Supplementary Information

Acess to Polyfunctionalized Carbazoles through π-extension of 2-Methyl-3-oxoacetate Indoles

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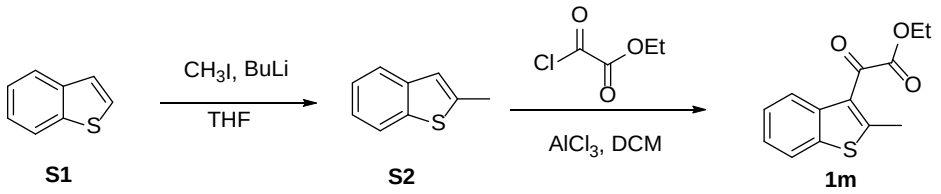
I: General Information

Commercially available materials were purchased from Alfa Aesar and Sigma-Aldrich. Toluene and DCM was dried over Pure Solv solvent purification system. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q–TOF Permier Spectrometer. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness).

II. General procedure

a) General procedure for the Synthesis of Indoles 1 and Naphthoquinone 2

Indoles **1a-1l**, **1o** were synthesized according to the literature.[1] **2p**, **2q**, **2r** and **4c** were synthesized according to the literatures.[2-5]

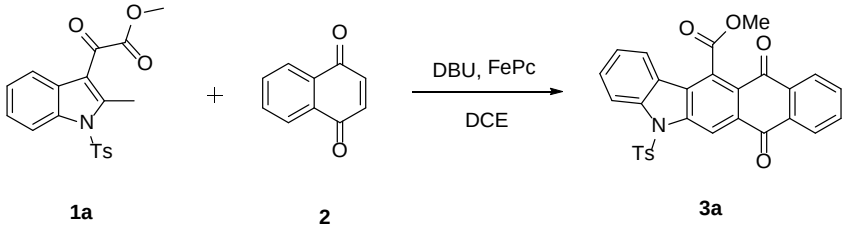


To a solution of benzothiophene **S1** (1.17 mL, 10.0 mmol) in dry THF, was added dropwise n-BuLi (6.56 mL, 10.5 mmol.) at -78 °C under N_2. The mixture was stirred at -78 °C for 1 h and then CH_3I (0.65 mL, 10.5 mmol.) was added. Afterwards it was allowed to reach room temperature and it was stirred for 1 h. The mixture was poured into water and extracted with Et_2O. The organic layer was then dried over $MgSO_4$ and it was concentrated under reduced Pressure. Further purifications were not necessary, obtaining 1.33 g of compound 2-methyl-benzothiophene **S2** as white crystals with 90% yield.

To a cooled (0 °C) and well stirred mixture of $AlCl_3$ (4.80 g, 36.0 mmol) and CH_2Cl_2 (20 ml) were added methyl-chlorooxoacetate (1.66 mL, 18.0 mmol) and a solution of 2-methyl-benzothiophene **S2** (1.33 g, 9.0 mmol) in the minimum amount of CH_2Cl_2. The mixture were stirred at room temperature for 2 h and quenched in a mixture of water. The crude mixture was extracted with CH_2Cl_2 and the organic phase was washed with a saturated solution of $NaHCO_3$ aq. The organic layer was dried over anhydrous sodium sulphate and taken to drieness under vacuo to give 1.90 g (90%) of methyl 2-(2-methylbenzo[*b*]thiophen-3-yl)-2-oxoacetate **1m** as a white solid.

1n was synthesized according to the above procedure.

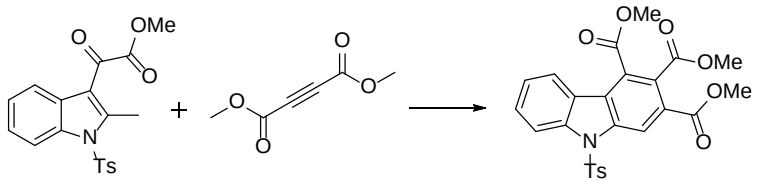
b) General procedure for the reactions of 1 with 2 to synthesize product 3 (3a as an example):



To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **1a** (37.1 mg, 0.10 mmol), **2** (24.2 mg, 0.15 mmol), FePc (6.2 mg, 0.01 mmol). To this mixture was added dry DCE (1.0 mL) and DBU (30 μL, 0.20 mmol) via a micro syringe, then the reaction mixture was stirred at 30 °C until **1a** disappeared (detected by TLC), the residue was purified by silica gel column chromatography (DCM) to afford 42.3 mg **3a** as a white solid in 83% yield.

c) Condition optimization and general procedure for the synthesis products 5 (5a as an example):

Table S1. Screening of various reaction conditions for the reaction of **5a**



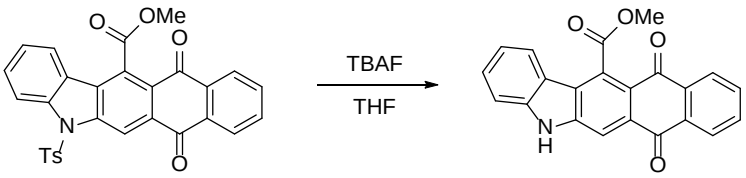
1a **4** **5a**

Entry[a]	Base	Solvent	Yield (%)[b]
1	DBU	THF	10
2	Et_3N	THF	15
3	K_2CO_3	THF	nd
4	Cs_2CO_3	THF	35
5	NaOAc	THF	nd
6	Cs_2CO_3	CH_3CN	40
7	Cs_2CO_3	DCM	nd
8	Cs_2CO_3	1,4-dioxane	trace
9	Cs_2CO_3	DCE	nd
10	Cs_2CO_3	DMF	63
11[c]	Cs_2CO_3	DMF	54
12[d]	Cs_2CO_3	DMF	53
13[e]	Cs_2CO_3	DMF	59
14[f]	Cs_2CO_3	DMF	66

[a] Standard condition: **1a** (0.1 mmol), **4** (3.0 equiv.), base (2.0 equiv.), solvent (1.0 mL), 30 °C, 12 h. [b] Isolated yields after column chromatography. [c] 1.5 equiv base was used. [d] 2.5 equiv. base was used. [e] 0 °C. [f] 1.5 equiv. **4** was used

To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **1a** (37.1 mg, 0.10 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol) . To this mixture was added dry DMF (1.0 mL) and **4** (19 μL, 0.15 mmol) via a micro syringe, then the reaction mixture was stirred at 30 °C until 1a disappeared (detected by TLC), the residue was purified by silica gel column chromatography (30% v/v EtOAc in hexane) to afford 31.2 mg **5a** as a white solid in 66% yield.

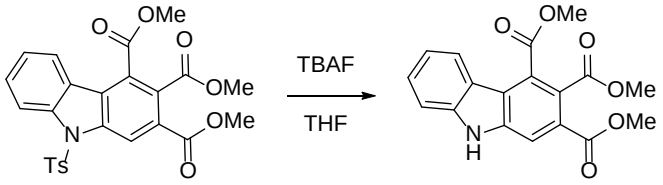
d) Synthetic transformation of 3a, 5a and 5g.



3a **6**

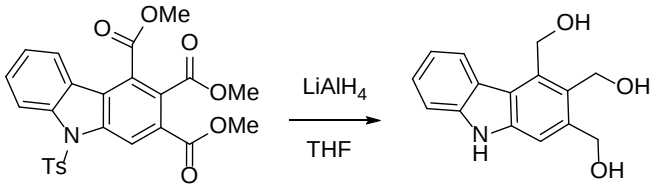
Synthesis of methyl 7,12-dioxo-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (6): To a solution of **3a** (0.20 mmol, 101.8 mg) in THF (1.0 mL) was

added 1.0 mL TBAF (1.0 M in THF). The mixture was stirred at refluxing temperature for 2 h. Then the residue was purified by silica gel column chromatography to afford **6** as a yellow solid in 96% yield.



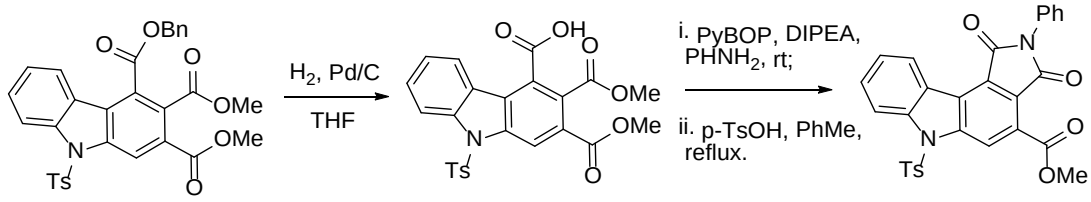
5a **7**

Synthesis of trimethyl 9H-carbazole-2,3,4-tricarboxylate (7): To a solution of **5a** (0.20 mmol, 99.0 mg) in THF (1.0 mL) was added 1.0 mL TBAF (1.0 M in THF). The mixture was stirred at refluxing temperature for 2 h. Then the residue was purified by silica gel column chromatographyto afford **7** as a yellow solid in 95% yield.



5a **8**

Synthesis of (9H-carbazole-2,3,4-triyl)trimethanol (8): To a suspension of lithium aluminium hydride (237.0 mg, 1.0 mmol) in anhydrous THF (5.0 mL) was added at 0 °C a solution of **5a** (99.0 mg, 0.2 mmol) in THF (5.0 mL). When the addition was completed the mixture was heated to reflux for 12 h. After addition of water (10.0 mL), the reaction mixture was thoroughly extracted with ethyl acetate; the organic fractions were combined, dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation, The residue was purified by column chromatography to give **8** (66.5 mg, 79%).



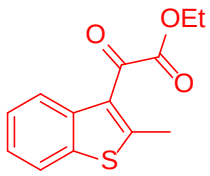
5g **9**, 98% yield **10**, 60% yield

Synthesis of 2,3-bis(methoxycarbonyl)-9-tosyl-9H-carbazole-4-carboxylic acid (9): A solution of **5g** (114.2 mg, 0.20 mmol) in THF (2.0 mL) with Pd/C (41.4 mg, 10% mol), was stirred 12 h under H_2. The catalyst was filtered through celite and washed with dichloromethane. The residue was purified by column chromatography to give **9** (94.3 mg, 98%).

Synthesis of methyl 1,3-dioxo-2-phenyl-6-tosyl-1,2,3,6-tetrahydropyrrolo[3,4-c]

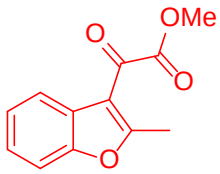
carbazole-4-carboxylate (10): To a suspension of PyBOP (116.8 mg, 0.22 mmol) in THF (1.0 mL) were sequentially added a solution of **9** (99.0 mg, 0.20 mmol) in THF (1.0 mL) and DIPEA (0.05 mL, 0.30 mmol) and the resulting mixture was stirred for 40 min at rt. Subsequently, $PhNH_2$ (0.02 mL, 0.22 mmol) was added and the mixture stirred at r.t. for 30 min. After **9** disappeared by TLC detection, spin the mixture and add toluene (2.0 mL), p-TsOH (4.0 mg). The mixturewas refluxed for 12 h. After cooling to rt, the mixture was successively washed with sat. aq $NaHCO_3$ solution (10.0 mL), brine (2×10 mL) and dried (Na_2SO_4). The residue was purified by column chromatography to give **10** (62.9 mg, 60%).

III. Characterizations of substrates and products, references.



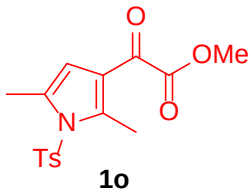
1m

Ethyl 2-(2-methylbenzo[b]thiophen-3-yl)-2-oxoacetate (1m): 90% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J = 7.2 Hz, 3H), 2.73 (s, 3H), 4.44 (q, J = 7.2 Hz, 2H), 7.34 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.42 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.68 – 7.76 (m, 1H), 8.28 (dt, J = 8.0, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 16.1, 62.6, 121.7, 123.8, 125.2, 126.0, 136.9, 138.2, 155.8, 164.9, 182.5; HRMS(ESI) calcd for $C_{13}H_{12}NaO_3S^+$ $(M+Na)^+$: 271.0399, Found: 271.0405.



1n

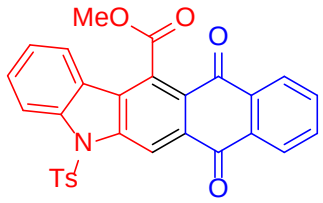
Methyl 2-(2-methylbenzofuran-3-yl)-2-oxoacetate (1n): 90% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 3H), 4.00 (s, 3H), 7.32 – 7.35 (m, 2H), 7.44 – 7.48 (m, 1H), 7.90 – 7.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 53.0, 111.1, 113.9, 121.5, 124.7, 125.2, 125.3, 153.67, 164.6, 166.3, 181.8; HRMS(ESI) calcd for $C_{12}H_{10}NaO_4^+$ $(M+Na)^+$: 241.0471, Found: 241.0475.



1o

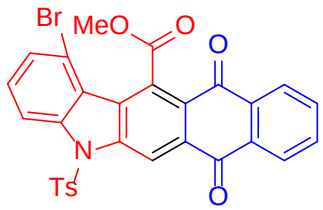
Methyl 2-(2,5-dimethyl-1-tosyl-1H-pyrrol-3-yl)-2-oxoacetate (1o): 60% yield, yellow solid; 1H NMR (400 MHz, $CDCl_3$) δ 2.43 (d, J = 3.9 Hz, 6H), 2.76 (s, 3H),

3.88 (s, 3H), 6.42 (s, 1H), 7.33 (d, J = 9.2 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 15.6, 21.8, 52.8, 112.6, 118.9, 126.9, 130.4, 132.4, 136.2, 142.0, 145.9, 163.8, 181.4; HRMS(ESI) calcd for $C_{16}H_{17}NNaO_5S^+$ $(M+Na)^+$: 358.0720, Found: 358.0723.



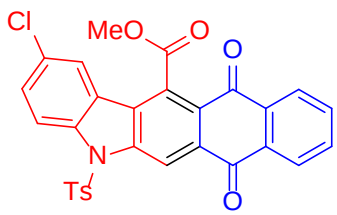
3a

Methyl 7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxy-Late (3a): 83% yield (42.3 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 4.23 (s, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.76 – 7.90 (m, 5H), 8.26 – 8.31 (m, 1H), 8.33 – 8.39 (m, 1H), 8.44 (d, J = 8.4 Hz, 1H), 9.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.4, 114.6, 115.1, 122.3, 123.1, 124.9, 125.8, 126.7, 126.8, 127.4, 127.5, 130.1, 132.4, 133.4, 134.4, 140.2, 141.2, 146.0, 169.2, 182.1; HRMS(ESI) calcd for $C_{29}H_{19}NNaO_6S^+$ $(M+Na)^+$: 532.0825, Found: 532.0830.



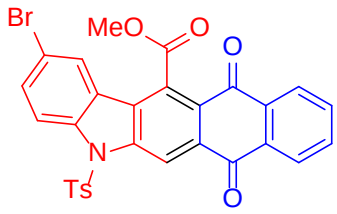
3b

Methyl 1-bromo-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13 -carboxylate (3b): 40% yield (23.5 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.14 (s, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.73 (dd, *J* = 11.2 8.0 Hz, 3H), 7.81 (dd, *J* = 5.6, 3.4 Hz, 2H), 8.26 – 8.34 (m, 2H), 8.58 (d, *J* = 8.4Hz, 1H), 9.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.5, 113.9, 114.6, 117.3, 124.0, 125.8, 126.8, 127.0, 127.1, 127.7, 130.1, 130.2, 130.4, 131.6, 132.9, 134.1, 134.5, 134.6, 141.8, 142.0, 146.4, 168.9, 181.9,182.4; HRMS(ESI) calcd for $C_{29}H_{18}BrNNaO_6S^+$ $(M+Na)^+$: 609.9930, Found: 609.9932.



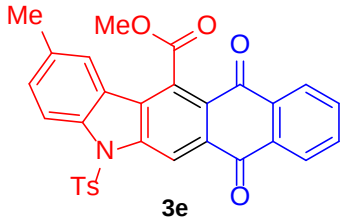
3c

Methyl 2-chloro-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3c): 79% yield (43.0 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.23 (s, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.62 (dd, J = 9.2, 2.0 Hz, 1H), 7.75– 7.88 (m, 5H), 8.31 (m, 1H), 8.36 – 8.42 (m, 2H), 9.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 29.7, 53.6, 114.8, 116.3, 122.1, 124.5, 125.7, 126.0, 126.7, 127.5, 127.6, 128.6, 130.3, 130.8, 132.9, 133.4, 134.2, 134.5, 138.5, 141.5, 146.3, 168.9, 182.0, 182.0; HRMS(ESI) calcd for $C_{29}H_{18}ClNNaO_6S^+$ $(M+Na)^+$: 566.0436, Found: 566.0443.



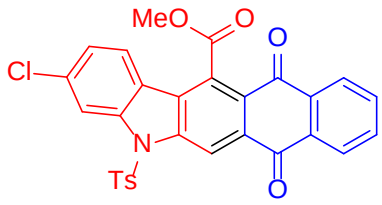
3d

Methyl 2-bromo-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3d): 61% yield (35.9 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.23 (s, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.80 (m, 5H), 7.94 (s, 1H), 8.27 – 8.42 (m, 3H), 9.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.6, 114.7, 116.5, 118.3, 124.9, 125.1, 125.6, 126.7, 127.5, 127.6, 128.6, 130.2, 133.0, 133.4, 134.1, 134.5, 138.9, 141.3, 146.3, 168.9, 181.9, 182.0; HRMS(ESI) calcd for $C_{29}H_{18}BrNNaO_6S^+$ $(M+Na)^+$: 609.9930, Found: 609.9935.



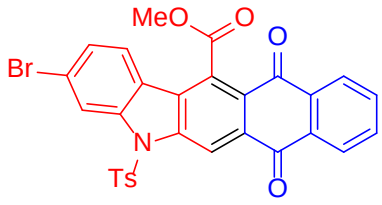
3e

Methyl 2-methyl-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3e): 78% yield (40.8 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.49 (s, 3H), 4.23 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.80 – 7.84 (m, 2H), 8.27 – 8.32 (m, 2H), 8.35 – 8.37 (m, 1H), 9.30 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.4, 114.6, 114.9, 122.1, 123.3, 125.8, 126.7, 126.8, 127.4, 127.5, 128.2, 130.1, 131.5, 132.2, 133.4, 134.4, 134.8, 138.4, 141.4, 145.9, 169.3, 182.1; HRMS(ESI) calcd for $C_{30}H_{21}NNaO_6S^+$ $(M+Na)^+$: 546.0982, Found: 546.0986.



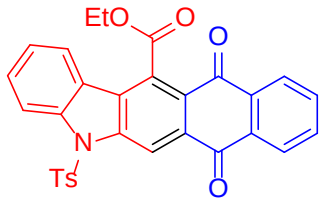
3f

Methyl 3-chloro-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3f): 75% yield (40.8 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 4.21 (s, 3H), 7.21 (d, J = 8.4 Hz, 2H), 7.42 (dd, J = 8.6, 1.8 Hz, 1H), 7.82 (m, 5H), 8.27 – 8.32 (m, 1H), 8.36 – 8.40 (m, 1H), 8.48 (d, J = 1.6 Hz, 1H), 9.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.5, 114.6, 115.4, 121.7, 123.0, 125.6, 126.1, 126.8, 127.5, 127.6, 130.3, 132.6, 133.4, 134.2, 134.5, 136.3, 140.7, 141.3, 146.4, 169.0, 181.9, 182.0; HRMS(ESI) calcd for $C_{29}H_{18}ClNNaO_6S^+$ $(M+Na)^+$: 566.0436, Found: 566.0441.



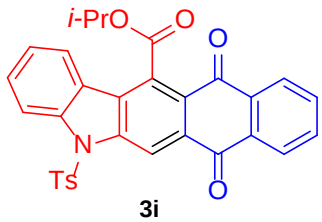
3g

Methyl 3-bromo-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3g): 75% yield (44.1 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 4.21 (s, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 9.2 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.83 (m, 4H), 8.30 (d, J = 8.2 Hz, 1H), 8.38 (d, J = 6.4 Hz, 1H), 8.65 (s, 1H), 9.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.5, 114.6, 118.3, 122.1, 123.2, 124.3, 126.1, 126.8, 127.5, 127.6, 128.3, 128.4, 130.3, 132.7, 133.4, 133.4, 134.2, 134.5, 140.8, 141.1, 146.4, 169.0, 181.9, 182.0. HRMS(ESI) calcd for $C_{29}H_{18}BrNNaO_6S^+$ $(M+Na)^+$: 609.9930, Found: 609.9936.



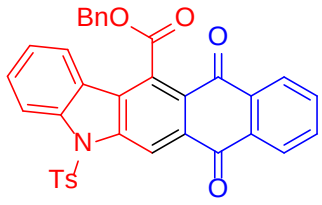
3h

Ethyl 7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3h): 88% yield (46.1 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 4.74 (s, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.46 (m, 1H), 7.63 – 7.68(m, 1H), 7.78 – 7.84 (m, 4H), 7.92 (d, *J* = 7.6 Hz, 1H), 8.28 – 8.37 (m, 2H), 8.45 (d, *J* = 8.4 Hz, 1H),9.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 62.6, 114.5, 115.1, 122.4, 123.3, 124.9, 125.8, 126.8, 126.8, 127.4, 127.5, 128.8, 130.1, 132.4, 133.4, 133.5, 134.3, 134.4, 140.2, 141.2, 146.0, 168.7, 182.1, 182.2. HRMS(ESI) calcd for $C_{30}H_{21}NNaO_6S^+$ $(M+Na)^+$: 546.0982, Found: 546.0985.



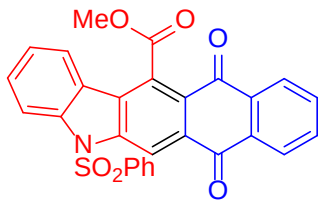
3i

Isopropyl 7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3i): 68% yield (36.6 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 6H), 2.28 (s, 3H), 5.70 (dt, *J* = 12.4, 6.4 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.80 – 7.82 (m, 4H), 7.99 (d, *J* = 7.6 Hz, 1H), 8.29 – 8.37 (m, 2H), 8.46 (d, *J* = 8.4 Hz, 1H), 9.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 70.2, 114.4, 115.1, 122.5, 123.3, 124.8, 125,8, 126.8, 127.3, 127.5, 129.3, 130.0, 130.1, 132.5, 133.4, 133.6, 134.3, 134.5, 140.2, 141.2, 146.0, 168.1, 182.0, 182.2; HRMS(ESI) calcd for $C_{31}H_{23}NNaO_6S^+$ $(M+Na)^+$: 560.1138, Found: 560.1142.



3j

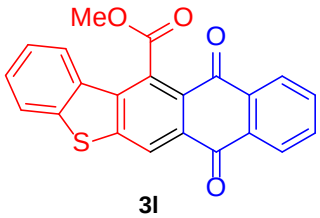
Benzyl 7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3j): 70% yield (41.0 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 5.76 (s, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.26 (m, 1H), 7.36 – 7.39 (m, 3H), 7.52 – 7.54 (m, 2H), 7.58 –7.63(m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.81 – 7.84 (m, 2H), 8.30 – 8.38 (m, 2H), 8.42 (d, *J* = 8.4 Hz, 1H), 9.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 68.7, 114.5, 115.0, 122.6, 123.1, 124.8, 125.9, 126.7, 126.9, 127.4, 127.5, 128.3, 128.7, 129.4, 130.0, 130.1, 132.4, 133.4, 133.5, 134.4, 134.9, 140.1, 141.2, 146.0, 168.6, 182.1; HRMS(ESI) calcd for $C_{35}H_{23}NNaO_6S^+$ $(M+Na)^+$: 608.1138, Found: 608.1140.



3k

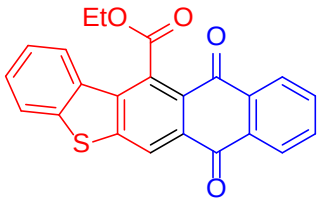
Methyl 7,12-dioxo-5-(phenylsulfonyl)-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3k): 82% yield (40.6 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 3H), 7.42 (dt, J = 15.8, 7.8 Hz, 3H), 7.53 (t, J = 7.4 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.79 – 7.90 (m, 3H), 7.93 (d, J = 7.6 Hz, 2H), 8.30 (m, 1H), 8.35 – 8.41 (m, 1H), 8.46 (d, J = 8.4 Hz, 1H), 9.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.5, 114.5,

115.1, 122.3, 123.2, 125.1, 126.7, 127.4, 127.6, 129.6, 130.2, 132.5, 133.4, 134.4, 134.7, 137.4, 140.1, 141.2, 169.2, 182.1, 182.2; HRMS(ESI) calcd for $C_{28}H_{17}NNaO_6S^+$ $(M+Na)^+$: 518.4942, Found: 518.4946.



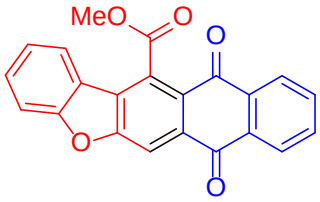
3l

Methyl 7,12-dioxo-7,12-dihydroanthra[2,3-b]benzo[d]thiophene-13-carboxylate (3l): 88% yield (32.8 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 (s, 3H), 7.50 –7.60(m, 2H), 7.79 – 7.82 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.30 – 8.33 (m, 2H), 8.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.4, 123.2, 123.3, 124.4, 125.7, 126.5, 127.3, 127.6, 128.9, 130.6, 132.8, 133.1, 133.7, 134.3, 134.4, 135.2, 141.5, 146.1, 169.7, 182.0, 182.4; HRMS(ESI) calcd for $C_{22}H_{12}NaO_4S^+$ $(M+Na)^+$: 395.0349, Found: 395.0345.



3m

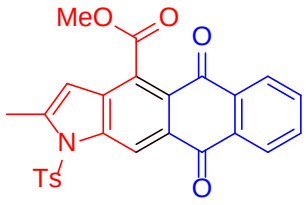
Ethyl 7,12-dioxo-7,12-dihydroanthra[2,3-b]benzo[d]thiophene-13-carboxylate (3m): 90% yield (34.8 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (t, *J* = 7.2 Hz, 3H), 4.83 (s, 2H), 7.51 – 7.62 (m, 2H), 7.81 – 7.84 (m, 2H), 7.92 – 7.94 (m, 1H), 8.18 – 8.21 (m, 1H), 8.33 – 8.35 (m, 2H), 8.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 62.5, 123.2, 123.2, 124.6, 125.7, 126.5, 127.3, 127.7, 128.8, 130.3, 130.7, 133.0, 133.2, 133.8, 134.3, 134.4, 135.3, 141.5, 146.1, 169.2, 182.2; HRMS(ESI) calcd for $C_{23}H_{14}NaO_4S^+$ $(M+Na)^+$: 409.0505, Found: 409.0508.



3n

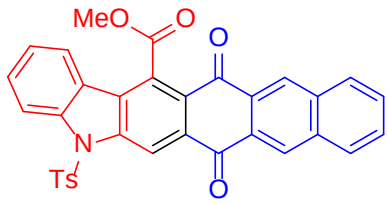
Methyl 7,12-dioxo-7,12-dihydroanthra[2,3-b]benzofuran-13-carboxylate (3n): 73% yield (26.0 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 3H), 7.38 – 7.42 (m, 1H), 7.56 – 7.65 (m, 2H), 7.77 – 7.80 (m, 2H), 7.86 (d, J = 7.6 Hz, 1H), 8.27 – 8.31 (m, 2H), 8.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.5, 111.6, 112.4, 121.4, 122.6, 124.4, 125.9, 126.6, 127.5, 127.6, 128.8, 130.3, 133.2, 133.4, 133.5, 134.4, 134.5, 158.1, 158.6, 168.9, 182.1; HRMS(ESI) calcd for $C_{22}H_{12}NaO_5^+$ $(M+Na)^+$:

379.0577, Found: 379.0579.



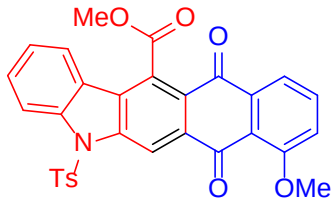
3o

Methyl 2-methyl-5,10-dioxo-1-tosyl-5,10-dihydro-1H-naphtho[2,3-f]indole-4-carboxylate (3o): 80% yield (37.9 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.70 (s, 3H), 4.09 (s, 3H), 6.47 (s, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.76 – 7.81 (m, 4H), 8.25 – 8.27 (m, 1H), 8.34 – 8.36 (m, 1H), 9.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 21.7, 53.3, 108.1, 114.7, 125.9, 126.5, 126.9, 127.4, 127.5, 129.6, 130.4, 131.6, 133.6, 133.7, 134.2, 134.3, 135.4, 139.2, 144.1, 146.1, 169.2, 182.5; HRMS(ESI) calcd for $C_{26}H_{19}NNaO_6S^+$ $(M+Na)^+$: 496.0825, Found: 496.0830.



3p

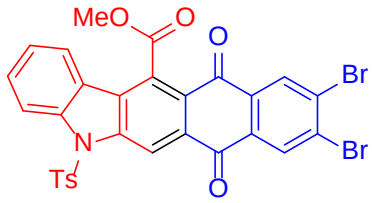
Methyl 7,14-dioxo-5-tosyl-7,14-dihydro-5H-anthra[2,3-b]carbazole-15-carboxyla-te (3p): 81% yield (45.3 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 4.26 (s, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.73– 7.65 (m, 3H), 7.82 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 8.15 – 8.08 (m, 2H), 8.46 (d, J = 8.4 Hz, 1H), 8.85 (s, 1H), 8.92 (s, 1H), 9.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 53.6, 114.8, 115.2, 122.4, 123.2, 125.0, 126.8, 126.9, 129.5, 129.5, 129.8, 129.8, 130.0, 130.2, 130.3, 133.5, 134.5, 135.4, 140.3, 146.1, 169.5, 182.0, 182.1; HRMS(ESI) calcd for $C_{33}H_{21}NNaO_6S^+$ $(M+Na)^+$: 582.0982, Found: 582.0987.



3q

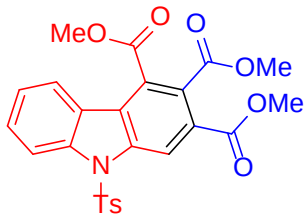
Methyl 8-methoxy-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (3q): 83% yield (44.8 mg), yellow solid; ^{1}H NMR (400 MHz, CDCl3) δ 2.28 (s, 3H), 4.11 (s, 3H), 4.21 (s, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.35 – 7.46 (m, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.74 (t, J = 8.2 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 8.47 (d, J = 8.8 Hz, 1H), 9.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.4, 56.6, 114.6, 115.1, 118.1, 120.1, 121.3, 122.2, 123.2,

124.8, 124.9, 126.3, 126.8, 127.5, 130.0, 130.1, 134.0, 134.5, 135.4, 135.7, 140.2, 141.4, 145.9, 160.6, 169.3, 181.3, 182.4; HRMS(ESI) calcd for $C_{30}H_{21}NNaO_7S^+$ $(M+Na)^+$: 562.0931, Found: 562.0938.



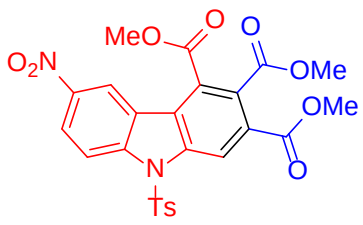
3r

Methyl 9,10-dibromo-7,12-dioxo-5-tosyl-7,12-dihydro-5H-naphtho[2,3-b]carbazo -le-13-carboxylate (3r): 63% yield (42.0 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.21 (s, 3H), 7.18 (d, J = 8.0 Hz, 2H),7.45 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.51 (s, 1H), 8.57 (s, 1H), 9.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 53.6, 114.8, 115.2, 122.4, 123.0, 125.2, 125.3, 126.8, 128.6, 130.3, 130.5, 131.9, 132.6, 132.7, 132.8, 134.4, 140.3, 141.4, 146.3, 168.9, 180.6, 180.7; HRMS(ESI) calcd for $C_{29}H_{17}Br_2NNaO_6S^+$ $(M+Na)^+$: 687.9036, Found: 687.9045.



5a

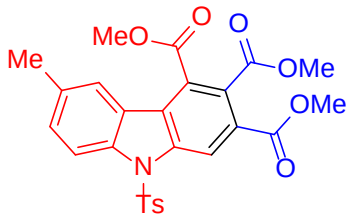
Trimethyl 9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5a): 66% yield (32.7 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.94 (s, 3H), 4.01 (d, *J* = 8.8 Hz, 6H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 9.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.1, 115.1, 118.0, 123.0, 123.3, 124.6, 125.8, 126.4, 126.5, 128.6, 129.0, 129.6, 130.1, 134.3, 138.7, 140.0, 145.8, 166.2, 167.1,167.8; HRMS(ESI) calcd for $C_{25}H_{21}NNaO_8S^+$ $(M+Na)^+$: 518.0880, Found: 518.0889.



5b

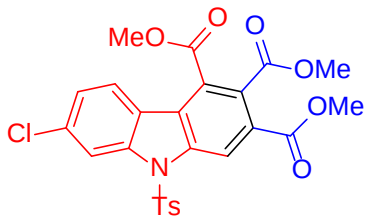
Trimethyl 6-nitro-9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5b): 50% yield (27.0 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.96 (s, 3H), 4.02 (s,

3H), 4.09 (s, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 8.46 – 8.50 (m, 2H), 8.92 (d, *J* = 2.0 Hz, 1H), 9.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.2, 53.3, 53.5, 115.2, 118.4, 119.7, 123.6, 124.4, 124.7, 126.6, 126.8, 130.1, 130.4, 133.8, 139.6, 143.0, 144.5, 146.8, 165.7, 166.3, 167.3; HRMS(ESI) calcd for $C_{25}H_{20}N_2NaO_{10}S^+$ $(M+Na)^+$: 563.0731, Found: 563.0740.



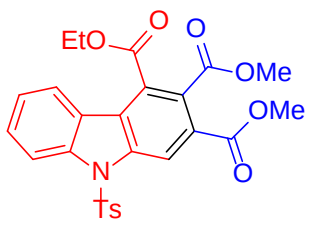
5c

Trimethyl 6-methyl-9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5c): 63% yield (32.1 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.45 (s, 3H), 3.94 (s, 3H), 4.01 (d, *J* = 12.0 Hz, 6H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 53.0, 53.1, 114.8, 118.0, 122.9, 123.5, 125.8, 126.4, 126.5, 128.4, 128.8, 130.0, 131.0, 134.2, 134.4, 138.2, 138.9, 145.7, 166.3, 167.1, 167.8; HRMS(ESI) calcd for $C_{26}H_{23}NNaO_8S^+$ $(M+Na)^+$: 532.1037, Found: 532.1039.



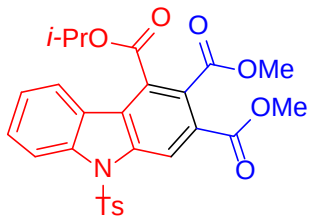
5d

Trimethyl 7-chloro-9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5d): 50% yield (26.5 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.93 (s, 3H), 4.00 (d, *J* = 2.4 Hz, 6H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 8.41 (d, *J* = 1.6 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.1, 53.2, 115.2, 118.1, 121.8, 124.1, 125.2, 126.1, 126.6, 128.7, 129.6, 130.2, 134.0, 135.7, 138.8, 140.6, 146.2, 166.0, 166.8, 167.7; HRMS(ESI) calcd for $C_{25}H_{20}ClNNaO_8S^+$ $(M+Na)^+$: 552.0490, Found: 552.0495.



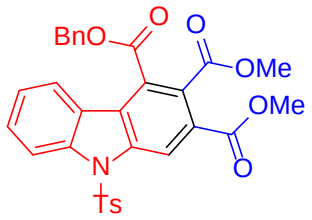
5e

4-Ethyl 2,3-dimethyl 9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5e): 65% yield (33.1 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.2 Hz, 3H), 2.29 (s, 3H), 3.94 (s, 3H), 4.00 (s, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.40 (m, 1H), 7.58 – 7.62 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 9.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 52.9, 53.1, 62.5, 115.1, 117.9, 123.1, 123.4, 124.5, 125.8, 126.6, 126.8, 128.6, 128.9, 129.6, 130.1, 134.3, 138.7, 140.0, 145.8, 166.2, 166.6, 167.7; HRMS(ESI) calcd for $C_{26}H_{23}NNaO_8S^+$ $(M+Na)^+$: 532.1037, Found: 532.1040.



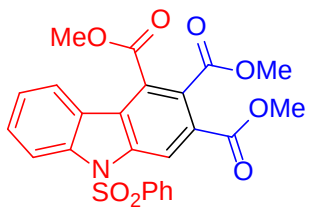
5f

4-Isopropyl 2,3-dimethyl 9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5f): 52% yield (27.2 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.4 Hz, 6H), 2.29 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 5.41 (dt, *J* = 12.8, 6.4 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.40 (m, 1H), 7.57 – 7.62 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 9.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.7, 52.9, 53.0, 70.6, 115.0, 117.7, 123.1, 123.4, 124.5, 125.6, 126.6, 127.1, 128.5, 128.7, 129.5, 130.1, 134.3, 138.6, 140.0, 145.8, 166.2, 166.3, 167.6; HRMS(ESI) calcd for $C_{27}H_{25}NNaO_8S^+$ $(M+Na)^+$: 546.1193, Found: 546.1197.



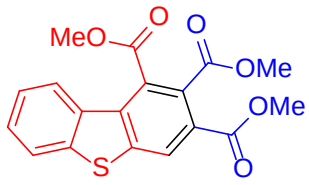
5g

4-Benzyl 2,3-dimethyl 9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5g): 50% yield (28.6 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.70 (s, 3H), 3.98 (s, 3H), 5.47 (s, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.40 (m, 3H), 7.46 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.55 – 7.59 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 9.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 52.8, 53.1, 68.4, 115.0, 117.9, 123.2, 123.3, 124.5, 125.8, 126.5, 126.6, 128.7, 128.8, 129.0, 129.5, 130.1, 134.3, 134.6, 138.7, 140.0, 145.8, 166.3, 166.5, 167.6; HRMS(ESI) calcd for $C_{31}H_{25}NNaO_8S^+$ $(M+Na)^+$: 594.1193, Found: 594.1195.



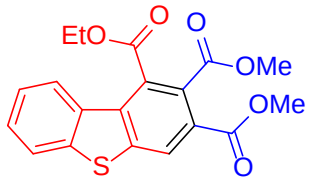
5h

Trimethyl 9-(phenylsulfonyl)-9H-carbazole-2,3,4-tricarboxylate (5h): 66% yield (31.8 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 4.00 (s, 3H), 4.02 (s, 3H), 7.38 (dd, *J* = 14.0, 7.2 Hz, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 9.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 53.2, 115.0, 118.0, 123.1, 123.3, 124.7, 125.9, 126.5, 128.7, 129.1, 129.5, 129.7, 134.6, 137.3, 138.7, 139.9, 166.2, 167.0, 167.7; HRMS(ESI) calcd for $C_{24}H_{19}NNaO_8S^+$ $(M+Na)^+$: 504.0724, Found: 504.0729.



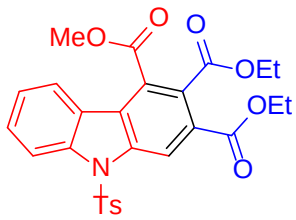
5i

Trimethyl dibenzo[b,d]thiophene-1,2,3-tricarboxylate (5i): 50% yield (17.9 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 6H), 4.09 (s, 3H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.52 – 7.56 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.9, 53.1, 53.2, 123.1, 124.3, 125.3, 127.6, 125.8, 128.4, 128.7, 128.9, 132.7, 133.6, 141.3, 141.9, 166.1, 167.7, 167.9; HRMS(ESI) calcd for $C_{18}H_{14}NaO_6S^+$ $(M+Na)^+$: 381.0403, Found: 381.0406.



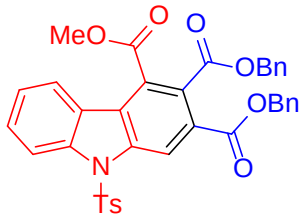
5j

1-Ethyl 2,3-dimethyl dibenzo[b,d]thiophene-1,2,3-tricarboxylate (5j): 45% yield (16.8 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (t, *J* = 7.2 Hz, 3H), 3.95 (d, *J* = 0.4 Hz, 6H), 4.57 (q, *J* = 7.0 Hz, 2H), 7.45 – 7.49 (m, 1H), 7.52 – 7.56 (m, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 52.9, 53.0, 62.5, 123.1, 124.5, 125.2, 125.7, 127.4, 128.3, 128.9, 132.8, 133.6, 141.3, 141.8, 166.1, 167.5; HRMS(ESI) calcd for $C_{19}H_{16}NaO_6S^+$ $(M+Na)^+$: 395.0560, Found: 395.0565.



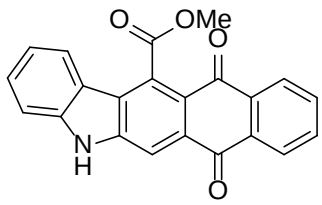
5k

2,3-Diethyl 4-methyl 9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5k): 67% yield (35.1 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (dt, J = 14.4, 7.2 Hz, 6H), 2.30 (s, 3H), 4.02 (s, 3H), 4.36 – 4.48 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H),7.35 – 7.41 (m, 1H), 7.57 – 7.62 (m, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.2, 21.5, 53.0, 62.1, 62.2, 76.70, 77.0, 77.3, 115.1, 117.8, 122.9, 123.4, 124.6, 125.5, 126.5, 126.6, 128.8, 129.4, 129.5, 130.0, 134.35, 138.7, 140.0, 145.8, 166.0, 167.2; HRMS(ESI) calcd for $C_{27}H_{25}NNaO_8S^+$ $(M+Na)^+$: 546.1193, Found: 546.1198.



5l

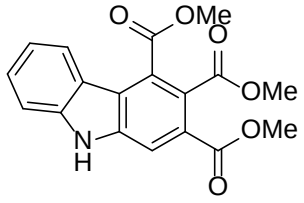
2,3-Dibenzyl 4-methyl 9-tosyl-9H-carbazole-2,3,4-tricarboxylate (5l): 52% yield (33.7 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.73 (s, 3H), 5.15 (s, 2H), 5.35 (s, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.36 – 7.32 (m, 6H), 7.42 – 7.40 (m, 3H), 7.46 (dd, J = 8.0, 4.0 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.63 (s, 1H), 7.65 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 9.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ21.7, 53.0, 67.9, 68.0, 115.1, 118.1, 123.1, 123.3, 124.7, 125.8, 126.7, 128.5, 128.6, 128.7, 128.8, 128.9, 129.7, 130.1, 134.3, 135.2, 135.4, 138.7, 140.1, 146.0, 165.8, 167.1; HRMS(ESI) calcd for $C_{37}H_{29}NNaO_8S^+$ $(M+Na)^+$: 670.1506, Found: 670.1510.



6

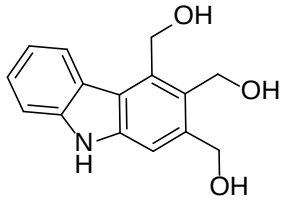
Methyl 7,12-dioxo-7,12-dihydro-5H-naphtho[2,3-b]carbazole-13-carboxylate (6): 96% yield (68.2 mg), yellow solid; ^{1}H NMR (400 MHz, DMSO-D6) δ 4.10 (s, 3H), 7.28 – 7.33 (m, 1H), 7.56 – 7.60 (m, 1H), 7.65 – 7.69 (m, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.88 – 7.91 (m, 2H), 8.16 – 8.22 (m, 2H), 8.34 – 8.35 (m, 1H),12.43 (s, 1H); ^{13}C NMR (100 MHz, DMSO-D6) δ 53.5, 111.2, 113.0, 120.7, 121.1, 121.6, 122.1, 122.9,

127.3, 127.4, 128.9, 129.3, 131.2, 133.7, 133.9, 134.9, 135.1, 142.5, 142.7, 169.7, 182.1,182.8; HRMS(ESI) calcd for $C_{22}H_{13}NNaO_4S^+$ $(M+Na)^+$: 378.0737, Found: 378.0742.



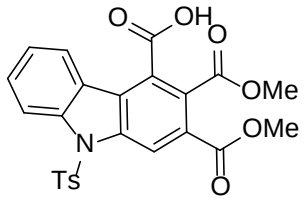
7

Trimethyl 9H-carbazole-2,3,4-tricarboxylate (7): 95% yield (64.8 mg), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.95 (s, 3H), 4.07 (s, 3H), 7.20 – 7.25 (m, 1H), 7.43 – 7.49 (m, 2H), 7.90 (s, 1H), 8.08 (d, J = 8.8 Hz, 1H), 8.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8, 53.0, 53.1, 76.8, 77.1, 77.4, 111.5, 114.4, 120.7, 122.3, 124.4, 126.3, 126.9, 128.2, 139.5, 141.4, 167.1, 168.2,169.0; HRMS(ESI) calcd for $C_{18}H_{15}NNaO_6S^+$ $(M+Na)^+$: 364.0792, Found: 364.0799.



8

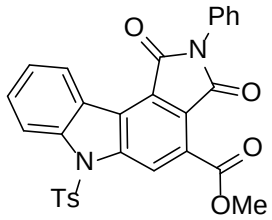
(9H-carbazole-2,3,4-triyl)trimethanol (8): 79% yield (40.7 mg), white solid; ^{1}H NMR (400 MHz, DMSO-D6) δ 4.67 – 4.91 (m, 5H), 5.02 (t, J = 5.0 Hz, 1H), 5.11 (d, J = 4.4 Hz, 2H), 5.18 – 5.24 (m, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 5.6 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 11.21 (s, 1H); ^{13}C NMR (100 MHz, DMSO-D6) δ 56.5, 58.1, 62.2, 109.6, 111.2, 118.9, 120.8, 122.9, 123.6, 125.3, 128.6, 135.0, 139.9, 140.0,140.6; HRMS(ESI) calcd for $C_{15}H_{15}NNaO_3S^+$ $(M+Na)^+$: 280.0944, Found: 280.0947.



9

2,3-Bis(methoxycarbonyl)-9-tosyl-9H-carbazole-4-carboxylic acid (9): 98% yield (94.4 mg), white solid; ^{1}H NMR (400 MHz, DMSO-D6) δ 2.21 (s, 3H), 3.71 (s, 3H), 3.87 (s, 3H), 7.27 (s, 1H), 7.29 (s, 1H), 7.34 – 7.38 (m, 1H), 7.57 – 7.61 (m, 1H), 7.66 (s, 1H), 7.68 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.47 (d, J = 7.6 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR (100 MHz, DMSO-D6) δ 21.5, 52.7, 53.4, 113.4, 114.6, 124.5, 124.8, 125.1, 125.3, 126.7, 127.6, 128.1, 129.3, 130.9, 133.8, 138.0, 139.2, 146.7, 167.0,

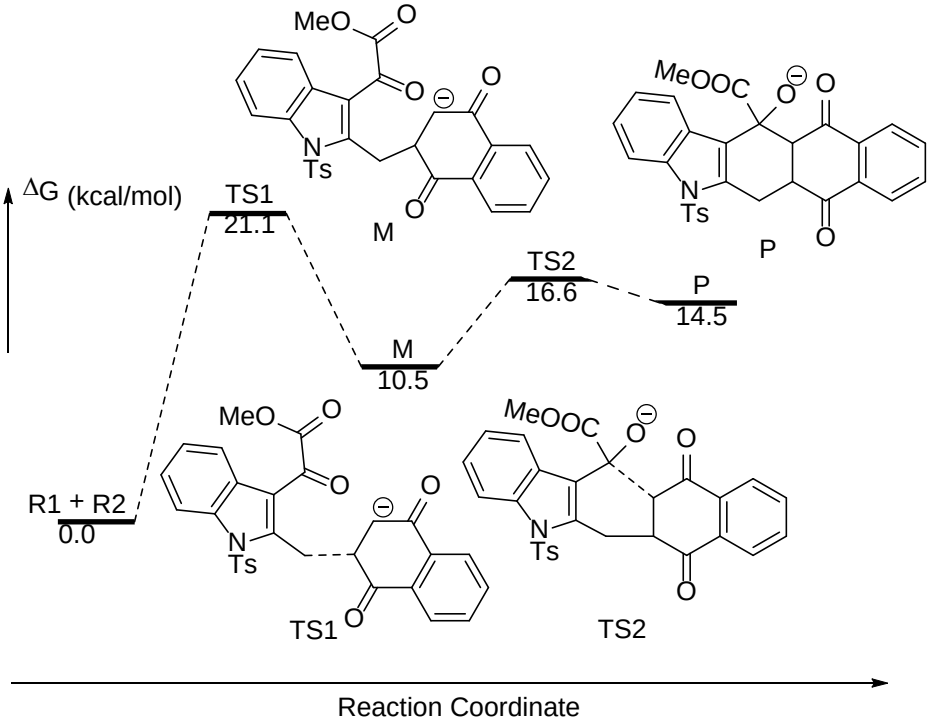
168.7,168.9; HRMS(ESI) calcd for $C_{24}H_{19}NNaO_8S^+$ $(M+Na)^+$: 504.0724, Found: 504.0728.



10

Methyl 1,3-dioxo-2-phenyl-6-tosyl-1,2,3,6-tetrahydropyrrolo[3,4-c]carbazole-4-carboxylate (10): 60% yield (62.9 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.09 (s, 3H), 7.17 (d, J = 8.4 Hz, 2H), 7.39 – 7.55 (m, 6H), 7.69 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.73 (t, J = 2.0 Hz, 1H), 7.75 (t, J = 2.0 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.96 (s, 1H), 9.15 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 53.4, 100.0, 114.8, 119.7, 123.0, 125.1, 125.3, 126.4, 126.7, 126.8, 126.9, 128.3, 128.4, 129.2, 130.2, 130.8, 131.6, 134.3, 140.6, 142.1, 146.2, 165.2, 166.3, 166.6; HRMS(ESI) calcd for $C_{29}H_{20}N_2NaO_6S^+$ $(M+Na)^+$: 547.0934, Found: 547.0938.

c) Computational Details



The Gaussian 09 software[6] was used for calculation in this work. All the optimizations were performed at b3lyp[7]/6-31g (d, p) level in DCE solvent

using the SMD model[8]. The energies discussed in this work were obtained by the addition of the free energy correction to the corresponding single energy at the same level.

d) References

1. D. H. Liu, Y. R. Gao, J. Huang, Z. Q. Fu and W. Huang, *J. Org. Chem.*, 2018, **83**, 14210.

2. L. Anaissi-Afonso, S. Oramas-Royo, J. Ayra-Plasencia, P. Martin-Rodriguez, J. Garcia-Luis, I. Lorenzo-Castrillejo, L. Fernandez-Perez, A. Estevez-Braun and F. Machin, *Acs. Chem. Biol.*, 2018, **13**, 1950.

3. Y. P. Hong, J. Z. Chen, Z. F. Zhang, Y. G. Liu and W. B. Zhang, *Org. Lett.*, 2016, **18**, 2640.

4. T. Yamakado, S. Takahashi, K. Watanabe, Y. Matsumoto, A. Osuka and S. Saito, *Angew. Chem. Int. Ed.*, 2018, **57**, 5438.

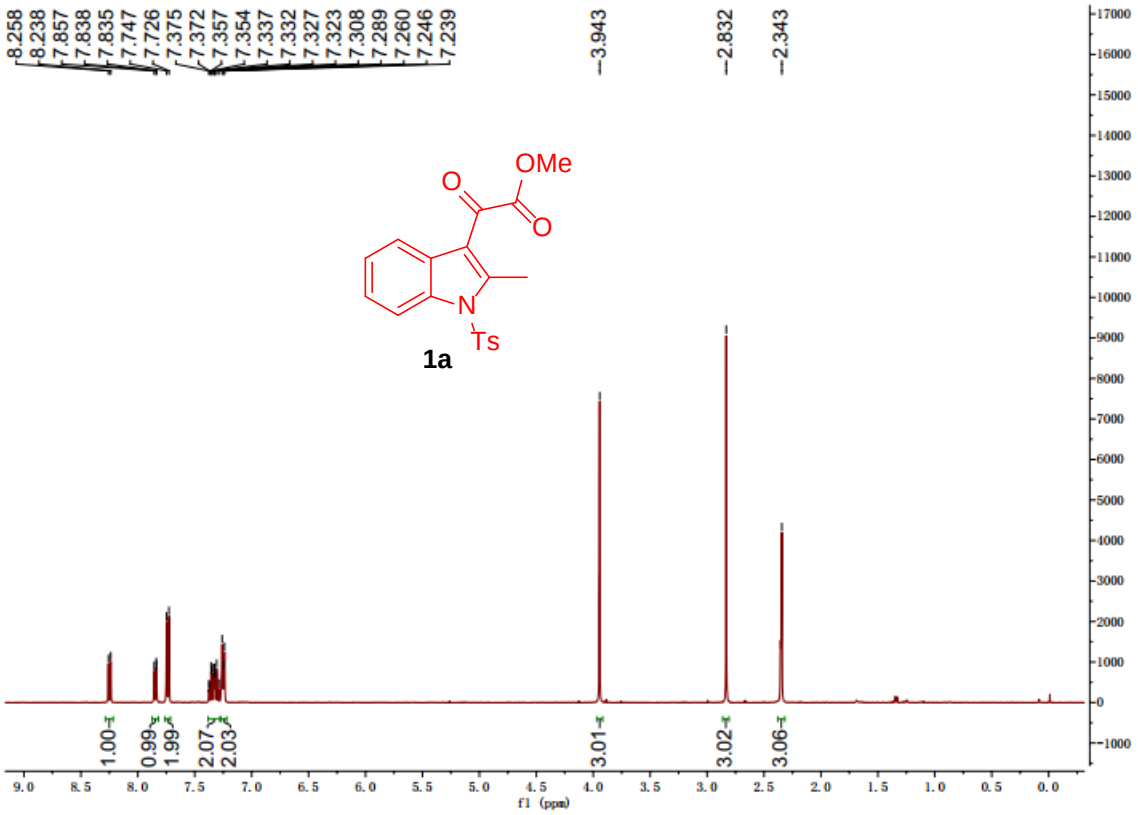
5. E. V. Kobylyansky, I. M. Vasilkevich and G. F. Dvorko, *Ukr. Khim. Zh.*, 1981, **47**, 646.

6. M. J.Frisch, G. W.Trucks, H. B.Schlegel, G. E.Scuseria, M. A.Robb, J. R.Cheeseman, G.Scalmani, V.Barone, B.Mennucci, G. A.Petersson, H.Nakatsuji, M.Caricato, X.Li, H. P.Hratchian, A. F.Izmaylov, J.Bloino, G.Zheng, J. L.Sonnenberg, M.Hada, M.Ehara, K.Toyota, R.Fukuda, J.Hasegawa, M.Ishida, T.Nakajima, Y.Honda, O.Kitao, H.Nakai, T.Vreven, J. A.Montgomery Jr., J. E.Peralta, F.Ogliaro, M.Bearpark, J. J.Heyd, E.Brothers, K. N.Kudin, V. N.Staroverov, T.Keith, R.Kobayashi, J.Normand, K.Raghavachari, A.Rendell, J. C.Burant, S. S.Iyengar, J.Tomasi, M.Cossi, N.Rega, J. M.Millam, M.Klene, J. E.Knox, J. B.Cross, V.Bakken, C.Adamo, J.Jaramillo, R.Gomperts, R. E.Stratmann, O.Yazyev, A. J.Austin, R.Cammi, C.Pomelli, J. W.Ochterski, R. L.Martin, K.Morokuma, V. G.Zakrzewski, G. A.Voth, P.Salvador, J. J.Dannenberg, S.Dapprich, A. D.Daniels, O.Farkas, J. B.Foresman, J. V.Ortiz, J.Cioslowski and D. J.Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010

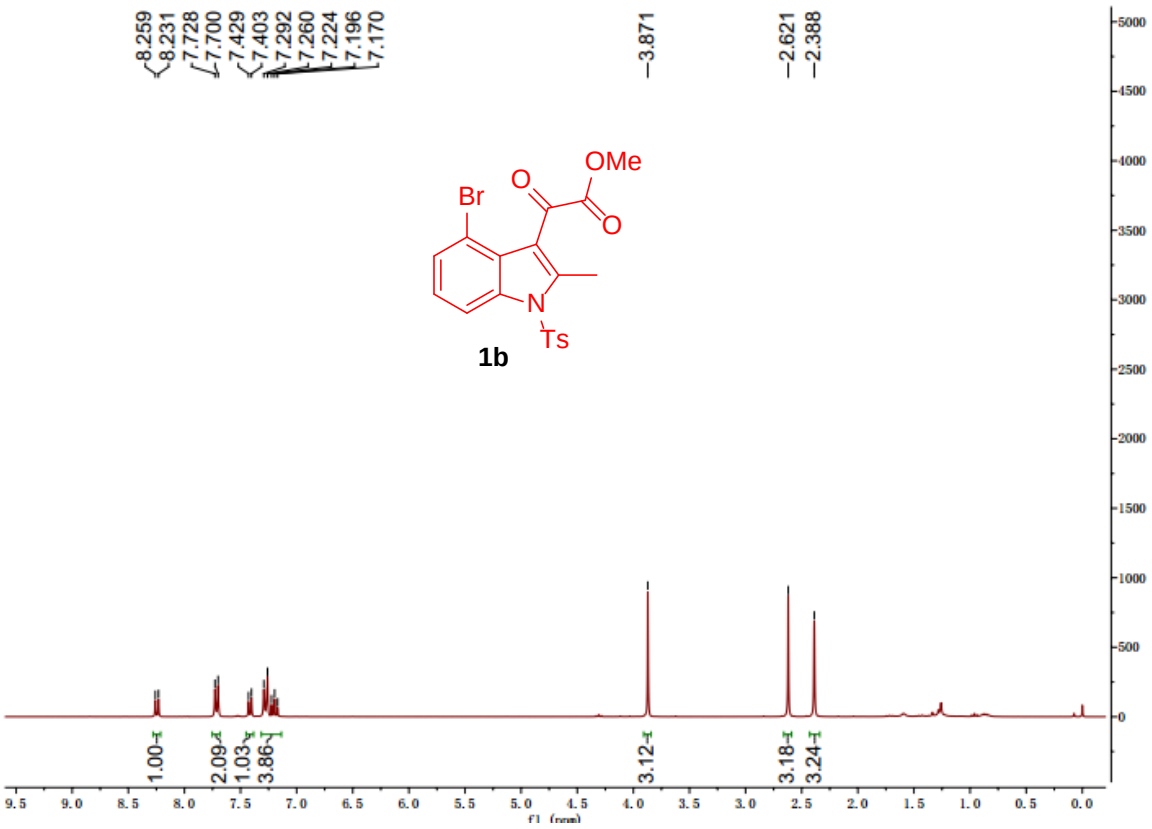
7. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. T. Lee, W. T. Yang, R.G. Parr, *Phys. Rev. B.*, 1988, **37**, 785

8. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378

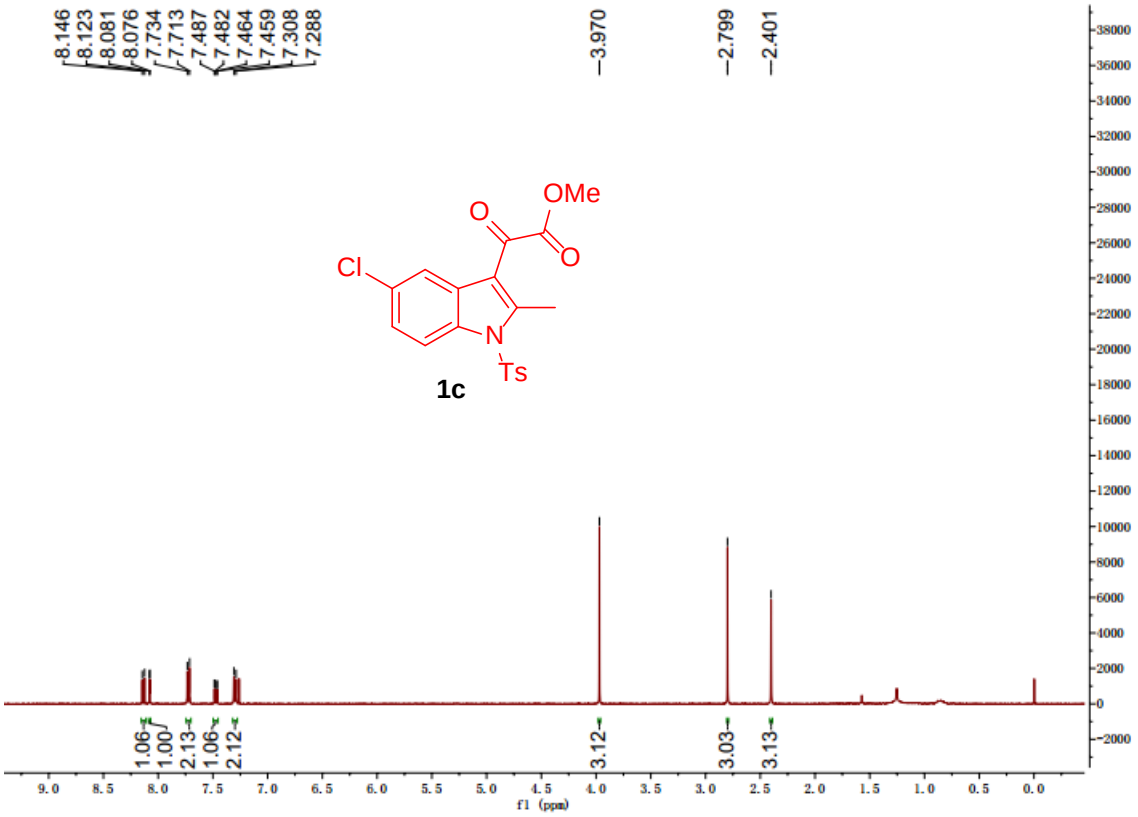
IV . ^{1}H and ^{13}C NMR spectra of substrates and products



1a



1b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O
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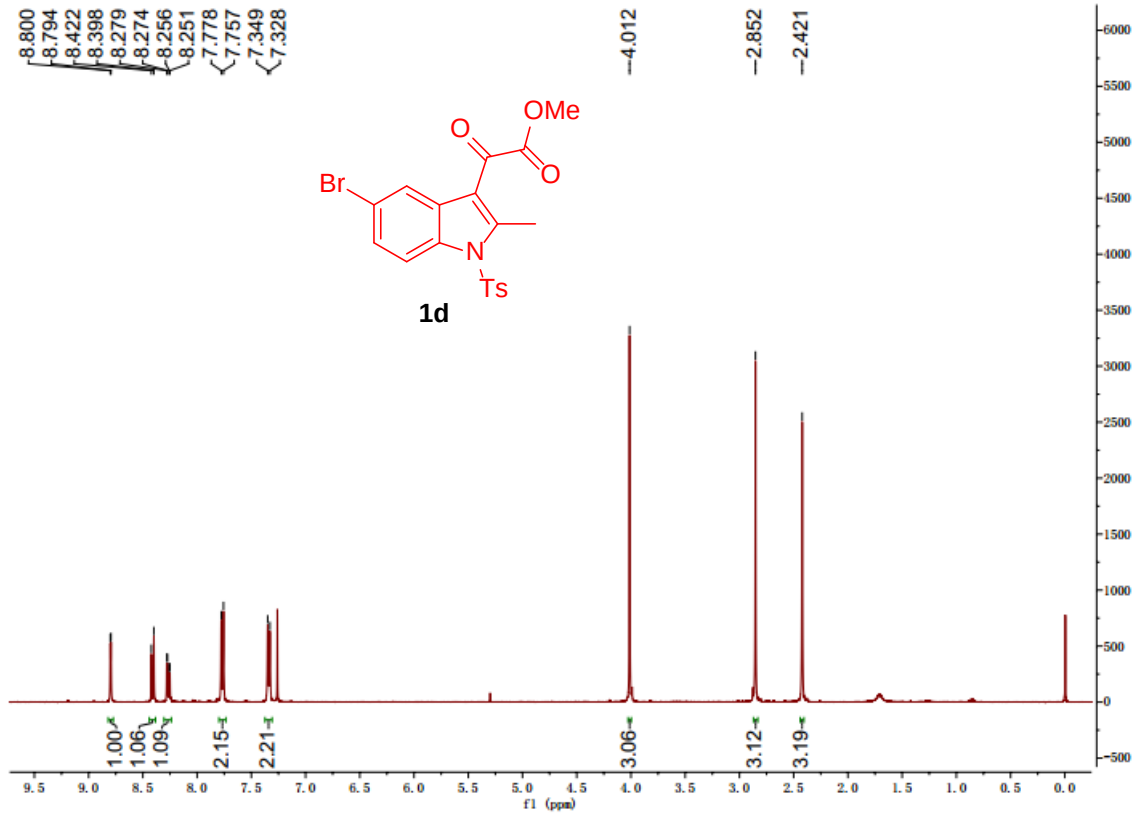
f1 (ppm)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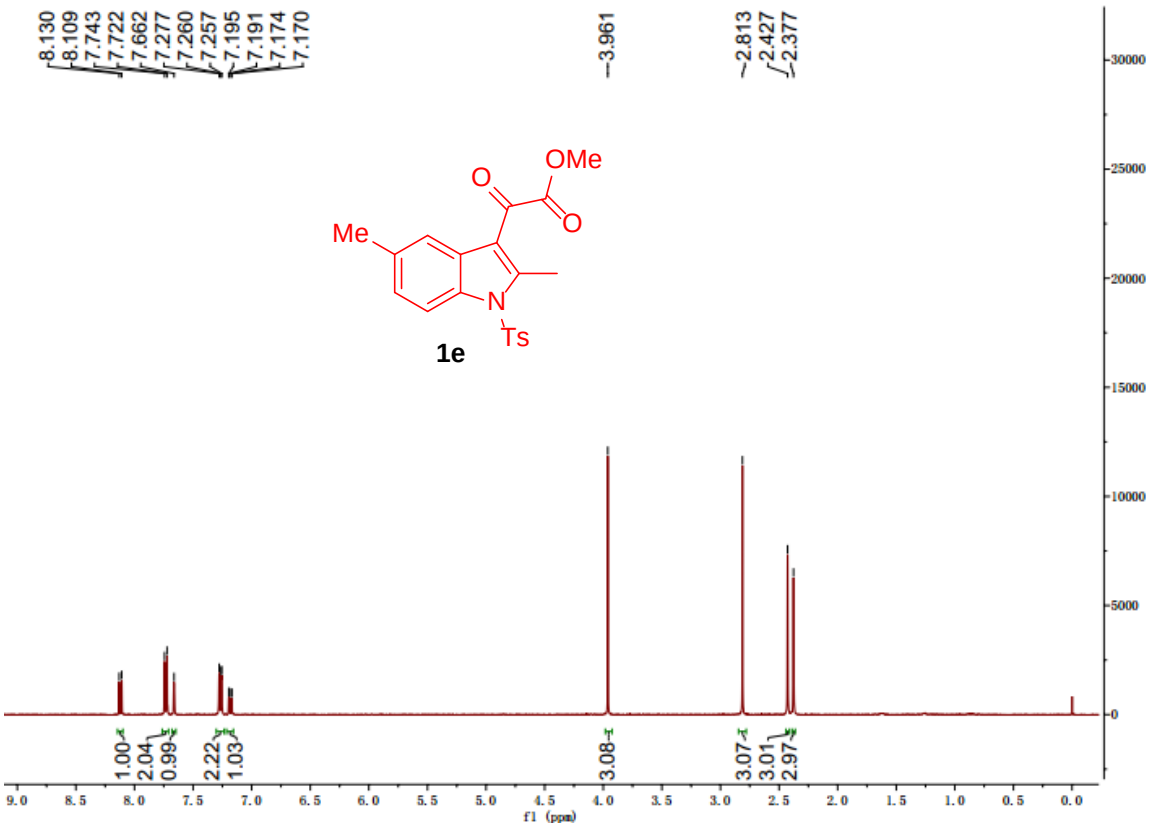
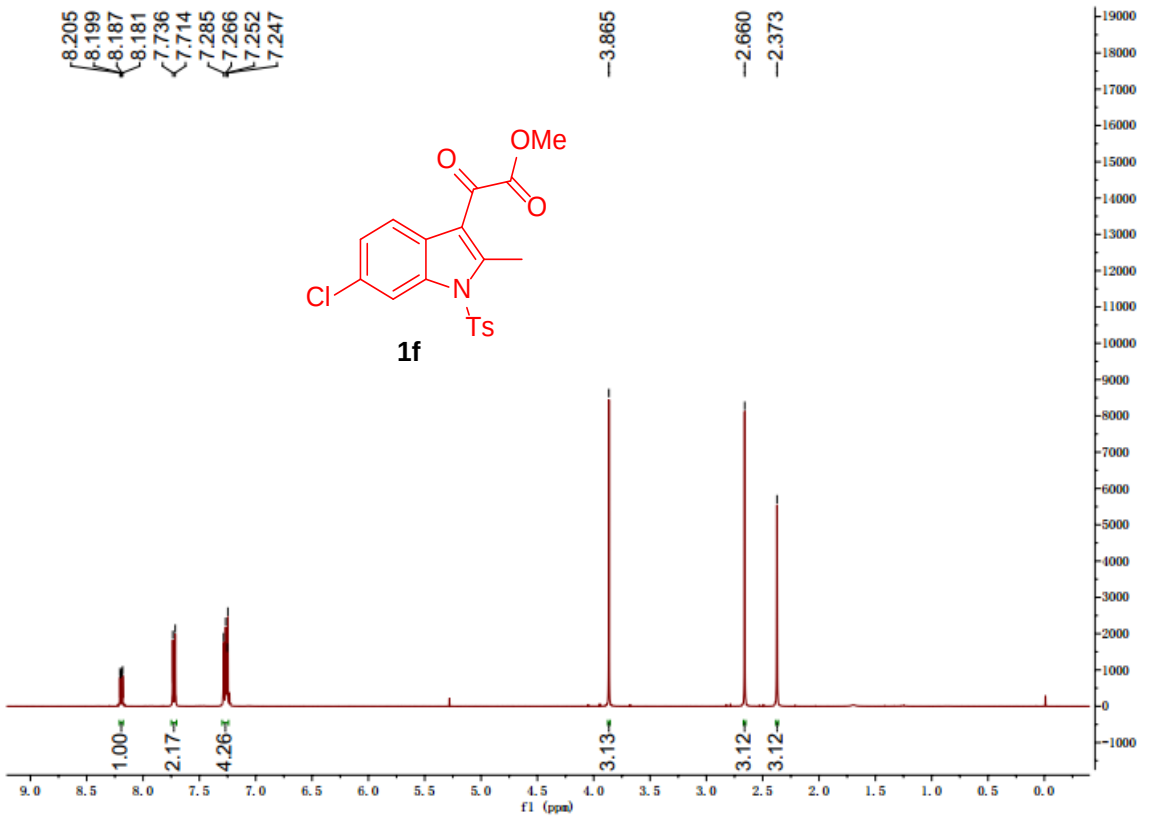
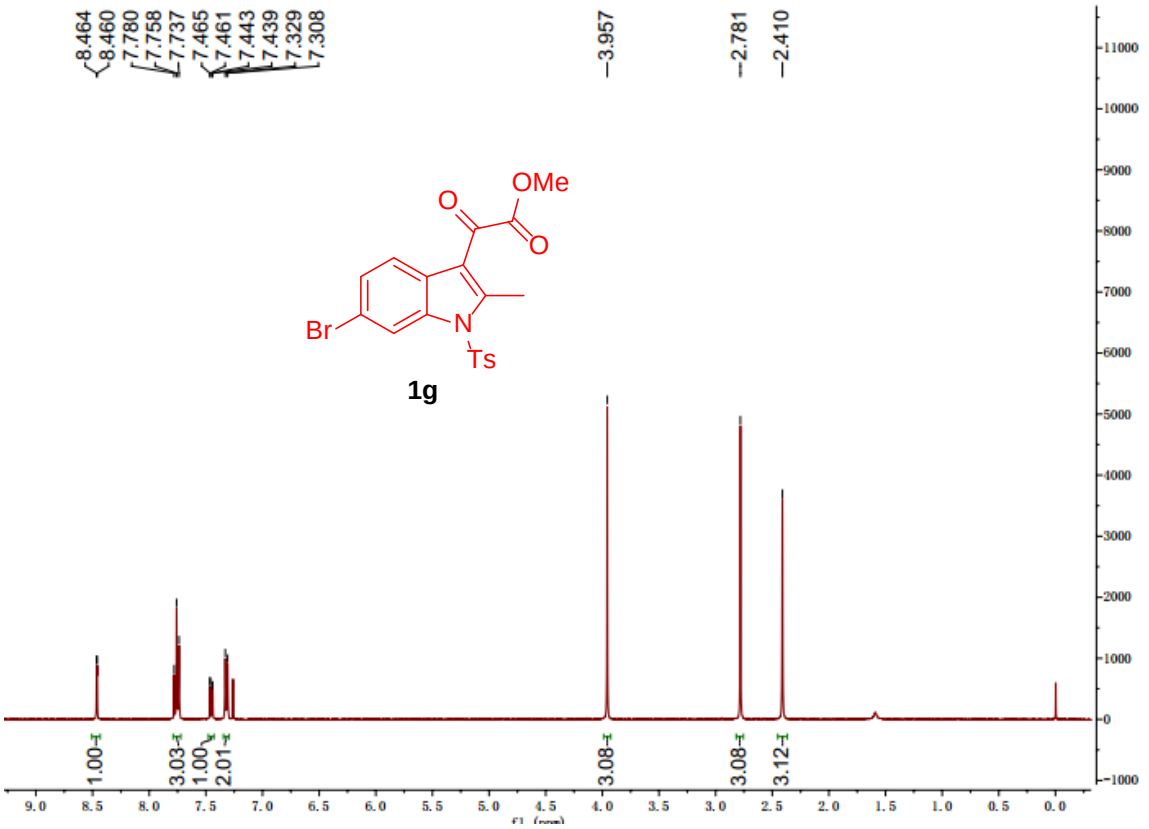
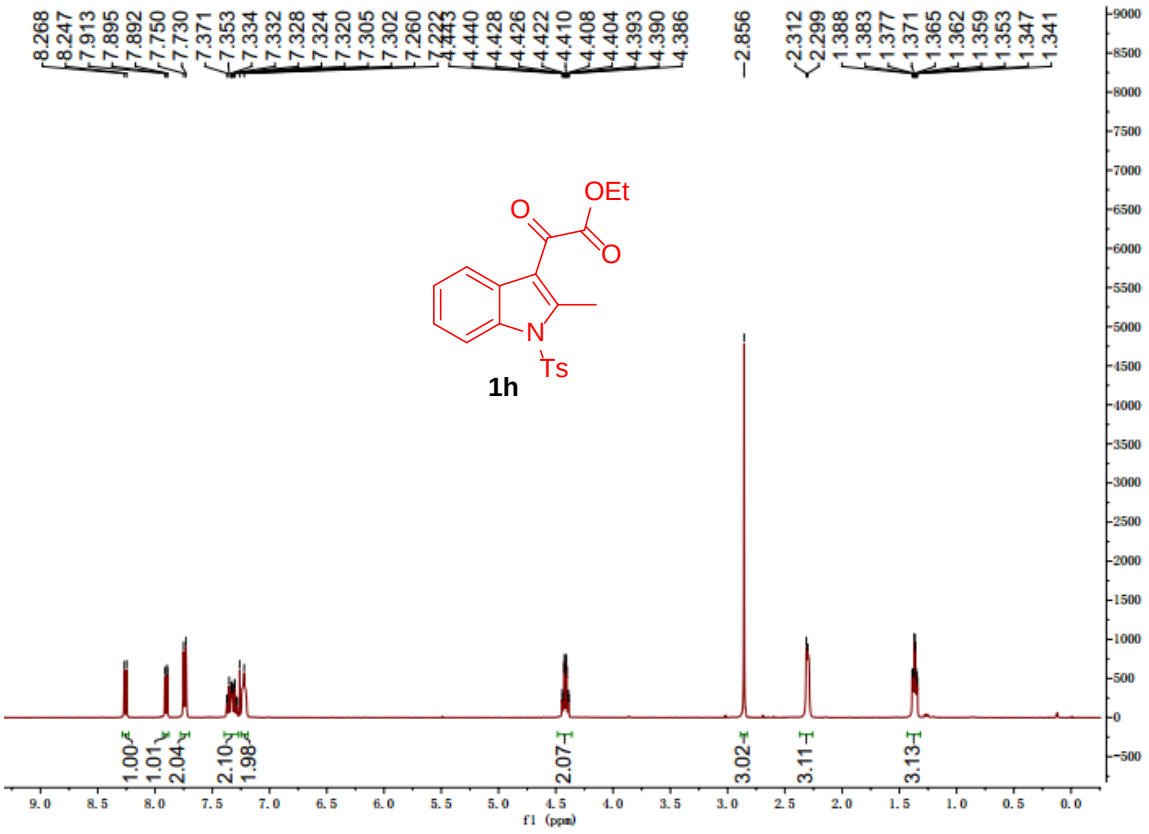
8.398
8.279
8.274
8.256
8.251
7.778
7.757
7.349
7.328
4.012
2.852
2.421
OMe
O
O
Br
N
Ts
1d
1.00
1.06
1.09
2.15
2.21
3.06
3.12
3.19
f1 (ppm)


8.130
8.109
7.743
7.722
7.662
7.277
7.260
7.257
7.195
7.191
7.174
7.170
3.961
2.813
2.427
2.377
OMe
O
O
Me
N
Ts
1e
1.00
2.04
0.99
2.22
1.03
3.08
3.07
3.01
2.97
f1 (ppm)

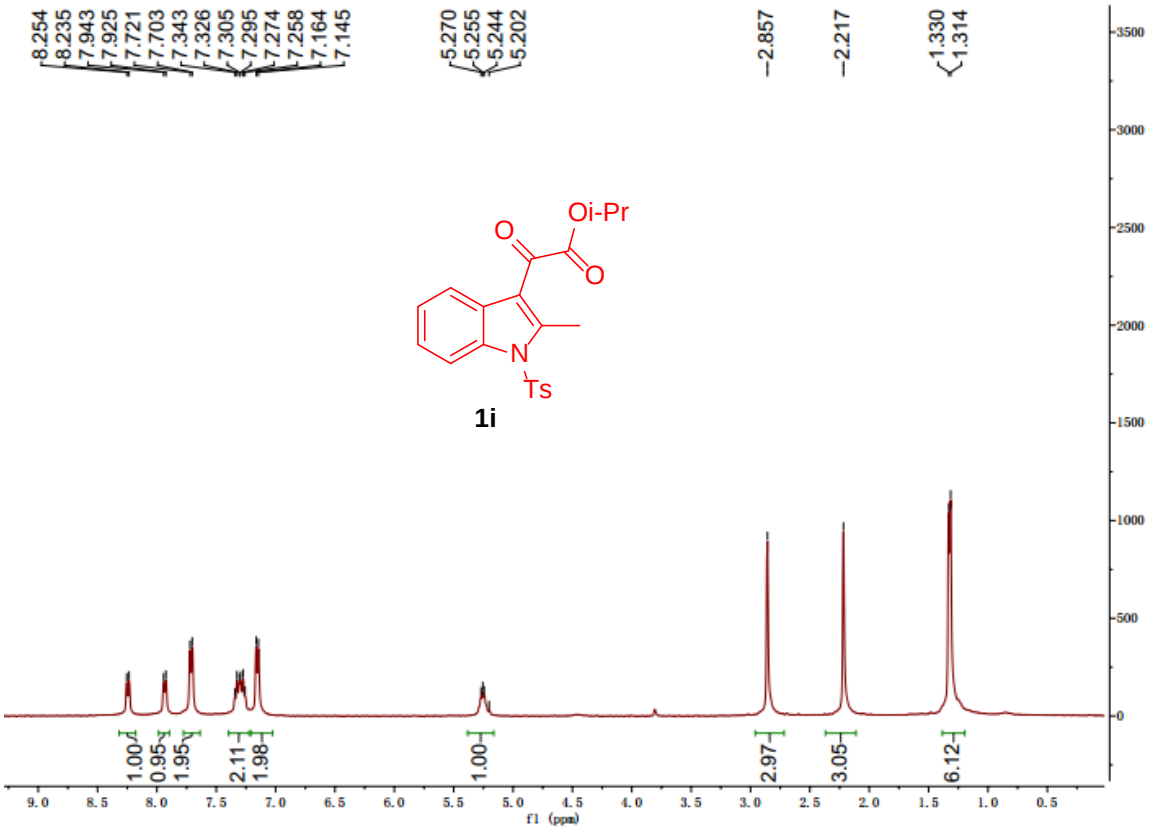

8.205
8.199
8.187
8.181
7.736
7.714
7.285
7.266
7.252
7.247
3.865
2.660
2.373
OMe
O
O
Cl
N
Ts
1f
1.00
2.17
4.26
3.13
3.12
3.12
f1 (ppm)


8.464
8.460
7.780
7.758
7.737
7.465
7.461
7.443
7.439
7.329
7.308
3.957
2.781
2.410
OMe
O
O
Br
N
Ts
1.00
3.03
1.00
2.01
3.08
3.08
3.12

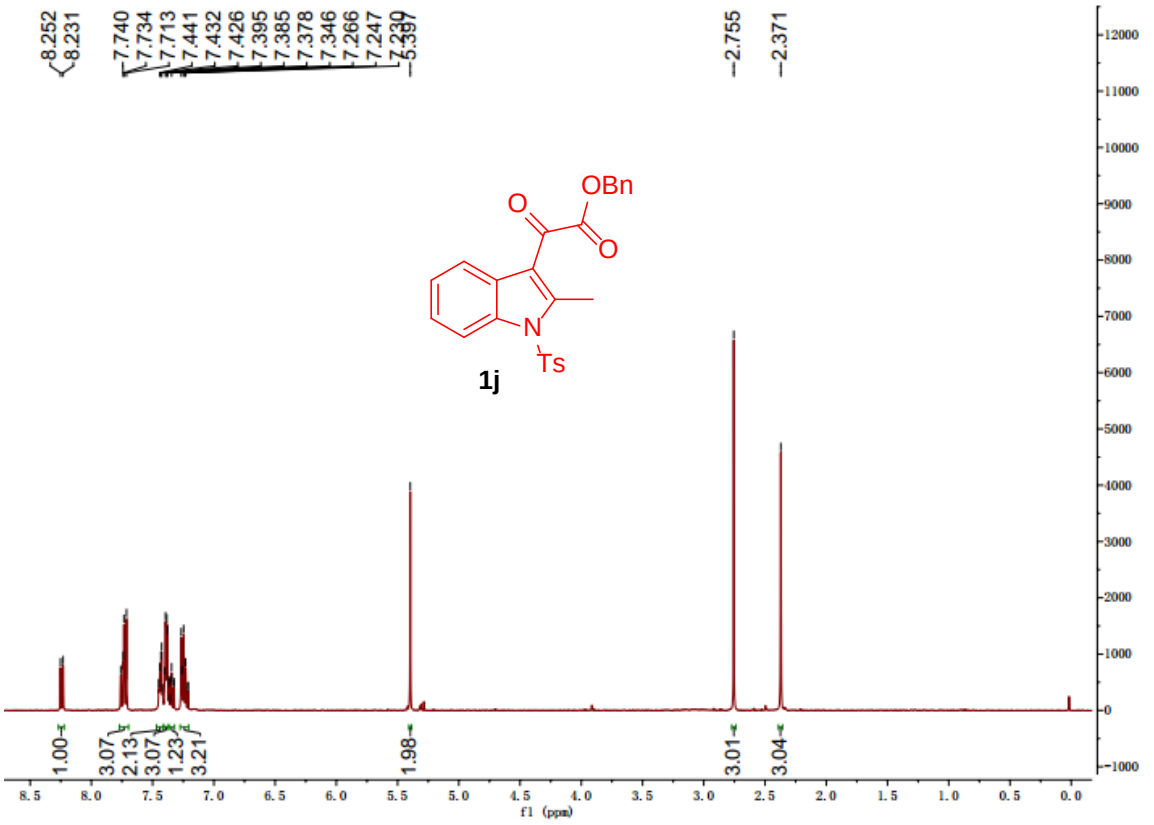
1g


8.268
8.247
7.913
7.895
7.892
7.750
7.730
7.371
7.353
7.334
7.332
7.328
7.324
7.320
7.305
7.302
7.260
4.440
4.428
4.426
4.422
4.410
4.408
4.404
4.393
4.390
4.386
2.856
2.312
2.299
1.388
1.383
1.377
1.371
1.365
1.362
1.359
1.353
1.347
1.341
OEt
O
O
N
Ts
1.00
1.01
2.04
2.10
1.98
2.07
3.02
3.11
3.13
f1 (ppm)

1h


8.254
8.235
7.943
7.925
7.721
7.703
7.343
7.326
7.305
7.295
7.274
7.258
7.164
7.145
5.270
5.255
5.244
5.202
2.857
2.217
1.330
1.314
Oi-Pr
O
O
N
Ts
1.00
0.95
1.95
2.11
1.98
1.00
2.97
3.05
6.12
f1 (ppm)

1i


8.252
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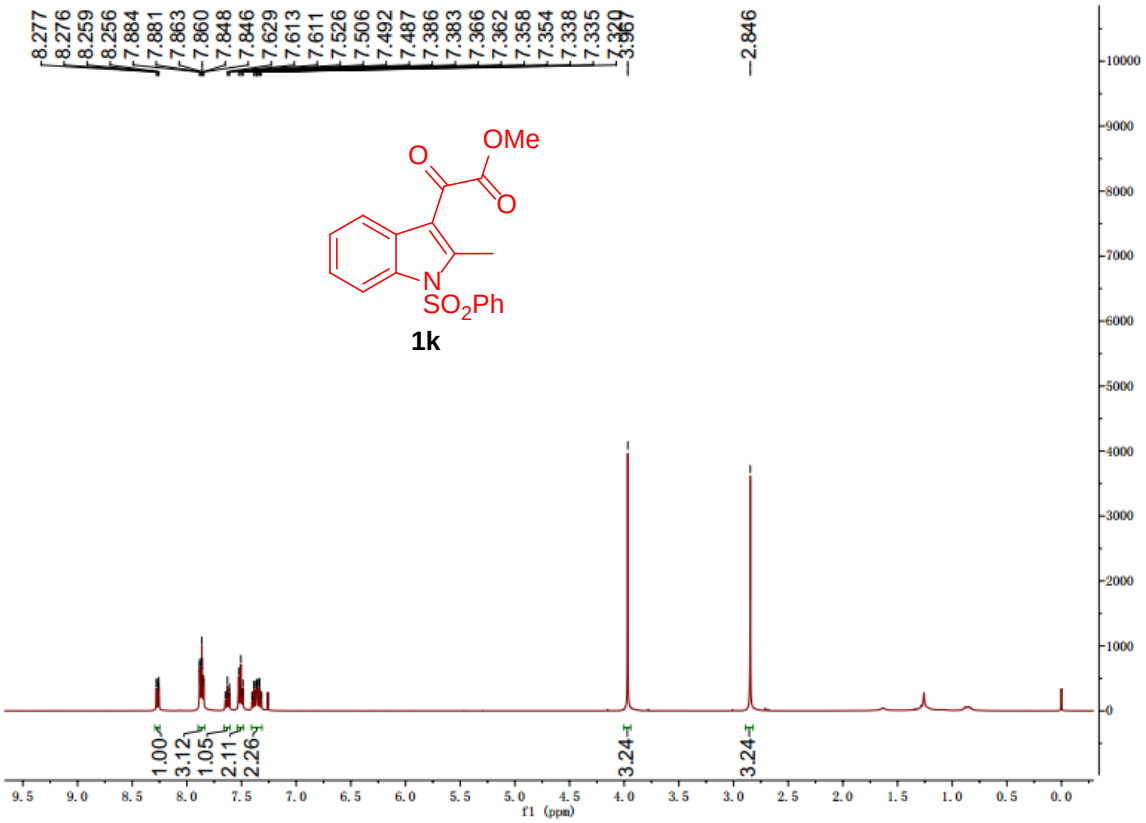
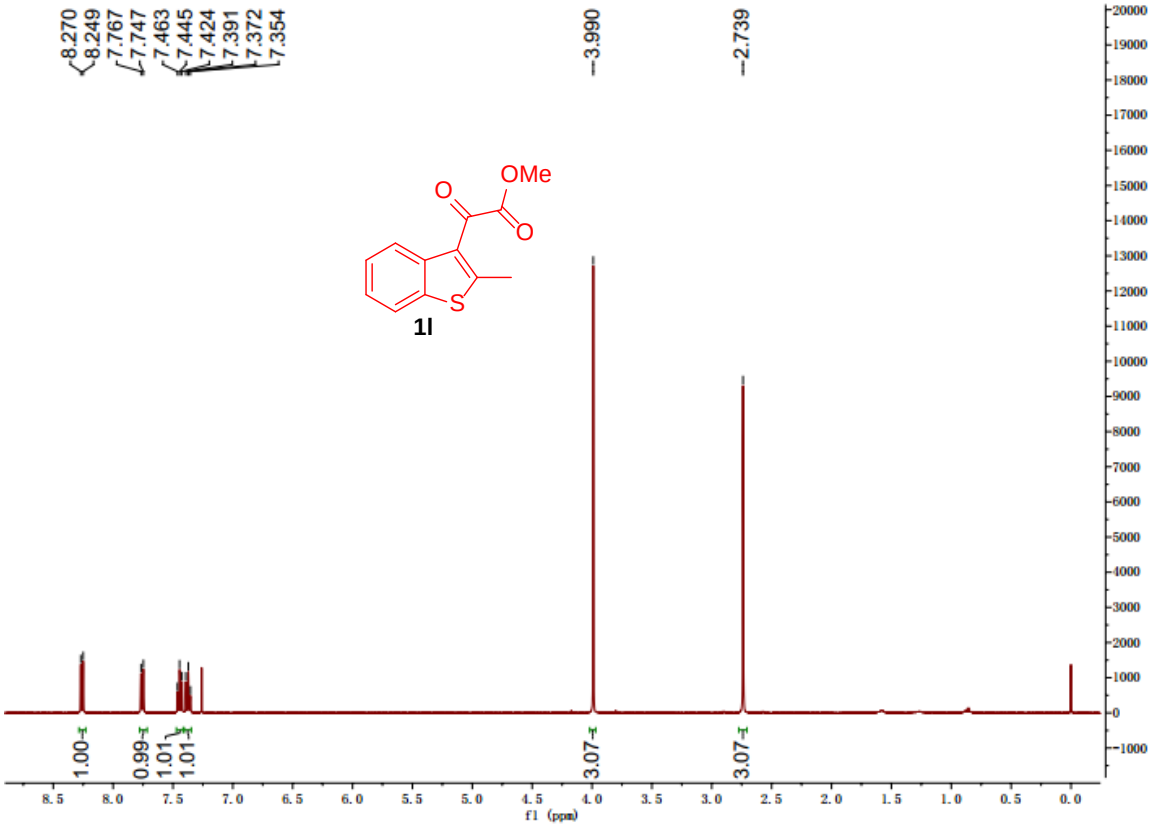
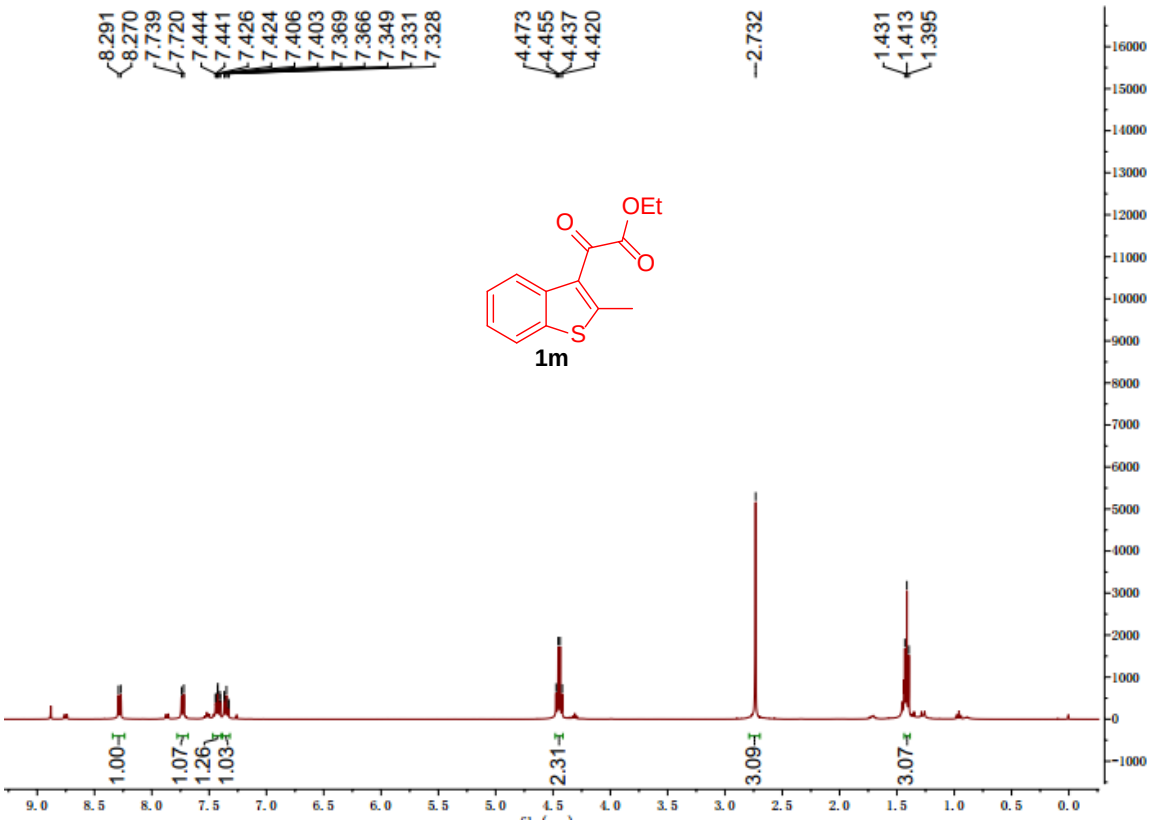
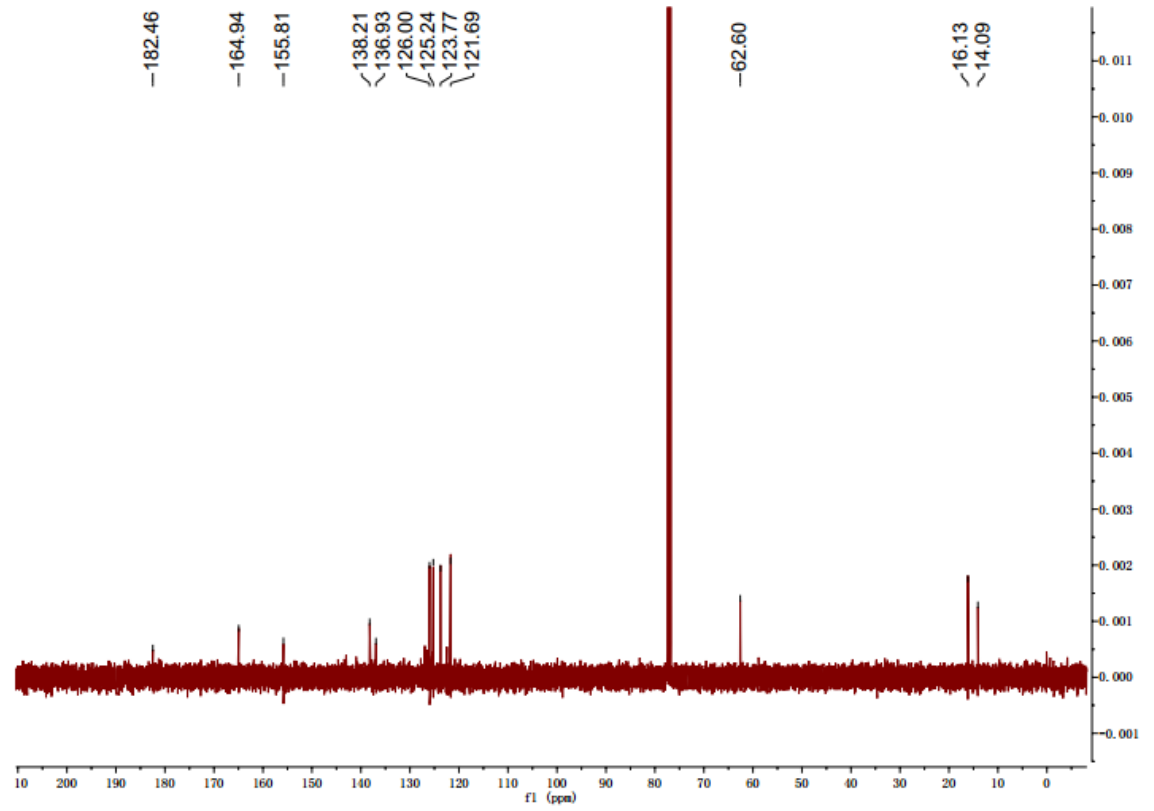
7.432
7.426
7.395
7.385
7.378
7.346
7.266
7.247
2.755
2.371
OBn
O
O
N
Ts
1.00
3.07
2.13
3.07
1.23
3.21
1.98
3.01
3.04
f1 (ppm)

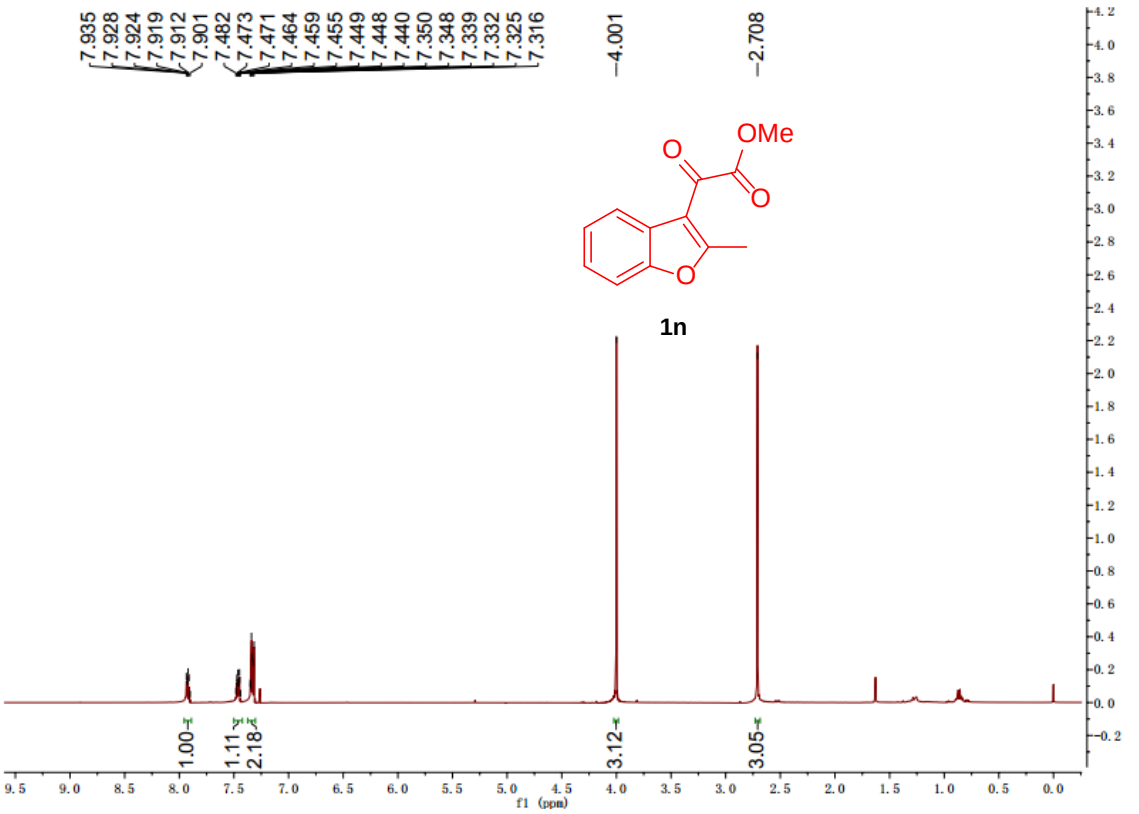
1j

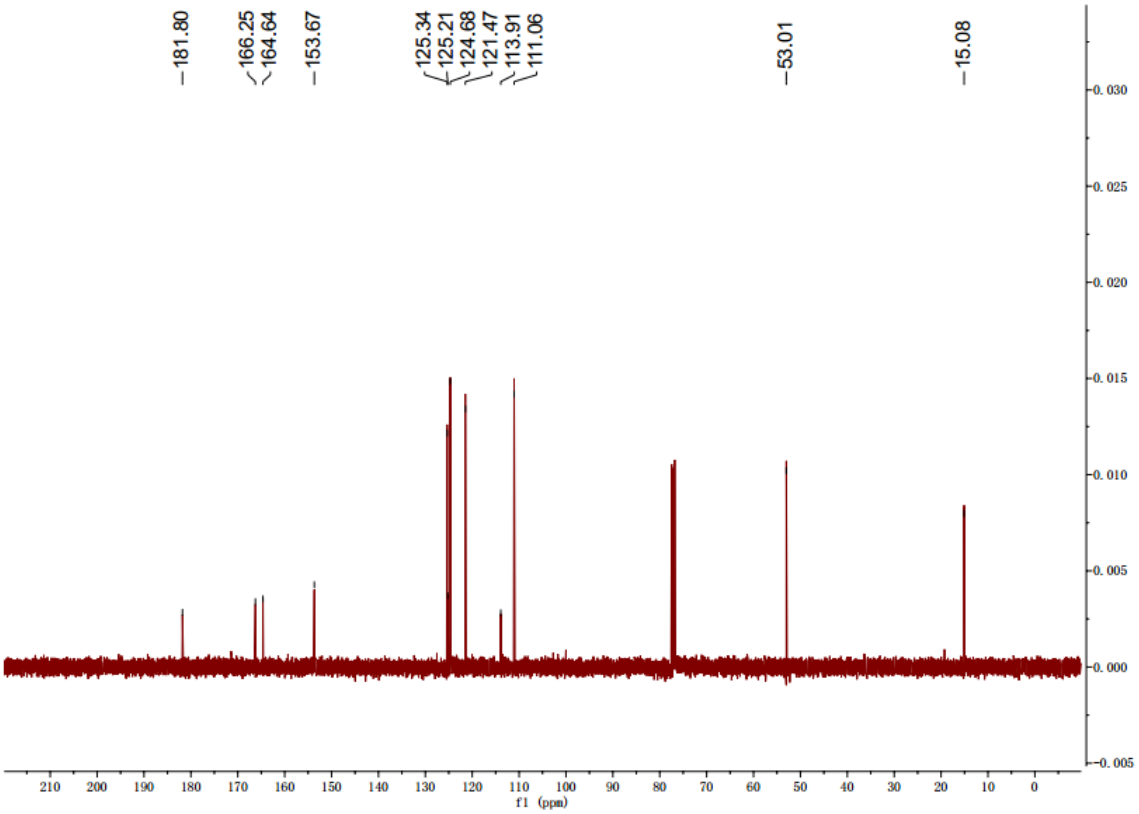

8.277
8.276
8.259
8.256
7.884
7.881
7.863
7.860
7.848
7.846
7.629
7.613
7.611
7.526
7.506
7.492
7.487
7.386
7.383
7.366
7.362
7.358
7.354
7.338
7.335
7.320
7.307
2.846
OMe
O
O
N
SO2Ph
1k
1.00
3.12
1.05
2.11
2.26
3.24
3.24
f1 (ppm)

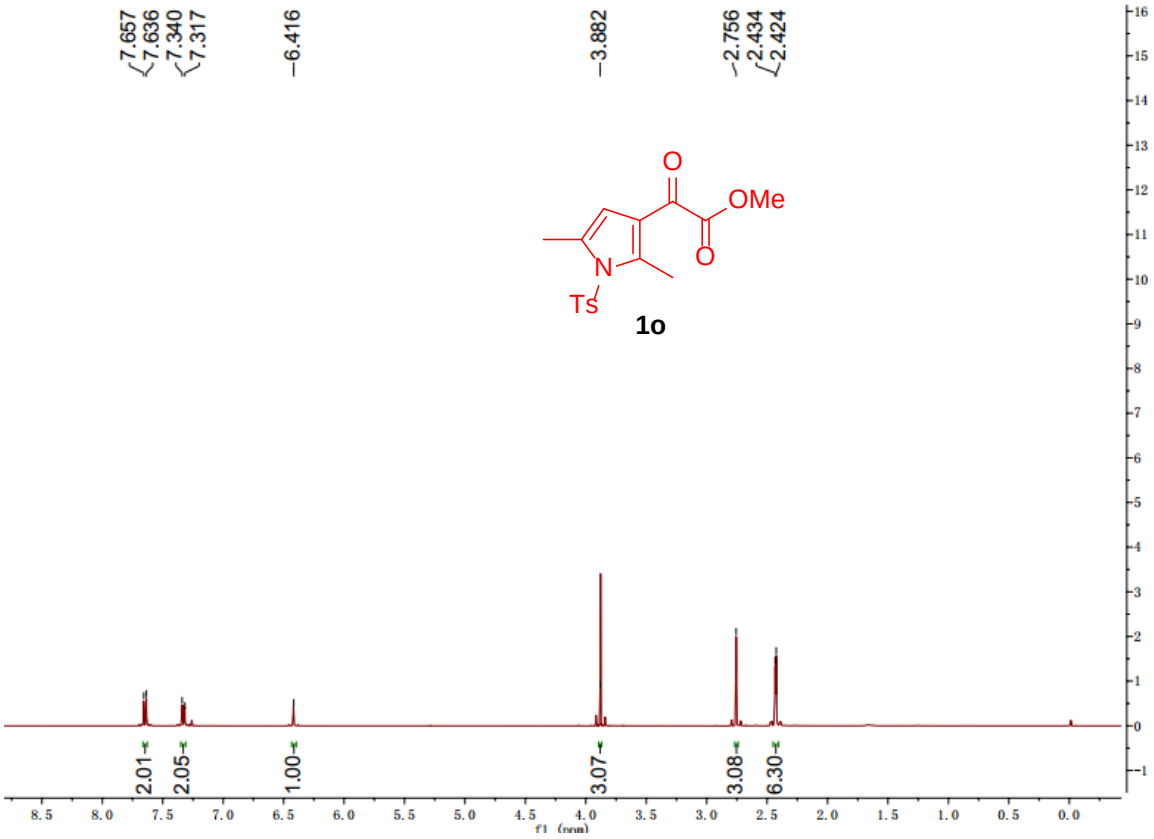

8.270
8.249
7.767
7.747
7.463
7.445
7.424
7.391
7.372
7.354
3.990
2.739
OMe
O
O
S
1l
1.00
0.99
1.01
1.01
3.07
3.07
f1 (ppm)


8.291
8.270
7.739
7.720
7.444
7.441
7.426
7.424
7.406
7.403
7.369
7.366
7.349
7.331
7.328
4.473
4.455
4.437
4.420
2.732
1.431
1.413
1.395
OEt
O
O
S
1m
1.00
1.07
1.26
1.03
2.31
3.09
3.07

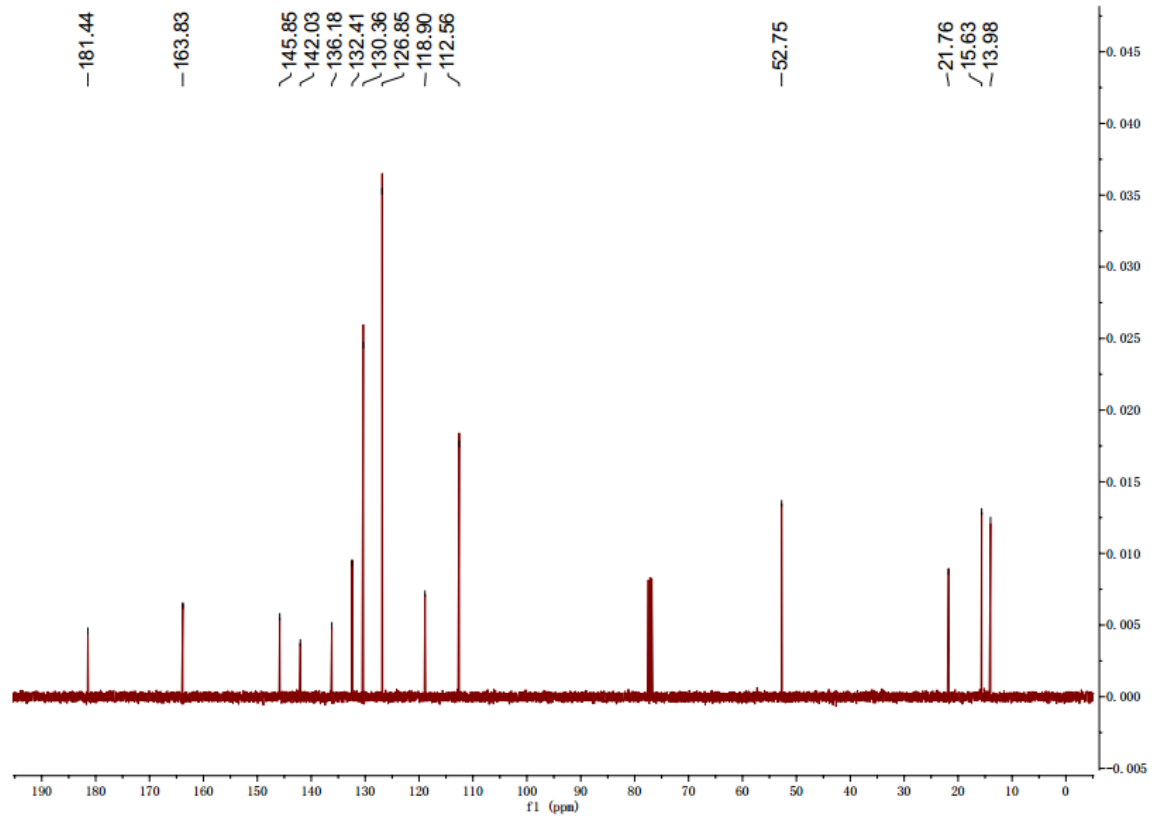

182.46
164.94
155.81
138.21
136.93
126.00
125.24
123.77
121.69
62.60
16.13
14.09
f1 (ppm)

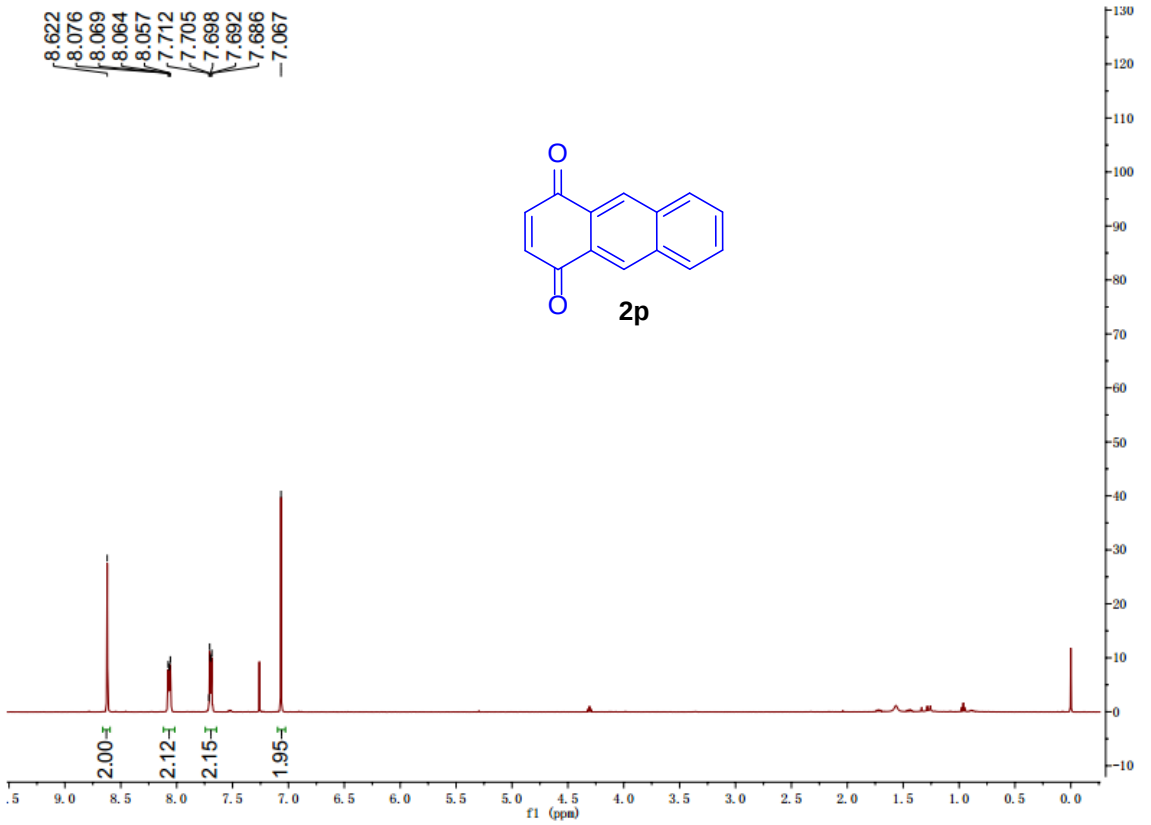

7.935
7.928
7.924
7.919
7.912
7.901
7.482
7.473
7.471
7.464
7.459
7.455
7.449
7.448
7.440
7.350
7.348
7.339
7.332
7.325
7.316
4.001
2.708
OMe
O
O
O
1n
1.00
1.11
2.18
3.12
3.05
f1 (ppm)

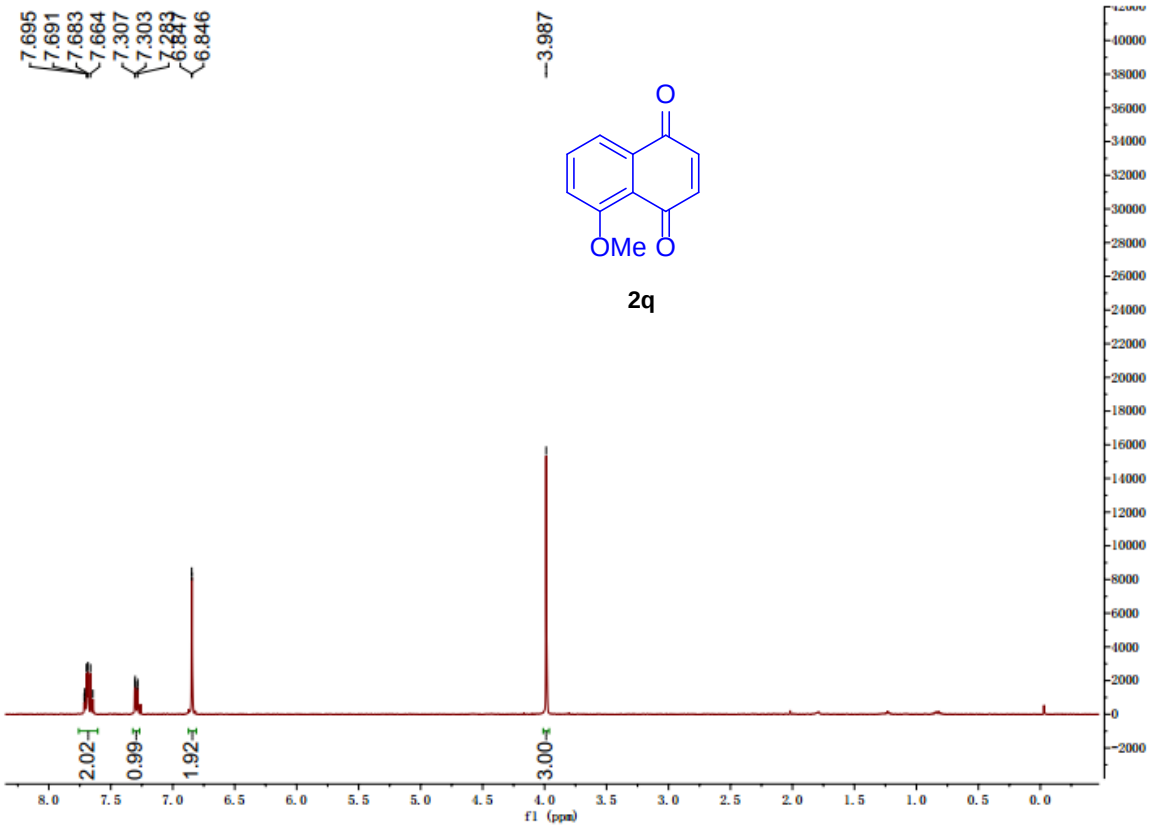

181.80
166.25
164.64
153.67
125.34
125.21
124.68
121.47
113.91
111.06
53.01
15.08
f1 (ppm)

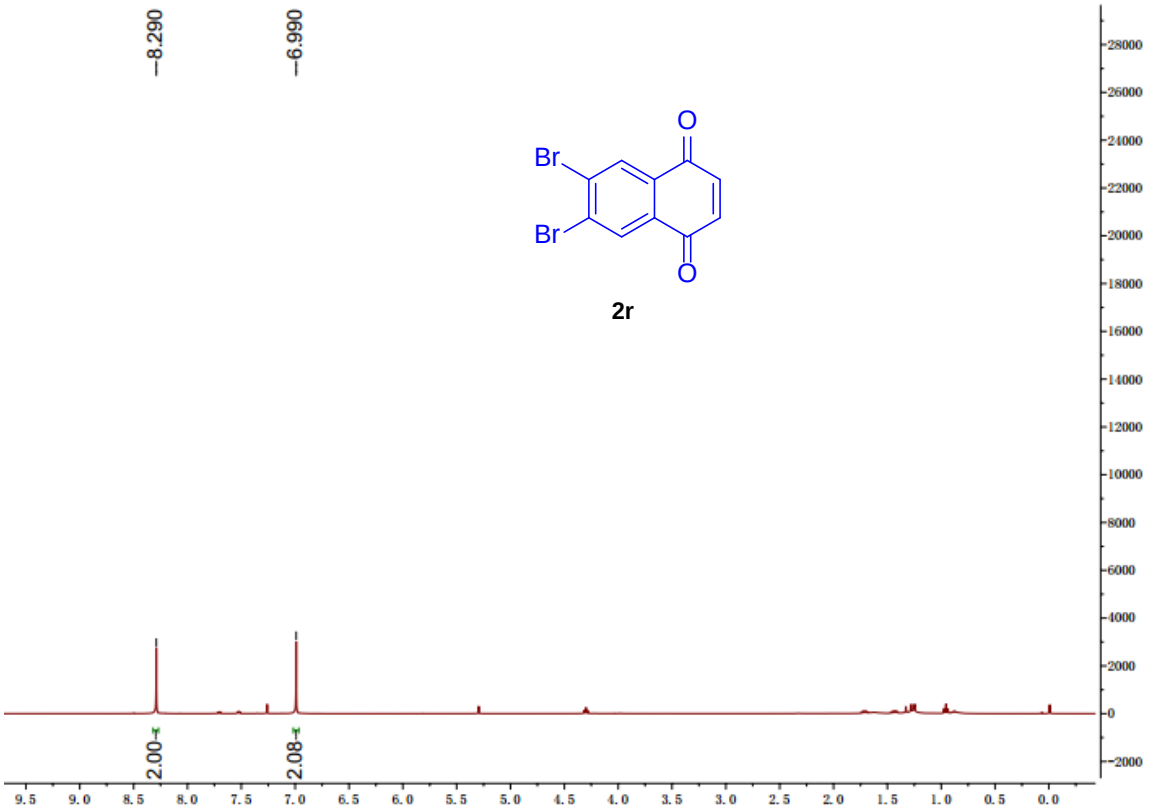

7.657
7.636
7.340
7.317
6.416
3.882
2.756
2.434
2.424
O
OMe
O
N
Ts
2.01
2.05
1.00
3.07
3.08
6.30
f1 (ppm)

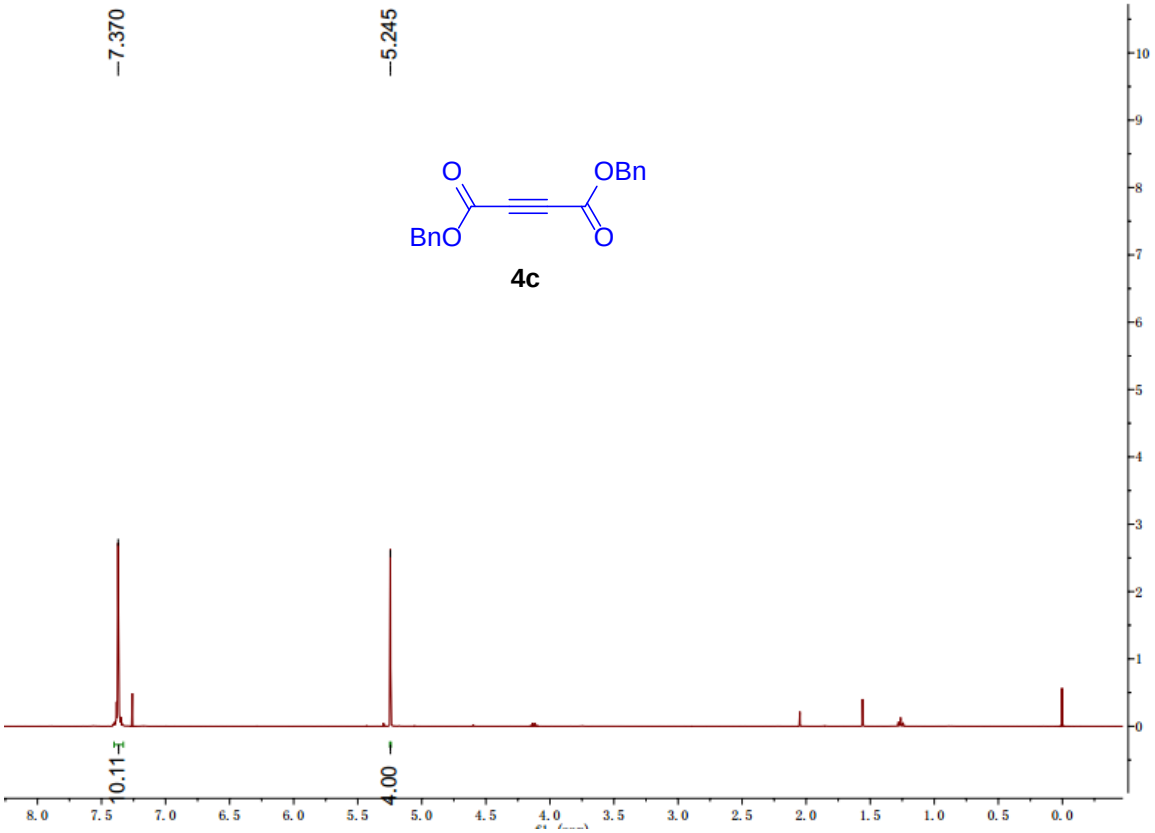
1o

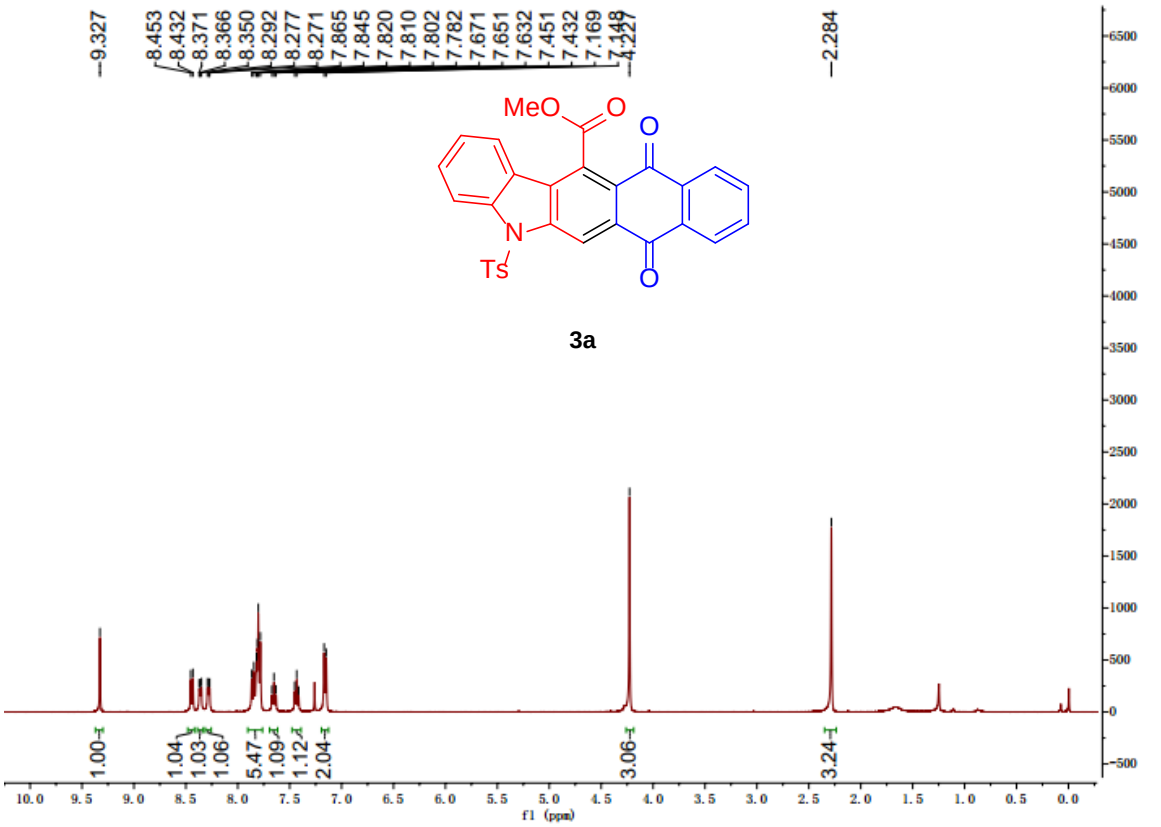

181.44
163.83
145.85
142.03
136.18
132.41
130.36
126.85
118.90
112.56
52.75
21.76
15.63
13.98
f1 (ppm)


8.622
8.076
8.069
8.064
8.057
7.712
7.705
7.698
7.692
7.686
7.067
O
O
2p
2.00
2.12
2.15
1.95
f1 (ppm)


7.695
7.691
7.683
7.664
7.307
7.303
7.283
6.847
6.846
3.987
O
OMe O
2q
2.02
0.99
1.92
3.00
f1 (ppm)


8.290
6.990
Br
Br
O
O
2r
2.00
2.08


7.370
5.245
O
OBn
BnO
O
4c
0.11
4.00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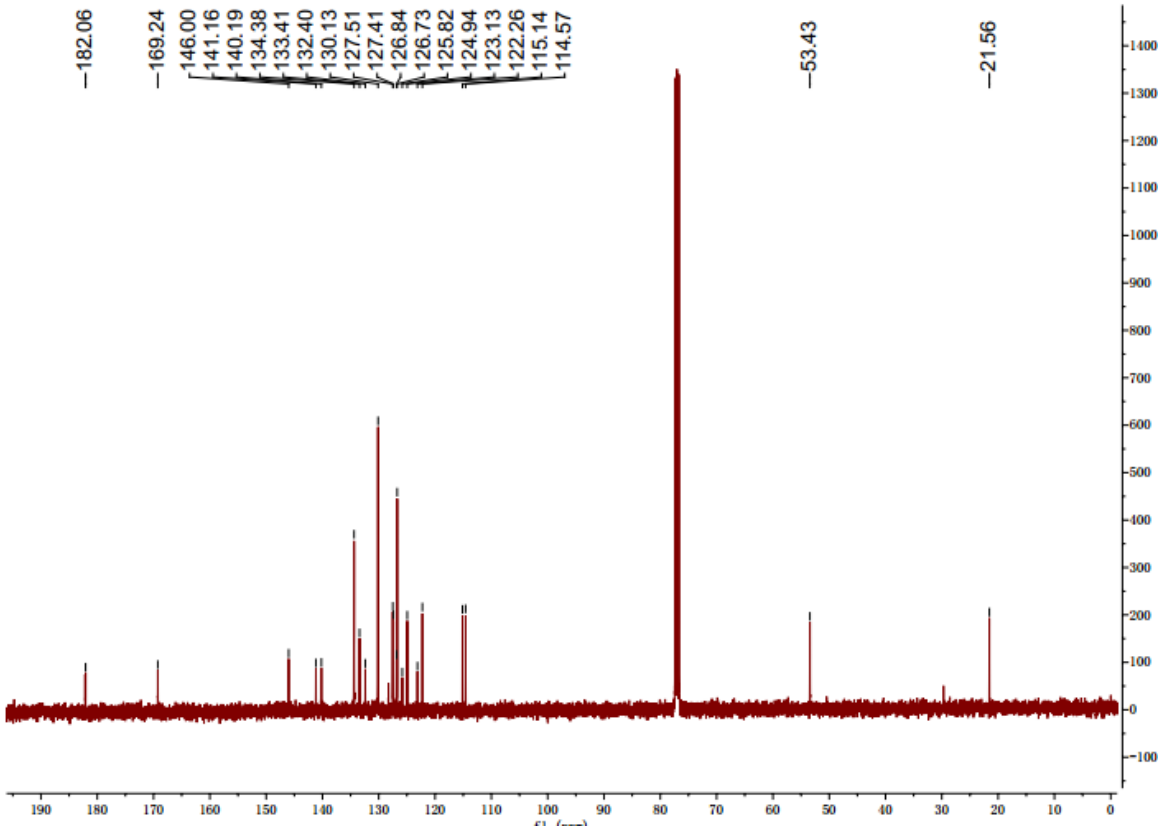
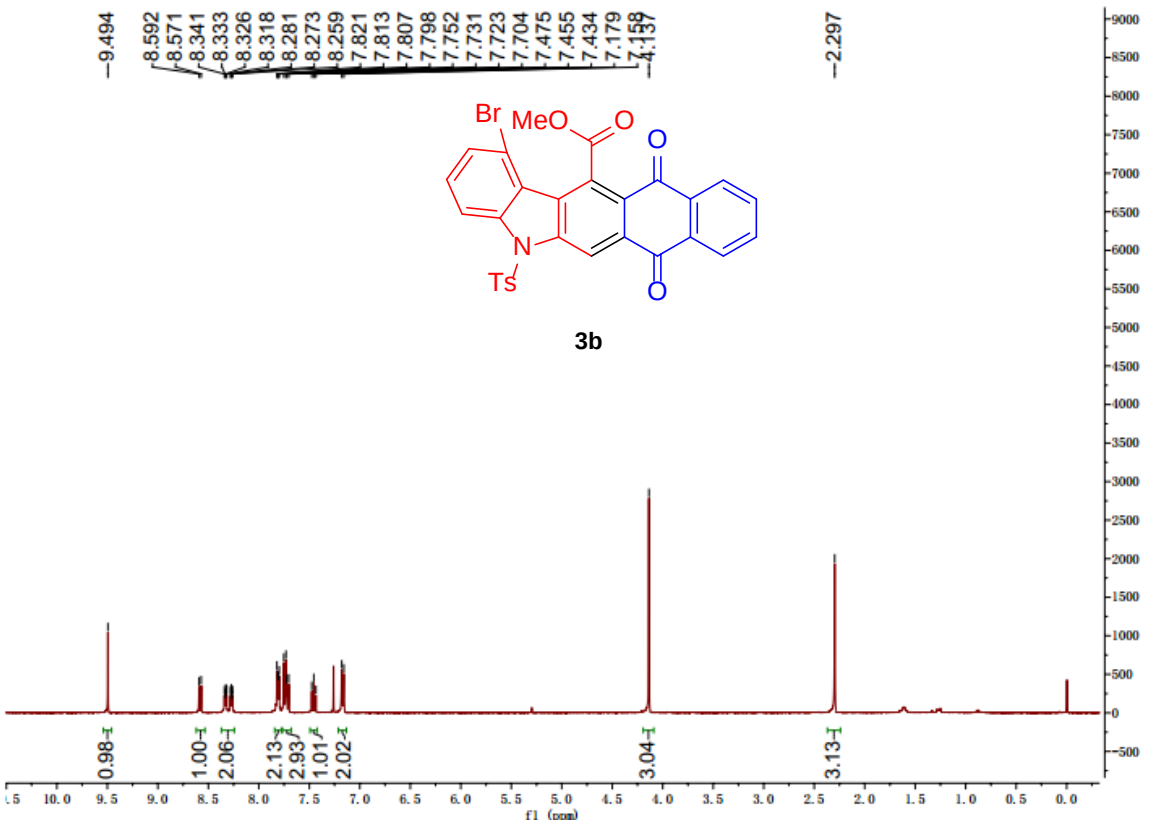
8.453
8.432
8.371
8.366
8.350
8.292
8.277
8.271
7.865
7.845
7.820
7.810
7.802
7.782
7.671
7.651
7.632
7.451
7.432
7.169
7.148
4.227
2.284
MeO
O
O
N
Ts
O
1.00
1.04
1.03
1.06
5.47
1.09
1.12
2.04
3.06
3.24
f1 (ppm)

3a


182.06
169.24
146.00
141.16
140.19
134.38
133.41
132.40
130.13
127.51
127.41
126.84
126.73
125.82
124.94
123.13
122.26
115.14
114.57
53.43
21.56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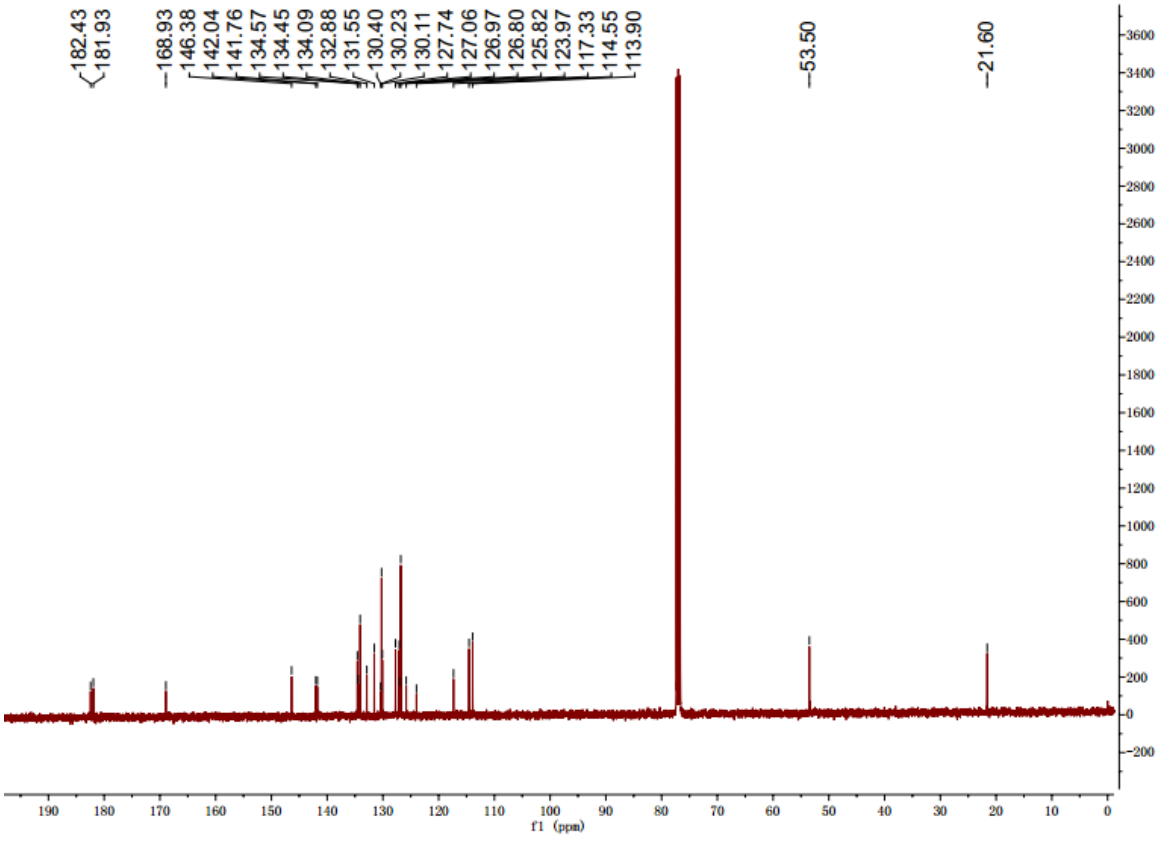
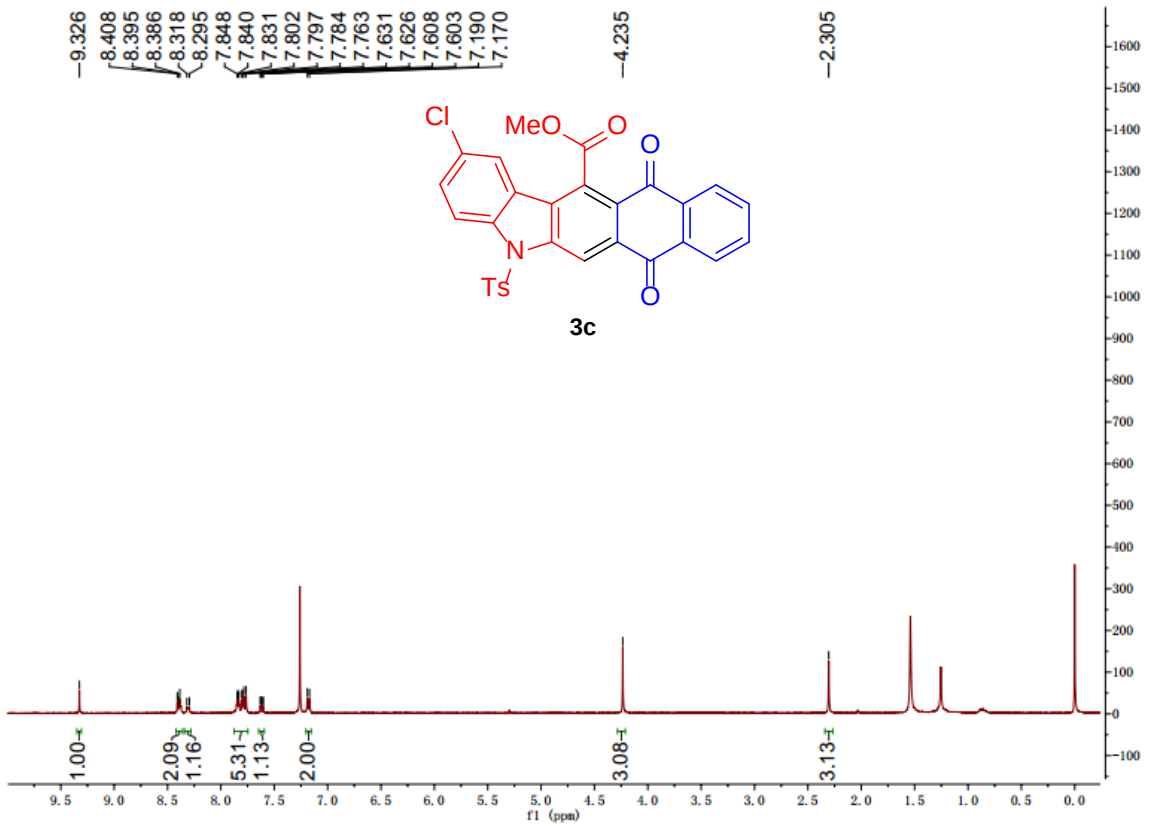
8.333
8.326
8.318
8.281
8.273
8.259
7.821
7.813
7.807
7.798
7.752
7.731
7.723
7.704
7.475
7.455
7.434
7.179
7.158
7.137
2.297
Br
MeO
O
O
N
Ts
O
0.98
1.00
2.06
2.13
2.93
1.01
2.02
3.04
3.13
f1 (ppm)

3b


182.43
181.93
168.93
146.38
142.04
141.76
134.57
134.45
134.09
132.88
131.55
130.40
130.23
130.11
127.74
127.06
126.97
126.80
125.82
123.97
117.33
114.55
113.90
53.50
21.60
f1 (ppm)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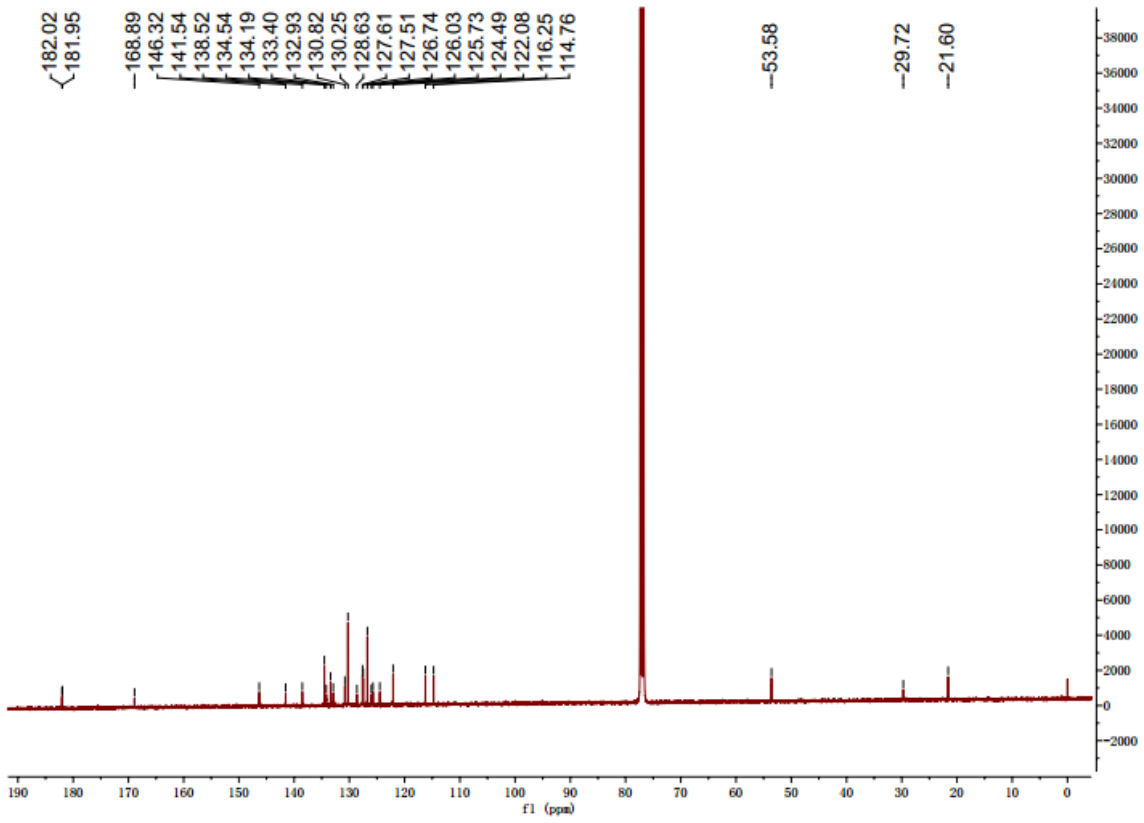
8.408
8.395
8.386
8.318
8.295
7.848
7.840
7.831
7.802
7.797
7.784
7.763
7.631
7.626
7.608
7.603
7.190
7.170
4.235
2.305
Cl
MeO
O
O
N
Ts
O
1.00
2.09
1.16
5.31
1.13
2.00
3.08
3.13
f1 (ppm)

3c


182.02
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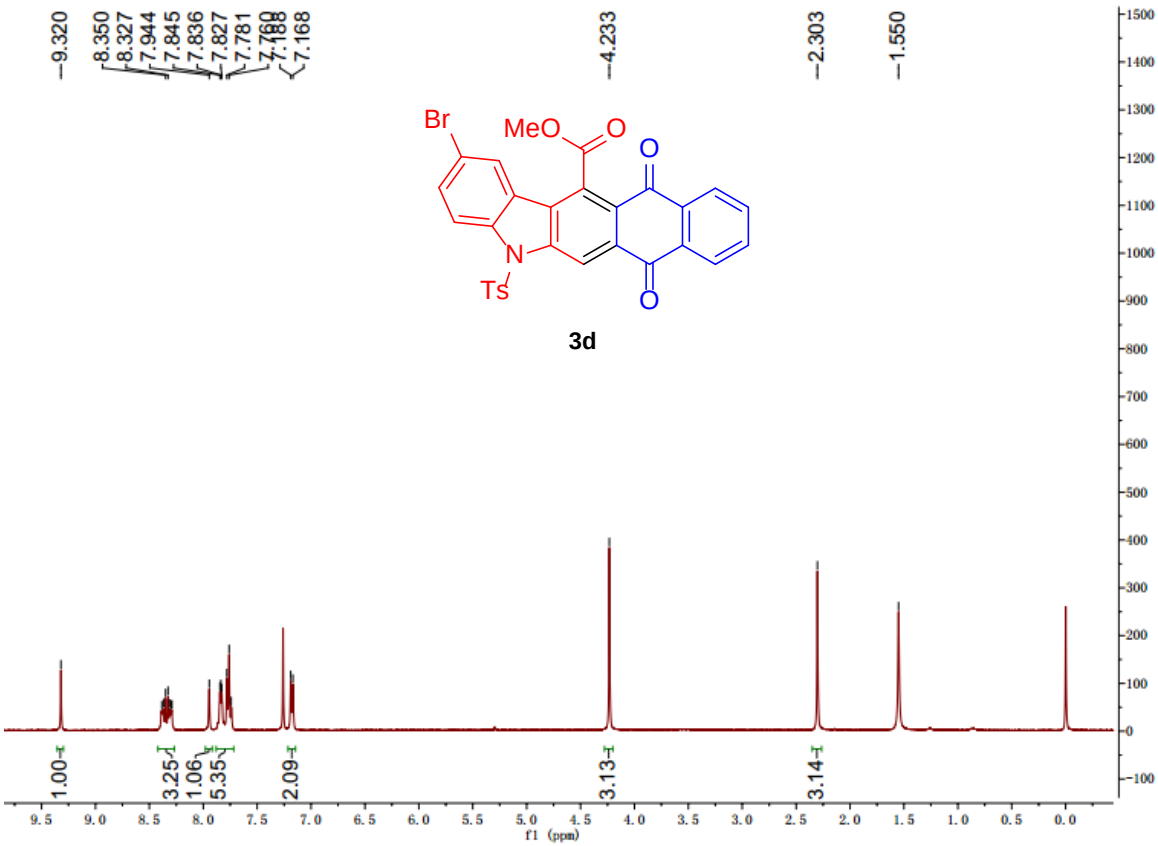
141.54
138.52
134.54
134.19
133.40
132.93
130.82
130.25
128.63
127.61
127.51
126.74
126.03
125.73
124.49
122.08
116.25
114.76
53.58
29.72
21.60
f1 (ppm)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8.350
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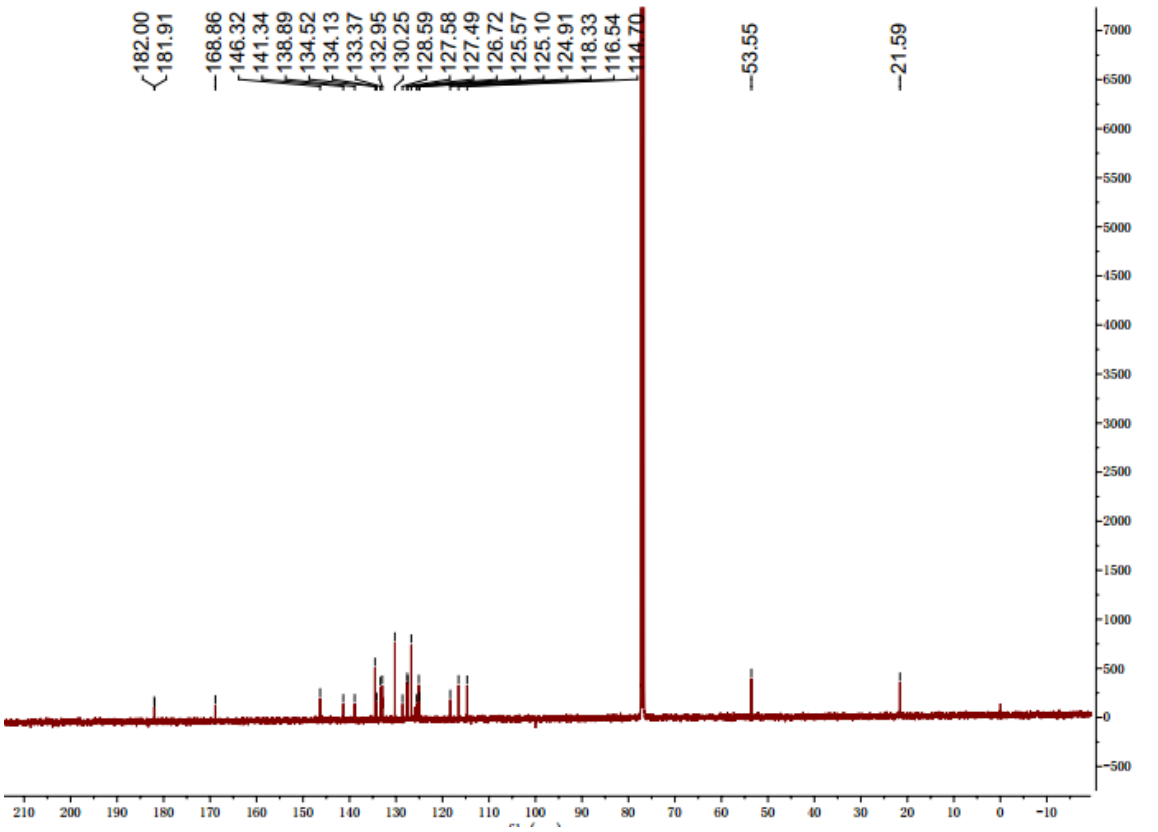
7.944
7.845
7.836
7.827
7.781
7.168
4.233
2.303
1.550
Br
MeO
O
O
N
Ts
O
1.00
3.25
1.06
5.35
2.09
3.13
3.14
f1 (ppm)

3d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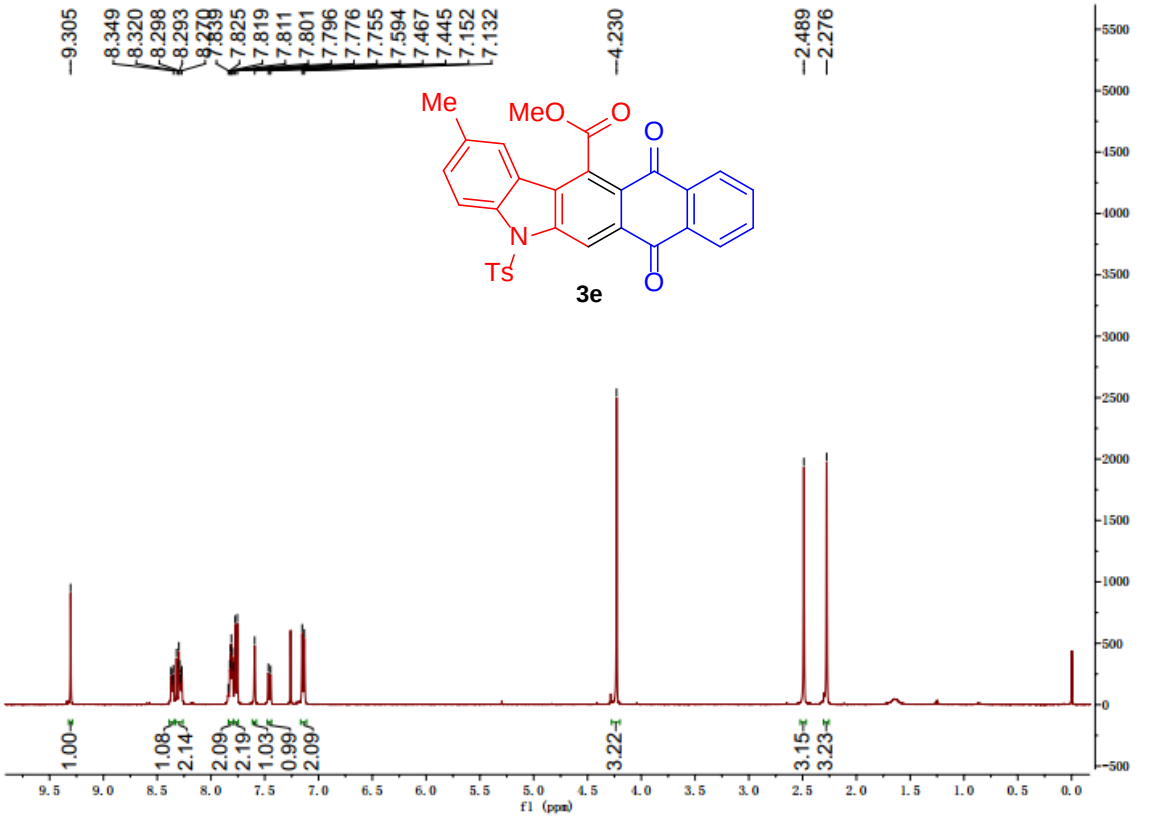
141.34
138.89
134.52
134.13
133.37
132.95
130.25
128.59
127.58
127.49
126.72
125.57
125.10
124.91
118.33
116.54
114.70
53.55
21.59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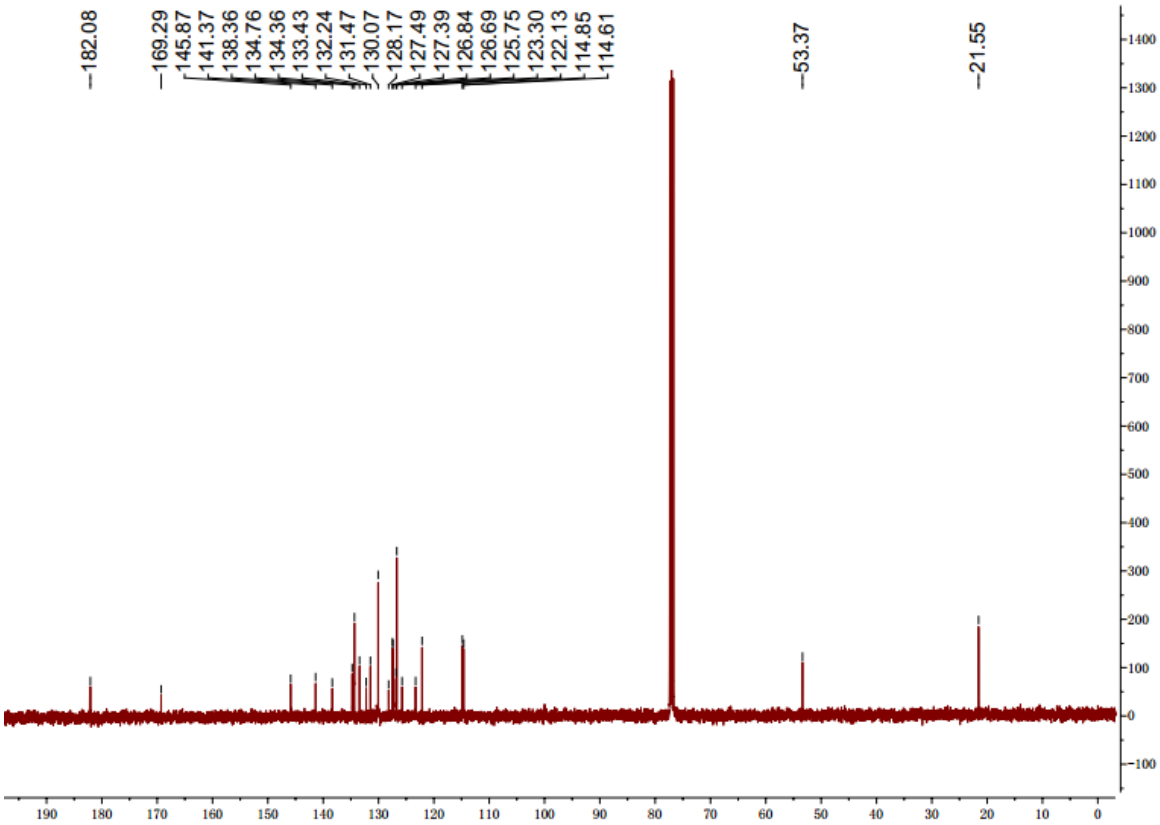
8.293
8.270
8.259
7.839
7.825
7.819
7.811
7.801
7.796
7.776
7.755
7.594
7.467
7.445
7.152
7.132
4.230
2.489
2.276
Me
MeO
O
O
N
Ts
O
3e
1.00
1.08
2.14
2.09
2.19
1.03
0.99
2.09
3.22
3.15
3.23
f1 (ppm)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145.87
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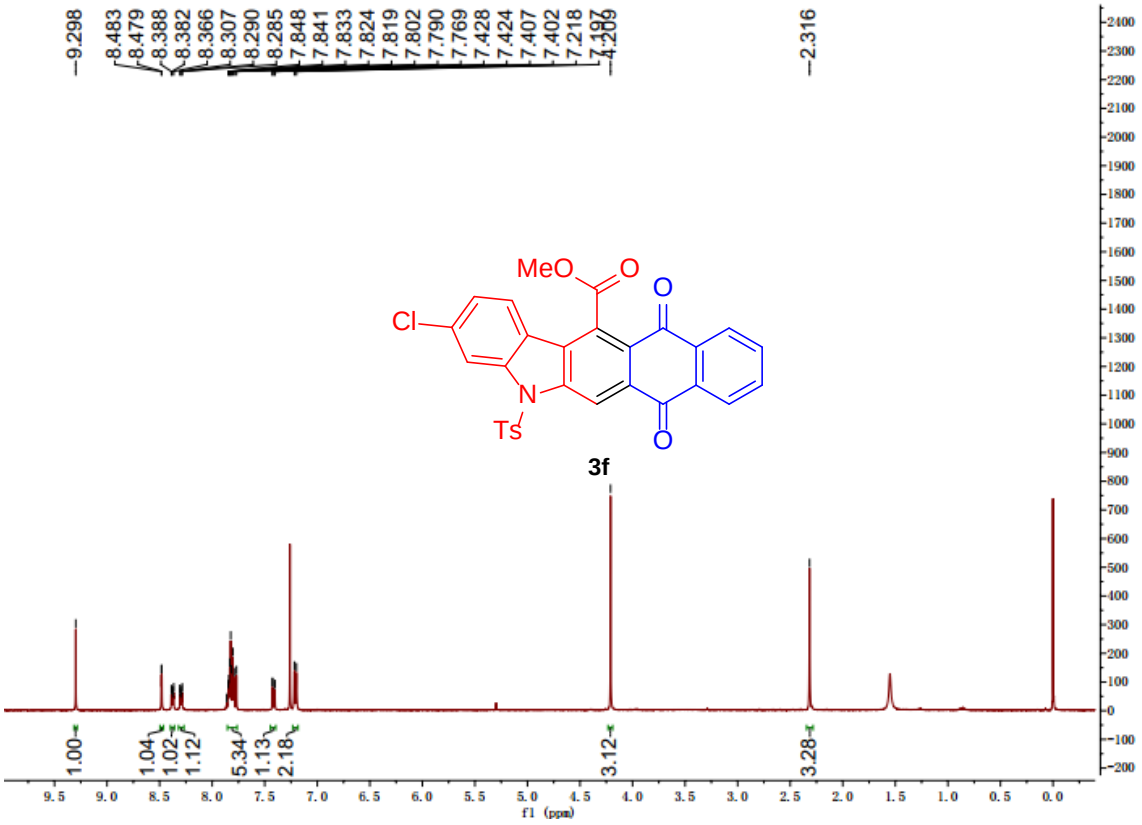
138.36
134.76
134.36
133.43
132.24
131.47
130.07
128.17
127.49
127.39
126.84
126.69
125.75
123.30
122.13
114.85
114.61
53.37
21.55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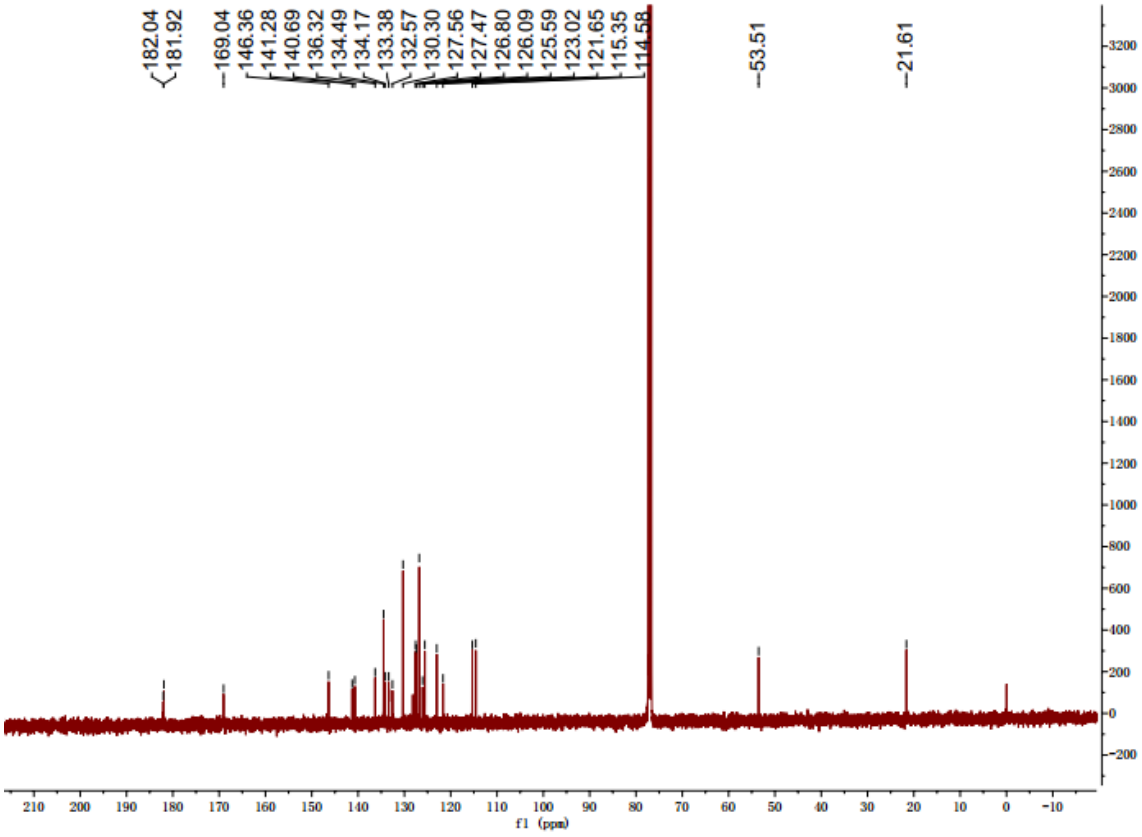
7.841
7.833
7.824
7.819
7.802
7.790
7.769
7.428
7.424
7.407
7.402
7.218
7.197
4.209
2.316
MeO
O
O
Cl
N
Ts
O
1.00
1.04
1.02
1.12
5.34
1.13
2.18
3.12
3.28
f1 (ppm)

3f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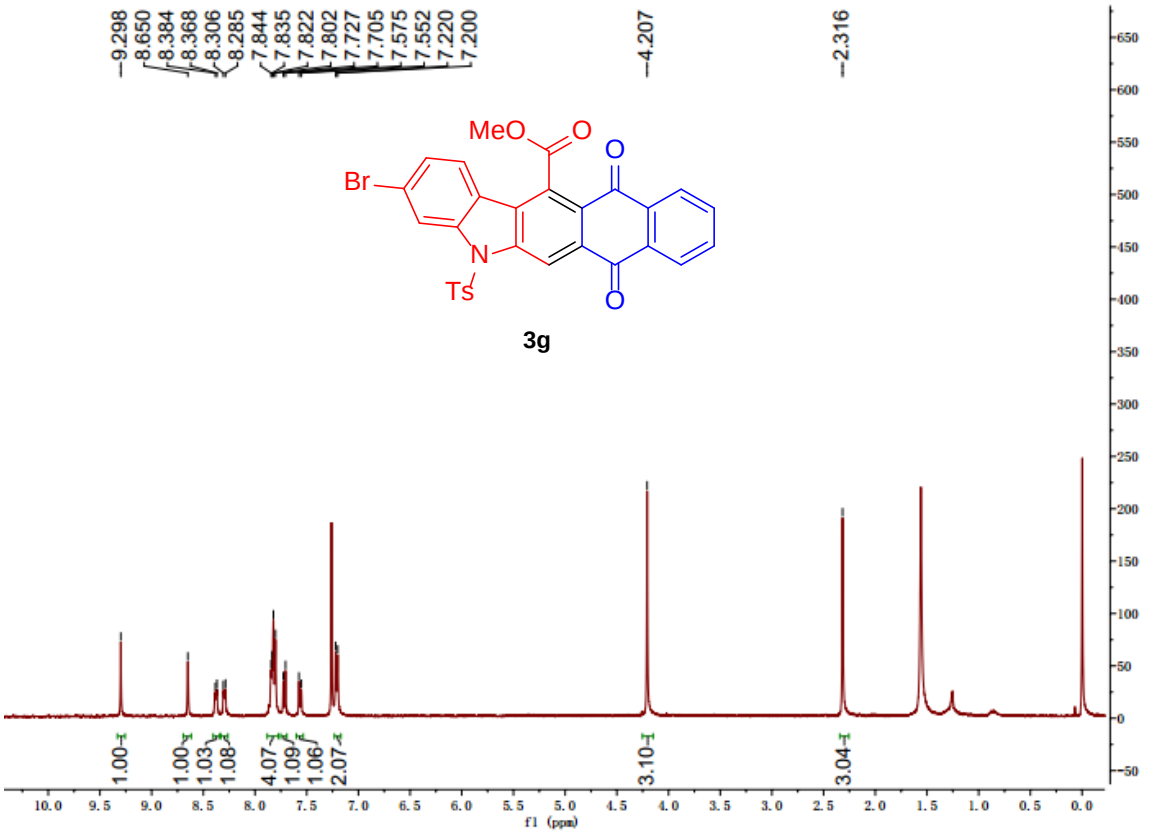
146.36
141.28
140.69
136.32
134.49
134.17
133.38
132.57
130.30
127.56
127.47
126.80
126.09
125.59
123.02
121.65
115.35
114.58
53.51
21.61
f1 (ppm)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7.575
7.552
7.220
7.200
4.207
2.316
MeO
O
O
Br
N
Ts
O
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1.08
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1.09
1.06
2.07
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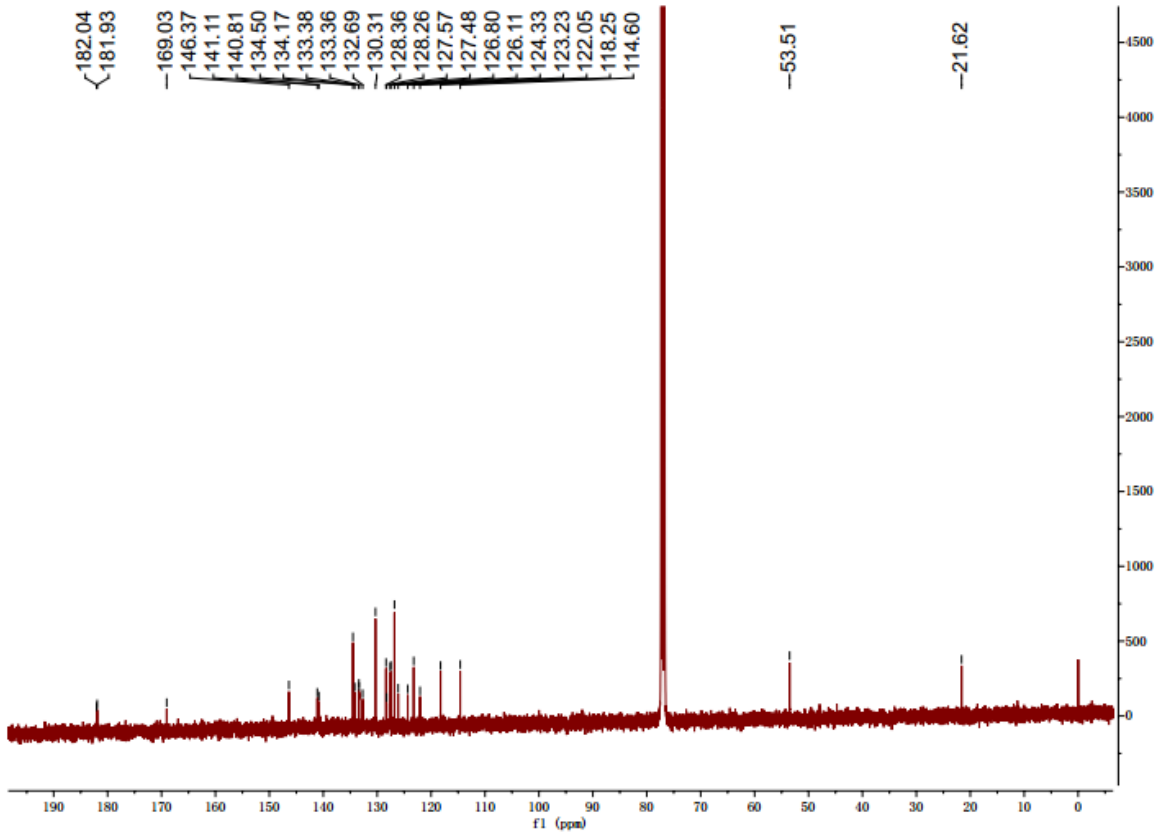
3.04
f1 (ppm)

3g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134.17
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130.31
128.36
128.26
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123.23
122.05
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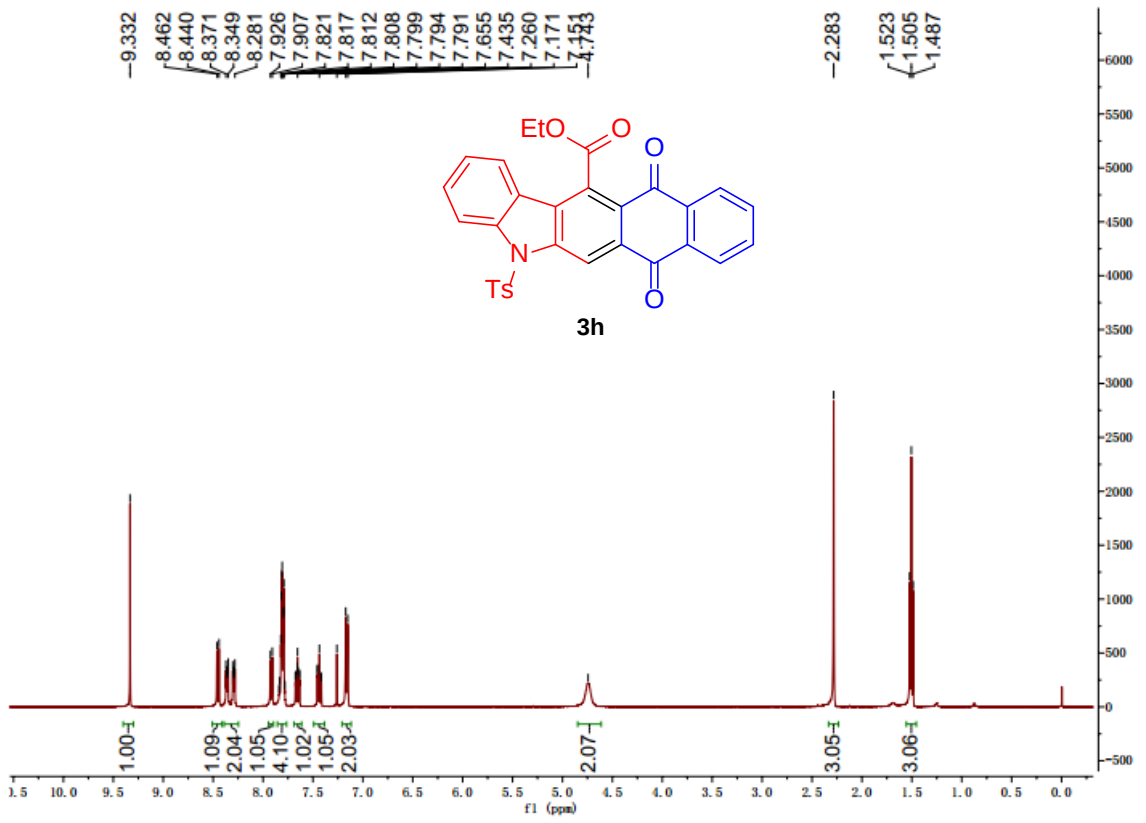
114.60
53.51
21.62
f1 (ppm)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7.794
7.791
7.655
7.435
7.260
7.171
7.151
4.743
2.283
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1.505
1.487
EtO
O
O
N
Ts
O
3h
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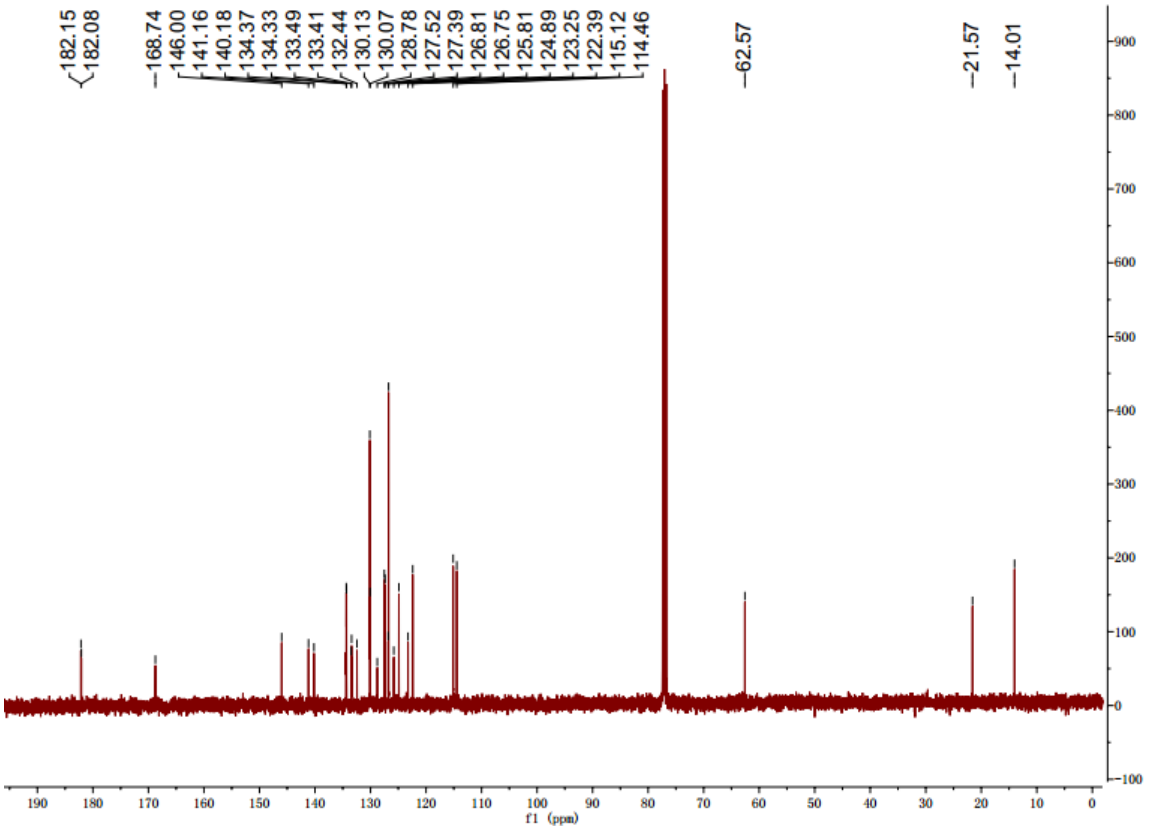
4.10
1.02
1.05
2.03
2.07
3.05
3.06
f1 (ppm)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130.07
128.78
127.52
127.39
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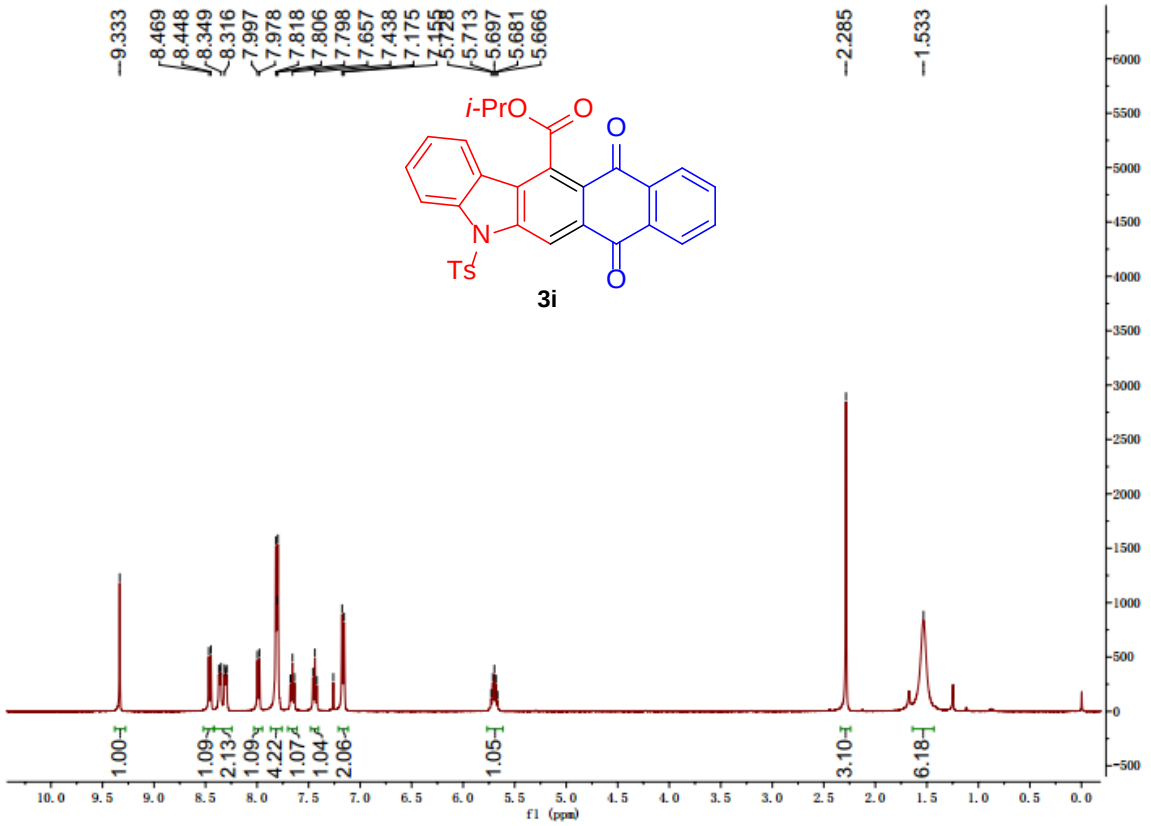
123.25
122.39
115.12
114.46
62.57
21.57
14.01
f1 (ppm)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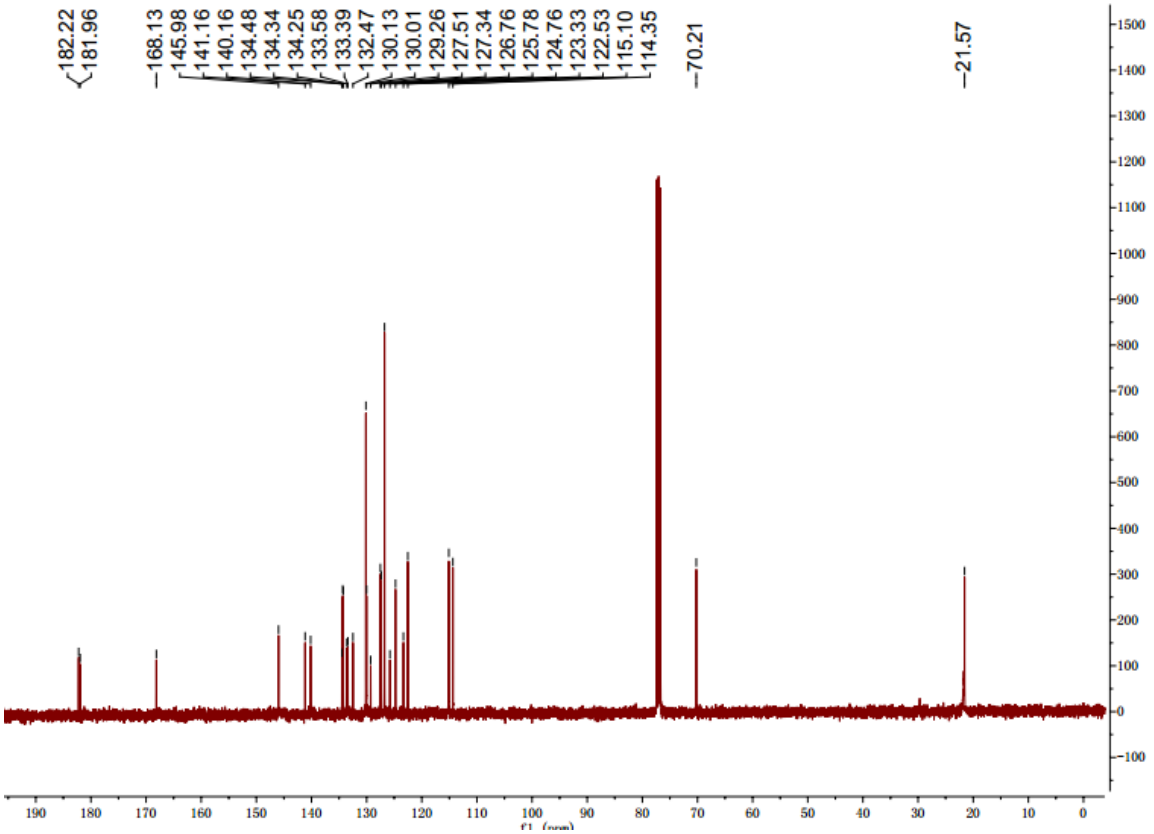
7.438
7.175
7.155
5.728
5.713
5.697
5.681
5.666
2.285
1.533
i-PrO
O
O
N
Ts
O
3i
1.00
1.09
2.13
1.09
4.22
1.07
1.04
2.06
1.05
3.10
6.18
f1 (ppm)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130.01
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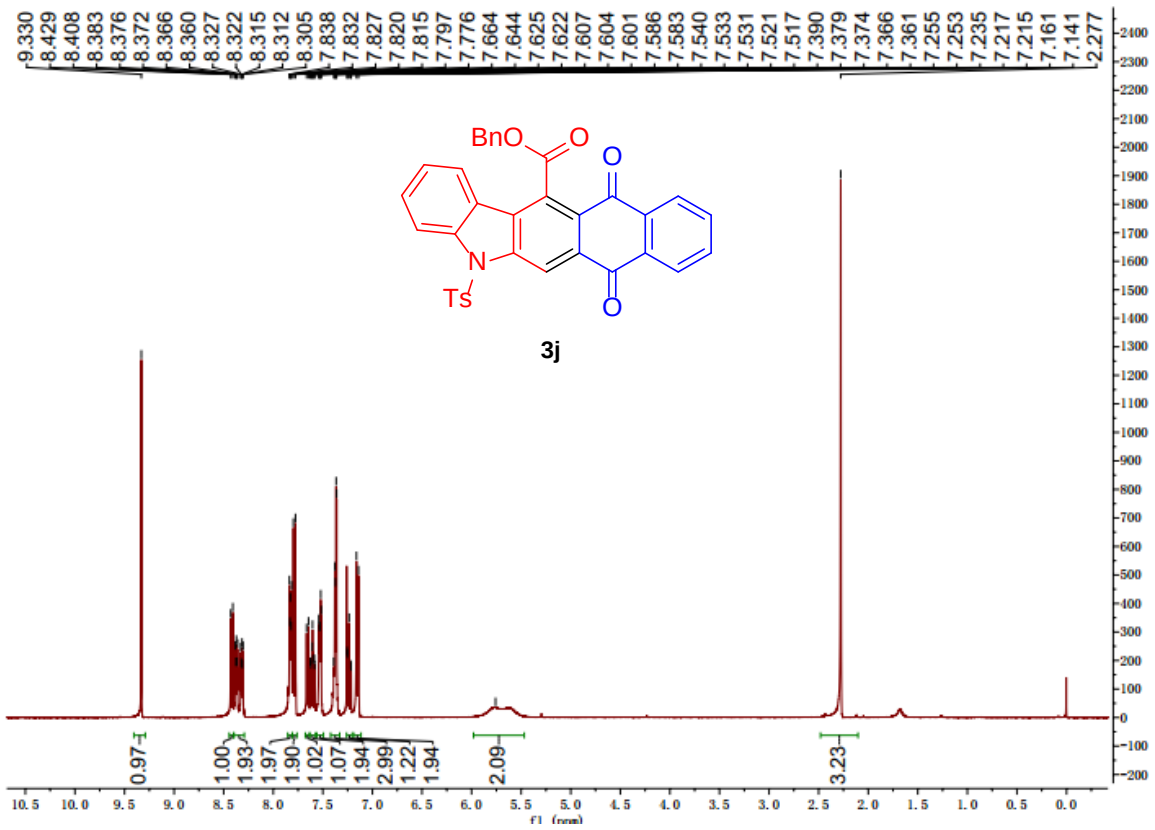
123.33
122.53
115.10
114.35
70.21
21.57
f1 (ppm)



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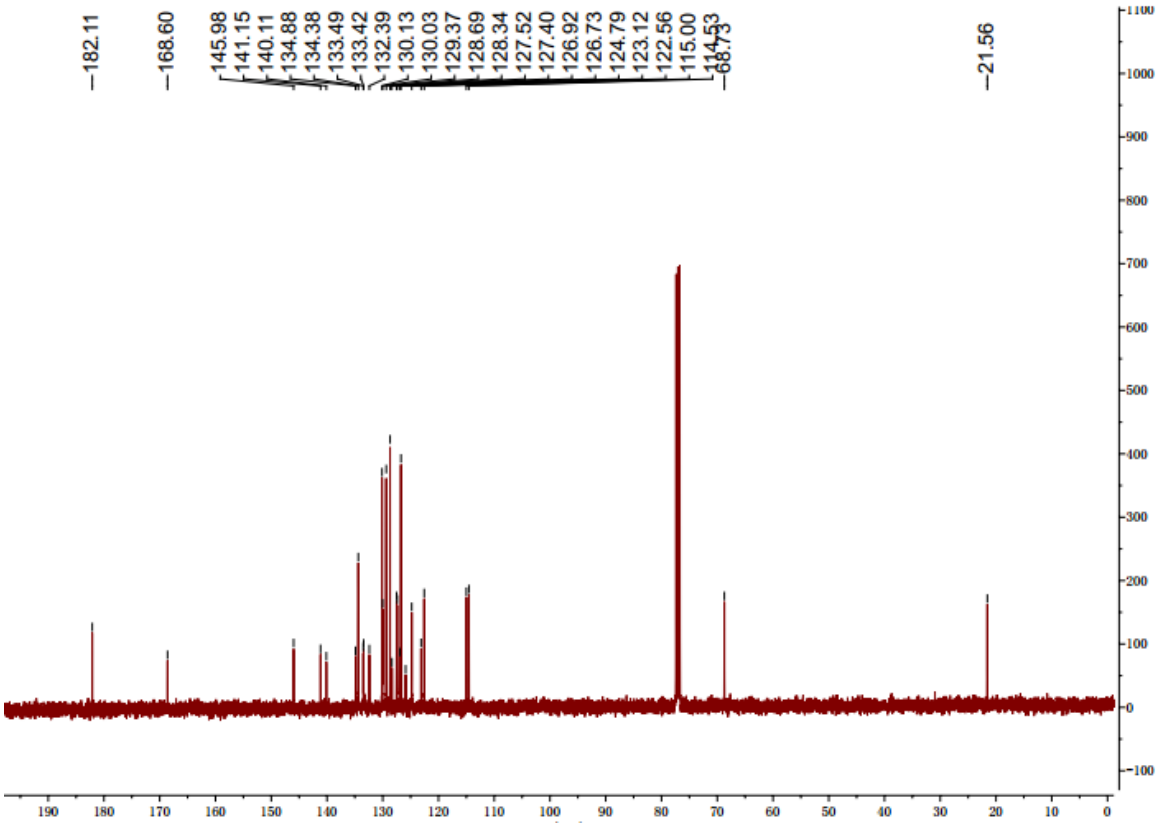

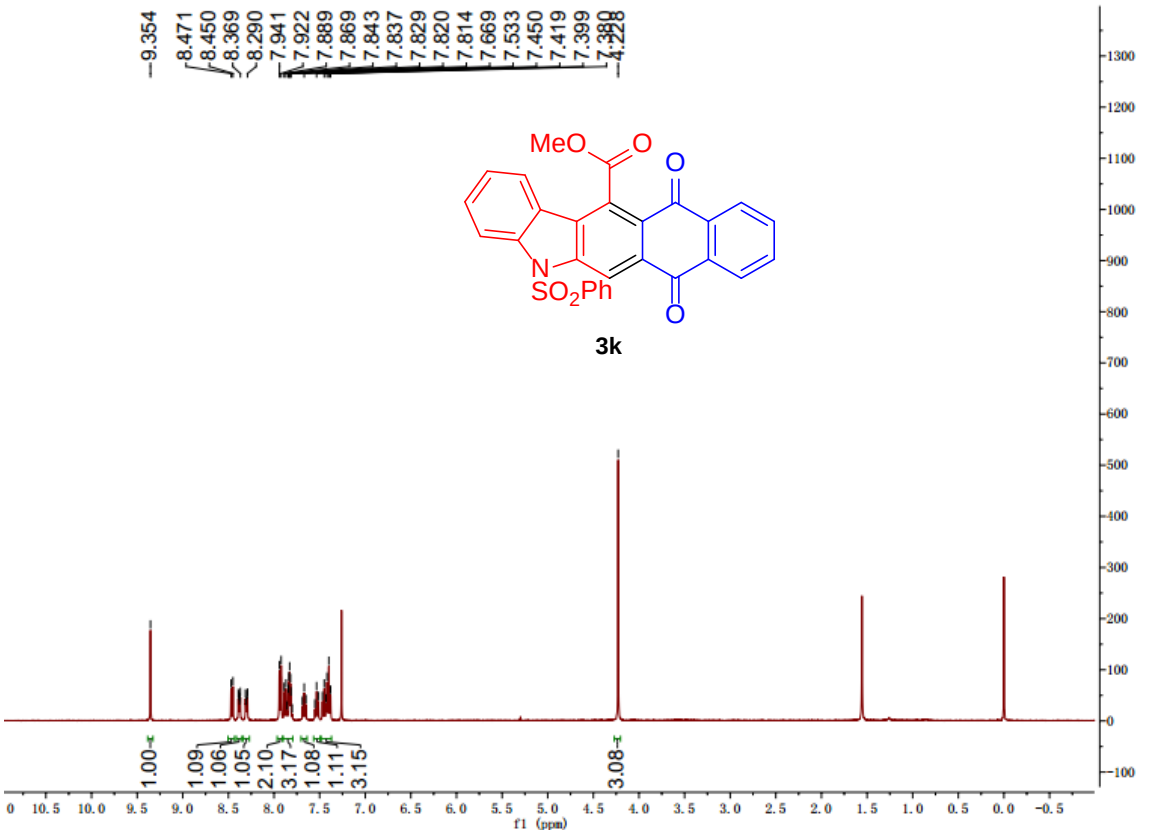
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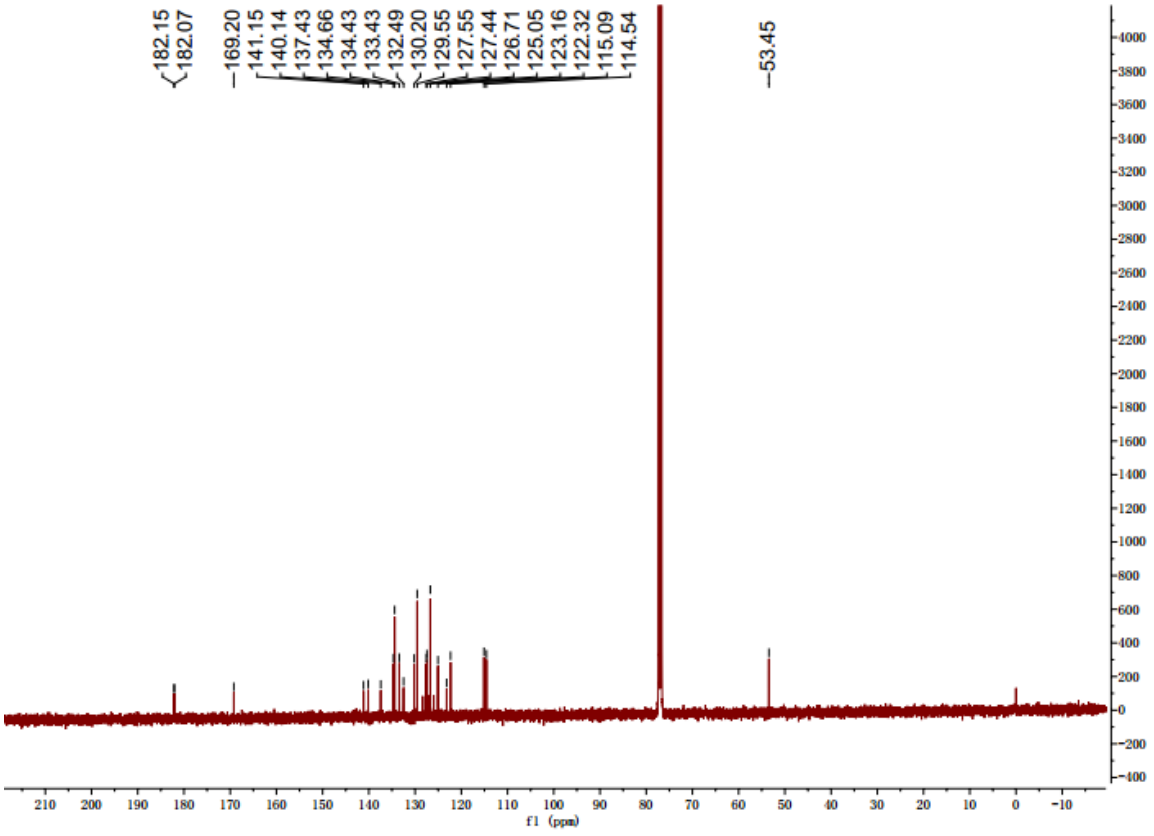
7.889
7.869
7.843
7.837
7.829
7.820
7.814
7.669
7.533
7.450
7.419
7.399
4.228
MeO
O
O
N
SO2Ph
O
3k
1.00
1.09
1.06
1.05
2.10
3.17
1.08
1.11
3.15
3.08
f1 (ppm)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137.43
134.66
134.43
133.43
132.49
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129.55
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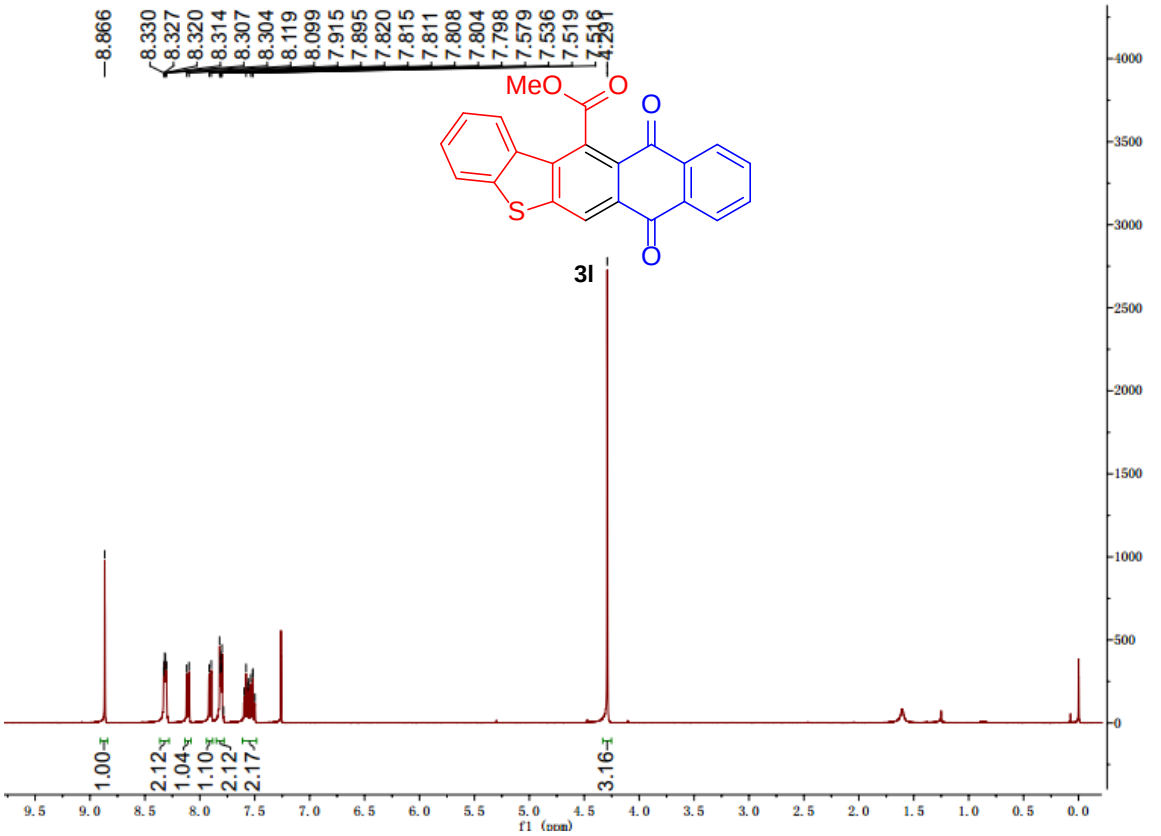
127.44
126.71
125.05
123.16
122.32
115.09
114.54
53.45
f1 (ppm)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8.307
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8.119
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7.915
7.895
7.820
7.815
7.811
7.808
7.804
7.798
7.579
7.536
7.519
7.516
4.291
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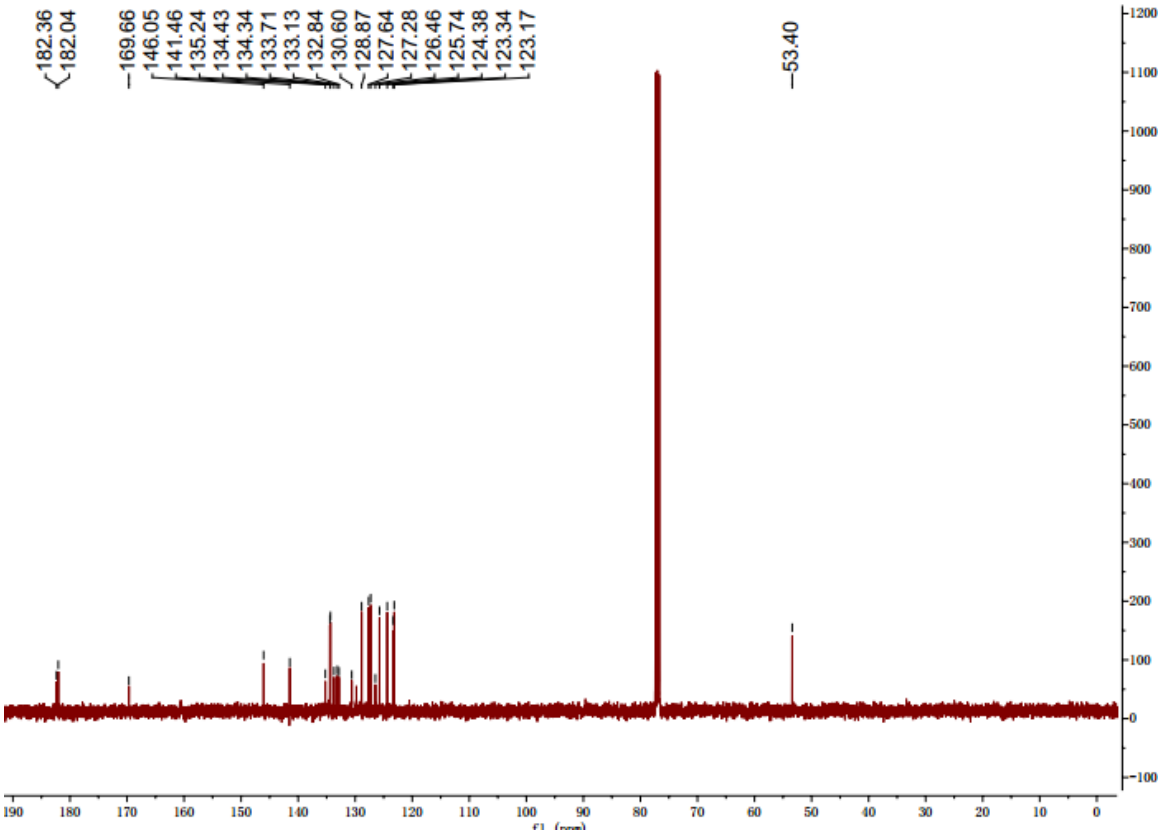
O
S
O
3l
1.00
2.12
1.04
1.10
2.12
2.17
3.16
f1 (ppm)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135.24
134.43
134.34
133.71
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132.84
130.60
128.87
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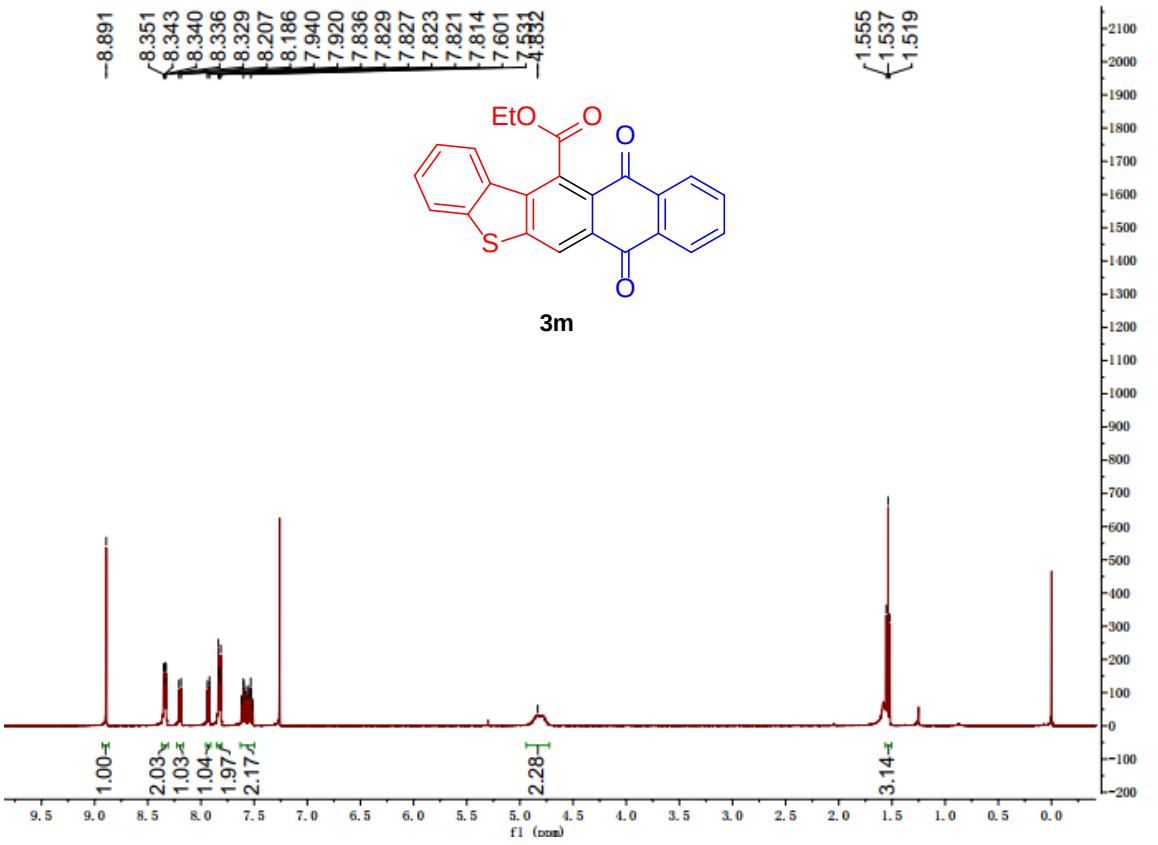
127.28
126.46
125.74
124.38
123.34
123.17
53.40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7.823
7.821
7.814
7.601
7.832
1.555
1.537
1.519
EtO
O
O
S
O
3m
1.00
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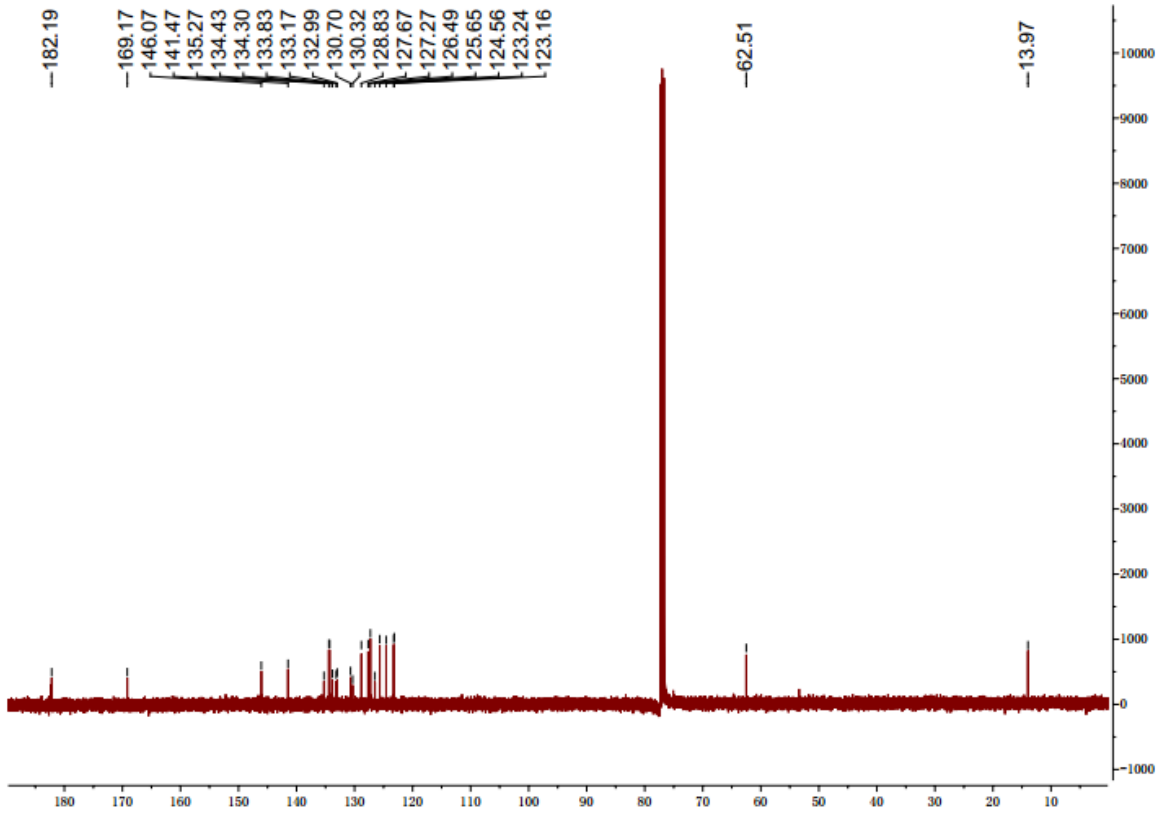
1.03
1.04
1.97
2.17
2.28
3.14
f1 (ppm)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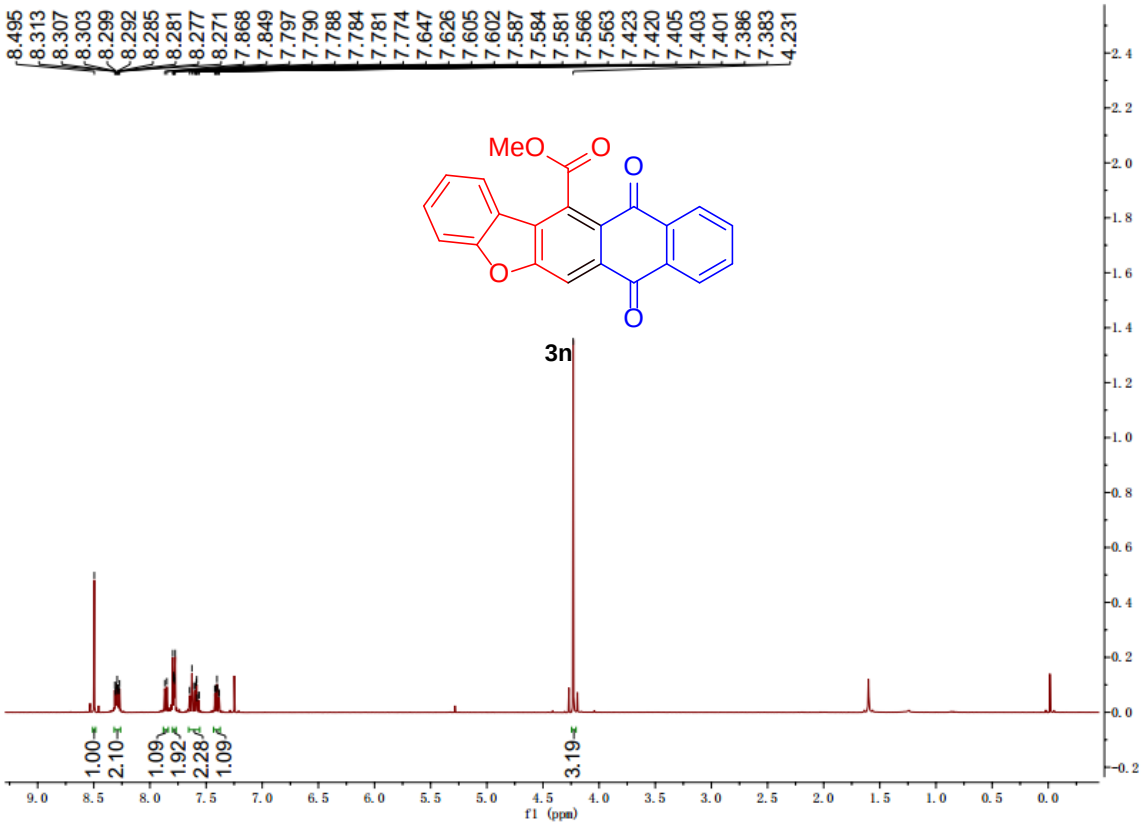
124.56
123.24
123.16
62.51
13.97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7.790
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7.784
7.781
7.774
7.647
7.626
7.605
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7.587
7.584
7.581
7.566
7.563
7.423
7.420
7.405
7.403
7.401
7.386
7.383
4.231
MeO
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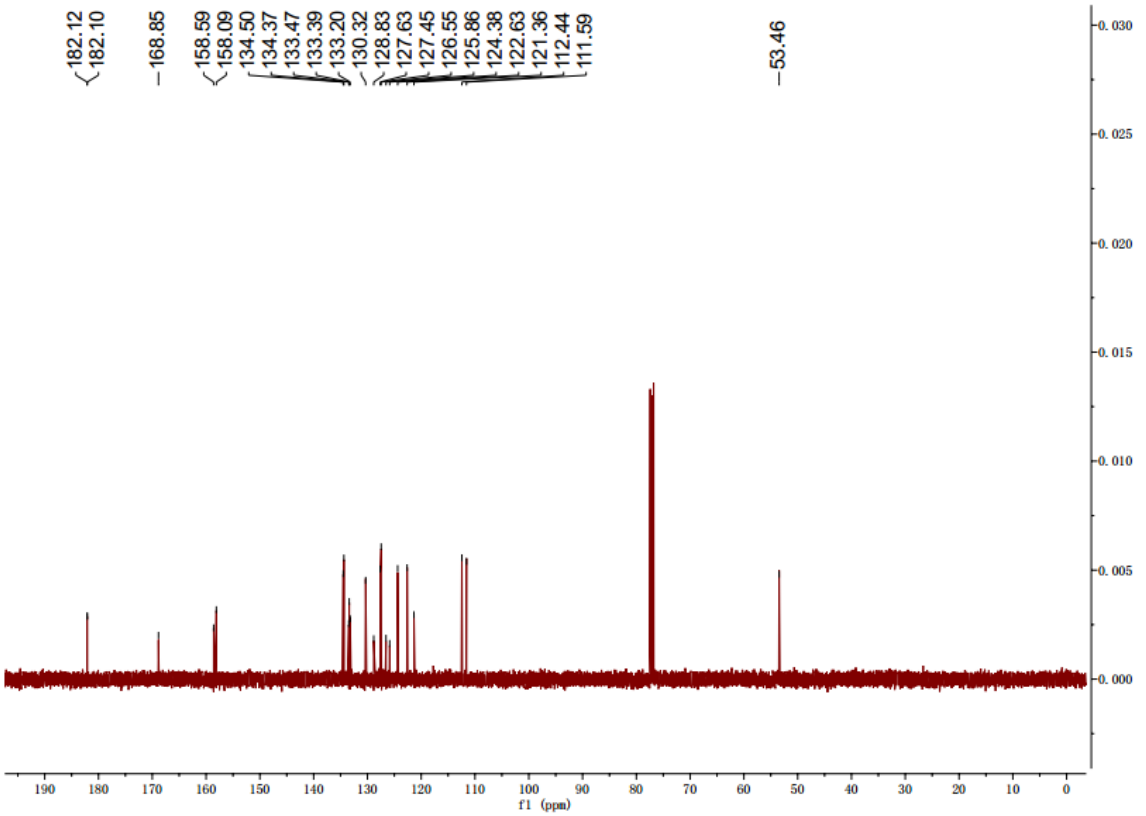
O
O
O
3n
1.00
2.10
1.09
1.92
2.28
1.09
3.19
f1 (ppm)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133.20
130.32
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126.55
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124.38
122.63
121.36
112.44
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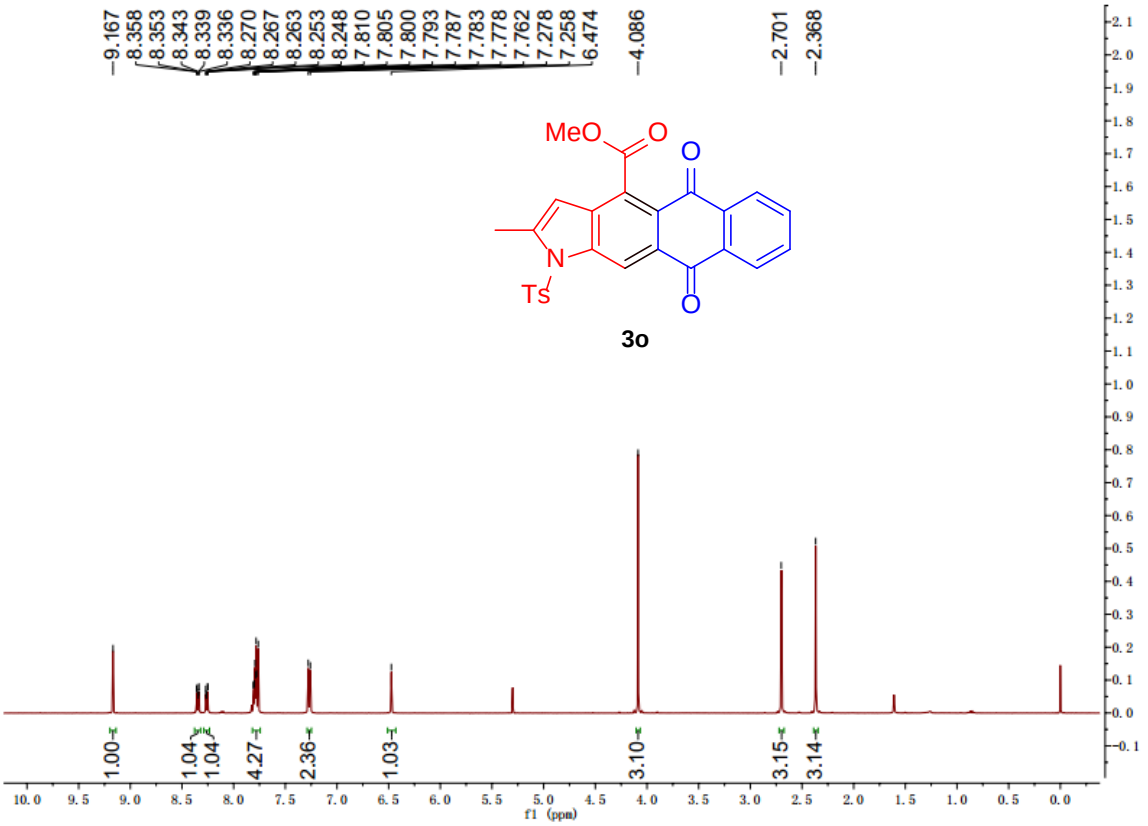
53.46
f1 (ppm)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8.248
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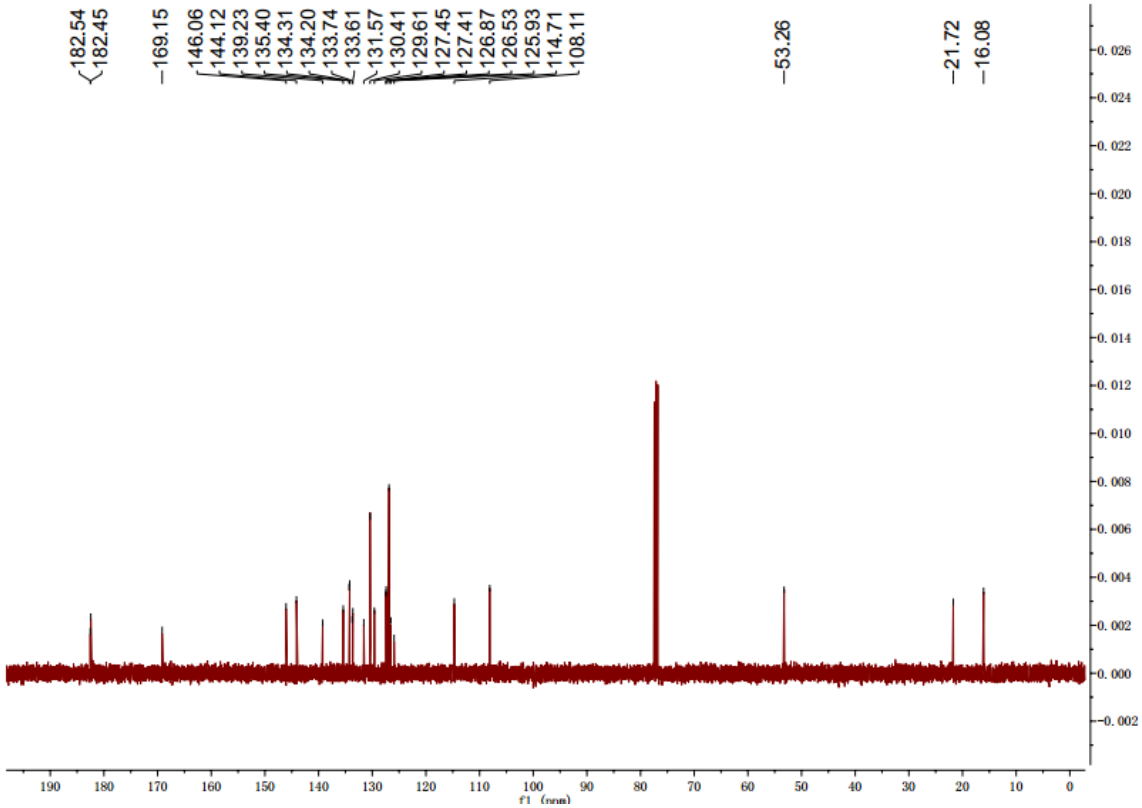
7.805
7.800
7.793
7.787
7.783
7.778
7.762
7.278
7.258
6.474
4.086
2.701
2.368
MeO
O
O
N
Ts
O
1.00
1.04
1.04
4.27
2.36
1.03
3.10
3.15
3.14
f1 (ppm)

3o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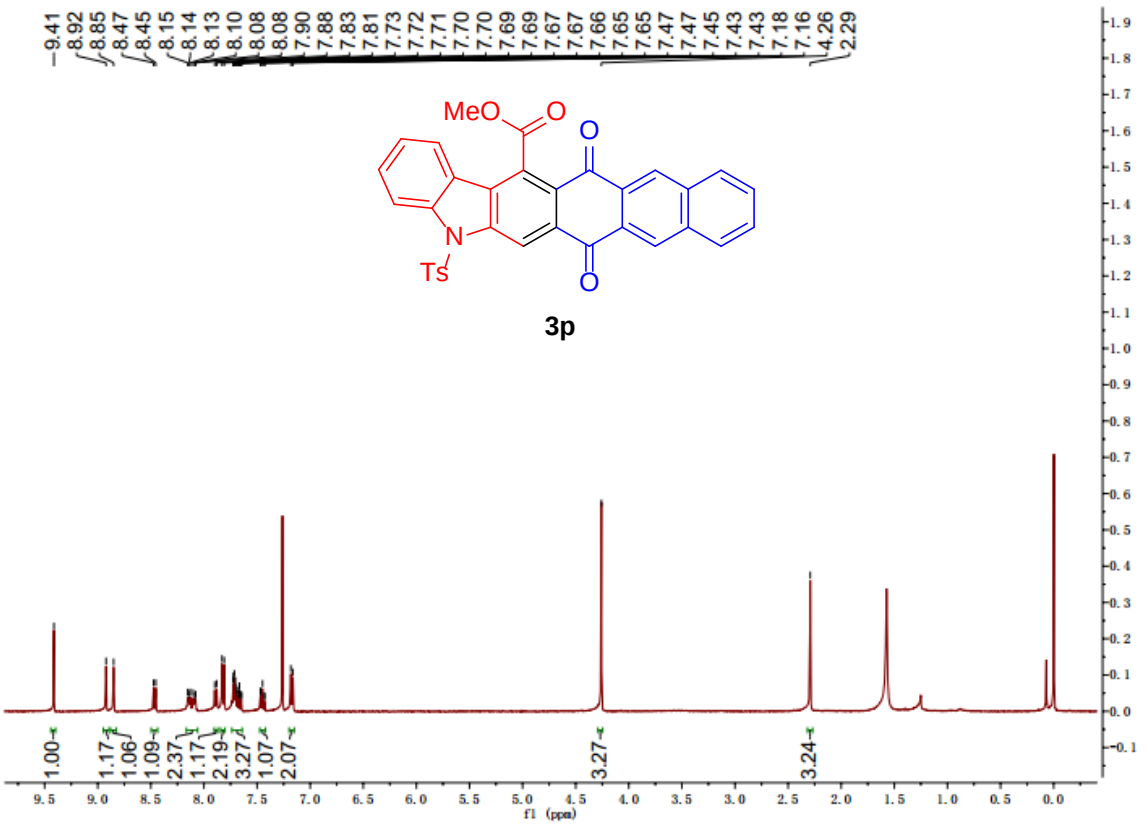
16.08
f1 (ppm)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7.71
7.70
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7.69
7.67
7.67
7.66
7.65
7.65
7.47
7.47
7.45
7.43
7.43
7.18
7.16
4.26
2.29
MeO
O
O
N
Ts
O
1.00
1.17
1.06
1.09
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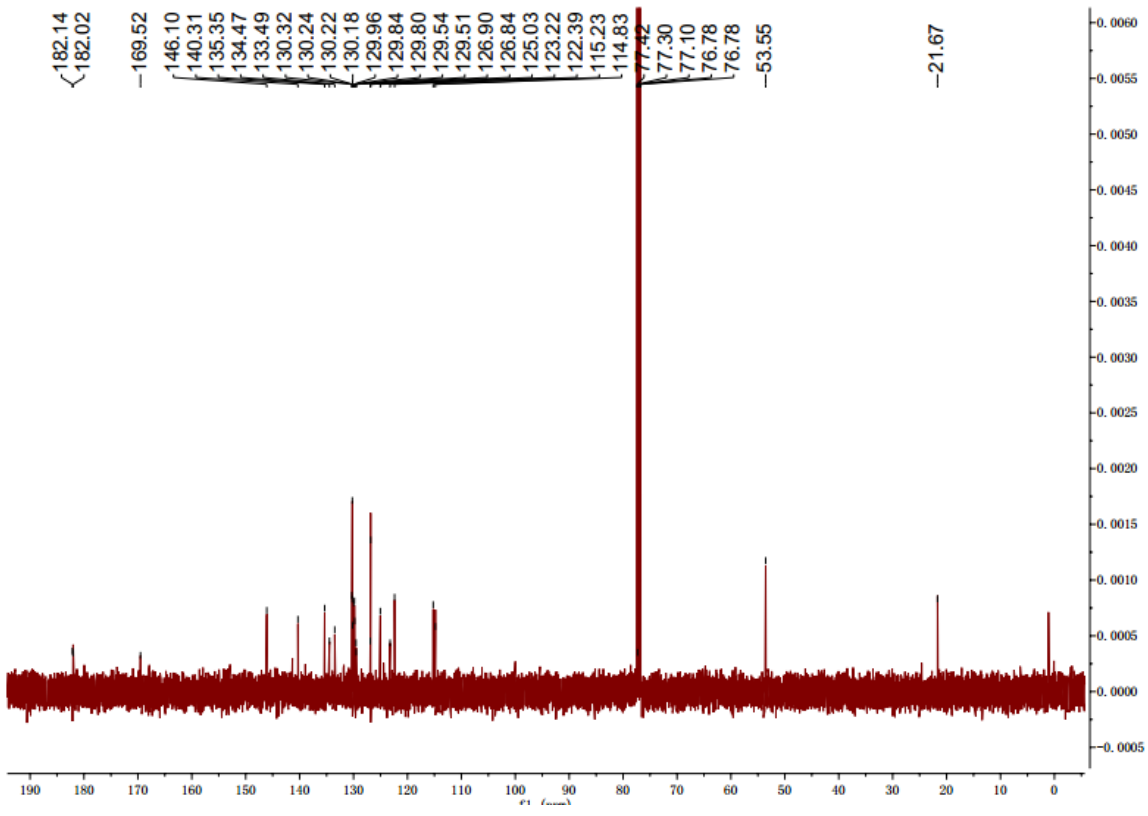
1.17
2.19
3.27
1.07
2.07
3.27
3.24
f1 (ppm)

3p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130.18
129.96
129.84
129.80
129.54
129.51
126.90
126.84
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122.39
115.23
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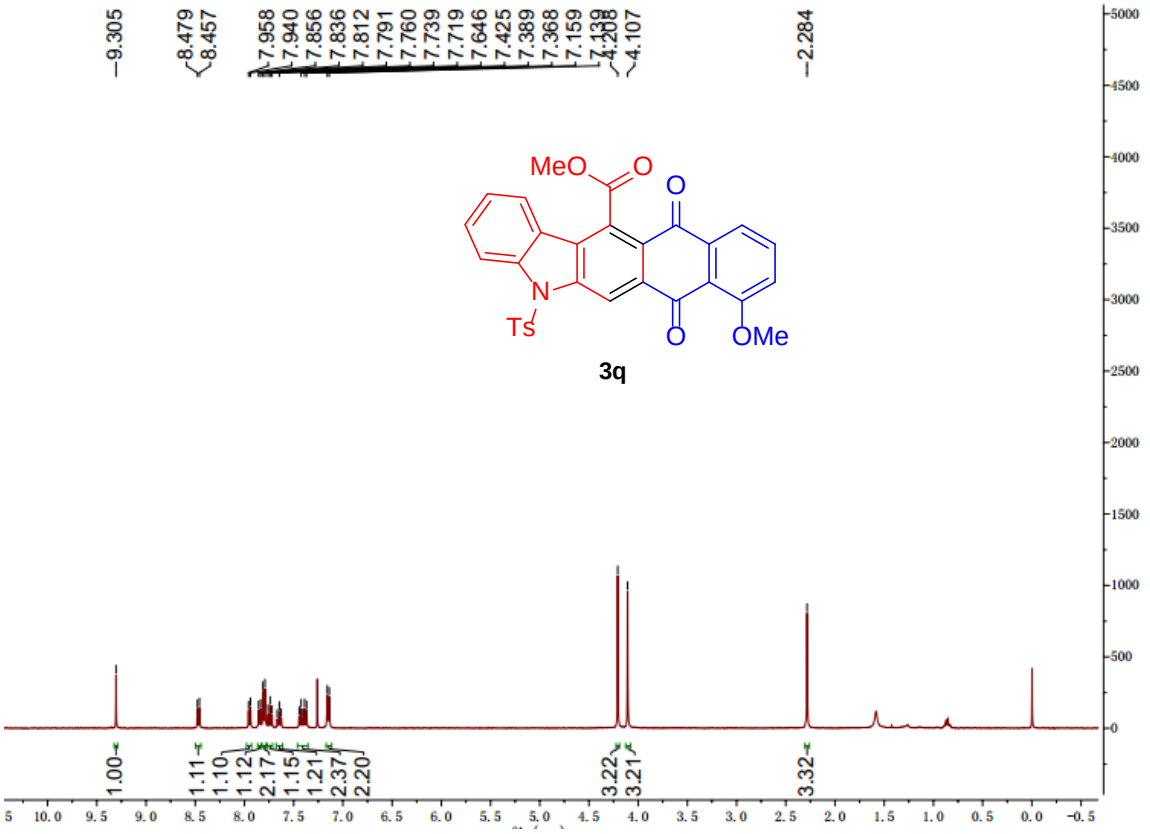
77.42
77.30
77.10
76.78
76.78
53.55
21.67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7.812
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7.646
7.425
7.389
7.368
7.159
7.139
4.208
4.107
2.284
MeO
O
O
N
Ts
O
OMe
1.00
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1.12
2.17
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1.21
2.37
2.20
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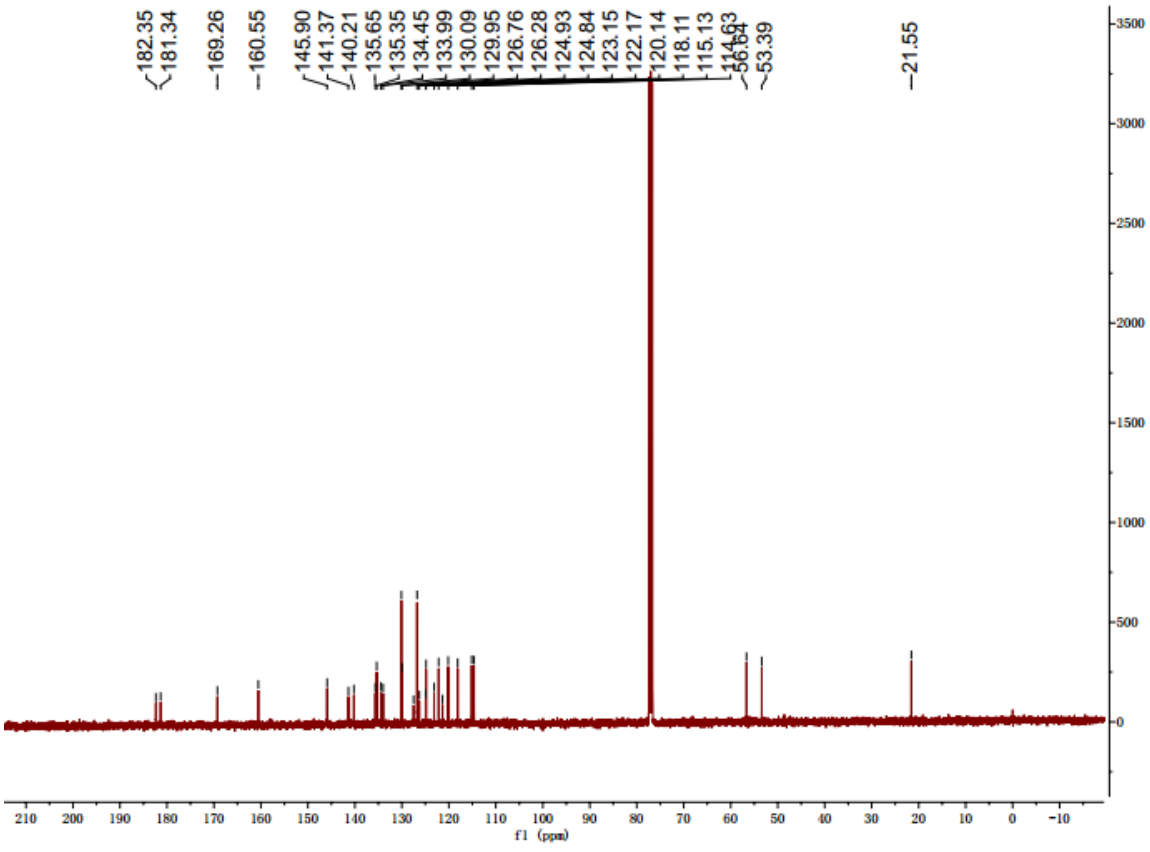
3.21
3.32

3q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141.37
140.21
135.65
135.35
134.45
133.99
130.09
129.95
126.76
126.28
124.93
124.84
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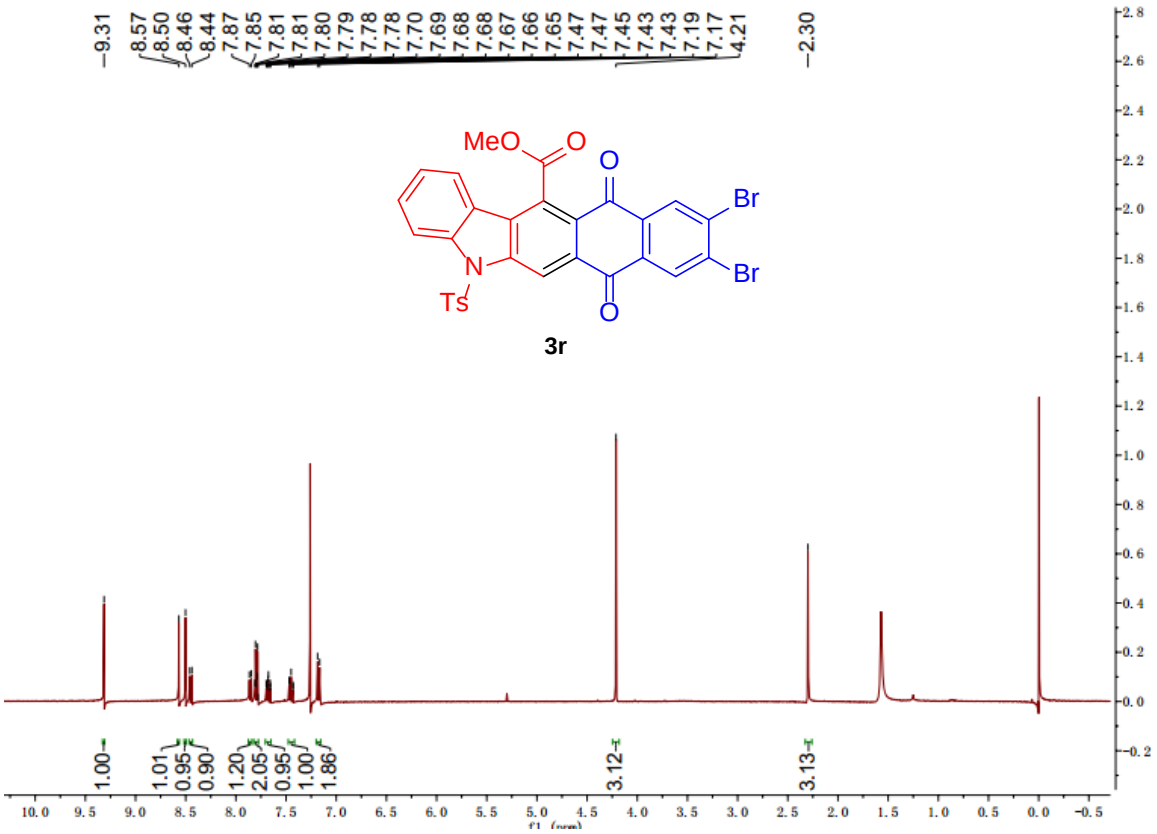
122.17
120.14
118.11
115.13
114.63
56.64
53.39
21.55
f1 (ppm)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8.44
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7.81
7.81
7.80
7.79
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7.78
7.70
7.69
7.68
7.68
7.67
7.66
7.65
7.47
7.47
7.45
7.43
7.43
7.19
7.17
4.21
2.30
MeO
O
O
Br
Br
N
Ts
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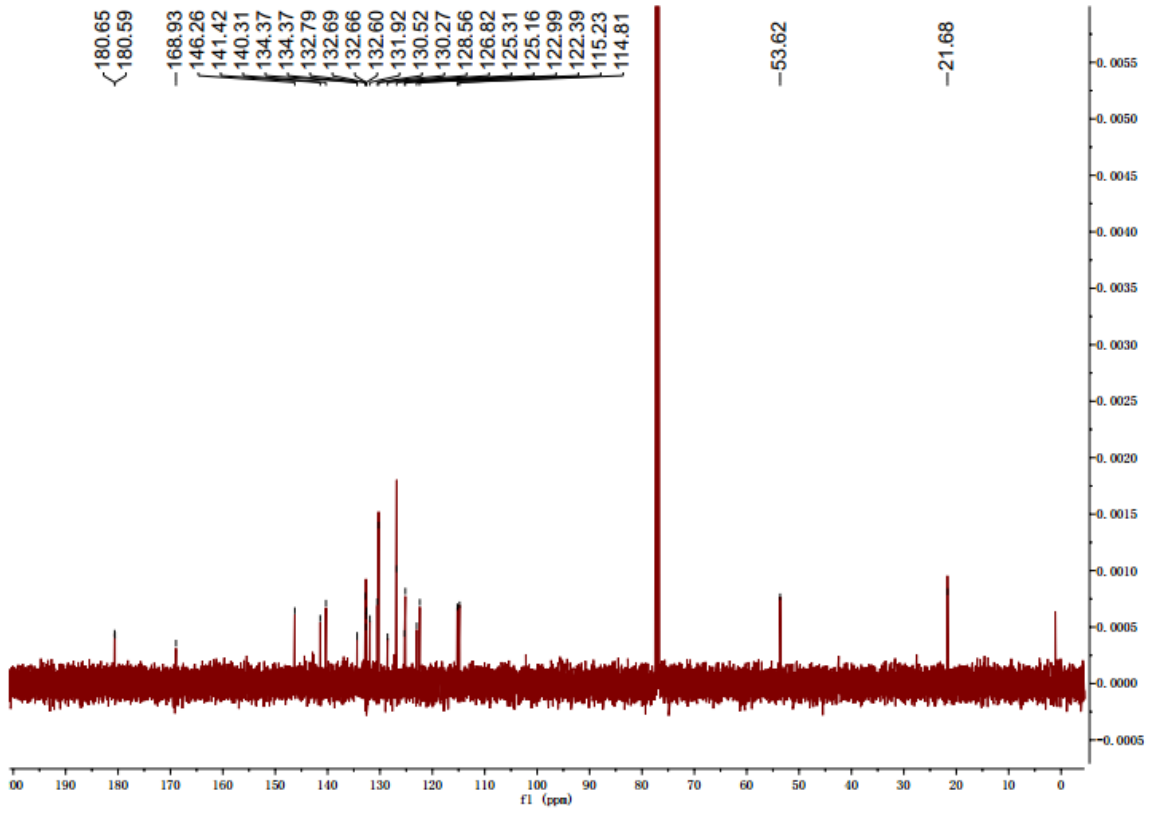
0.90
1.20
2.05
0.95
1.00
1.86
3.12
3.13

3r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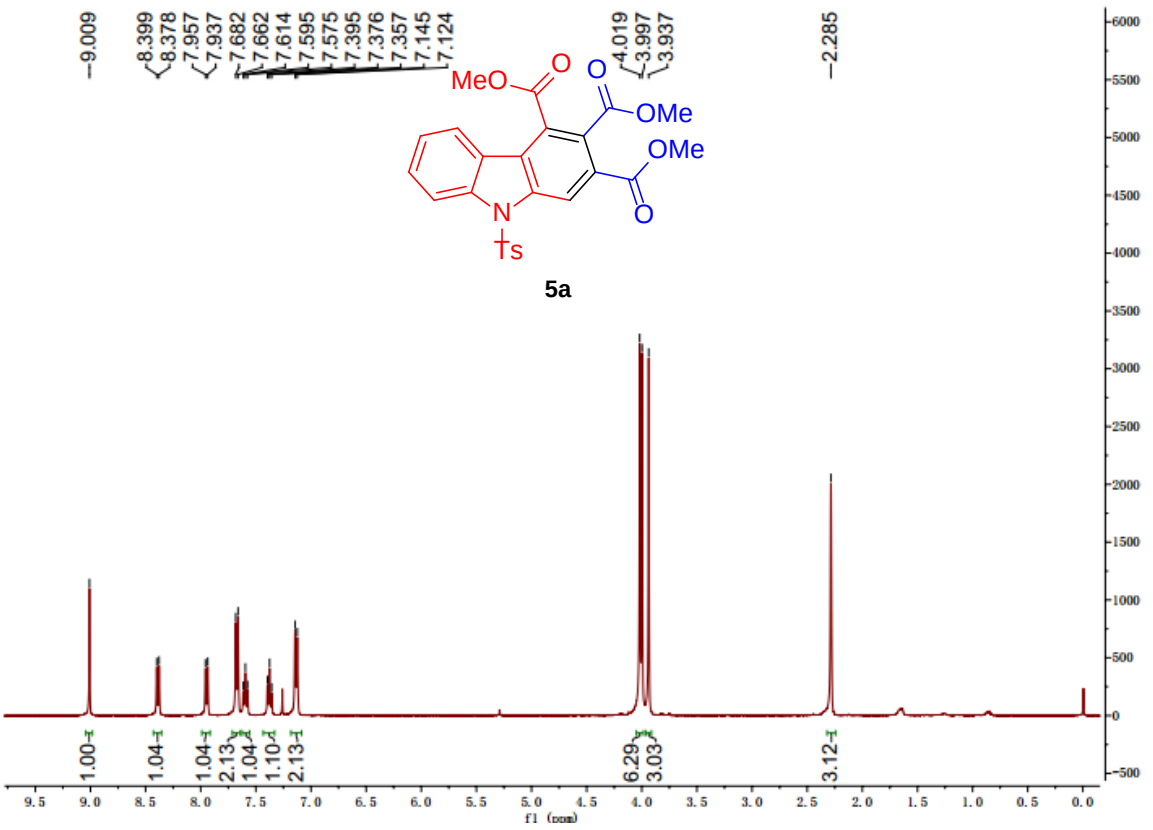
140.31
134.37
134.37
132.79
132.69
132.66
132.60
131.92
130.52
130.27
128.56
126.82
125.31
125.16
122.99
122.39
115.23
114.81
53.62
21.68
f1 (ppm)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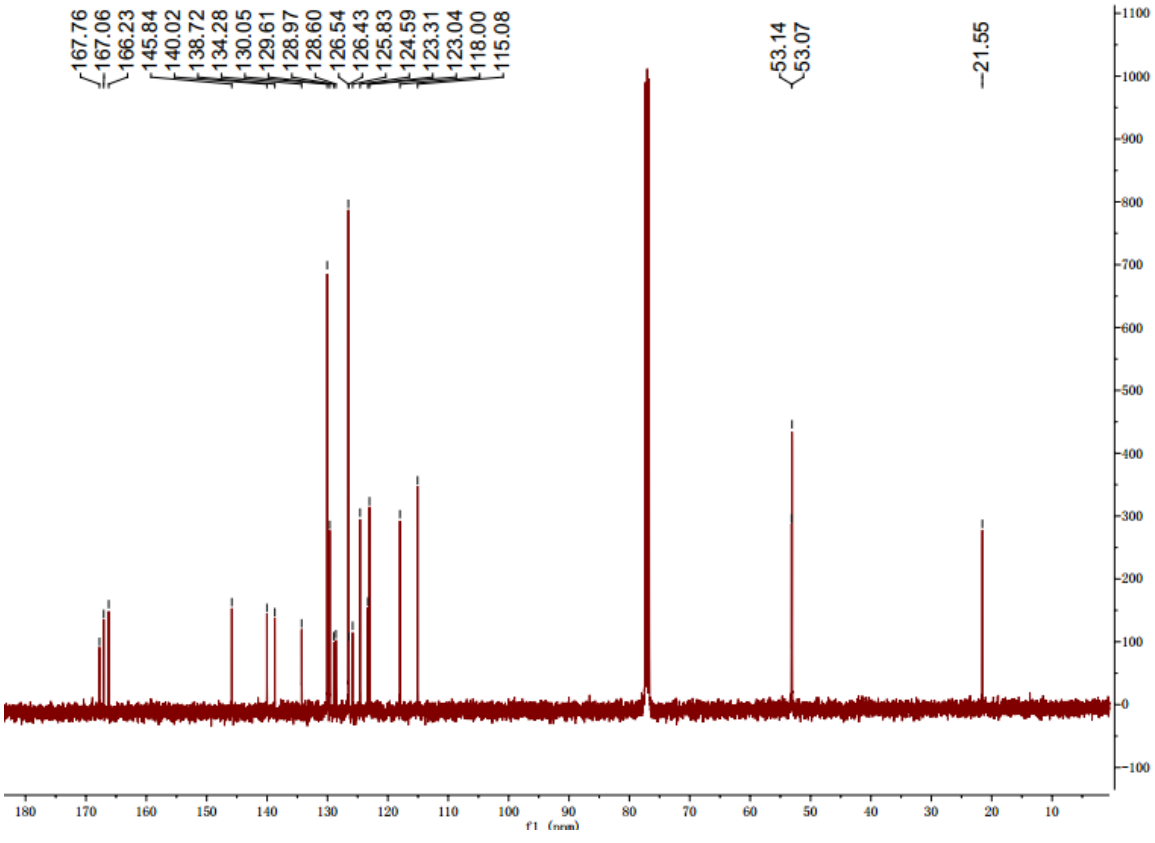
7.575
7.395
7.376
7.357
7.145
7.124
4.019
3.997
3.937
2.285
MeO
O
O
OMe
OMe
O
N
Ts
1.00
1.04
1.04
2.13
1.04
1.10
2.13
6.29
3.03
3.12
f1 (ppm)

5a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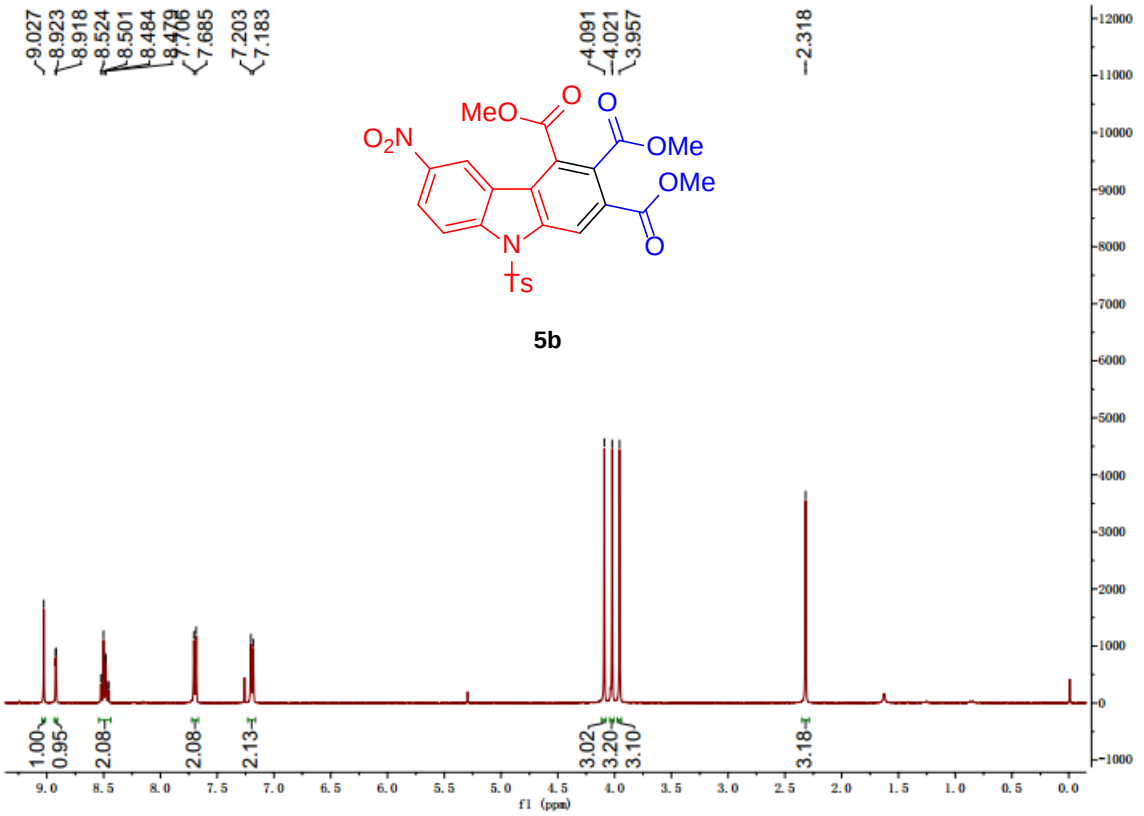
167.06
166.23
145.84
140.02
138.72
134.28
130.05
129.61
128.97
128.60
126.54
126.43
125.83
124.59
123.31
123.04
118.00
115.08
53.14
53.07
21.55
f1 (ppm)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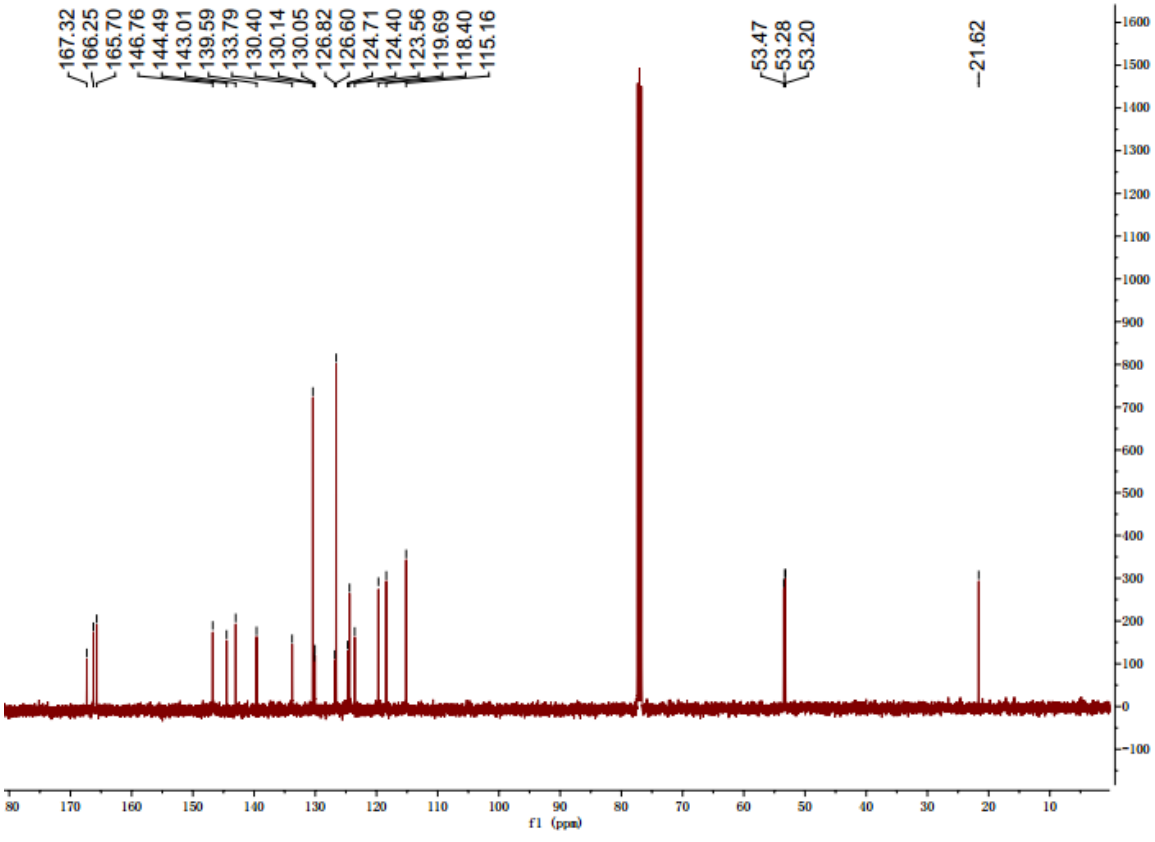
8.484
8.479
7.708
7.685
7.203
7.183
4.091
4.021
3.957
2.318
MeO
O
O
OMe
OMe
O
O2N
N
Ts
1.00
0.95
2.08
2.08
2.13
3.02
3.20
3.10
3.18
f1 (ppm)

5b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166.25
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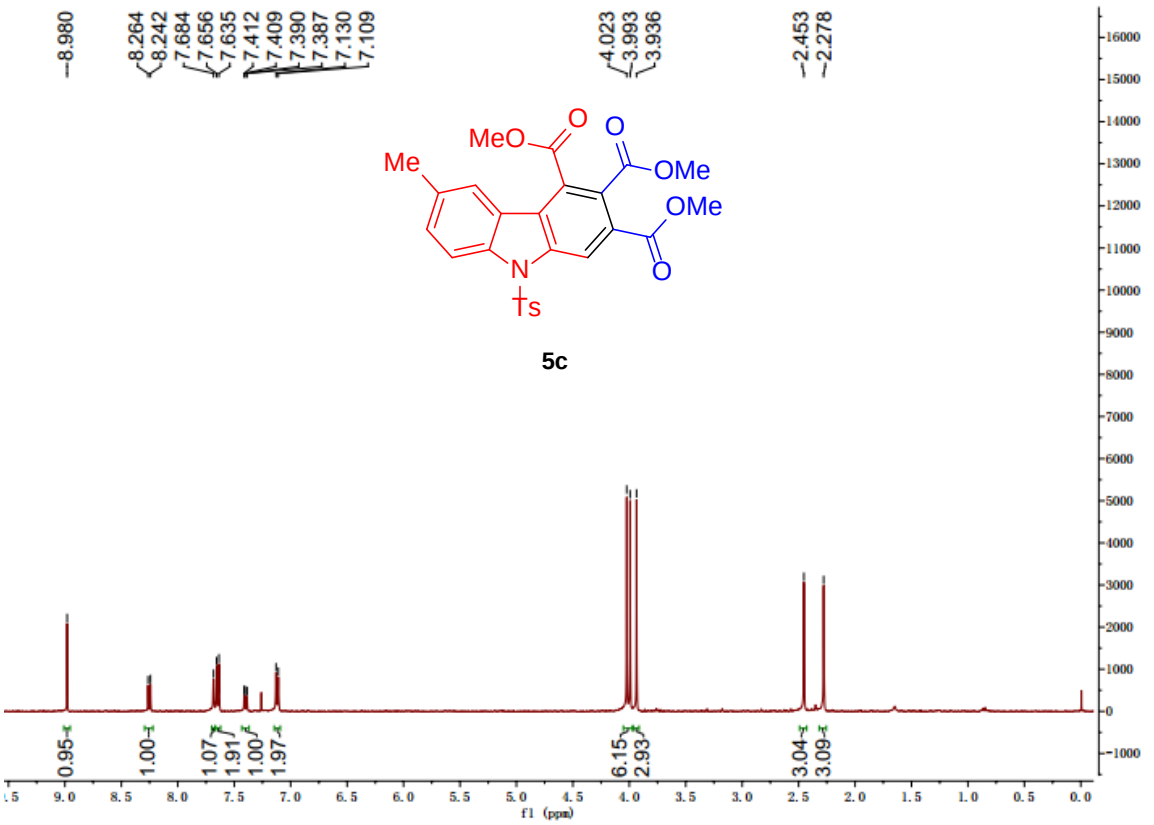
144.49
143.01
139.59
133.79
130.40
130.14
130.05
126.82
126.60
124.71
124.40
123.56
119.69
118.40
115.16
53.47
53.28
53.20
21.62
f1 (ppm)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7.635
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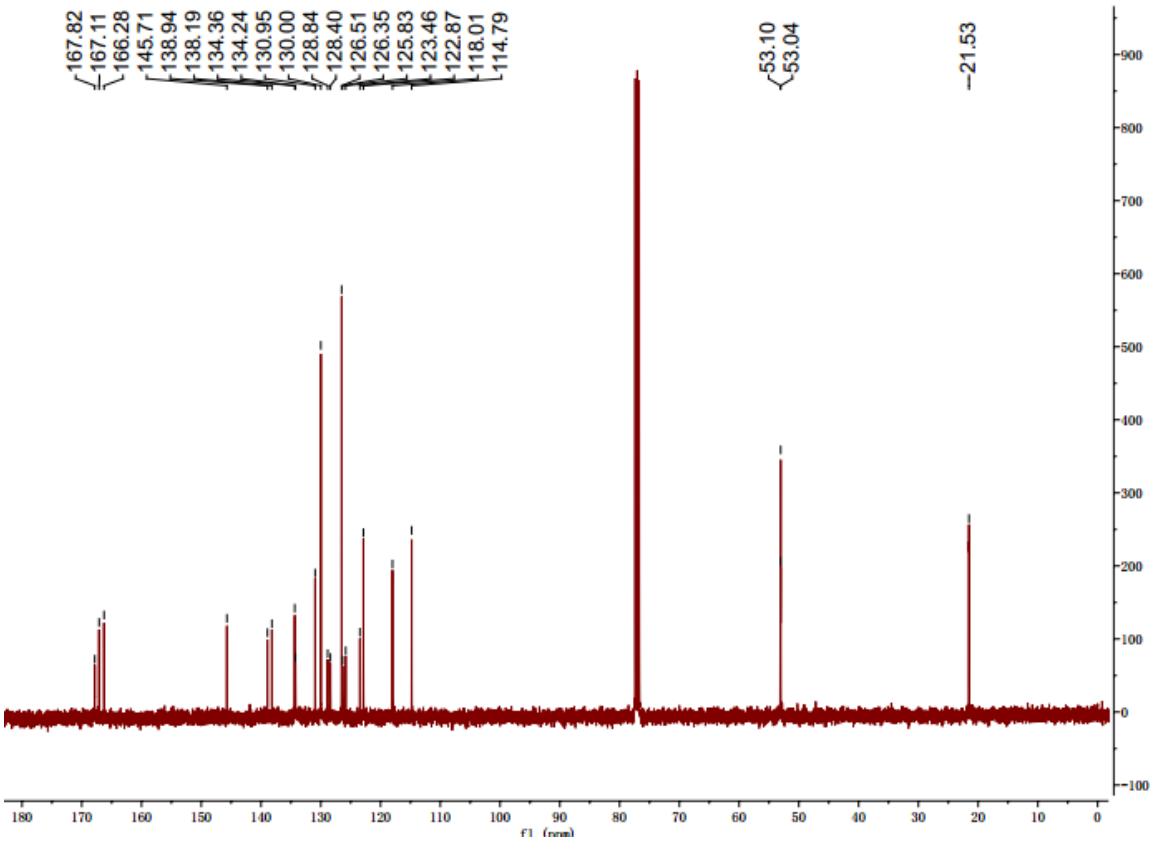
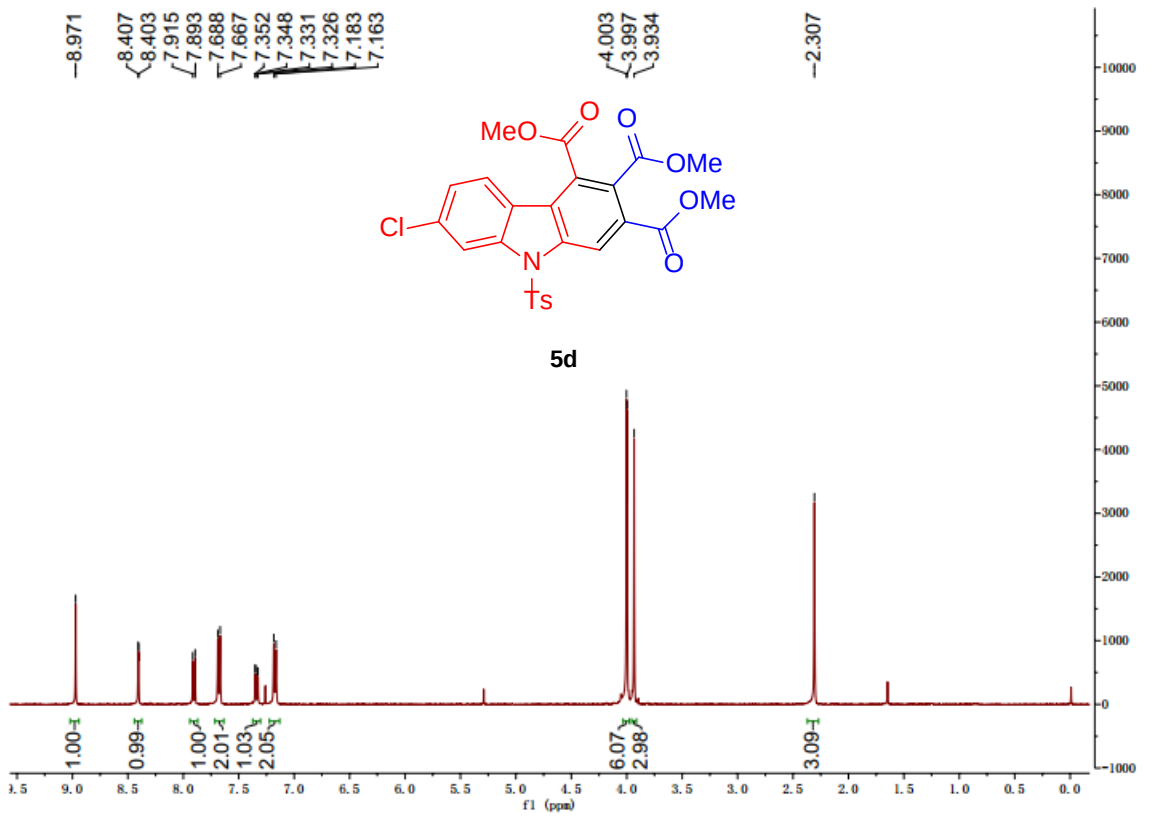
7.390
7.387
7.130
7.109
4.023
3.993
3.936
2.453
2.278
MeO
O
O
OMe
OMe
O
Me
N
Ts
0.95
1.00
1.07
1.91
1.00
1.97
6.15
2.93
3.04
3.09
f1 (ppm)

5c


167.82
167.11
166.28
145.71
138.94
138.19
134.36
134.24
130.95
130.00
128.84
128.40
126.51
126.35
125.83
123.46
122.87
118.01
114.79
53.10
53.04
21.53
f1 (ppm)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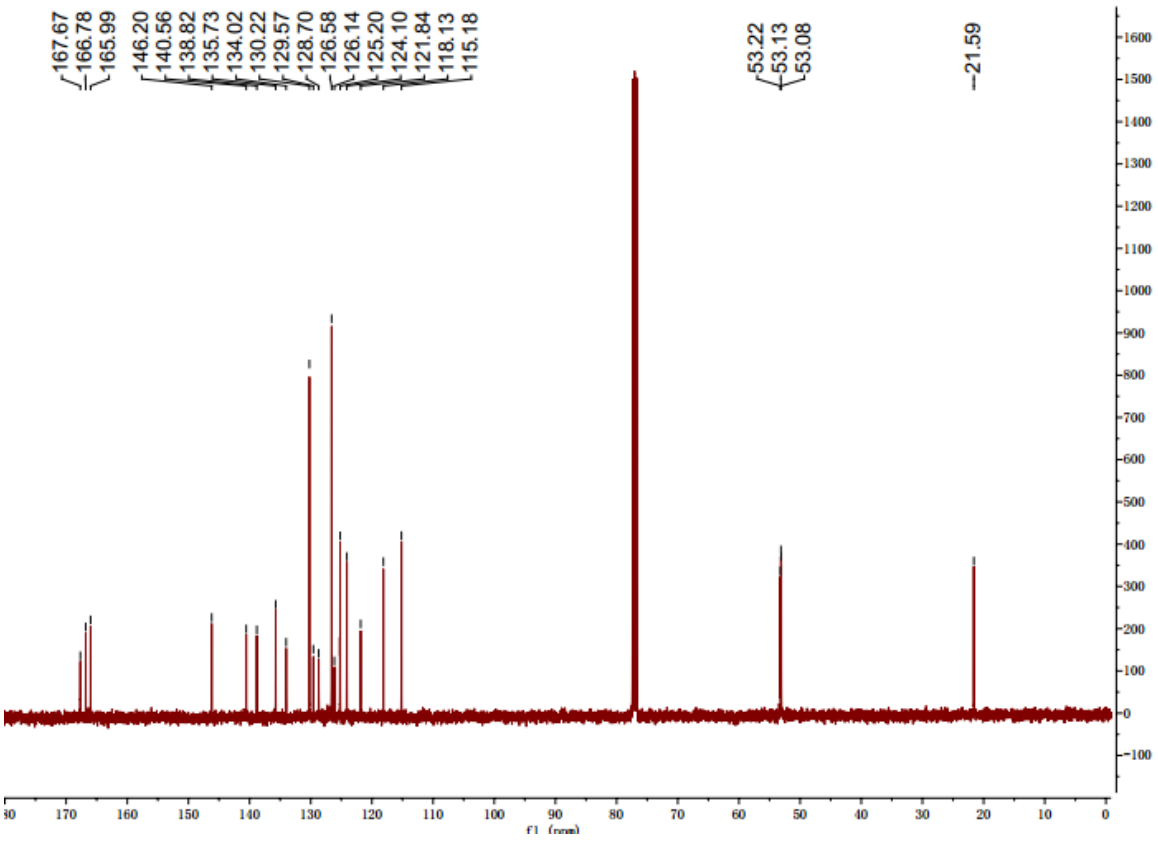
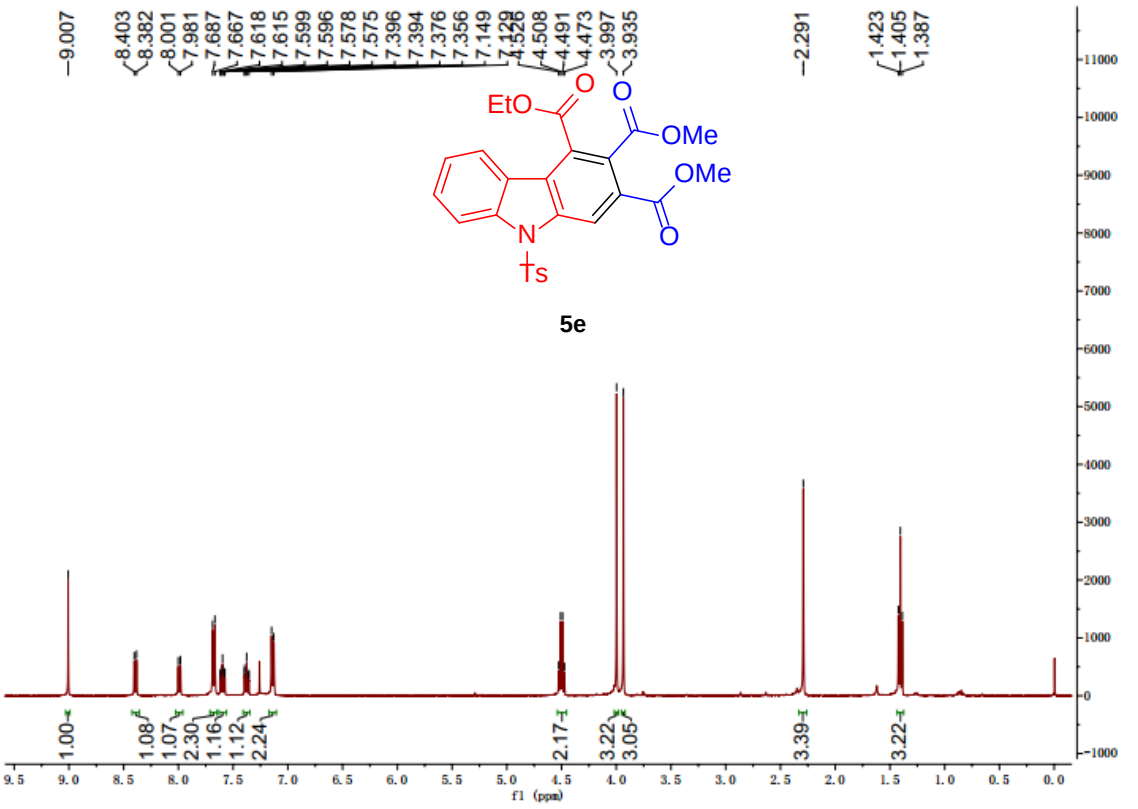
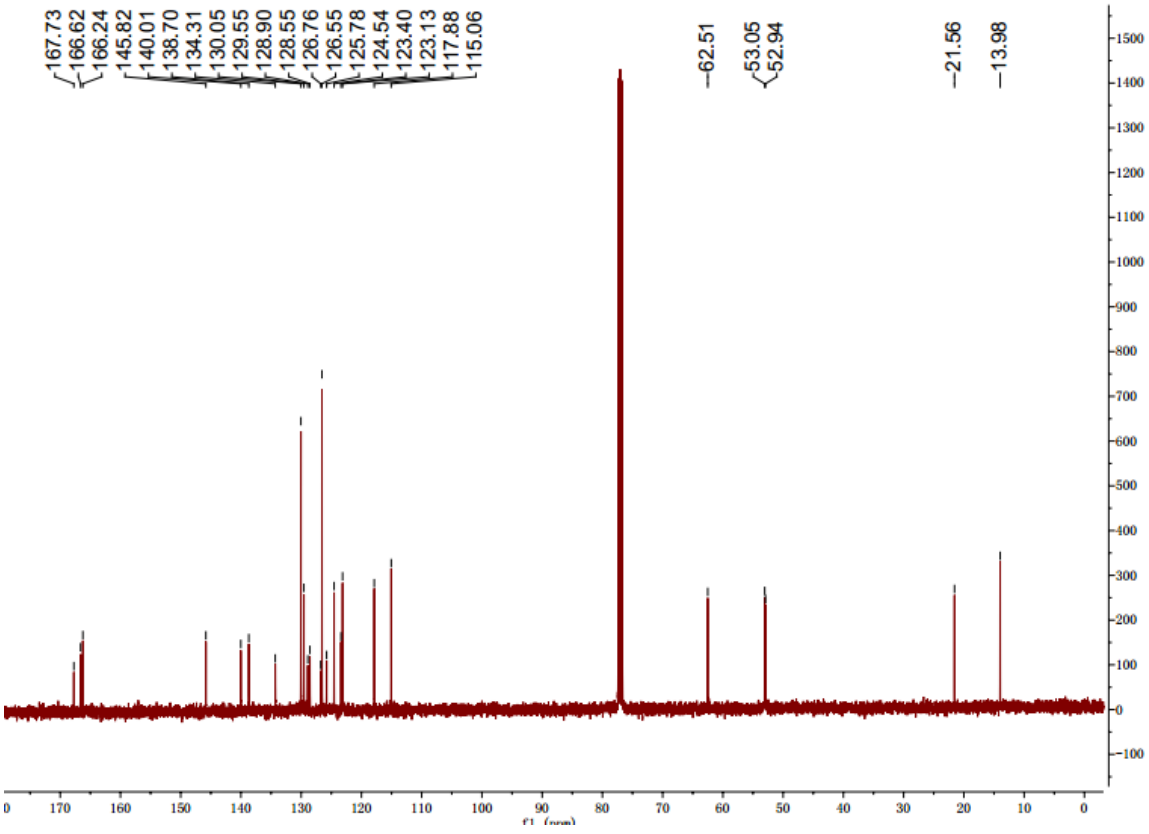
8.403
7.915
7.893
7.688
7.667
7.352
7.348
7.331
7.326
7.183
7.163
4.003
3.997
3.934
2.307
MeO
O
O
OMe
OMe
O
Cl
N
Ts
1.00
0.99
1.00
2.01
1.03
2.05
6.07
2.98
3.09
f1 (ppm)

5d


167.67
166.78
165.99
146.20
140.56
138.82
135.73
134.02
130.22
129.57
128.70
126.58
126.14
125.20
124.10
121.84
118.13
115.18
53.22
53.13
53.08
21.59
f1 (ppm)


9.007
8.403
8.382
8.001
7.981
7.687
7.667
7.618
7.615
7.599
7.596
7.578
7.575
7.396
7.394
7.376
7.356
7.149
4.508
4.491
4.473
3.997
3.935
2.291
1.423
1.405
1.387
EtO
O
O
OMe
OMe
O
N
Ts
1.00
1.08
1.07
2.30
1.16
1.12
2.24
2.17
3.22
3.05
3.39
3.22
f1 (ppm)

5e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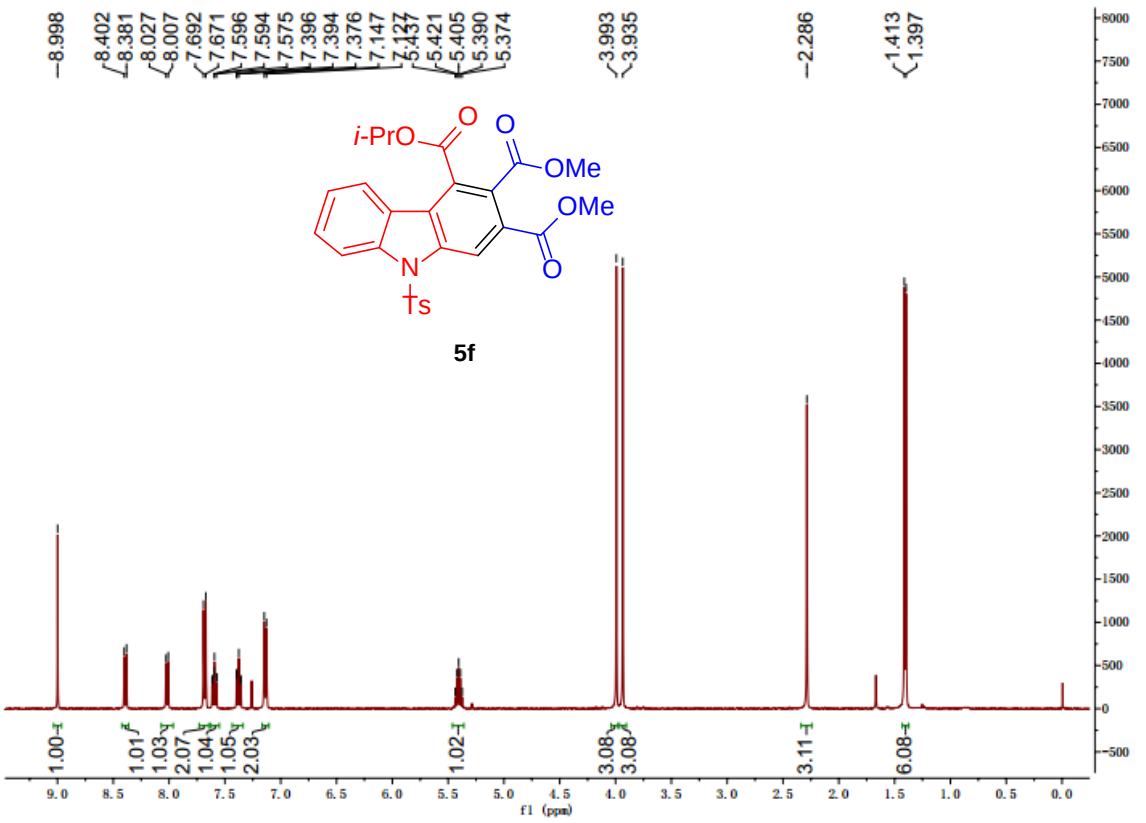
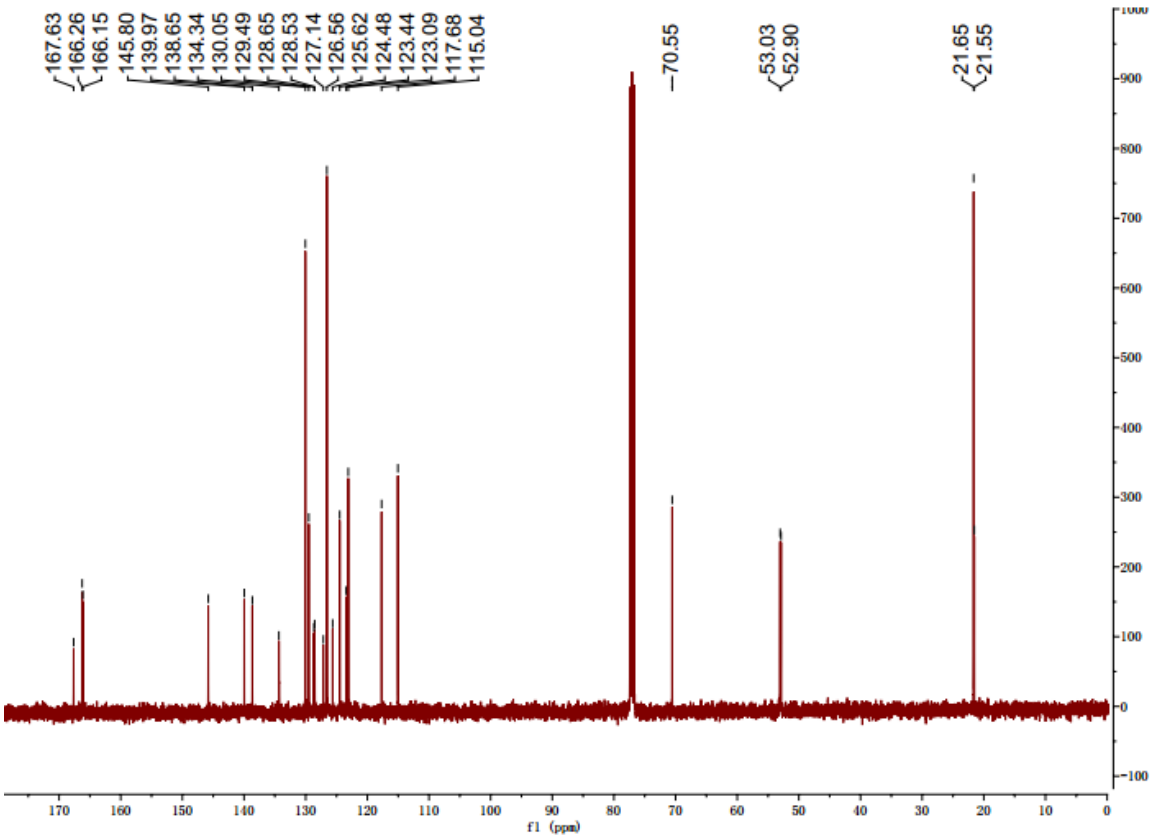
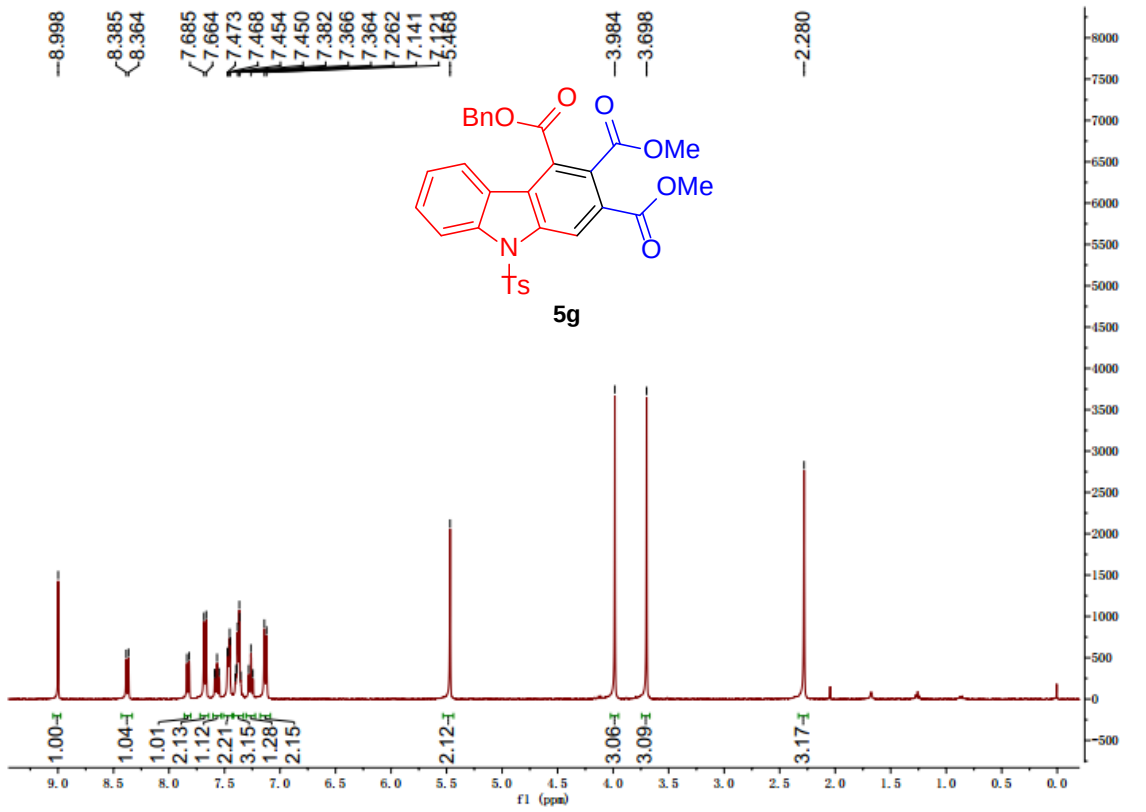
166.62
166.24
145.82
140.01
138.70
134.31
130.05
129.55
128.90
128.55
126.76
126.55
125.78
124.54
123.40
123.13
117.88
115.06
62.51
53.05
52.94
21.56
13.98

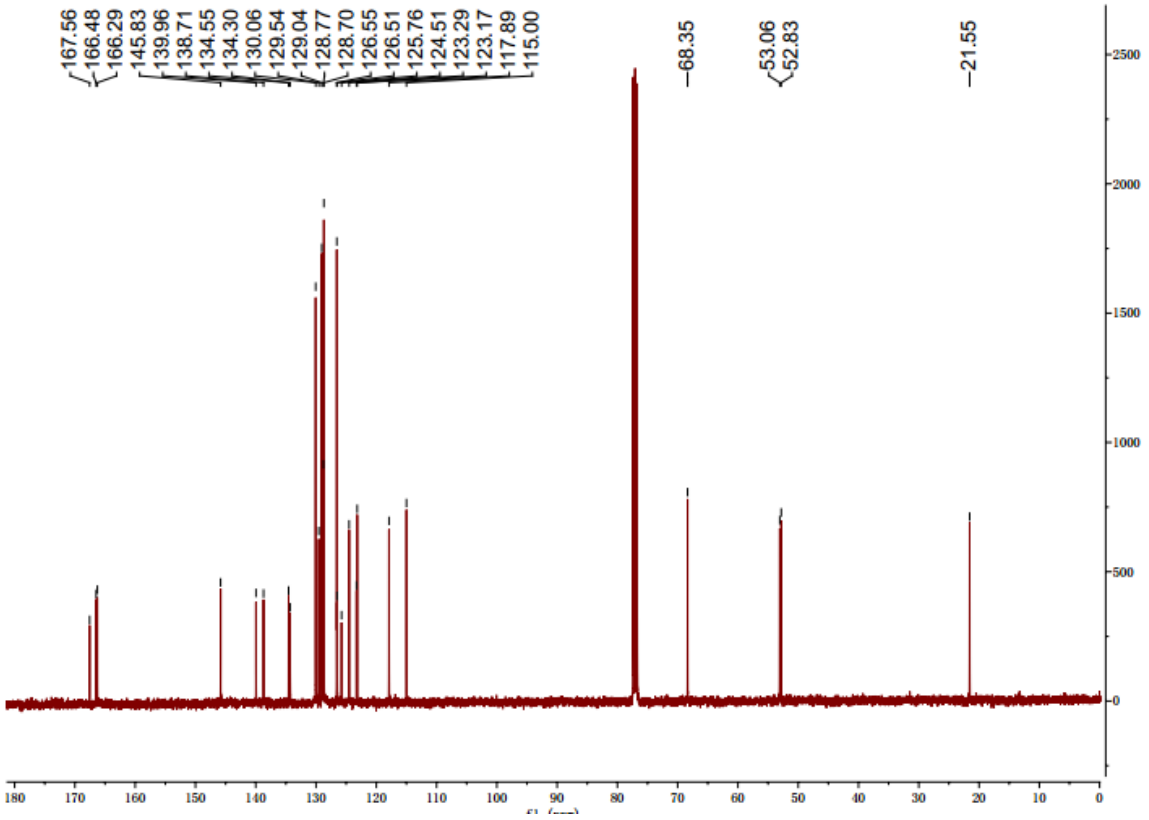

8.998
8.402
8.381
8.027
8.007
7.692
7.671
7.596
7.594
7.575
7.396
7.394
7.376
7.147
7.127
5.437
5.421
5.405
5.390
5.374
3.993
3.935
2.286
1.413
1.397
i-PrO
O
O
OMe
OMe
O
N
Ts
1.00
1.01
1.03
2.07
1.04
1.05
2.03
1.02
3.08
3.08
3.11
6.08
f1 (ppm)

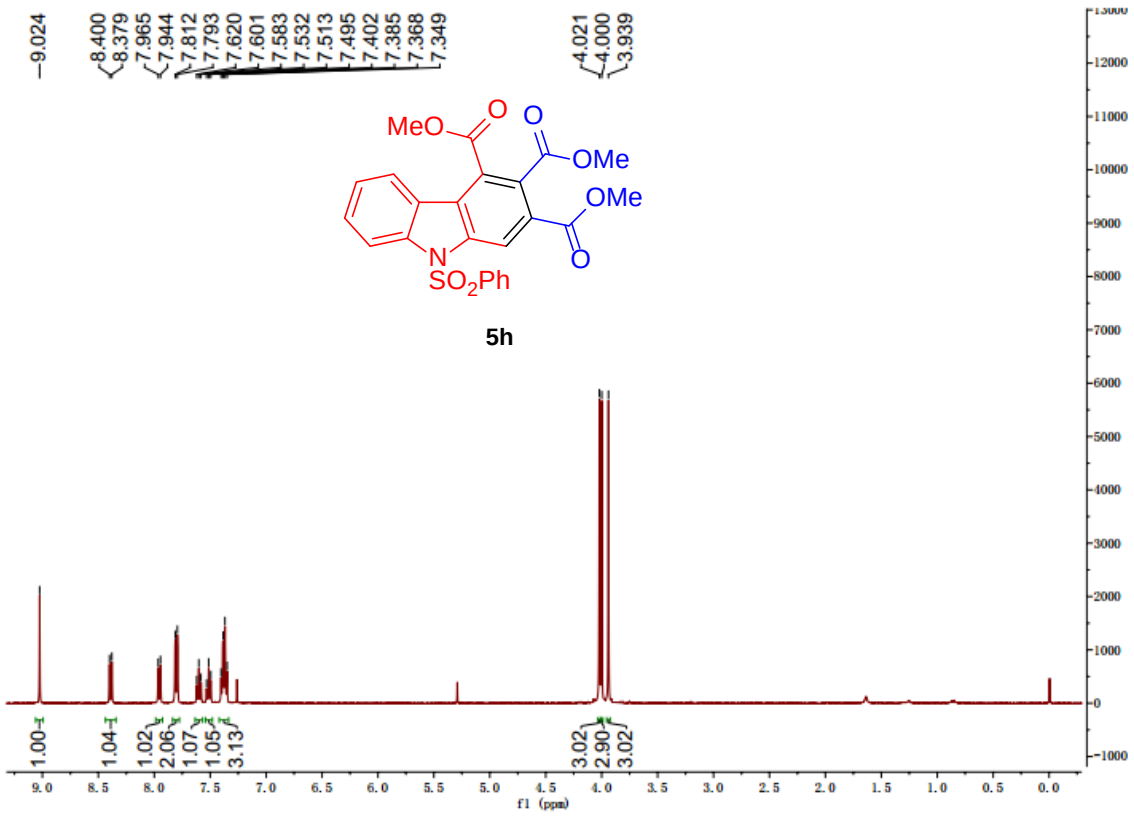
5f


167.63
166.26
166.15
145.80
139.97
138.65
134.34
130.05
129.49
128.65
128.53
127.14
126.56
125.62
124.48
123.44
123.09
117.68
115.04
70.55
53.03
52.90
21.65
21.55
f1 (ppm)

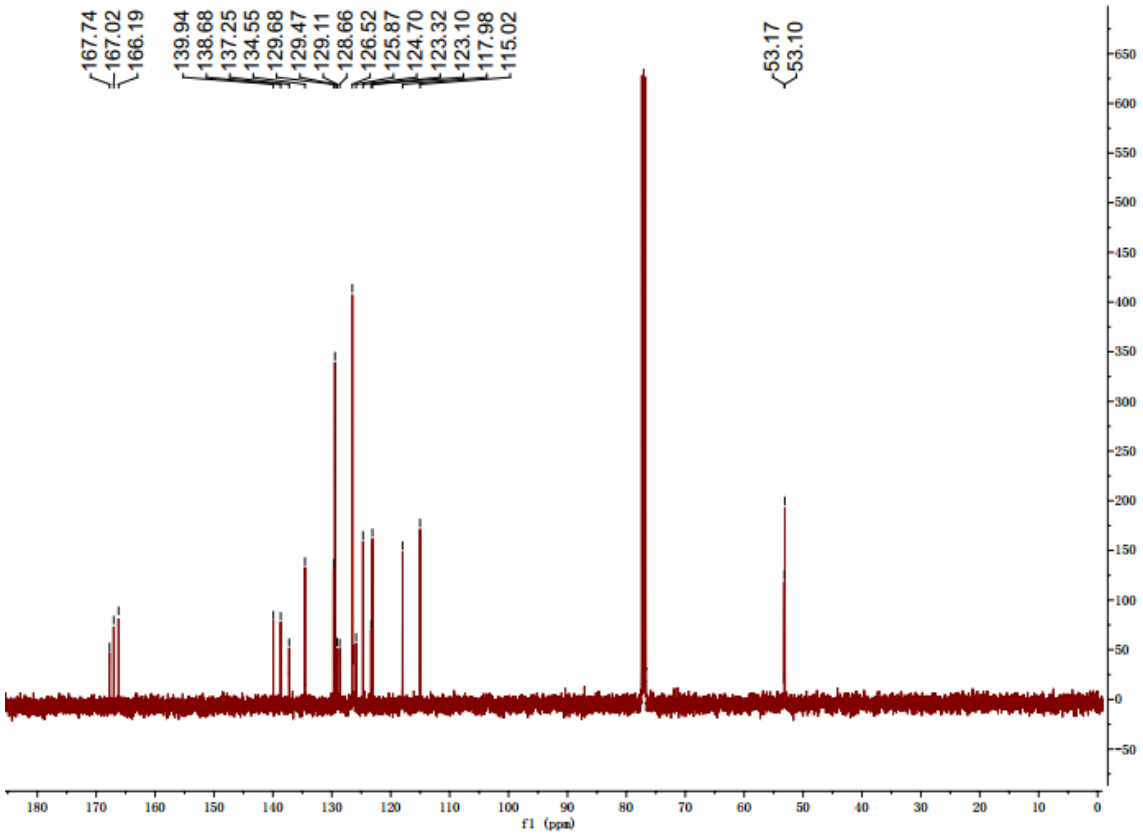

8.998
8.385
8.364
7.685
7.664
7.473
7.468
7.454
7.450
7.382
7.366
7.364
7.262
7.141
7.121
5.468
3.984
3.698
2.280
BnO
O
O
OMe
OMe
O
N
Ts
1.00
1.04
1.01
2.13
1.12
2.21
3.15
1.28
2.15
2.12
3.06
3.09
3.17
f1 (ppm)

5g


167.56
166.48
166.29
145.83
139.96
138.71
134.55
134.30
130.06
129.54
129.04
128.77
128.70
126.55
126.51
125.76
124.51
123.29
123.17
117.89
115.00
68.35
53.06
52.83
21.55


9.024
8.400
8.379
7.965
7.944
7.812
7.793
7.620
7.601
7.583
7.532
7.513
7.495
7.402
7.385
7.368
7.349
4.021
4.000
3.939
MeO
O
O
OMe
OMe
O
N
SO2Ph
1.00
1.04
1.02
2.06
1.07
1.05
3.13
3.02
2.90
3.02
f1 (ppm)

5h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167.02
166.19
139.94
138.68
137.25
134.55
129.68
129.47
129.11
128.66
126.52
125.87
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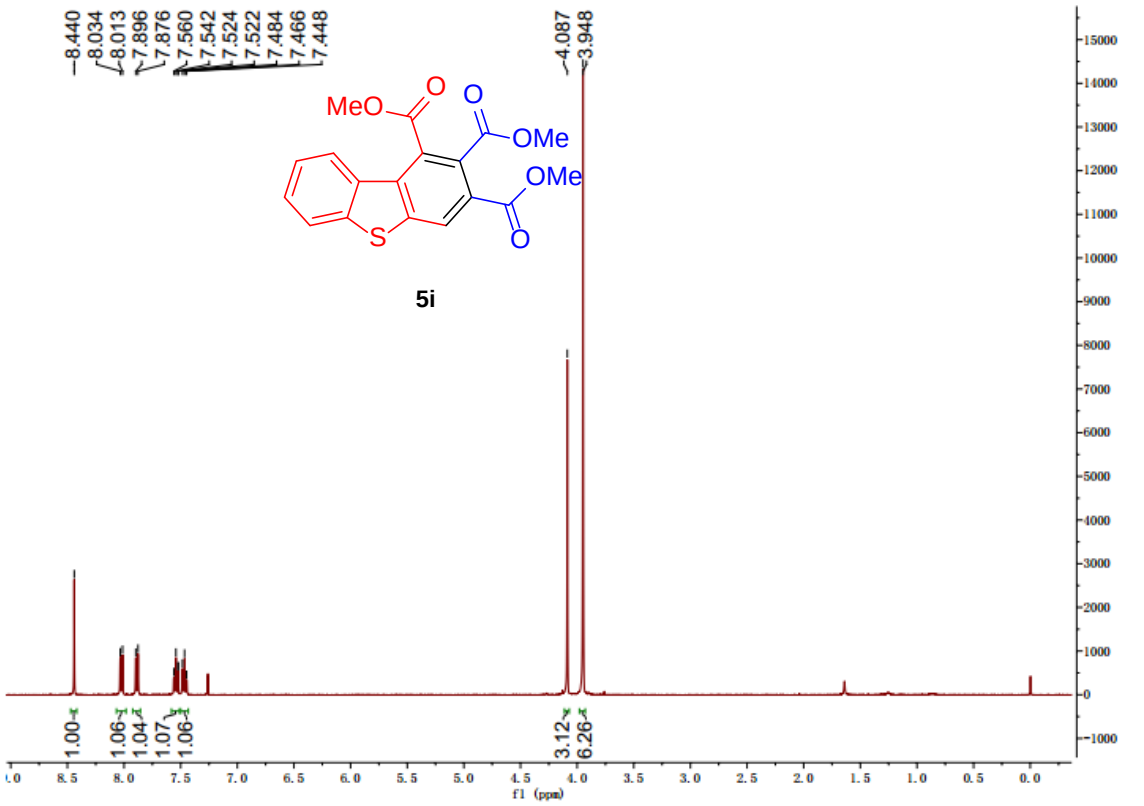
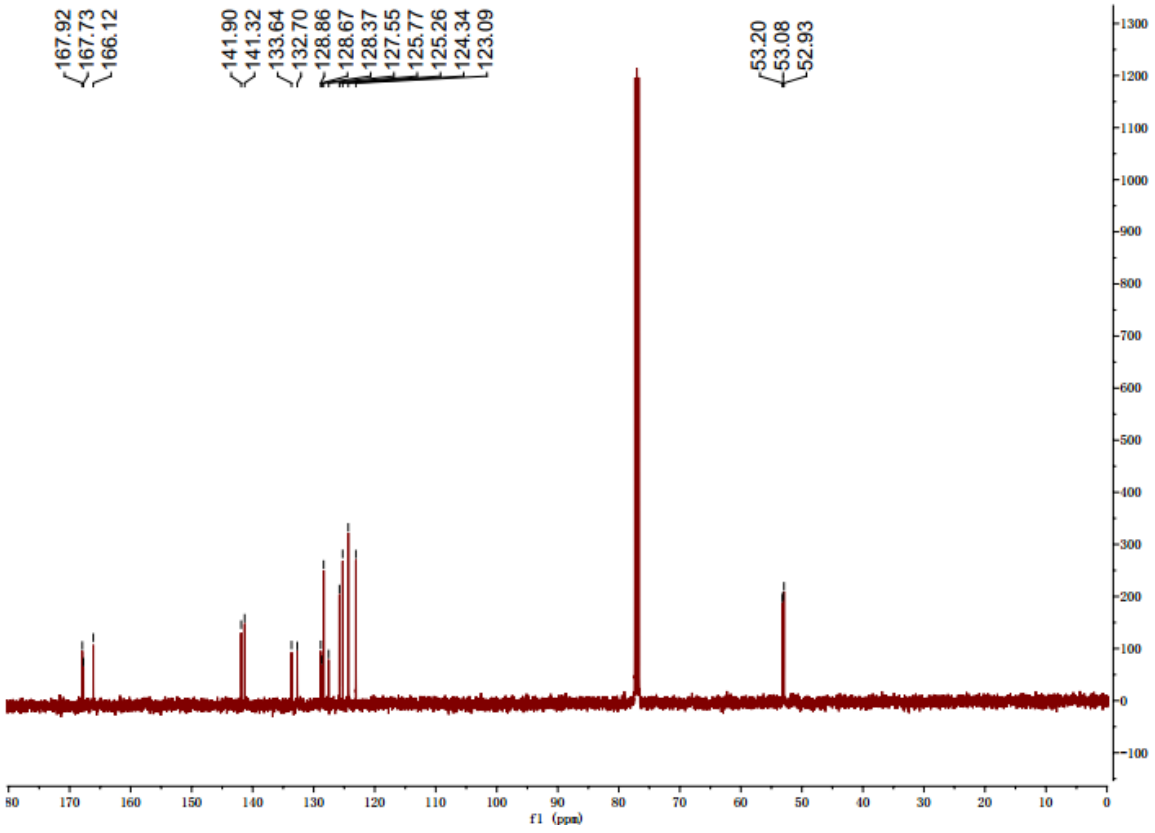
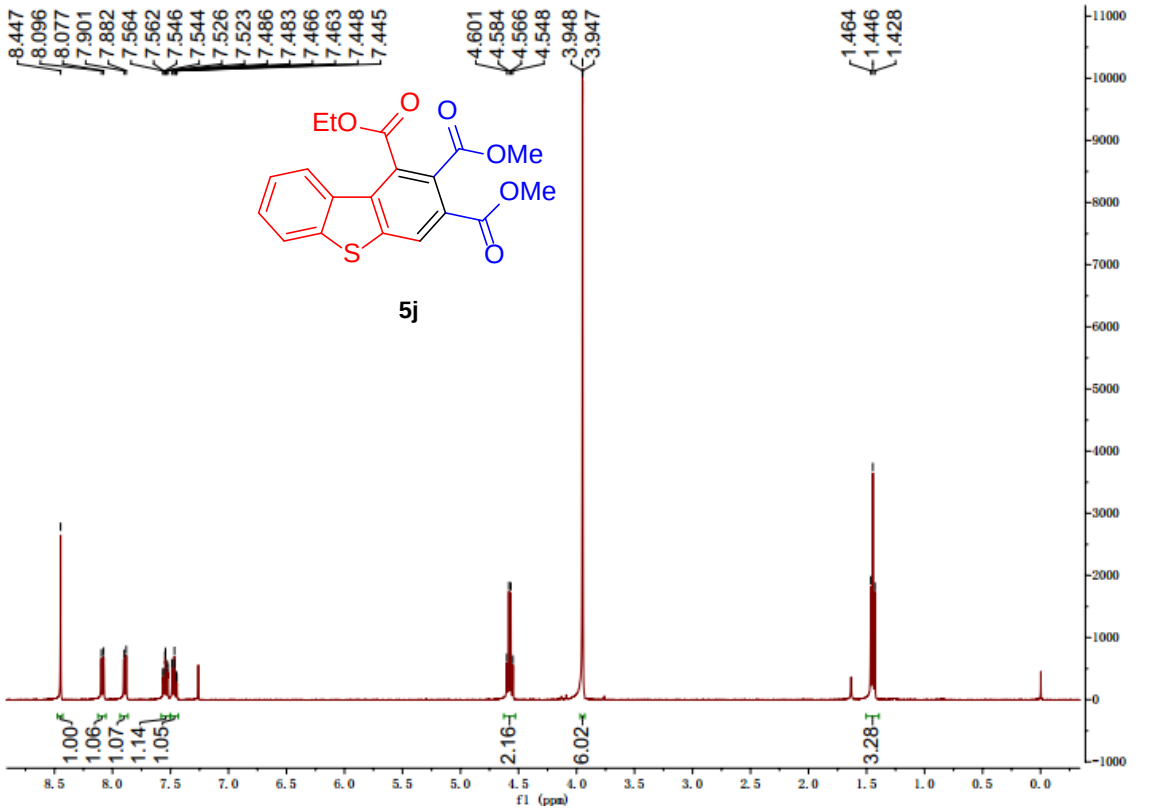
123.32
123.10
117.98
115.02
53.17
53.10
f1 (ppm)


8.440
8.034
8.013
7.896
7.876
7.560
7.542
7.524
7.522
7.484
7.466
7.448
4.087
3.948
MeO
O
O
OMe
OMe
O
S
1.00
1.06
1.04
1.07
1.06
3.12
6.26
f1 (ppm)

5i


167.92
167.73
166.12
141.90
141.32
133.64
132.70
128.86
128.67
128.37
127.55
125.77
125.26
124.34
123.09
53.20
53.08
52.93
f1 (ppm)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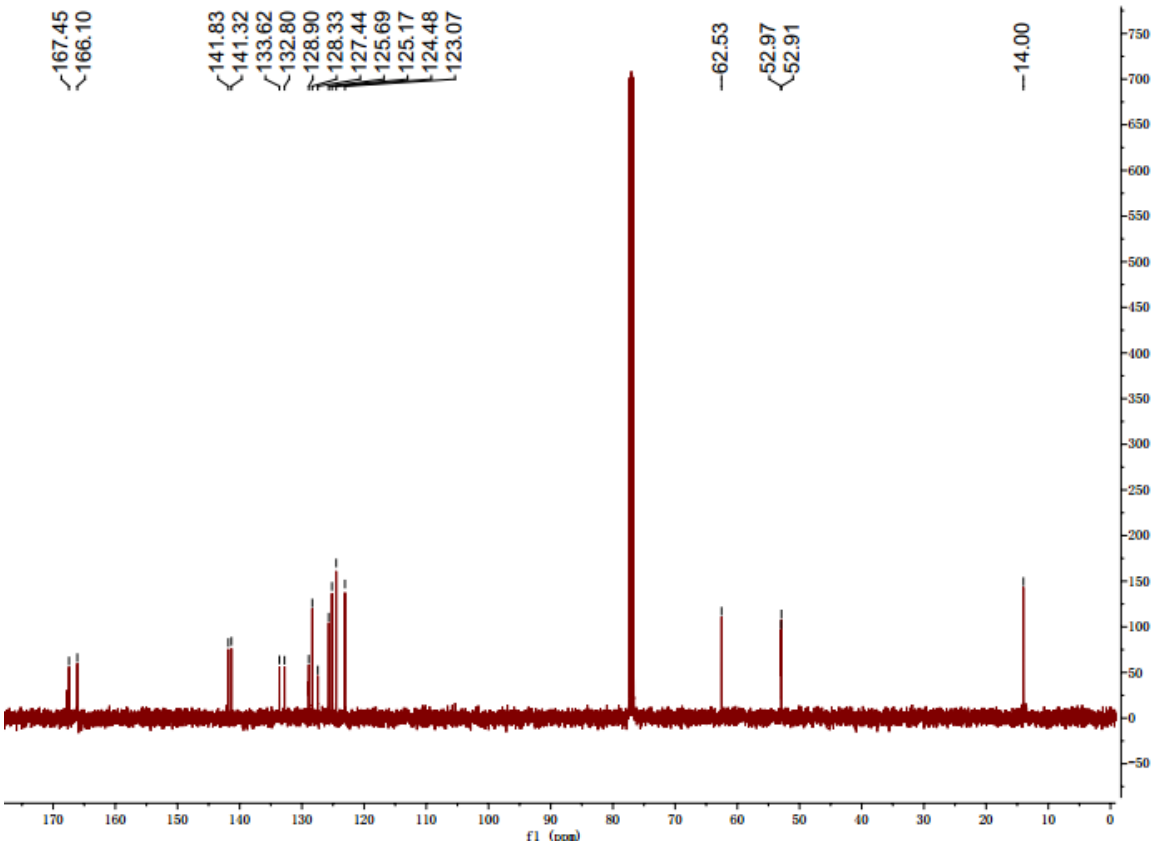
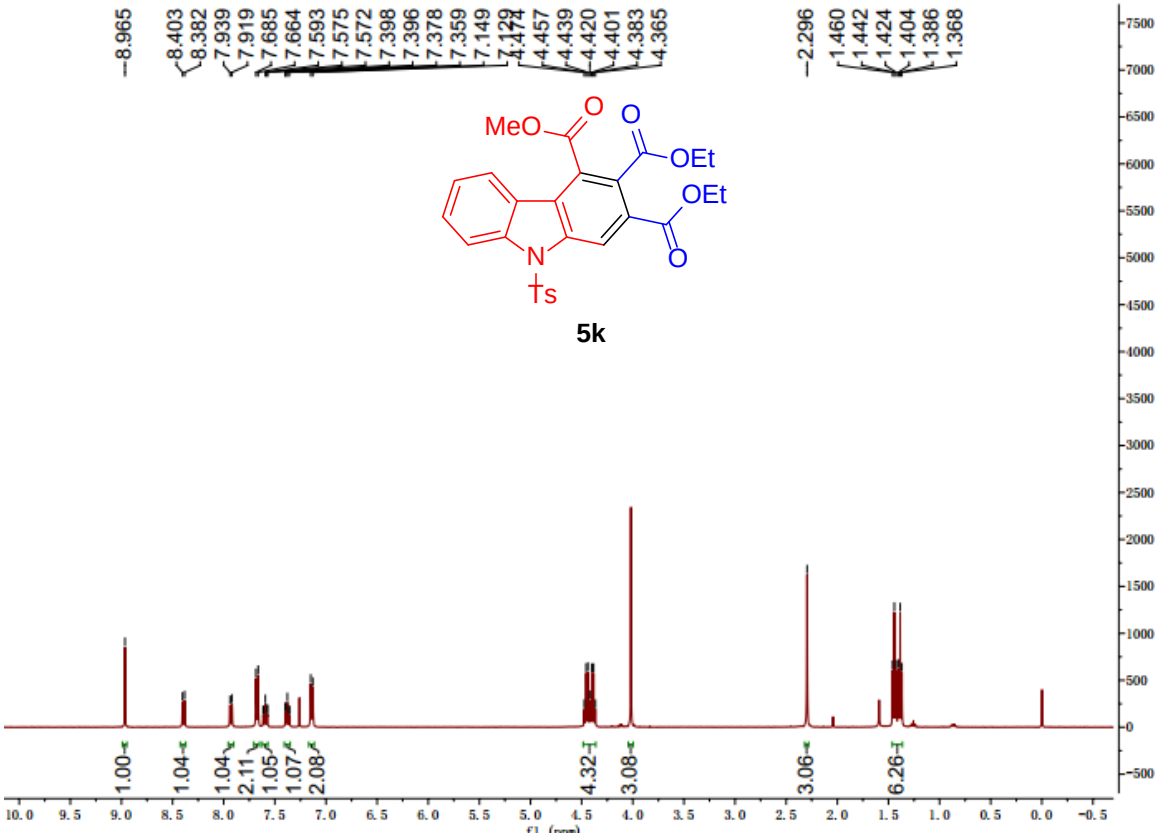
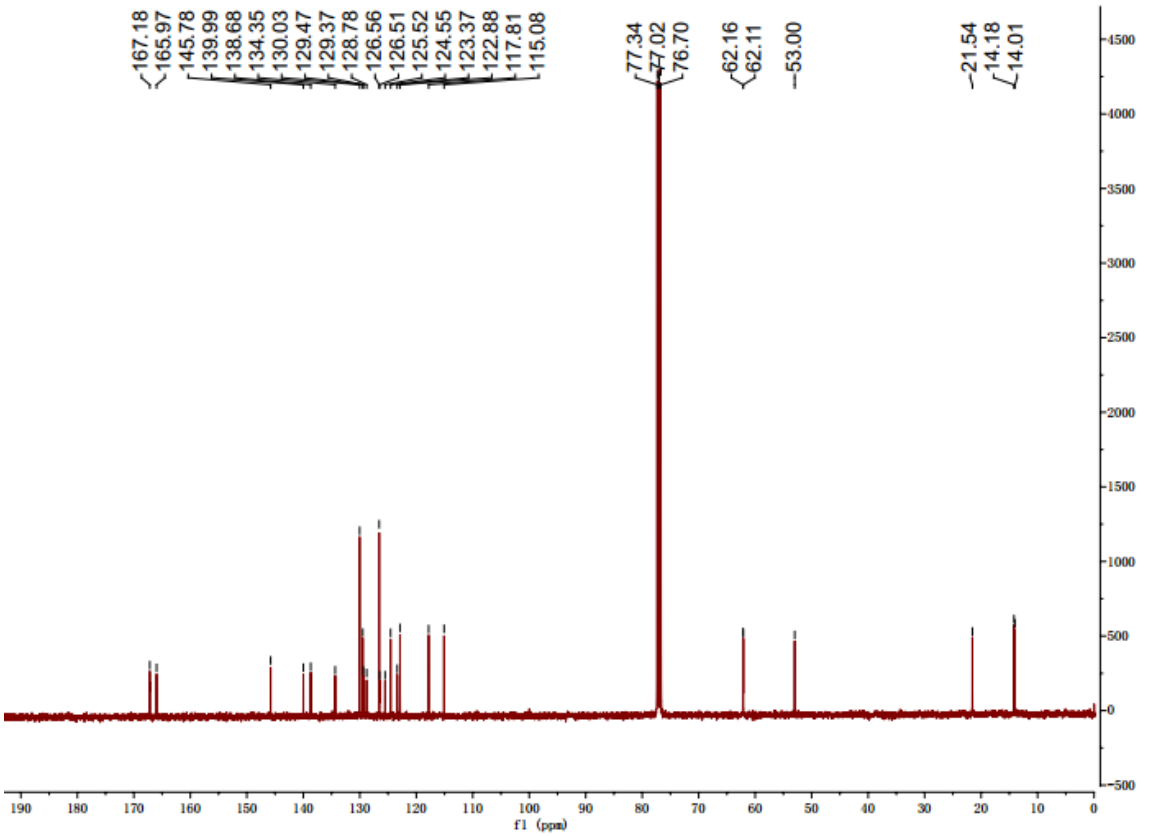
8.096
8.077
7.901
7.882
7.564
7.562
7.546
7.544
7.526
7.523
7.486
7.483
7.466
7.463
7.448
7.445
4.601
4.584
4.566
4.548
3.948
3.947
1.464
1.446
1.428
EtO
O
O
OMe
OMe
O
S
1.00
1.06
1.07
1.14
1.05
2.16
6.02
3.28
f1 (ppm)

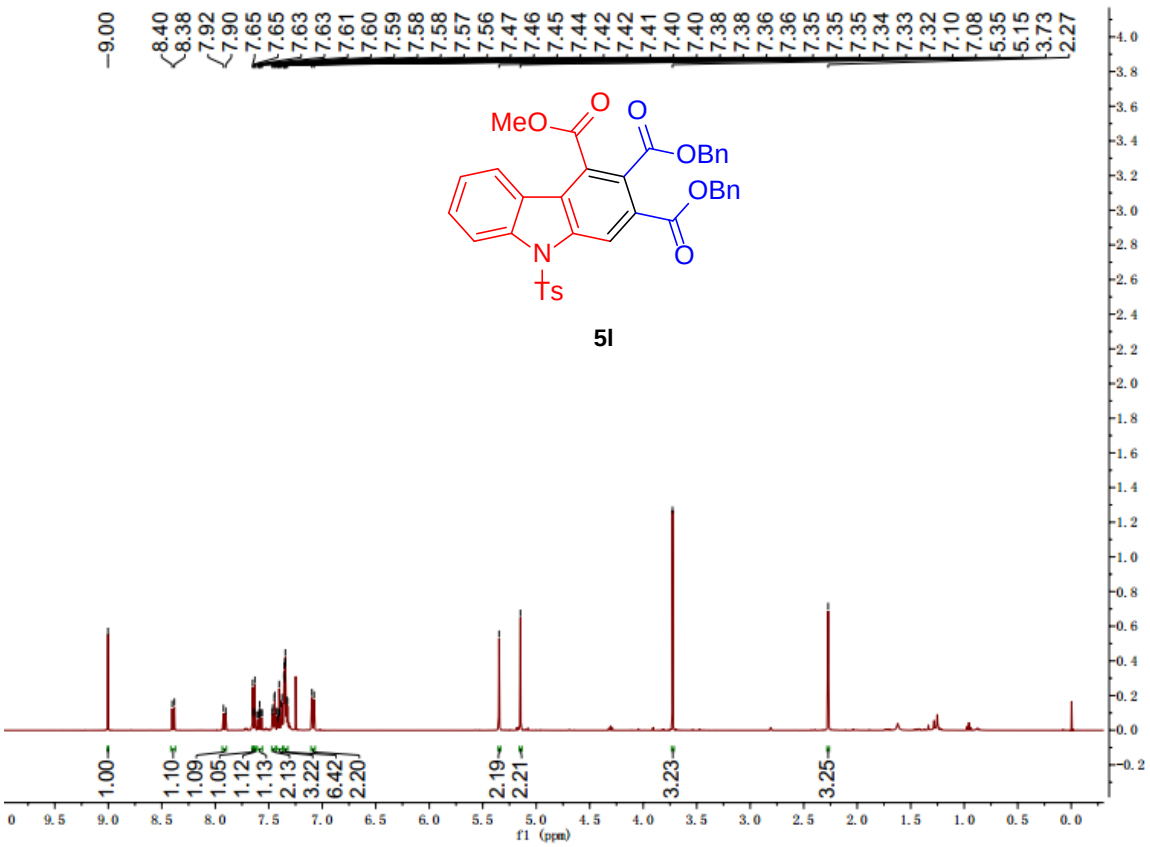
5j


167.45
166.10
141.83
141.32
133.62
132.80
128.90
128.33
127.44
125.69
125.17
124.48
123.07
62.53
52.97
52.91
14.00
f1 (ppm)

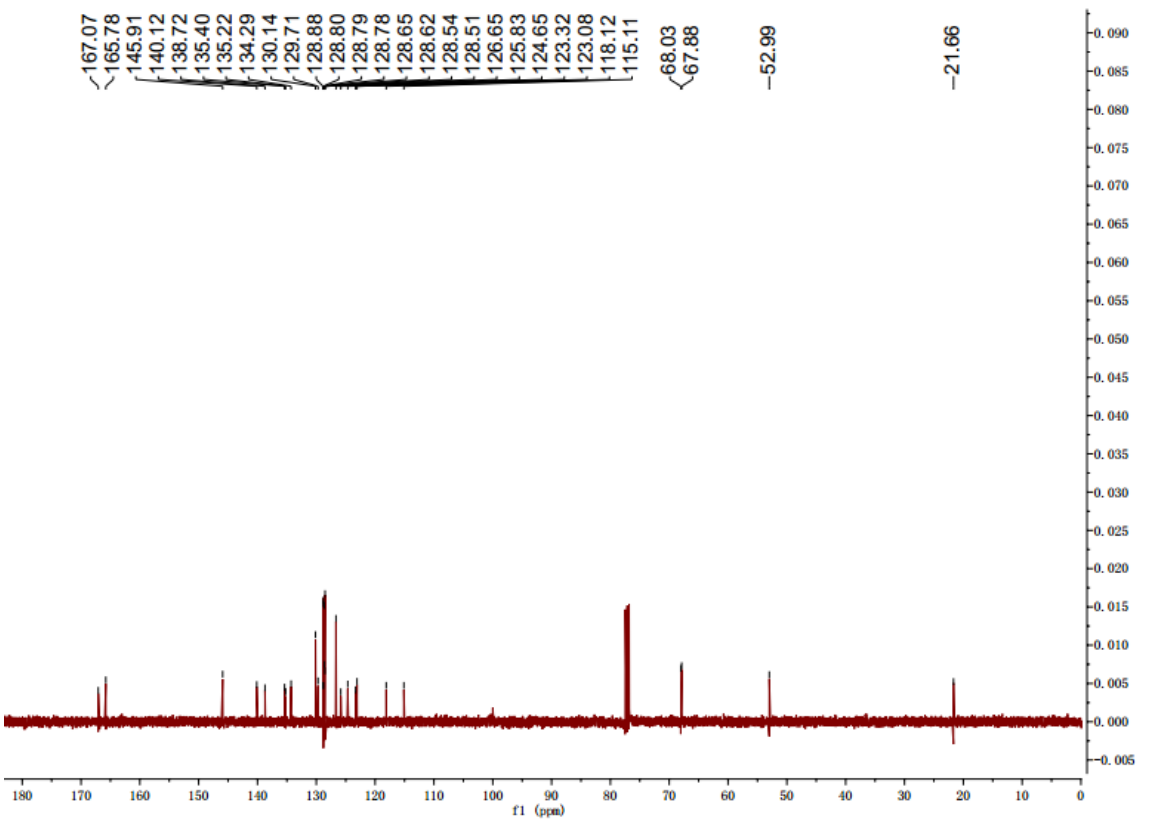

8.965
8.403
8.382
7.939
7.919
7.685
7.664
7.593
7.575
7.572
7.398
7.396
7.378
7.359
7.149
4.457
4.439
4.420
4.401
4.383
4.365
2.296
1.460
1.442
1.424
1.404
1.386
1.368
MeO
O
O
OEt
OEt
O
N
Ts
1.00
1.04
1.04
2.11
1.05
1.07
2.08
4.32
3.08
3.06
6.26

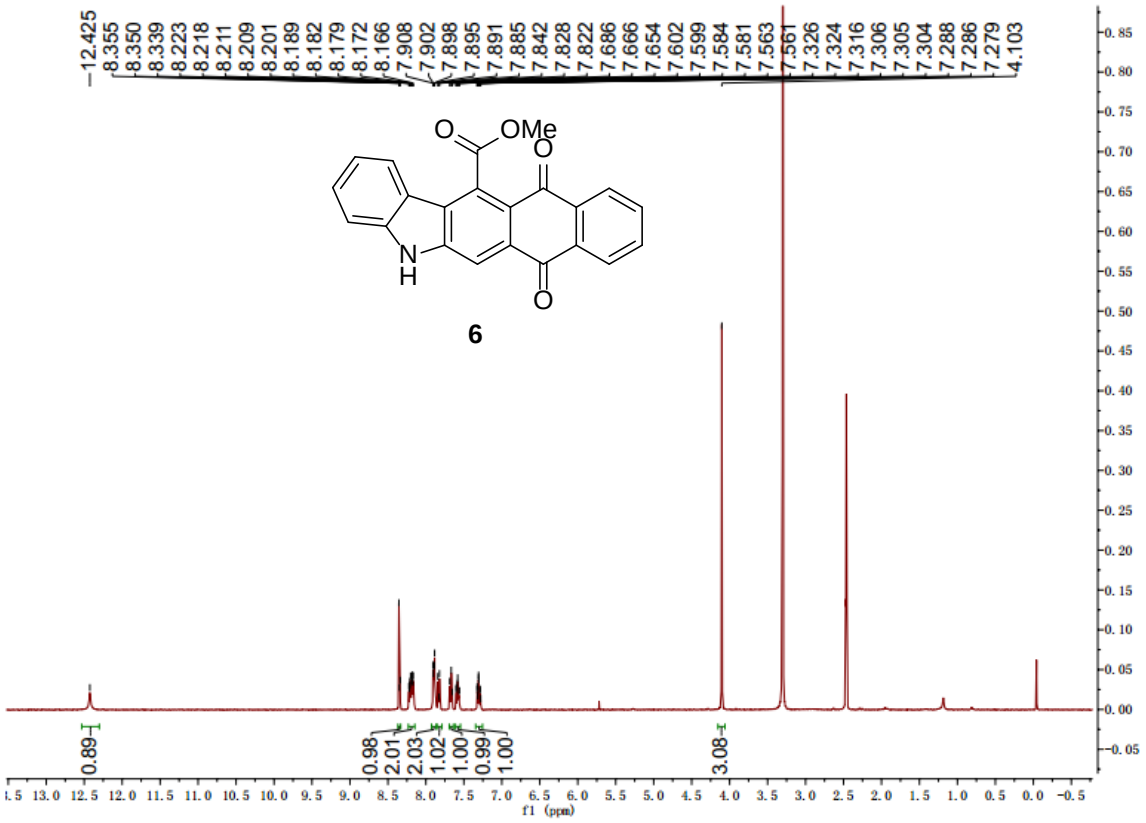
5k


167.18
165.97
145.78
139.99
138.68
134.35
130.03
129.47
129.37
128.78
126.56
126.51
125.52
124.55
123.37
122.88
117.81
115.08
77.34
77.02
76.70
62.16
62.11
53.00
21.54
14.18
14.01
f1 (ppm)



5l

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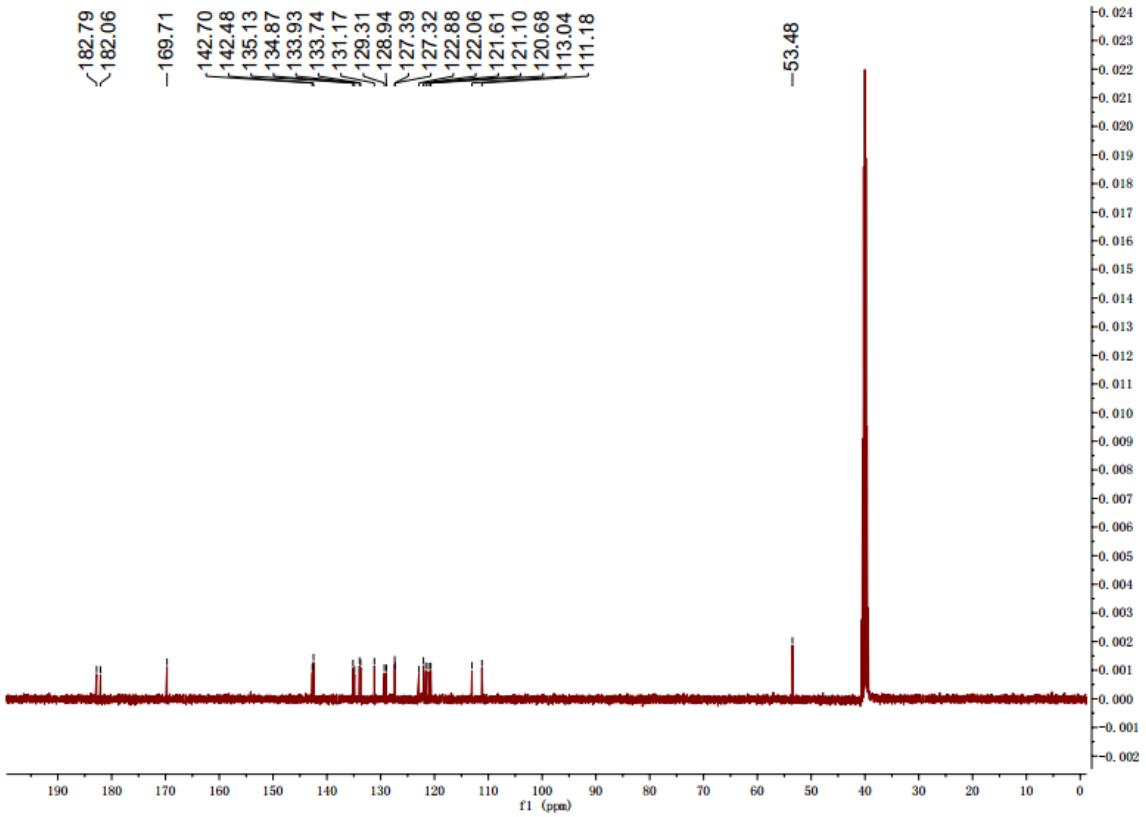
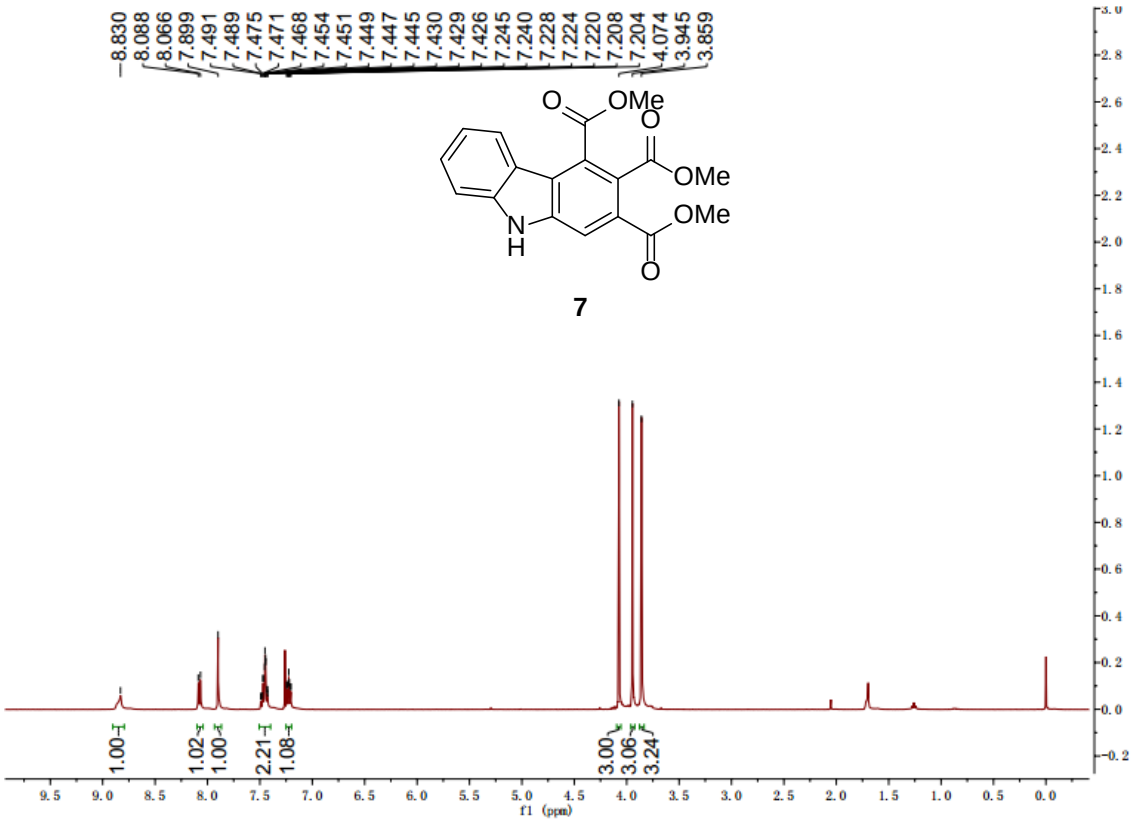
8.339
8.223
8.218
8.211
8.209
8.201
8.189
8.182
8.179
8.172
8.166
7.908
7.902
7.898
7.895
7.891
7.885
7.842
7.828
7.822
7.686
7.666
7.654
7.602
7.599
7.584
7.581
7.563
7.561
7.326
7.324
7.316
7.306
7.305
7.304
7.288
7.286
7.279
4.103
O
OMe
O
N
H
O
6
0.89
0.98
2.01
2.03
1.02
1.00
0.99
1.00
3.08
f1 (ppm)


182.79
182.06
169.71
142.70
142.48
135.13
134.87
133.93
133.74
131.17
129.31
128.94
127.39
127.32
122.88
122.06
121.61
121.10
120.68
113.04
111.18
53.48
f1 (ppm)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8.088
8.066
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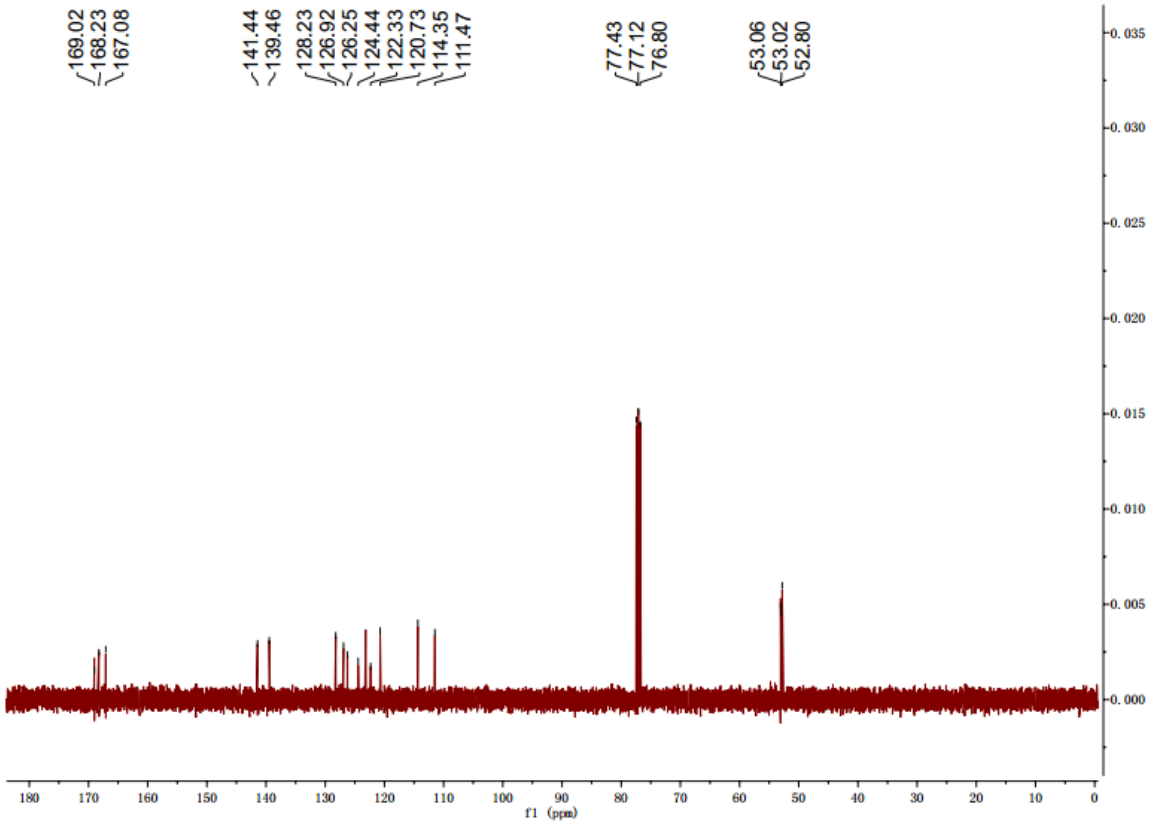
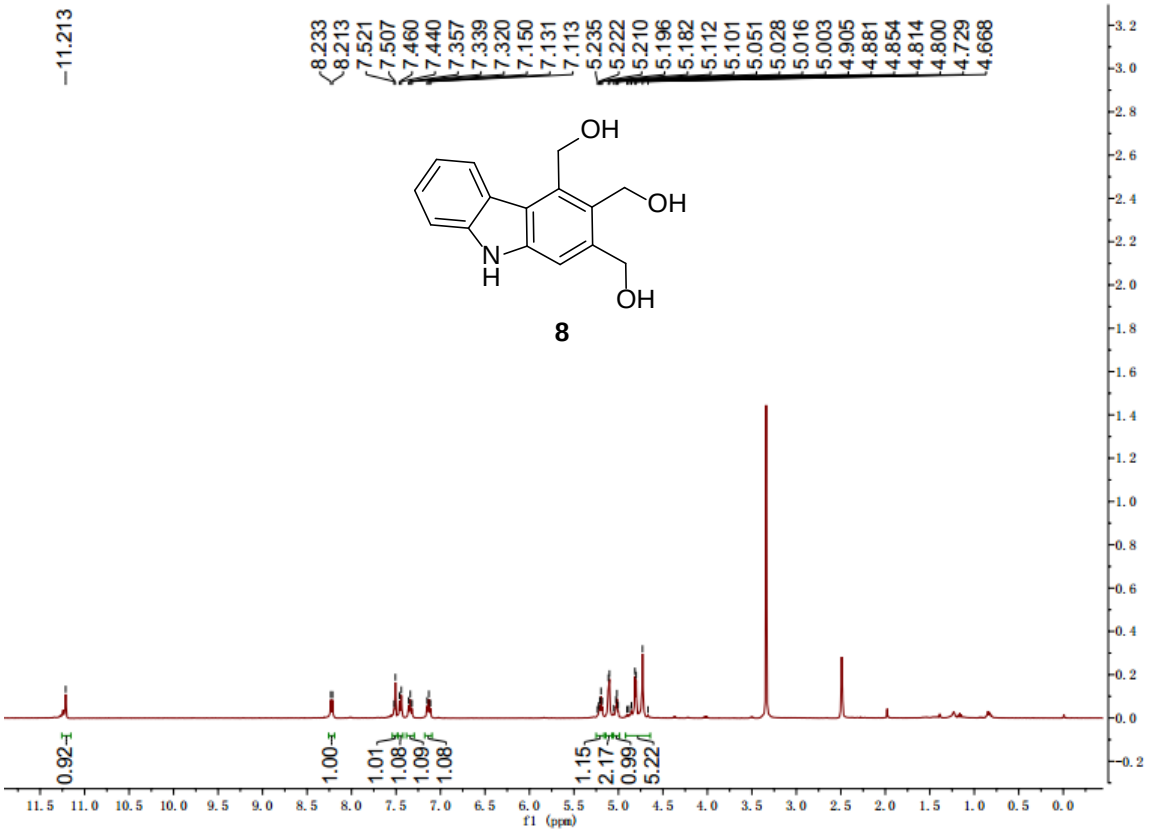
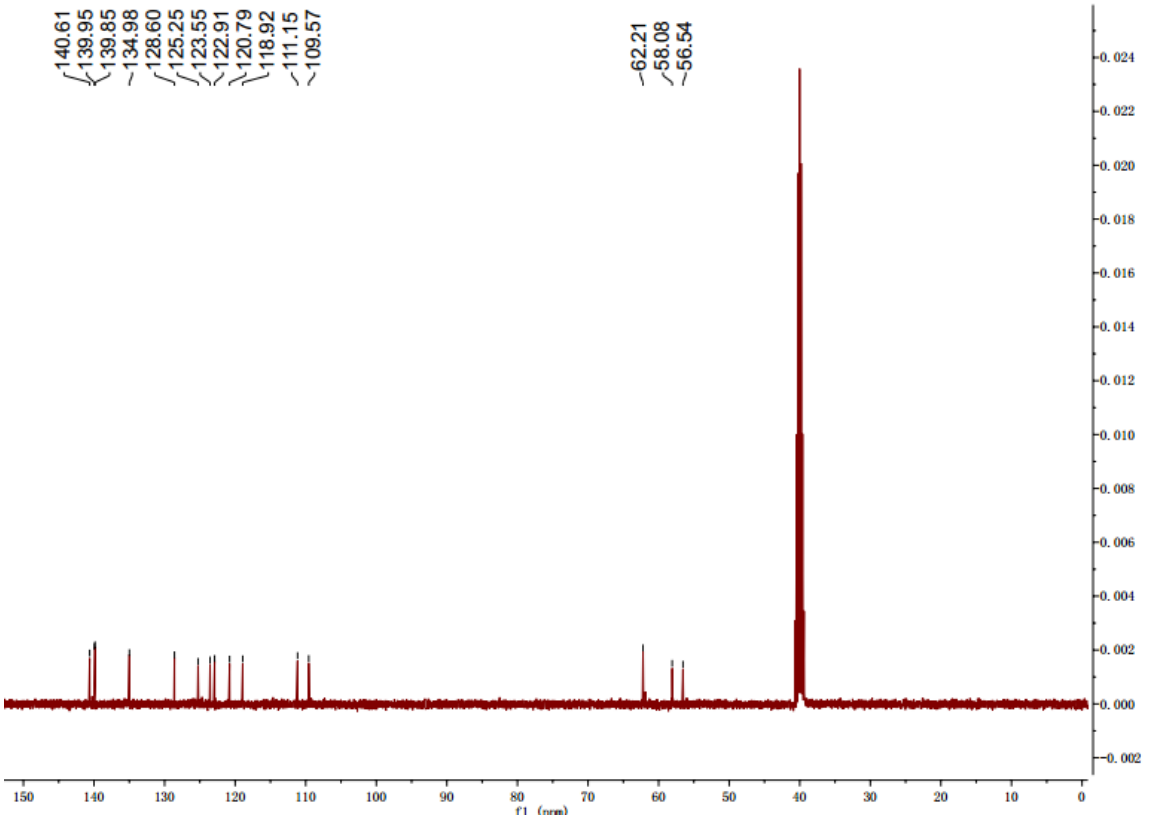
7.491
7.489
7.475
7.471
7.468
7.454
7.451
7.449
7.447
7.445
7.430
7.429
7.426
7.245
7.240
7.228
7.224
7.220
7.208
7.204
4.074
3.945
3.859
O
OMe
O
OMe
OMe
N
H
O
1.00
1.02
1.00
2.21
1.08
3.00
3.06
3.24
f1 (ppm)

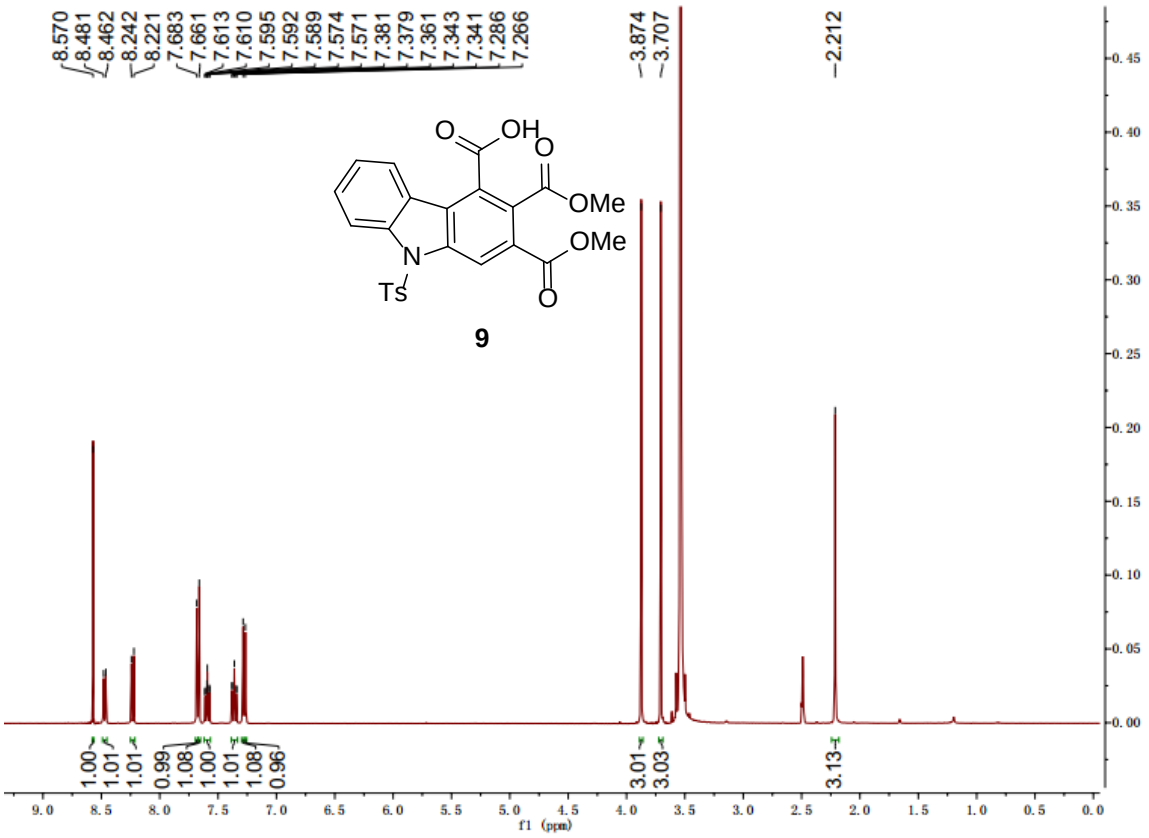
7


169.02
168.23
167.08
141.44
139.46
128.23
126.92
126.25
124.44
122.33
120.73
114.35
111.47
77.43
77.12
76.80
53.06
53.02
52.80
f1 (ppm)


11.213
8.233
8.213
7.521
7.507
7.460
7.440
7.357
7.339
7.320
7.150
7.131
7.113
5.235
5.222
5.210
5.196
5.182
5.112
5.101
5.051
5.028
5.016
5.003
4.905
4.881
4.854
4.814
4.800
4.729
4.668
OH
OH
OH
N
H
0.92
1.00
1.01
1.08
1.09
1.08
1.15
2.17
0.99
5.22
f1 (ppm)

8


140.61
139.95
139.85
134.98
128.60
125.25
123.55
122.91
120.79
118.92
111.15
109.57
62.21
58.08
56.54
f1 (ppm)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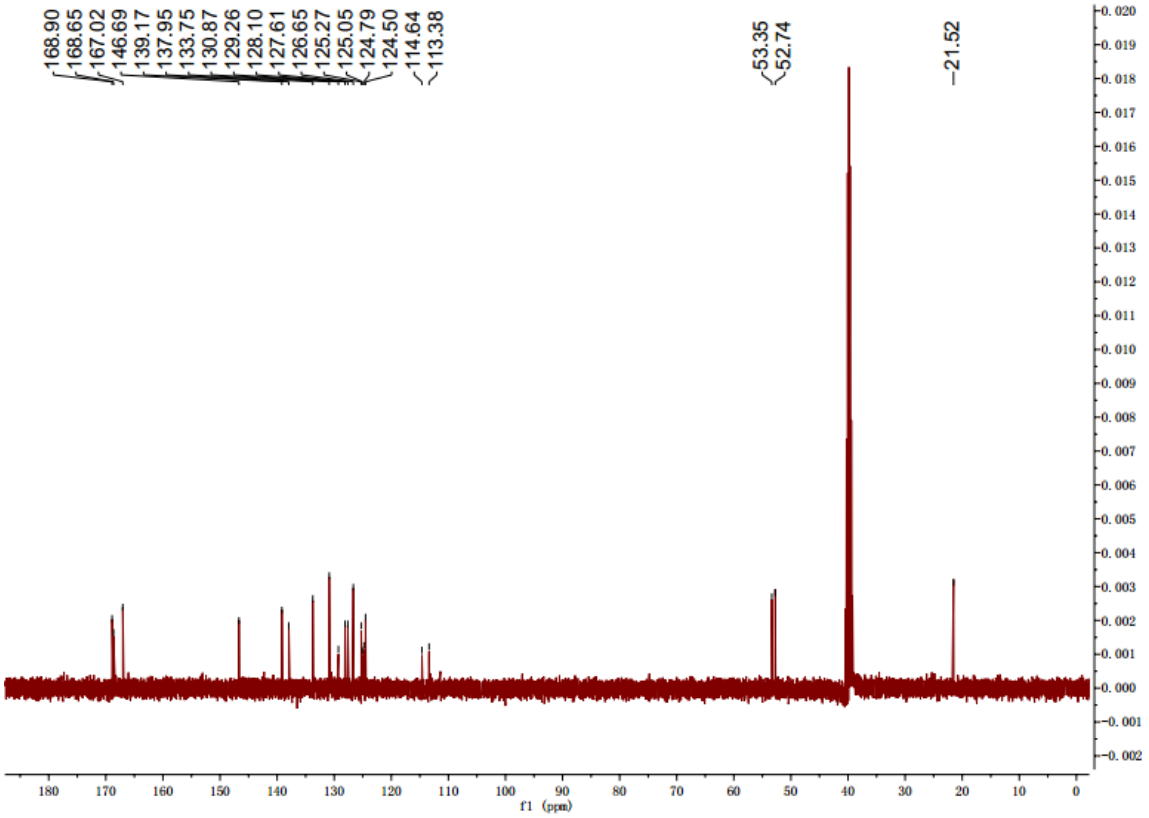
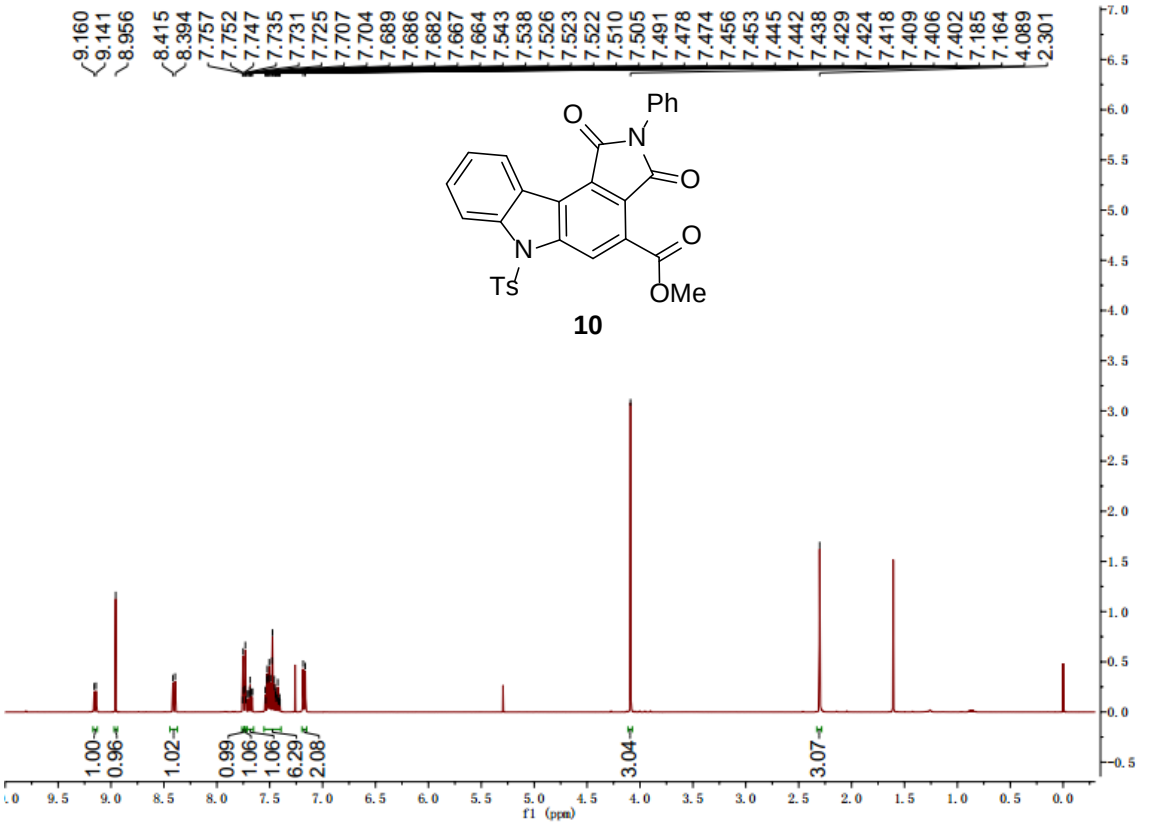
8.462
8.242
8.221
7.683
7.661
7.613
7.610
7.595
7.592
7.589
7.574
7.571
7.381
7.379
7.361
7.343
7.341
7.286
7.266
3.874
3.707
2.212
O
OH
O
OMe
OMe
N
Ts
O
9
1.00
1.01
1.01
0.99
1.08
1.00
1.01
1.08
0.96
3.01
3.03
3.13
f1 (ppm)


168.90
168.65
167.02
146.69
139.17
137.95
133.75
130.87
129.26
128.10
127.61
126.65
125.27
125.05
124.79
124.50
114.64
113.38
53.35
52.74
21.52
f1 (ppm)


9.160
9.141
8.956
8.415
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7.747
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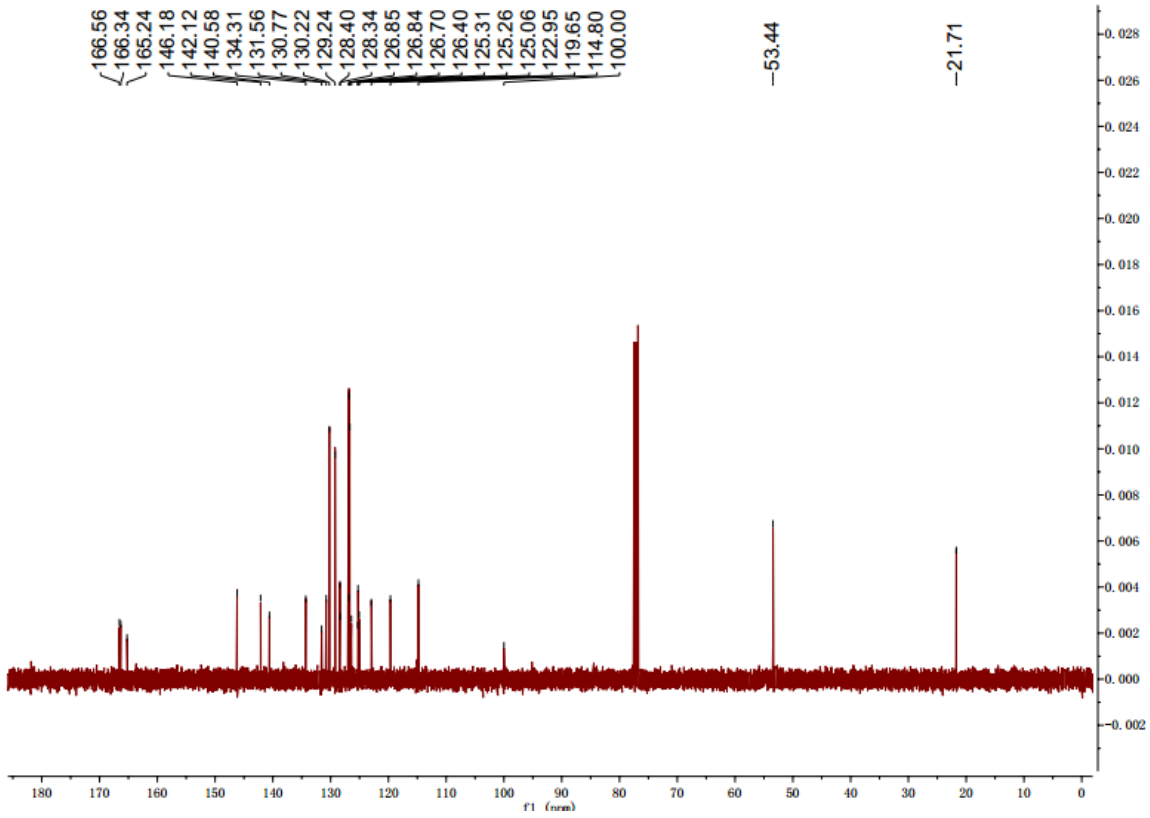
7.731
7.725
7.707
7.704
7.689
7.686
7.682
7.667
7.664
7.543
7.538
7.526
7.523
7.522
7.510
7.505
7.491
7.478
7.474
7.456
7.453
7.445
7.442
7.438
7.429
7.424
7.418
7.409
7.406
7.402
7.185
7.164
4.089
2.301
O
Ph
N
O
O
N
Ts
OMe
1.00
0.96
1.02
0.99
1.06
1.06
6.29
2.08
3.04
3.07
f1 (ppm)

10


166.56
166.34
165.24
146.18
142.12
140.58
134.31
131.56
130.77
130.22
129.24
128.40
128.34
126.85
126.84
126.70
126.40
125.31
125.26
125.06
122.95
119.65
114.80
100.00
53.44
21.71
f1 (ppm)