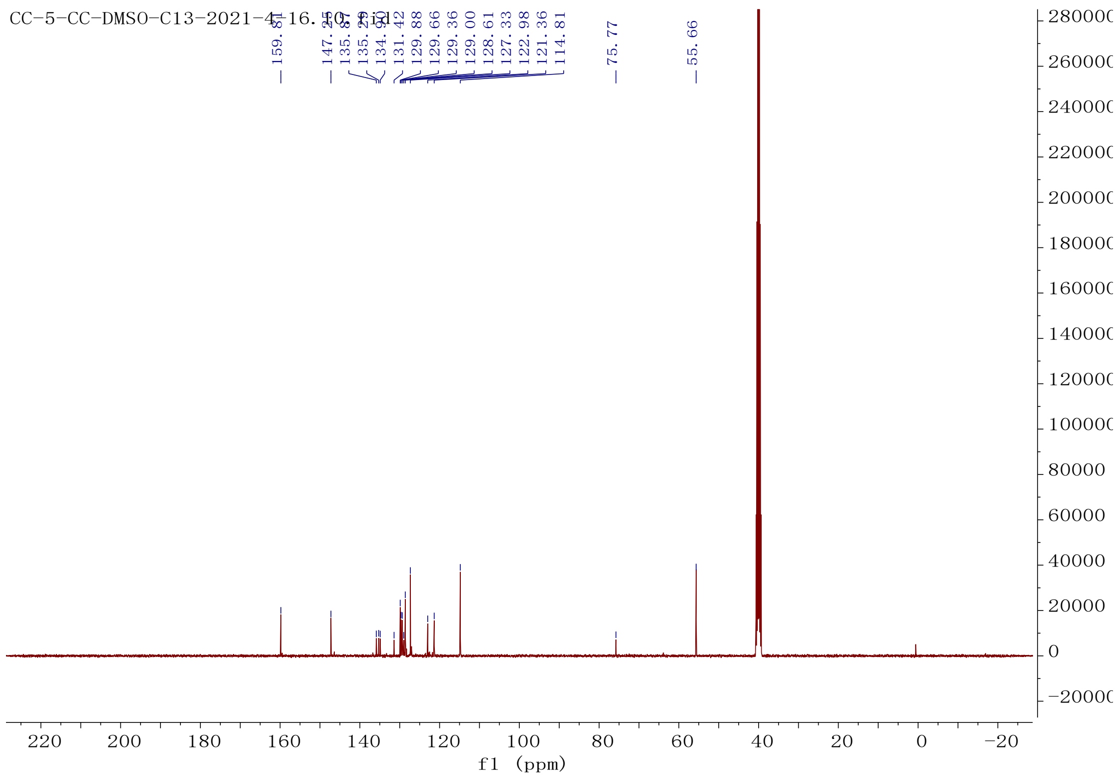
CC-5-13-2_H1_DMSO_2021-4-2.40.fid
7.32
7.30
7.04
7.02
6.97
6.95
6.92
6.89
6.36
3.79
3.76
1.96
MeO
OMe
OMe
5j
1.93
1.00
4.08
1.10
4.13
3.44
1.00
9.29
3.11
f1 (ppm)

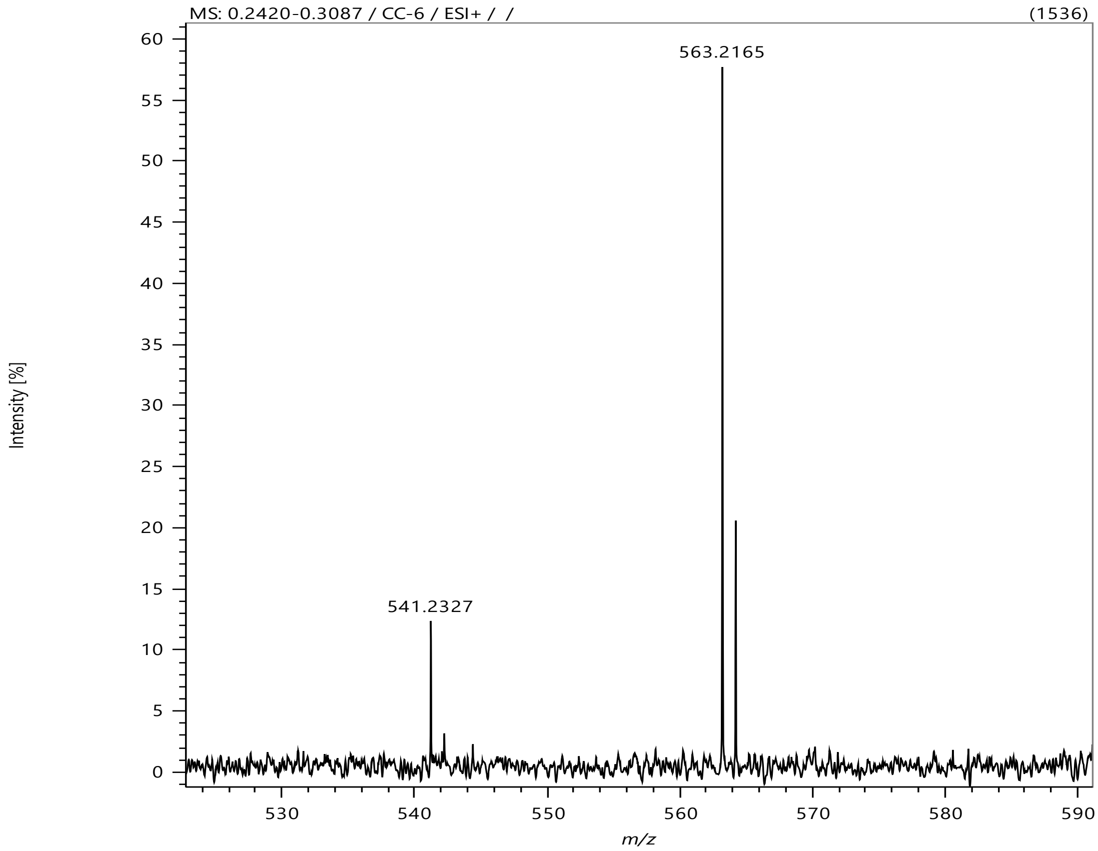


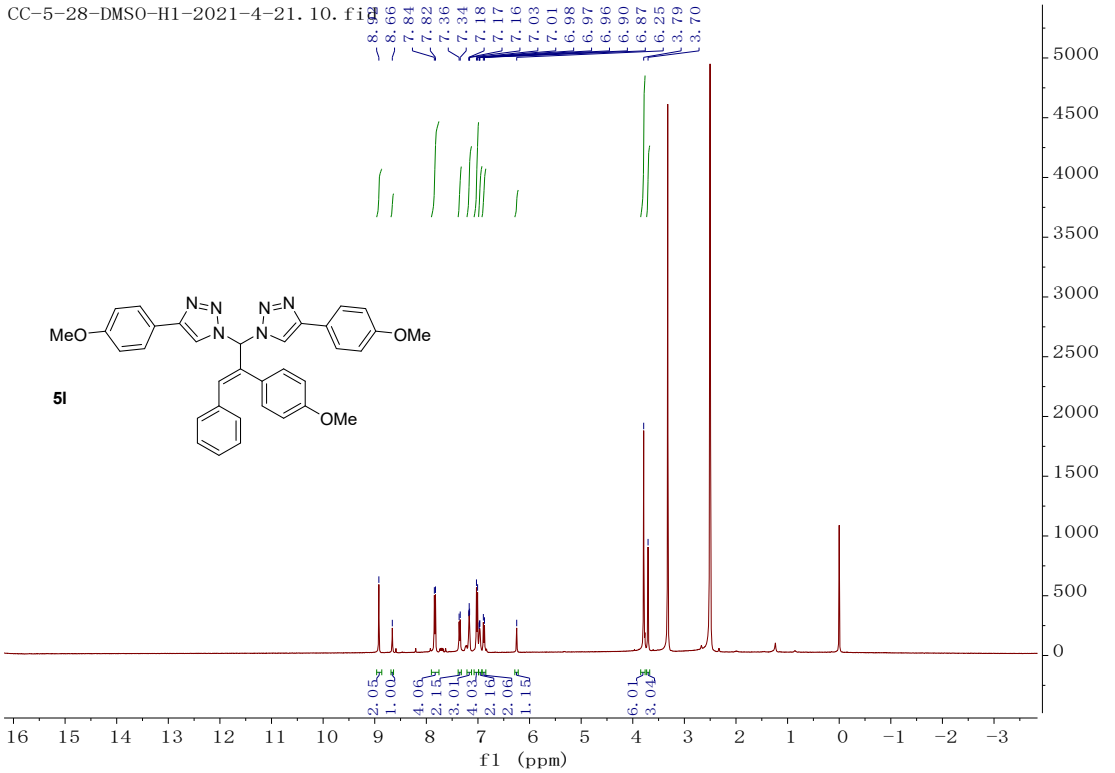
CC-5-13-2_C13_DMSO_2021-4-6
CC-5-13-2 C13 DMSO 2021-4-6
159.77
159.59
147.35
137.06
131.35
131.02
129.87
127.34
123.02
121.95
120.89
114.91
114.75
113.99
76.78
55.62
15.92
f1 (ppm)

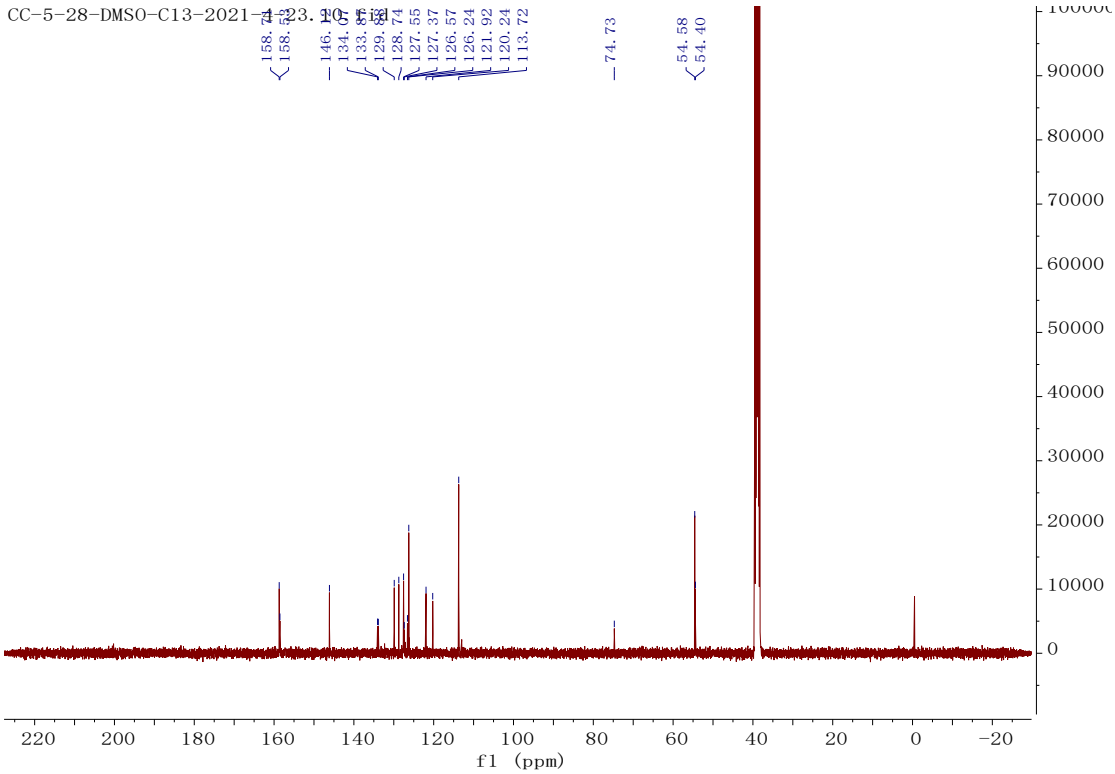

MS: 0.5419-0.6919 / CC-11 / ESI+ / /
(471)
531.2119
Intensity [%]
m/z

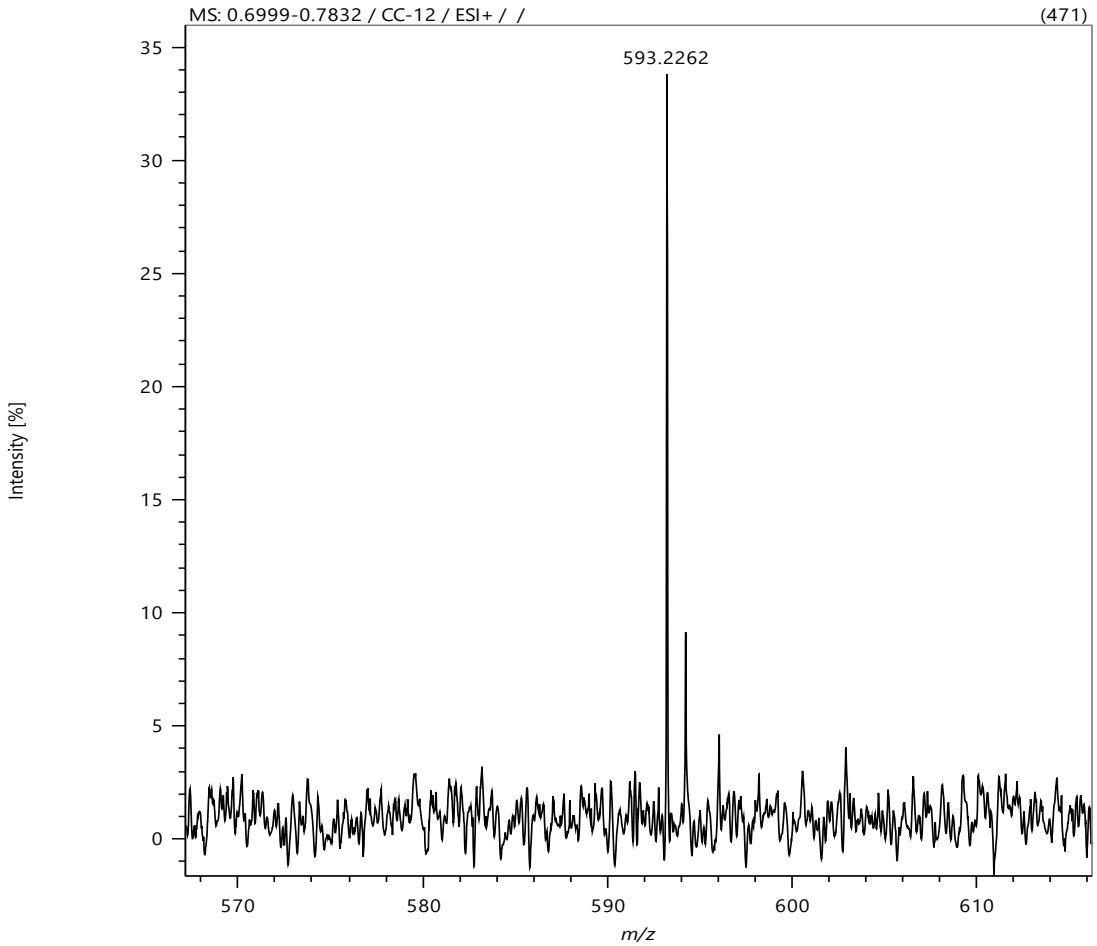

CC-5-CC_H1_DMSO_2021-4-16.80.fid
MeO
OMe
5l
f1 (ppm)

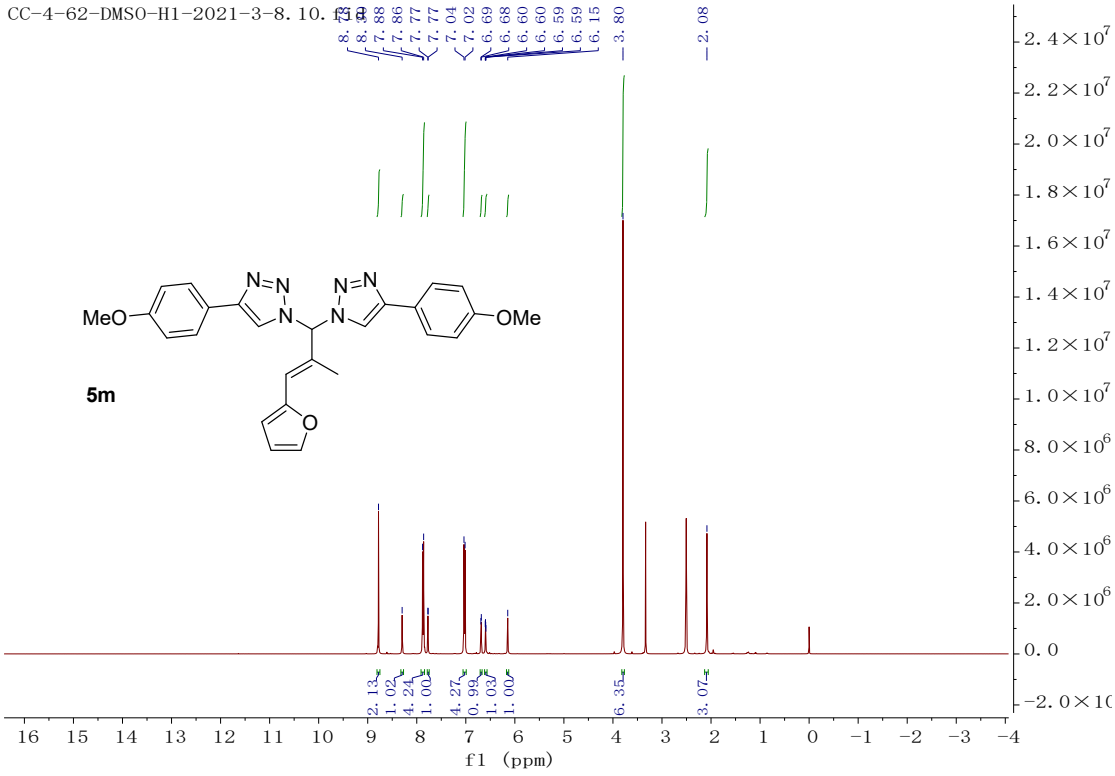

CC-5-CC-DMSO-C13-2021-4-16.10.fid
159.81
147.25
135.87
135.29
134.90
131.42
129.88
129.66
129.36
129.00
128.61
127.33
122.98
121.36
114.81
75.77
55.66
f1 (ppm)

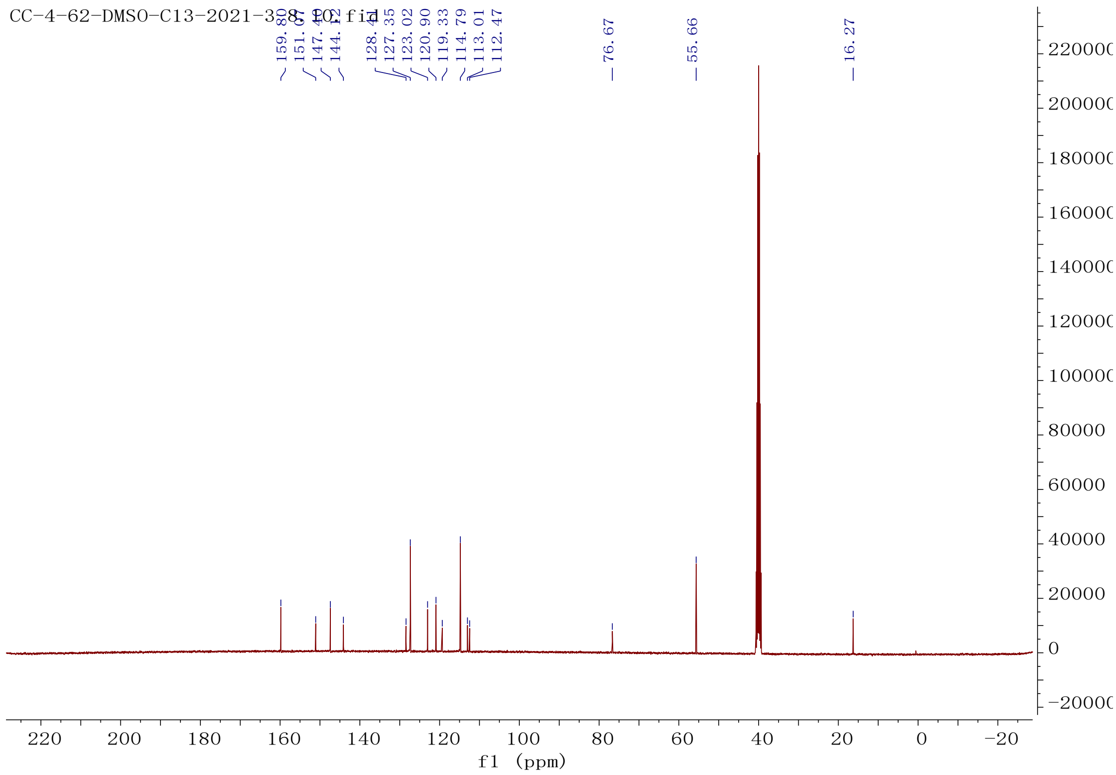

MS: 0.2420-0.3087 / CC-6 / ESI+ / /
(1536)
563.2165
541.2327
Intensity [%]
m/z

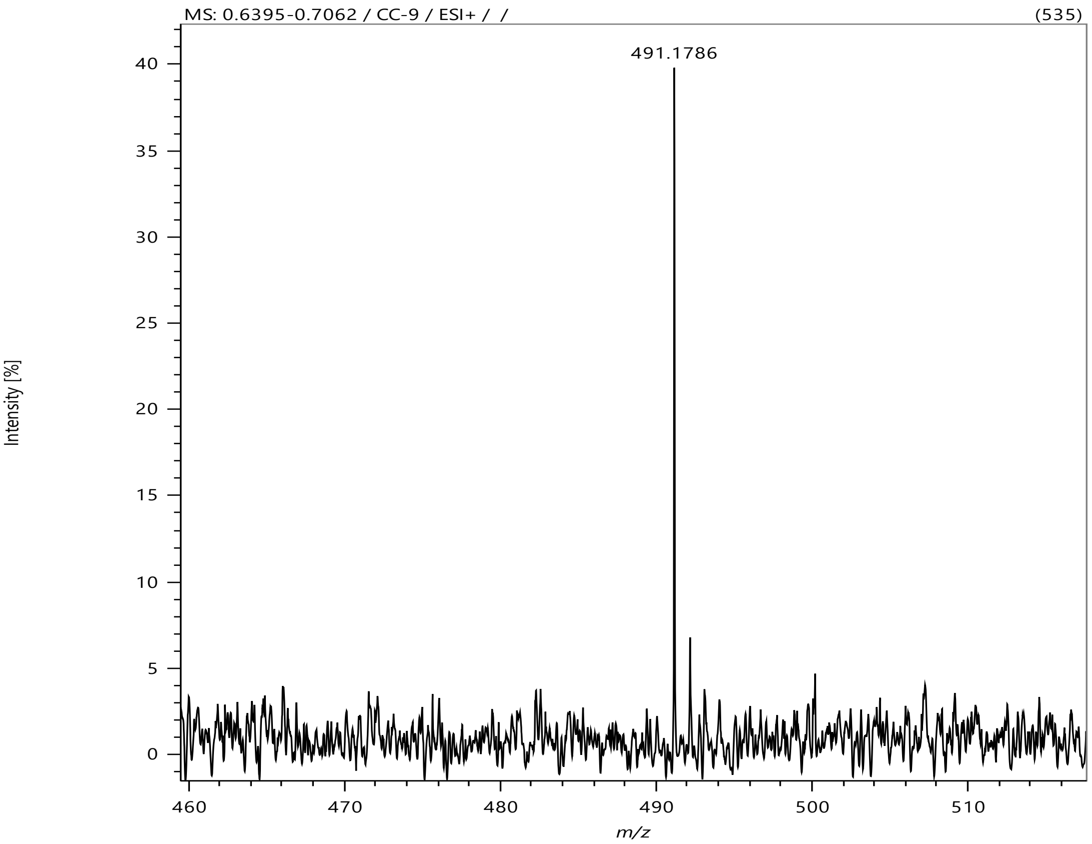

CC-5-28-DMSO-H1-2021-4-21.10.fid
8.84
8.66
7.84
7.82
7.36
7.34
7.18
7.17
7.16
7.03
7.01
6.98
6.97
6.96
6.90
6.87
6.25
3.79
3.70
MeO
OMe
OMe
5l
2.05
1.00
4.06
2.15
3.01
4.03
2.10
2.06
1.15
6.01
3.04
f1 (ppm)

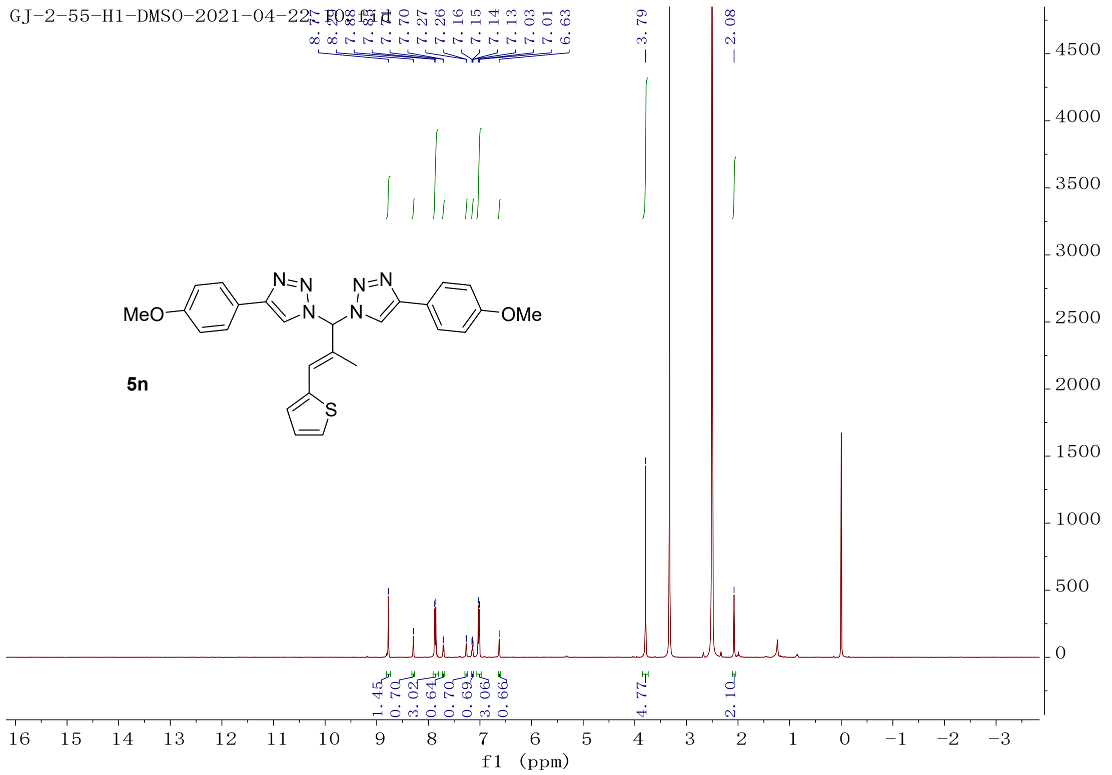

CC-5-28-DMSO-C13-2021-4-23.10.fid
158.74
158.52
146.10
134.06
133.84
129.82
128.74
127.55
127.37
126.57
126.24
121.92
120.24
113.72
74.73
54.58
54.40
f1 (ppm)

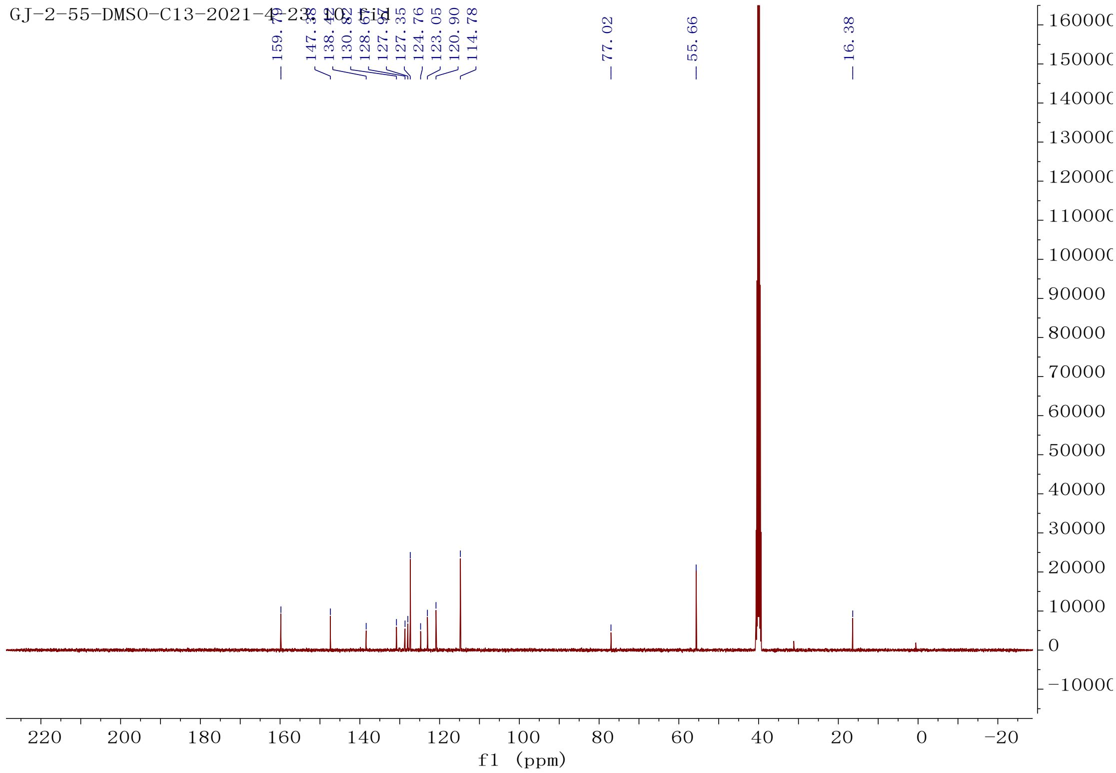

MS: 0.6999-0.7832 / CC-12 / ESI+ / /
(471)
593.2262
Intensity [%]
m/z

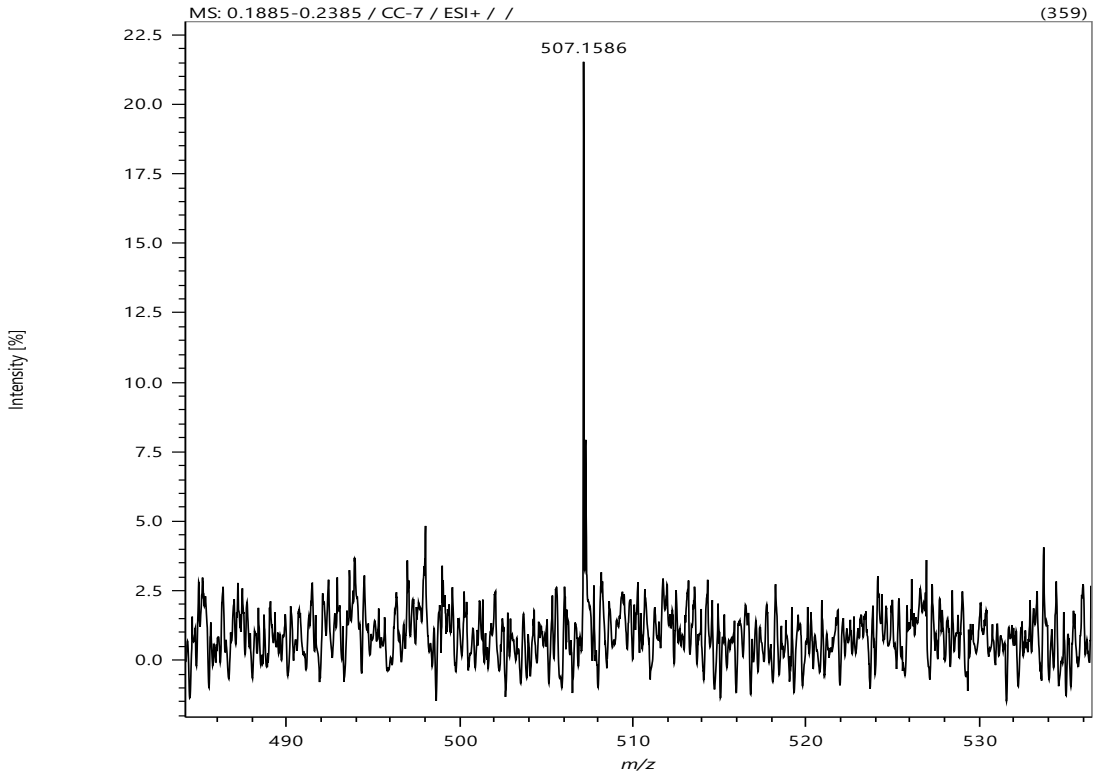

MeO
OMe
5m
f1 (ppm)

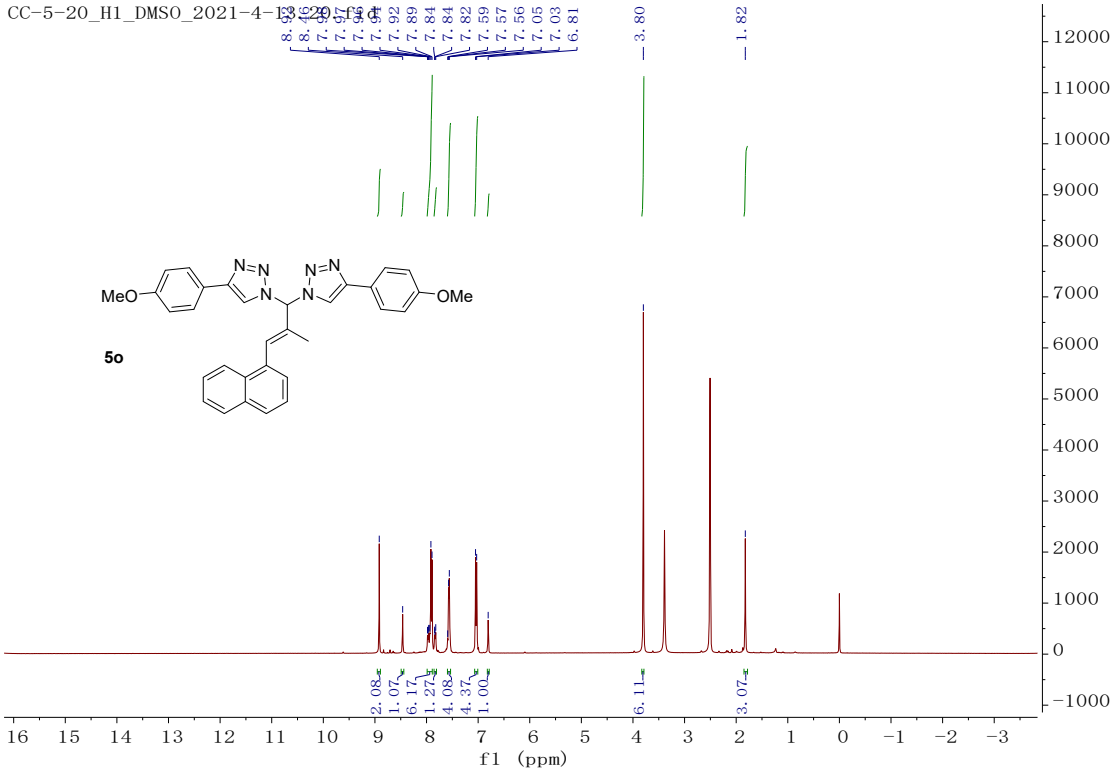

CC-4-62-DMSO-C13-2021-3-8.10.fid
159.80
147.40
127.35
123.02
120.90
119.33
114.79
113.01
112.47
76.67
55.66
16.27
f1 (ppm)

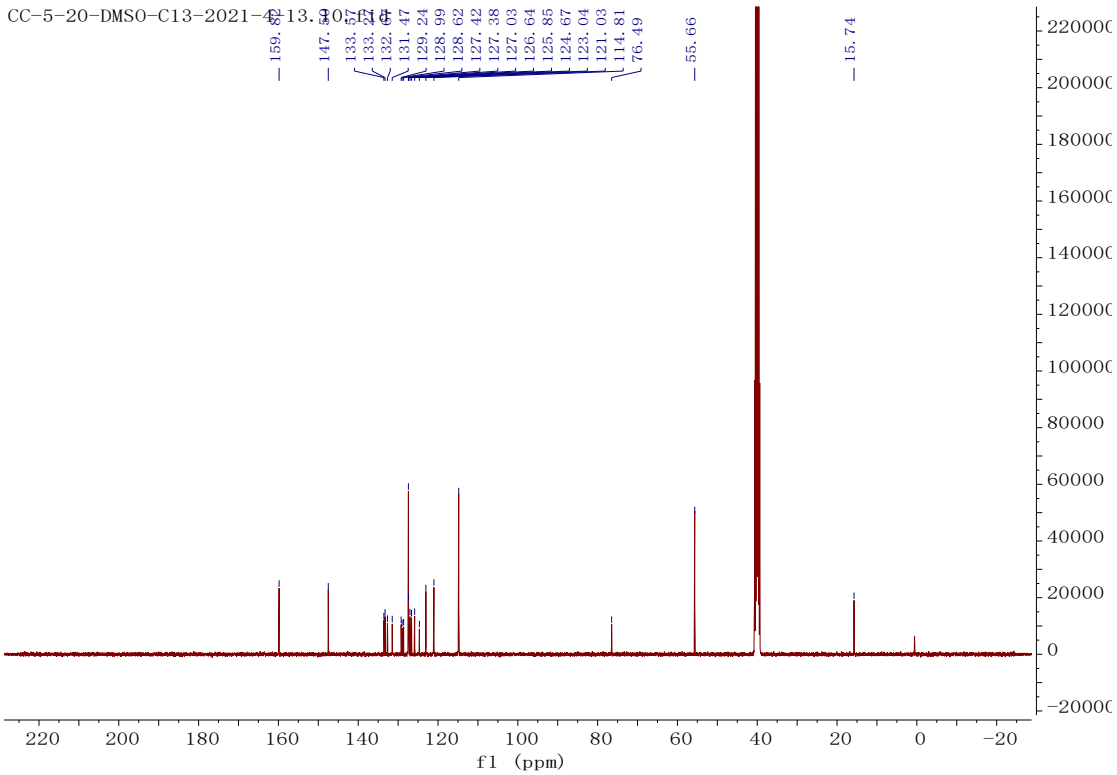

MS: 0.6395-0.7062 / CC-9 / ESI+ / /
(535)
491.1786
Intensity [%]
m/z

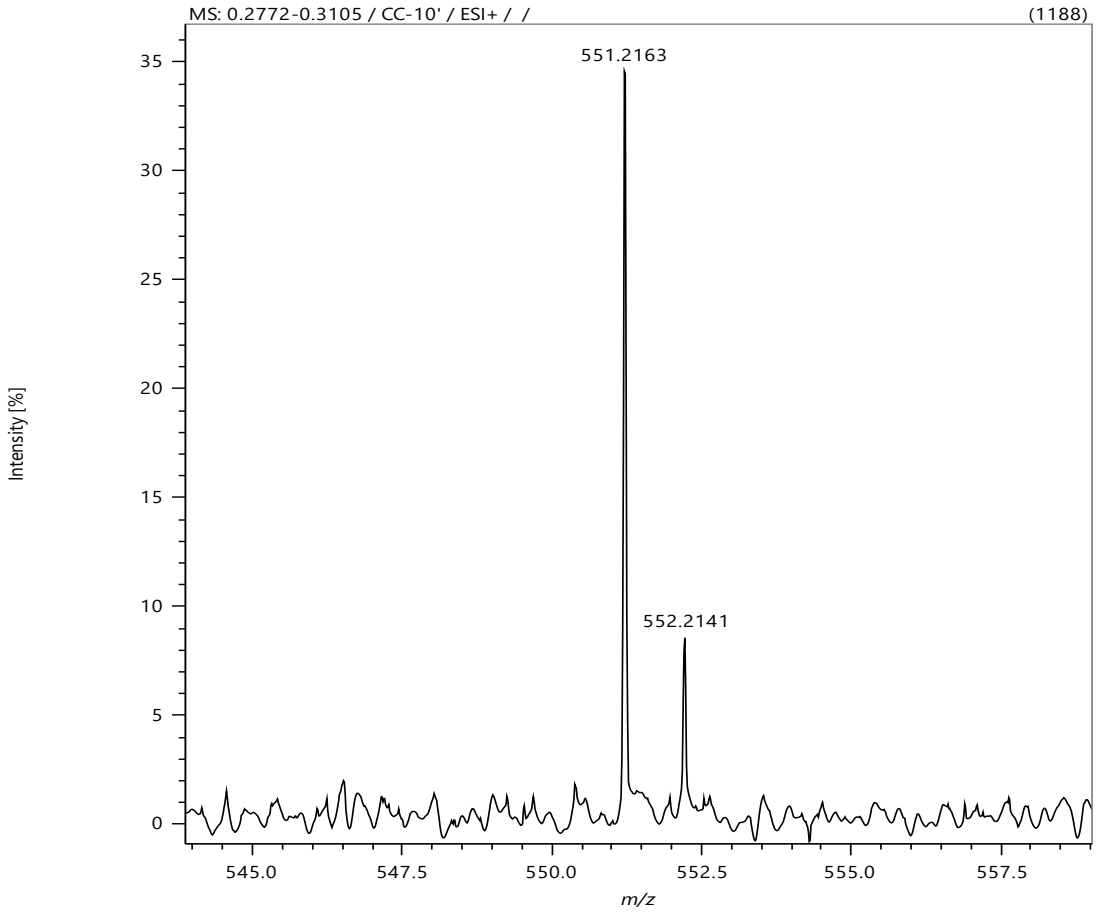

GJ-2-55-H1-DMSO-2021-04-22
7.70
7.27
7.26
7.16
7.15
7.14
7.13
7.03
7.01
6.63
3.79
2.08
MeO
OMe
N
S
5n
1.45
0.70
3.02
0.64
0.70
0.69
3.06
0.66
4.77
2.10
f1 (ppm)

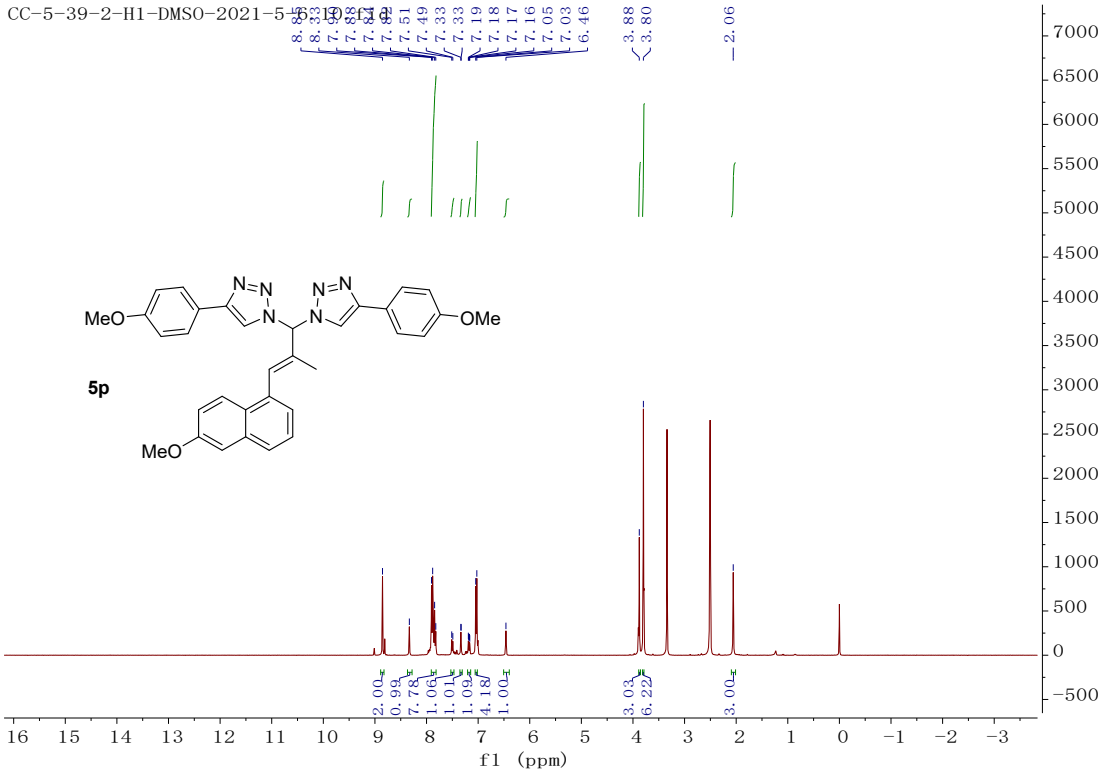

GJ-2-55-DMSO-C13-2021-4-23
147.3
138.4
130.8
127.35
124.76
123.05
120.90
114.78
77.02
55.66
16.38
f1 (ppm)

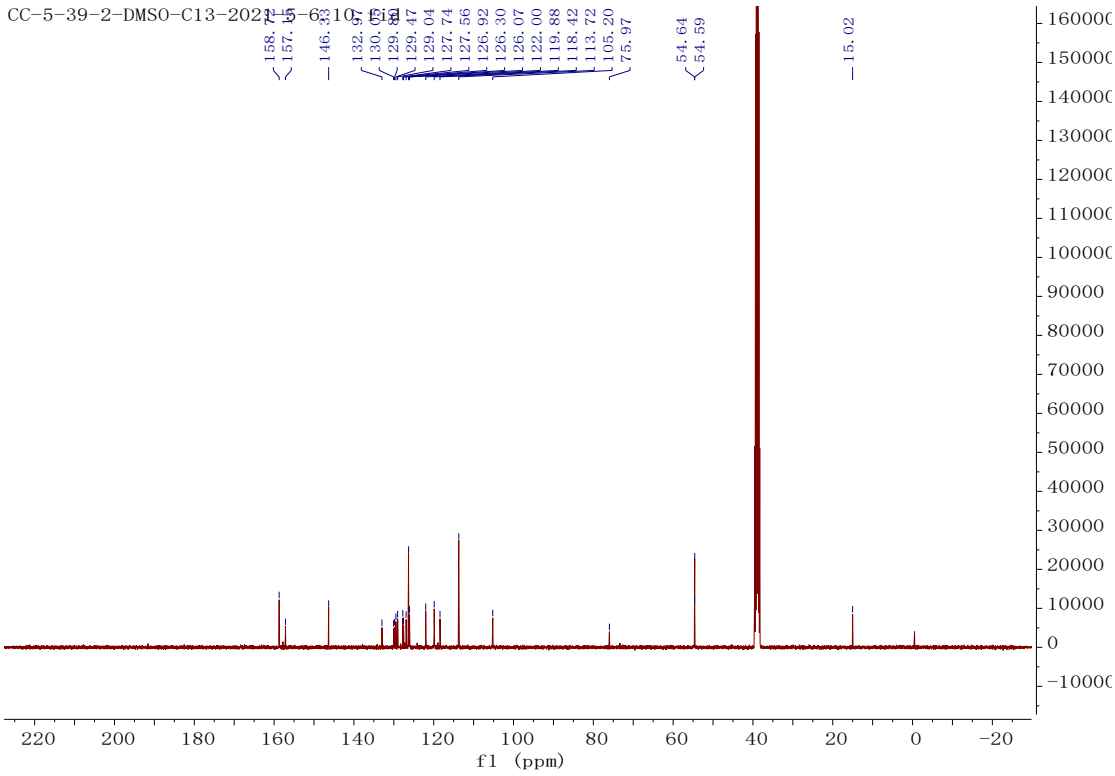

MS: 0.1885-0.2385 / CC-7 / ESI+ / /
(359)
507.1586
Intensity [%]
m/z

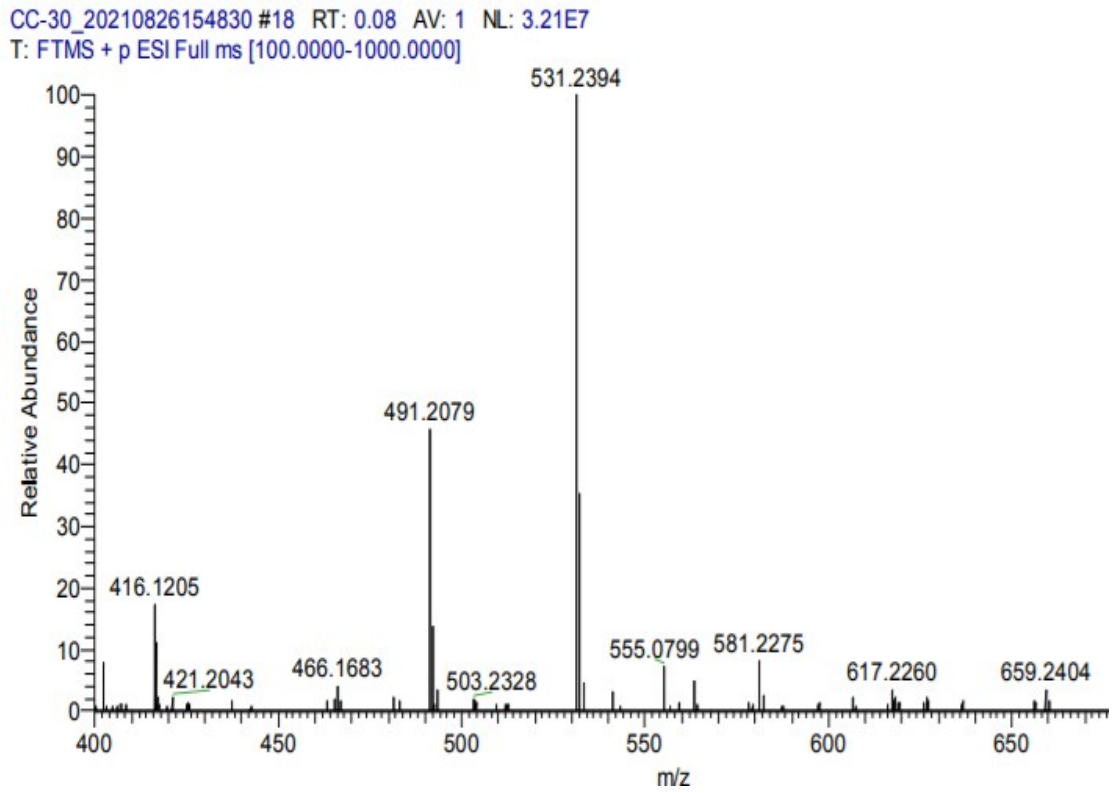

MeO
OMe
5o
f1 (ppm)

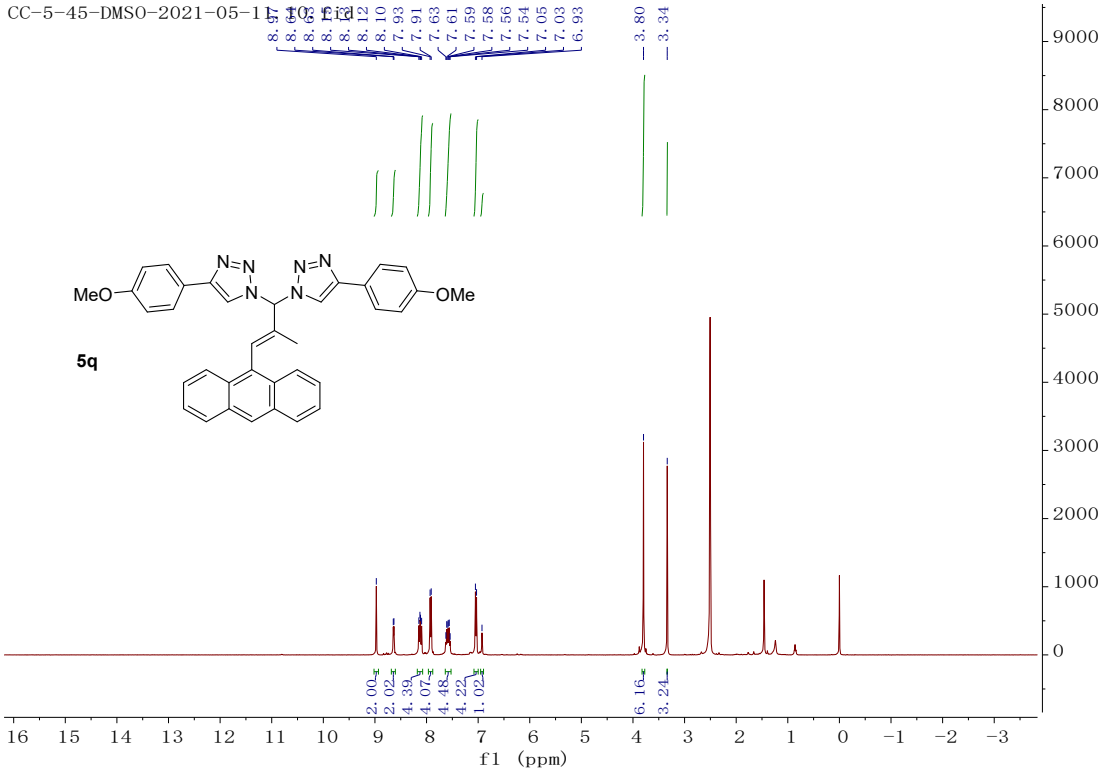

CC-5-20-DMSO-C13-2021-4-13.40.fid
159.82
147.50
133.74
133.46
132.67
131.47
129.24
128.99
128.62
127.42
127.38
127.03
126.64
125.85
124.67
123.04
121.03
114.81
76.49
55.66
15.74
f1 (ppm)

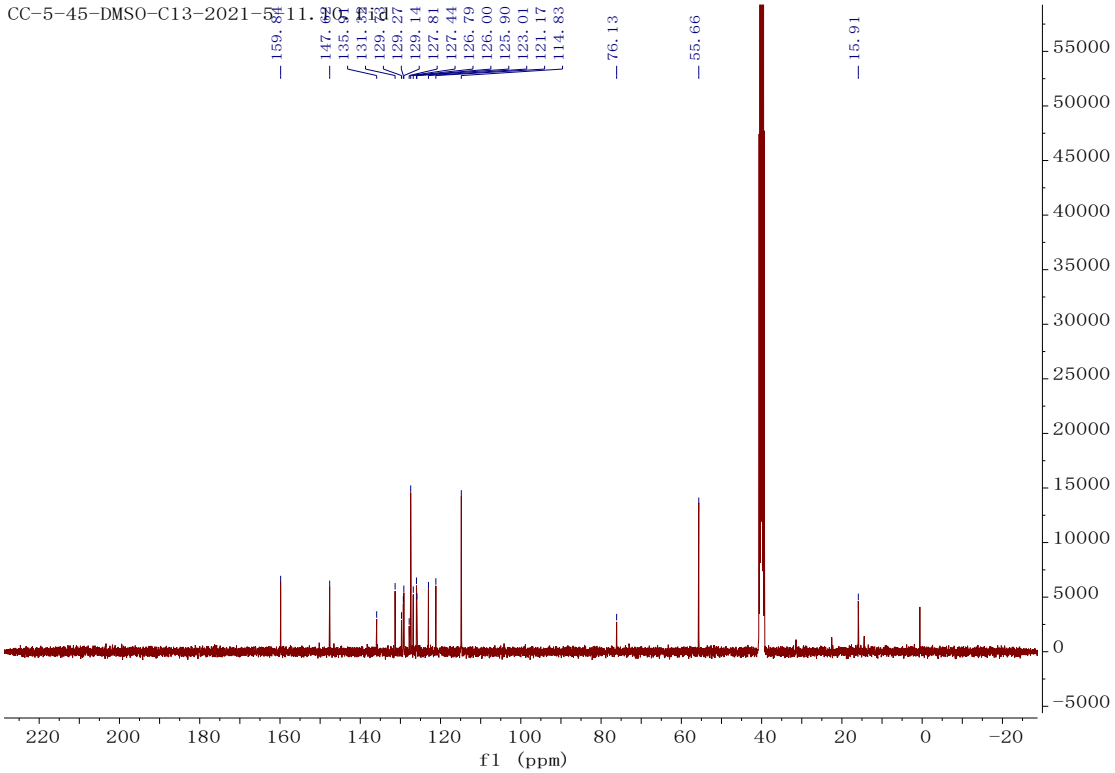

MS: 0.2772-0.3105 / CC-10' / ESI+ / /
(1188)
551.2163
552.2141
Intensity [%]
m/z

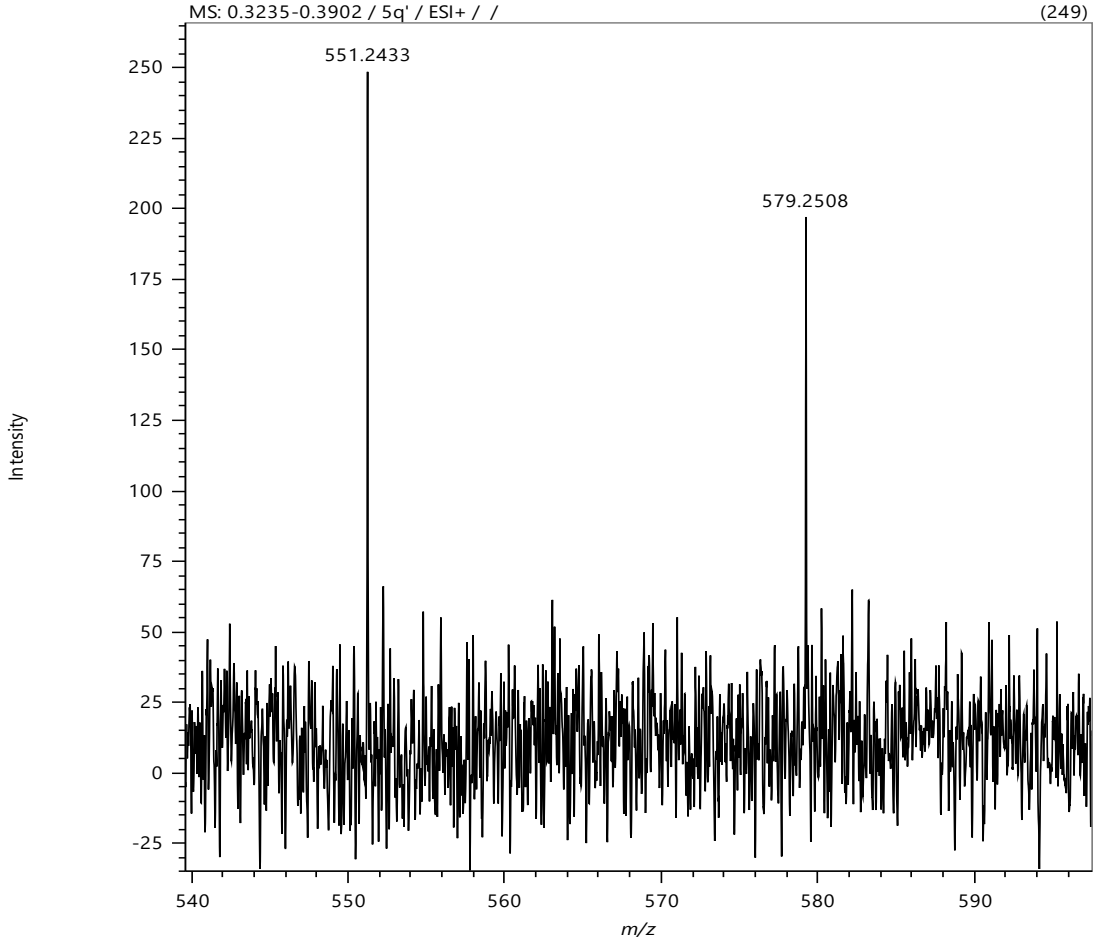

8.46
8.33
7.82
7.51
7.49
7.33
7.19
7.18
7.17
7.16
7.05
7.03
6.46
3.88
3.80
2.06
MeO
OMe
MeO
5p
2.00
0.93
7.78
1.06
1.01
1.05
4.18
1.00
3.03
6.22
3.00
f1 (ppm)

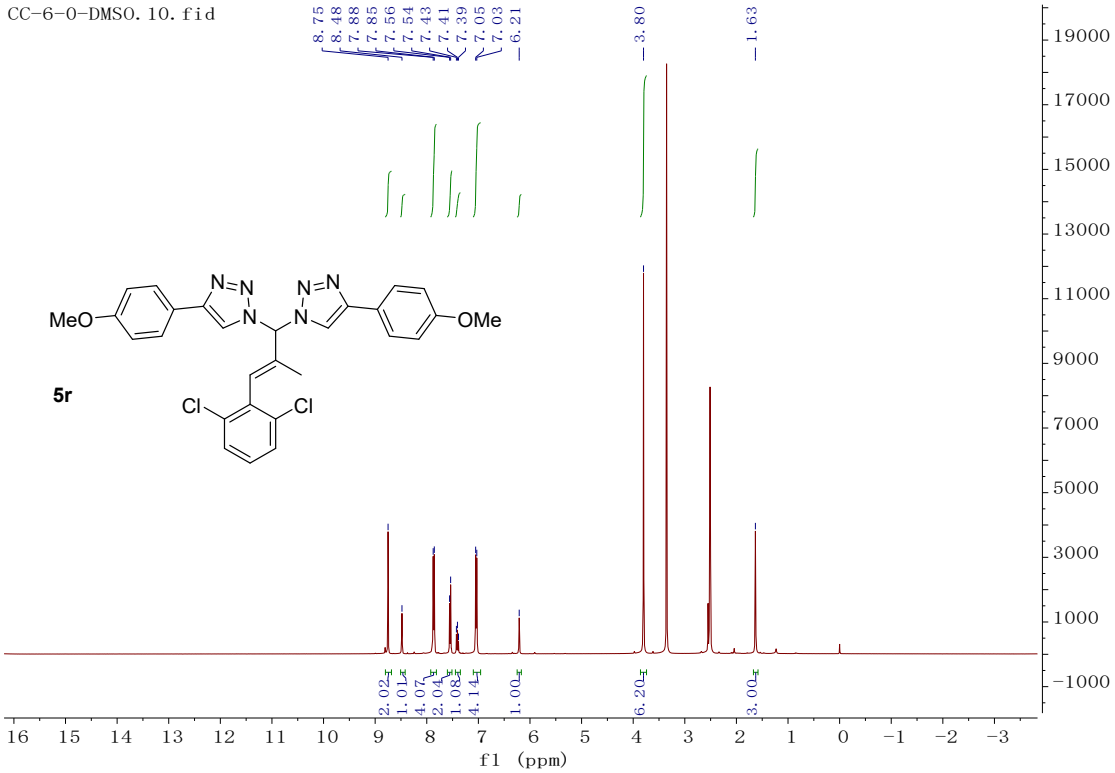

158.72
157.15
146.33
132.97
130.05
129.84
129.47
129.04
127.74
127.56
126.92
126.30
126.07
122.00
119.88
118.42
113.72
105.20
75.97
54.64
54.59
15.02
f1 (ppm)

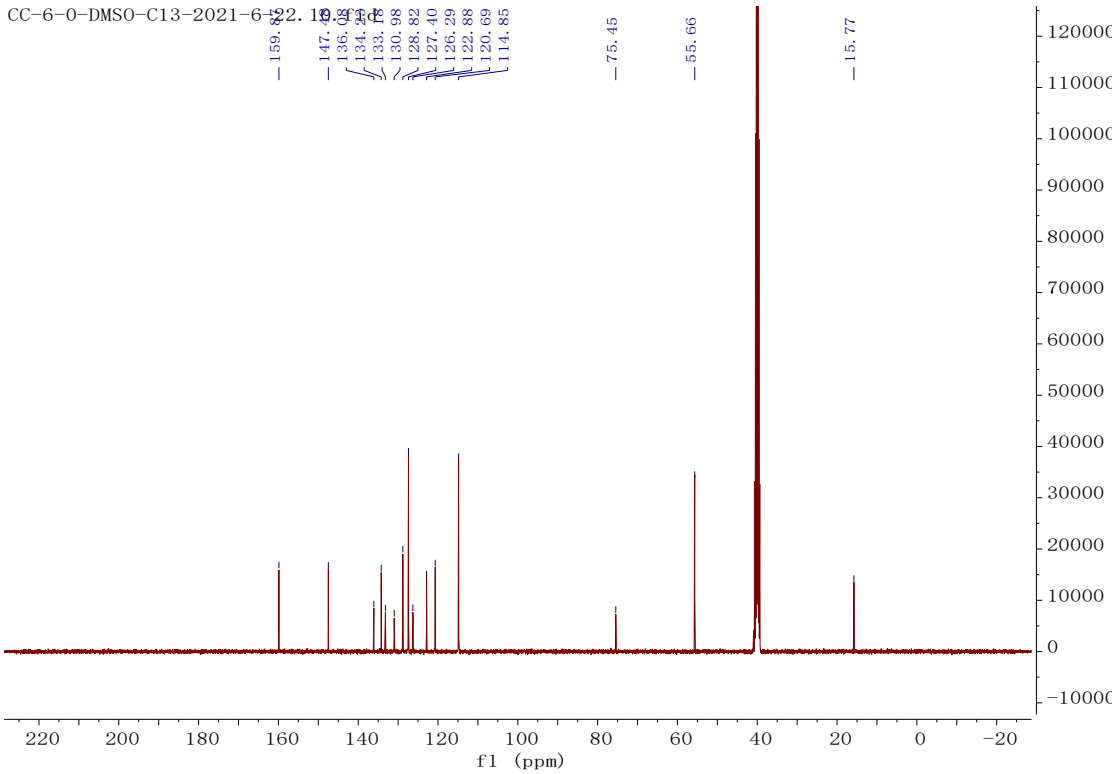

CC-30_20210826154830 #18 RT: 0.08 AV: 1 NL: 3.21E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]
Relative Abundance
m/z
531.2394
491.2079
416.1205
421.2043
466.1683
503.2328
555.0799
581.2275
617.2260
659.2404

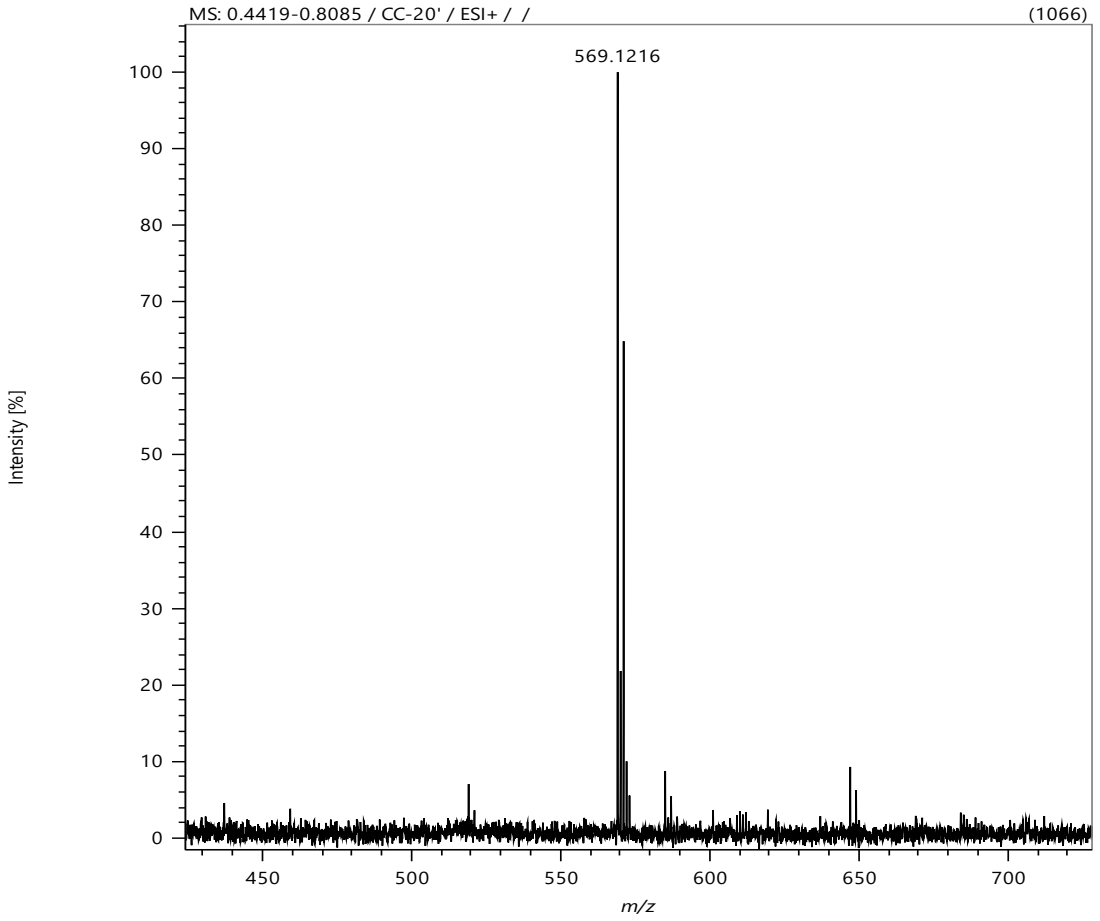

CC-5-45-DMSO-2021-05-11
MeO
OMe
5q
f1 (ppm)

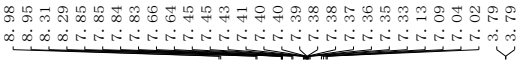

CC-5-45-DMSO-C13-2021-5
159.84
147.60
135.54
131.42
129.27
129.14
127.81
127.44
126.79
126.00
125.90
123.01
121.17
114.83
76.13
55.66
15.91
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
220
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)

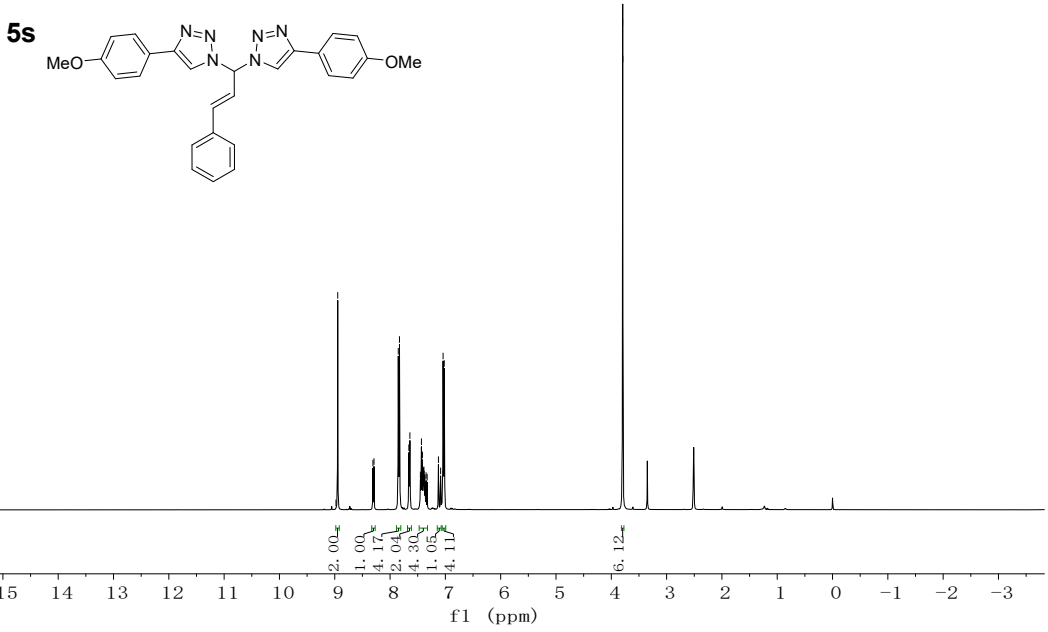

MS: 0.3235-0.3902 / 5q' / ESI+ / /
(249)
551.2433
579.2508
Intensity
250
225
200
175
150
125
100
75
50
25
0
-25
540
550
560
570
580
590
m/z

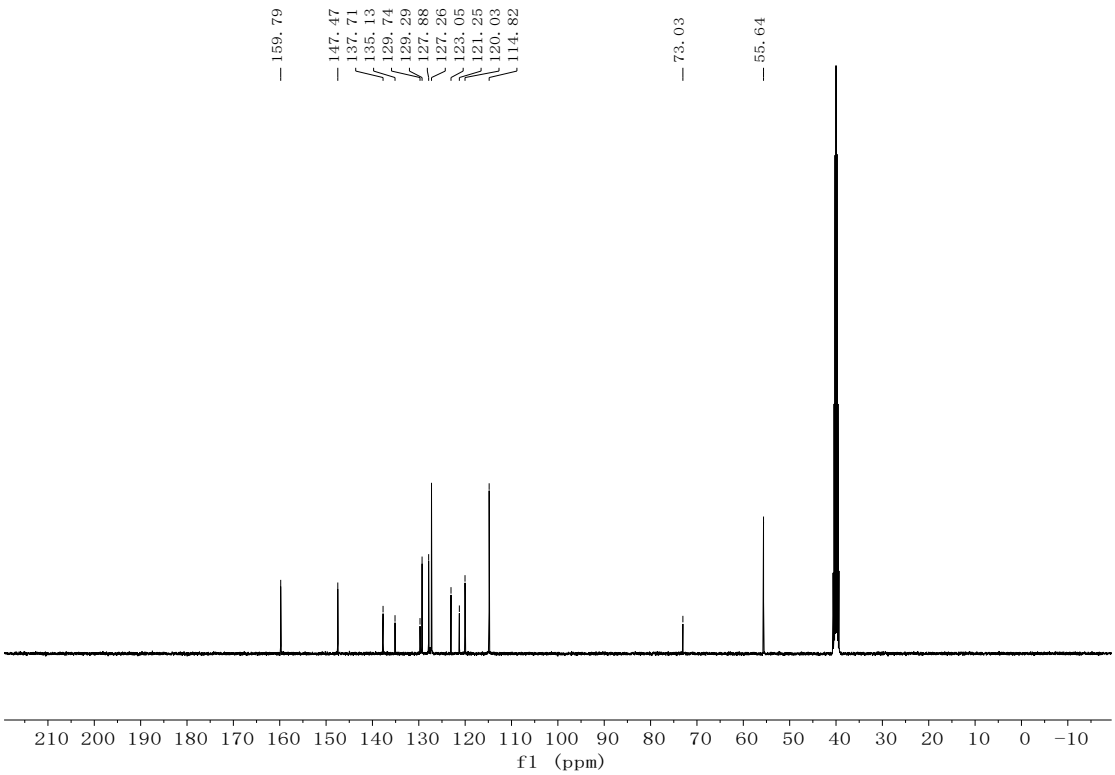

CC-6-0-DMSO.10.fid
8.75
8.48
7.88
7.85
7.56
7.54
7.43
7.41
7.39
7.05
7.03
6.21
3.80
1.63
MeO
OMe
Cl
Cl
5r
2.02
1.01
4.07
2.04
1.08
4.14
1.00
6.20
3.00
f1 (ppm)

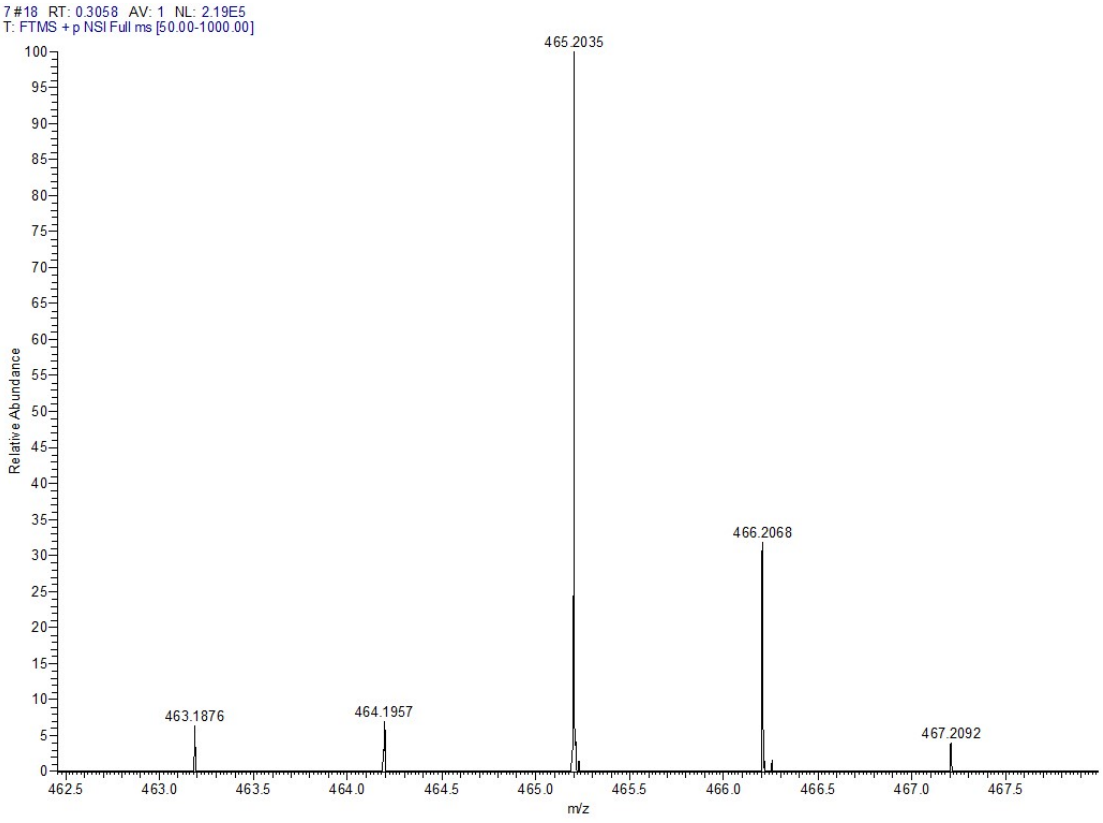

CC-6-0-DMSO-C13-2021-6-22.19.fid
159.82
147.47
136.04
134.44
133.78
130.98
128.82
127.40
126.29
122.88
120.69
114.85
75.45
55.66
15.77
f1 (ppm)

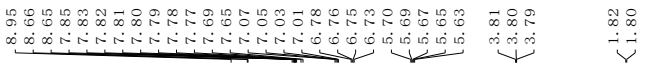

MS: 0.4419-0.8085 / CC-20' / ESI+ / /
(1066)
569.1216
Intensity [%]
m/z


8.98
8.95
8.31
8.29
7.85
7.85
7.84
7.83
7.66
7.64
7.45
7.45
7.43
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.33
7.13
7.09
7.04
7.02
3.79
3.79

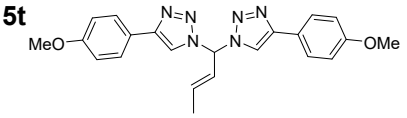

5s
MeO
OMe
2.00
1.00
4.17
2.04
4.30
1.05
4.11
6.12
f1 (ppm)

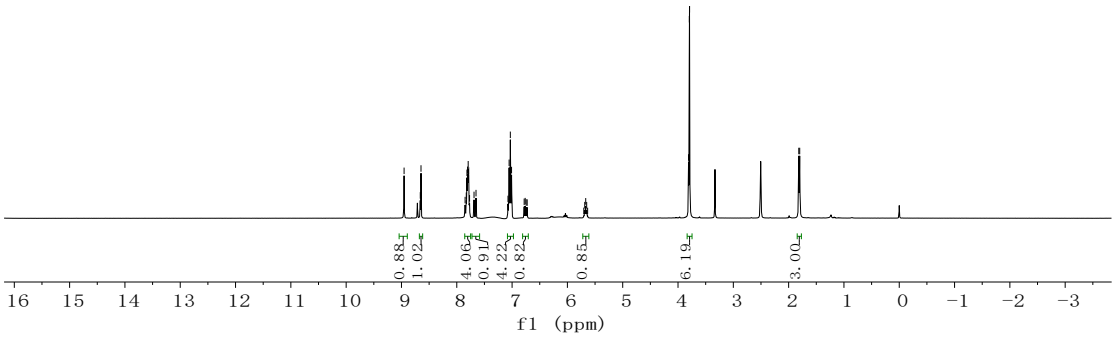

159.79
147.47
137.71
135.13
129.74
129.29
127.88
127.26
123.05
121.25
120.03
114.82
73.03
55.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

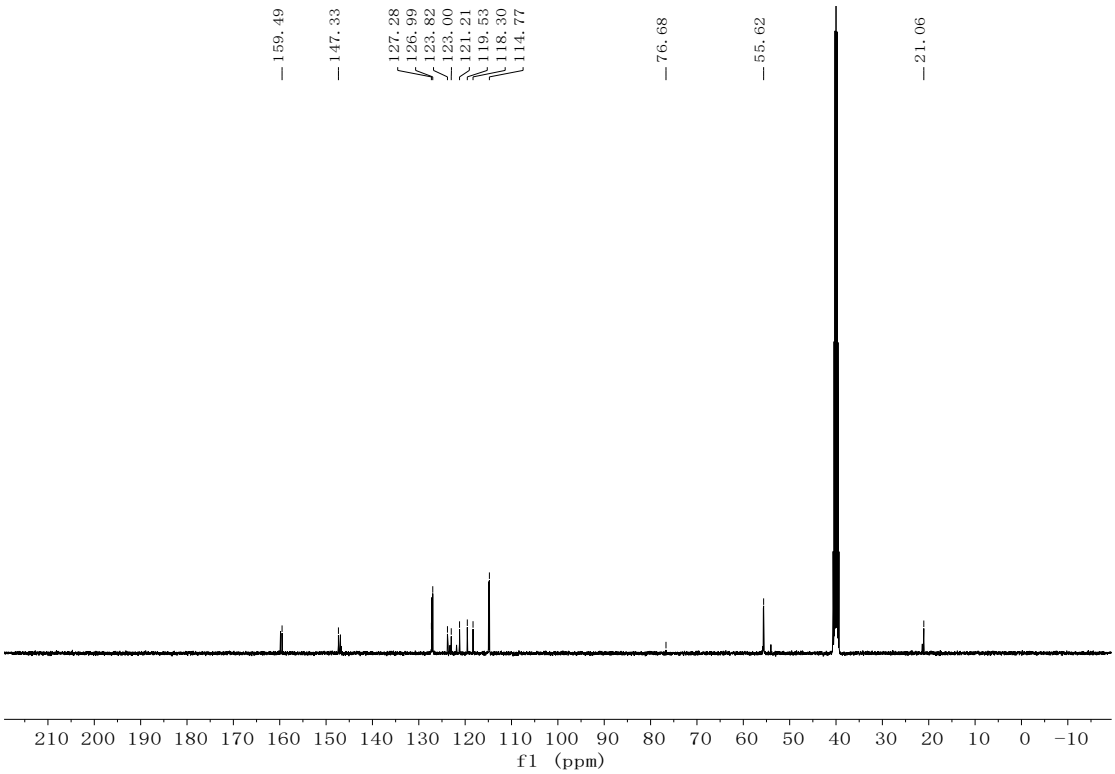

7 #18 RT: 0.3058 AV: 1 NL: 2.19E5
T: FTMS + p NSI Full ms [50.00-1000.00]
Relative Abundance
m/z
465.2035
466.2068
463.1876
464.1957
467.2092

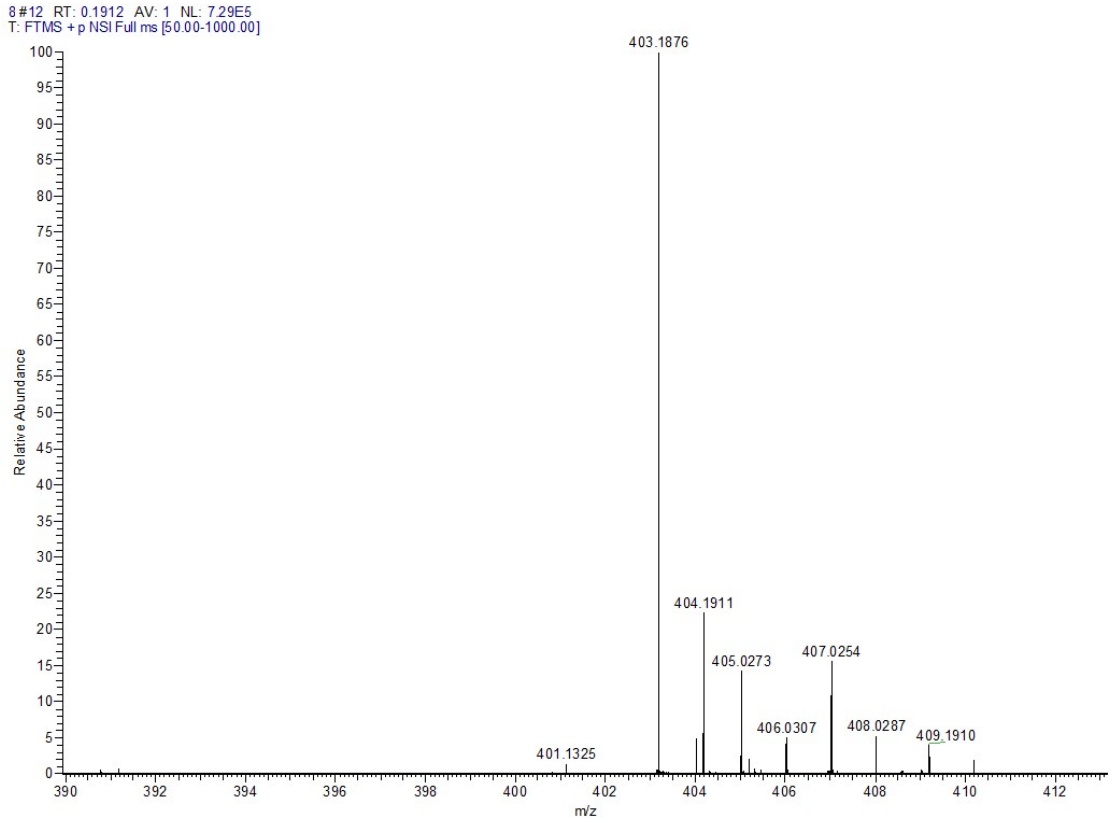

8.95
8.66
8.65
7.85
7.83
7.82
7.81
7.80
7.79
7.78
7.77
7.69
7.65
7.07
7.05
7.03
7.01
6.78
6.76
6.75
6.73
5.70
5.69
5.67
5.65
5.63
3.81
3.80
3.79
1.82
1.80

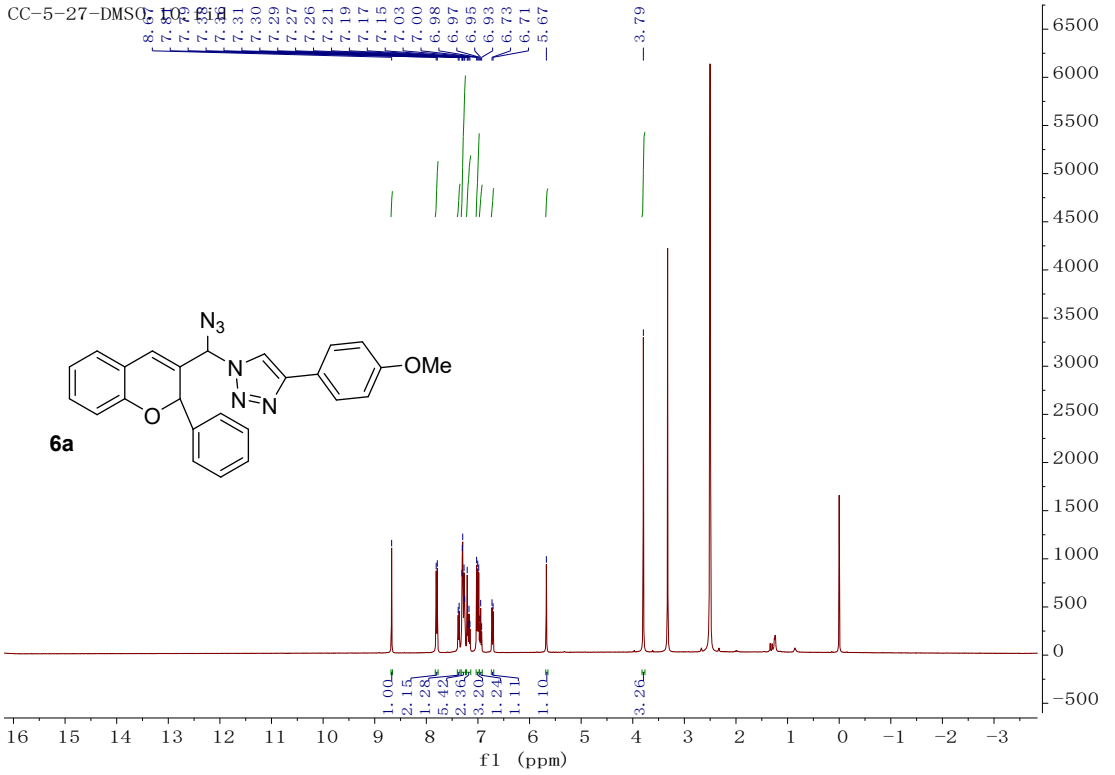
5t

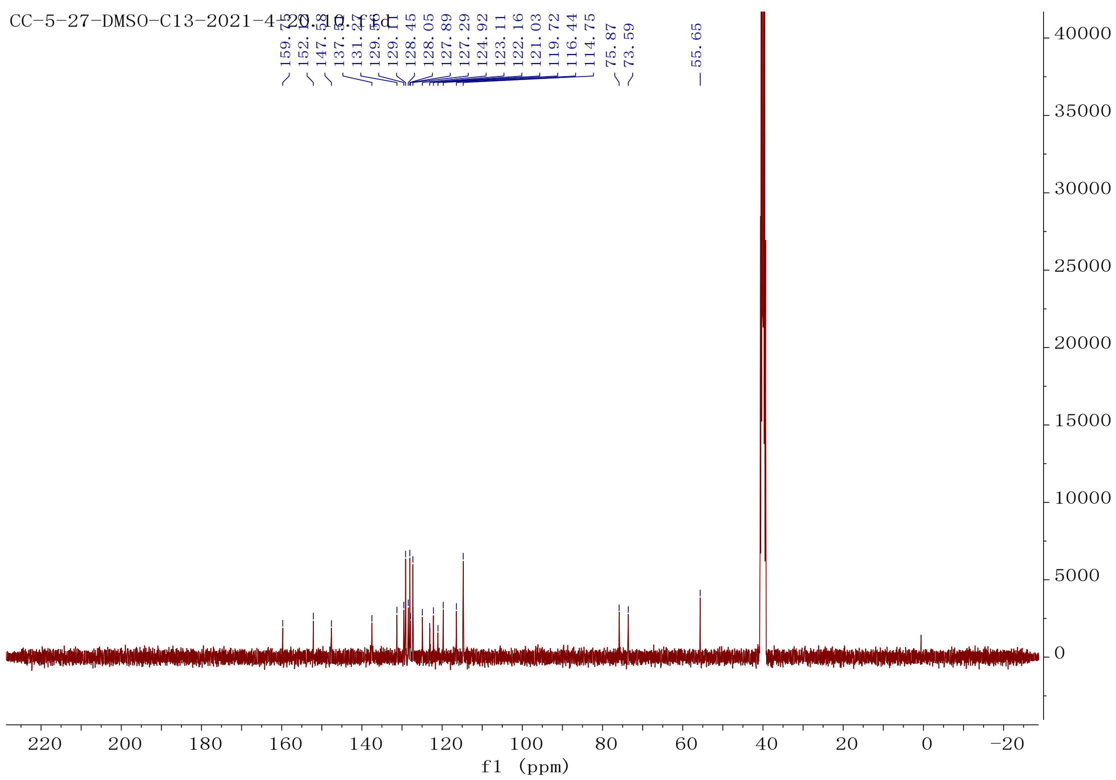

MeO
OMe

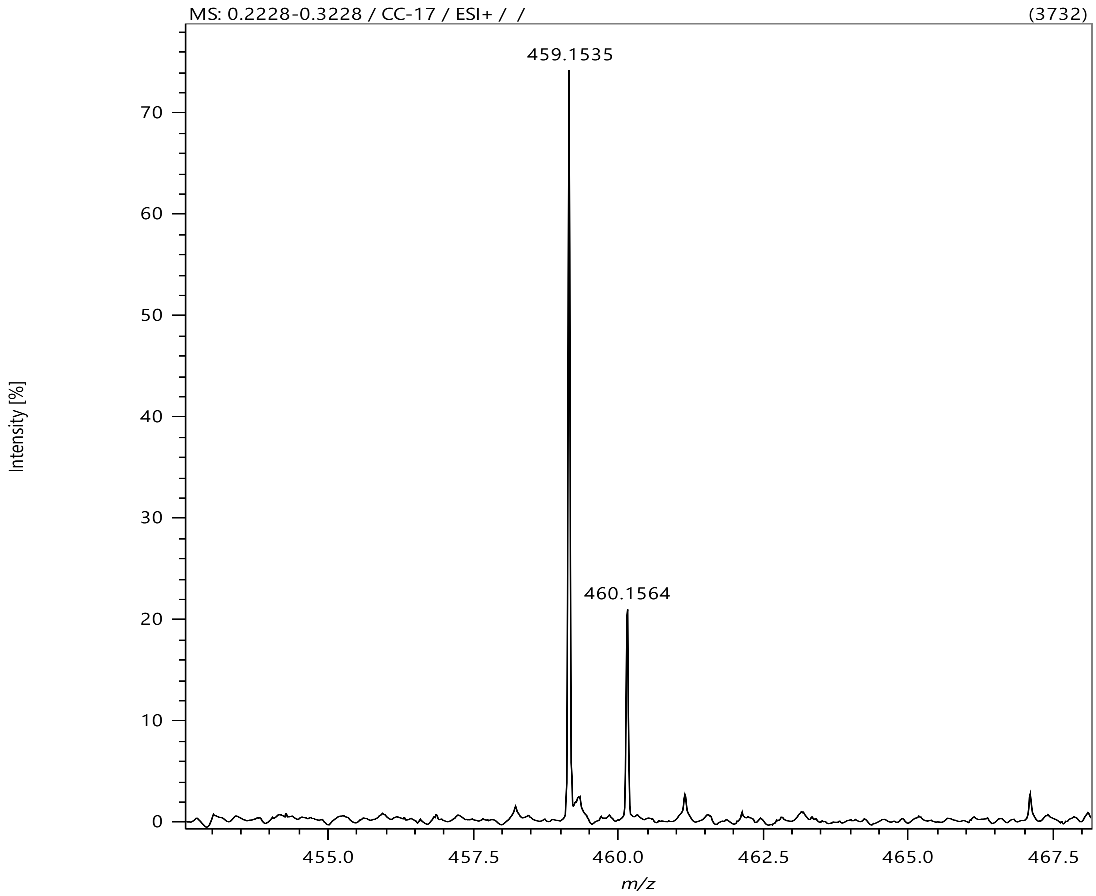

0.88
1.02
4.06
0.91
4.22
0.82
0.85
6.19
3.00
f1 (ppm)

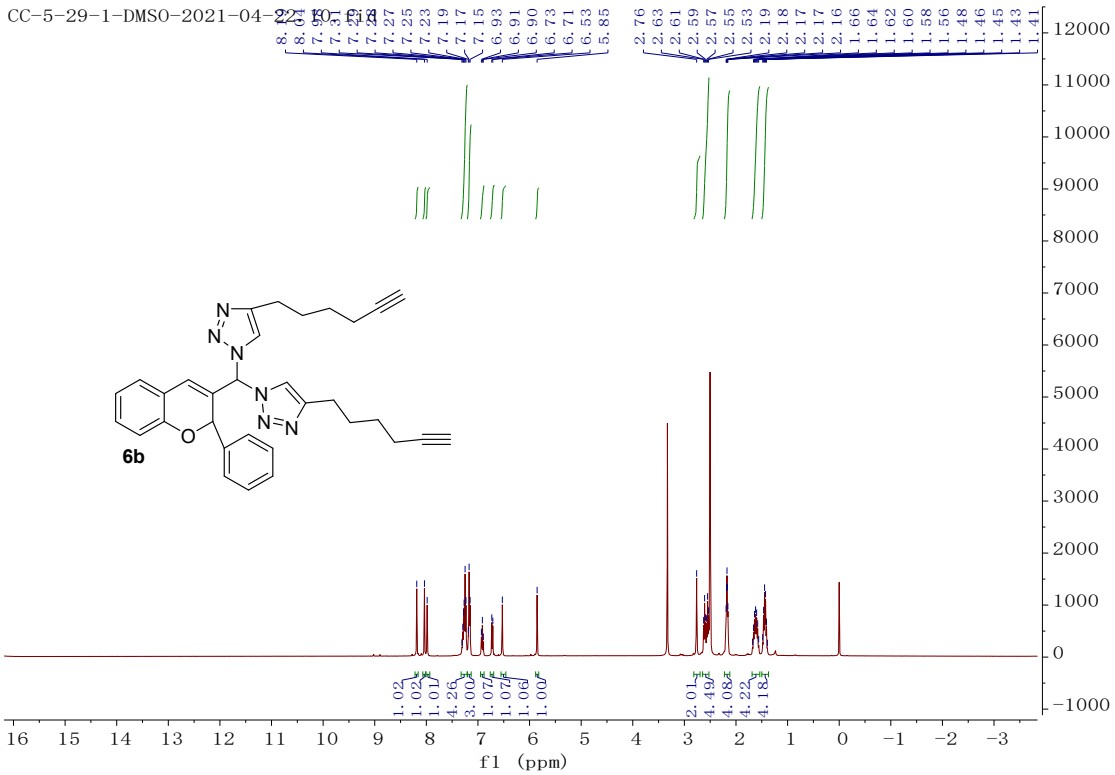

159.49
147.33
127.28
126.99
123.82
123.00
121.21
119.53
118.30
114.77
76.68
55.62
21.06
f1 (ppm)

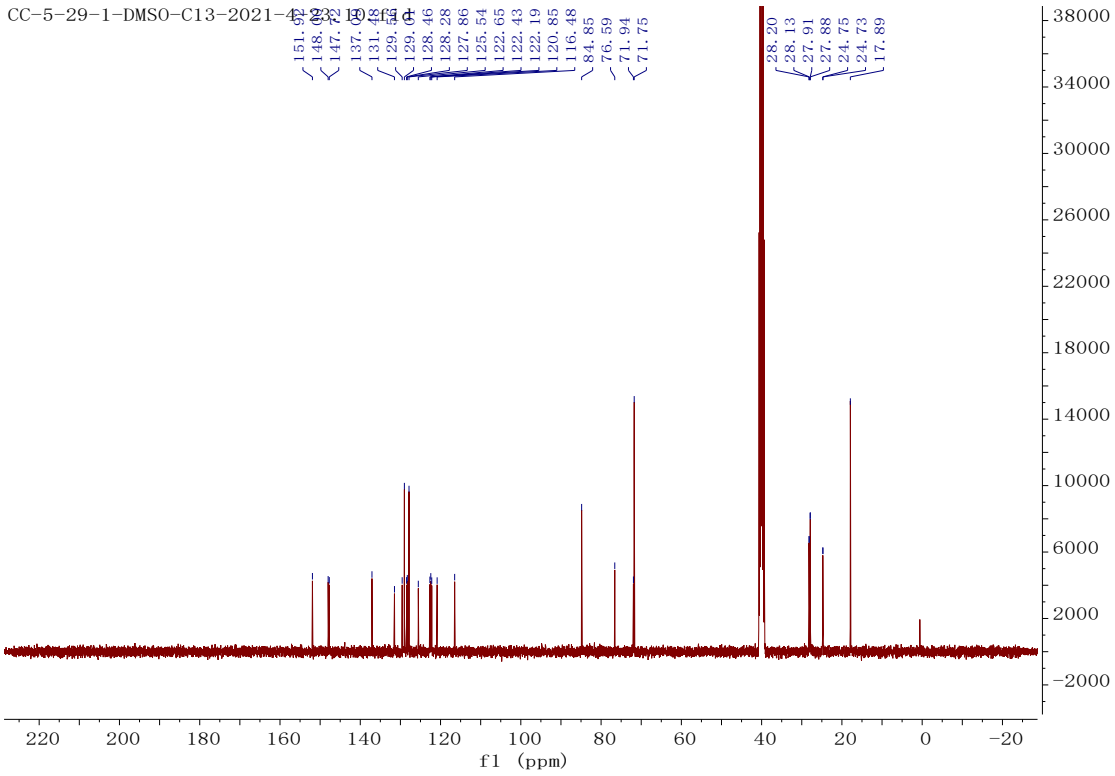

8 #12 RT: 0.1912 AV: 1 NL: 7.29E5
T: FTMS + p NSI Full ms [50.00-1000.00]
Relative Abundance
m/z
403.1876
404.1911
405.0273
407.0254
406.0307
408.0287
409.1910
401.1325

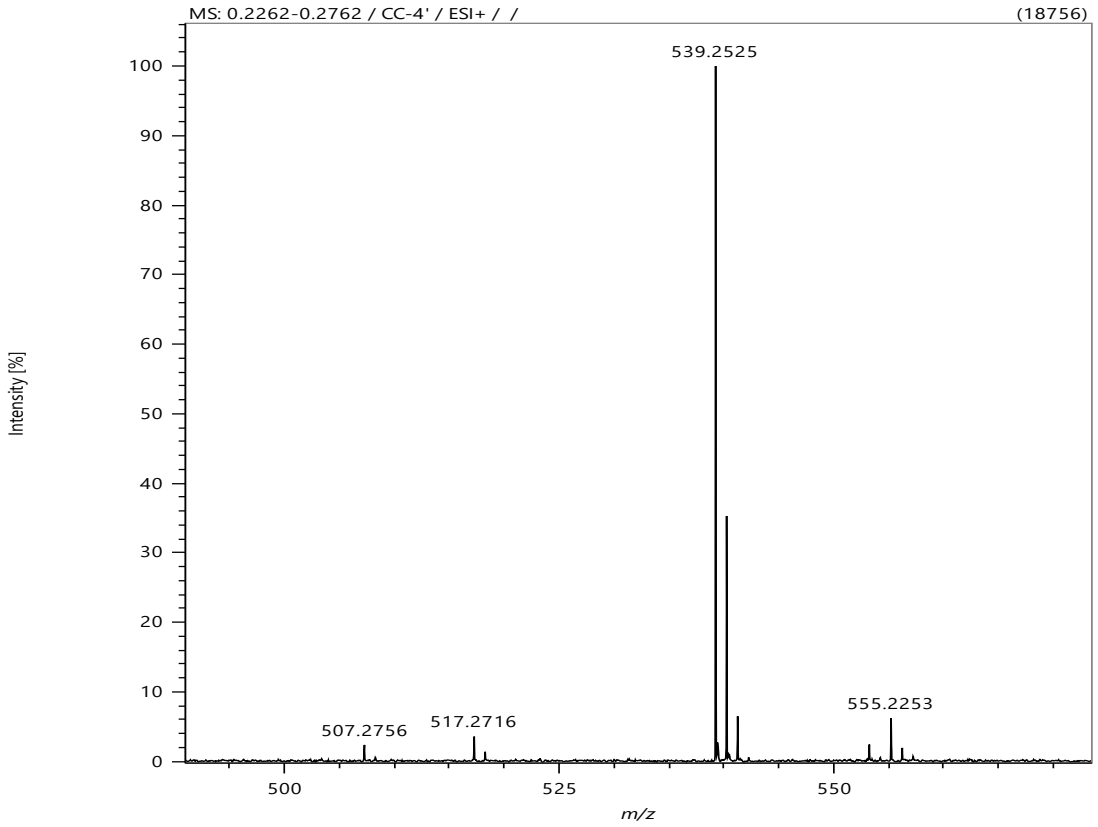

CC-5-27-DMSO-1H.esp
f1 (ppm)
OMe
N3
6a

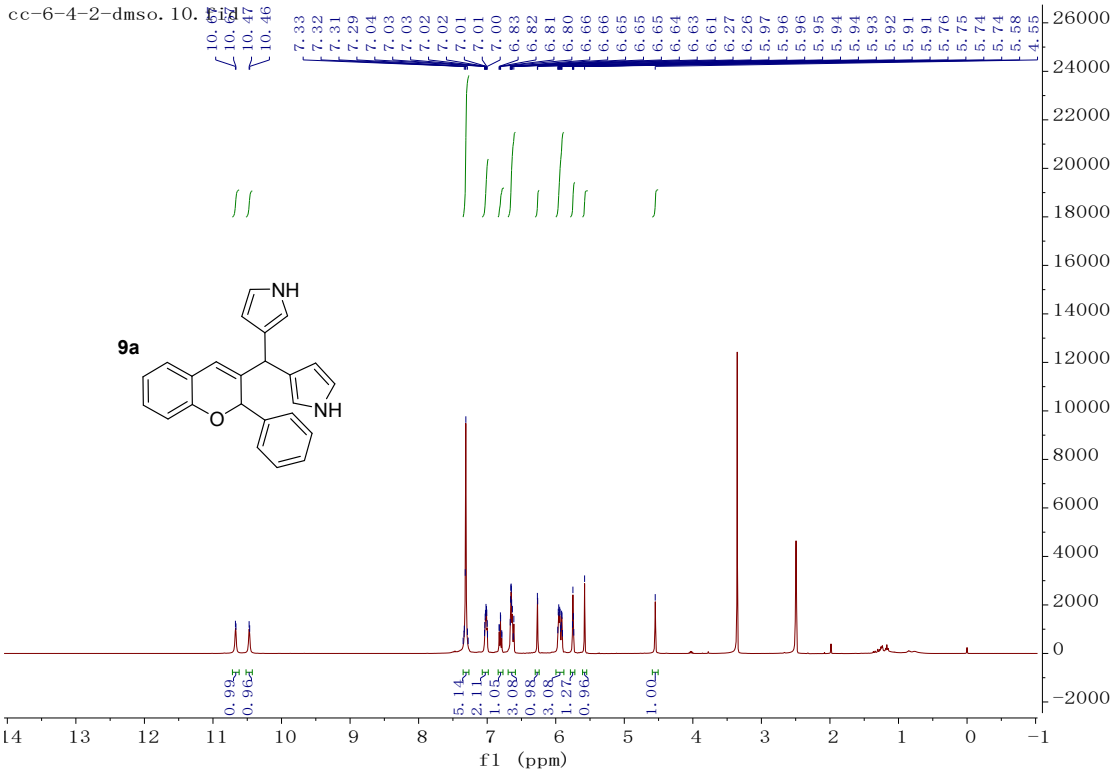

CC-5-27-DMSO-C13-2021-4-20.10.fid
159.75
152.
147.58
137.3
131.2
129.5
129.1
128.45
128.05
127.89
127.29
124.92
123.11
122.16
121.03
119.72
116.44
114.75
75.87
73.59
55.65
f1 (ppm)

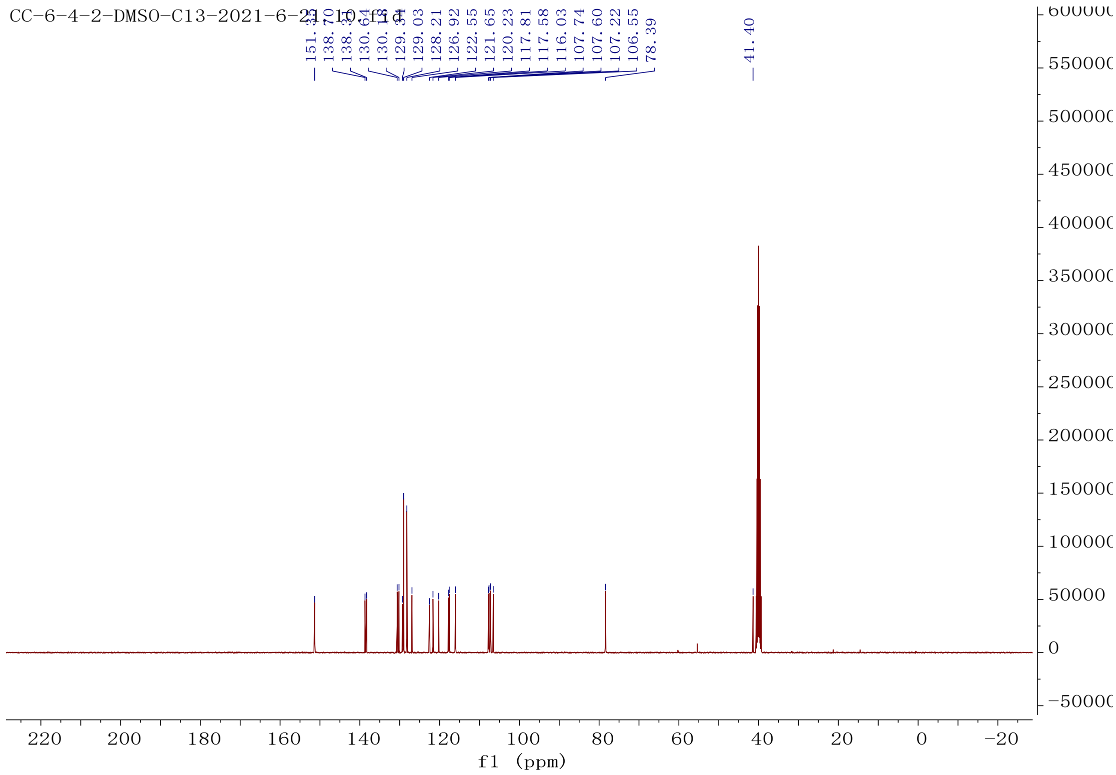

MS: 0.2228-0.3228 / CC-17 / ESI+ / /
(3732)
459.1535
460.1564
Intensity [%]
m/z

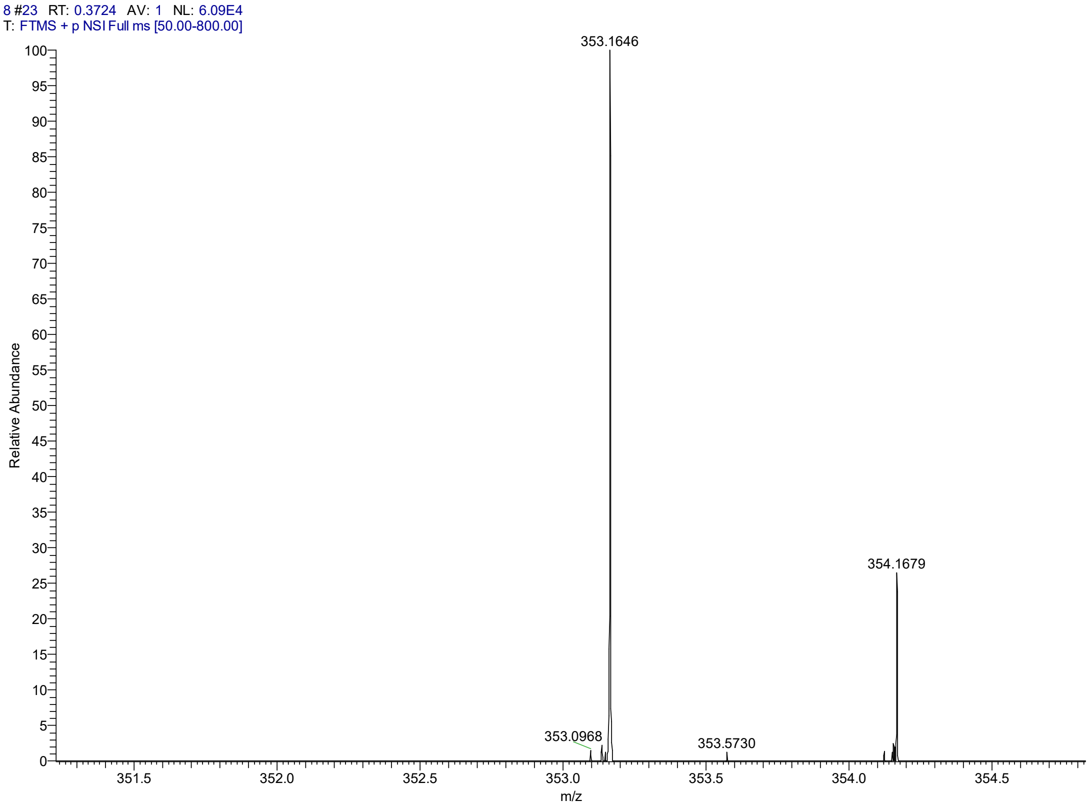

CC-5-29-1-DMSO-2021-04-22 10:16:18
6b
f1 (ppm)

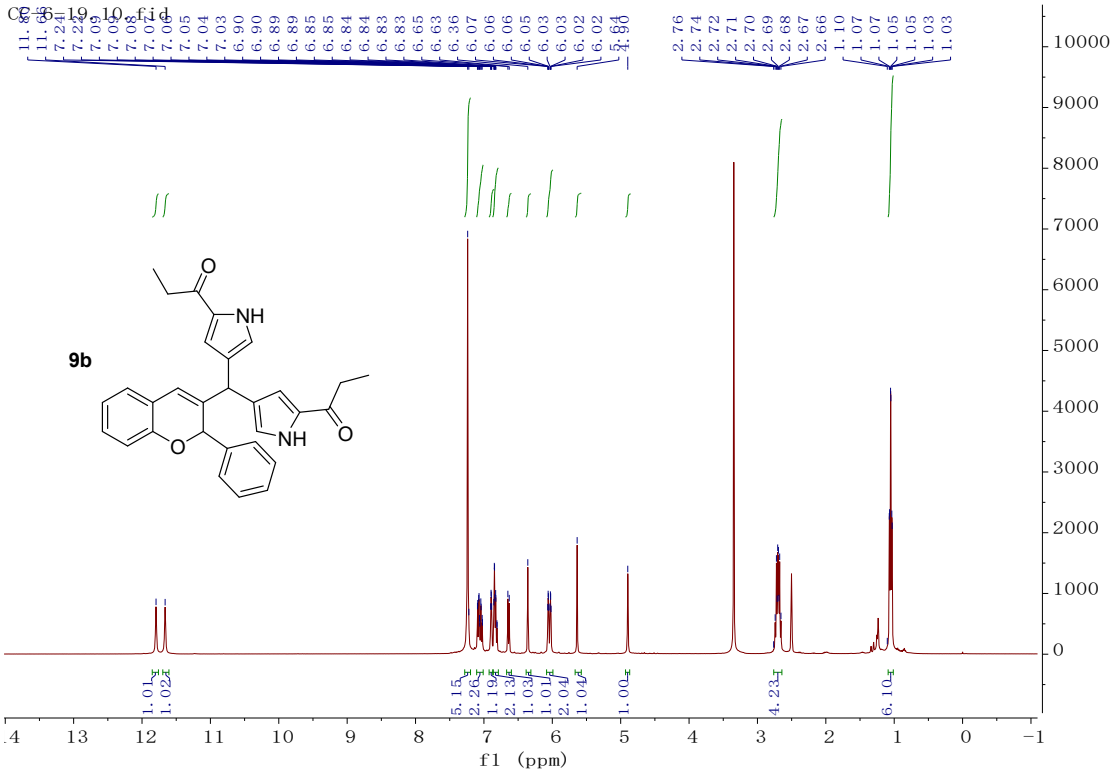

CC-5-29-1-DMSO-C13-2021-4-22 19:06:51
f1 (ppm)

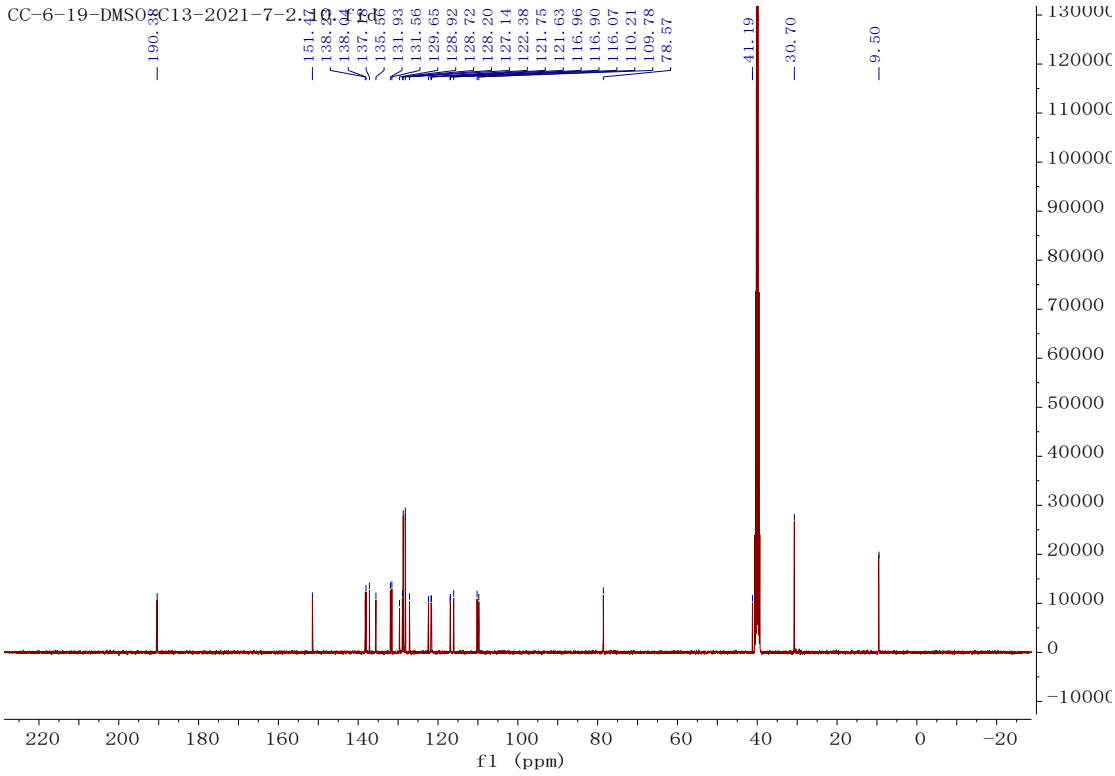

MS: 0.2262-0.2762 / CC-4' / ESI+ / /
(18756)
539.2525
507.2756
517.2716
555.2253
Intensity [%]
m/z

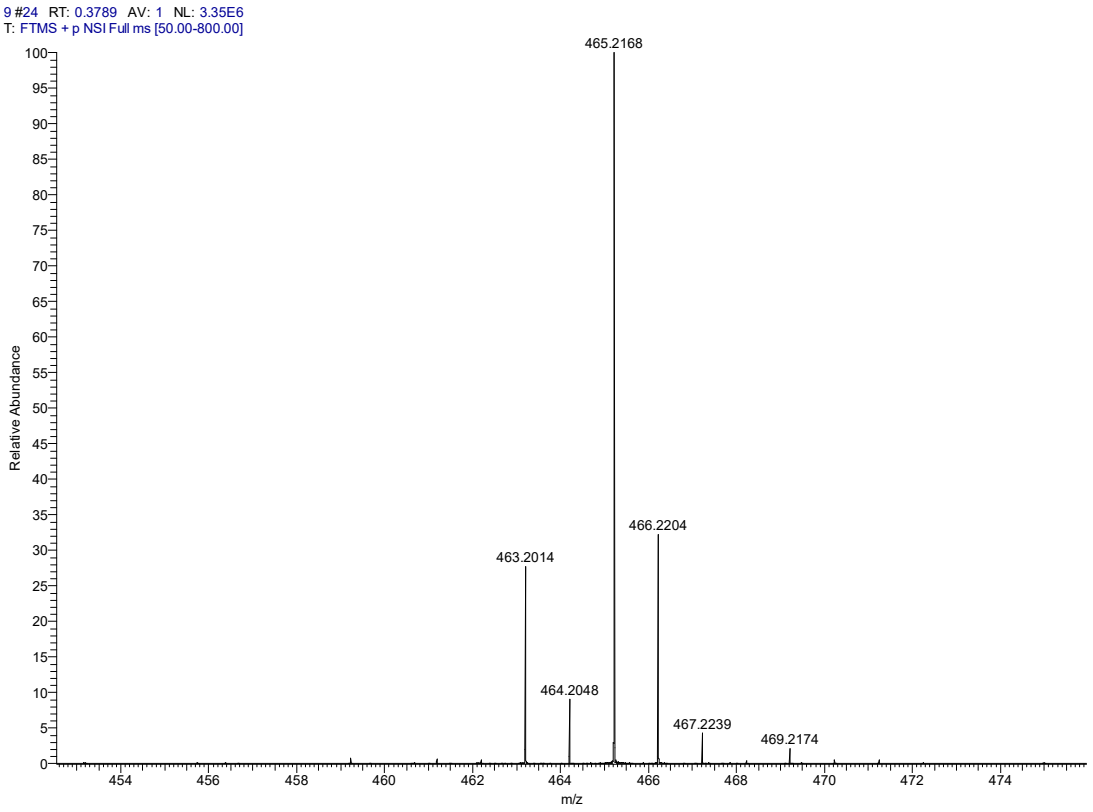

cc-6-4-2-dmso.10.fid
9a
NH
NH
O
f1 (ppm)

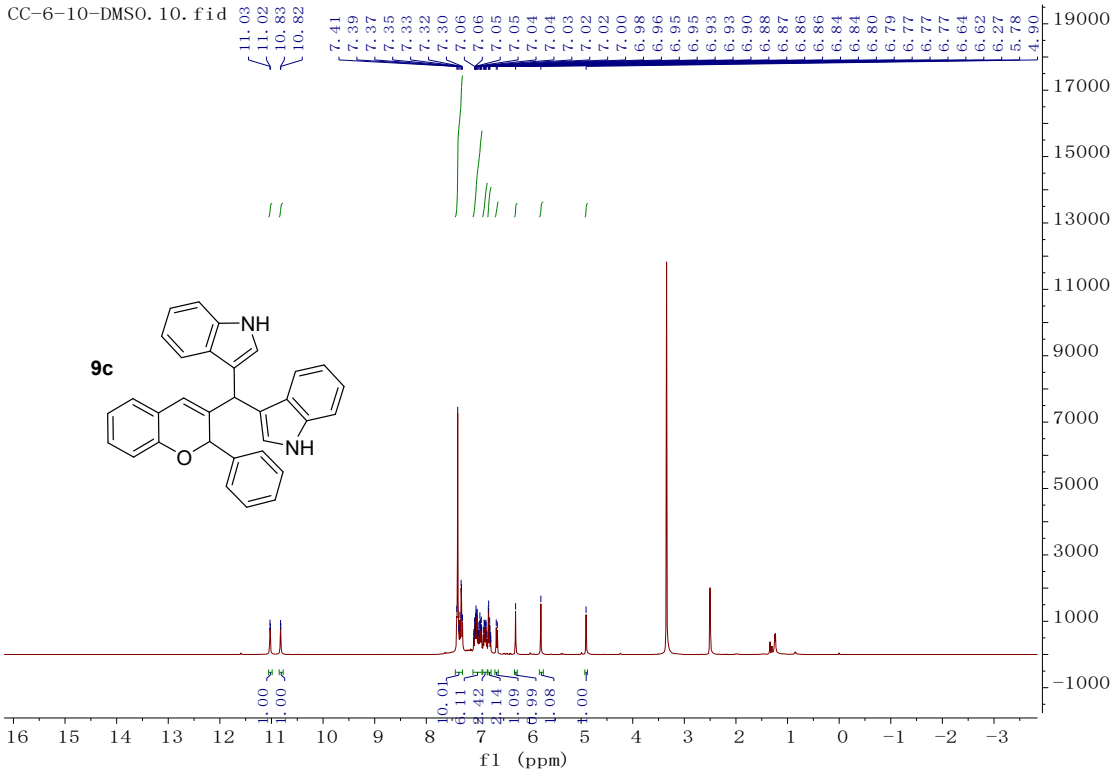

CC-6-4-2-DMSO-C13-2021-6-21.10.fid
151.31
138.70
138.33
130.61
130.37
129.34
129.03
128.21
126.92
122.55
121.65
120.23
117.81
117.58
116.03
107.74
107.60
107.22
106.55
78.39
41.40
f1 (ppm)

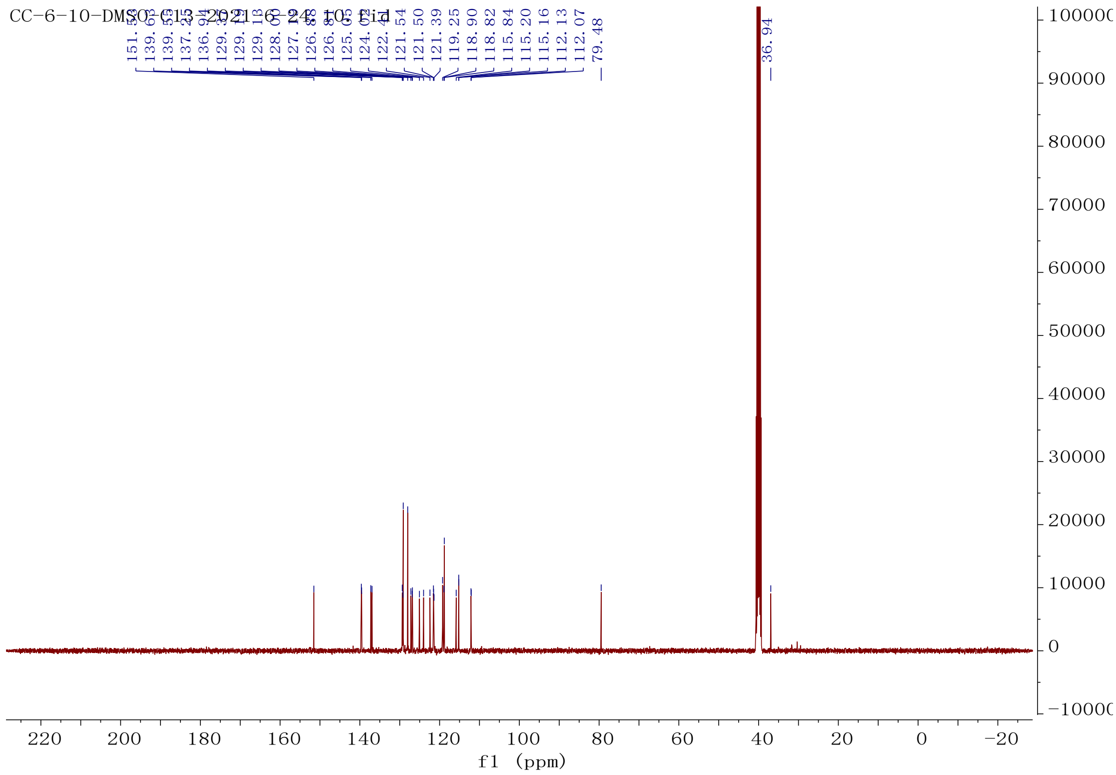

8 #23 RT: 0.3724 AV: 1 NL: 6.09E4
T: FTMS + p NSI Full ms [50.00-800.00]
353.1646
354.1679
353.0968
353.5730
Relative Abundance
m/z

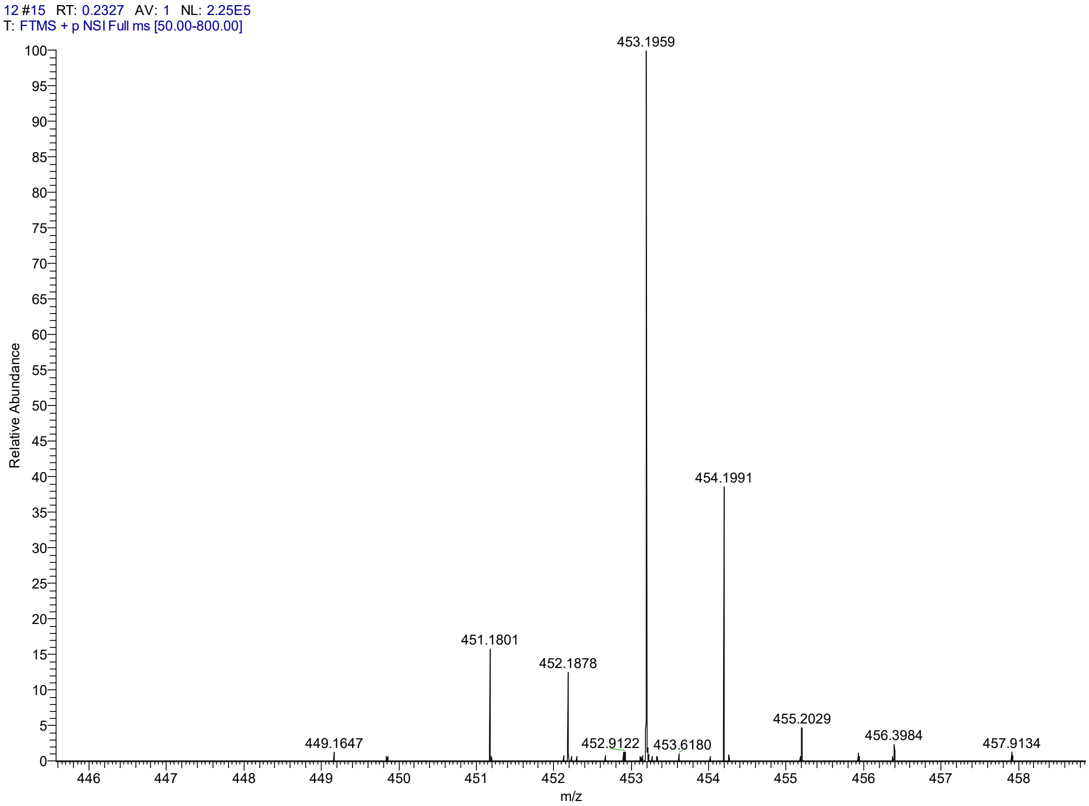

CC-6-19-10.fid
9b
NH
NH
O
O
O
f1 (ppm)

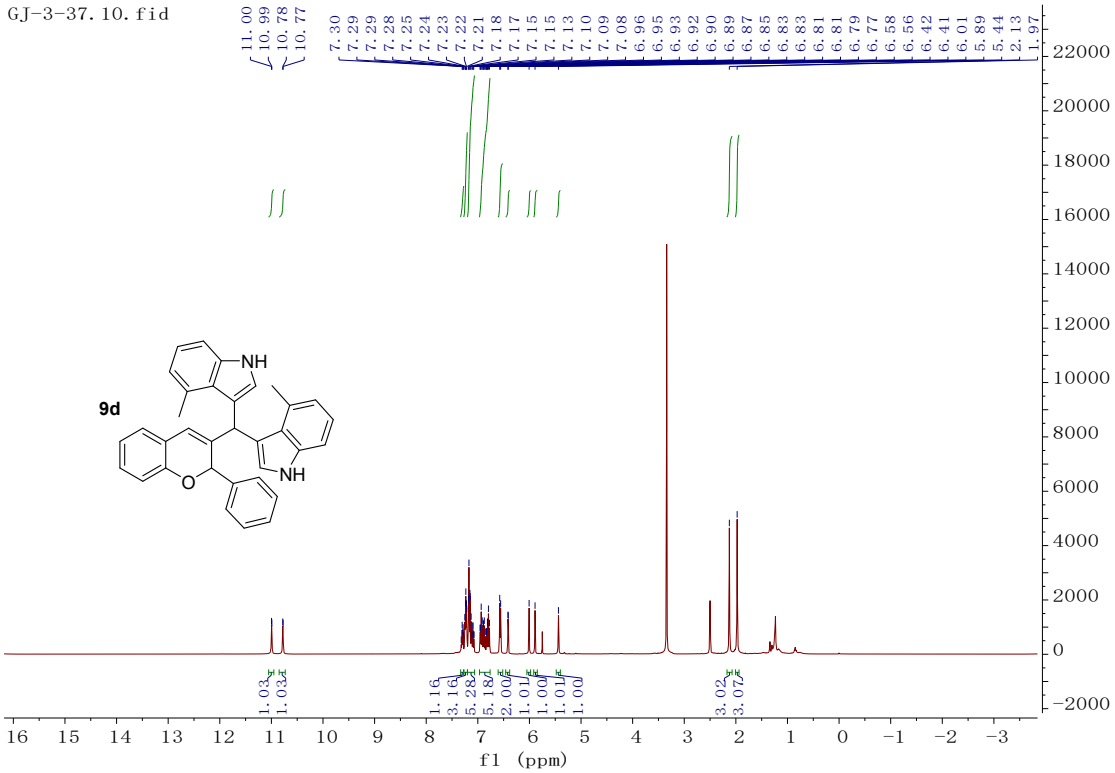

CC-6-19-DMSO-C13-2021-7-2.10.fid
f1 (ppm)

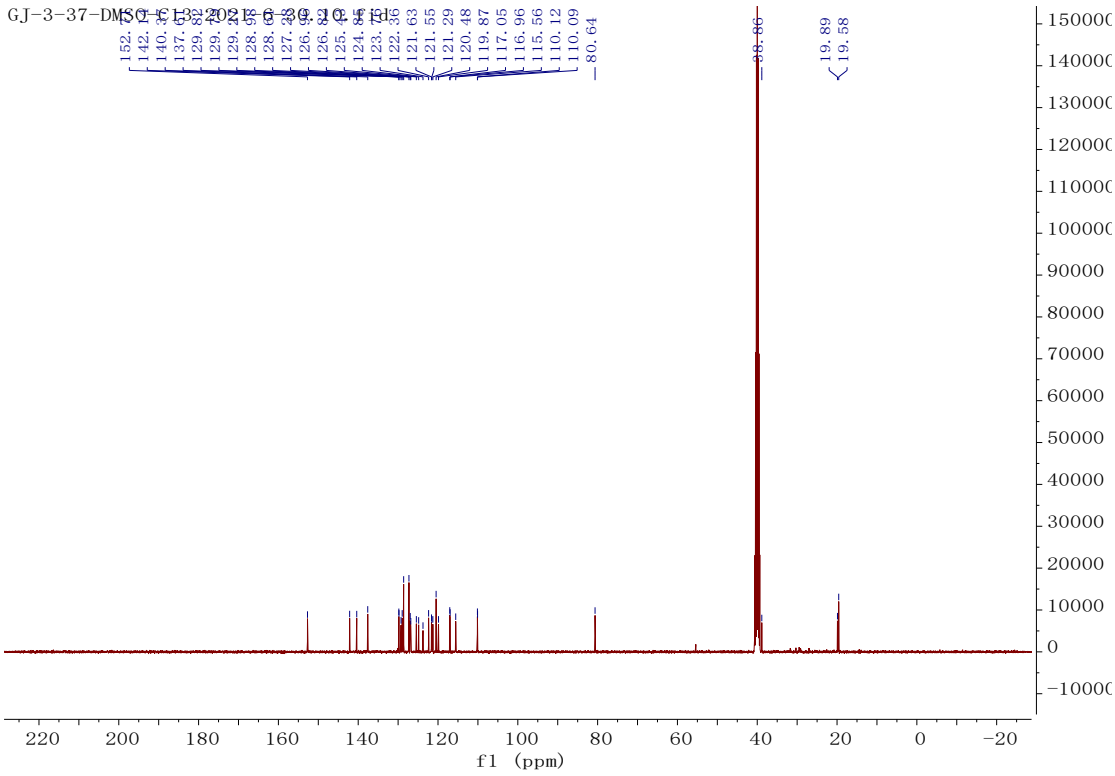

9 #24 RT: 0.3789 AV: 1 NL: 3.35E6
T: FTMS + p NSI Full ms [50.00-800.00]
Relative Abundance
m/z
465.2168
466.2204
463.2014
464.2048
467.2239
469.2174

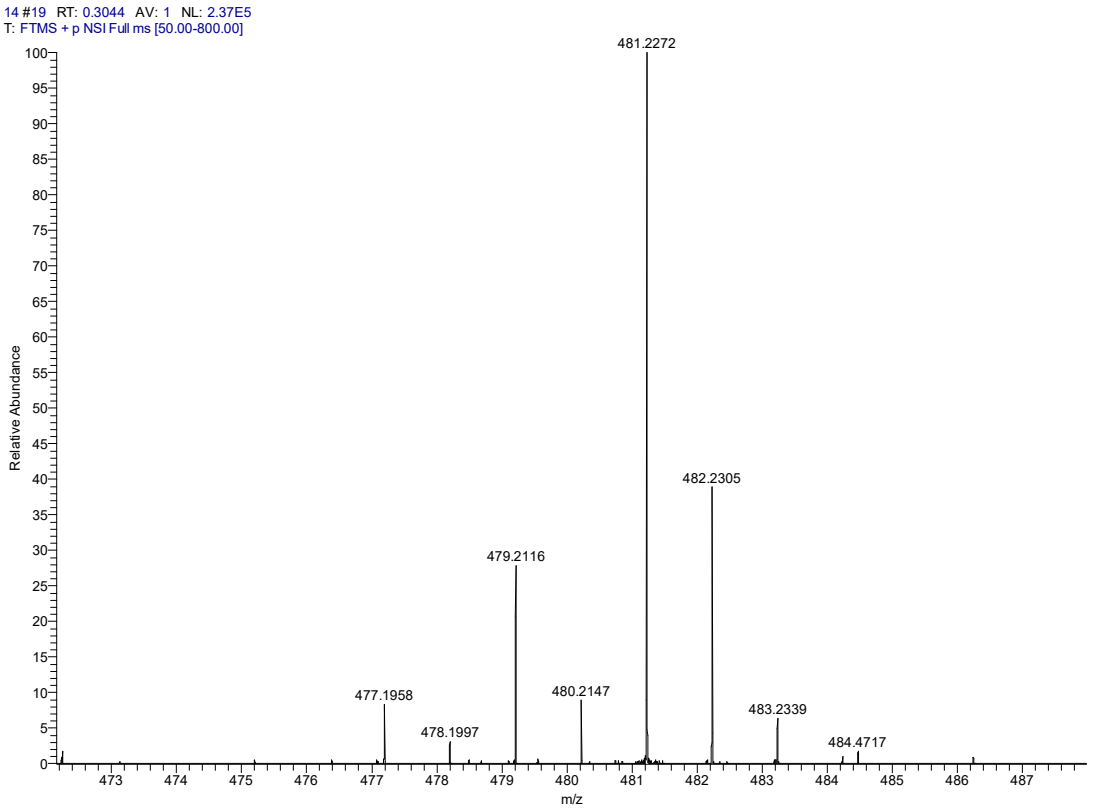

CC-6-10-DMSO.10.fid
9c
NH
NH
O
f1 (ppm)

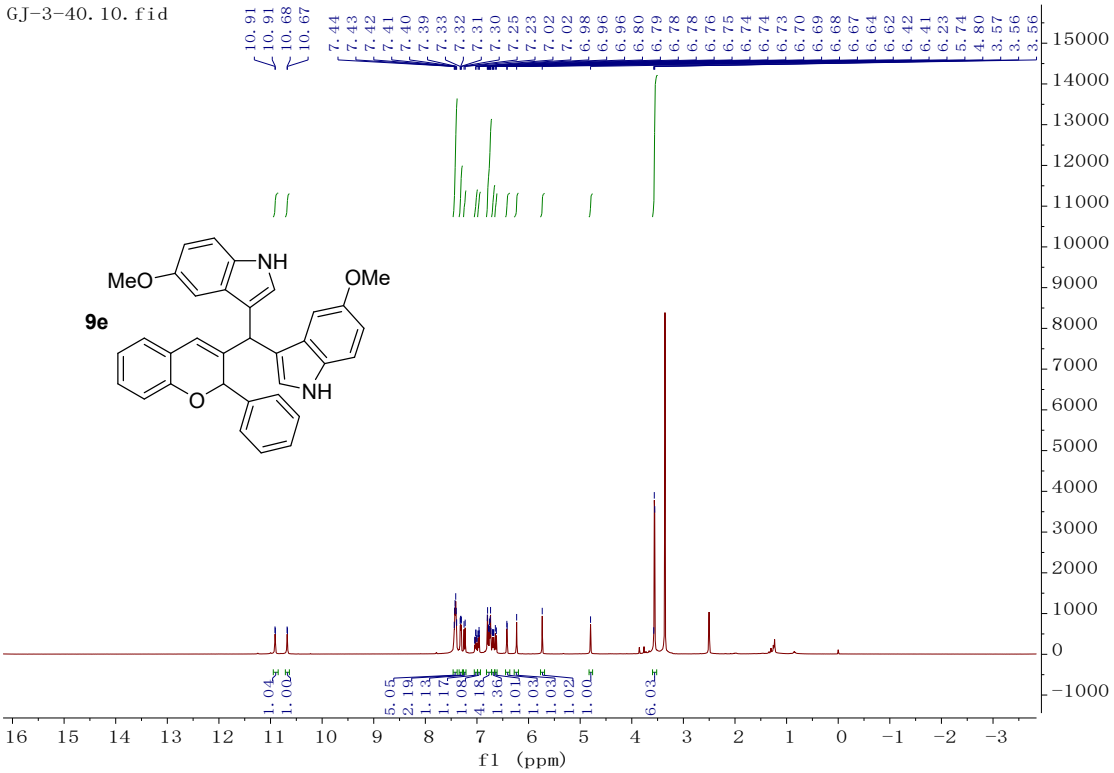

CC-6-10-DMSO-C13-2021-6-24.10.fid
79.48
36.94
f1 (ppm)

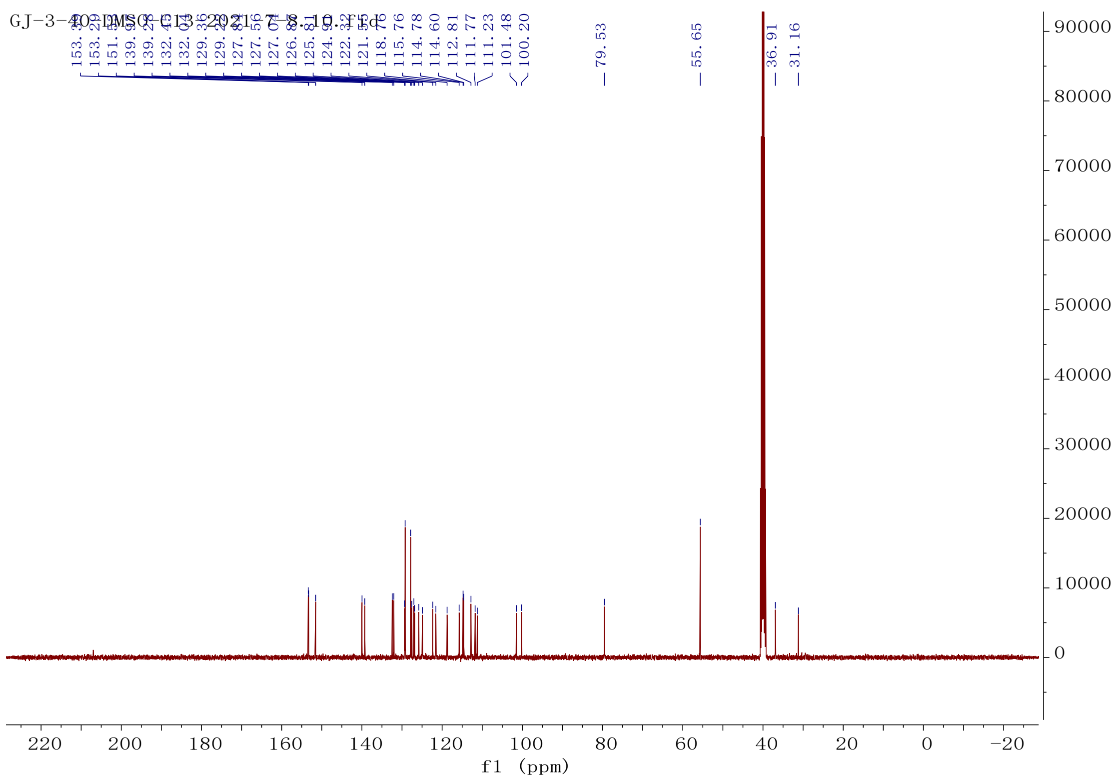

12 #15 RT: 0.2327 AV: 1 NL: 2.25E5
T: FTMS + p NSI Full ms [50.00-800.00]
453.1959
454.1991
451.1801
452.1878
455.2029
449.1647
452.9122
453.6180
456.3984
457.9134
Relative Abundance
m/z


GJ-3-37.10.fid
9d
NH
NH
O
f1 (ppm)

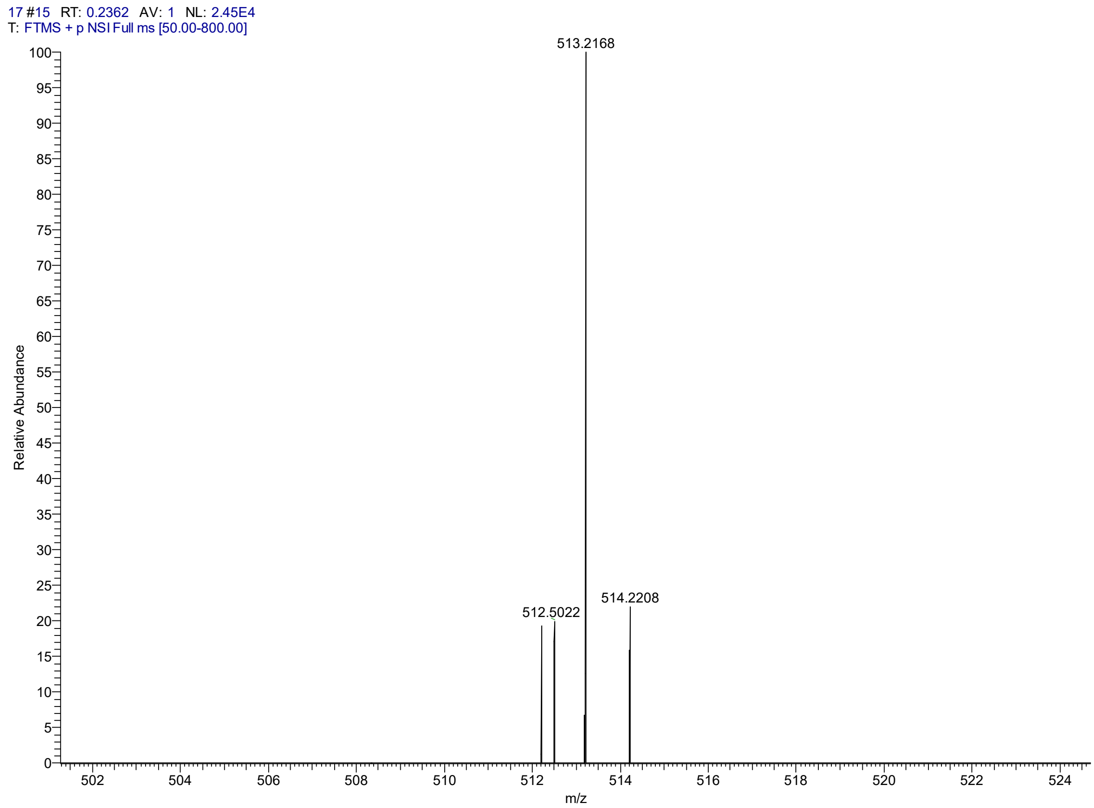

GJ-3-37-DMSO-C13-2021-6-30-10.fid
f1 (ppm)


14 #19 RT: 0.3044 AV: 1 NL: 2.37E5
T: FTMS + p NSI Full ms [50.00-800.00]
481.2272
482.2305
479.2116
477.1958
480.2147
478.1997
483.2339
484.4717
Relative Abundance
m/z

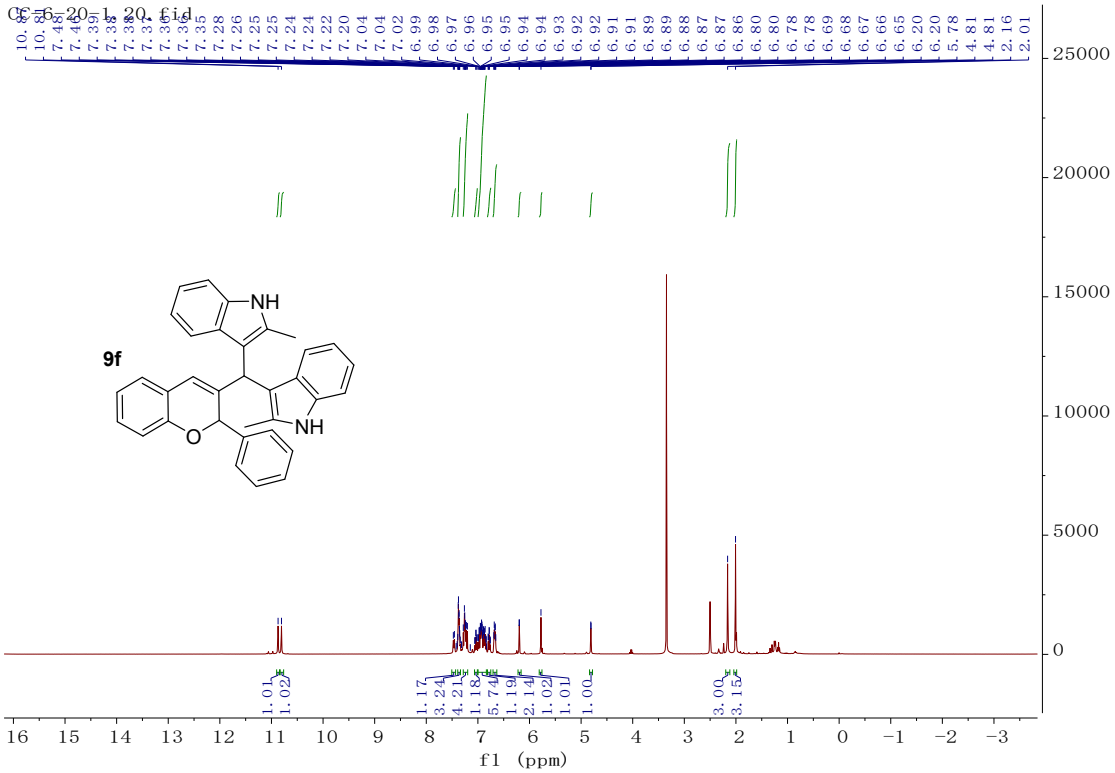

GJ-3-40.10.fid
9e
MeO
OMe
NH
NH
O
f1 (ppm)

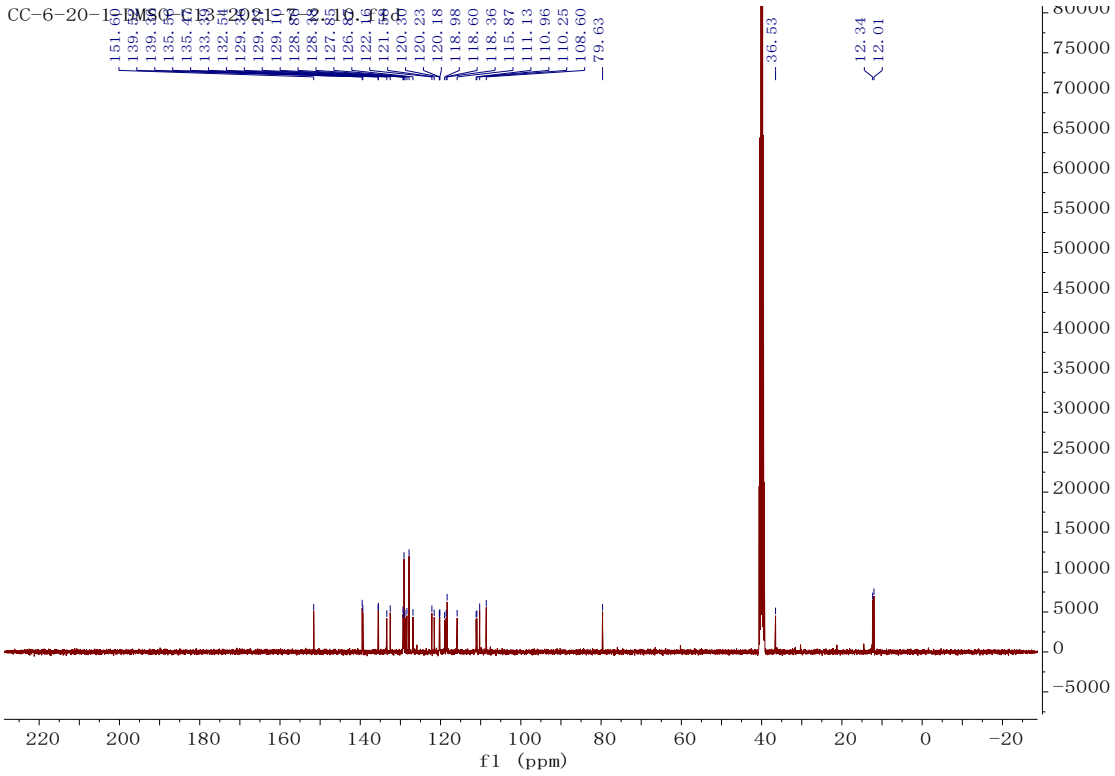


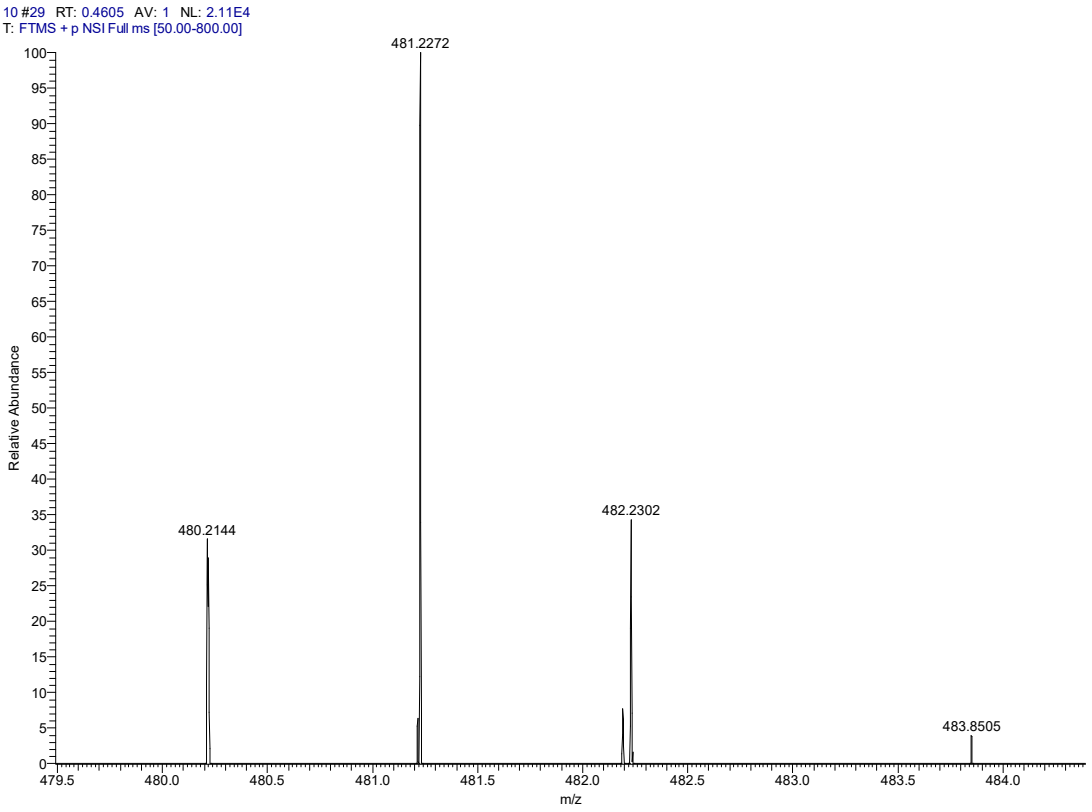
GJ-3-40-DMSO-C13-2021-7-8-10.fid
79.53
55.65
36.91
31.16
f1 (ppm)

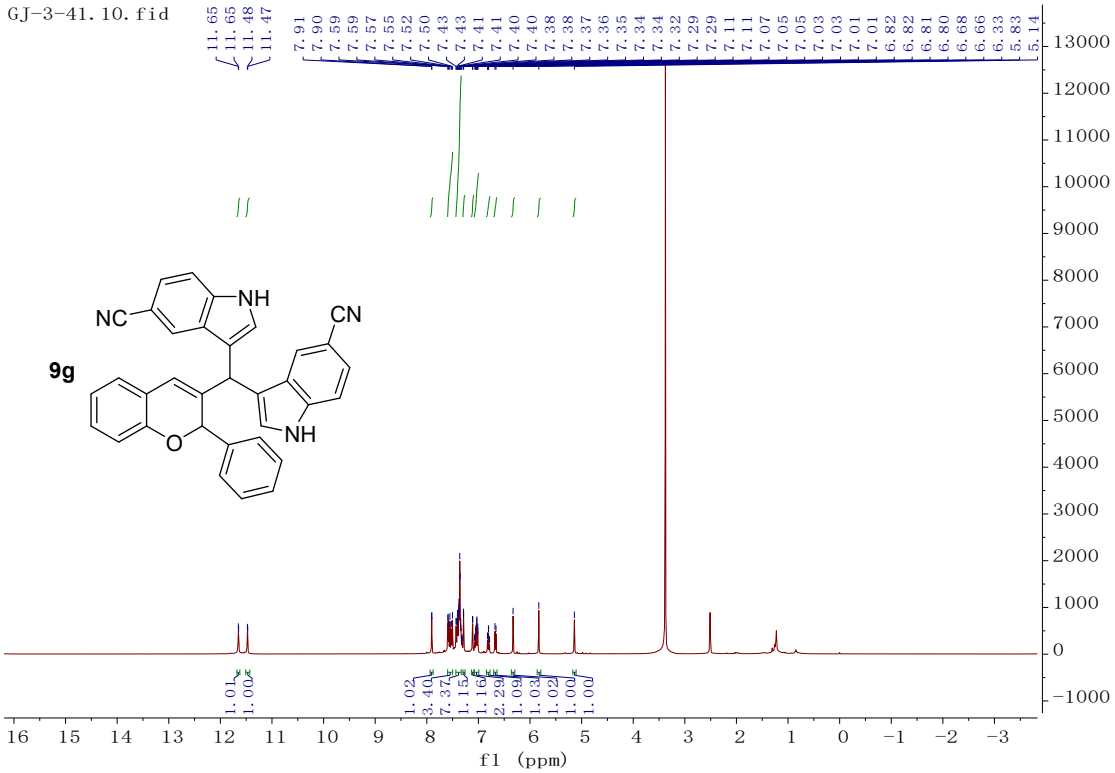


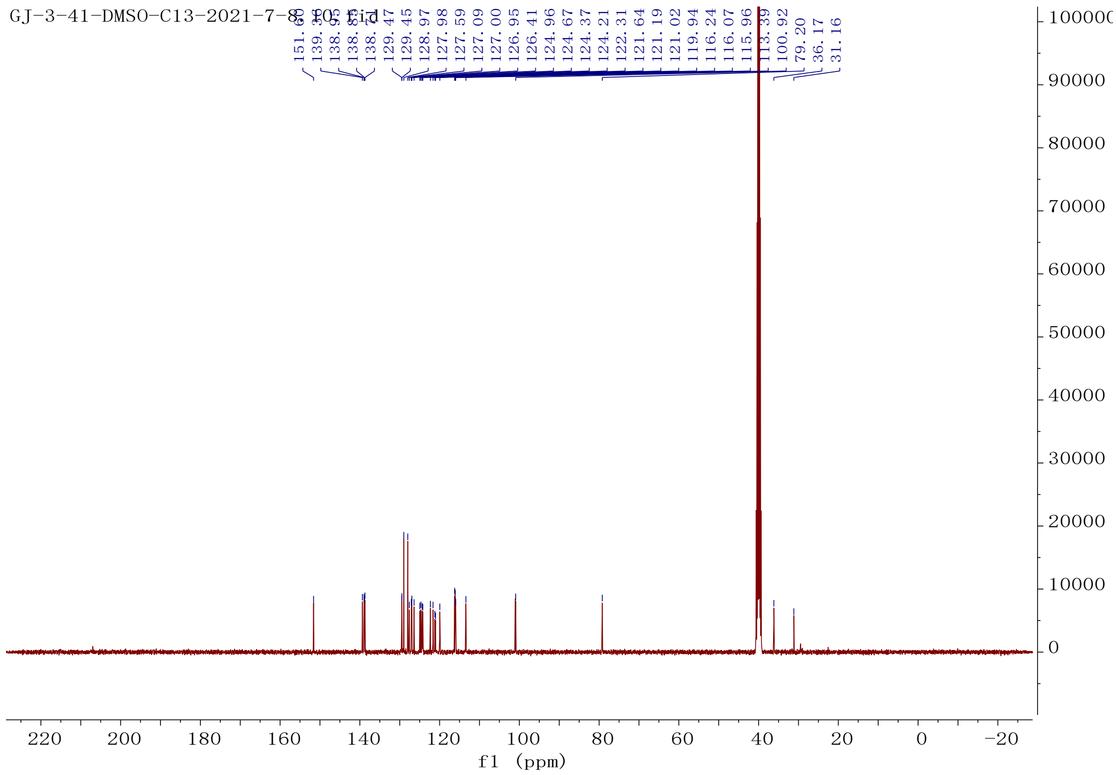
17 #15 RT: 0.2362 AV: 1 NL: 2.45E4
T: FTMS + p NSI Full ms [50.00-800.00]
513.2168
512.5022
514.2208
Relative Abundance
m/z

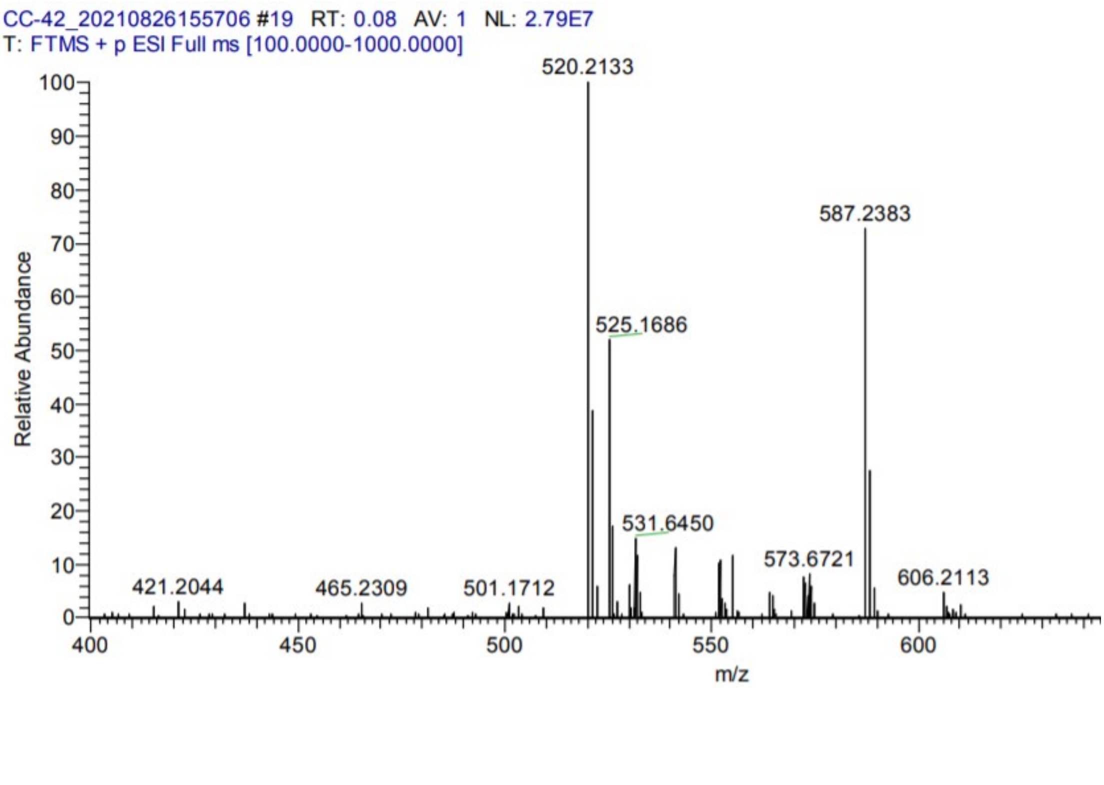

CC-6-20-1-20.fid
9f
NH
NH
O
f1 (ppm)

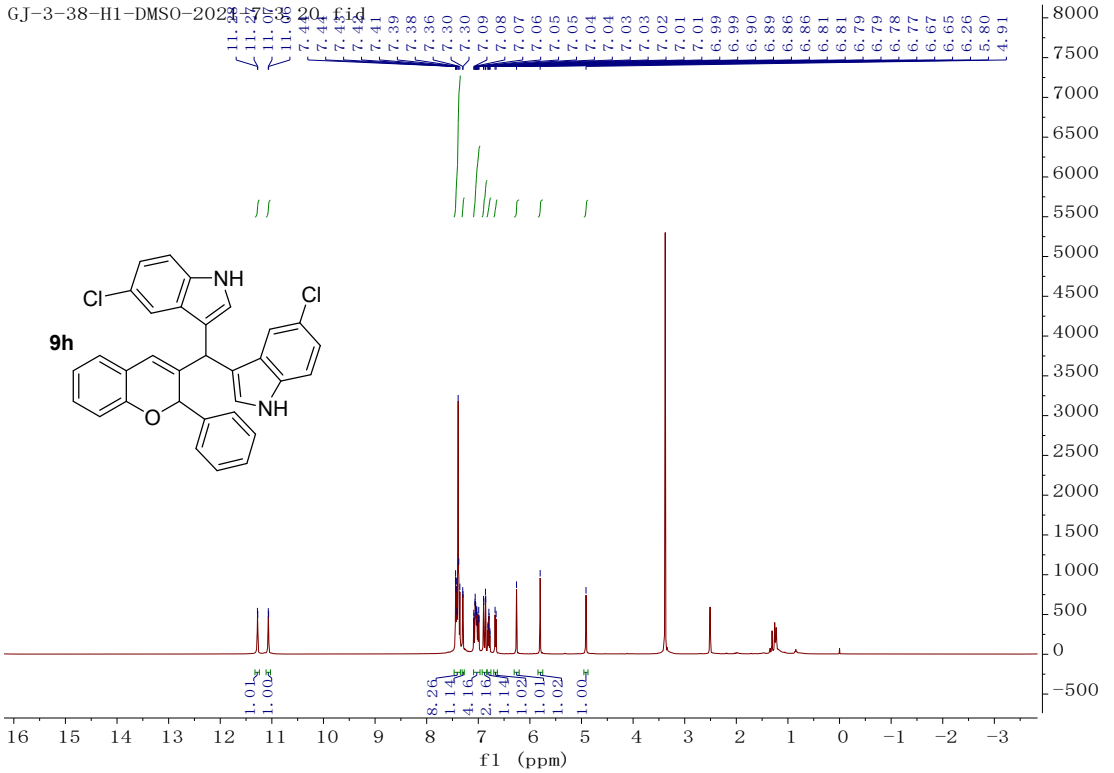

CC-6-20-1-DMSO-C13-2021-7-2-19-54.fid
f1 (ppm)

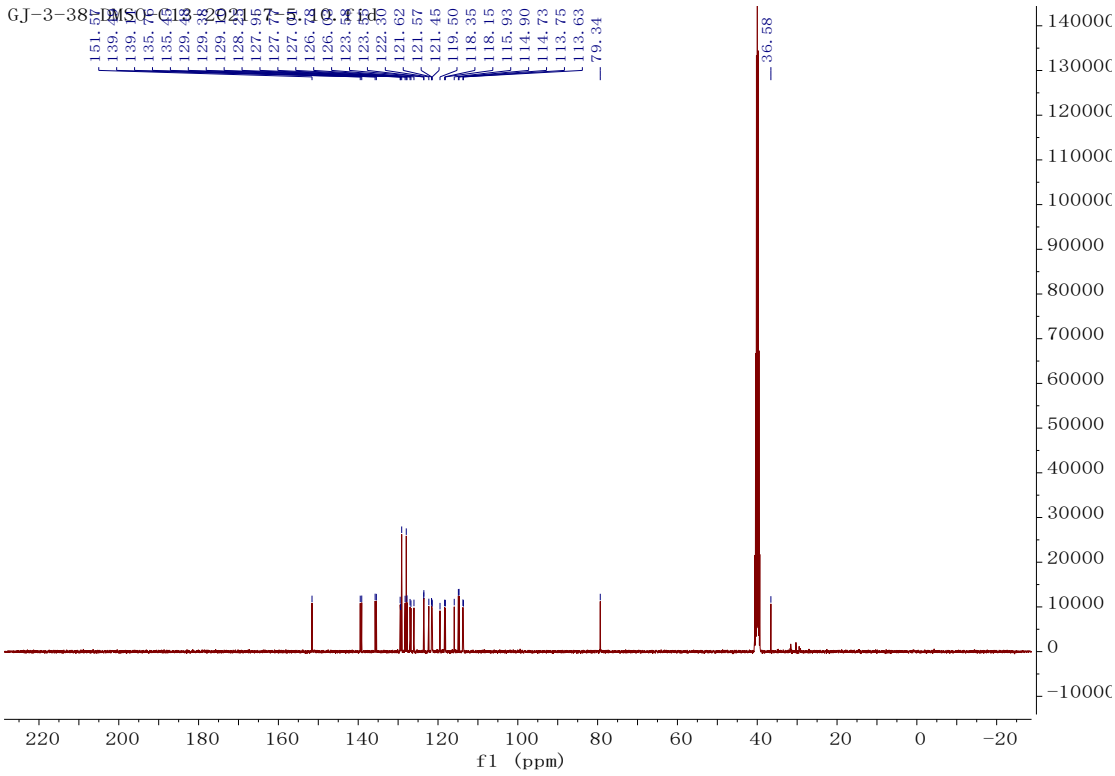

10 #29 RT: 0.4605 AV: 1 NL: 2.11E4
T: FTMS + p NSI Full ms [50.00-800.00]
481.2272
480.2144
482.2302
483.8505
Relative Abundance
m/z

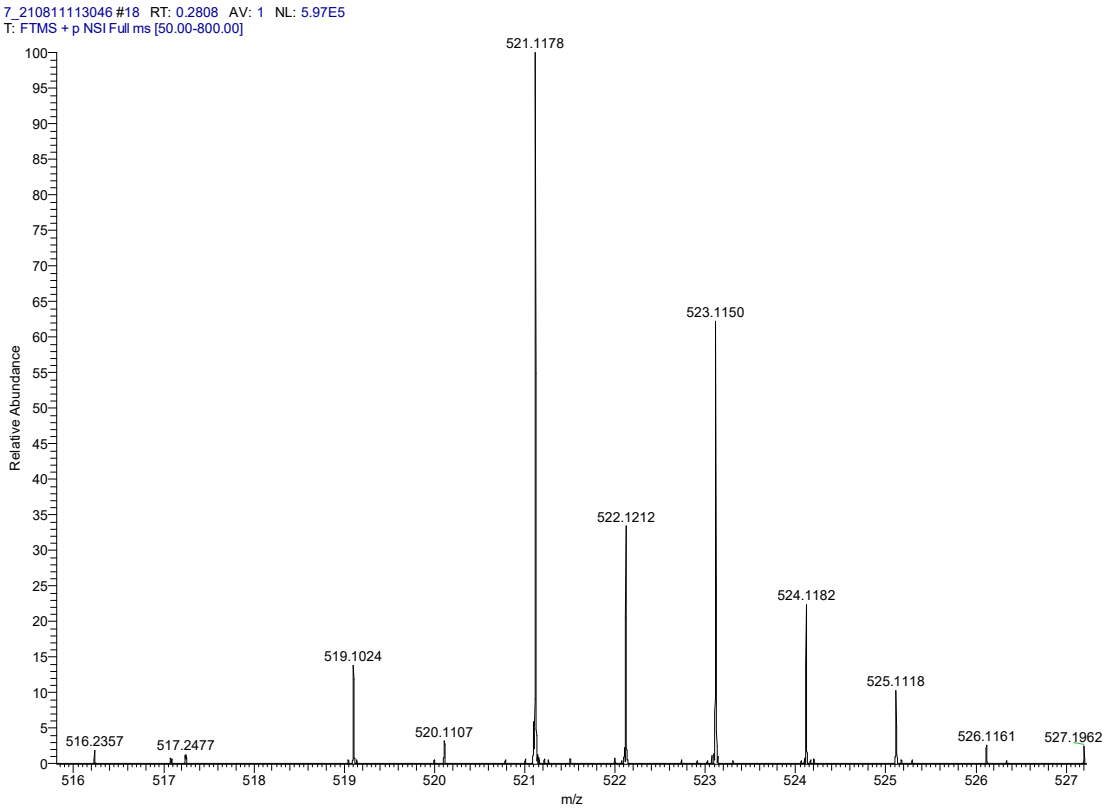

GJ-3-41.10.fid
9g
NC
NH
CN
NH
O
f1 (ppm)

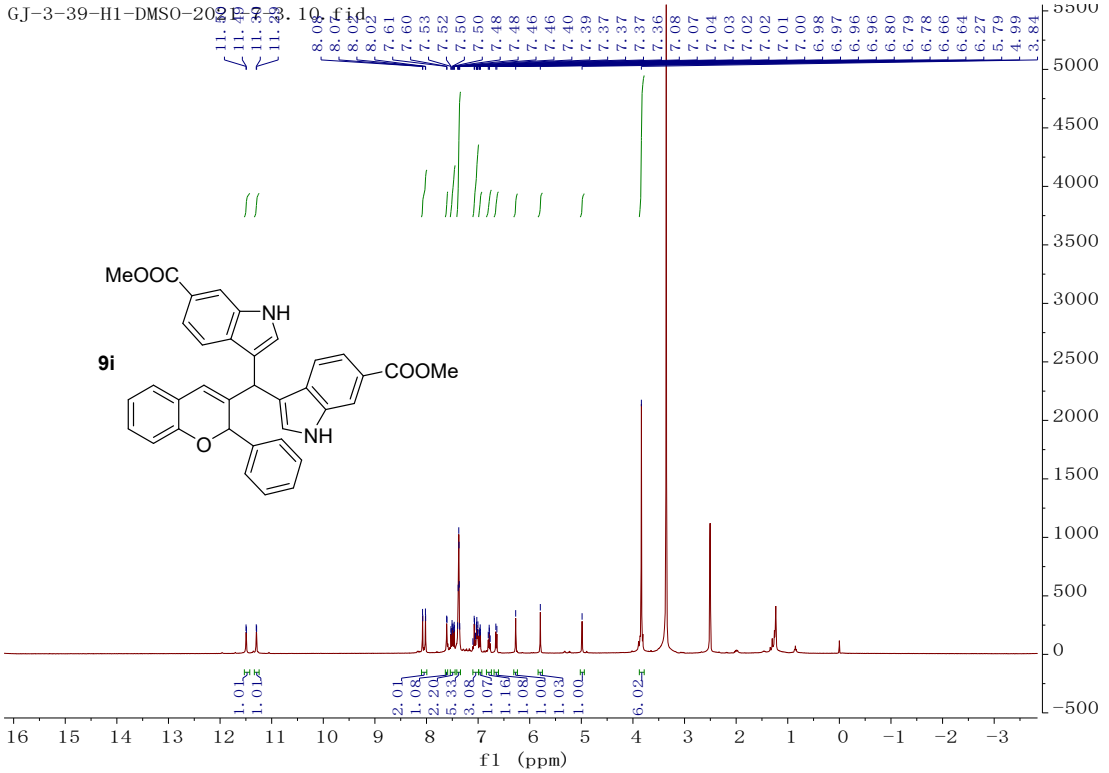

GJ-3-41-DMSO-C13-2021-7-8.10.fid
129.47
129.45
128.97
127.98
127.59
127.09
127.00
126.95
126.41
124.96
124.67
124.37
124.21
122.31
121.64
121.19
121.02
119.94
116.24
116.07
115.96
113.39
100.92
79.20
36.17
31.16
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220 200 180 160 140 120 100 80 60 40 20 0 −20
f1 (ppm)

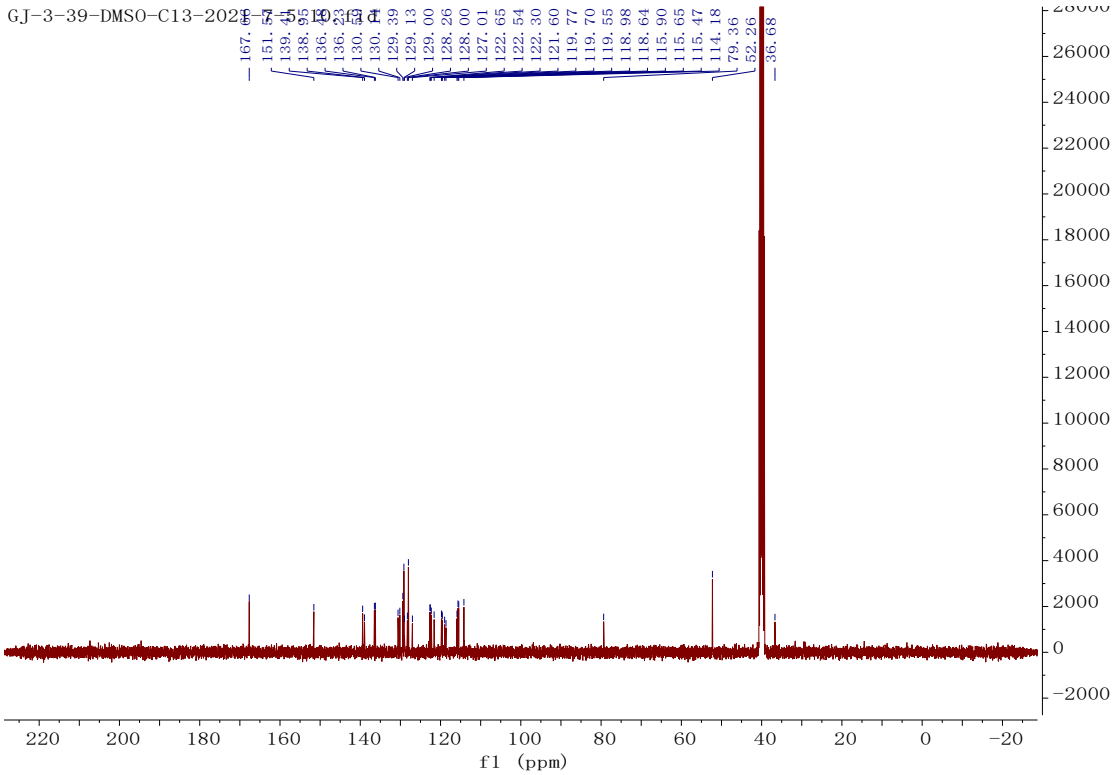

CC-42_20210826155706 #19 RT: 0.08 AV: 1 NL: 2.79E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]
520.2133
587.2383
525.1686
531.6450
573.6721
606.2113
421.2044
465.2309
501.1712
Relative Abundance
m/z
400 450 500 550 600

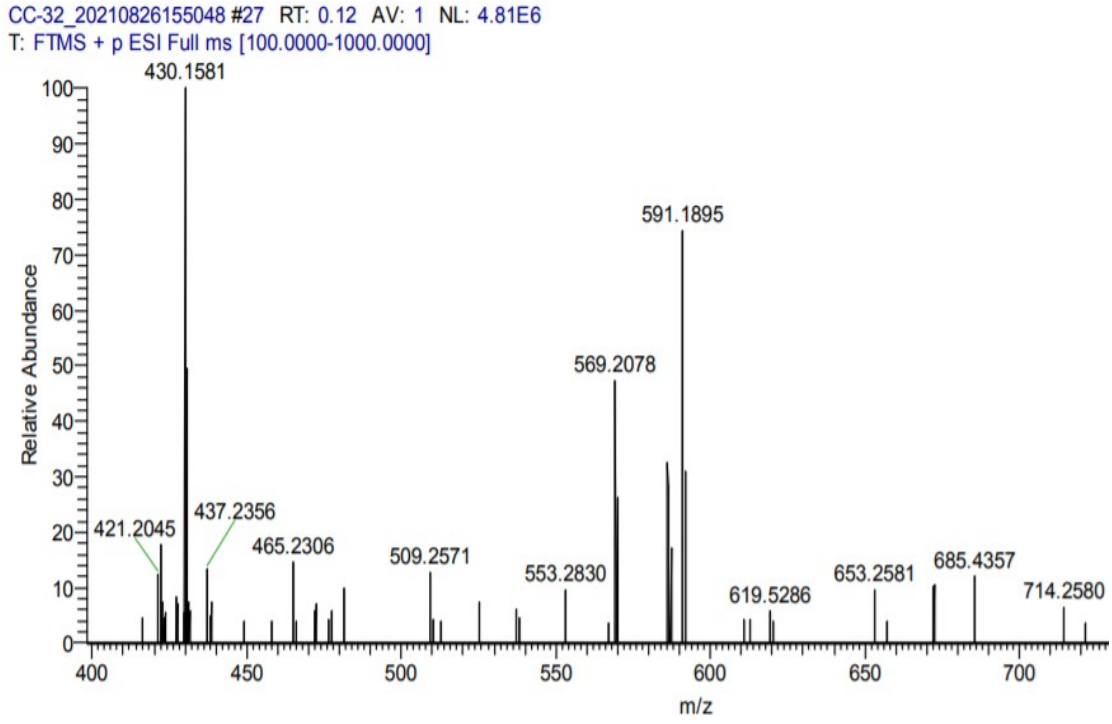

GJ-3-38-H1-DMSO-2022.4.7-5.30.20.fid
9h
Cl
NH
Cl
NH
O
f1 (ppm)

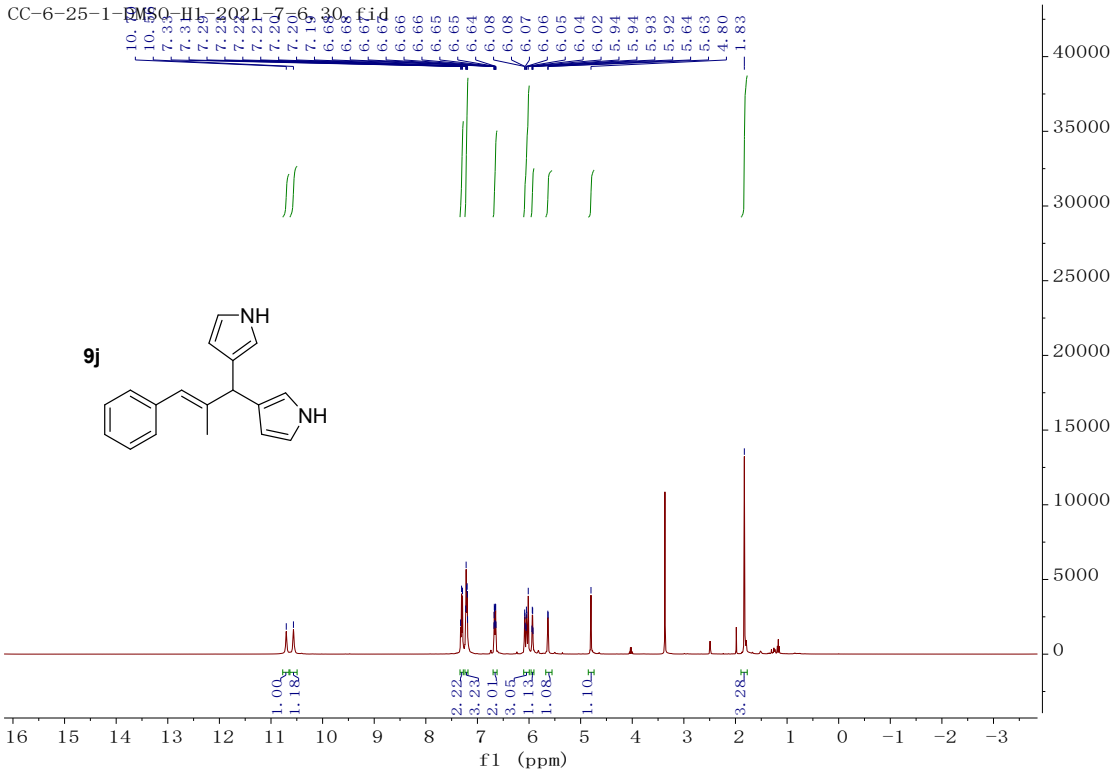

GJ-3-38-DMSO-C13-2021.7.5-10.2.fid
f1 (ppm)

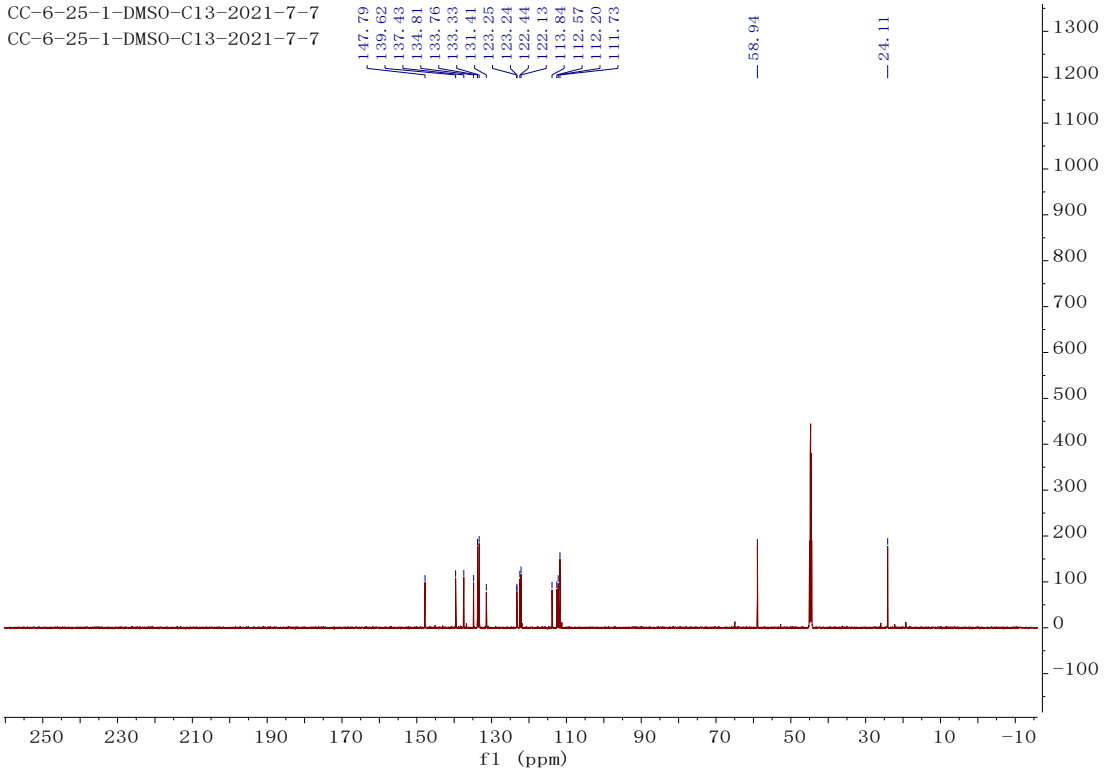

7_210811113046 #18 RT: 0.2808 AV: 1 NL: 5.97E5
T: FTMS + p NSI Full ms [50.00-800.00]
Relative Abundance
m/z
521.1178
523.1150
522.1212
524.1182
519.1024
525.1118
520.1107
526.1161
527.1962
516.2357
517.2477

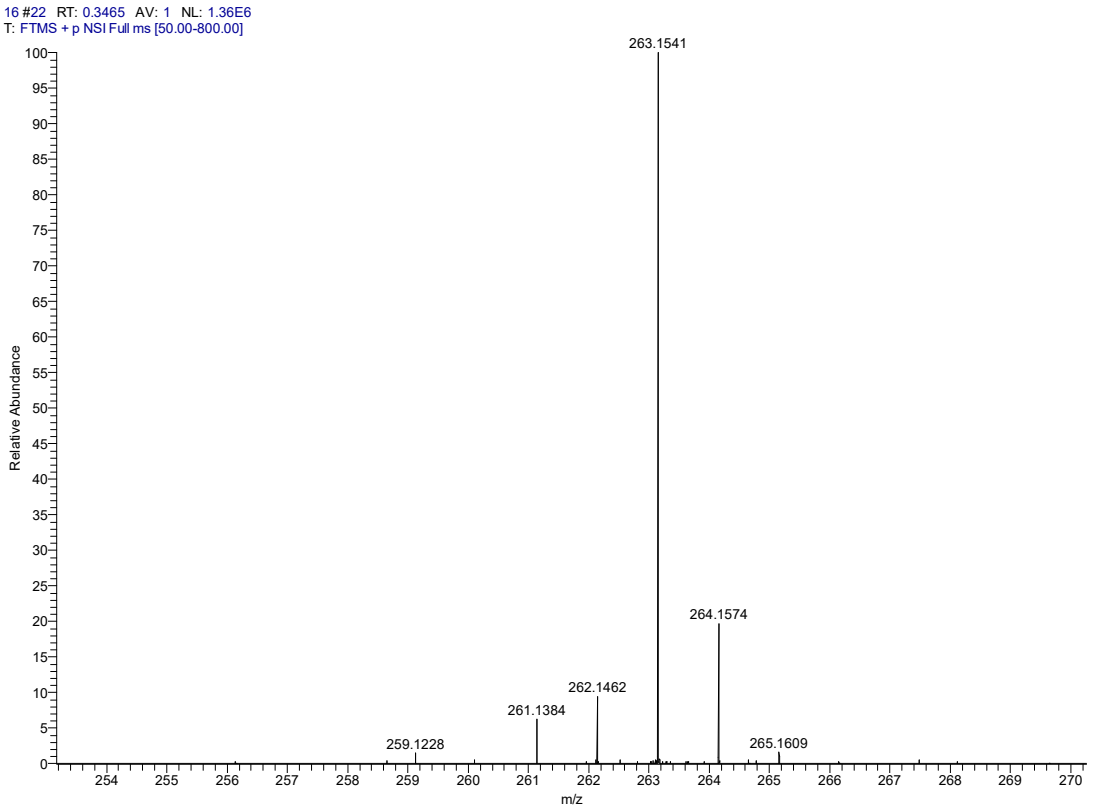

GJ-3-39-H1-DMSO-2021-3-3.10.fid
MeOOC
NH
9i
COOMe
NH
O
f1 (ppm)

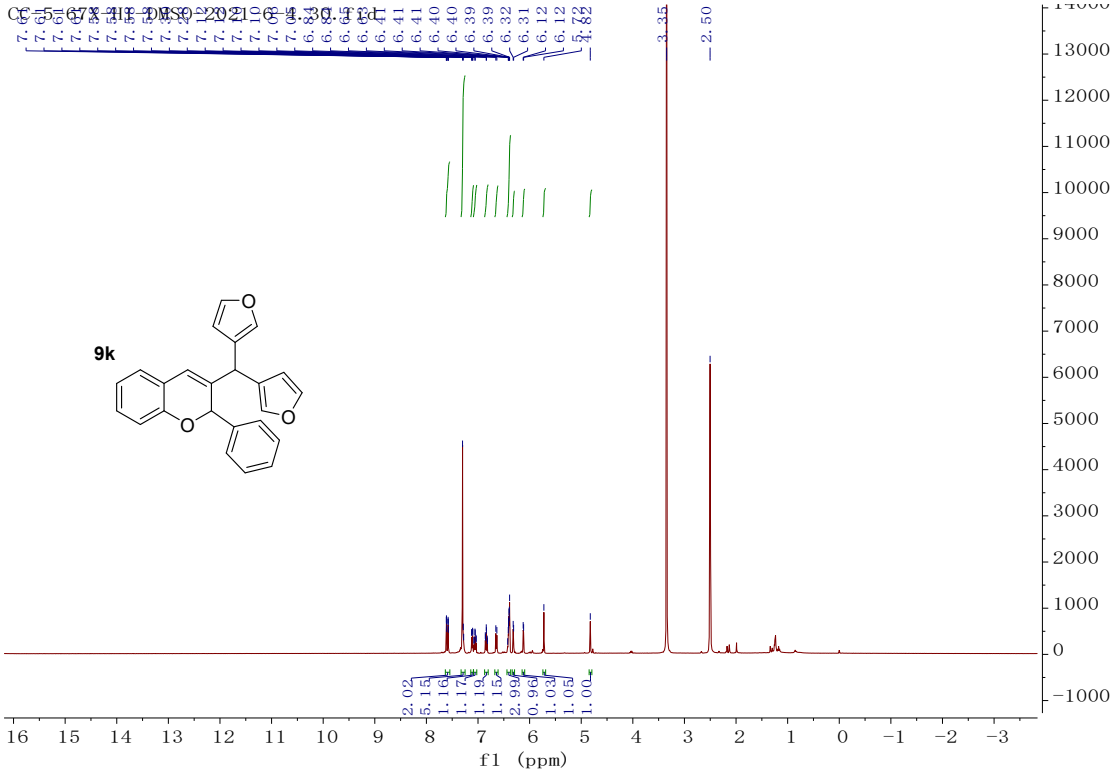

GJ-3-39-DMSO-C13-2020
167.65
151.57
139.41
138.95
136.43
136.23
130.53
130.14
129.39
129.13
129.00
128.26
128.00
127.01
122.65
122.54
122.30
121.60
119.77
119.70
119.55
118.98
118.64
115.90
115.65
115.47
114.18
79.36
52.26
36.68
f1 (ppm)

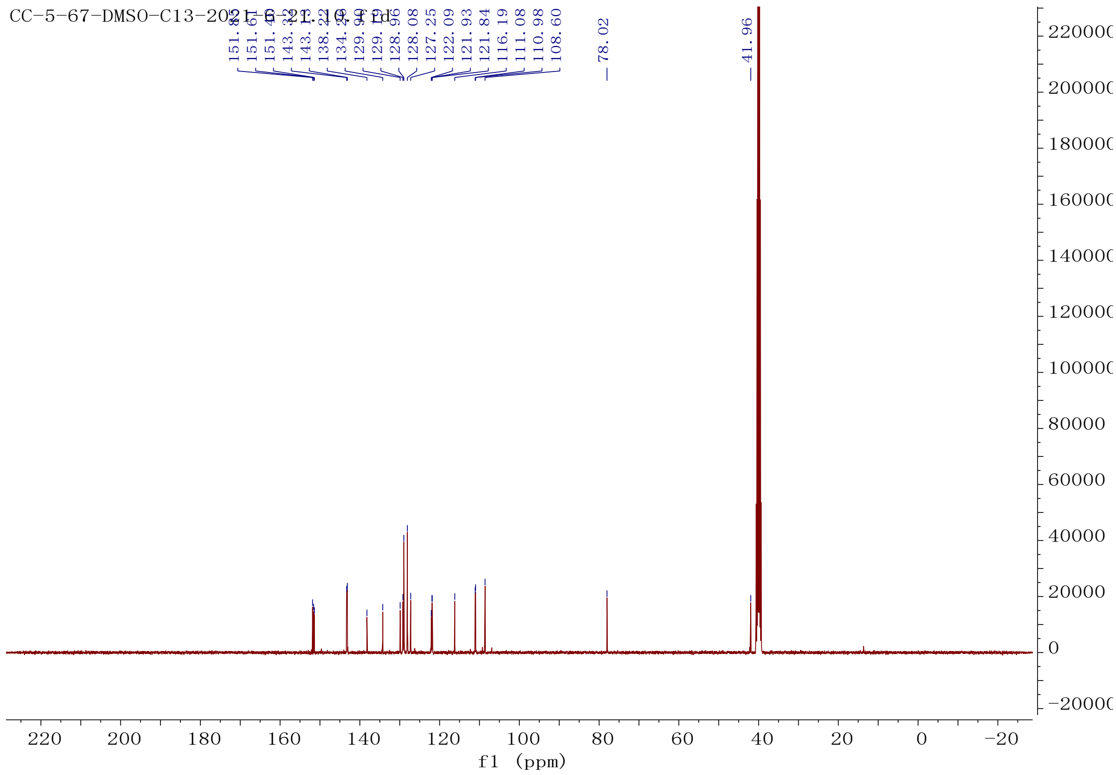

CC-32_20210826155048 #27 RT: 0.12 AV: 1 NL: 4.81E6
T: FTMS + p ESI Full ms [100.0000-1000.0000]
430.1581
591.1895
569.2078
421.2045
437.2356
465.2306
509.2571
553.2830
619.5286
653.2581
685.4357
714.2580
Relative Abundance
m/z

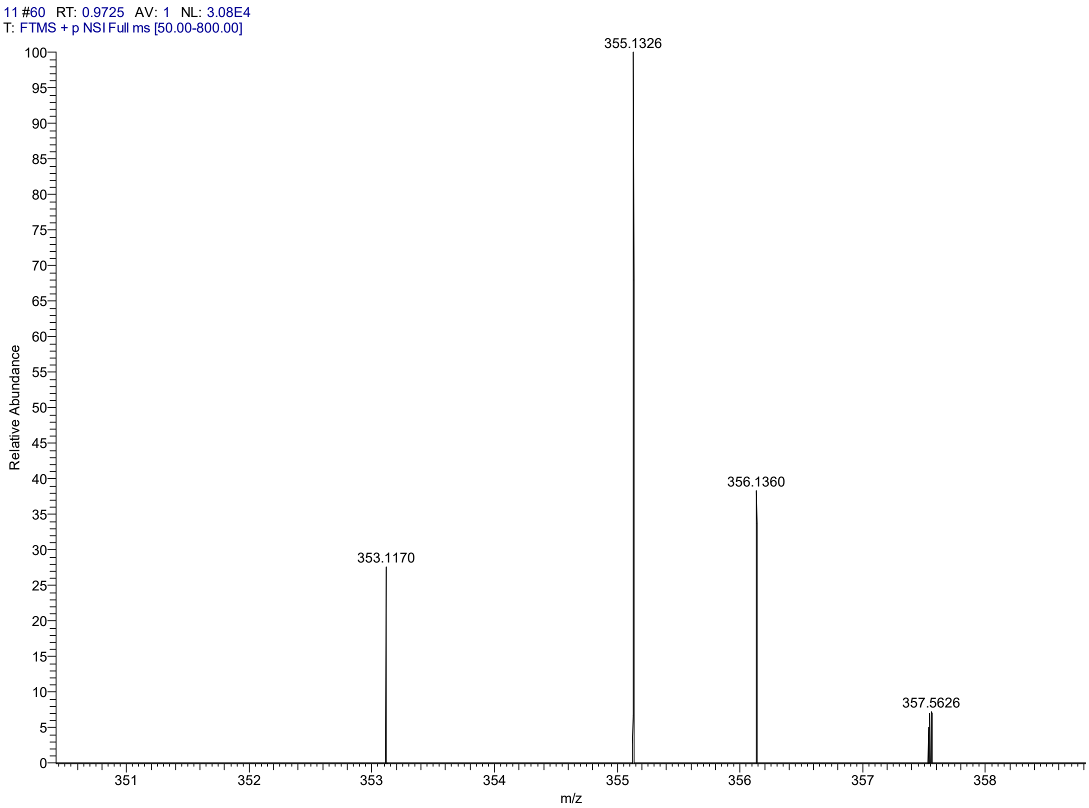

CC-6-25-1-DMSO-H1-2021-7-6-30.fid
9j
NH
NH
f1 (ppm)

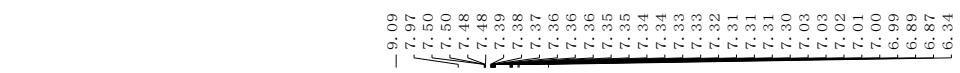

CC-6-25-1-DMSO-C13-2021-7-7
CC-6-25-1-DMSO-C13-2021-7-7
f1 (ppm)

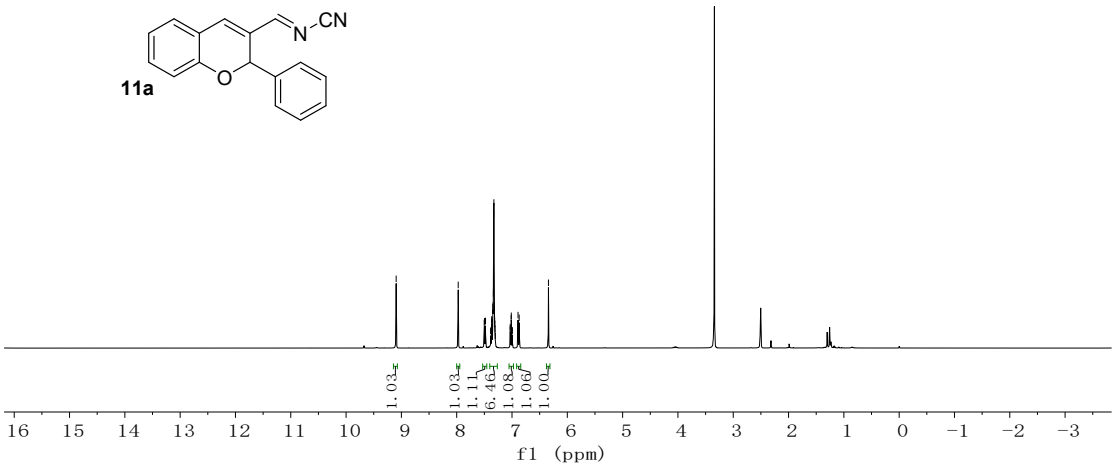

16 #22 RT: 0.3465 AV: 1 NL: 1.36E6
T: FTMS + p NSI Full ms [50.00-800.00]
263.1541
264.1574
262.1462
261.1384
259.1228
265.1609
Relative Abundance
m/z

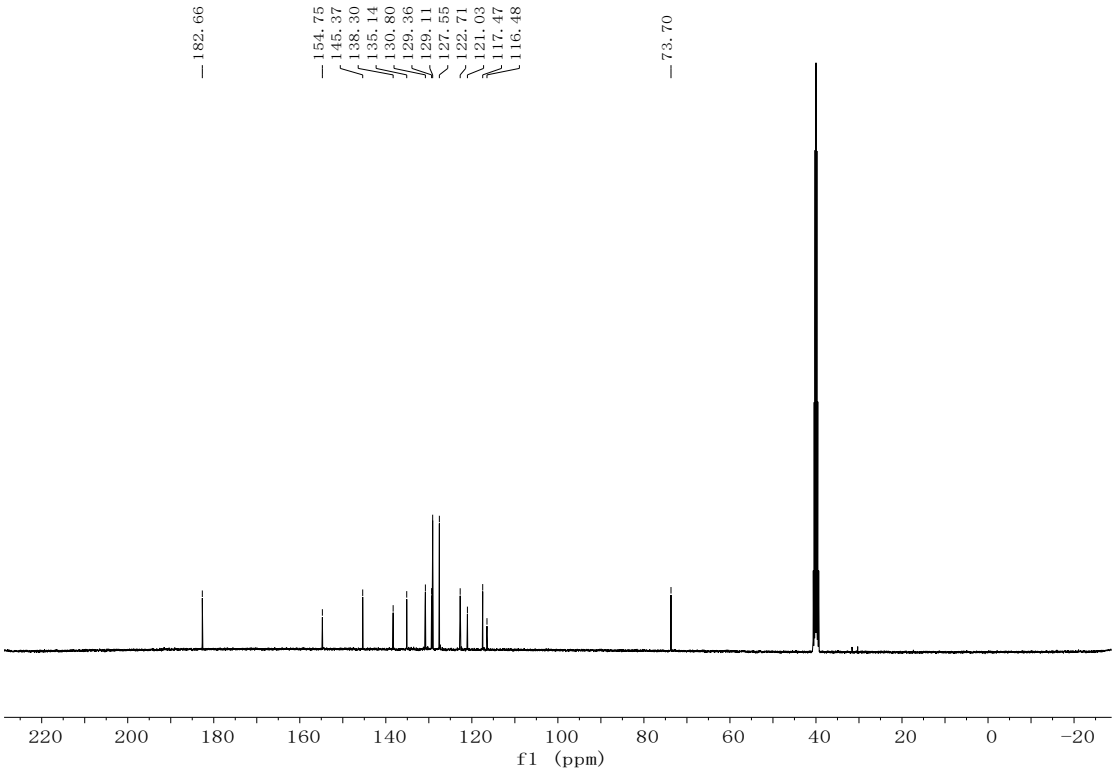

9k
f1 (ppm)

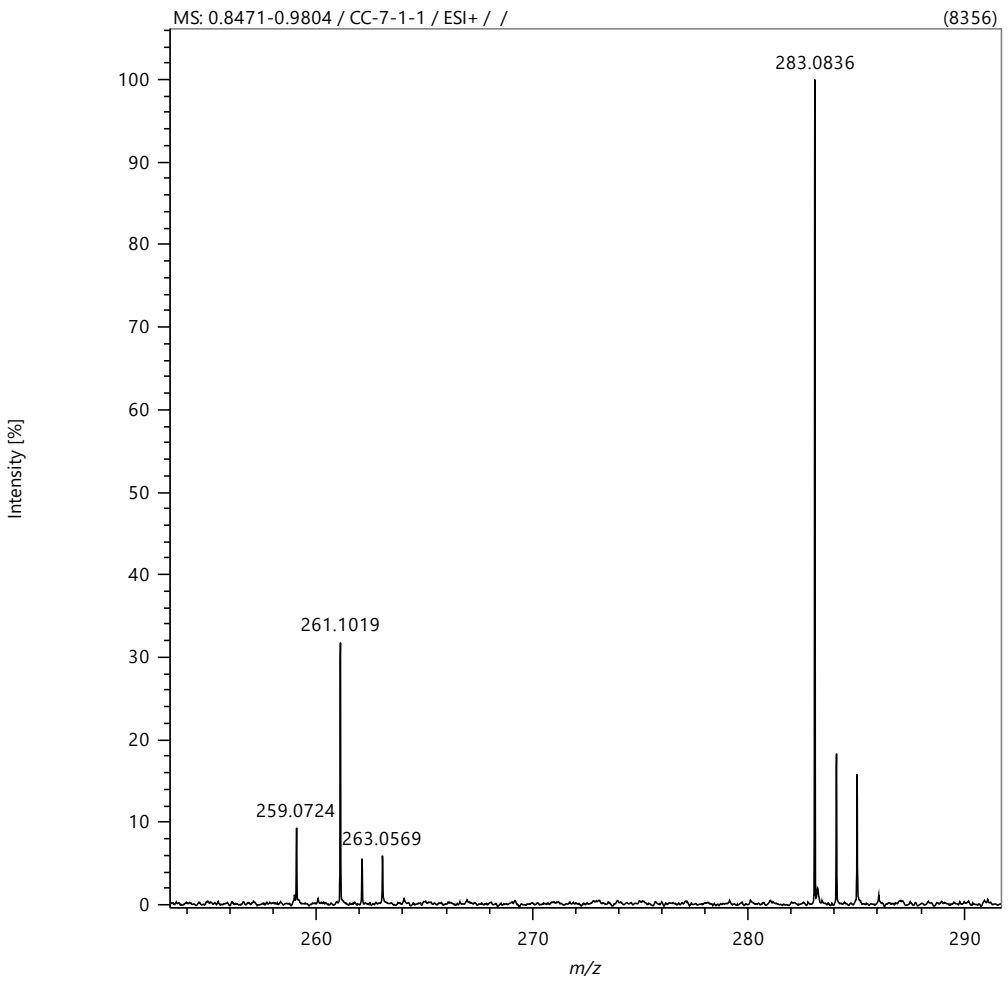

CC-5-67-DMSO-C13-2021-6-21.10.fid
78.02
41.96
f1 (ppm)

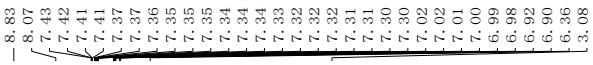

11 #60 RT: 0.9725 AV: 1 NL: 3.08E4
T: FTMS + p NSI Full ms [50.00-800.00]
355.1326
356.1360
353.1170
357.5626
Relative Abundance
m/z

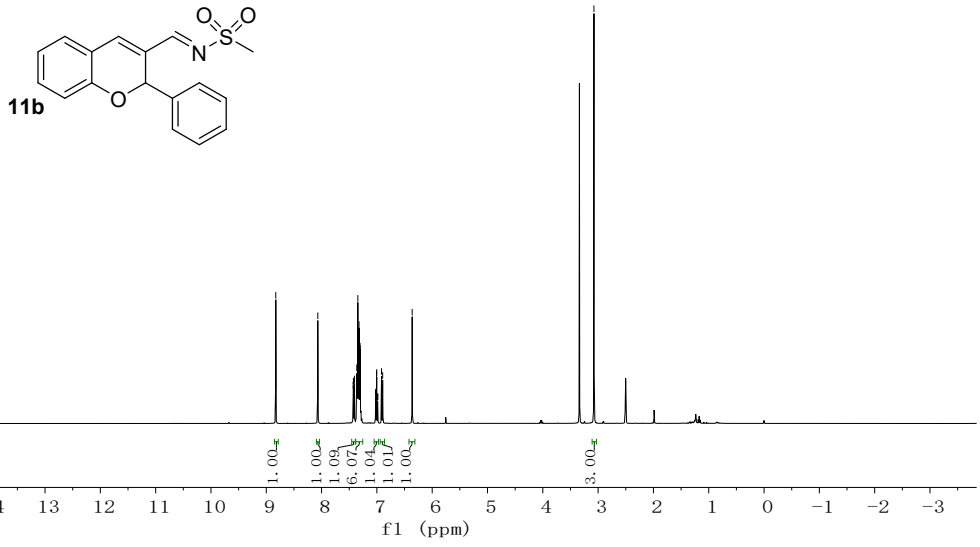

9.09
7.97
7.50
7.50
7.48
7.48
7.39
7.38
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.03
7.03
7.02
7.01
7.00
6.99
6.89
6.87
6.34

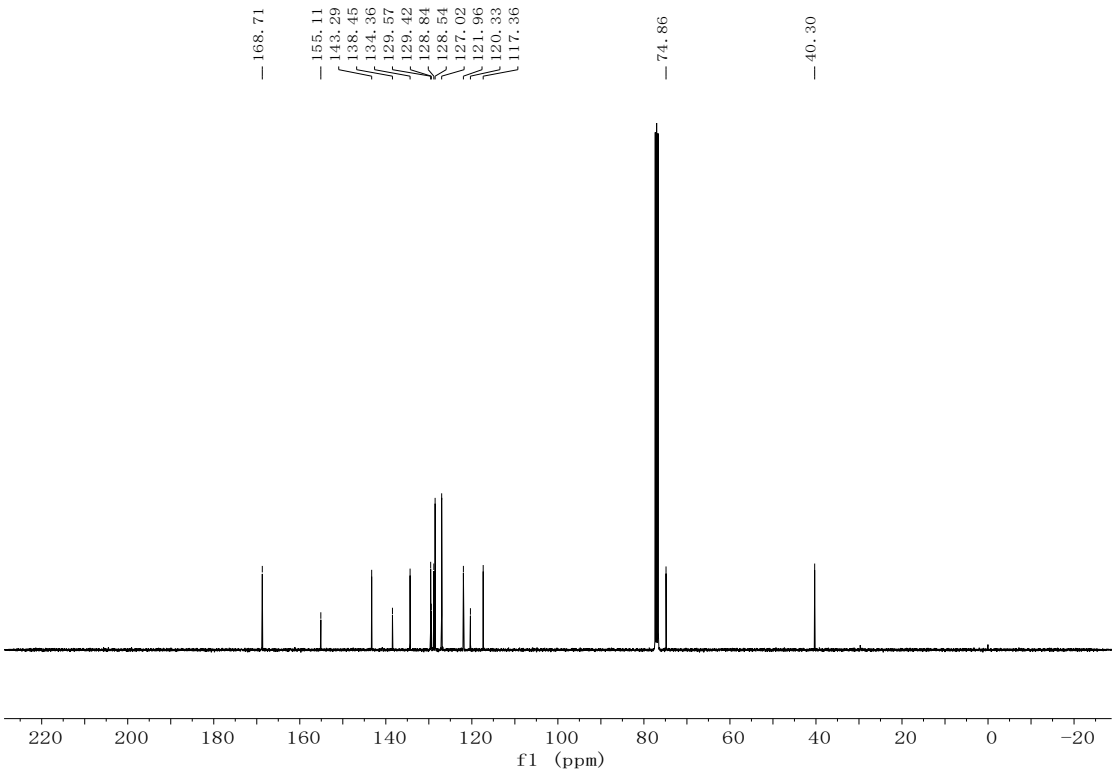

N
CN
O
11a
1.03
1.03
1.11
6.46
1.08
1.06
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

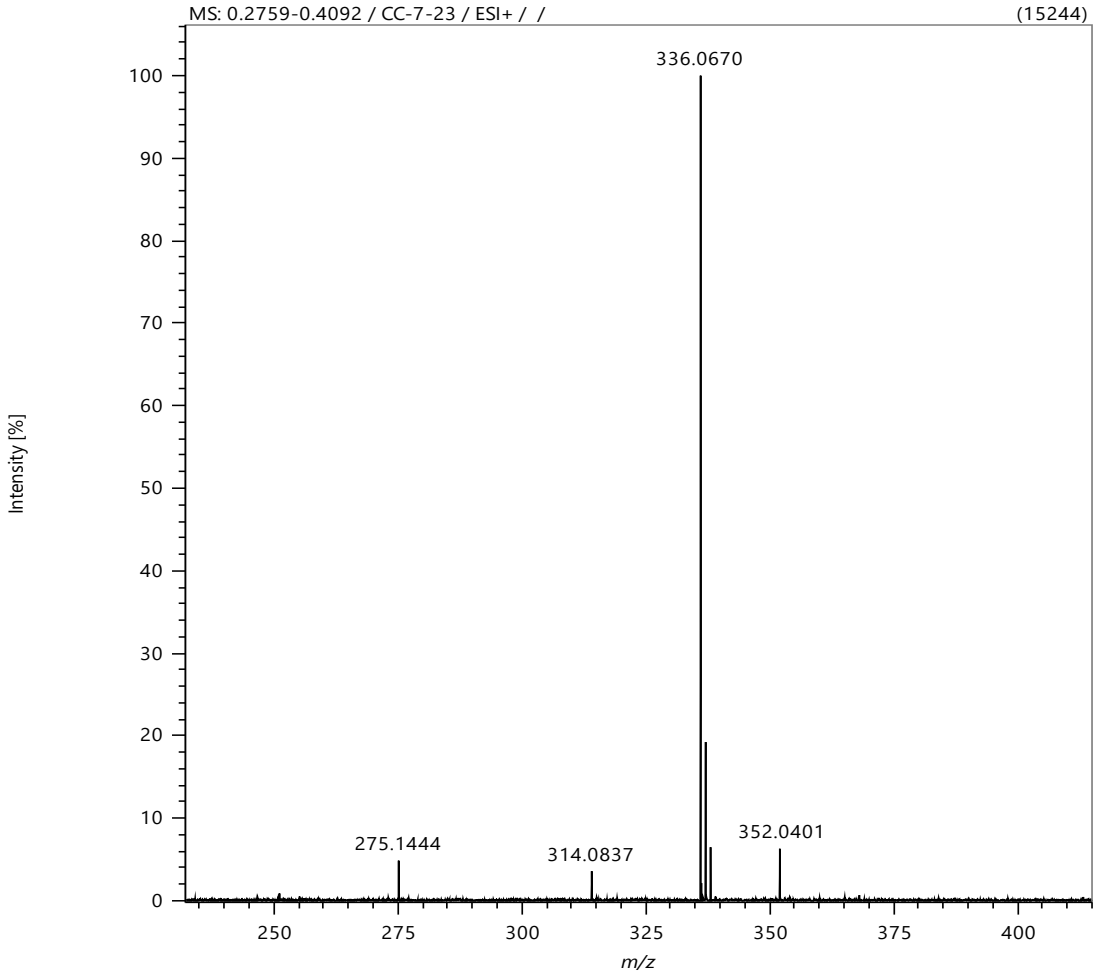

182.66
154.75
145.37
138.30
135.14
130.80
129.36
129.11
127.55
122.71
121.03
117.47
116.48
73.70
220 200 180 160 140 120 100 80 60 40 20 0 −20
f1 (ppm)

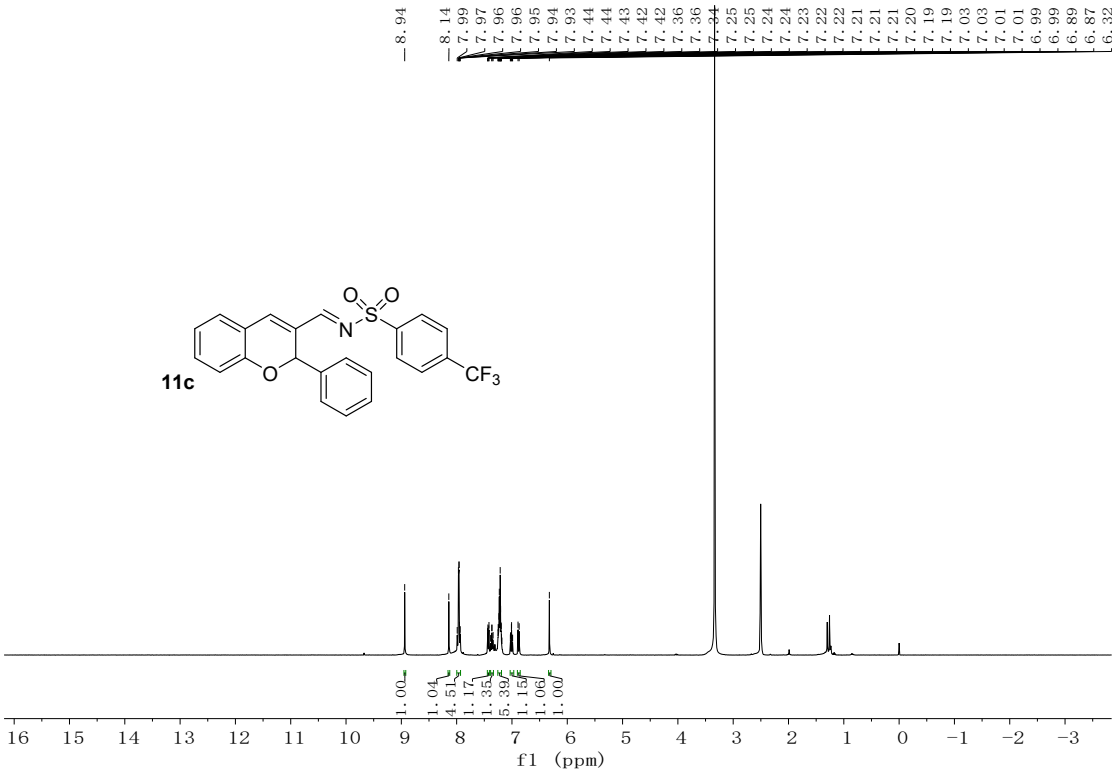

MS: 0.8471-0.9804 / CC-7-1-1 / ESI+ / /
(8356)
283.0836
261.1019
259.0724
263.0569
Intensity [%]
m/z

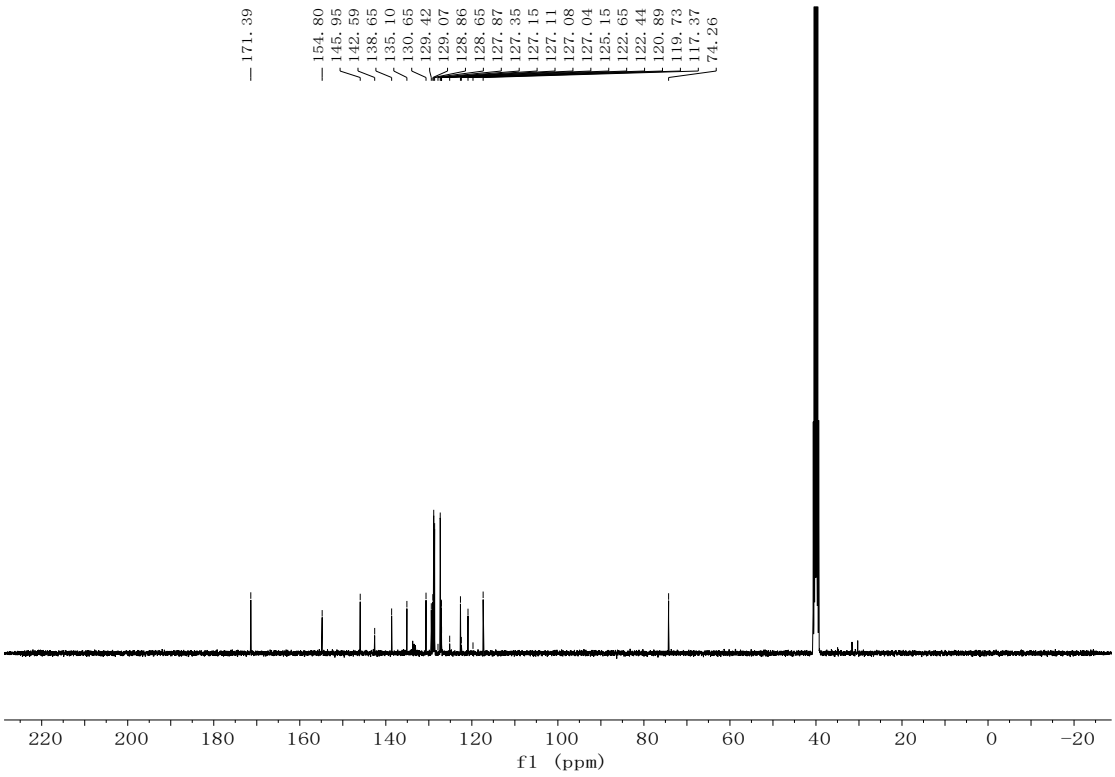

8.83
8.07
7.43
7.42
7.41
7.41
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.02
7.02
7.01
7.00
6.99
6.98
6.92
6.90
6.36
3.08

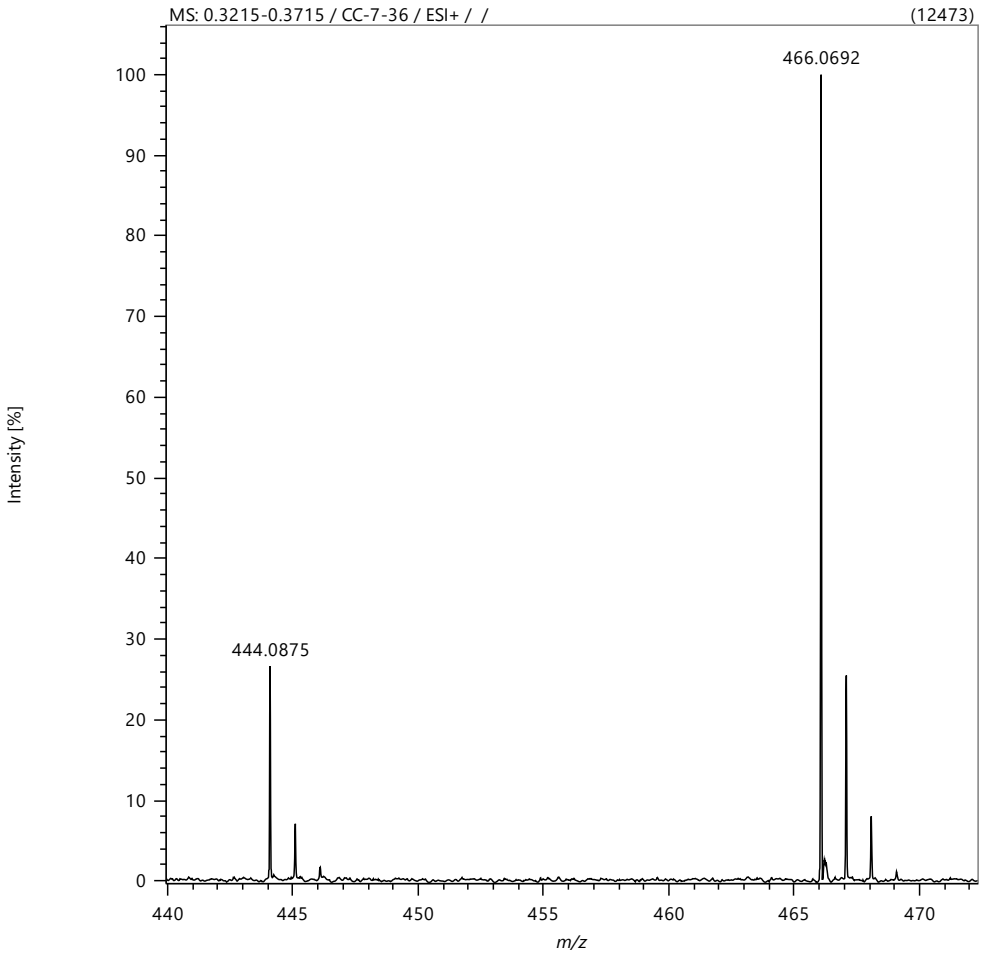

11b
O
S
O
N
O
1.00
1.00
1.09
6.07
1.04
1.01
1.00
3.00
f1 (ppm)


168.71
155.11
143.29
138.45
134.36
129.57
129.42
128.84
128.54
127.02
121.96
120.33
117.36
74.86
40.30
220
200
180
160
140
120
100
80
60
40
20
0
−20
f1 (ppm)


MS: 0.2759-0.4092 / CC-7-23 / ESI+ / /
(15244)
336.0670
352.0401
314.0837
275.1444
Intensity [%]
m/z
100
90
80
70
60
50
40
30
20
10
0
250
275
300
325
350
375
400


8.94
8.14
7.99
7.97
7.96
7.96
7.95
7.94
7.93
7.44
7.44
7.43
7.42
7.42
7.36
7.36
7.34
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.19
7.19
7.03
7.03
7.01
7.01
6.99
6.99
6.89
6.87
6.32
O
O
S
N
O
CF3
11c
1.00
1.04
4.51
1.17
1.35
5.39
1.15
1.06
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


171.39
154.80
145.95
142.59
138.65
135.10
130.65
129.42
129.07
128.86
128.65
127.87
127.35
127.15
127.11
127.08
127.04
125.15
122.65
122.44
120.89
119.73
117.37
74.26
220 200 180 160 140 120 100 80 60 40 20 0 −20
f1 (ppm)



5. Crystallographic data

Crystallographic data for 2a

Table 1 Crystal data and structure refinement for 2a.

CCDC	2121586
Empirical formula	$C_{16}H_{12}N_6O$
Formula weight	304.32
Temperature/K	293.4(2)
Crystal system	orthorhombic
Space group	Pccn
a/Å	25.5258(11)
b/Å	16.0414(7)
c/Å	7.3397(3)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	3005.4(2)
Z	8
ρ_{calc}g/cm^3	1.345
μ/mm^{-1}	0.742
F(000)	1264.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.926 to 142.722
Index ranges	-28 ≤ h ≤ 30, -19 ≤ k ≤ 13, -7 ≤ l ≤ 8
Reflections collected	7901
Independent reflections	2850 [R_{int} = 0.0355, R_{sigma} = 0.0334]
Data/restraints/parameters	2850/0/208
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0598, wR_2 = 0.1651
Final R indexes [all data]	R_1 = 0.0702, wR_2 = 0.1827
Largest diff. peak/hole / e Å^{-3}	0.21/-0.24

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
O001	3930.2(6)	4712.0(9)	5543.8(19)	58.4(4)
N002	5100.0(6)	6222.9(11)	2634(3)	59.6(5)
N003	4429.8(8)	6553.5(13)	-1272(3)	68.1(5)
N004	4241.7(8)	6491.4(13)	267(3)	67.7(5)
N005	4955.6(7)	5666.0(12)	1578(3)	65.4(5)
C006	4060.9(7)	5601.5(11)	2857(3)	47.4(4)
C007	3738.9(7)	4133.1(11)	2546(2)	46.0(4)
C008	3783.5(8)	6203.3(11)	3650(3)	50.6(5)
C009	4072.0(7)	4731.6(11)	3648(3)	48.4(4)
C00A	3499.9(7)	6043.2(12)	5322(3)	48.5(4)
C00B	3579.0(7)	5281.5(12)	6200(3)	49.1(5)
C00C	4384.3(8)	5705.5(12)	1171(3)	54.4(5)
N00D	5270.0(9)	6702.5(15)	3578(4)	86.0(7)
C00E	3197.8(8)	4207.4(13)	2483(3)	58.0(5)
C00F	3327.7(9)	5090.9(14)	7811(3)	59.0(5)
C00G	3976.1(9)	3507.2(12)	1554(3)	58.8(5)
N00H	4584.4(11)	6674.6(18)	-2681(3)	97.4(8)
C00I	3160.1(8)	6613.7(13)	6134(3)	59.6(5)

C00J	2984.7(9)	5663.1(16)	8570(3)	66.5(6)
C00K	2901.2(9)	6418.3(16)	7725(3)	68.7(6)
C00L	3147.1(11)	3042.7(15)	457(3)	72.6(7)
C00M	2904.7(9)	3654.7(16)	1456(3)	68.0(6)
C00N	3682.6(11)	2969.6(14)	499(4)	73.9(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	67.6(9)	55.3(8)	52.4(8)	3.8(6)	-0.6(6)	15.2(6)
N002	45.5(9)	63.2(10)	70.1(11)	6.2(9)	-1.8(8)	-3.4(7)
N003	55.7(11)	80.8(13)	67.7(12)	14(1)	-9.8(9)	-17.5(9)
N004	66.7(11)	70.0(12)	66.3(12)	13.6(9)	5.1(9)	-2.0(9)
N005	49.5(10)	70.1(11)	76.7(12)	-10.4(10)	4.8(9)	-1.3(8)
C006	41.1(9)	48.2(9)	53(1)	-0.1(8)	-3.7(8)	-3.4(7)
C007	46.2(9)	40.1(9)	51.8(10)	4.4(7)	3.9(7)	0.5(6)
C008	49.3(10)	43.9(9)	58.5(11)	0.4(8)	-3.8(8)	-1.3(7)
C009	43.0(9)	47.6(9)	54.6(11)	0.3(8)	-1.3(8)	5.5(7)
C00A	44.5(9)	47.5(9)	53.6(11)	-6.5(8)	-5.5(8)	-1.0(7)
C00B	47.2(10)	51.6(10)	48.4(10)	-6.5(8)	-5.3(8)	-0.8(7)
C00C	51.6(11)	52.8(10)	58.8(11)	-1.7(9)	2.5(9)	-6.2(7)
N00D	70.3(14)	82.4(14)	105.4(18)	-9.5(13)	-21.6(13)	-8.2(11)
C00E	48.4(11)	62.1(11)	63.4(12)	-5.3(10)	6.1(8)	-0.6(8)
C00F	62.9(12)	64.6(12)	49.7(10)	-0.8(9)	-2.8(9)	-3.1(9)
C00G	56.2(11)	49.7(10)	70.4(13)	-4.4(9)	5.0(9)	5.1(8)
N00H	86.9(16)	138(2)	67.0(13)	27.0(15)	-2.2(12)	-25.5(15)
C00I	57.4(11)	54.7(11)	66.8(13)	-9.8(10)	-5.4(10)	6.4(8)
C00J	62.6(13)	83.0(15)	54.0(12)	-9.5(11)	5.3(10)	-4.7(10)
C00K	61.7(13)	76.5(14)	68.1(14)	-19.5(12)	6.4(11)	7.6(10)
C00L	79.7(16)	62.2(13)	75.9(15)	-7.5(11)	-0.8(12)	-22.3(11)
C00M	50.8(12)	77.9(14)	75.2(15)	-4.1(12)	1.7(10)	-13.9(10)
C00N	85.2(17)	54.2(12)	82.2(16)	-18.5(12)	5.9(13)	0.2(10)

Table 4 Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C009	1.438(2)	C007	C00G	1.380(3)
O001	C00B	1.367(2)	C008	C00A	1.447(3)
N002	N005	1.239(3)	C00A	C00B	1.396(3)
N002	N00D	1.123(3)	C00A	C00I	1.395(3)
N003	N004	1.231(3)	C00B	C00F	1.380(3)

N003	N00H	1.124(3)	C00E	C00M	1.384(3)
N004	C00C	1.470(3)	C00F	C00J	1.385(3)
N005	C00C	1.490(3)	C00G	C00N	1.380(3)
C006	C008	1.332(3)	C00I	C00K	1.378(3)
C006	C009	1.512(2)	C00J	C00K	1.377(4)
C006	C00C	1.496(3)	C00L	C00M	1.373(4)
C007	C009	1.516(3)	C00L	C00N	1.372(4)
C007	C00E	1.387(3)			

Table 5 Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00B	O001	C009	119.40(14)	C00I	C00A	C00B	117.84(19)
N00D	N002	N005	174.5(2)	O001	C00B	C00A	121.14(18)
N00H	N003	N004	174.3(3)	O001	C00B	C00F	117.29(18)
N003	N004	C00C	112.7(2)	C00F	C00B	C00A	121.49(19)
N002	N005	C00C	112.68(17)	N004	C00C	N005	111.67(16)
C008	C006	C009	120.74(18)	N004	C00C	C006	109.39(17)
C008	C006	C00C	125.04(17)	N005	C00C	C006	111.69(17)
C00C	C006	C009	114.21(16)	C00M	C00E	C007	120.1(2)
C00E	C007	C009	121.44(17)	C00B	C00F	C00J	119.4(2)
C00G	C007	C009	119.74(17)	C00N	C00G	C007	120.8(2)
C00G	C007	C00E	118.81(18)	C00K	C00I	C00A	120.8(2)
C006	C008	C00A	120.54(18)	C00K	C00J	C00F	120.0(2)
O001	C009	C006	112.78(15)	C00J	C00K	C00I	120.5(2)
O001	C009	C007	111.17(15)	C00N	C00L	C00M	119.9(2)
C006	C009	C007	111.66(15)	C00L	C00M	C00E	120.4(2)
C00B	C00A	C008	118.31(17)	C00L	C00N	C00G	120.0(2)
C00I	C00A	C008	123.84(19)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	*x*	*y*	*z*	U(eq)
H008	3772	6731	3127	61
H009	4435	4534	3563	58
H00C	4300	5247	341	65
H00E	3032	4629	3133	70
H00F	3388	4583	8384	71
H00G	4338	3447	1597	71
H00I	3108	7132	5596	72
H00J	2811	5537	9649	80

H00K 2668	6799	8232	82
H00L 2949	2678	-247	87
H00M 2541	3698	1442	82
H00N 3848	2558	-183	89

Experimental

Single crystals of $C_{16}H_{12}N_6O$ **[2a]** were obtained by slow evaporation of a mixture solution (*n*-hexane and ether) of the compound. A suitable crystal was selected and mounte in oil on a **New Gemini, Dual, Cu at home/near, EosS2** diffractometer. The crystal was kept at 293.4(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [hl-cc-2-1]

Crystal Data for $C_{16}H_{12}N_6O$ (M =304.32 g/mol): orthorhombic, space group Pccn (no. 56), a = 25.5258(11) Å, b = 16.0414(7) Å, c = 7.3397(3) Å, V = 3005.4(2) Å^3, Z = 8, T = 293.4(2) K, μ(CuKα) = 0.742 mm^{-1}, *Dcalc* = 1.345 g/cm^3, 7901 reflections measured (6.926° ≤ 2Θ ≤ 142.722°), 2850 unique (R_{int} = 0.0355, R_{sigma} = 0.0334) which were used in all calculations. The final R_1 was 0.0598 (I > 2σ(I)) and wR_2 was 0.1827 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2.a Ternary CH refined with riding coordinates:

C009(H009), C00C(H00C)

2.b Aromatic/amide H refined with riding coordinates:

C008(H008), C00E(H00E), C00F(H00F), C00G(H00G), C00I(H00I), C00J(H00J), C00K(H00K), C00L(H00L), C00M(H00M), C00N(H00N)

Crystallographic data for 11a

Table 1 Crystal data and structure refinement for 11a.

CCDC	2121587
Empirical formula	$C_{17}H_{12}N_2O$
Formula weight	260.29
Temperature/K	293.15
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	6.1263(19)
b/Å	28.328(3)
c/Å	11.289(4)
α/°	90
β/°	136.87(6)
γ/°	90
Volume/Å^3	1339.5(12)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.082
F(000)	544.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.012 to 52.744
Index ranges	$-7 \le h \le 7$, $-35 \le k \le 31$, $-9 \le l \le 14$
Reflections collected	5598
Independent reflections	2734 [R_{int} = 0.0201, R_{sigma} = 0.0343]
Data/restraints/parameters	2734/0/181
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1133
Final R indexes [all data]	R_1 = 0.0757, wR_2 = 0.1338
Largest diff. peak/hole / e Å^{-3}	0.15/-0.18

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	-1752(3)	1427.4(5)	549.2(15)	58.5(4)
N1	7555(3)	833.7(5)	4477.5(18)	49.0(4)
N2	12865(4)	445.6(7)	6484(2)	76.1(6)
C1	1558(3)	1315.5(6)	2119(2)	44.6(4)
C2	1986(4)	815.3(6)	2700(2)	42.2(4)
C3	-495(4)	563.0(6)	2127(2)	45.6(4)
C4	-3664(4)	752.1(6)	881(2)	46.2(4)
C5	-6277(4)	515.0(7)	332(2)	57.9(5)
C6	-9278(4)	707.0(9)	-902(3)	69.1(6)
C7	-9704(4)	1140.9(10)	-1602(2)	74.0(7)
C8	-7181(4)	1384.2(8)	-1090(2)	65.4(6)
C9	-4158(4)	1188.1(7)	148(2)	49.8(5)

C10	2890(4)	1673.3(6)	3503(2)	44.0(4)
C11	5079(5)	1999.2(7)	3978(3)	69.1(6)
C12	6350(6)	2329.5(9)	5232(4)	97.9(9)
C13	5442(6)	2337.4(9)	6021(4)	98.4(9)
C14	3250(6)	2018.0(9)	5572(3)	83.6(7)
C15	1988(4)	1683.5(7)	4314(2)	59.4(5)
C16	5098(4)	610.1(6)	3902(2)	46.9(4)
C17	10378(4)	607.7(7)	5574(2)	53.5(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 11a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	45.6(7)	58.4(8)	44.1(7)	12.9(6)	24.0(6)	6.6(6)
N1	40.1(8)	50.1(9)	47.8(8)	-0.7(7)	29.1(7)	1.3(7)
N2	42.7(9)	74.1(12)	79.3(12)	-4.2(10)	34.2(9)	5.1(9)
C1	38.6(9)	48.0(10)	40.9(9)	2.9(8)	27.0(8)	2.5(7)
C2	38.1(8)	41.2(9)	38.6(8)	-2.4(8)	25.2(7)	1.3(7)
C3	43.3(9)	39.0(9)	43.5(9)	-2.4(8)	28.1(8)	-0.1(7)
C4	37.6(9)	51.8(10)	37.0(8)	-9.6(8)	23.4(7)	-1.6(8)
C5	47.0(10)	66.7(13)	52.7(10)	-18.0(10)	34.0(9)	-9.2(9)
C6	39.8(10)	95.7(17)	56.9(12)	-25.9(13)	30.5(10)	-10.1(11)
C7	38.9(11)	102.6(19)	44.9(11)	-11.2(13)	19.2(9)	12.2(12)
C8	50.2(11)	73.5(14)	41.6(9)	1.3(10)	23.6(9)	14.0(10)
C9	39.0(9)	57.5(11)	33.6(8)	-5.0(8)	20.3(8)	3.9(8)
C10	40.8(9)	36.7(9)	45.3(9)	4.0(8)	28.5(8)	5.4(7)
C11	71.8(13)	50.3(12)	87.6(15)	-8.4(12)	58.9(12)	-10.5(10)
C12	89.7(18)	60.4(15)	129(2)	-35.8(16)	75.3(18)	-24.2(13)
C13	86.0(18)	77.1(18)	93.5(18)	-43.6(15)	53.2(16)	-8.6(14)
C14	84.8(16)	89.3(17)	74.3(14)	-16.6(14)	57.2(14)	8.9(14)
C15	58.8(11)	59.8(12)	59.6(11)	-5.0(10)	43.2(10)	-0.2(9)
C16	42.5(9)	42.8(10)	44.8(9)	0.9(8)	28.6(8)	2.8(8)
C17	41.4(10)	50.9(11)	57.0(10)	-6.8(9)	32.3(9)	-3.5(8)

Table 4 Bond Lengths for 11a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.452(3)	C4	C9	1.392(3)
O1	C9	1.365(2)	C5	C6	1.370(3)
N1	C16	1.289(2)	C6	C7	1.379(3)
N1	C17	1.345(2)	C7	C8	1.376(3)
N2	C17	1.141(2)	C8	C9	1.383(3)

C1	C2	1.502(2)	C10	C11	1.374(2)
C1	C10	1.507(2)	C10	C15	1.373(2)
C2	C3	1.343(2)	C11	C12	1.370(3)
C2	C16	1.428(2)	C12	C13	1.352(4)
C3	C4	1.431(3)	C13	C14	1.373(3)
C4	C5	1.397(2)	C14	C15	1.382(3)

Table 5 Bond Angles for 11a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C1	120.31(14)	C7	C8	C9	119.2(2)
C16	N1	C17	118.29(17)	O1	C9	C4	121.99(15)
O1	C1	C2	112.46(13)	O1	C9	C8	117.47(19)
O1	C1	C10	109.63(14)	C8	C9	C4	120.47(18)
C2	C1	C10	113.10(14)	C11	C10	C1	119.53(17)
C3	C2	C1	121.07(15)	C15	C10	C1	121.88(16)
C3	C2	C16	119.86(17)	C15	C10	C11	118.59(18)
C16	C2	C1	119.06(14)	C12	C11	C10	121.3(2)
C2	C3	C4	121.36(17)	C13	C12	C11	119.7(2)
C5	C4	C3	123.33(18)	C12	C13	C14	120.5(2)
C9	C4	C3	117.86(15)	C13	C14	C15	119.6(2)
C9	C4	C5	118.79(17)	C10	C15	C14	120.3(2)
C6	C5	C4	120.9(2)	N1	C16	C2	122.48(17)
C5	C6	C7	119.3(2)	N2	C17	N1	174.3(2)
C8	C7	C6	121.37(19)				

Table 6 Torsion Angles for 11a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C2	C3	-18.6(2)	C5	C4	C9	O1	-176.26(15)
O1	C1	C2	C16	162.48(14)	C5	C4	C9	C8	0.6(3)
O1	C1	C10	C11	-108.51(18)	C5	C6	C7	C8	0.1(3)
O1	C1	C10	C15	71.7(2)	C6	C7	C8	C9	0.2(3)
C1	O1	C9	C4	-19.3(2)	C7	C8	C9	O1	176.37(16)
C1	O1	C9	C8	163.78(15)	C7	C8	C9	C4	-0.6(3)
C1	C2	C3	C4	3.0(3)	C9	O1	C1	C2	26.4(2)
C1	C2	C16	N1	-1.9(2)	C9	O1	C1	C10	-100.30(17)
C1	C10	C11	C12	-179.89(19)	C9	C4	C5	C6	-0.2(3)
C1	C10	C15	C14	-179.73(17)	C10	C1	C2	C3	106.29(19)
C2	C1	C10	C11	125.12(18)	C10	C1	C2	C16	-72.7(2)
C2	C1	C10	C15	-54.7(2)	C10	C11	C12	C13	0.0(4)
C2	C3	C4	C5	-175.75(16)	C11	C10	C15	C14	0.5(3)

C2	C3	C4	C9	6.3(3)	C11	C12	C13	C14	-0.2(4)
C3	C2	C16	N1	179.10(16)	C12	C13	C14	C15	0.6(4)
C3	C4	C5	C6	-178.13(16)	C13	C14	C15	C10	-0.7(3)
C3	C4	C9	O1	1.8(2)	C15	C10	C11	C12	-0.1(3)
C3	C4	C9	C8	178.65(16)	C16	C2	C3	C4	-178.04(14)
C4	C5	C6	C7	-0.2(3)	C17	N1	C16	C2	-178.35(15)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 11a.

Atom	*x*	*y*	*z*	U(eq)
H1	2752.08	1348.86	1850.43	53
H3	-147.02	259.08	2548.37	55
H5	-5976.77	222.97	810.39	69
H6	-11007.26	546.56	-1263.05	83
H7	-11739.07	1271.77	-2437.88	89
H8	-7504.87	1676.95	-1571.27	78
H11	5709.86	1995.34	3438.62	83
H12	7829.8	2547.39	5537.94	117
H13	6308.36	2560.87	6875.17	118
H14	2618.68	2026.65	6111.33	100
H15	520.84	1464.31	4016.04	71
H16	5363.25	303.51	4285.05	56

Experimental

Single crystals of $C_{17}H_{12}N_2O$ **[11a]** were obtained by slow evaporation of a mixture solution (*n*-hexane and ether) of the compound. A suitable crystal was selected and mounted in oil on a **Xcalibur, Eos** diffractometer. The crystal was kept at 293.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [11a]

Crystal Data for $C_{17}H_{12}N_2O$ (M =260.29 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 6.1263(19) Å, b = 28.328(3) Å, c = 11.289(4) Å, β = 136.87(6)°, V = 1339.5(12) Å^3, Z = 4, T = 293.15 K, μ(MoKα) = 0.082 mm^{-1},*Dcalc* = 1.291 g/cm^3, 5598 reflections measured (6.012° ≤ 2Θ ≤ 52.744°), 2734 unique (R_{int} = 0.0201, R_{sigma} = 0.0343) which were used in all calculations. The final R_1 was 0.0503 (I > 2σ(I)) and wR_2 was 0.1338 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

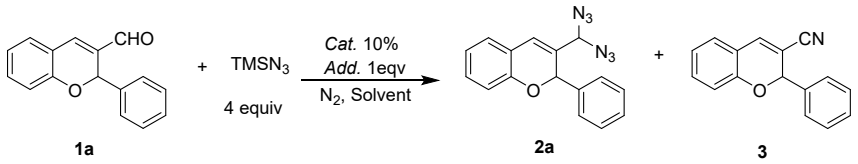
2.a Ternary CH refined with riding coordinates:

C1(H1)

2.b Aromatic/amide H refined with riding coordinates:

C3(H3), C5(H5), C6(H6), C7(H7), C8(H8), C11(H11), C12(H12), C13(H13), C14(H14), C15(H15), C16(H16)

6. Optimization of The Reaction Conditions



1a **2a** **3**

Entry[a]	*Cat.* 10%mol	*Add.* 1 eqv.	Solvent	**2a** *Cmpd.* %[b]	**3** *Cmpd.* %[b]	**2a:3**
1	$Fe(acae)_3$	-	DCM	0		0:100
2	$Cu(AcO)_2$	-	DCM	0		0:100
3	$Rh_2(AcO)_2$	-	DCM	0		0:100
4	$AlCl_3$	-	DCM	NR[c]	-	-
5	$Cu(TfO)_2$	-	DCM	42	20	2.07:1
6	AgTfO	-	DCM	44	18	2.38:1
7	$Bi(TfO)_3$	-	DCM	30	4.	7.09:1
8	**$Yb(TfO)_3$**	**-**	**DCM**	**70**	**0**	**100:0**
9	LiTfO	-	DCM	NR	-	-
10	$In(TfO)_3$	-	DCM	39	16	2.40:1
11	$Cu(ClO_4)_2$	-	DCM	41	29	1.42:1
12	$Zn(TfO)_2$	-	DCM	36	0	100:0
13	$AgSbF_6$	-	DCM	NR		-
14	$Sm(TfO)_3$	-	DCM	22	0	100:0
15	$Cu[(CH_3CN)_4ClO_4]$	-	DCM	22	4	5.37:1
16	$CoMoO_4$	-	DCM	NR	-	-
17	$LiClO_4$	-	DCM	NR	-	-
18	$Bi(NO_3)_3.5H_2O$	-	DCM	trace	-	-

19	$RuCl_3$	-	DCM	NR	-	-
20	$NiCl_2$	-	DCM	NR	-	-
21	$Sc(TfO)_3$	-	DCM	47	0	100:0
22	$Yb(TfO)_3$	K_2CO_3	DCM	trace	0	-
23	$Yb(TfO)_3$	PhCOOH	DCM	27	4	6.52:1
24	$Yb(TfO)_3$	TMSTfO	DCM	0		0:100
25	$Yb(TfO)_3$	-	CH_3OH	ND[d]	ND	-
26	$Yb(TfO)_3$	-	CH_3CN	9	0	100:0
27	$Yb(TfO)_3$	-	THF	22	0	100:0
28	$Yb(TfO)_3$	-	Toluene	19	0	100:0
29	$Yb(TfO)_3$	-	$CHCl_3$	20	0	100:0
30	$Yb(TfO)_3$	40℃	DCM	20	4	4.99:1
31	$Yb(TfO)_3$	50℃	DCM	17	6	2.82:1
32	$Yb(TfO)_3$	60℃	DCM	16	8	1.92:1

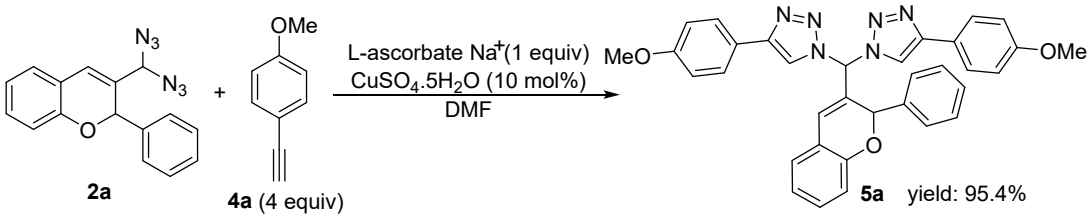
[a]**1a** (0.21 mmol), $TMSN_3$ (0.84 mmol), catalyst (0.02 mmol). [b]Isolated yields. [c]No reaction. [d]Not detected.

7. Antiproliferative Activity Data

In 5% CO_2 humidified incubator, the A549 was cultured in RPMI 1640 medium which mixed with 10% FBS at 37 °C. Cells were plated in a 96-well plate raged 2000–4000 cells per well. After 24 h culturing, different concentrations of the compounds were added and cultured for 48 h. After treating with 10% trichloroacetic acid (TCA) at 4 °C for 1 hour, each well was washed with distilled water for 5 times and dry naturally. Subsequently, the cells were stained by 0.4% (w/v) SRB at room temperature for 20 minutes, followed washing with 1% glacial acetic acid for 5 times to remove the excess unbound SRB dye. After the SRB bounded protein was dissolved in 10 mm tris(hydroxy-methylamino)methane (Tris) for 15 min, the absorbance was read by a microtiter-plate reader at 540 nm and the IC_{50} values were calculated according to the corresponding concentrations and the inhibitory ratios.

Concentration (μM)	10.0000	1.111111	0.37037	0.123457	0.041152	0.013717	0.004572	0
OD Value	0.9317	2.5665	2.8071	2.8099	2.8385	2.8766	2.8892	3.5295
background OD Value	0.1184	-	-	-	-	-	-	-

8. Quantitative Transformation of α, β-Unsaturated Diazides into Bistriazole



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