Electroreduction cross-coupling of thiosulfonates with (hetero)aryl boronic acids to access thioethers

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Supporting Information

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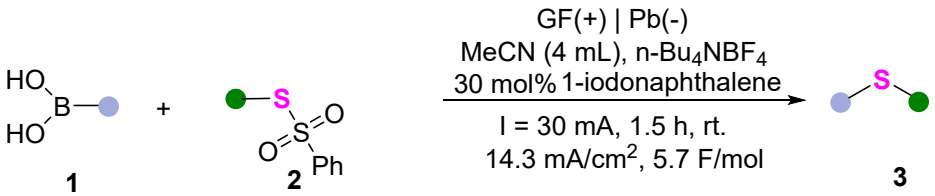
1. Materials and equipment

Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. And all the solvents were used as received without further purification. The instrument for electrolysis was dual display potentiostat (HY3005B) (made in China, HYELEC), the GF anode (5.25 × 0.8 × 0.2 cm^3) and Pb cathode (5.25 × 0.8 × 0.2 cm^3) were purchased from Shanghai Fanyue Electronic Technology Co., LTD. Thin layer chromatography (TLC) employed glass 0.20-0.25 mm silica gel plates (GF254). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90°C). Gradient flash chromatography was conducted eluting with PE (petroleum)/EA (ethyl acetate), they are listed as volume/volume ratios. (Hetero)aryl boronic acids were purchased from JiaHe Co., LTD., (Shanghai). Thiosulfonates were purchased from EYu Co., LTD., (Wuhan). Amino acids used were L-Amino Acids. NMR spectra were recorded on a Bruker Avance III spectrometer (^{1}H NMR: 400 MHz; ^{13}C NMR: 101 MHz; ^{19}F NMR: 376.8 MHz) or a JEOL-ECX500 instrument (^{1}H NMR: 500 MHz; ^{13}C NMR: 125 MHz). Chemical shifts were reported in ppm downfield. Coupling constants were quoted in Hz (*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High resolution mass spectra (HRMS) were measured using Thermo Scientic Q Exactive. Mass spectra (MS) were measured using electron ionization (EI) method by GC-MS.

2. Experimental procedure

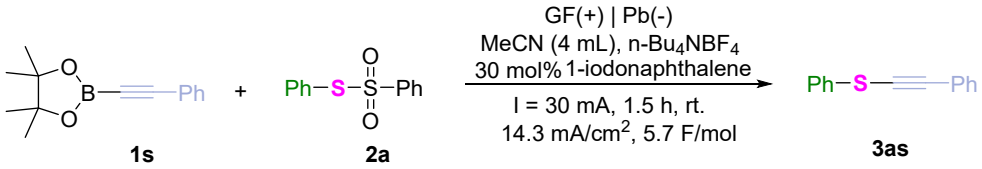
2.1 General procedure for the synthesis of 3



A 10-mL undivided three-necked bottle was equipped with a GF anode (5.25 × 0.8 × 0.2 cm^3) and Pb cathode (5.25 × 0.8 × 0.2 cm^3) which was connected to a DC regulated power supply. Under N_2 atmosphere, **1** (0.2 mmol), **2** (0.26 mmol), 1-

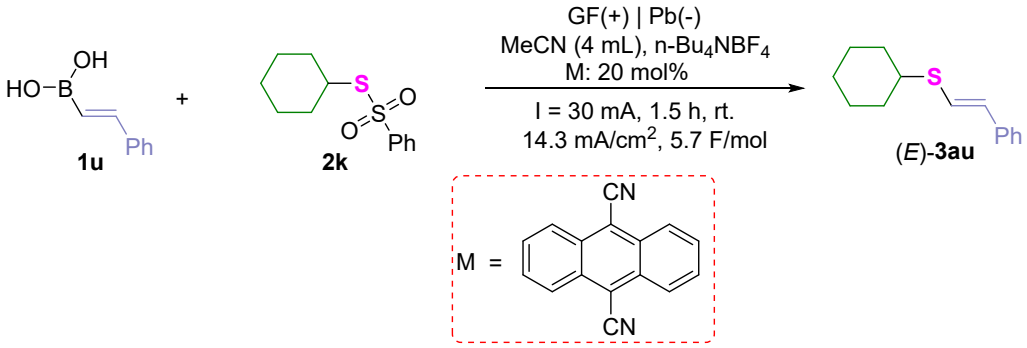
iodonaphthalene (0.06 mmol) and n-Bu_4NBF_4 (0.4 mmol) were dissolved in 4 mL MeCN, and the cell was electrolyzed at a constant current of 30 mA (~14.3 mA/cm^2), and the mixture was stirred for 1.5 h at environment temperature. The electrolysis was terminated when the starting materials were consumed as determined by TLC. Then the reaction mixture was diluted with 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA) to afford the desired products **3**.

2.2 Experimental procedure for the synthesis of 3as



A 10-mL undivided three-necked bottle was equipped with a GF anode (5.25 × 0.8 × 0.2 cm^3) and Pb cathode (5.25 × 0.8 × 0.2 cm^3) which was connected to a DC regulated power supply. Under N_2 atmosphere, **1s** (0.2 mmol, 45.6 mg), **2a** (0.26 mmol, 65.1 mg), 1-iodonaphthalene (0.06 mmol) and n-Bu_4NBF_4 (0.4 mmol) were dissolved in 4 mL MeCN, and the cell was electrolyzed at a constant current of 30 mA (~14.3 mA/cm^2) for 1.5 h at environment temperature. The electrolysis was terminated when the starting materials were consumed as determined by TLC. Then the reaction mixture was diluted with 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA) to afford the desired products **3as**.

2.3 Experimental procedure for the synthesis of 3au



A 10-mL undivided three-necked bottle was equipped with a GF anode (5.25 × 0.8 × 0.2 cm^3) and Pb cathode (5.25 × 0.8 × 0.2 cm^3) which was connected to a DC regulated power supply. Under N_2 atmosphere, (*E*)-styrylboronic acid **1u** (0.2 mmol, 29.6 mg), **2k** (0.26 mmol, 74.5 mg), 9,10-anthracenedicarbonitrile (0.04 mmol, 9.1 mg) and n-Bu_4NBF_4 (0.4 mmol) were dissolved in 4 mL MeCN, and the cell was electrolyzed at a constant current of 30 mA (~14.3 mA/cm^2) for 1.5 h at environment temperature. The electrolysis was terminated when the starting materials were consumed as determined by TLC. Then the reaction mixture was diluted with 30 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA) to afford the desired products **3au**.

2.4 Scale-up reaction procedure

A 100-mL undivided three-necked bottle was equipped with a GF anode (5.25 × 0.8 × 0.2 cm^3) and Pb cathode (5.25 × 0.8 × 0.2 cm^3) which was connected to a DC regulated power supply. Under N_2 atmosphere, **1a** (5 mmol, 610 mg), **2a** (6.5 mmol, 1.63 g), 1-iodonaphthalene (1.5 mmol) and n-Bu_4NBF_4 (10.0 mmol) were dissolved in 20 mL MeCN, and the cell was electrolyzed at a constant current of 30 mA (~14.3 mA/cm^2) for 1.5 h at environment temperature. The electrolysis was terminated when the starting materials were consumed as determined by TLC. Then the reaction mixture was diluted with 100 mL ethyl acetate, washed with a saturated solution of brine (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting

residue was purified by silica gel column chromatography (eluent: PE/EA = 100:1) to afford the desired products **3aa**.

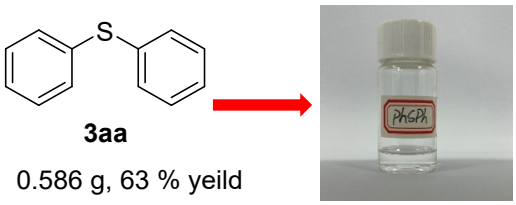
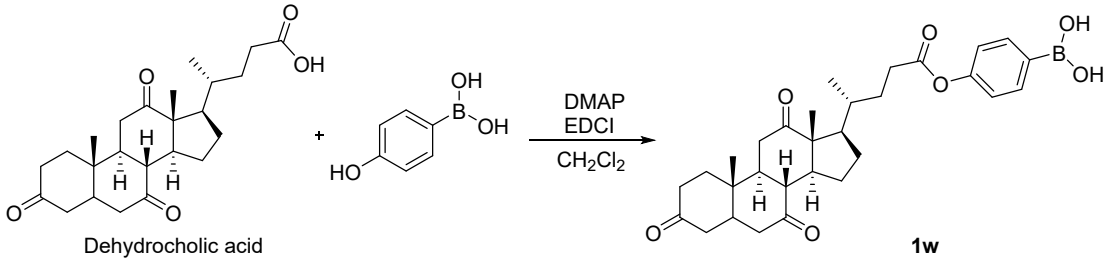
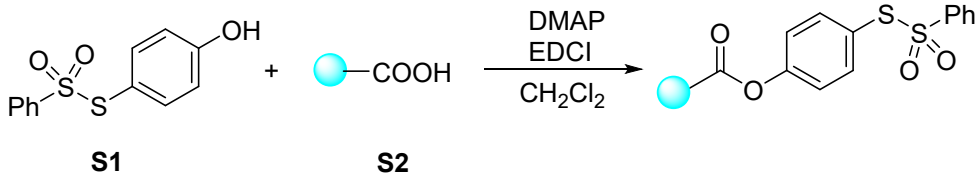


Figure S1. Product **3aa**.

2.5 General procedure for the synthesis of intermediate



To a stirred solution of **Dehydrocholic acid** (1.2 mmol), **4-Hydroxyphenylboronic acid** (1.0 mmol, 266.33 mg) and 4-dimethylaminopyridine (DMAP, 12.22 mg, 0.1mmol) in CH_2Cl_2 (5 mL), a CH_2Cl_2 solution (2 mL) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 1.2 mmol, 230.04 mg) was added dropwise. The mixture was stirred at room temperature overnight. After completion, the mixture was filtered through a thin pad of celite and rinsed with additional CH_2Cl_2 (20 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel to afford the desired intermediate **1w**.



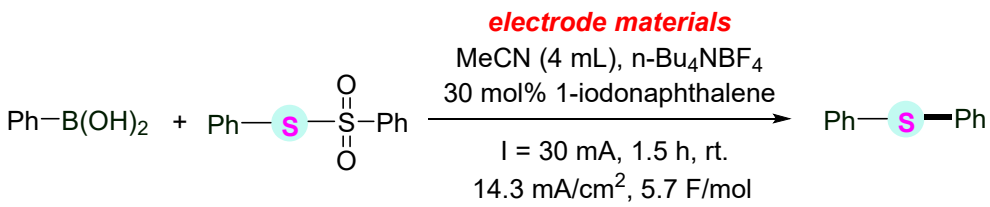
S1 **S2**

To a stirred solution of acid **S2** (1.2 mmol), thiosulfonate **S1** (1.0 mmol, 266.33 mg) and 4-dimethylaminopyridine (DMAP, 12.22 mg, 0.1mmol) in CH_2Cl_2 (5 mL), a CH_2Cl_2 solution (2 mL) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 1.2 mmol, 230.04 mg) was added dropwise. The mixture was stirred at room temperature overnight. After completion, the mixture was filtered through a thin pad of celite and rinsed with additional CH_2Cl_2 (20 mL). The filtrate

was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel to afford the desired intermediate **2o** and **2p**.

3. Optimization of reaction

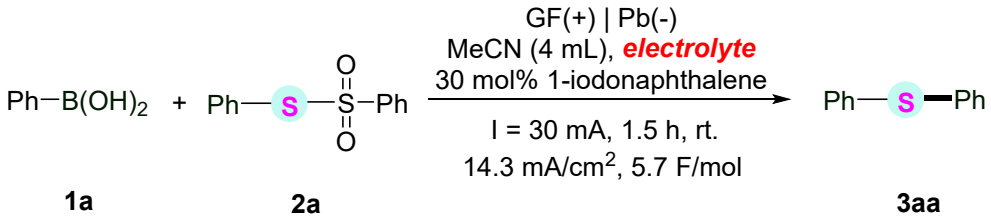
Table S1 Screening for electrode materials



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

Entry	Variation from the standard conditions	Isolated yield (%)
1	none	81
2	C(+) | Pb(-) instead of GF(+) | Pb(-)	22
3	GF(+) | Ni(-) instead of GF(+) | Pb(-)	n.d.
4	RVC(+) | Ni(-) instead of GF(+) | Pb(-)	45
5	GF(+) | GF(-) instead of GF(+) | Pb(-)	n.d.

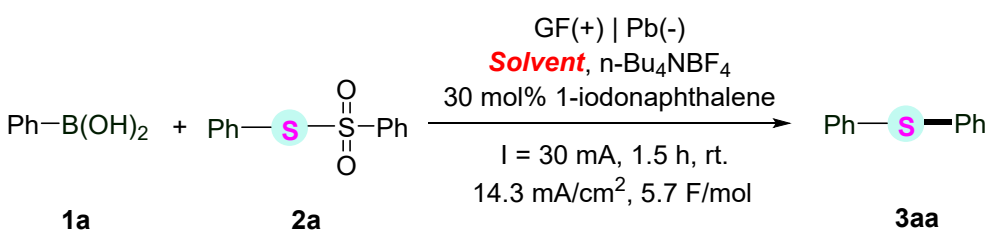
Table S2 Screening for electrolytes



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

Entry	Variation from the standard conditions	Isolated yield (%)
1	none	81
2	n-Bu_4NPF_6 instead of n-Bu_4NBF_4	58
3	n-Bu_4NI instead of n-Bu_4NBF_4	41
4	Et_4NBF_4 instead of n-Bu_4NBF_4	60
5	NH_4Br instead of n-Bu_4NBF_4	55
6	NaBr instead of n-Bu_4NBF_4	64

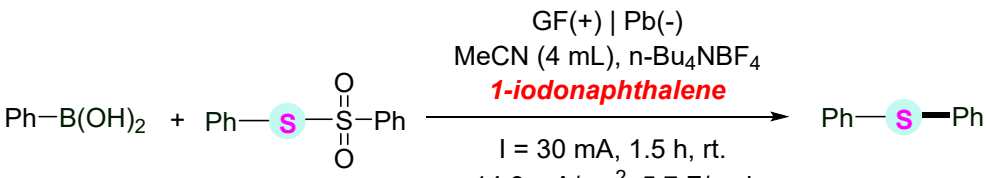
Table S3 Screening for solvents



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

Entry	Variation from the standard conditions	Isolated yield (%)
1	none	81
2	DMF instead of MeCN	n.d.
3	MeOH instead of MeCN	14
4	DMSO instead of MeCN	23
5	MeOH/H_2O (4:1, 5 mL) instead of MeCN	56

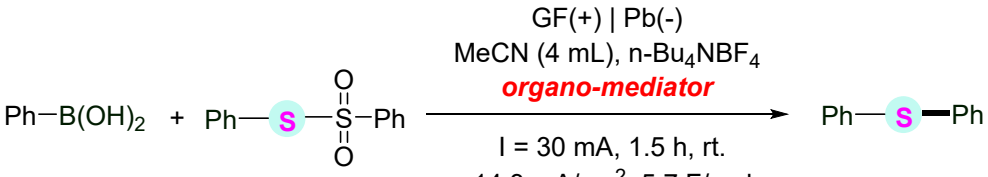
Table S4 Screening for of 1-iodonaphthalene dosage



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

Entry	Variation from the standard conditions	Isolated yield (%)
1	none	81
2	1-iodonaphthalene (10 mol%) instead of 1-iodonaphthalene (30 mol%)	32
3	1-iodonaphthalene (20 mol%) instead of 1-iodonaphthalene (30 mol%)	65
4	1-iodonaphthalene (40 mol%) instead of 1-iodonaphthalene (30 mol%)	81
5	1-iodonaphthalene (50 mol%) instead of 1-iodonaphthalene (30 mol%)	80
6	1-iodonaphthalene (0 mol%) instead of 1-iodonaphthalene (30 mol%)	0

Table S5 Screening for organo-mediators



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

Entry	Variation from the standard conditions	Isolated yield (%)
1	none	81
2	Naphthalene instead of 1-Iodonaphthalene	29
3	1-Methylnaphthalene instead of 1-Iodonaphthalene	23
4	1-Bromonaphthalene instead of 1-Iodonaphthalene	54
5	1-Naphthylbenzene instead of 1-Iodonaphthalene	n.d.
6	9,10-Dicyanoanthracen instead of 1-Iodonaphthalene	50
7	Triethyl phosphite instead of 1-Iodonaphthalene	36

4. Cyclic voltammetry experiments

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 4 mL of MeCN containing 0.1 M n-Bu_4NBF_4 were poured into the electrochemical cell in all experiments. The scan rate is 0.01 V/s, ranging from 0.0 V to -3.0 V.

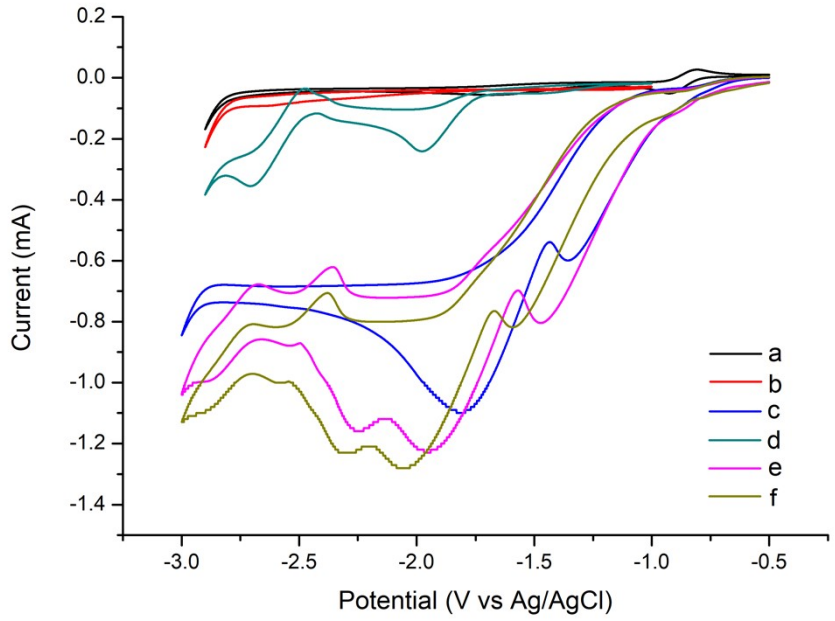


Figure S2. plotting convention (IUPAC)

In **Figure S2**, Cyclic voltammograms of 0.1 mol L^{-1} of n-Bu_4NBF_4 in 4 mL of MeCN solution containing different compounds: (a) blank experiment; (b) **1a** (0.2 mmol); (c) **2a** (0.26 mmol); (d) 1-iodonaphthalene (0.06 mmol); (e) **2a** (0.26 mmol) + 1-iodonaphthalene (0.06 mmol); (f) **1a** (0.2 mmol) + **2a** (0.26 mmol) + 1-iodonaphthalene (0.06 mmol); with a GC disk working electrode, Pt counter electrode, and Ag/AgCl reference electrode at 0.01 V/s scan rate.

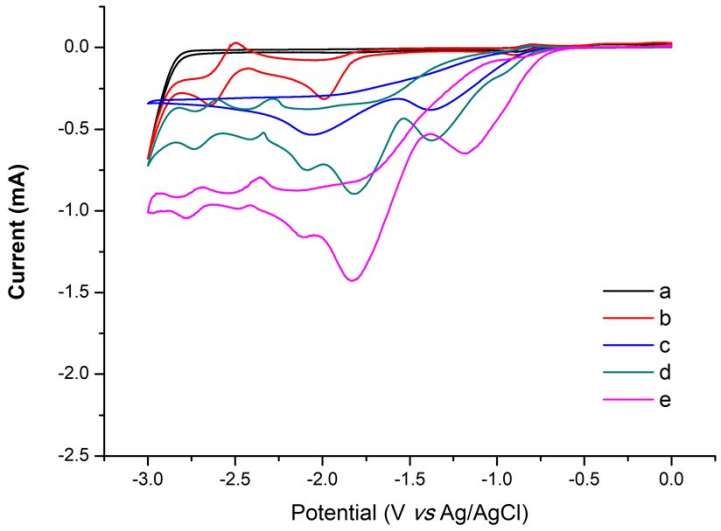


Figure S3. CV analyses of **2a** and 1-iodonaphthalene

In **Figure S3**, Cyclic voltammograms of 0.1 mol L^{-1} of n-Bu_4NBF_4 in 4 mL of MeCN solution containing different compounds: (a) blank experiment; (b) 1-iodonaphthalene (0.06 mmol); (c) **2a** (0.13 mmol); (d) **2a** (0.13 mmol) + 1-iodonaphthalene (0.06 mmol); (e) **2a** (0.26 mmol) + 1-iodonaphthalene (0.06 mmol); with a GC disk working electrode, Pt counter electrode, and Ag/AgCl reference electrode at 0.01 V/s scan rate.

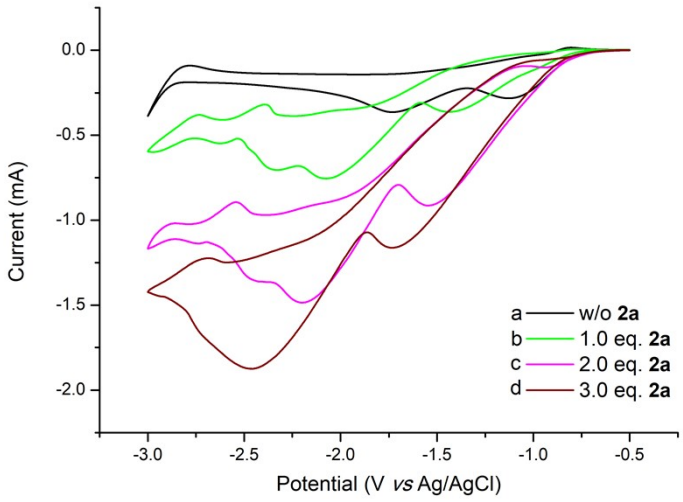


Figure S4. CVs of 1-iodonaphthalene performed in the presence of increasing equivalents of **2a**.

In **Figure S4**, Cyclic voltammograms of 0.1 mol L^{-1} of n-Bu_4NBF_4 in 4 mL of MeCN solution containing different compounds: (a) blank experiment; (b) **2a** (0.13 mmol) + 1-iodonaphthalene (0.06 mmol); (c) **2a** (0.26 mmol) + 1-iodonaphthalene (0.06 mmol); (d) **2a** (0.39 mmol) + 1-iodonaphthalene (0.06 mmol); with a GC disk working electrode, Pt counter electrode, and Ag/AgCl reference electrode at 0.01 V/s scan rate.

5. Analysis of by-product

5.1 High-resolution mass spectra of disulfide

Reaction conditions: Reaction conditions: GF anode (5.25 × 0.8 × 0.2 cm^3), Pb cathode (5.25 × 0.8 × 0.2 cm^3), **1a** (0.2 mmol, 1 equiv.), *S*-(4-methoxyphenyl) benzenesulfonothioate (0.26 mmol, 1.3 equiv.), 1-iodonaphthalene (30 mol%), n-Bu_4NBF_4 (0.4 mmol, 2 equiv), MeCN (4.0 mL), undivided cell, room temperature, 30 mA, 1.5 h. The corresponding reaction mixture was detected by HRMS. We successfully detected the desired disulfide.

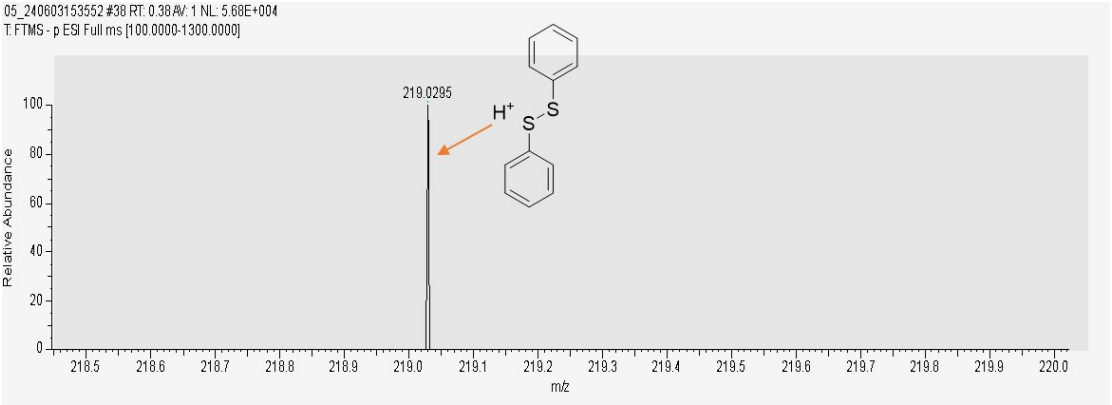


Figure S5. HMRS spectra of disulfide

5.2 GC-mass spectra of naphthalene

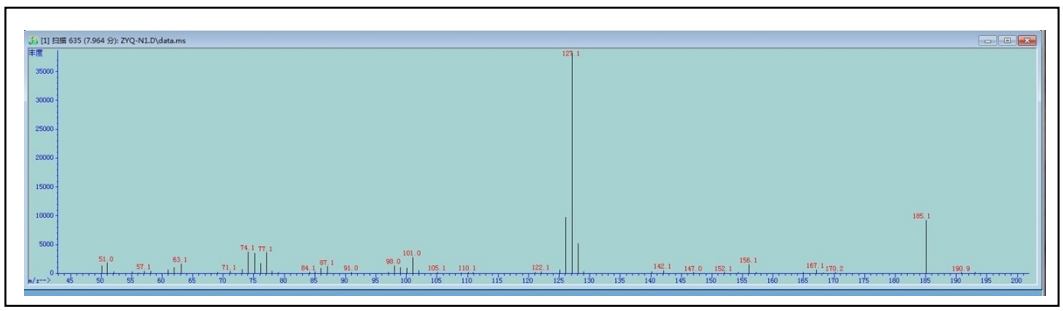
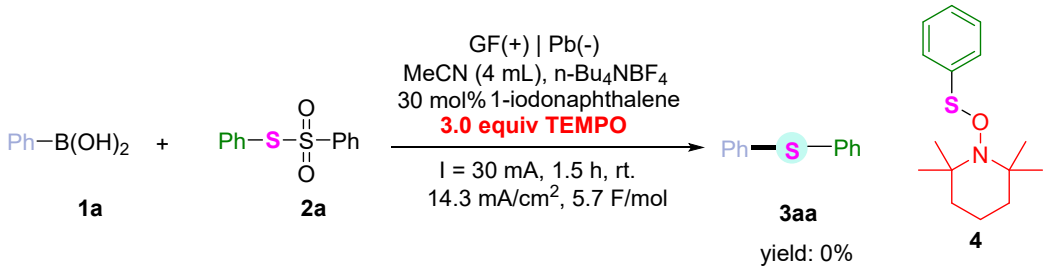


Figure S6. GC-mass spectra of naphthalene

Reaction conditions: Reaction conditions: GF anode (5.25 × 0.8 × 0.2 cm^3), Pb cathode (5.25 × 0.8 × 0.2 cm^3), **1a** (0.2 mmol, 1 equiv.), *S*-(4-methoxyphenyl) benzenesulfonothioate (0.26 mmol, 1.3 equiv.), 1-iodonaphthalene (30 mol%), n-

Bu_4NBF_4 (0.4 mmol, 2 equiv), MeCN (4.0 mL), undivided cell, room temperature, 30 mA, 1.5 h. The corresponding reaction mixture was detected by GC-mass. We successfully detected the desired naphthalene.

6. Radical trapping experiments



Reaction conditions: GF anode, Pb cathode, **1a** (0.2 mmol, 1 equiv.), *S*-(4-methoxyphenyl) benzenesulfonothioate (0.26 mmol, 1.3 equiv.), 1-iodonaphthalene (30 mol%), n-Bu_4NBF_4 (0.4 mmol, 2 equiv), TEMPO (0.6 mmol, 3 equiv), MeCN (4.0 mL), undivided cell, room temperature, 30 mA, 1.5 h. The corresponding reaction mixture was detected by HRMS, and intermediate **4** was successfully detected.

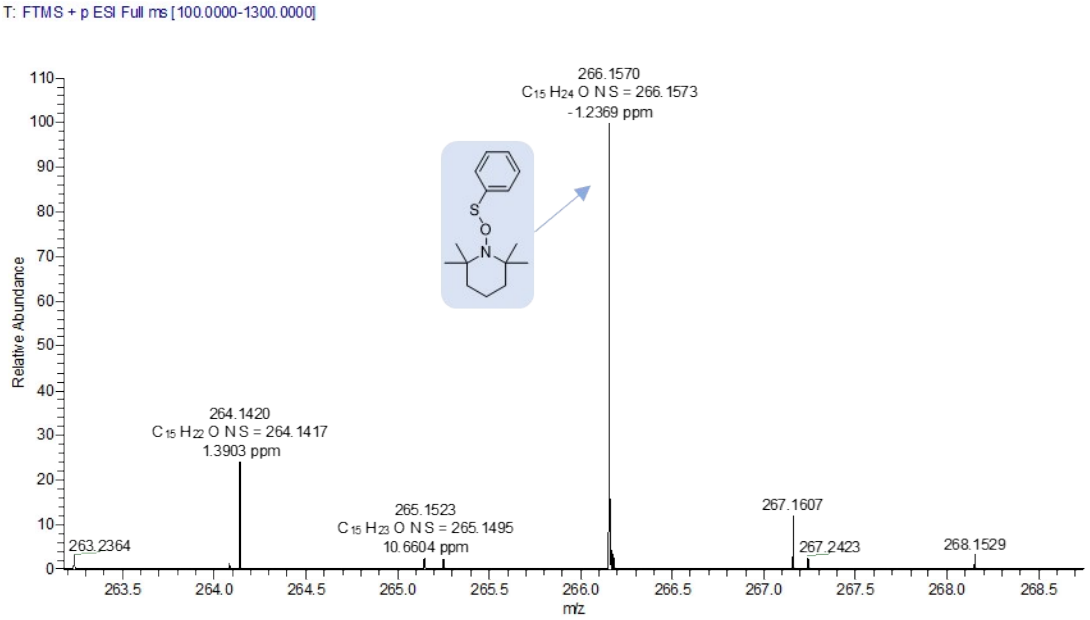
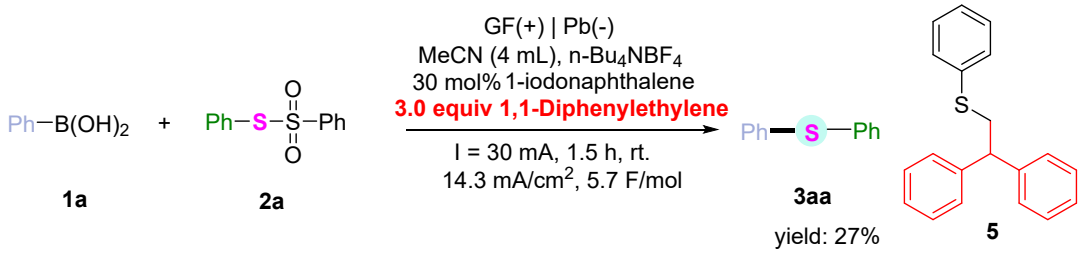


Figure S7. HRMS analysis was performed for **4**



Reaction conditions: GF anode, Pb cathode, **1a** (0.2 mmol, 1 equiv.), *S*-(4-methoxyphenyl) benzenesulfonothioate (0.26 mmol, 1.3 equiv.), 1-iodonaphthalene (30 mol%), n-Bu_4NBF_4 (0.4 mmol, 2 equiv), 1,1-diyldibenzene (0.6 mmol, 3 equiv), MeCN (4.0 mL), undivided cell, room temperature, 30 mA, 1.5 h. The corresponding reaction mixture was detected by HRMS, and intermediate **5** was successfully detected.

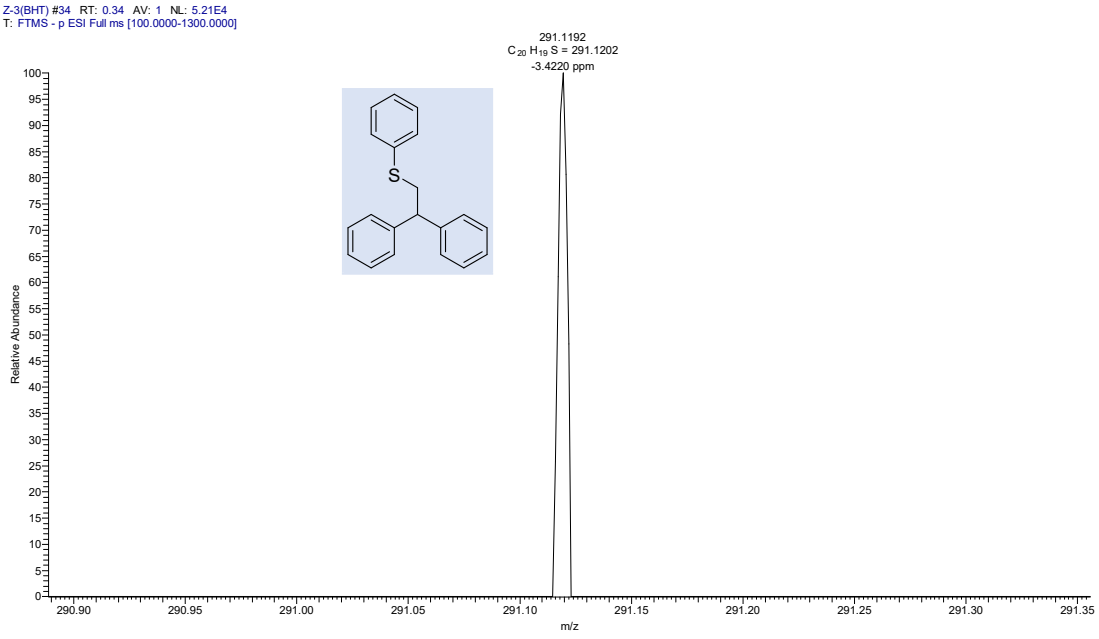
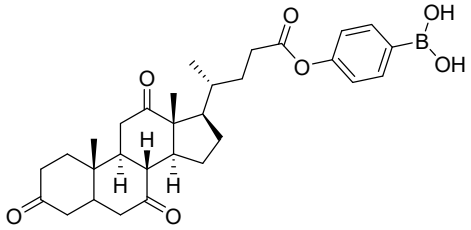


Figure S8. HRMS analysis was performed for **5**

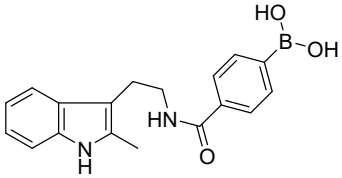
7. Characterization data of products

(4-(((4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl)oxy)phenyl)boronic acid (1w)



Overall Yield: 36% (151 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.25 (s, 2H), 7.04 – 7.00 (m, 2H), 2.55 – 2.31 (m, 12H), 2.10 – 2.03 (m, 1H), 1.92 – 1.83 (m, 3H), 1.73 (m, 1H), 1.67 – 1.53 (m, 4H), 1.52 – 1.43 (m, 2H), 1.36 – 1.26 (m, 1H), 0.99 (s, 3H), 0.87 (dd, *J* = 6.7, 1.5 Hz, 3H), 0.84 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.2, 210.4, 209.4, 172.4, 151.7, 135.7, 135.7, 134.1, 121.5, 121.5, 56.4, 51.1, 49.7, 49.6, 46.0, 44.9, 44.4, 43.9, 39.3, 38.0, 35.9, 35.6, 35.0, 32.3, 31.4, 27.4, 25.7, 18.8, 12.9, 12.5. HRMS (ESI): m/z for $C_{30}H_{39}BO_7$ $[M+H]^+$ calcd 522.2789, found 522.2791.

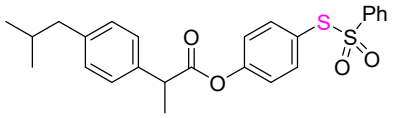
(4-((2-(2-Methyl-1H-indol-3-yl)ethyl)carbamoyl)phenyl)boronic acid (1x)[1]



The synthesis of the compound followed the reported method [1]. The NMR data matched those previously reported. Overall Yield: 45% (80.5 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: DCM/MeOH = 7:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.71 (s, 1H), 8.58 (t, *J* = 5.8 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 6.93 (t, *J* = 6.8 Hz, 1H), 3.43 - 3.39 (m, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.2, 136.0, 135.2, 133.9, 132.1, 128.4, 126.0, 125.9, 121.0, 119.8,

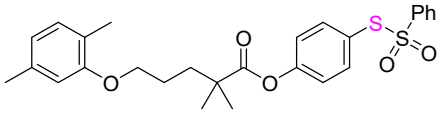
117.3, 110.5, 107.7, 40.4, 24.1, 11.2. HRMS (ESI): m/z for $C_{18}H_{19}BN_2O_3$ $[M+H]^+$ calcd 323.1562, found 323.1558.

4-((Phenylsulfonyl)thio)phenyl 2-(4-isobutylphenyl) propanoate (2r)



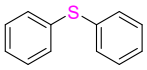
Overall Yield: 94% (429.3 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 3H), 7.44 - 7.40 (m, 2H), 7.33 - 7.27 (m, 4H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.93 (q, *J* = 7.1 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.92 - 1.82 (m, 1H), 1.61 (d, *J* = 7.1 Hz, 3H), 0.92 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 153.5, 142.8, 141.1, 137.7, 136.8, 133.7, 129.6, 128.9, 127.5, 127.1, 124.9, 122.7, 45.3, 45.0, 30.2, 22.4, 18.4. HRMS (ESI): m/z for $C_{25}H_{26}O_4S_2$ $[M+H]^+$ calcd 455.1345, found 455.1340.

4-((Phenylsulfonyl)thio)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (2s)



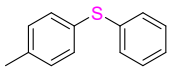
Overall Yield: 64% (318.5 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.57 (m, 3H), 7.47 - 7.43 (m, 2H), 7.37 - 7.33 (m, 2H), 7.04 - 7.00 (m, 3H), 6.68 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 3.99 (t, *J* = 5.4 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 1.95 - 1.81 (m, 4H), 1.38 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 156.7, 153.7, 142.8, 137.8, 136.5, 133.7, 130.4, 128.9, 127.6, 124.8, 123.5, 122.8, 120.8, 111.9, 67.6, 42.6, 37.0, 25.2, 25.0, 21.4, 15.8. HRMS (ESI): m/z for $C_{27}H_{30}O_5S_2$ $[M+Na]^+$ calcd 521.1427, found 521.1430.

Diphenyl sulfane (3aa)[2]



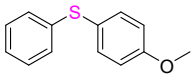
Overall Yield: 81% (30.0 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.32 (m, 4H), 7.31 - 7.28 (m, 4H), 7.25 - 7.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 131.5, 129.2, 127.0; HRMS (ESI): m/z for $C_{12}H_{10}S$ $[M+H]^+$ Calcd 187.0576, found 187.0578.

Phenyl 4-methylphenyl sulfide (3ab) [2]



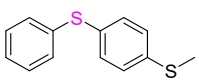
Overall Yield: 79% (35.2 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 - 7.25 (m, 6H), 7.20 - 7.16 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 2.34(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.1, 132.3, 131.3, 130.0, 129.8,129.0, 126.4, 21.1; HRMS (ESI): m/z for $C_{13}H_{12}S$ $[M+H]^+$ calcd 201.0733, found 201.0734.

(4-Methoxyphenyl)(phenyl)sulfane (3ac)[2]



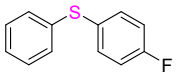
Overall Yield: 75% (29.0 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.34 - 7.20 (m, 5H), 6.99 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 138.6, 134.9, 128.9, 128.2, 126.3, 124.7, 115.3, 54.8; HRMS (ESI): m/z for $C_{13}H_{12}OS$ $[M+H]^+$ calcd 217.0682, found 217.0681.

Methyl(4-(phenylthio)phenyl)sulfane (3ad)[2]



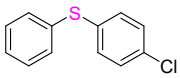
Overall Yield: 61% (28.3 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.28 (m, 2H), 7.24 - 7.19 (m, 1H), 2.48 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 136.5, 132.3, 131.4, 130.2, 129.1, 127.1, 126.7, 15.7; HRMS (ESI): m/z for $C_{13}H_{12}S_2$ $[M+H]^+$ calcd 233.0453, found 233.0455.

(4-Fluorophenyl)(phenyl)sulfane (3ae)[2]



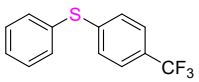
Overall Yield: 64 % (26.1 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.35 (m, 2H), 7.30 - 7.27 (m, 4H), 7.23 - 7.20 (m, 1H), 7.02 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, J = 247.8 Hz), 136.6, 134.1 (d, J = 8.2 Hz), 130.2 (d, J = 3.4 Hz), 129.9, 129.2, 126.8, 116.4 (d, J = 22.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0. HRMS (ESI): m/z for $C_{12}H_9FS$ $[M+H]^+$ calcd 205.0482, found 204.0480.

(4-Chlorophenyl)(phenyl)sulfane (3af)[2]



Overall Yield: 72% (31.8 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.26 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 134.6, 133.0, 132.0, 131.3, 129.3, 129.3, 127,4; HRMS (ESI): m/z for $C_{12}H_9ClS$ $[M+H]^+$ calcd 221.0186, found 221.0188.

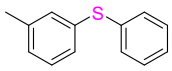
Phenyl(4-(trifluoromethyl)phenyl)sulfane (3ag) [2]



Overall Yield: 60% (30.5 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 90:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 4H), 7.38 (d, *J* = 5.5 Hz, 3H), 7.26 (d, *J* =

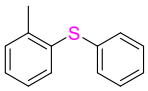
8.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 133.5, 132.5, 129.7, 128.6, 128.2, 128.0 (q, J = 32.6 Hz), 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 271.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (ESI): m/z for $C_{13}H_9F_3S$ $[M+H]^+$ calcd 255.0450, found 255.0448.

Phenyl(m-tolyl)sulfane (3ah)[2]



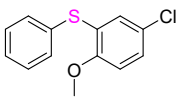
Overall Yield: 70% (28.0 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 4H), 7.24 - 7.14 (m, 4H), 7.06 (d, J = 6.0 Hz, 2H), 2.30(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 136.1, 135.2, 131.8, 130.7, 129.1, 129.0, 128.3, 128.0, 126.8, 21.2; HRMS (ESI): m/z for $C_{13}H_{12}S$ $[M+H]^+$ calcd 201.7863, found 201.7861.

Phenyl(*o*-tolyl)sulfane (3ai)[2]



Overall Yield: 68% (27.2 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.23 (m, 5H), 7.21 -7.17 (m, 3H), 7.16-7.10 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 136.1, 133.7, 132.9, 130.6, 129.6, 129.1, 127.9, 126.7, 126.3, 20.6; HRMS (ESI): m/z for $C_{13}H_{12}S$ $[M+H]^+$ calcd 201.0799, found 201.0985.

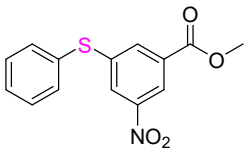
(5-Chloro-2-methoxyphenyl)(phenyl)sulfane (3aj)[3]



Overall Yield: 73% (36.6 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR

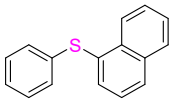
(400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.5 Hz, 2H), 7.42-34 (m, 3H), 7.14 (dd, *J* = 7.2, 2.4 Hz, 1H), 6.87 (s, 1H), 6.87 – 6.79 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 133.0, 132.3, 129.5, 129.1, 128.1, 127.4, 127.1, 126.0, 111.5, 56.2. HRMS (ESI): m/z for $C_{13}H_{11}ClOS$ $[M+H]^+$ calcd 251.0292, found 251.0289.

Methyl 3-nitro-5-(phenylthio)benzoate (3ak)



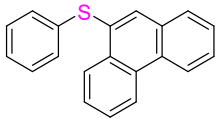
Overall Yield: 27% (15.6 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (t, *J* = 1.8 Hz, 1H), 8.78 (t, *J* = 2.0 Hz, 1H), 8.73 (t, *J* = 1.7 Hz, 1H), 7.40 - 7.35 (m, 5H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 147.1, 134.7, 133.6, 131.9, 131.6, 129.3, 127.4, 125.8, 124.6, 53.1. HRMS (ESI): m/z for $C_{14}H_{11}NO_4S$ $[M+H]^+$ calcd 290.0482, found 290.0480.

1-(4-(Phenylthio)phenyl)ethan-1-one (3al)[3]



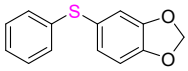
Overall Yield: 67% (31.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.40–8.36 (m, 1H), 7.90–7.86 (m, 2H), 7.68–7.67 (m, 1H), 7.54–7.51 (m, 2H), 7.46–7.44 (m, 1H), 7.24–7.14 (m, 5H);; ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 134.2, 133.5, 132.6, 131.1, 129.2, 129.1, 128.9, 128.5, 126.9, 126.4, 126.1, 125.8, 125.6; HRMS (ESI): m/z for $C_{16}H_{12}S$ $[M+H]^+$ calcd 237.0733, found 237.0735.

Phenanthren-9-yl(phenyl)sulfane (3am)[4]



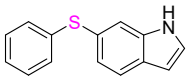
Overall Yield: 78% (44.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.0, 1.2 Hz, 2H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.72 - 7.68 (m, 2H), 7.64 - 7.60 (m, 2H), 7.28 - 7.22 (m, 4H), 7.22 - 7.16 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 134.0, 131.6, 131.5, 131.0, 130.6, 129.5, 129.1, 128.8, 128.5, 127.4, 127.2, 127.1, 127.0, 126.5, 126.1, 123.0, 122.6; HRMS (ESI): m/z for $C_{20}H_{14}S$ $[M+H]^+$ calcd 287.0889, found 286.0891.

5-(Phenylthio)benzo[*d*][1,3]dioxole (3an)



Overall Yield: 51% (23.4 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 7.01 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.91 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 147.9, 137.9, 129.0, 128.9, 127.4, 126.2, 126.2, 113.6, 109.0, 101.4. HRMS (ESI): m/z for $C_{13}H_{10}O_2S$ $[M+H]^+$ calcd 231.0474, found 231.0476.

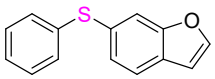
6-(Phenylthio)-1*H*-indole (3ao)[5]



Overall Yield: 51% (23.0 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 - 7.25 (m, 2H), 7.22 - 7.15 (m, 5H), 7.12 - 7.10 (m, 1H), 6.57 - 6.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 135.6, 128.9, 128.8, 128.2,

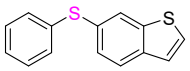
127.6, 127.4, 125.3, 125.1, 123.0, 112.1, 102.8. HRMS (ESI): m/z for $C_{14}H_{11}NS$ $[M+H]^+$ calcd 266.1685, found 266.1681.

6-(Phenylthio)benzofuran (3ap) [5]



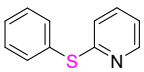
Overall Yield: 60% (27.1 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.43 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.31 - 7.23 (m, 4H), 7.19 – 7.17 (m, 1H), 6.77 – 7.76 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 145.9, 138.1, 129.6, 129.0, 128.9, 128.6, 127.8, 126.4, 126.1, 112.3, 106.4. HRMS (ESI): m/z for $C_{14}H_{10}OS$ $[M+H]^+$ calcd 227.2525, found 227.2527.

6-(Phenylthio)benzo[*b*]thiophene (3aq)[5]



Overall Yield: 53% (25.7mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.36 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.28 - 7.22 (m, 5H), 7.20 - 7.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 139.1, 137.1, 130.6, 129.9, 129.1, 128.3, 127.5, 127.4, 126.5, 123.5, 123.2. HRMS (ESI): m/z for $C_{14}H_{10}S_2$ $[M+H]^+$ calcd 243.0297, found 243.0230.

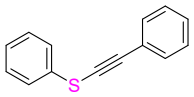
2-(Phenylthio)pyridine (3ar)[5]



Overall Yield: 44% (16.4 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 3.7, 1.7 Hz, 1H), 7.60 (td, *J* = 6.7, 1.6 Hz, 1H), 7.51 - 7.42 (m, 2H), 7.37 - 7.27 (m, 3H), 7.23 (dd, *J* = 6.6, 1.4 Hz, 1H), 7.19 - 7.17

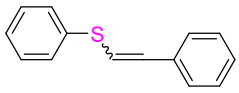
(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 149.7, 137.0, 136.8, 131.5, 129.1, 127.8, 124.4, 121.2; HRMS (ESI): m/z for $C_{11}H_9NS$ $[M+H]^+$ calcd 188.3529, found 188.3531.

Phenyl(phenylethynyl)sulfane (3as)[5]



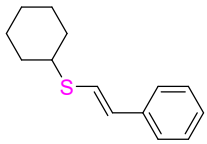
Overall Yield: 32% (13.4 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.38 (m, 4H), 7.25 - 7.24 (m, 5H), 7.17 - 7.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.1, 131.9, 129.4, 128.8, 128.4, 126.8, 126.3, 123.1, 98.0, 75.3. HRMS (ESI): m/z for $C_{14}H_{10}S$ $[M+H]^+$ calcd 211.1576, found 211.1578.

(*Z*/*E*)-Phenyl(styryl)sulfane (3at)[5]



Overall Yield: 50% (21.2 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.33 (m, 4H), 7.29 - 7.28 (m, 5H), 7.27 - 7.26 (m, 1H), 6.91(d, *J* = 12.4 Hz, 1H), 6.76 (d, *J* = 12.4Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 135.2, 132.8, 131.8, 129.8, 129.2, 138.7, 128.7, 127.6, 126.0. HRMS (ESI): m/z for $C_{14}H_{12}S$ $[M+H]^+$ calcd 213.4733, found 213.4734.

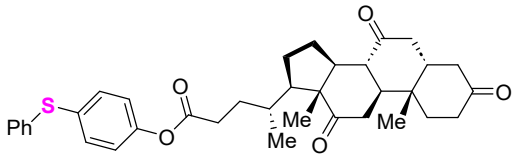
(*E*)-Cyclohexyl(styryl)sulfane (3au)[6]



Overall Yield: 45% (19.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 - 7.45 (m, 2H), 7.38 - 7.31 (m, 3H), 6.80 (d, *J* = 15.6 Hz,

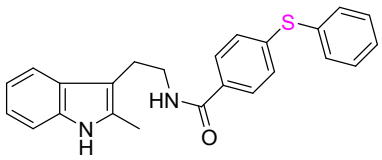
1H), 6.62 (dd, *J* = 14.1, 1.6 Hz, 1H), 3.16 – 3.14 (m, 1H), 1.75 – 1.64 (m, 2H), 1.63 - 1.53 (m, 5H), 1.43 - 1.38 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.1, 129.2, 129.0, 127. 7, 127.6, 126.0, 44.8, 35.5, 25.5, 24.7. HRMS (ESI): m/z for $C_{14}H_{18}S$ $[M+H]^+$ calcd 219.1202, found 219.1201.

4-(Phenylthio)phenyl (4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12- tri oxohexadeca hydro- 1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (3aw)



Overall Yield: 52% (60.9 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (m, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 2.94 - 2.82 (m, 3H), 2.64 (m, 1H), 2.52 (m, 1H), 2.38 - 2.00 (m, 12H), 1.95 (m, 2H), 1.86 (td, *J* = 11.3, 7.0 Hz, 1H), 1.61 (td, *J* = 14.4, 4.6 Hz, 1H), 1.52 (ddt, *J* = 14.0, 9.0, 4.5 Hz, 1H), 1.40 (s, 3H), 1.36 - 1.33 (m, 1H), 1.31 - 1.25 (m, 1H), 1.08 (s, 3H), 0.90 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.9, 209.0, 208.7, 171.8, 153.3, 142.7, 137.8, 133.7, 128.9, 127.5, 124.8, 122.7, 56.8, 51.7, 48.9, 46.8, 45.5, 44.9, 42.7, 38.6, 36.4, 35.9, 35.4, 35.2, 31.5, 30.2, 27.6, 25.1, 21.9, 18.6, 11.8. HRMS (ESI): m/z for $C_{36}H_{42}O_5S$ $[M+Na]^+$ calcd 609.2645, found 609.2647.

N-(2-(2-methyl-1H-indol-3-yl)ethyl)-4-(phenylthio)benzamide (3ax)

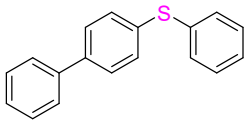


Overall Yield: 50% (38.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 13.0 Hz, 1H), 7.69 - 7.60 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.43 - 7.41 (m, 2H), 7.38 - 7.31 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* =

8.4 Hz, 2H), 7.14 - 7.05 (m, 2H), 3.68 (q, J = 6.4 Hz, 2H), 3.02 (q, J = 6.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 141.6, 135.3, 133.2, 132.9, 132.2, 132.1, 129.5, 128.6, 128.5, 128.2, 127.4, 121.2, 119.4, 117.7, 110.4, 108.4, 40.4, 24.0, 11.6. HRMS (ESI): m/z for $C_{24}H_{22}N_2OS$ $[M+H]^+$ calcd 387.1526, found 387.1529.

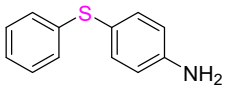
52.9, 45.8, 25.2, 17.8. HRMS (ESI): m/z for $C_{35}H_{34}N_7O_3S_2$ $[M+Na]^+$ calcd 722.1745, found 722.1742.

[1,1'-Biphenyl]-4-yl(phenyl)sulfane (3ba)[5]



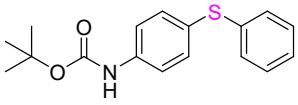
Overall Yield: 51% (26.8 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.51 (m, 4H), 7.45 - 7.24 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 140.0, 135.7, 134.9, 131.3, 131.2, 129.2, 128.8, 127.8, 127.5, 127.2, 127.0. HRMS (ESI): m/z for $C_{18}H_{14}S$ $[M+H]^+$ calcd 263.0889, found 263.0891.

4-(Phenylthio)aniline (3ca)[5]



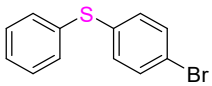
Overall Yield: 49% (19.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.55 (m, 3H), 7.45 - 7.41 (m, 2H), 7.12 - 7.09 (m, 2H), 6.63 - 6.59 (m, 2H), 4.33 (s, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 143.1, 138.3, 133.4, 128.7, 127.6, 115.7, 115.6. HRMS (ESI): m/z for $C_{12}H_{11}NS$ $[M+H]^+$ calcd 202.2685, found 202.2681.

***tert*-Butyl (4-(phenylthio)phenyl)carbamate (3da)**[7]



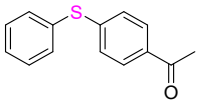
Overall Yield: 50% (30.1 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.32 (m, 4H), 7.32 - 7.26 (m, 4H), 7.25 -7.21 (m, 1H), 6.51 (s, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 139.1, 136.7, 131.3, 129.6, 129.1, 128.9, 127.1, 120.4, 28.2. HRMS (ESI): m/z for $C_{17}H_{19}NO_2S$ $[M+H]^+$ calcd 302.1209, found 302.1231.

(4-Bromophenyl)(phenyl)sulfane (3ea)[2]



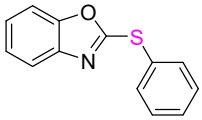
Overall Yield: 54% (28.6 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.37 - 7.36 (m, 4H), 7.31 - 7.26 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 134.8, 133.2, 132.1, 131.5, 129.4, 127.5, 120.5. HRMS (ESI): m/z for $C_{12}H_9BrS$ [M+H]+ calcd 264.9681, found 264.9683.

1-(4-(Phenylthio)phenyl)ethan-1-one (3fa)[5]



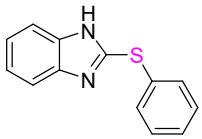
Overall Yield: 47% (21.5 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.80 (m, 2H), 7.51 - 7.48 (m, 2H), 7.43 - 7.38 (m, 3H), 7.23 - 7.20 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 144.9, 134.5, 133.8, 132.1, 129.7, 128.9, 128.8, 127.4, 26.4; HRMS (ESI): m/z for $C_{14}H_{12}OS$ $[M+H]^+$ calcd 229.0682, found 229.0680.

2-(Phenylthio)benzo[*d*]oxazole (3ga)[8]



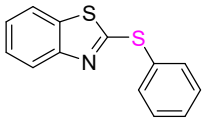
Overall Yield: 50% (24.6 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 - 7.68 (m, 2H), 7.60 - 7.58 (m, 1H), 7.46 - 7.38 (m, 3H), 7.28 - 7.20 (m, 1H), 7.28 - 7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 151.8, 141.9, 134.4, 129.8, 129.6, 127.1, 124.3, 124.2, 119.0, 110.0; HRMS (ESI): m/z for $C_{13}H_9NOS$ $[M+H]^+$ calcd 288.0478, found 288.0480.

2-(Phenylthio)-1*H*-benzo[*d*]imidazole (3ha)[9]



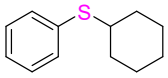
Overall Yield: 48% (22.3 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 - 7.75 (m, 1H), 7.49 - 7.40 (m, 3H), 7.36 - 7.28 (m, 3H), 7.21 - 7.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 142.3, 138.7, 136.6, 130.6, 129.1, 127.8, 124.6, 122.3, 117.7, 111.9. HRMS (ESI): m/z for $C_{13}H_{10}NOS$ $[M+H]^+$ calcd 227.0638, found 227.0635.

2-(Phenylthio)benzo[*d*]thiazole (3ia)[10]



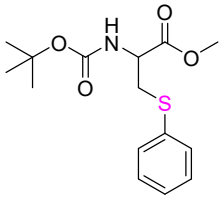
Overall Yield: 55% (26.8 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 - 7.73 (m, 1H), 7.66 - 7.64 (m, 2H), 7.52 - 7.46 (m, 1H), 7.43 - 7.39 (m, 3H), 7.29 – 7.27 (m, 1H), 7.27 - 7.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 153.7, 135.4, 135.4, 130.5, 129.9, 129.9, 126.2, 124.4, 121.9, 120.8. HRMS (ESI): m/z for $C_{13}H_9NS_2$ $[M+H]^+$ calcd 244.0250, found 244.0249.

Cyclohexyl(phenyl)sulfane (3ja)[5]



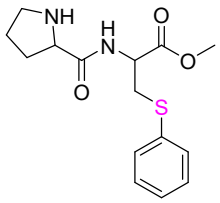
Overall Yield: 72% (27.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 100:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 - 7.29 (m, 5H), 3.40 – 3.39 (m, 1H), 1.86 – 1.81 (m, 2H), 1.66 - 1.53 (m, 5H), 1.49 - 1.40 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 131.5, 129.0, 127.9, 46.7, 33.7, 25.5, 24.8. HRMS (ESI): m/z for $C_{12}H_{16}S$ $[M+H]^+$ calcd 193.1046, found 193.1049.

Methyl N-(tert-butoxycarbonyl)-S-phenyl-*L*-cysteinate (3ka)[11]



Overall Yield: 61% (37.7 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.40 (m, 2H), 7.40 - 7.42 (m, 2H), 7.30 - 7.26 (m, 1H), 7.23 - 7.21(m, 1H), 5.35 (d, *J* = 8.0 Hz, 1H), 4.58 - 4.56 (m, 1H), 3.53 (s, 3H), 3.38 - 3.37 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 155.0, 134.7, 131.0, 129.0, 127.0, 80.1, 53.2, 52.3, 37.2, 28.2. HRMS (ESI): m/z for $C_{15}H_{21}NO_4S$ $[M+H]^+$ calcd 312.1264, found 312.1262.

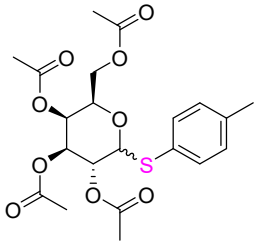
Methyl phenyl-N-prolylcysteinate (3la)



Overall Yield: 56% (14.5 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.36 - 7.24 (m, 5H), 4.74 (dt, *J* = 5.1, 2.6 Hz, 1H), 4.40 (dt, *J* = 8.8, 5.0 Hz, 1H), 3.70 - 3.64 (m, 4H), 3.39 (dd, *J* = 14.4, 5.0

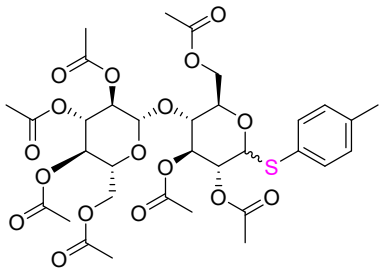
Hz, 1H), 3.29 (dd, *J* = 14.4, 5.0 Hz, 1H), 3.02 - 2.87 (m, 2H), 1.92 - 1.84 (m, 1H), 1.81 - 1.74 (m, 2H), 1.73 - 1.68 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 171.8, 137.9, 131.8, 130.5, 128.1, 61.1, 52.3, 52.3, 47.6, 35.4, 31.6, 26.4. HRMS (ESI): m/z for $C_{15}H_{20}N_2O_3S^+$ $[M+H]^+$ calcd 309.1267, found 309.1269.

(2R,3S,4S,5R,6R)-2-(Acetoxymethyl)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3ma)[12]



Overall Yield: 56% (39.1 mg). Nature: White solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.40 (d, *J* = 3.2 Hz, 1H), 5.23 (t, *J* = 10.0 Hz, 1H), 5.04 (dd, *J* = 10.0, 3.2 Hz, 1H), 4.65 (d, *J* = 10.0 Hz, 1H), 4.52 (m, 2H), 3.92 (t, *J* = 6.4 Hz, 1H), 2.33 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 170.2, 170.0, 169.4, 138.4, 133.1, 129.6, 128.6, 86.9, 74.3, 72.0, 67.2, 67.2, 61.5, 21.1, 20.8, 20.6, 20.6, 20.5; HRMS (ESI): m/z for $C_{21}H_{26}O_9S$ $[M+Na]^+$ calcd 477.1190, found 477.1192.

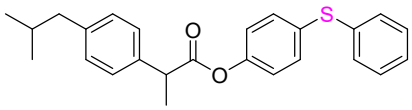
(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-(((2R,3R,4S,5R,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(*p*-tolylthio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3na) [12]



Overall Yield: 47% (13.5 mg). Nature: White solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 1:1). ^{1}H NMR (400

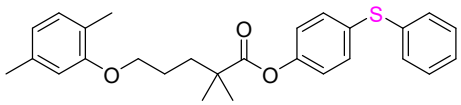
MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.34 (d, *J*= 2.8 Hz, 1H), 5.07 (t, *J* = 9.2 Hz, 1H), 5.07 - 5.02 (m, 1H), 4.94 - 4.90 (m, 1H), 4.86 (t, *J* = 9.8 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.51 - 4.47 (m, 2H), 4.12 - 4.00 (m, 3H), 3.72 (t, *J* = 9.6 Hz, 1H), 3.65 - 3.61 (m, 1H), 3.60 - 3.58 (m, 1H), 2.33 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.01 (s, 9H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.2, 170.0, 169.7, 169.5, 169.3, 169.0, 138.6, 133.7, 129.6, 127.7, 100.7, 85.7, 76.3,75.2, 73.6, 71.6, 70.7, 70.1, 69.4, 67.7, 61.9, 61.5, 60.9, 21.2, 20.8, 20.8, 20.7, 20.6, 20.6, 20.5. HRMS (ESI): m/z for $C_{33}H_{42}O_{17}S$ $[M+Na]^+$ calcd 765.2035, found 765.2032.

4-(Phenylthio)phenyl 2-(4-isobutylphenyl)propanoate (3oa)



Overall Yield: 61% (47.6 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.30 (m, 4H), 7.30 - 7.16 (m, 5H), 7.15 (dd, *J* = 8.3, 2.5 Hz, 2H), 7.01 - 6.94 (m, 2H), 3.96 - 3.91 (m, 1H), 2.48 (dd, *J* = 7.3, 2.7 Hz, 2H), 1.92 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.61 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 2.7 Hz, 3H), 0.91 (d, *J* = 2.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 150.2, 141.5, 137.1, 132.6, 132.5, 130.6, 129.5, 129.3, 129.2, 127.2, 127.0, 122.3, 45.3, 45.0, 30.1, 22.4, 18.4. HRMS (ESI): m/z for $C_{25}H_{26}O_2S$ $[M+H]^+$ caled 391.1726, found 391.1730.

4-(Phenylthio)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3pa)



Overall Yield: 54% (46.9 mg). Nature: Colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.41 (m, 2H), 7.39 - 7.28 (m, 5H), 7.08 - 7.03 (m, 3H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 1.6 Hz, 1H), 4.08 - 4.01 (m, 2H), 2.36 (s, 3H), 2.23 (s, 3H), 1.97 - 1.90 (m, 4H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 156.8,

150.3, 136.5, 136.1, 132.7, 132.4, 130.5, 130.3, 129.2, 126.9, 123.6, 122.4, 120.8, 111.9, 67.7, 42.5, 37.1, 29.7, 25.2, 25.1, 21.4, 15.8. HRMS (ESI): m/z for $C_{27}H_{30}O_3S$ $[M+H]^+$ calcd 453.1988, found 453.1990.

8. References

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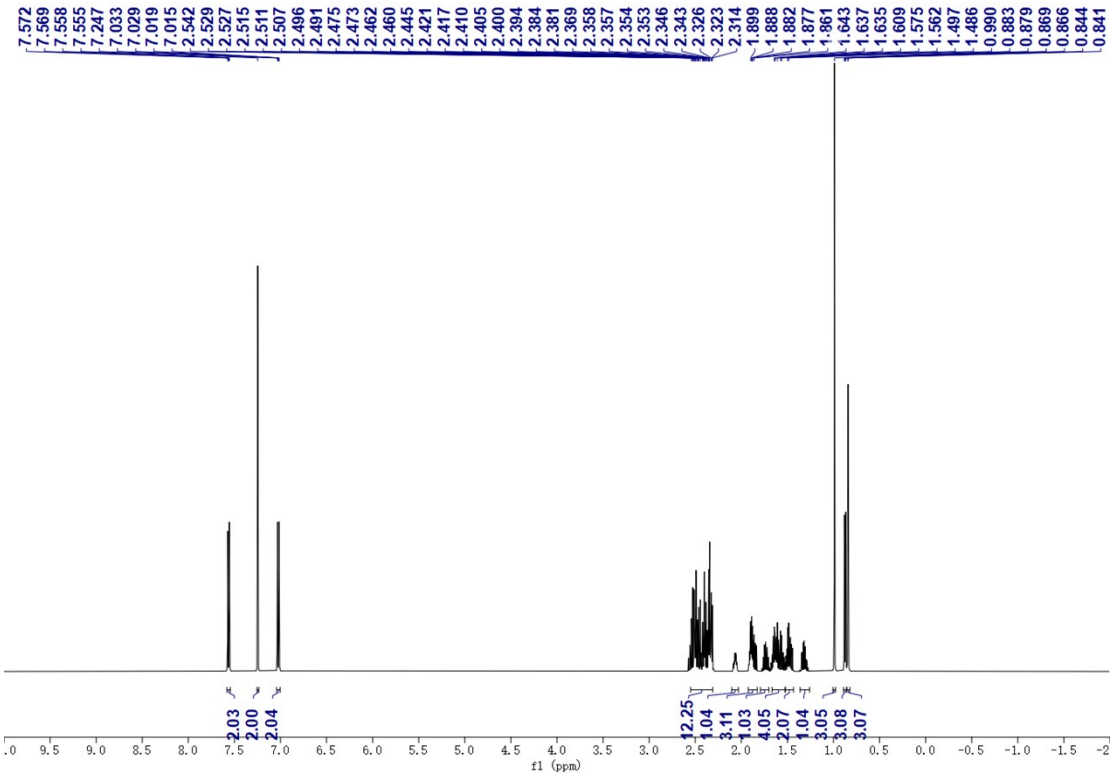
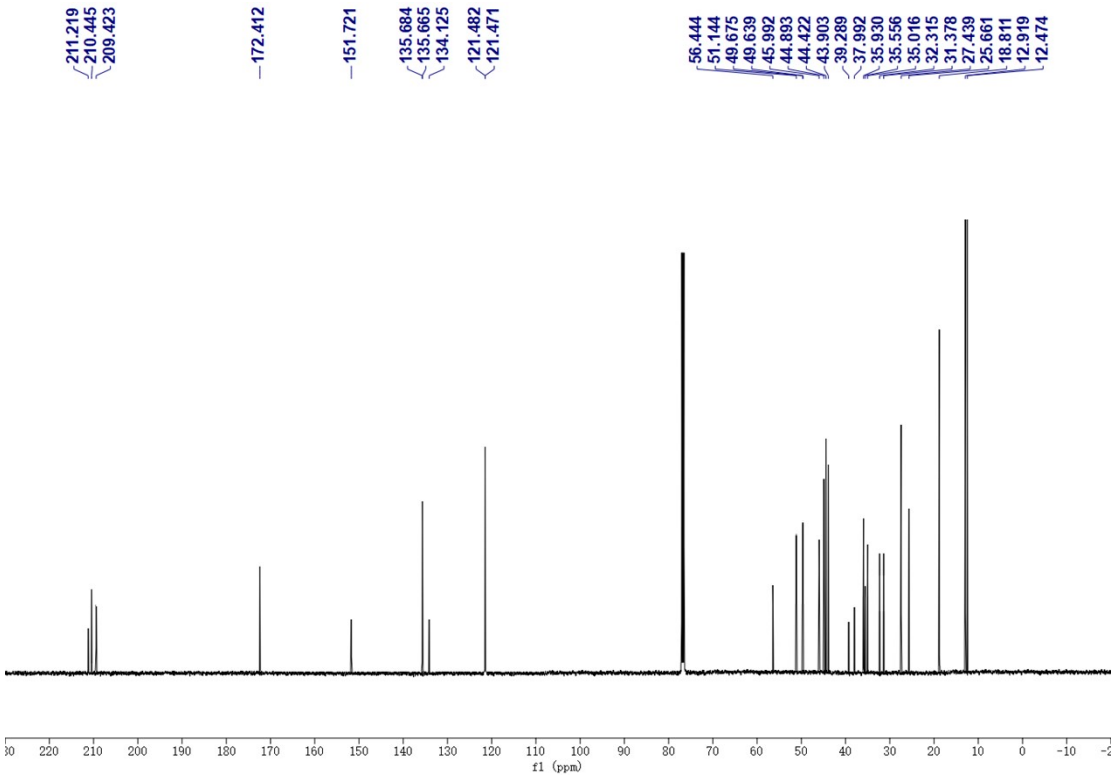
9. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra



1w-^{1}H NMR



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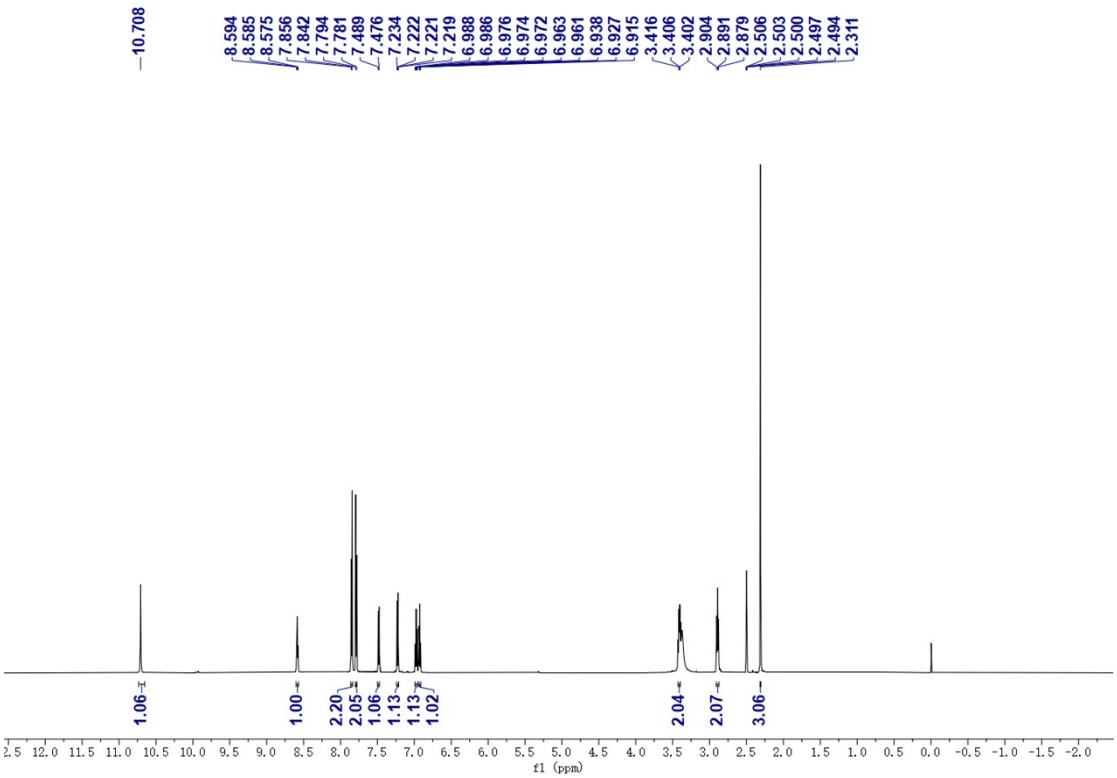

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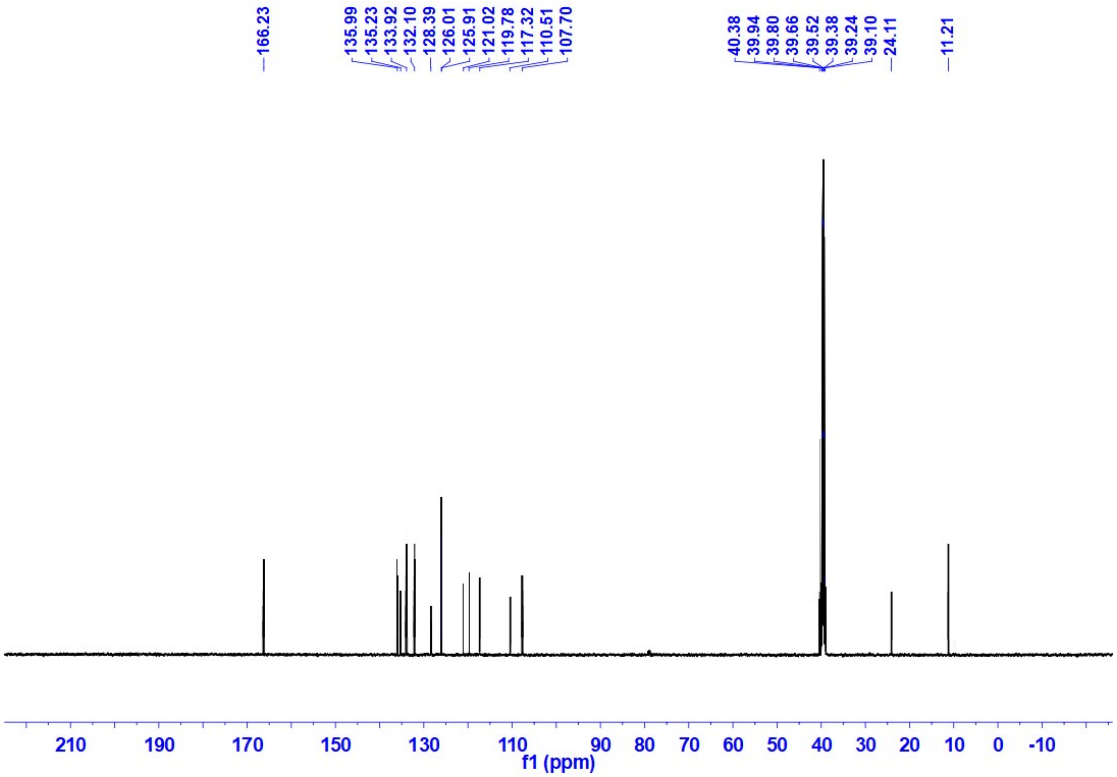

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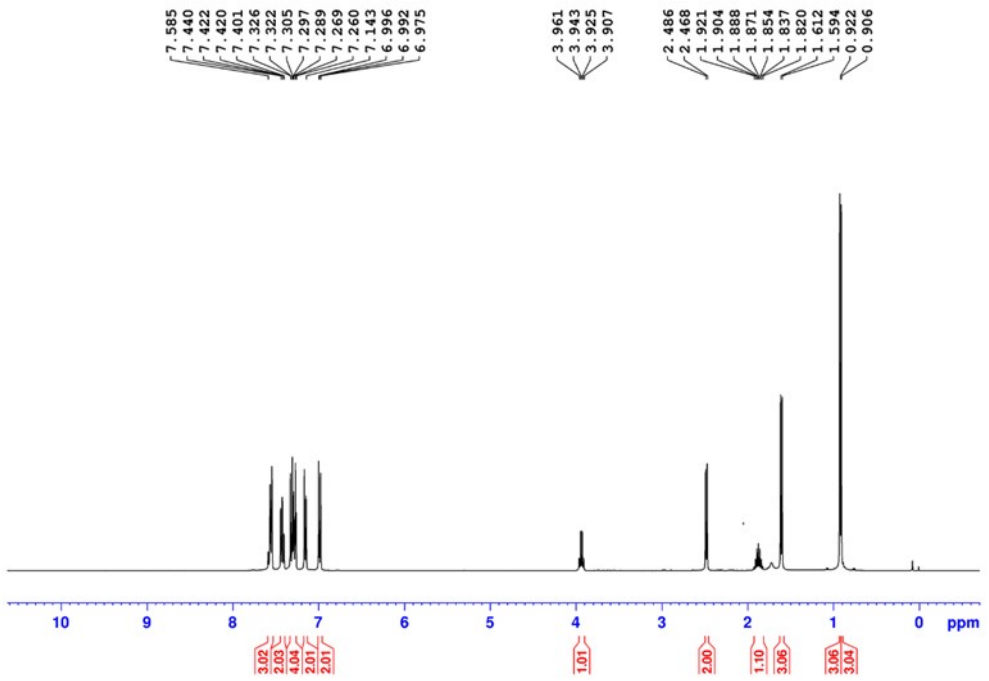

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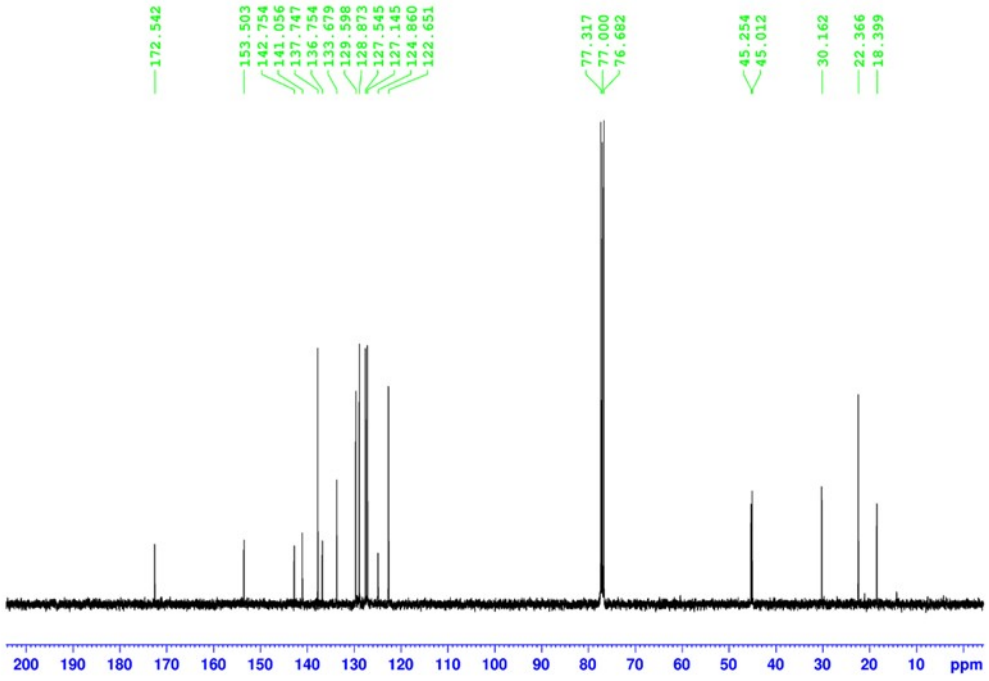

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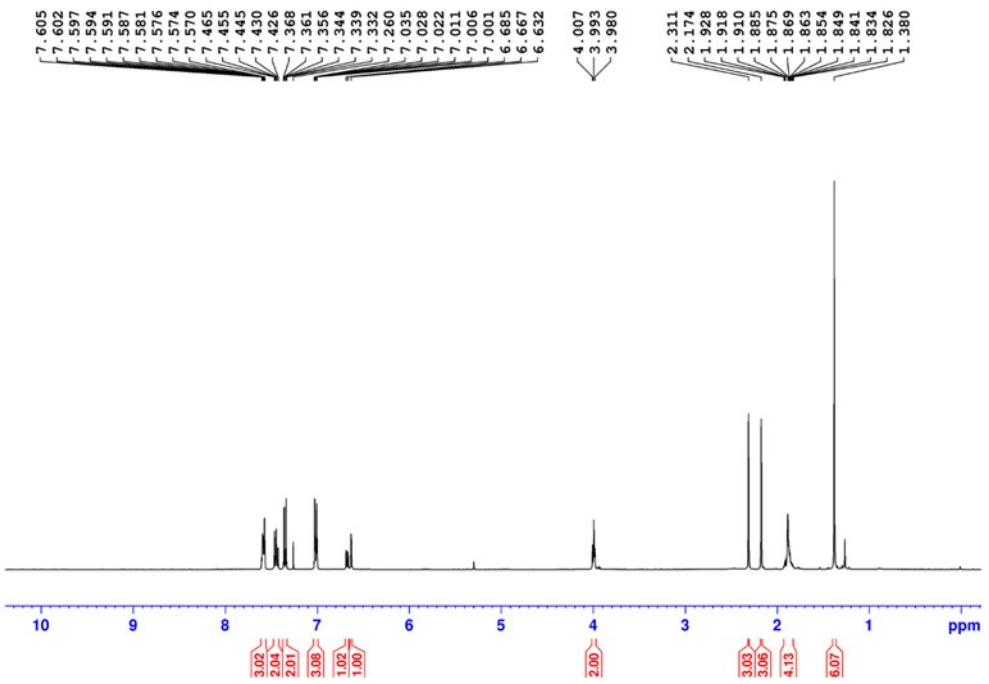

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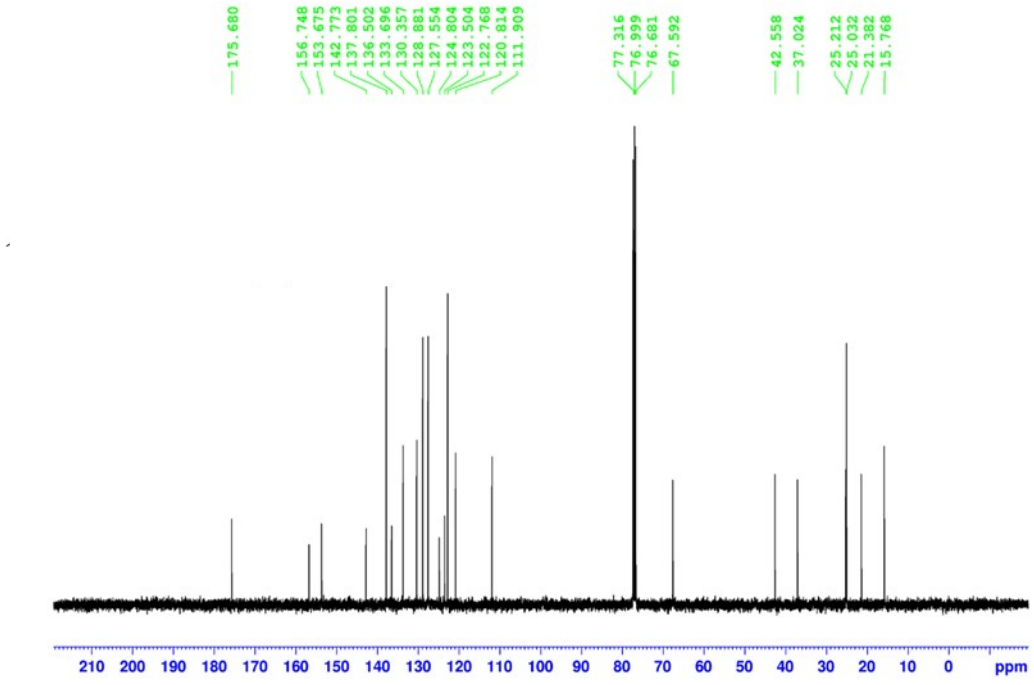

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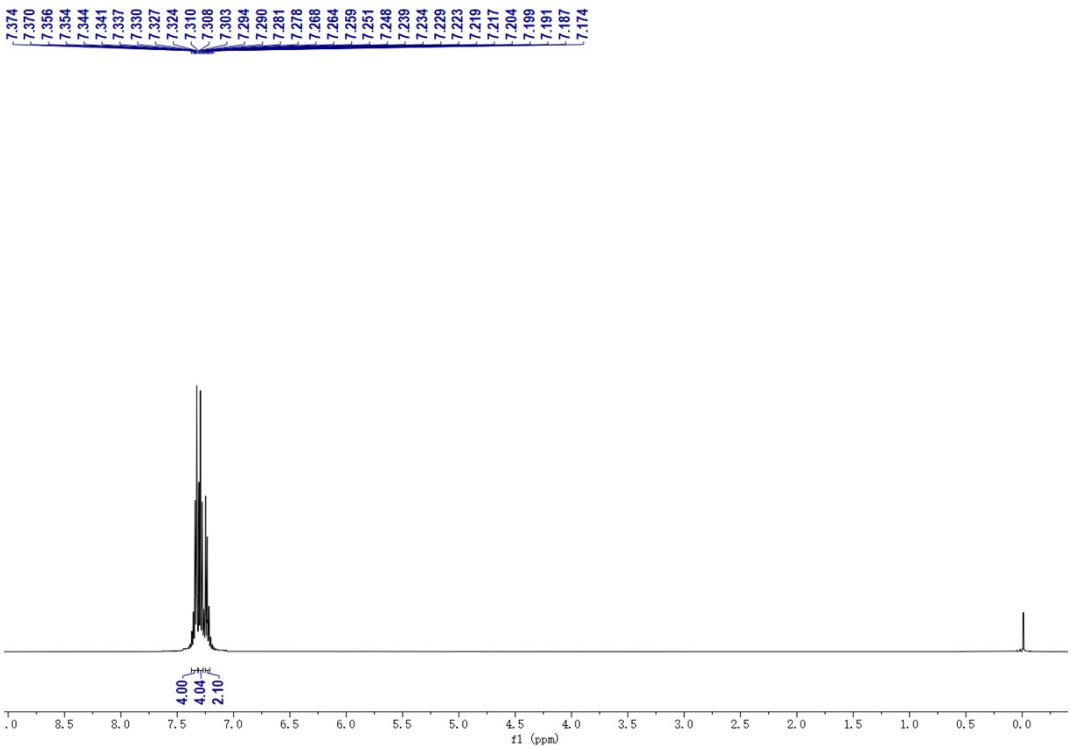

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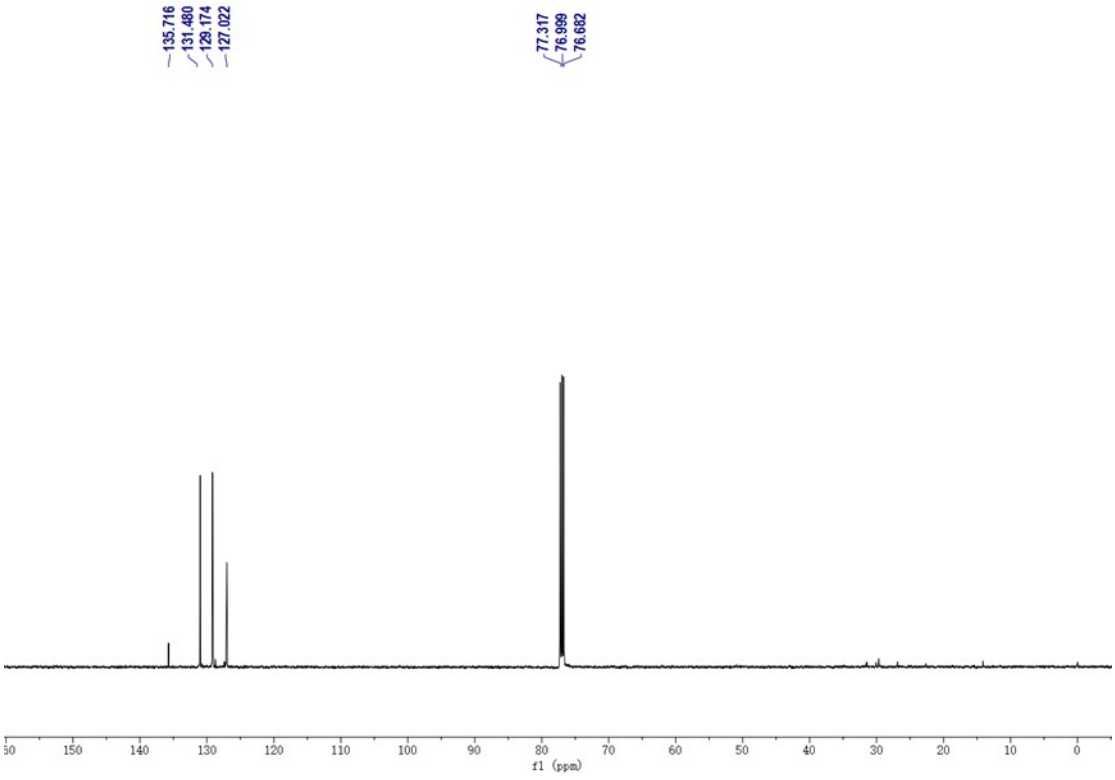

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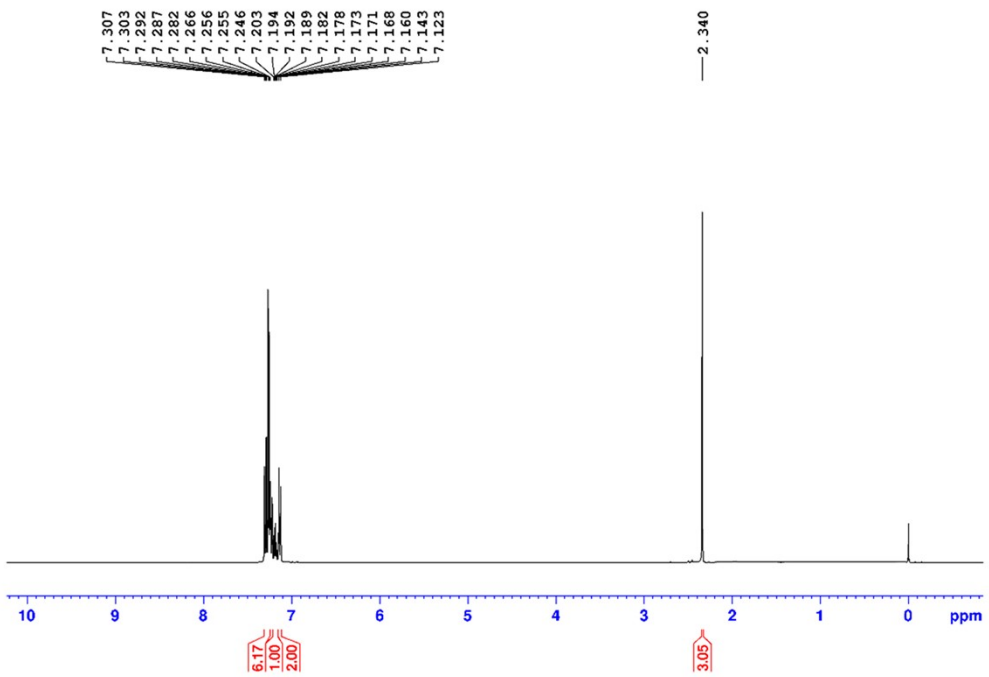

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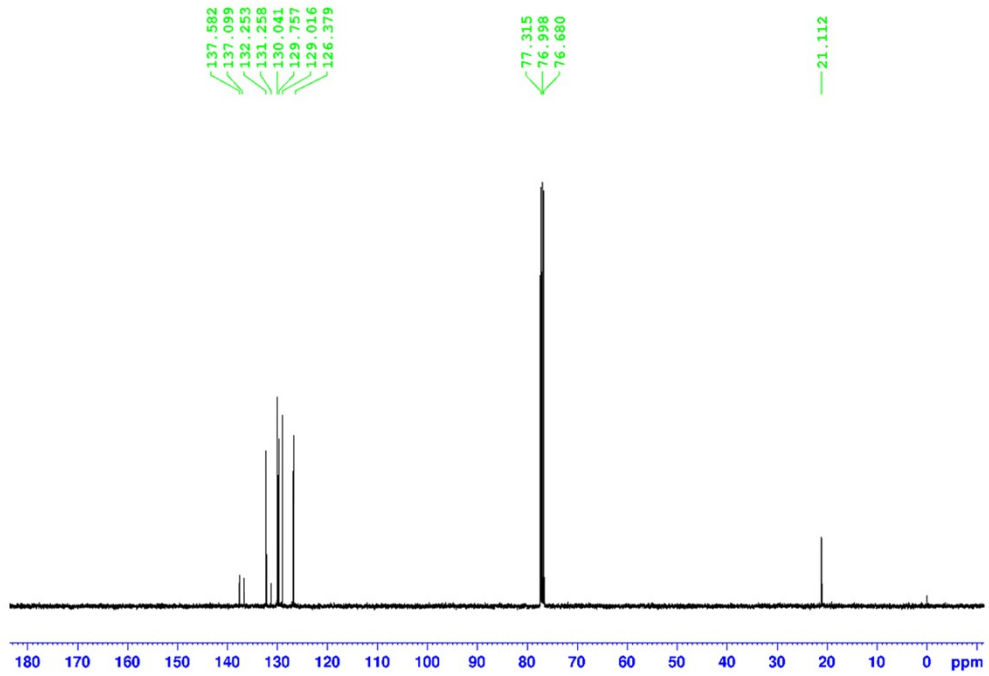

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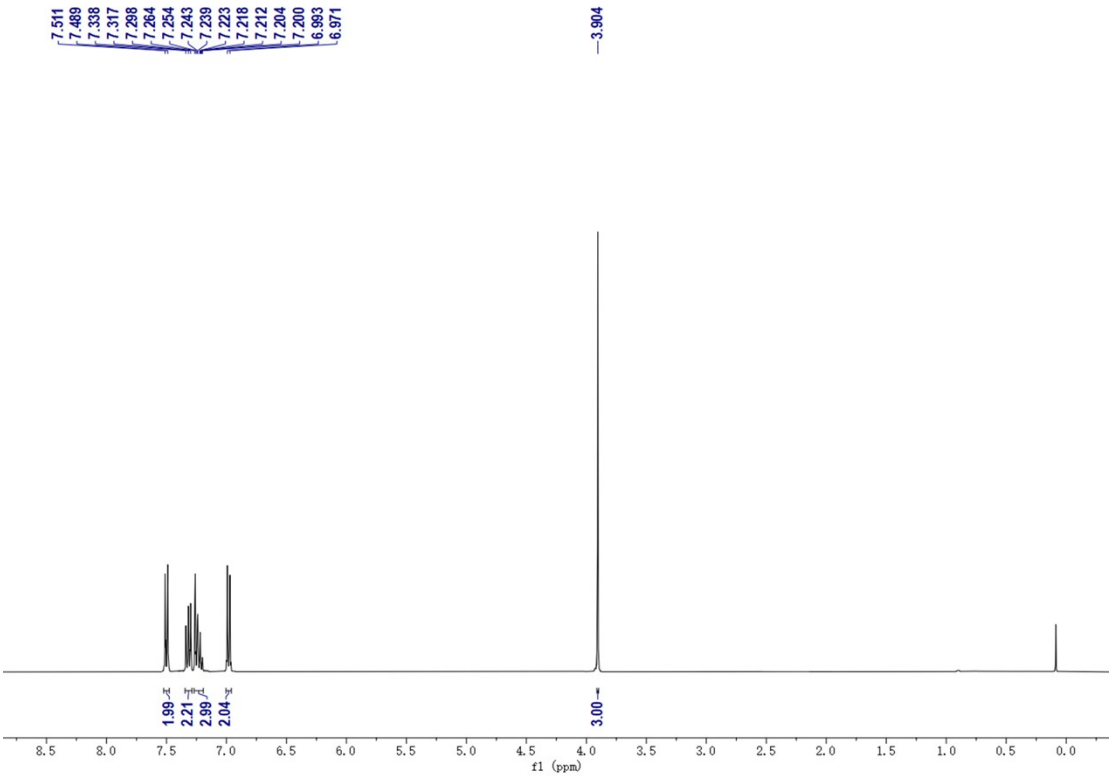

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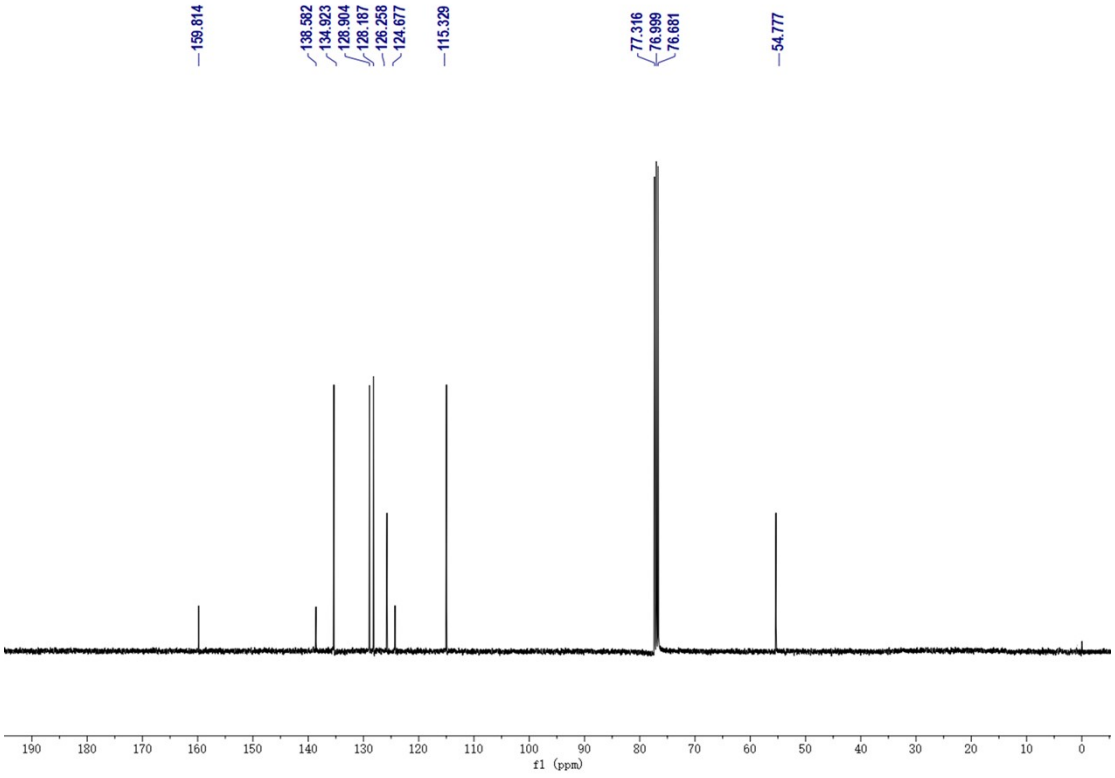

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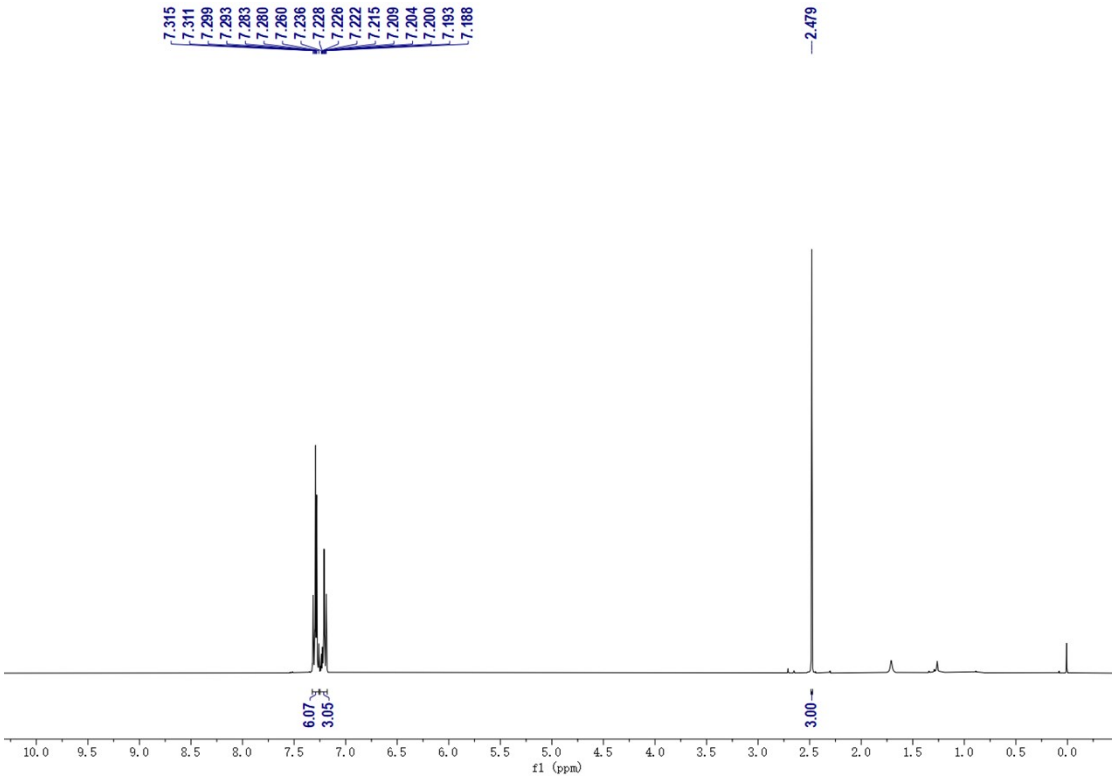

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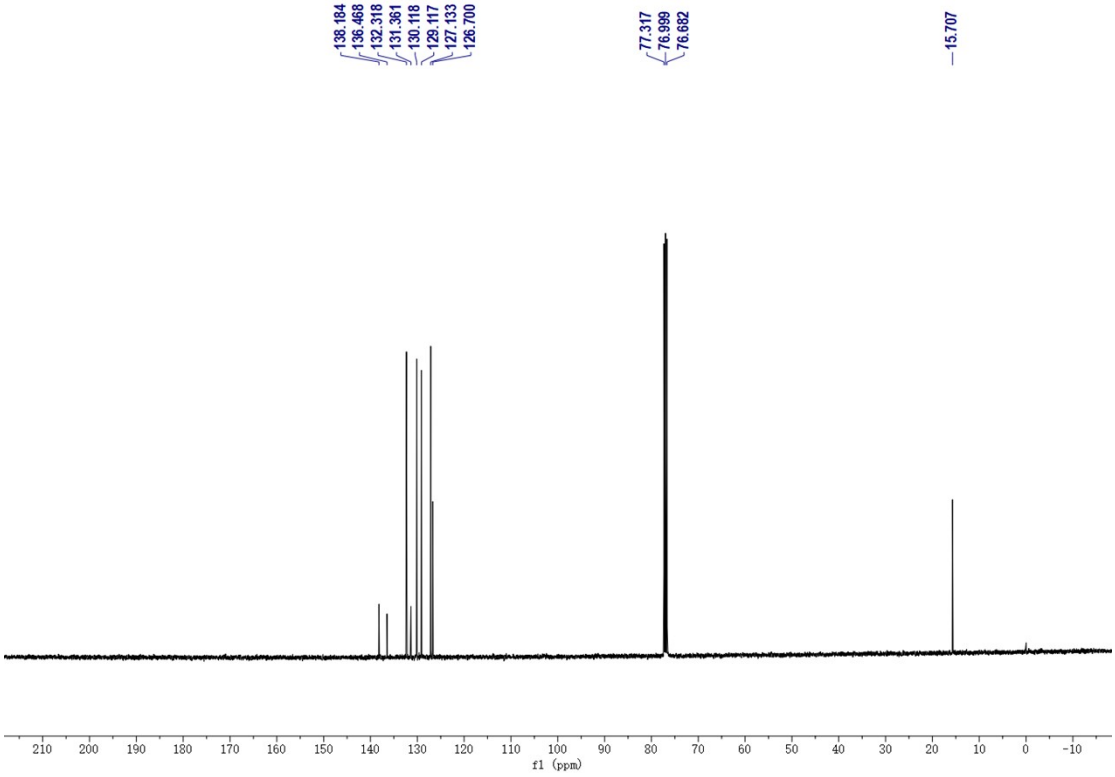

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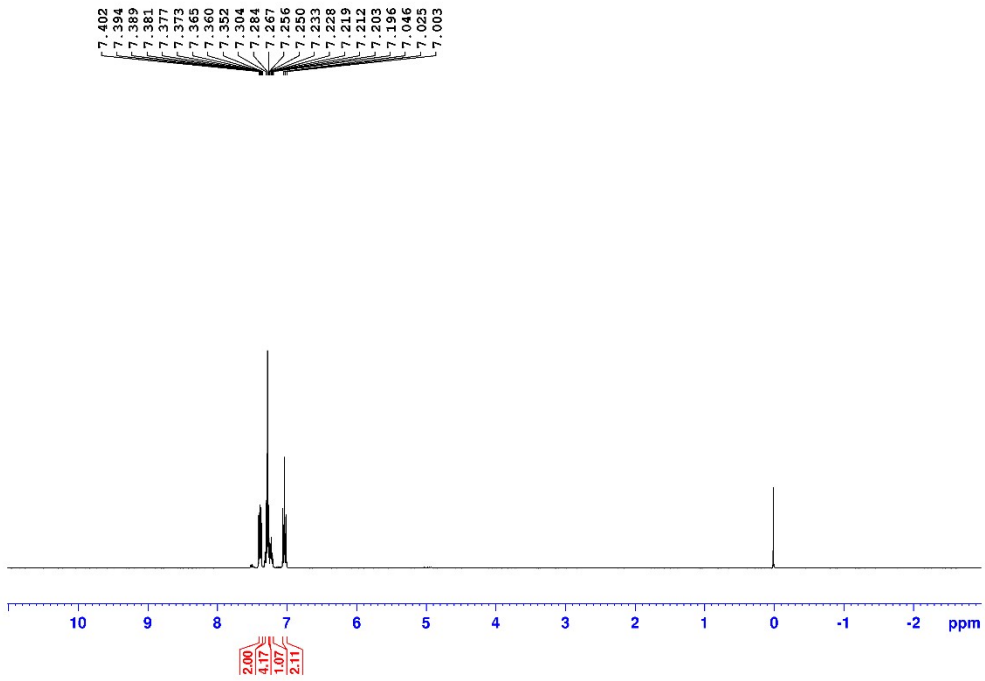

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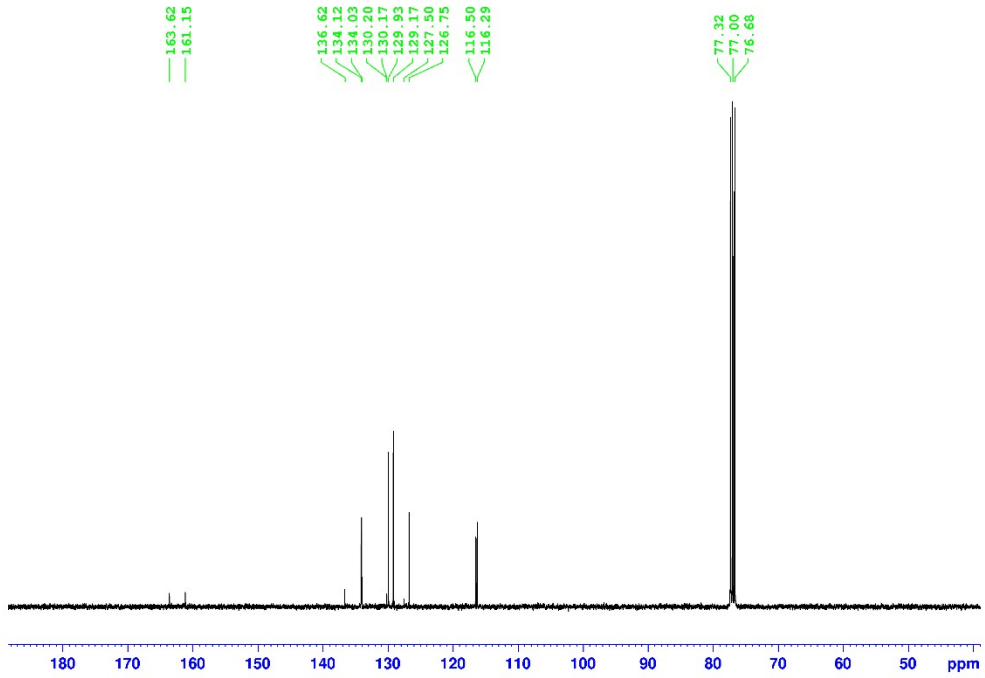

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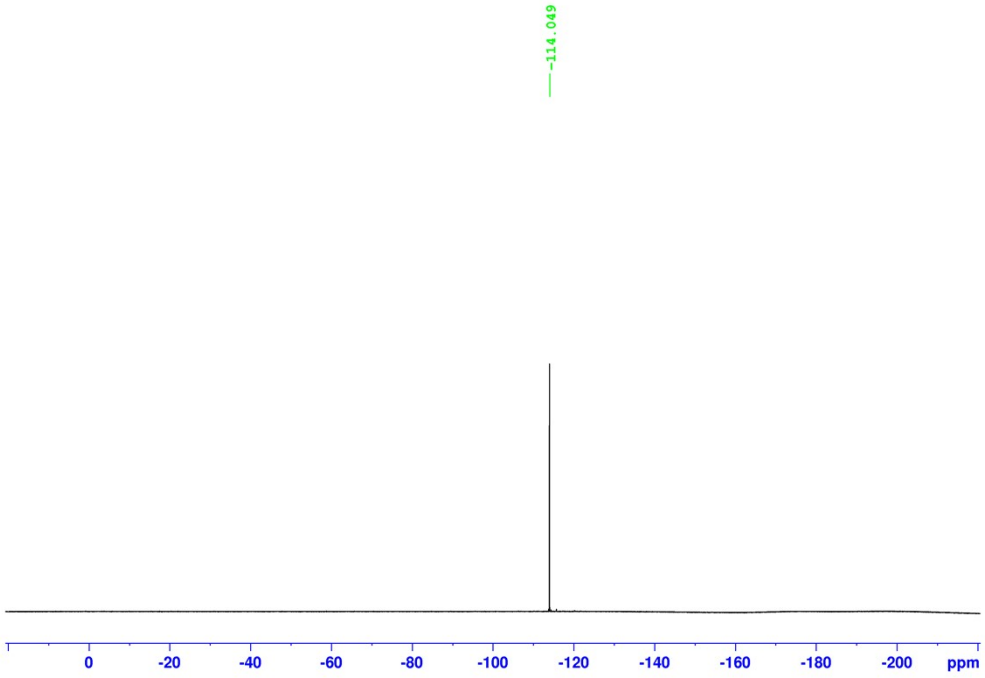

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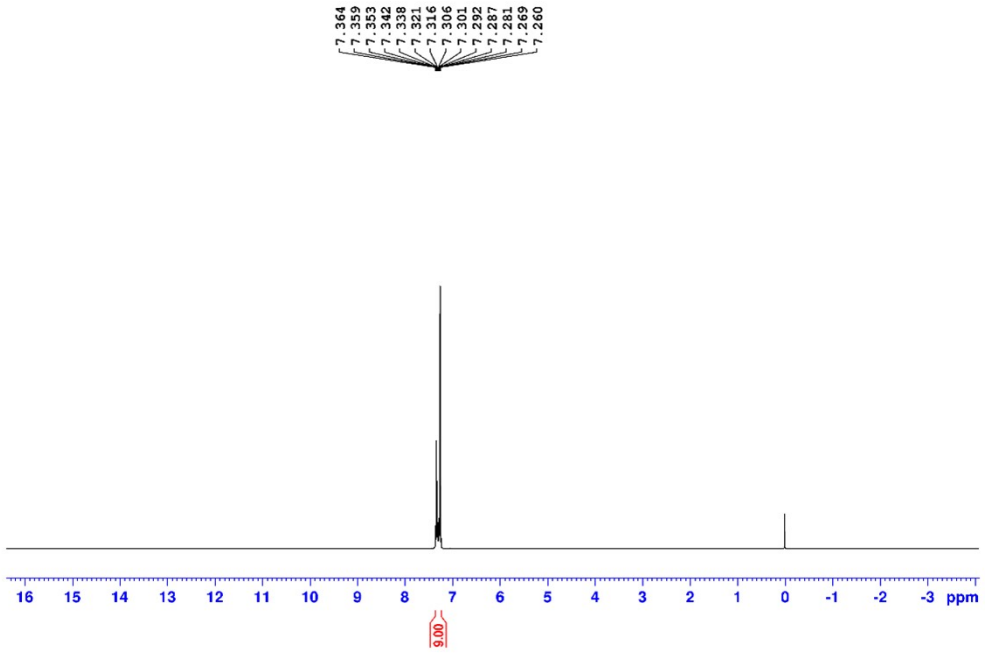

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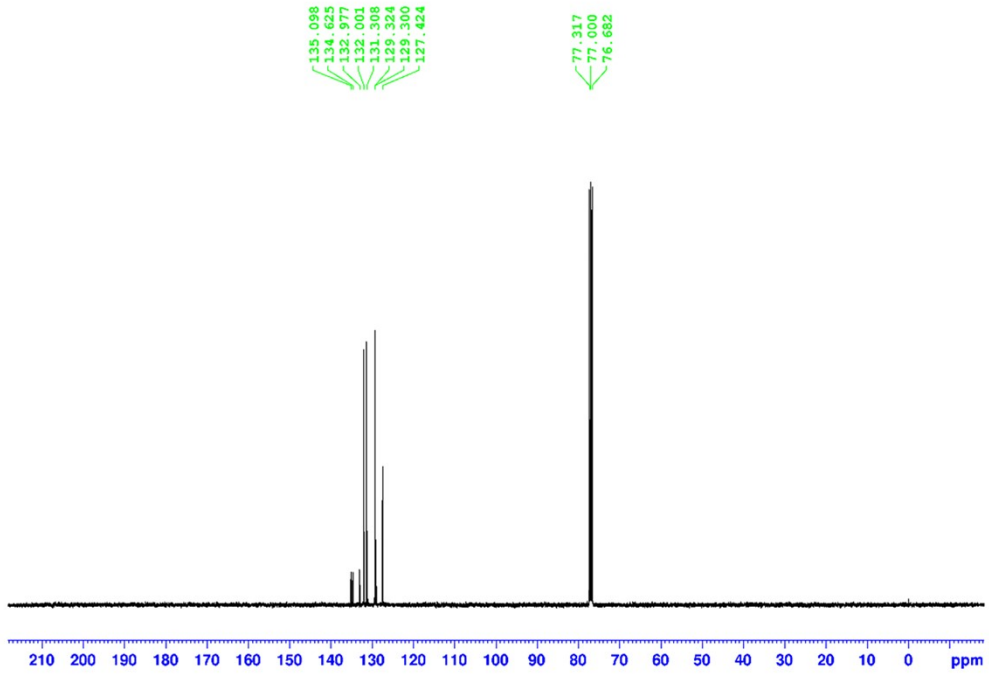

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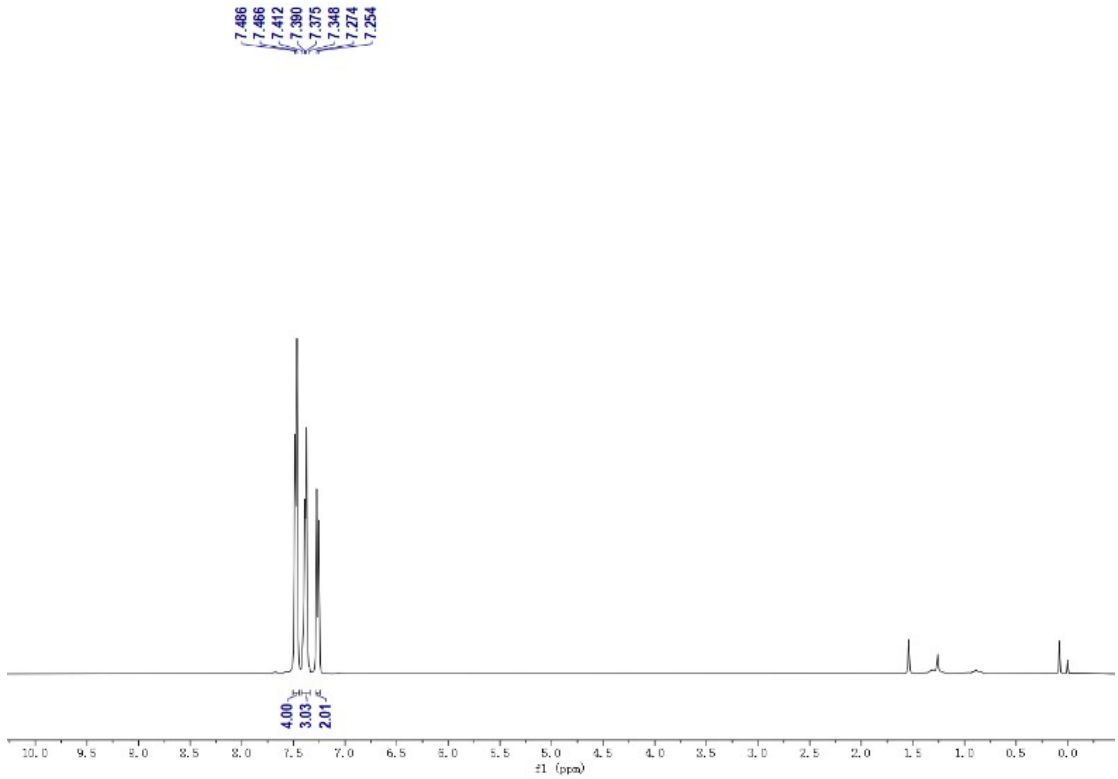

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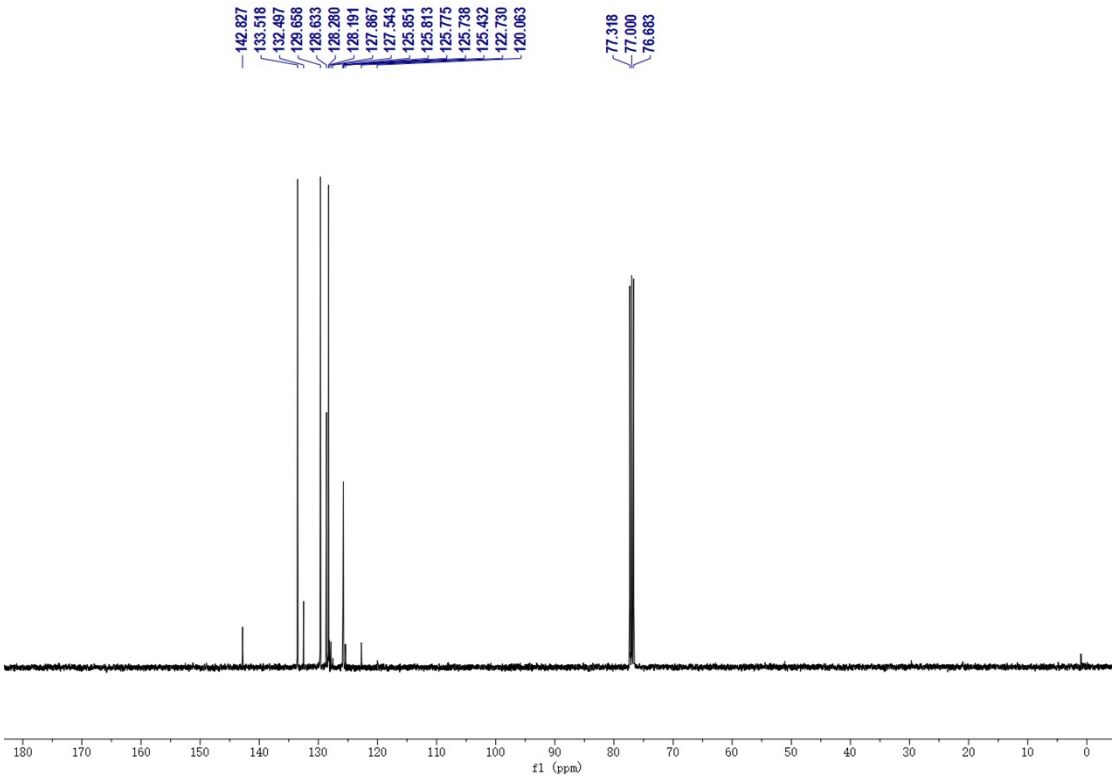

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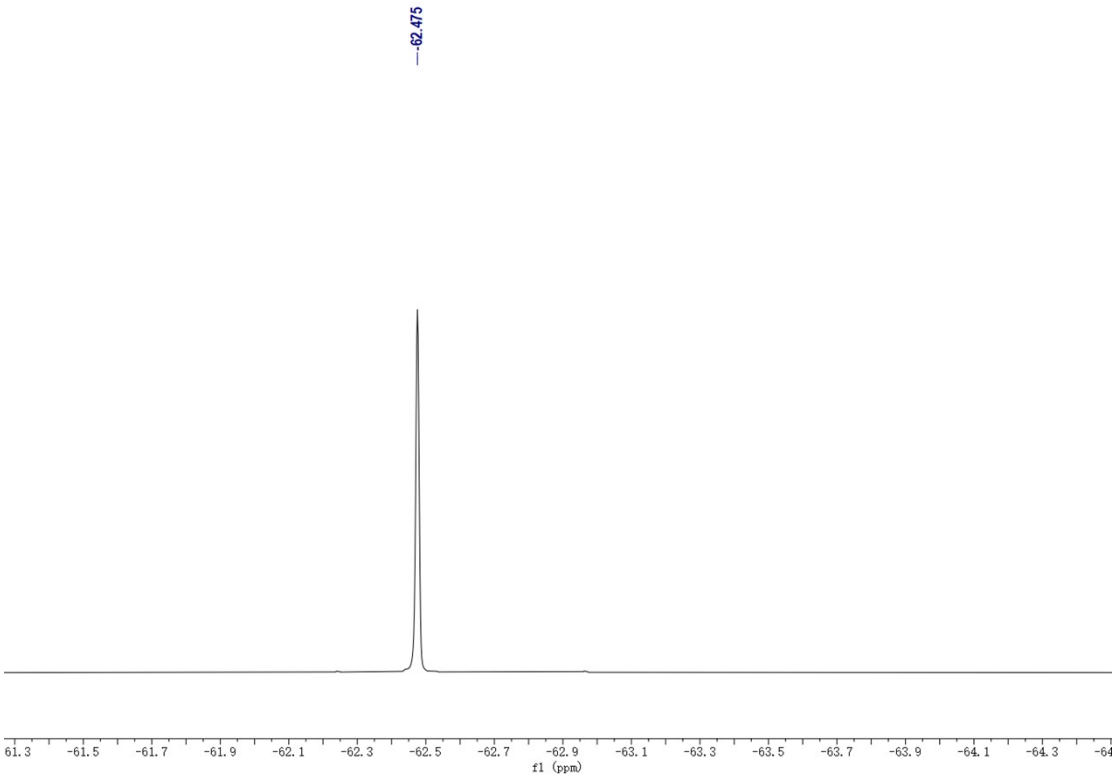

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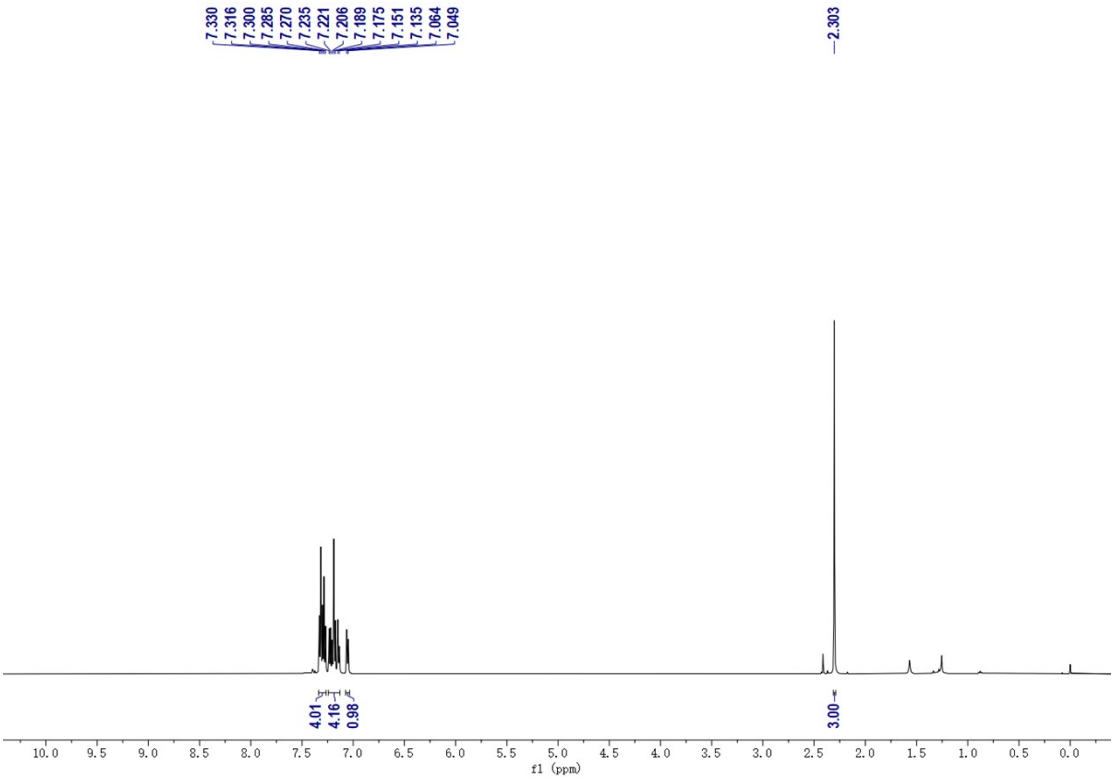

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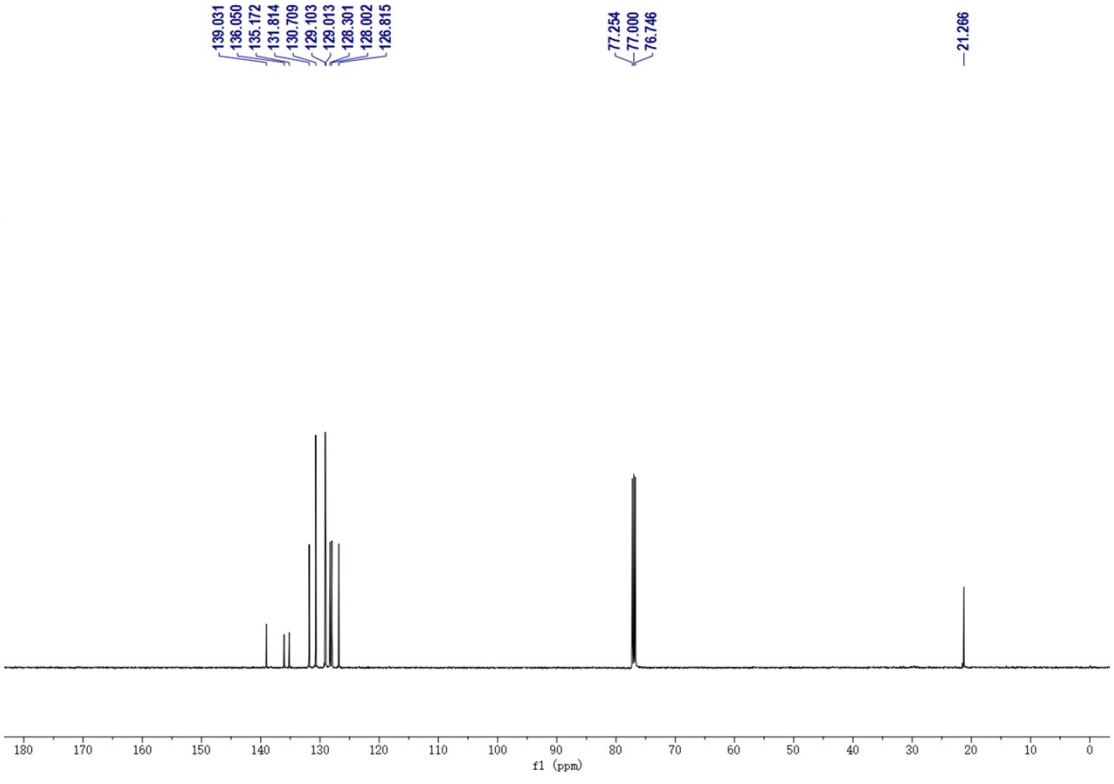

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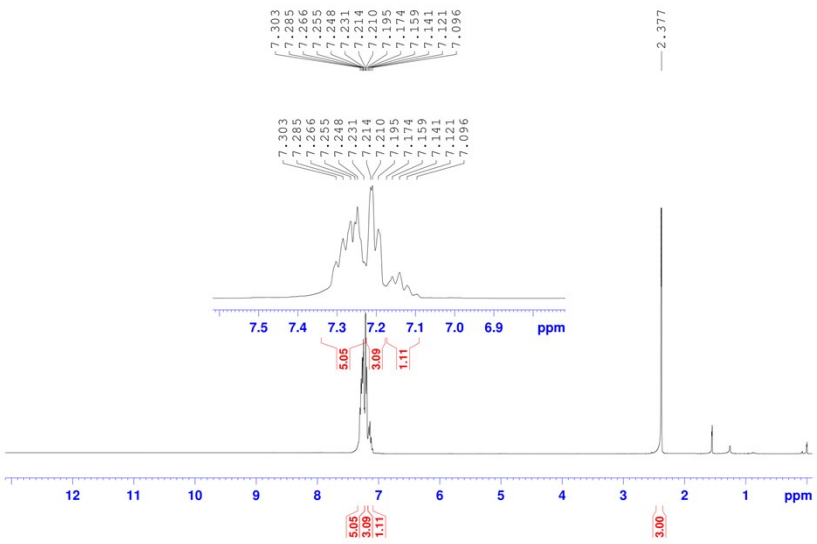

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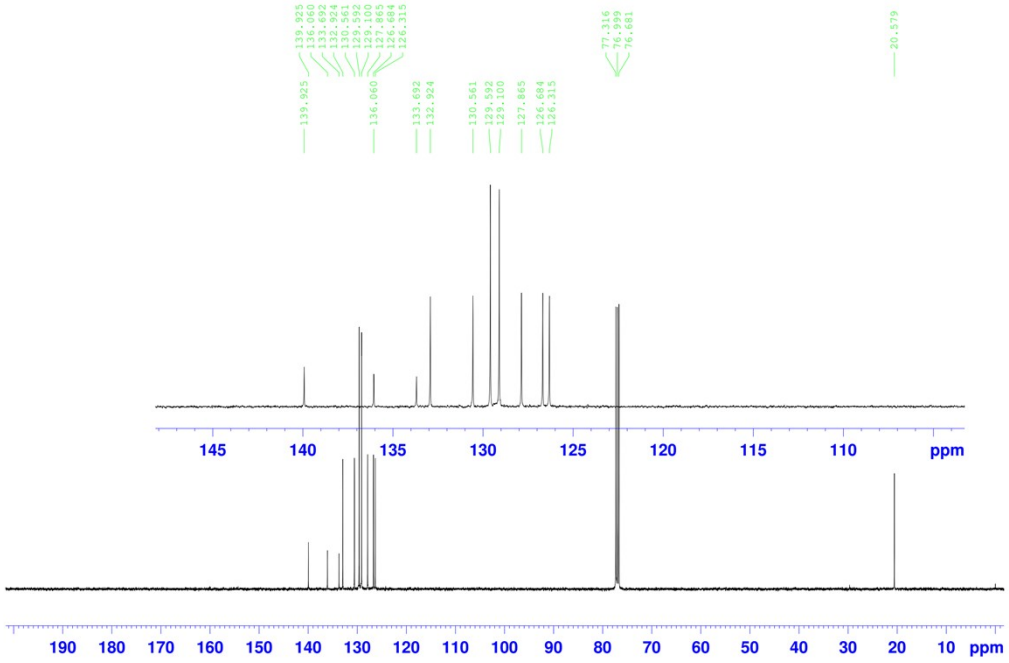

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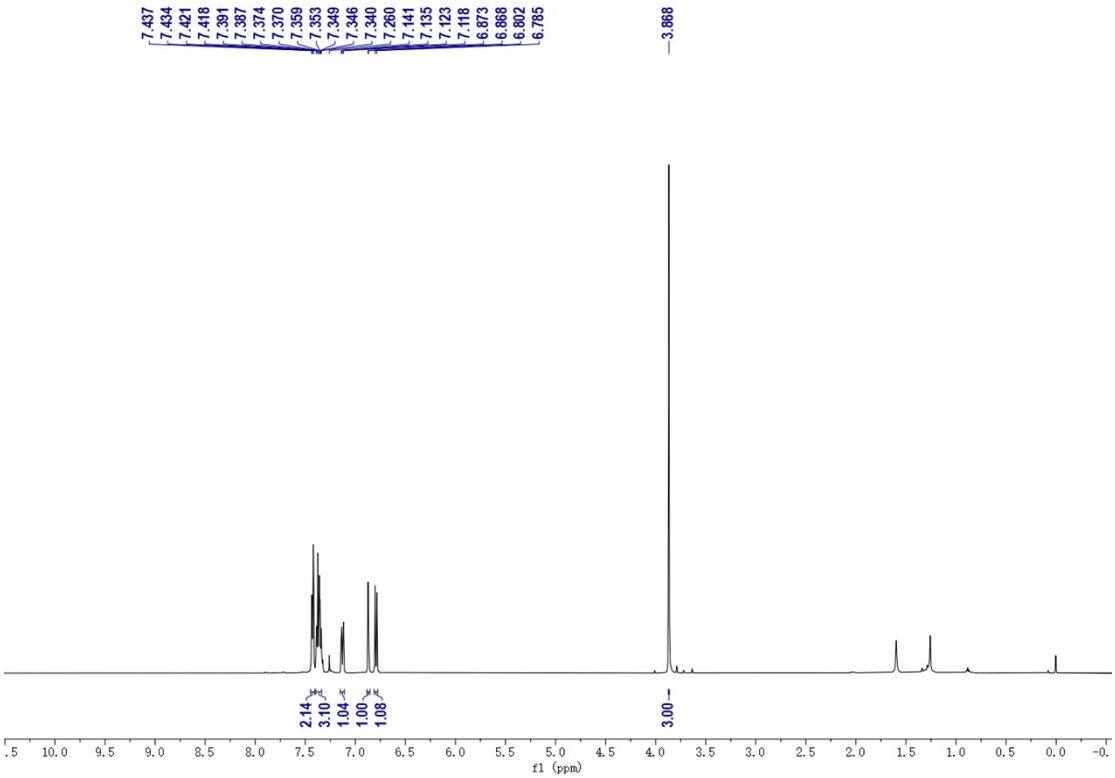

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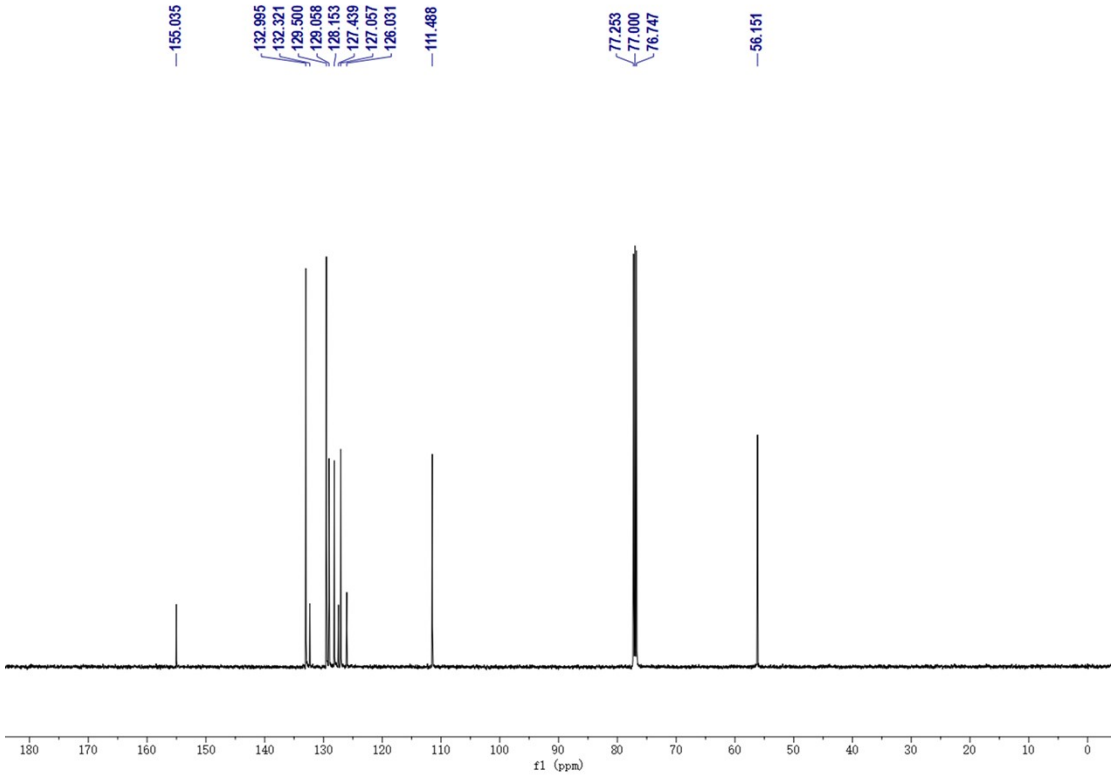

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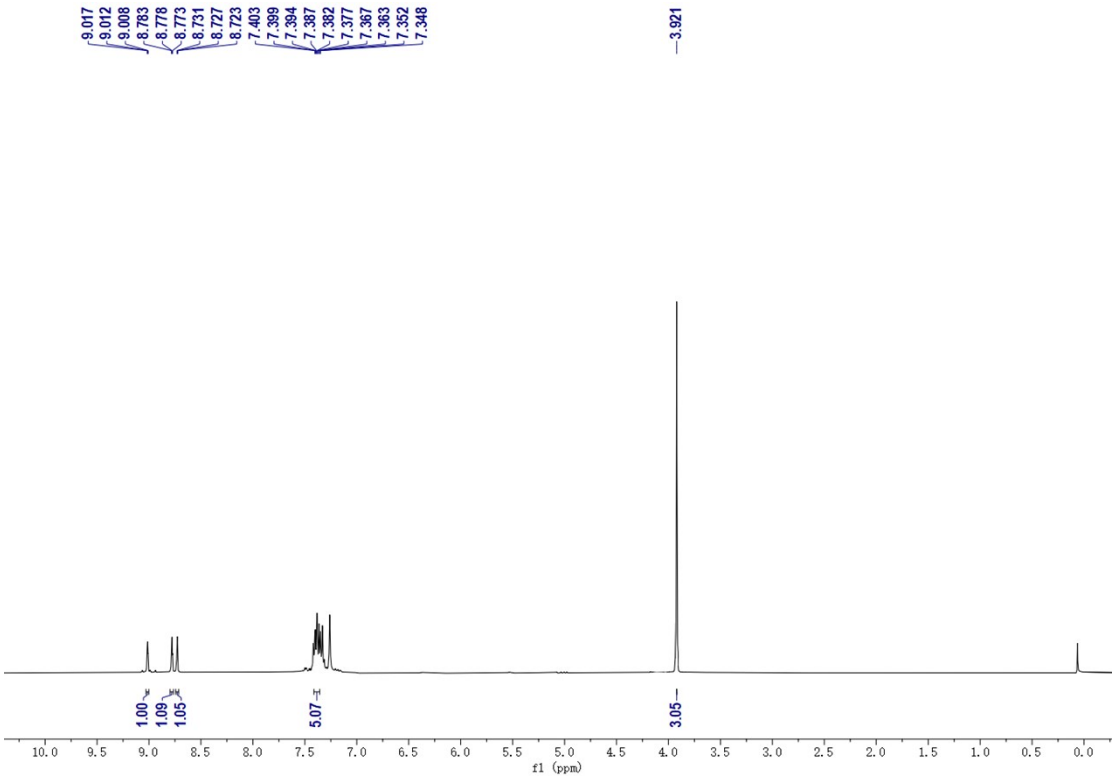

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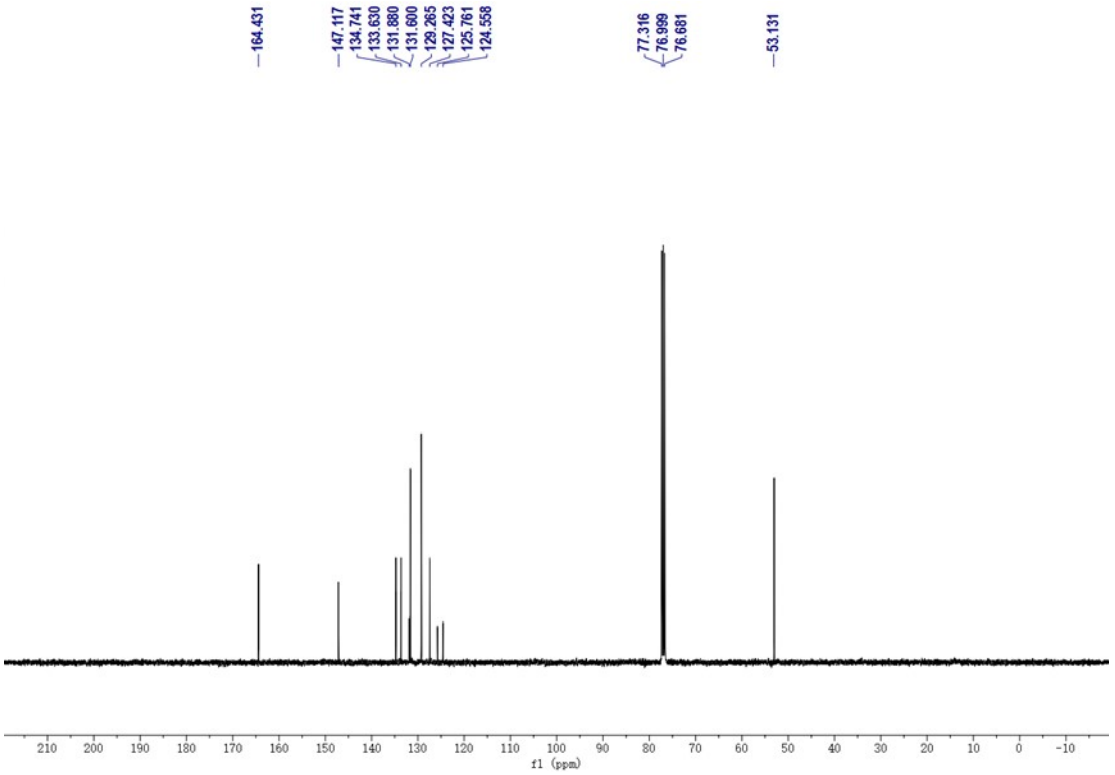

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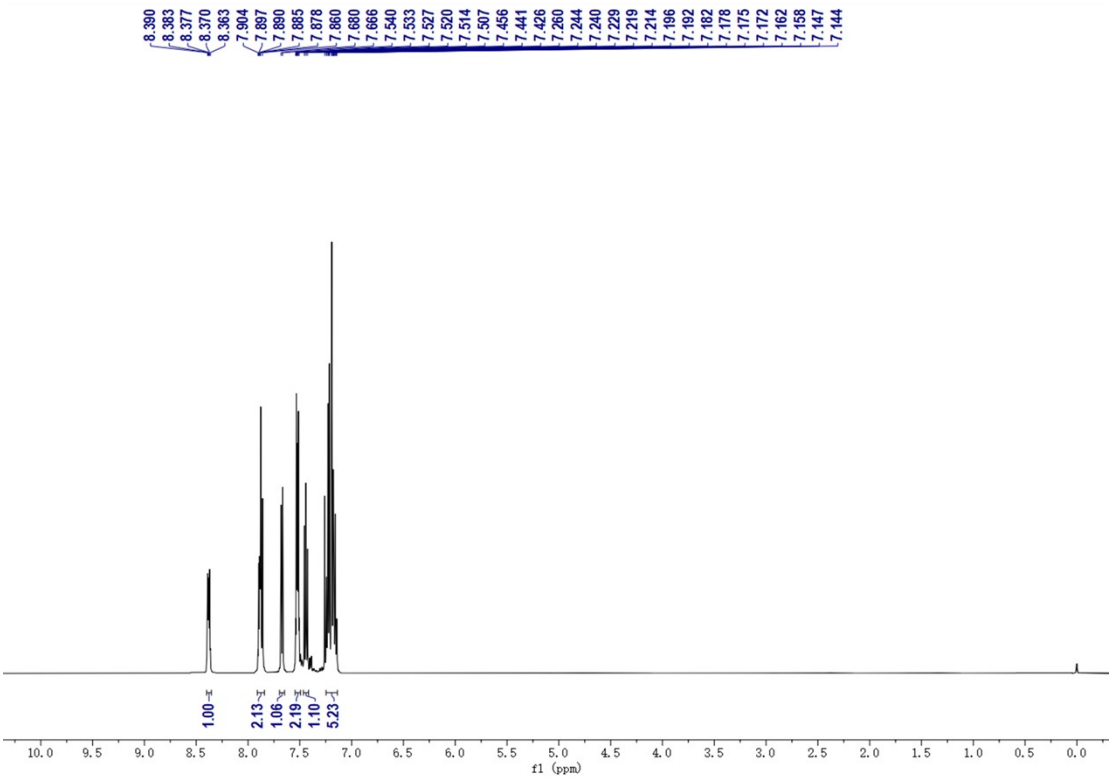

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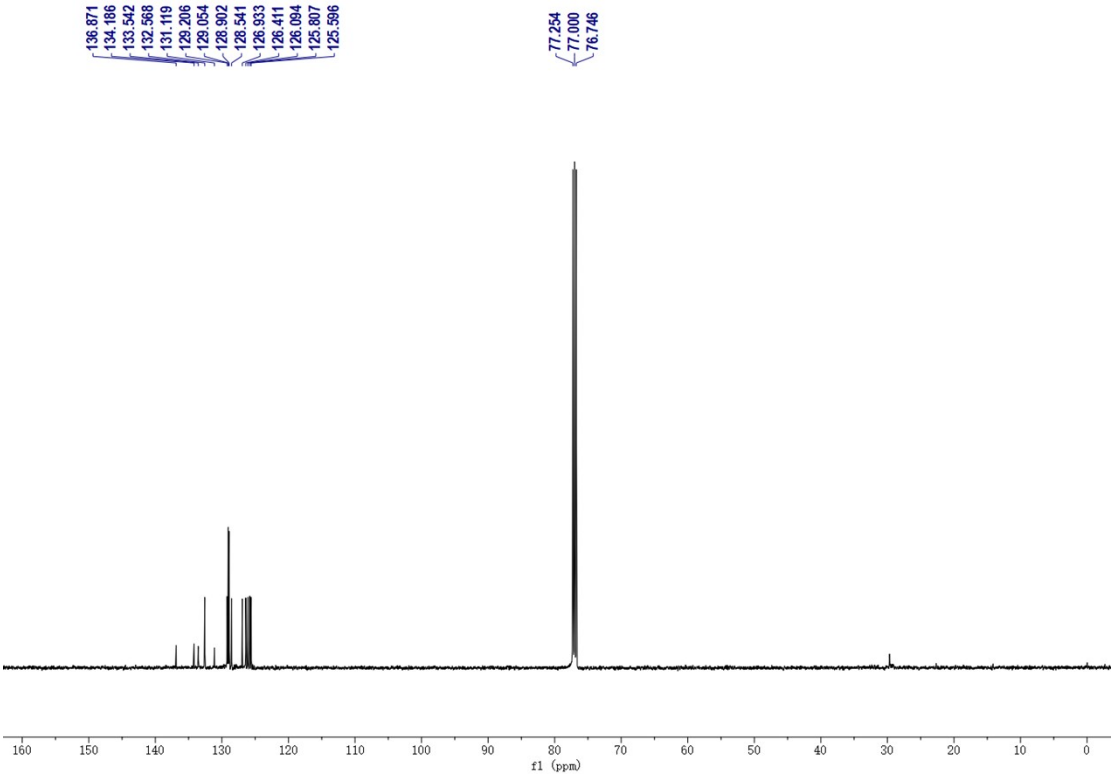

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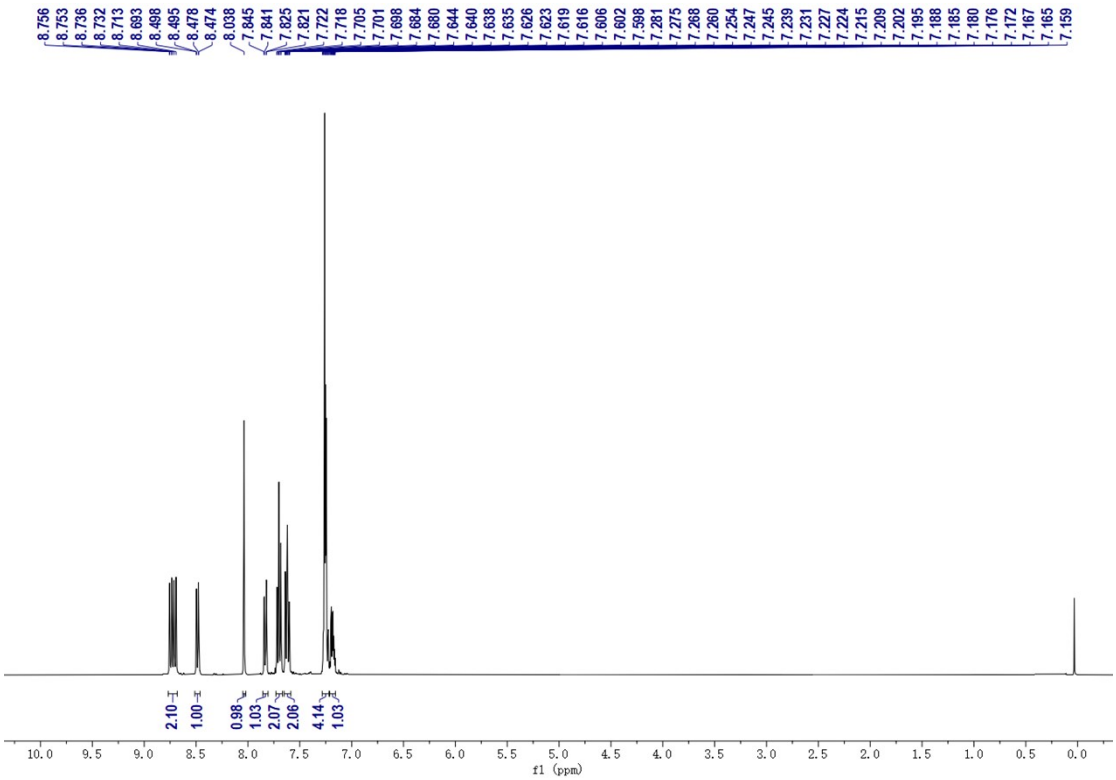

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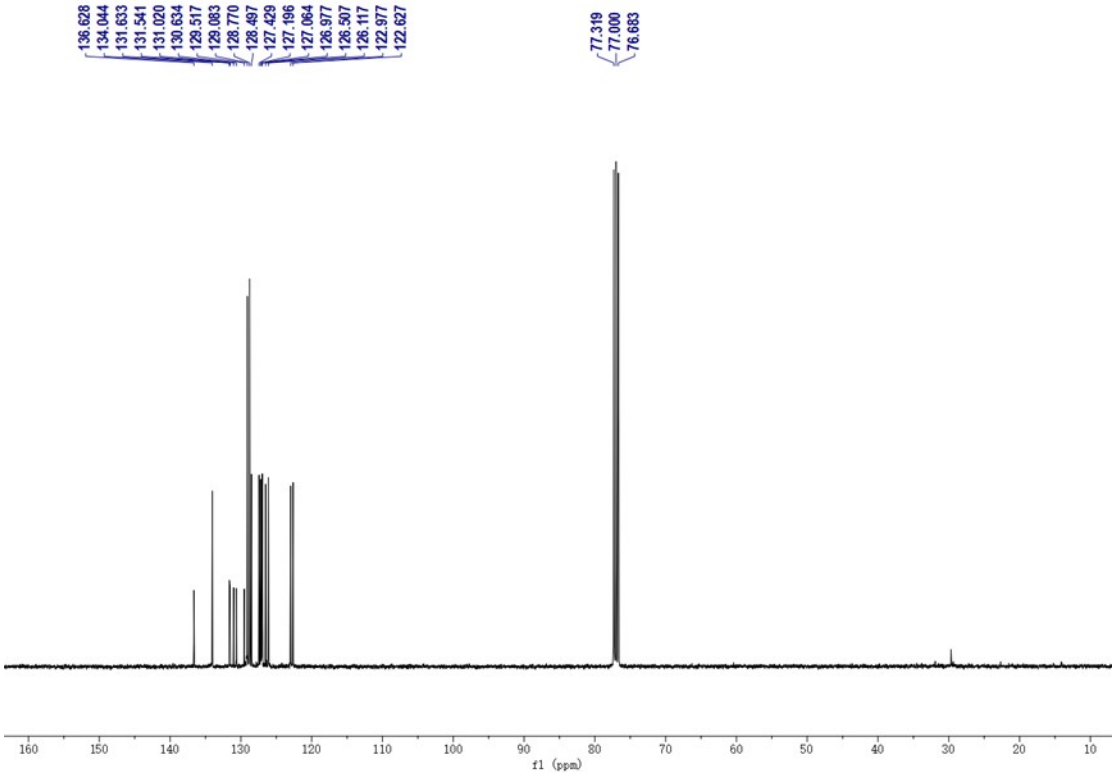

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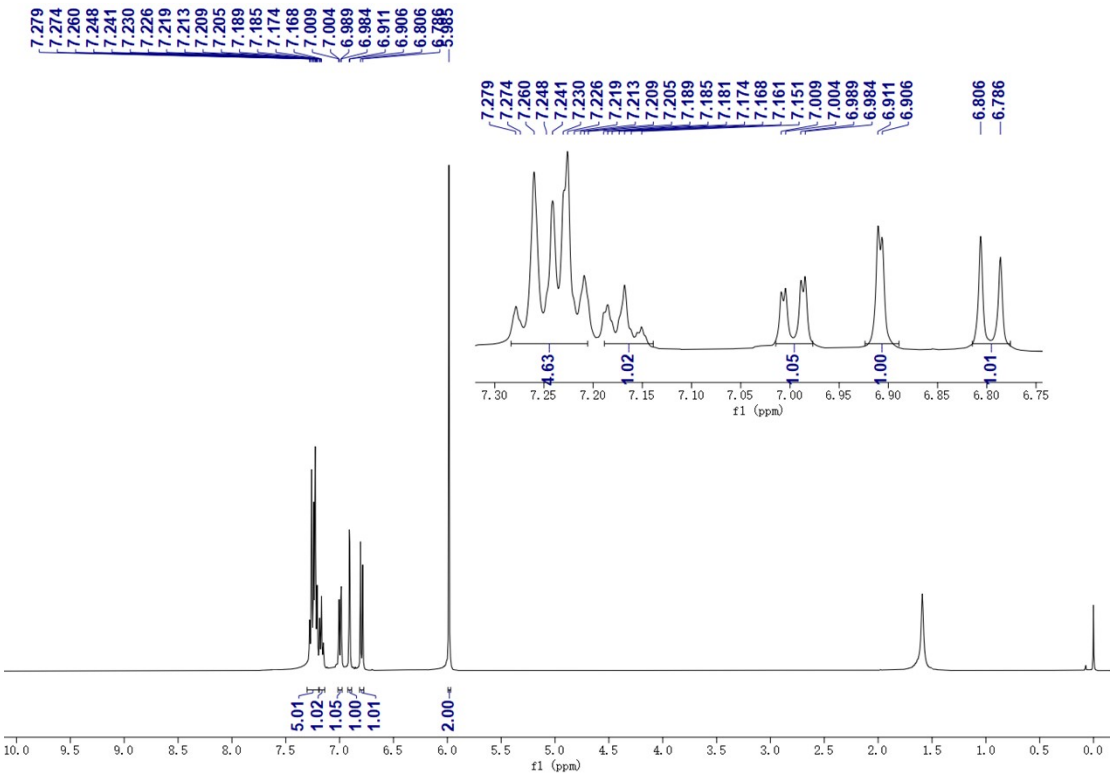

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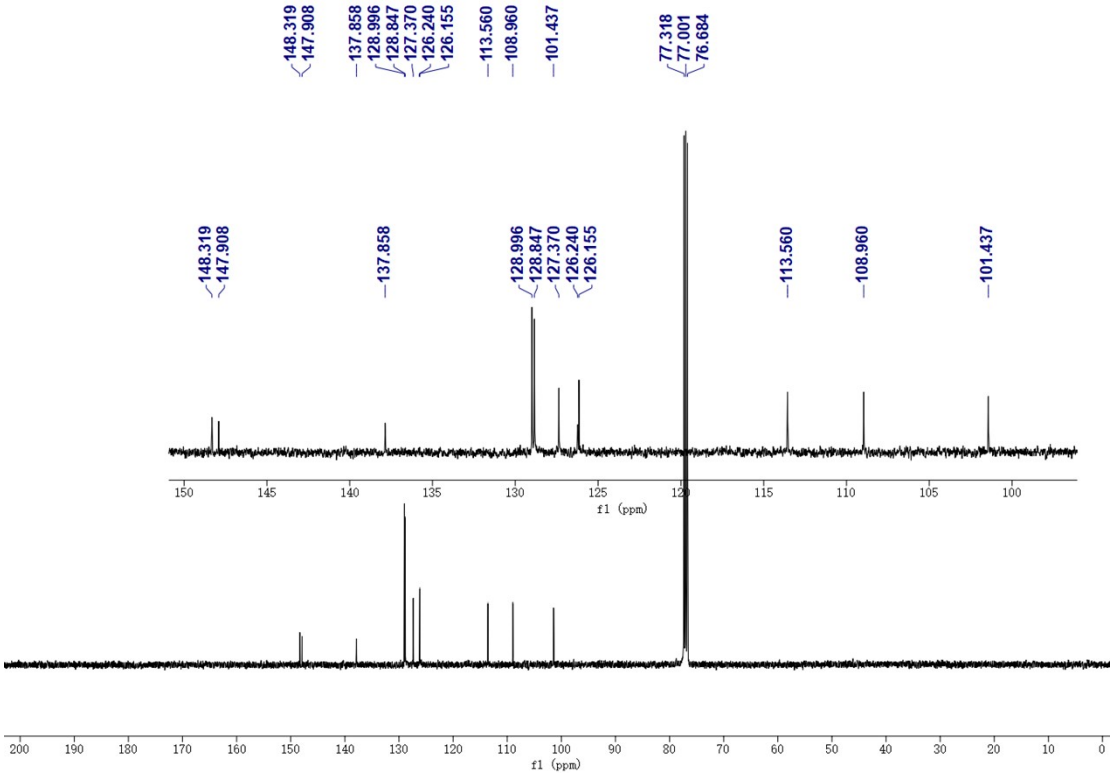

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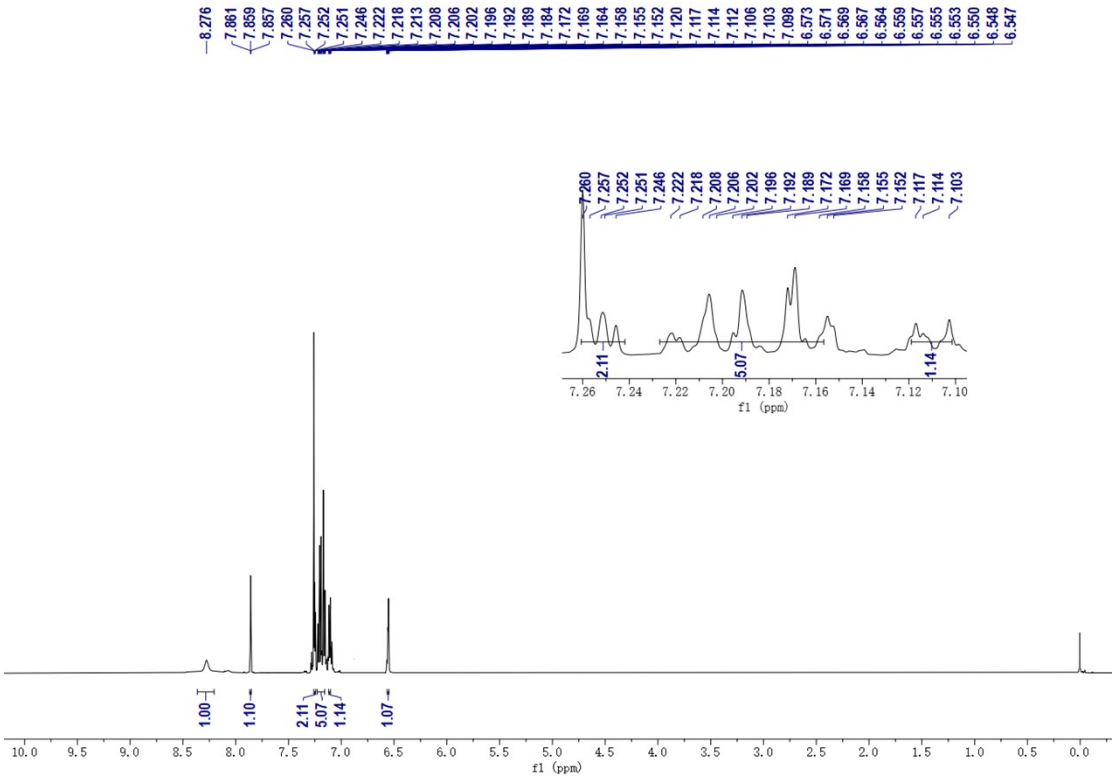

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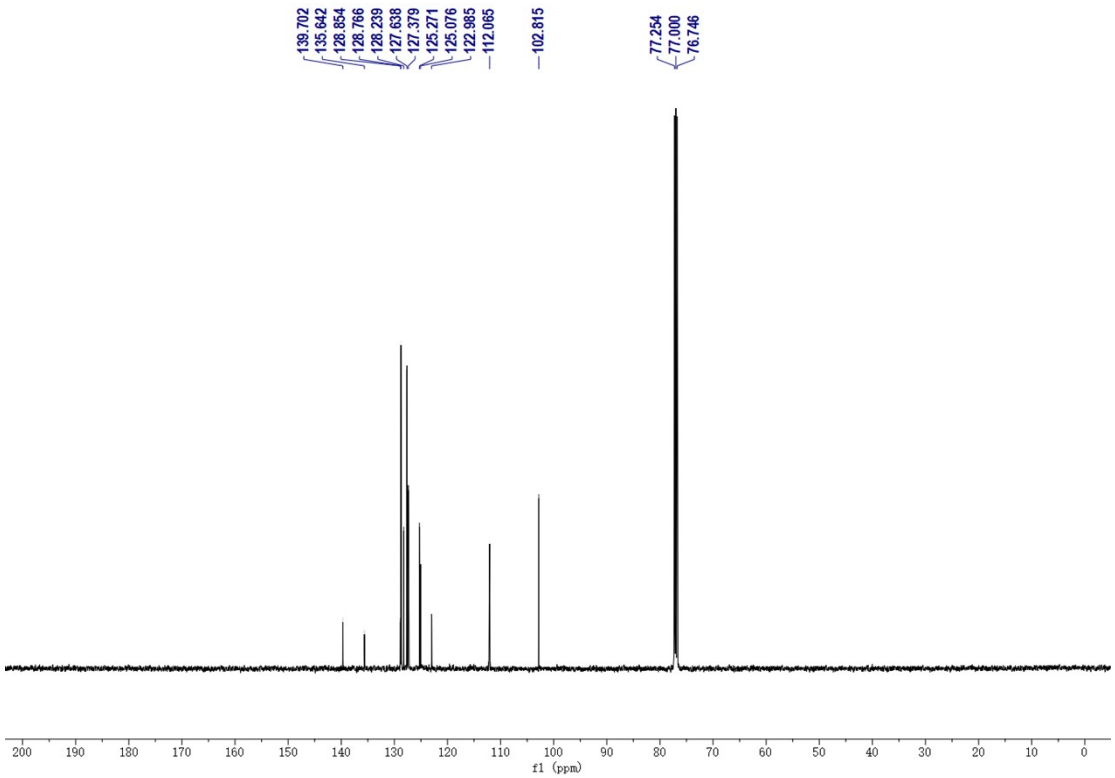

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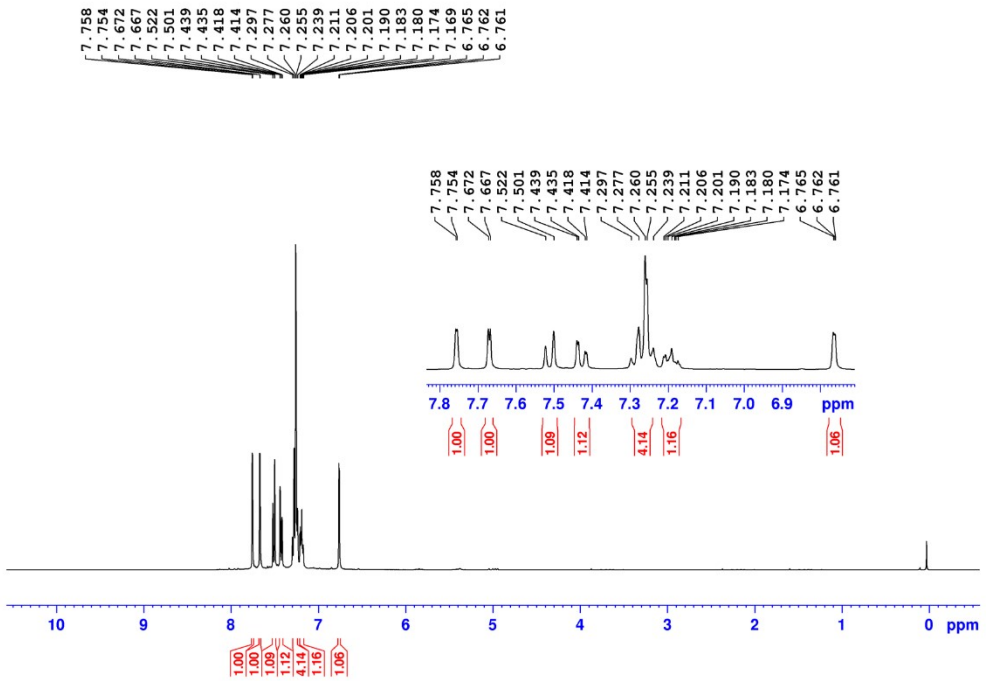

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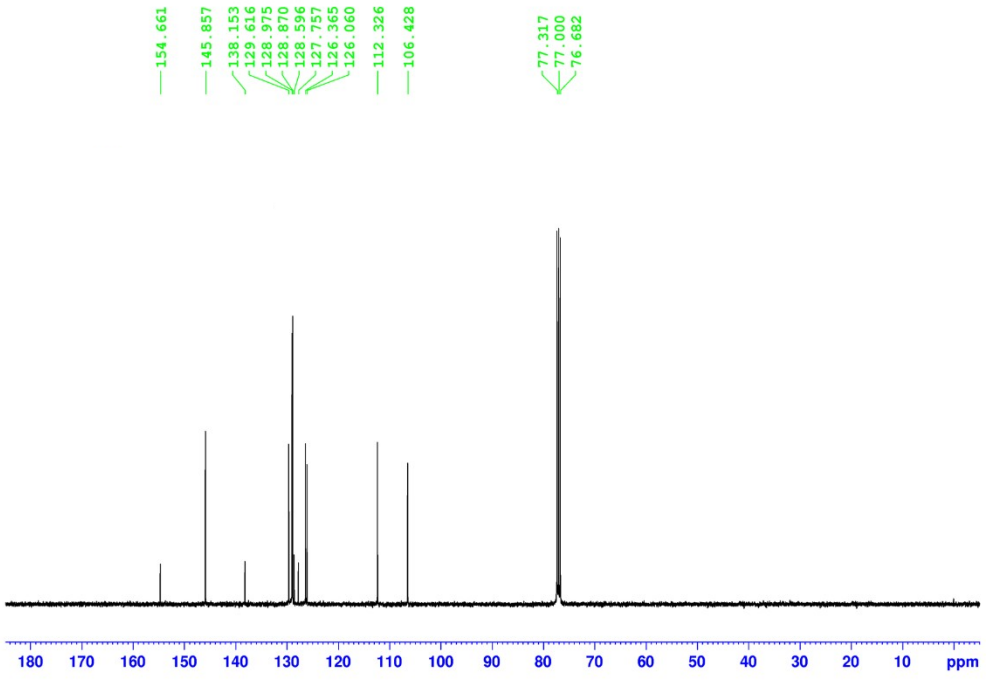
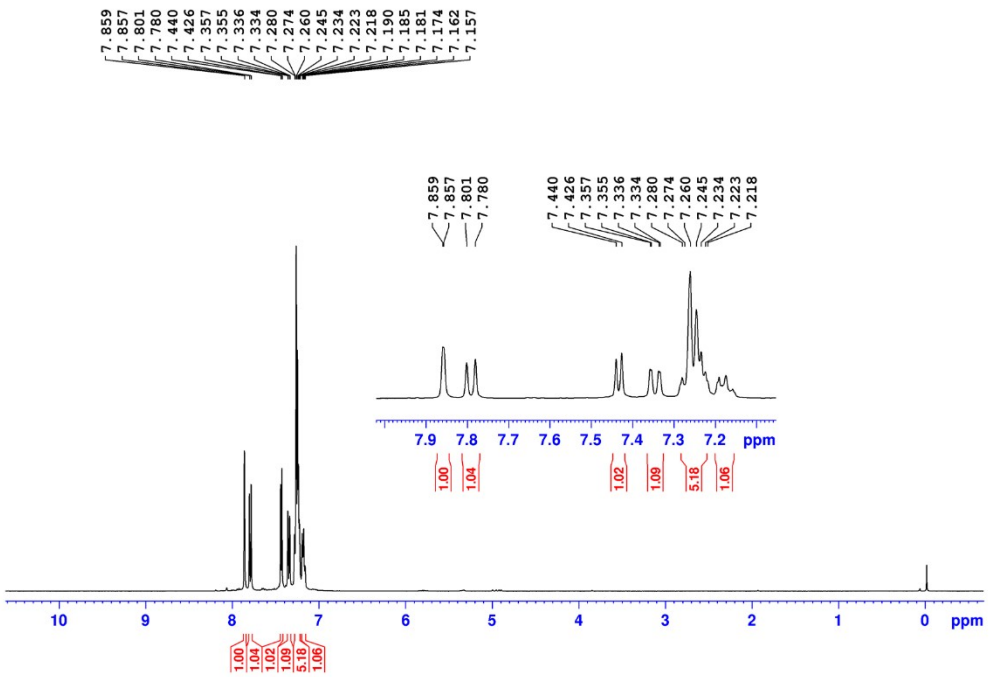
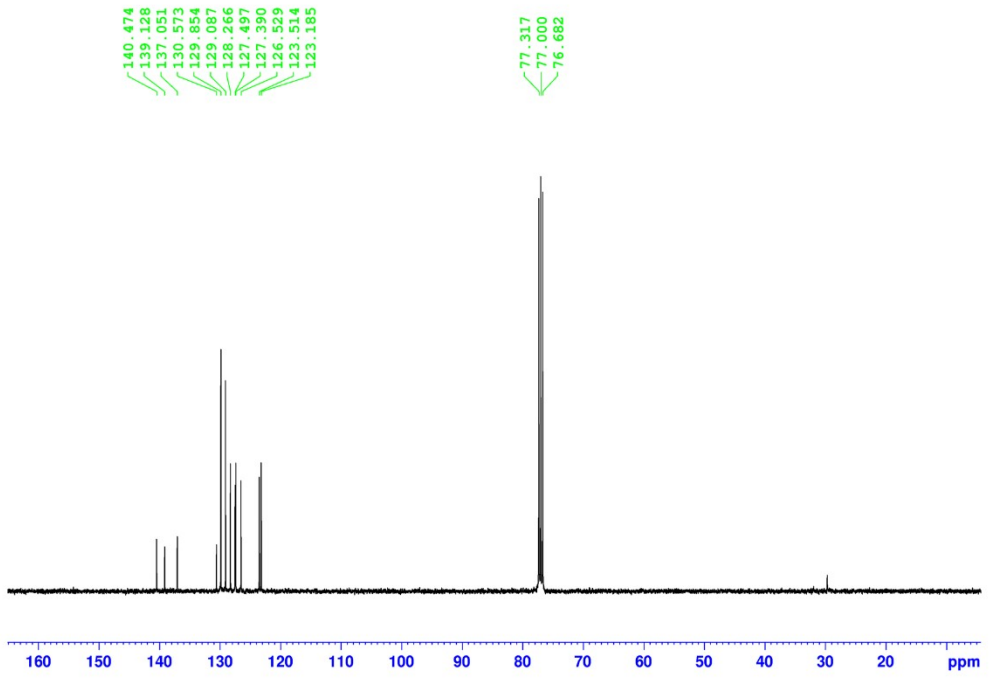


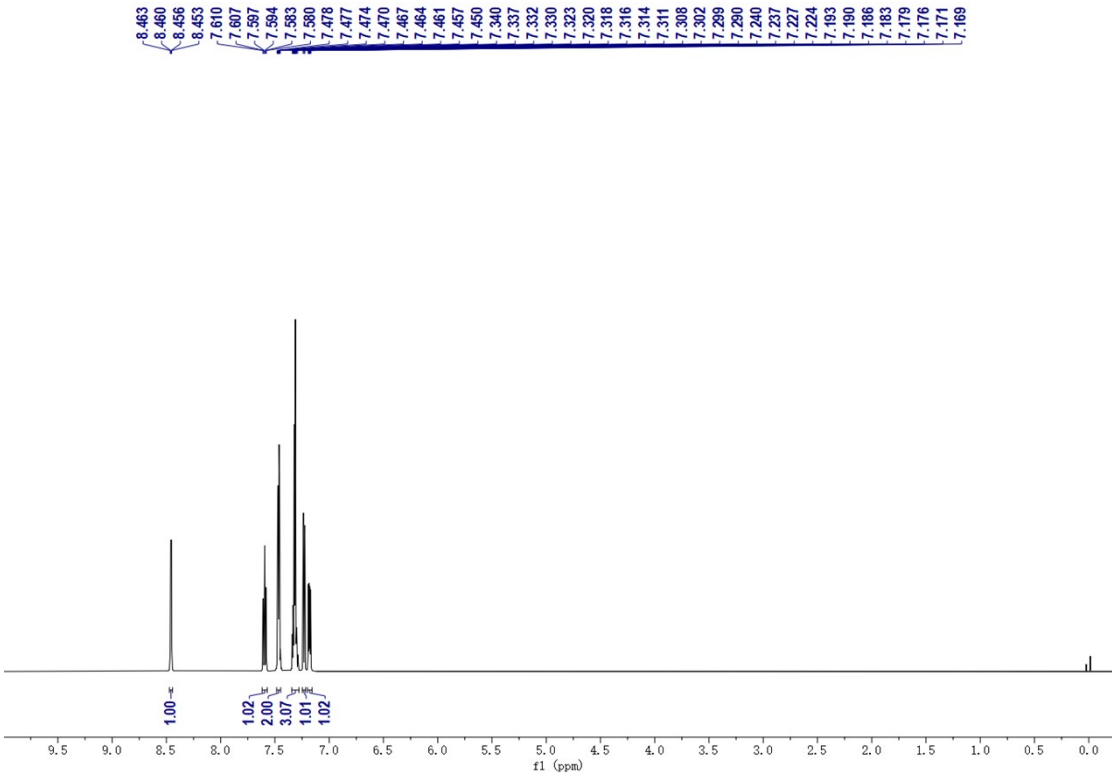
3ap-^{13}C NMR



3aq-^{1}H NMR



3aq-^{13}C NMR



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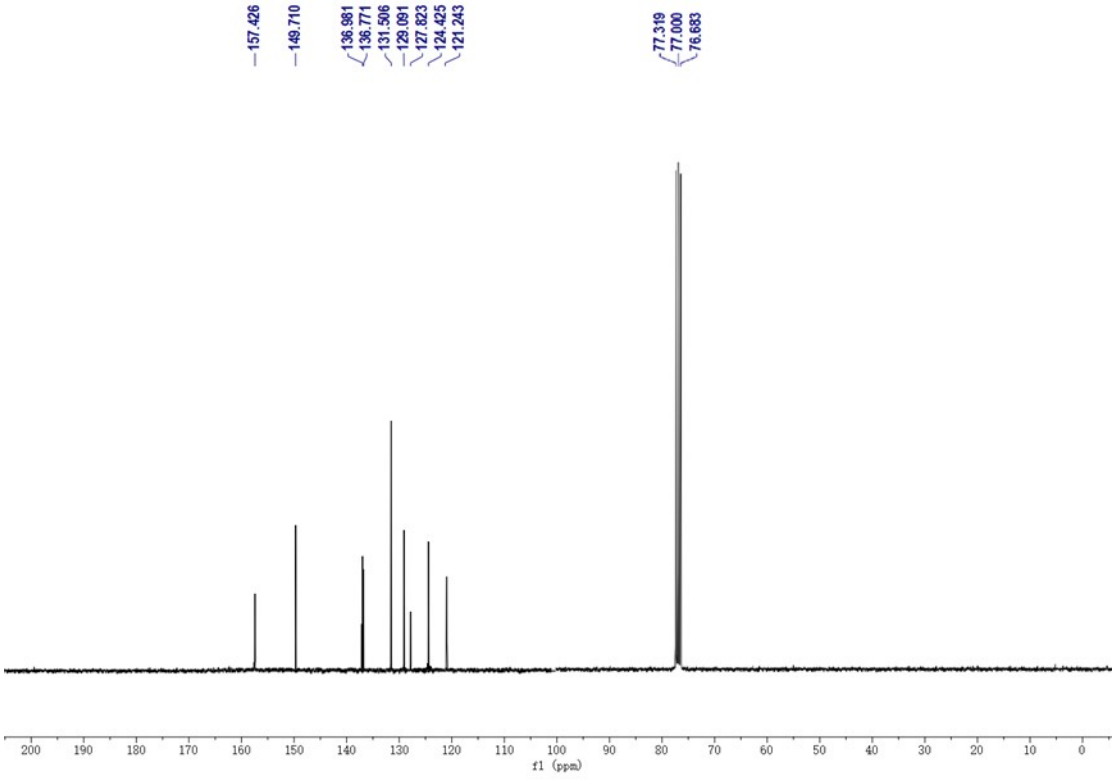
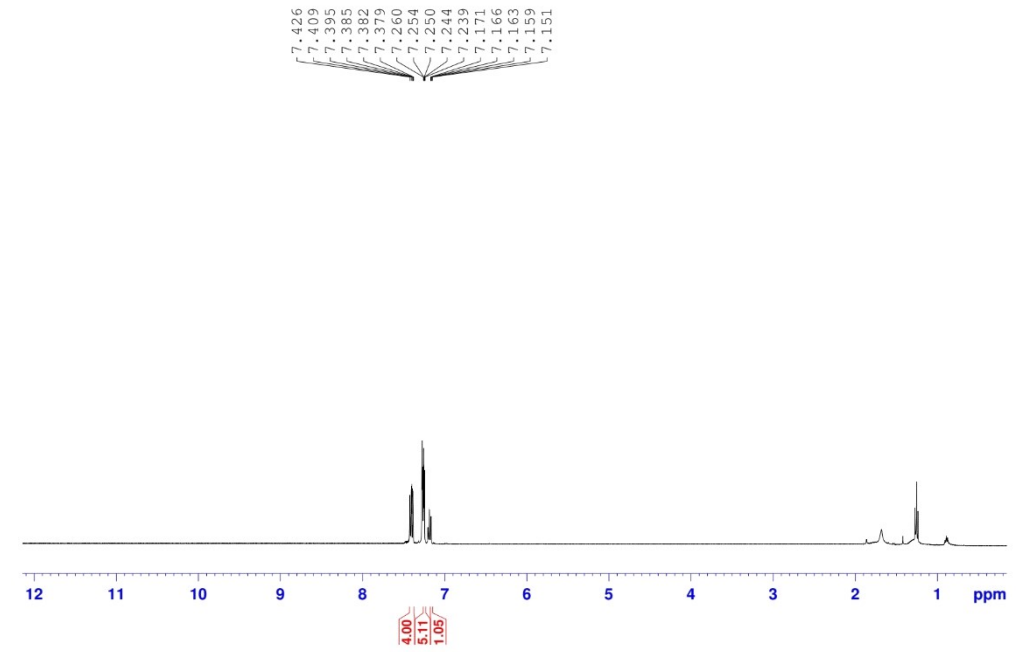


3ar-^{13}C NMR



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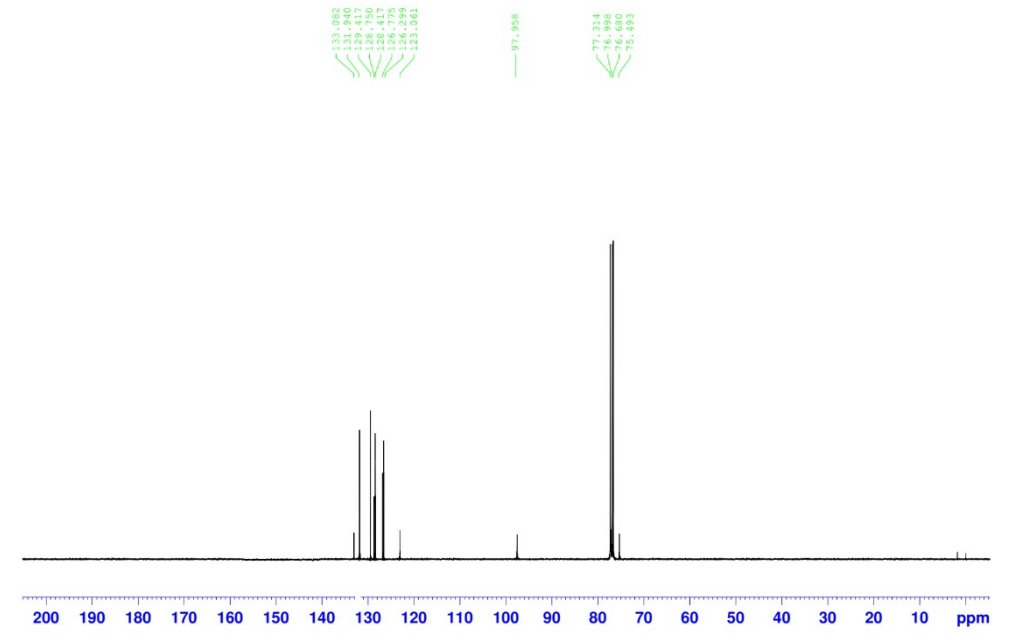

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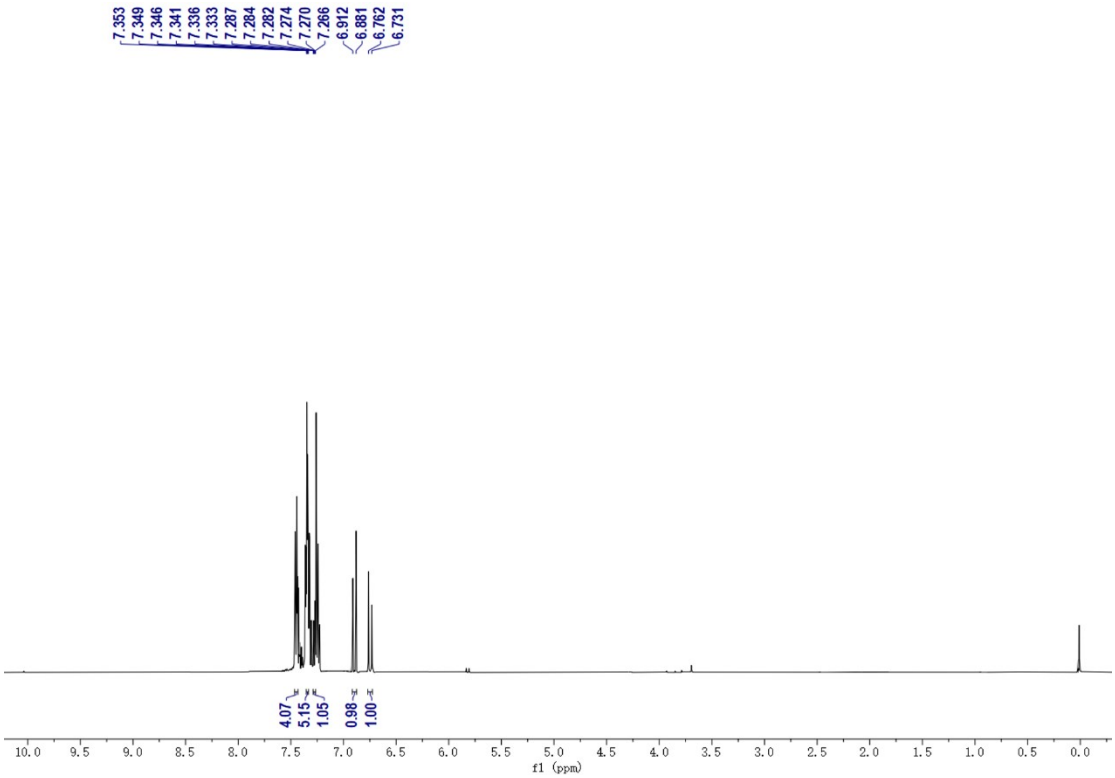
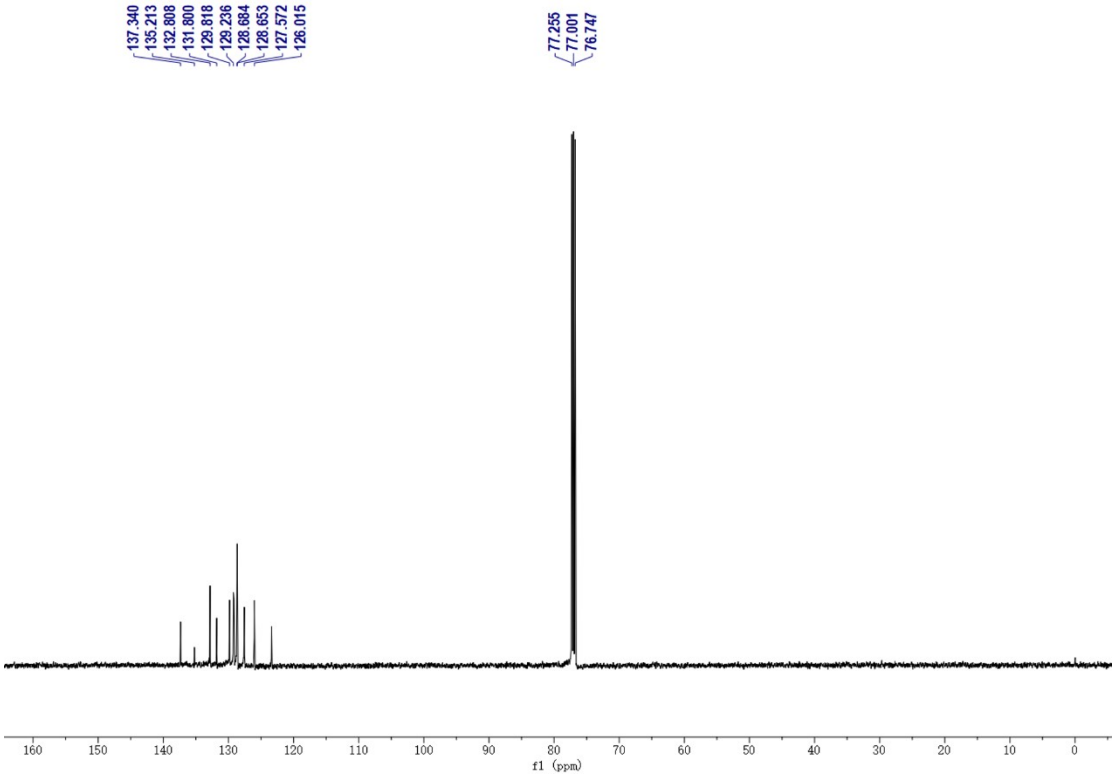


3at-^{1}H NMR



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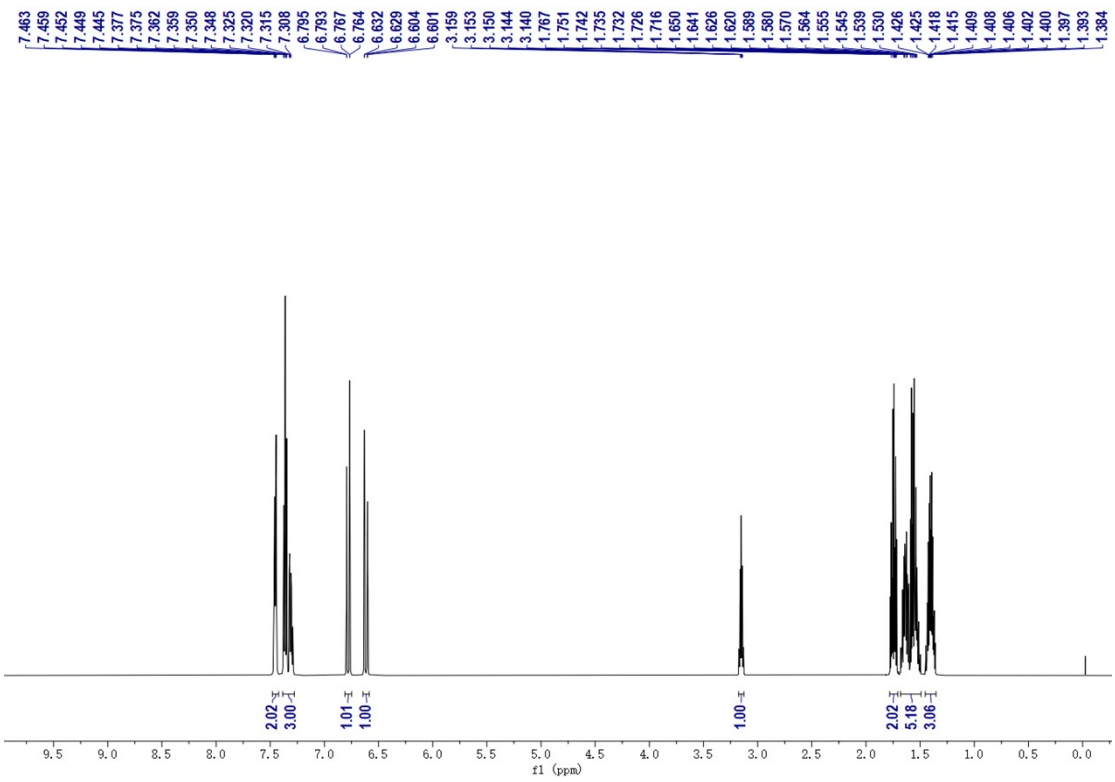

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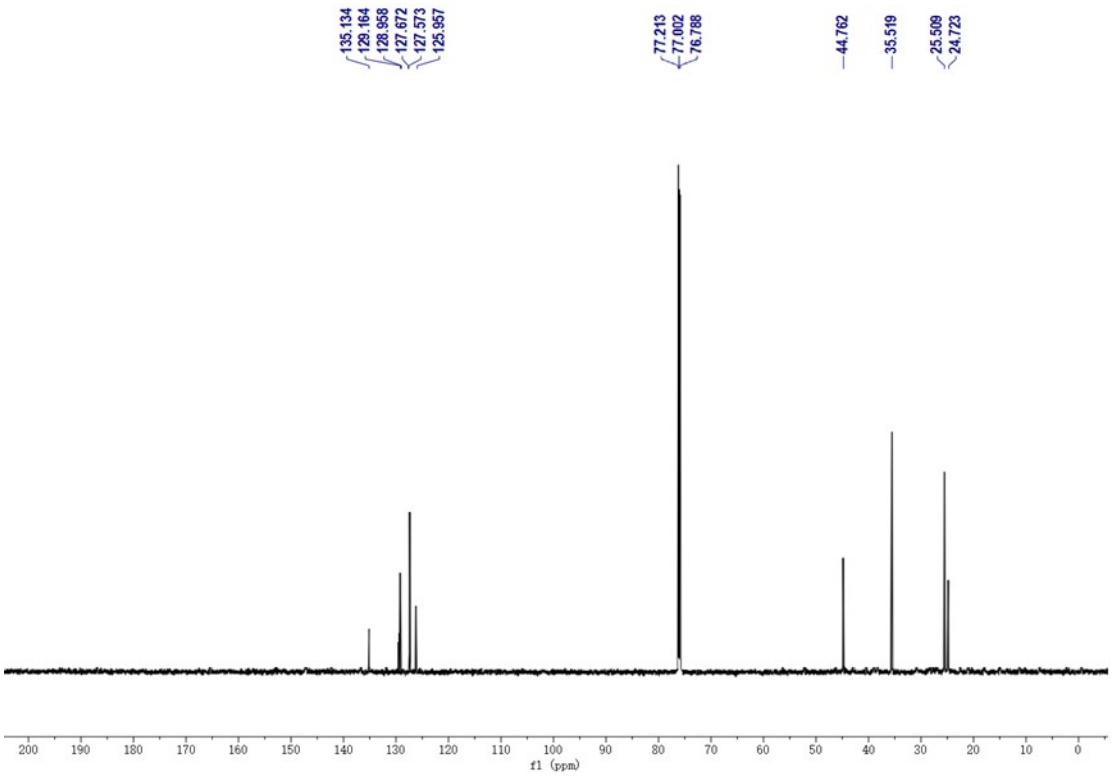
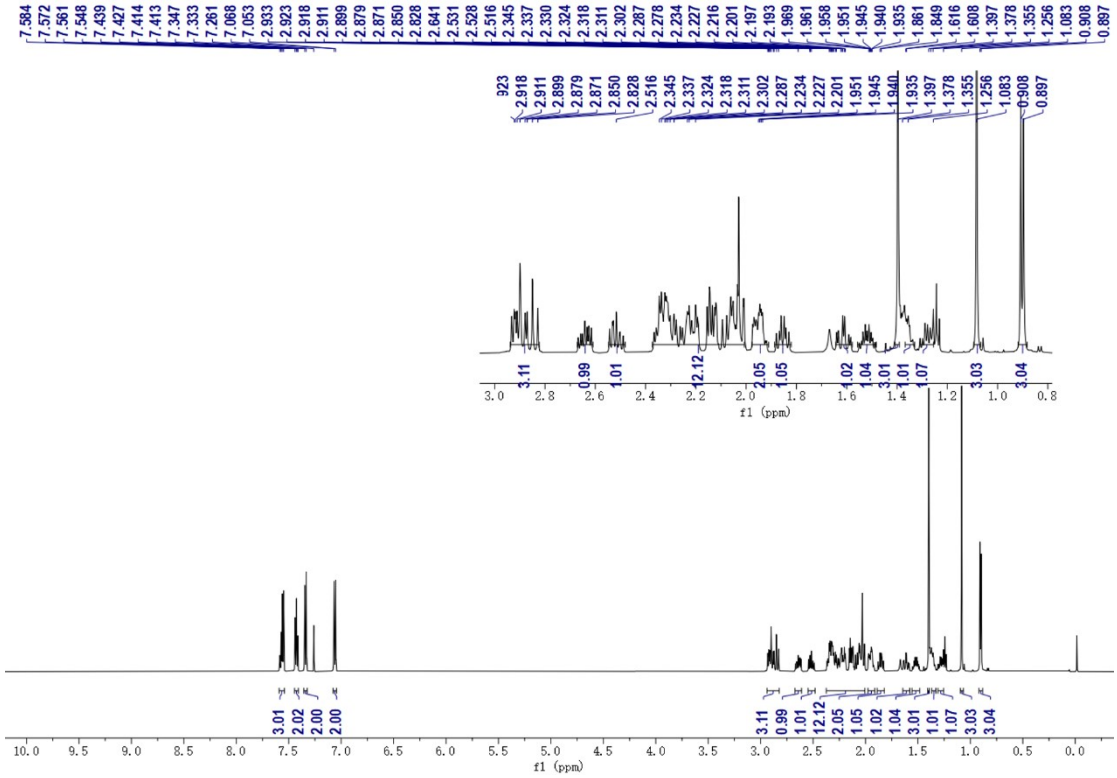
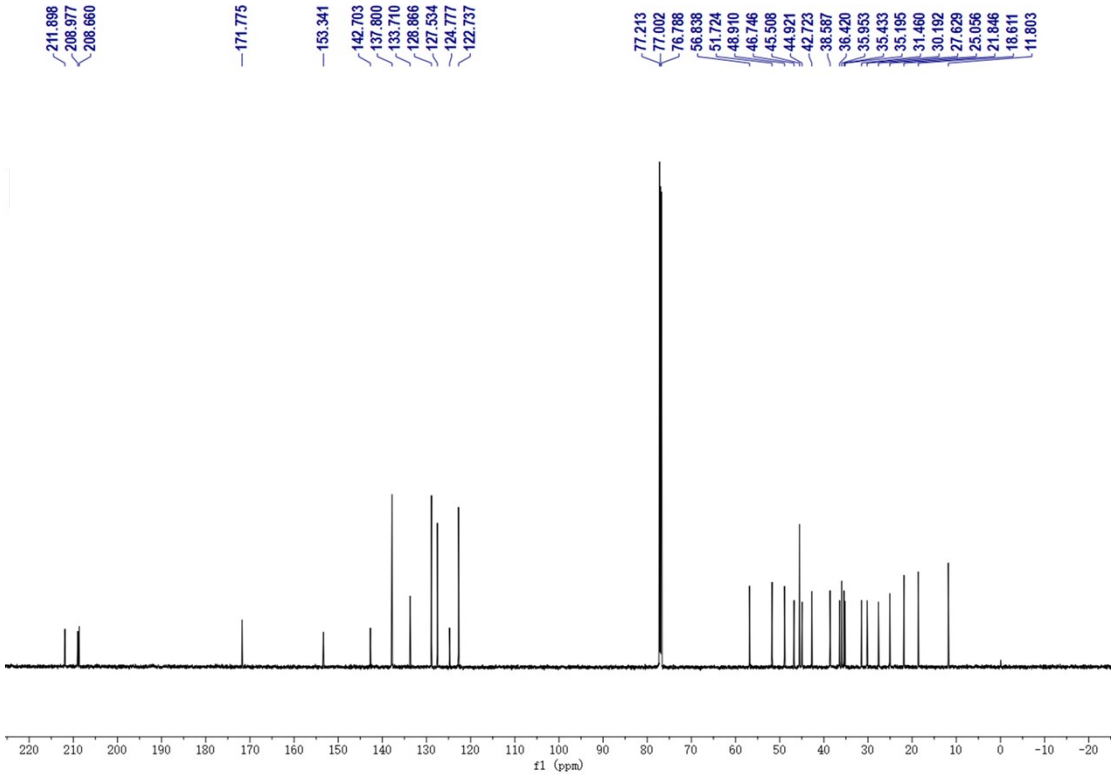


3au-^{13}C NMR



3aw-^{1}H NMR



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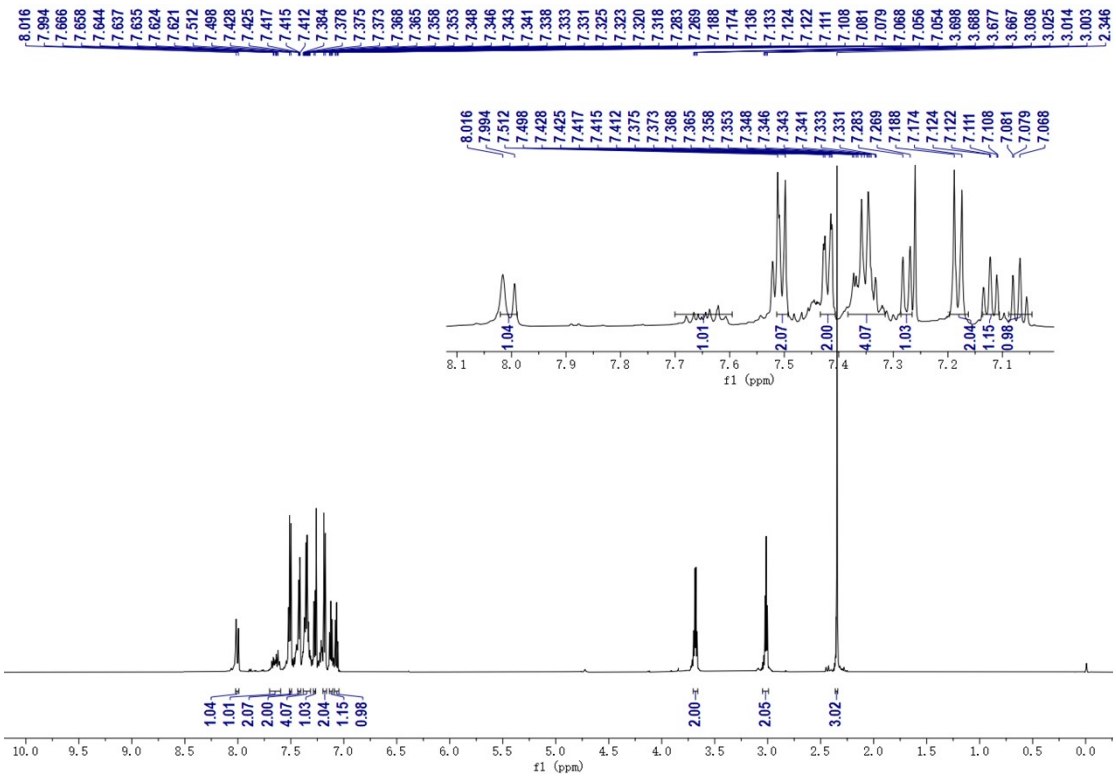
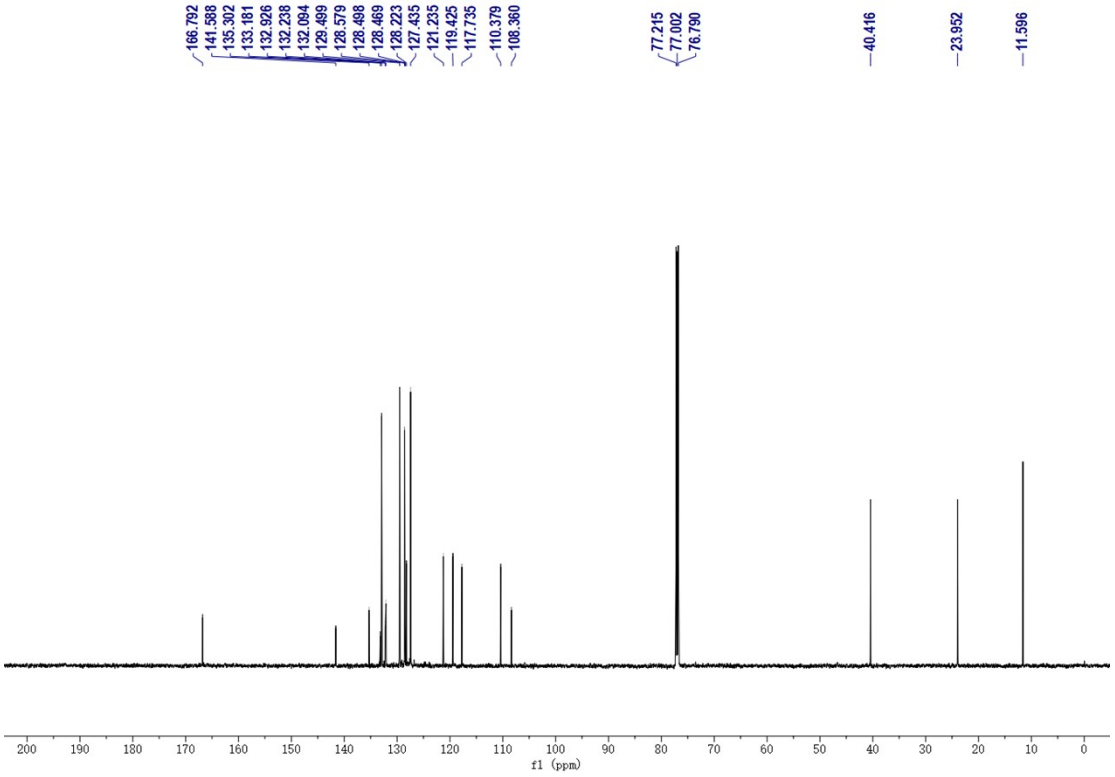
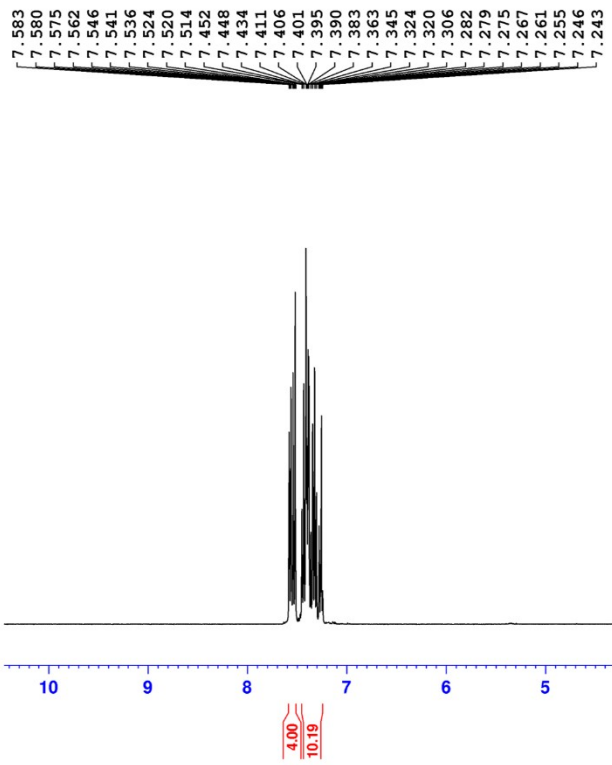


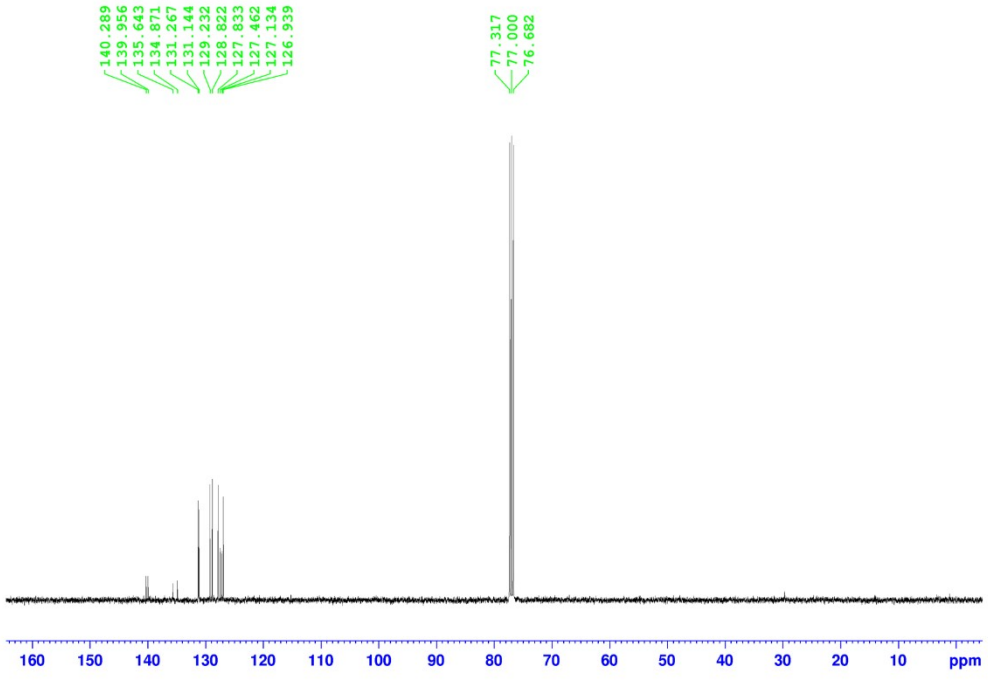
3ax-^{1}H NMR



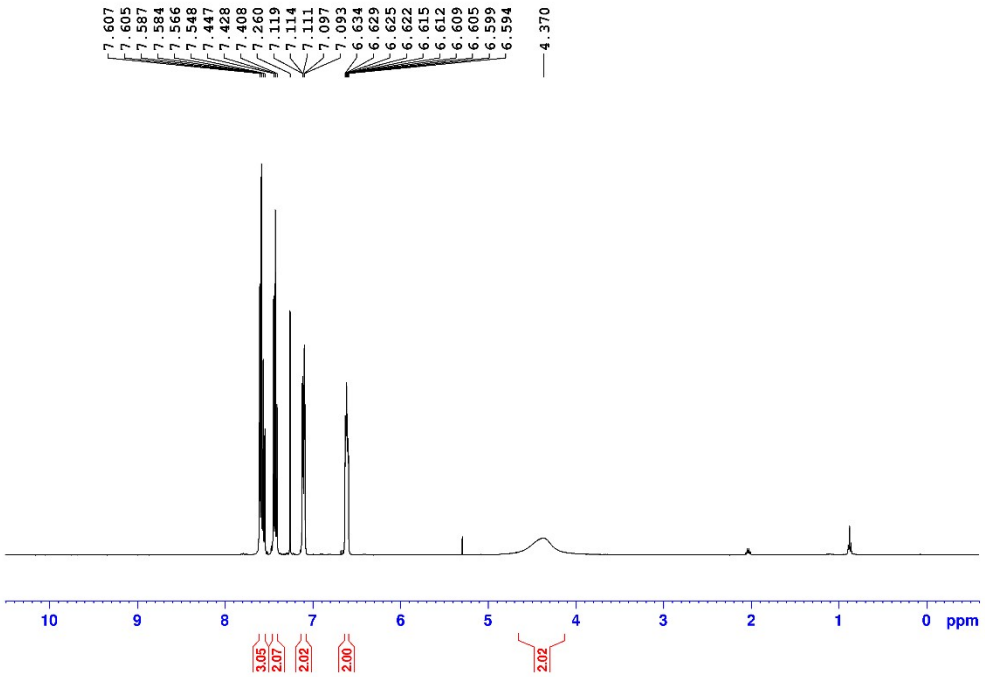
3ax-^{13}C NMR



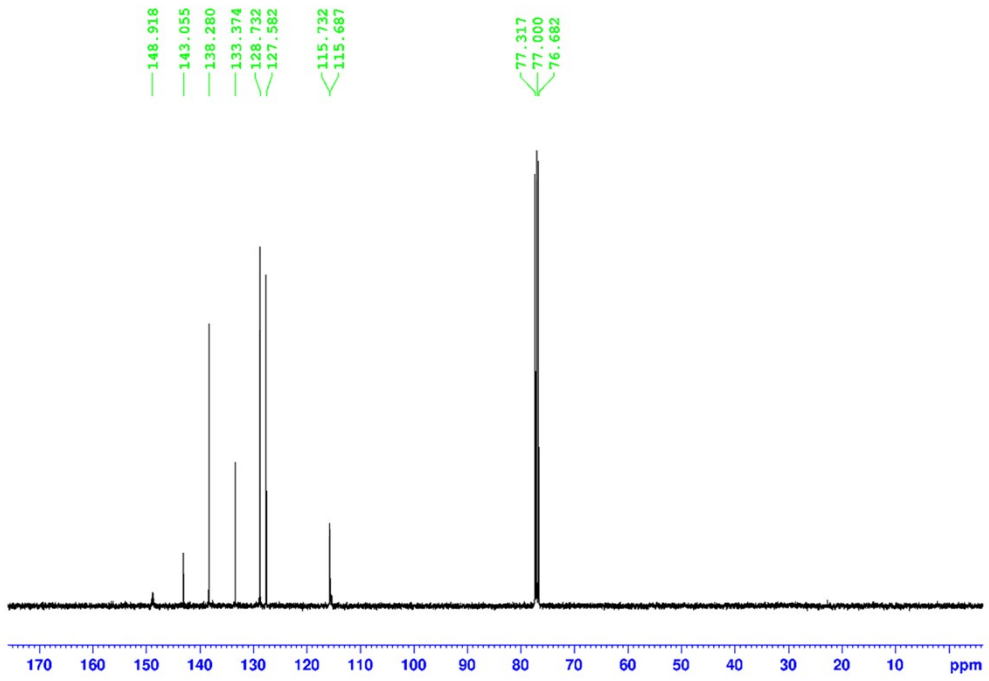
3ba-^{1}H NMR



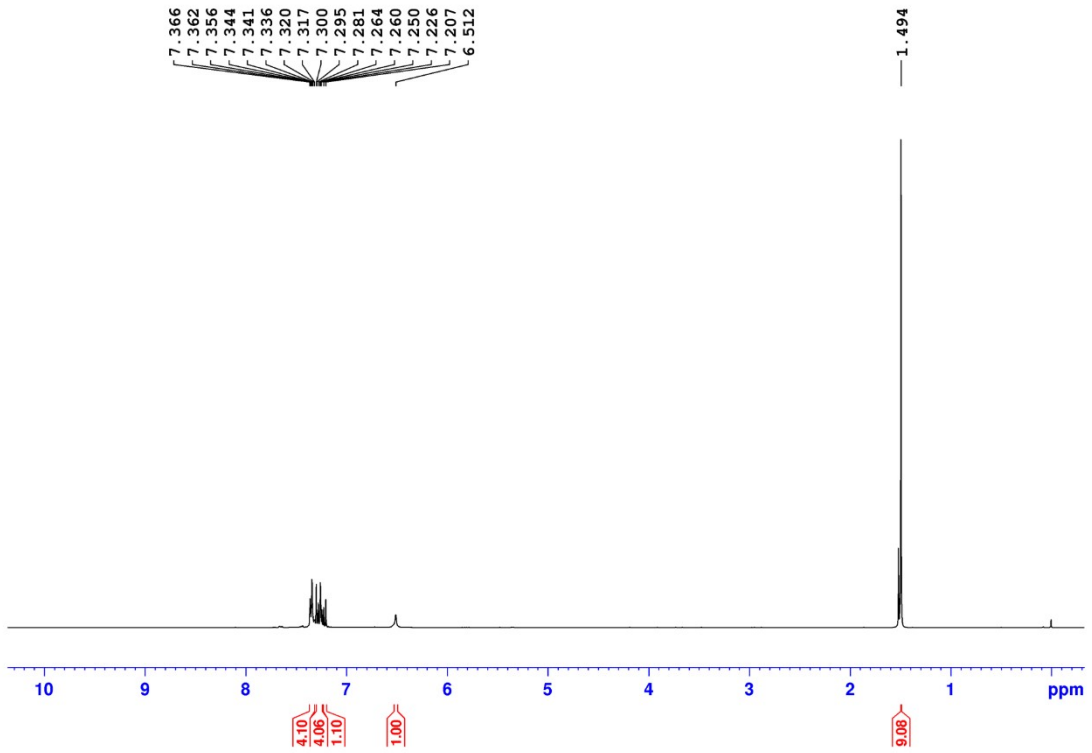
3ba-^{13}C NMR



3ca-^{1}H NMR



3ca-^{13}C NMR



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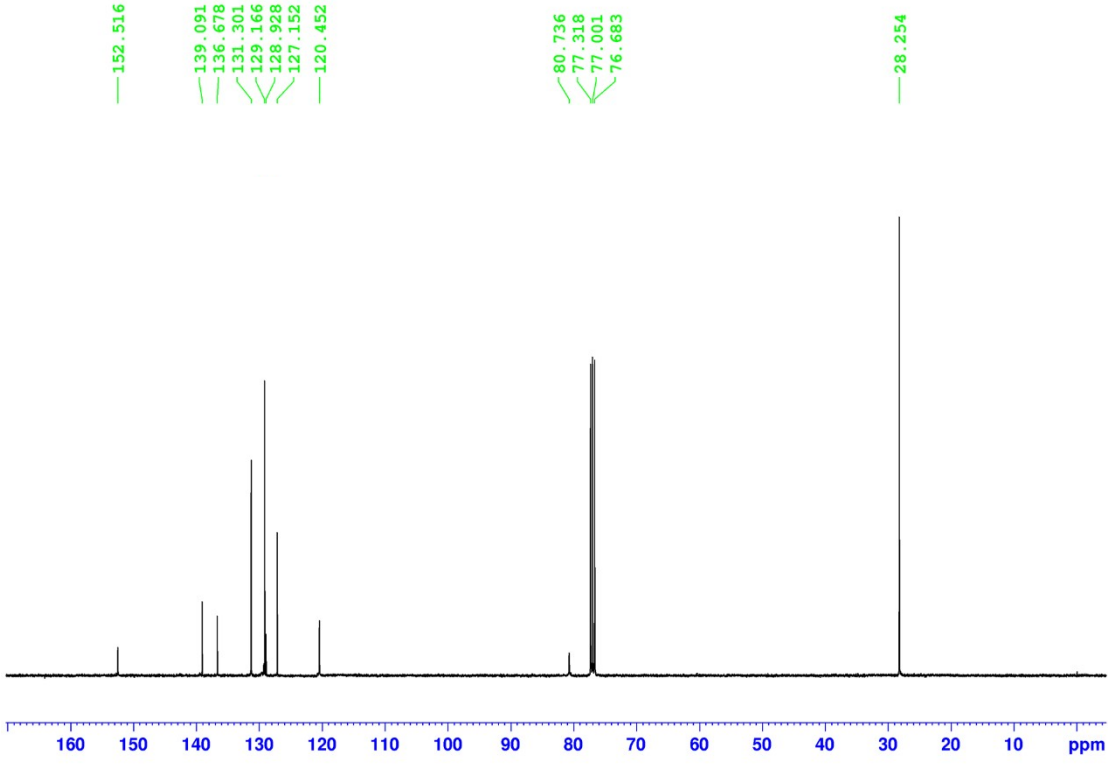
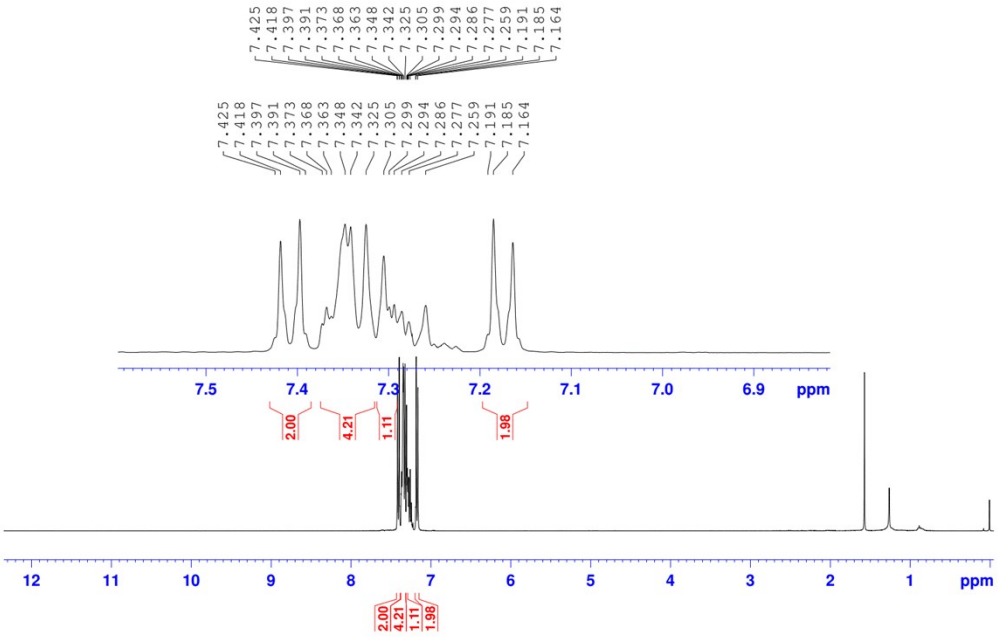
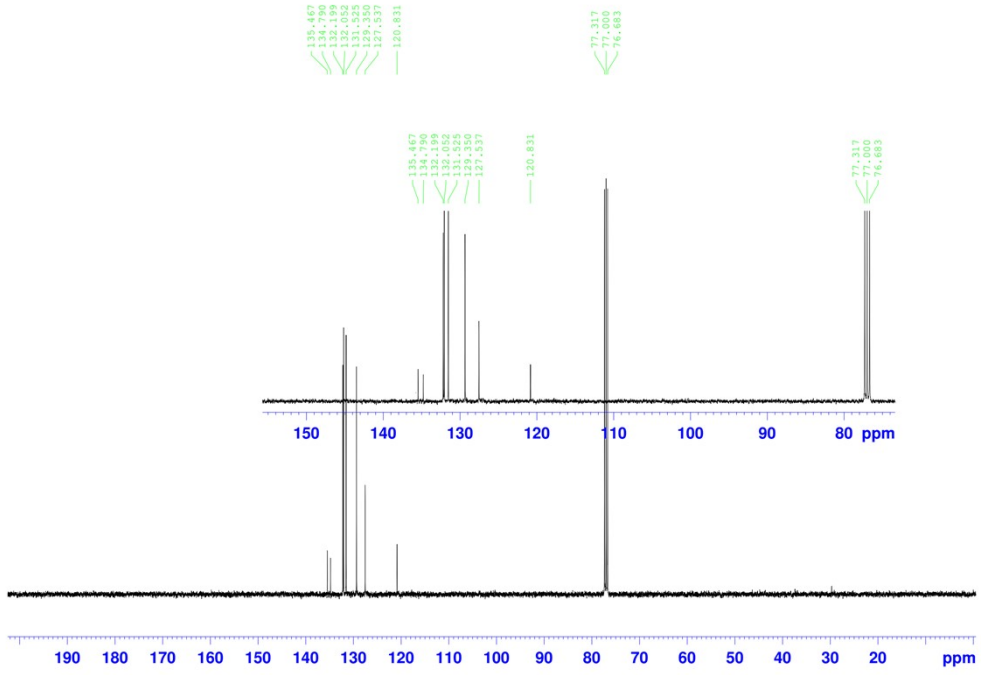


3da-^{13}C NMR



3ea-^{1}H NMR



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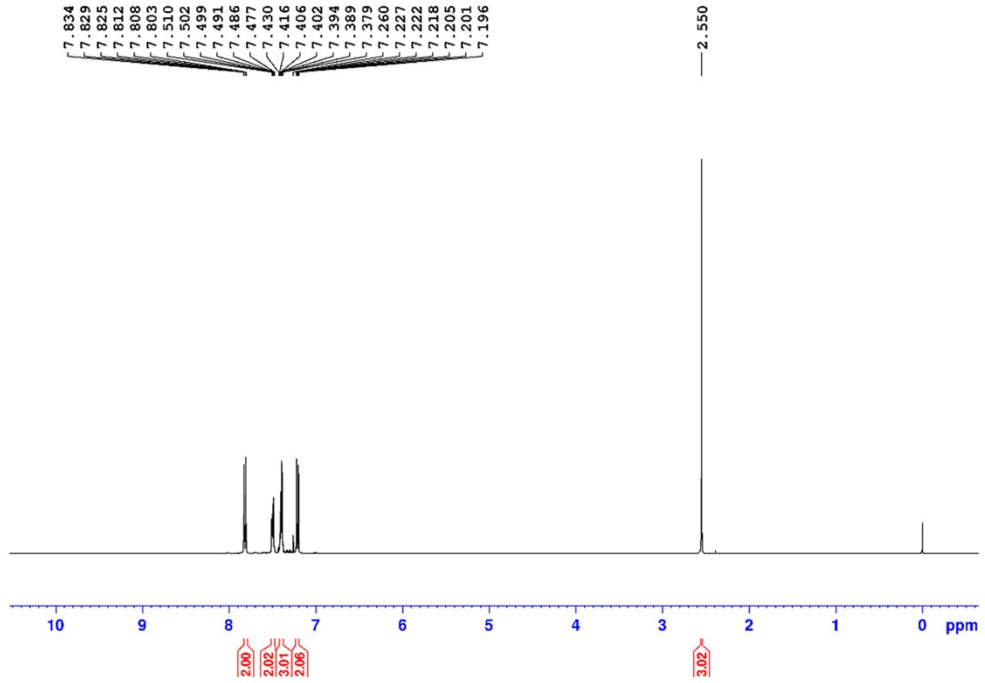
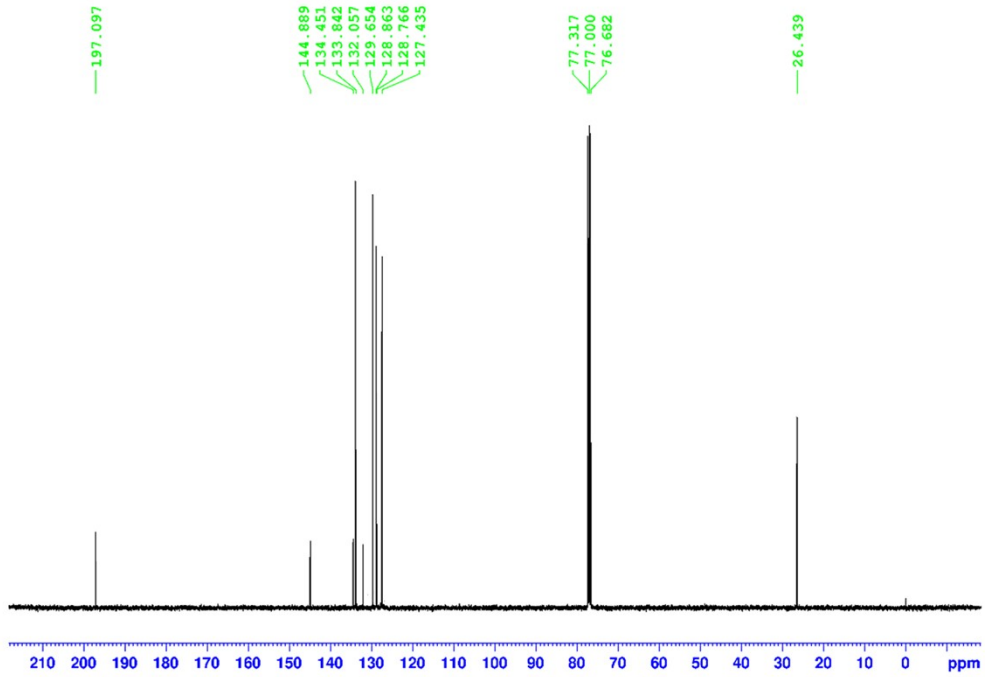
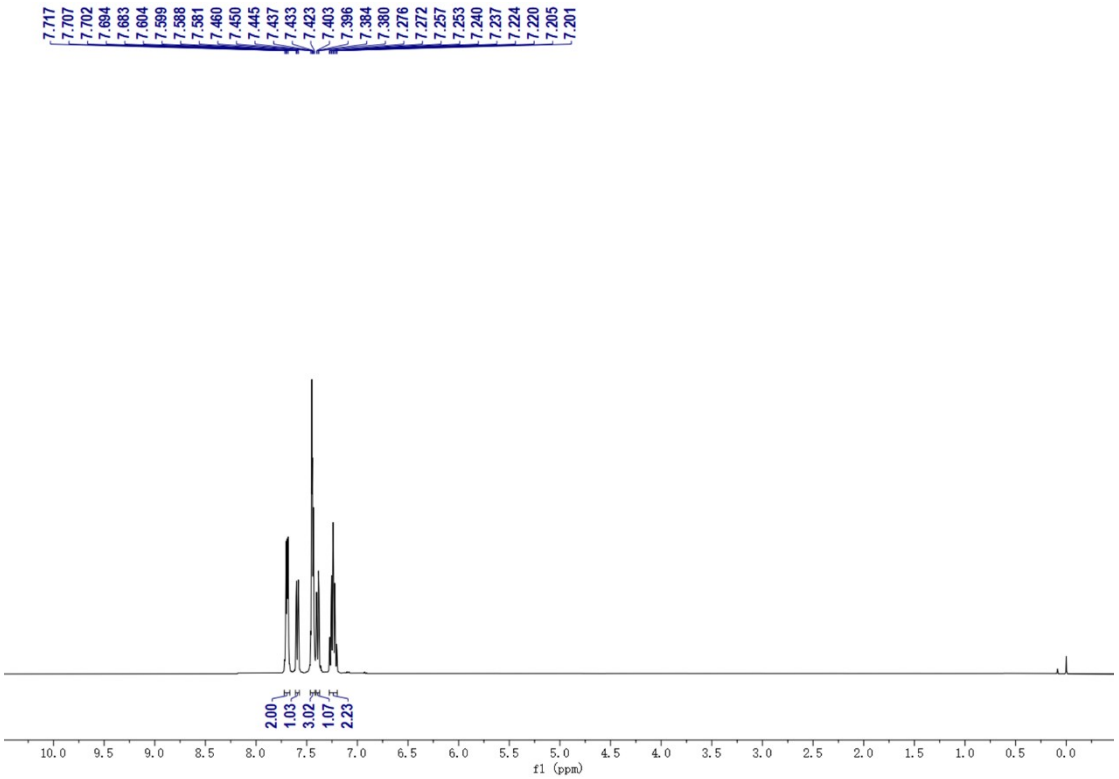
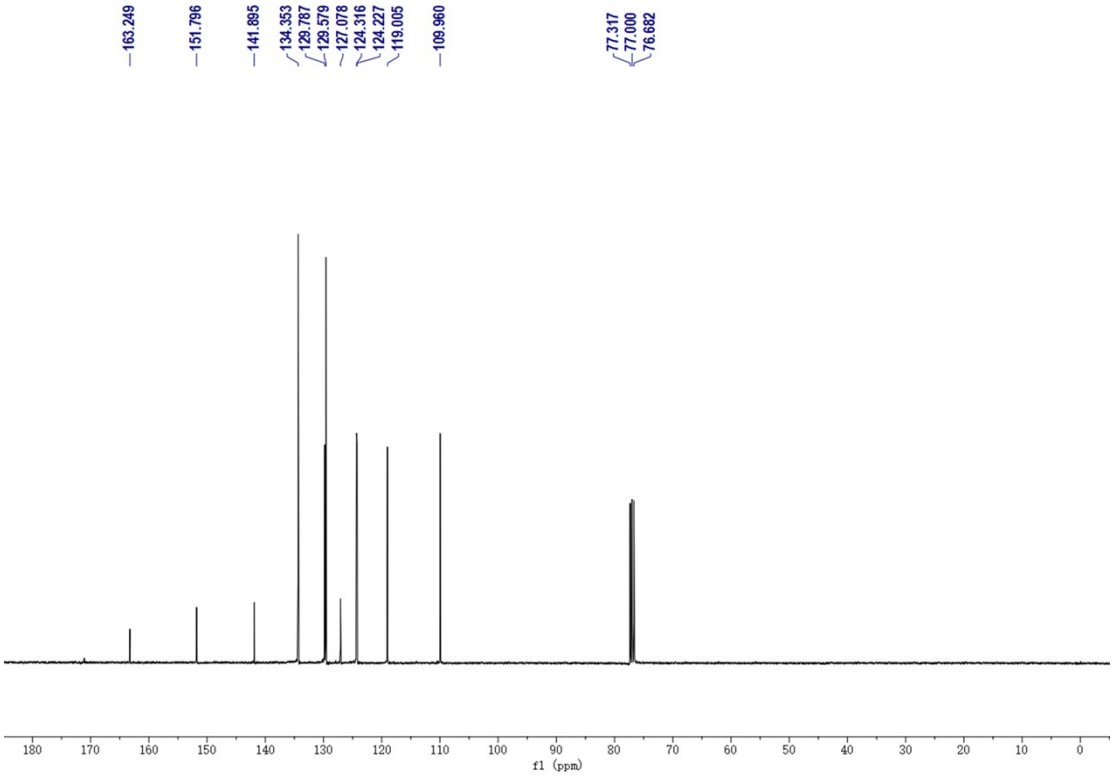

7.834
7.829
7.825
7.812
7.808
7.803
7.510
7.502
7.499
7.491
7.486
7.477
7.430
7.416
7.406
7.402
7.394
7.389
7.379
7.260
7.227
7.222
7.218
7.205
7.201
7.196
2.550
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
2.02
3.01
2.06
3.02

3fa-^{1}H NMR

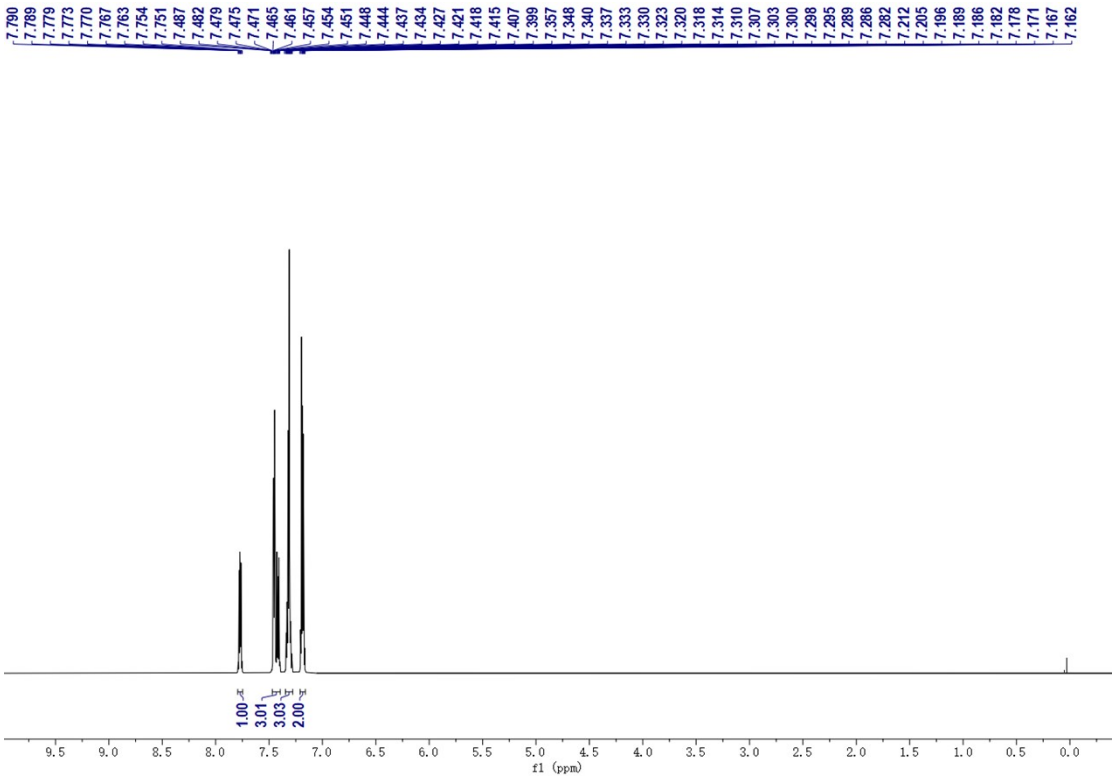

197.097
144.889
134.451
133.842
132.057
129.654
128.863
128.766
127.435
77.317
77.000
76.682
26.439
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3ga-^{1}H NMR



3ga-^{13}C NMR



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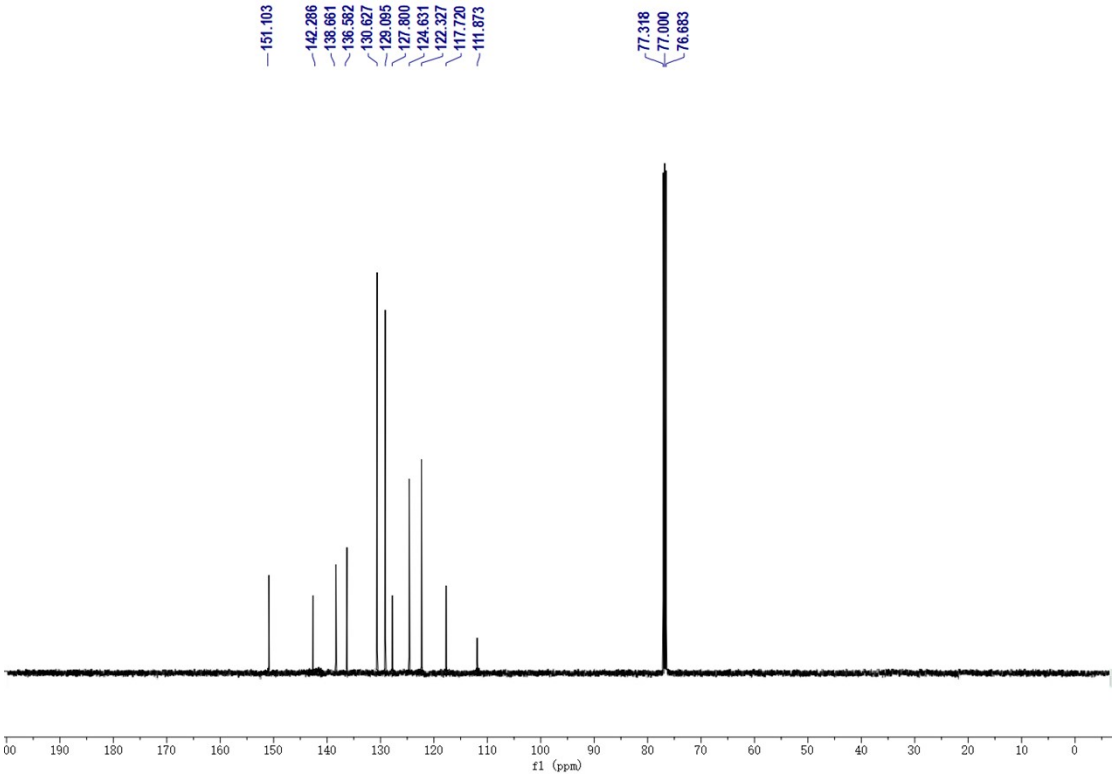
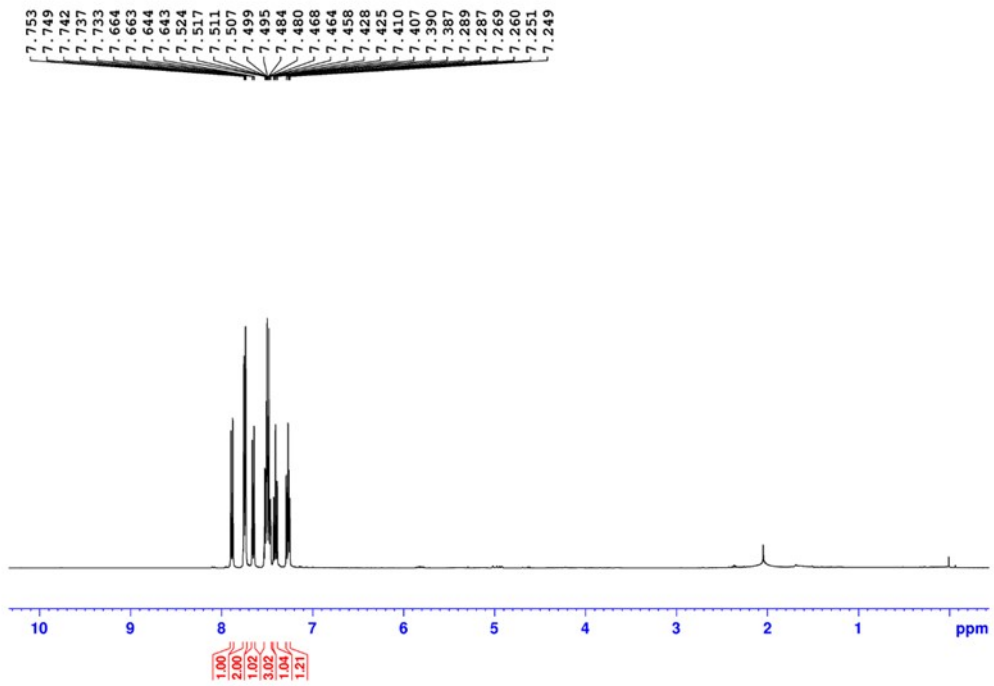
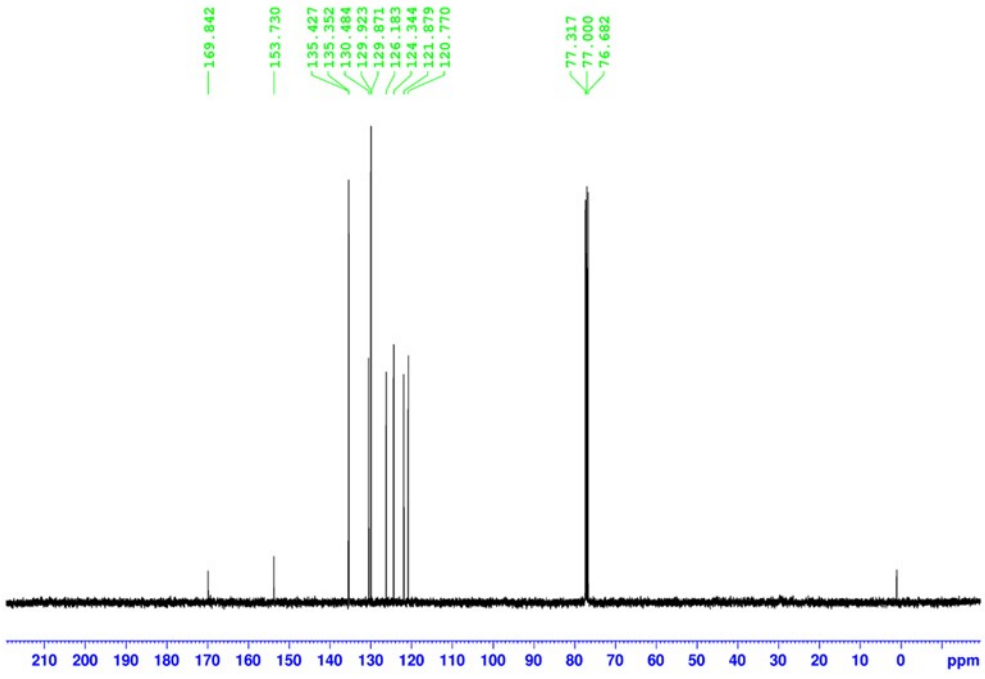


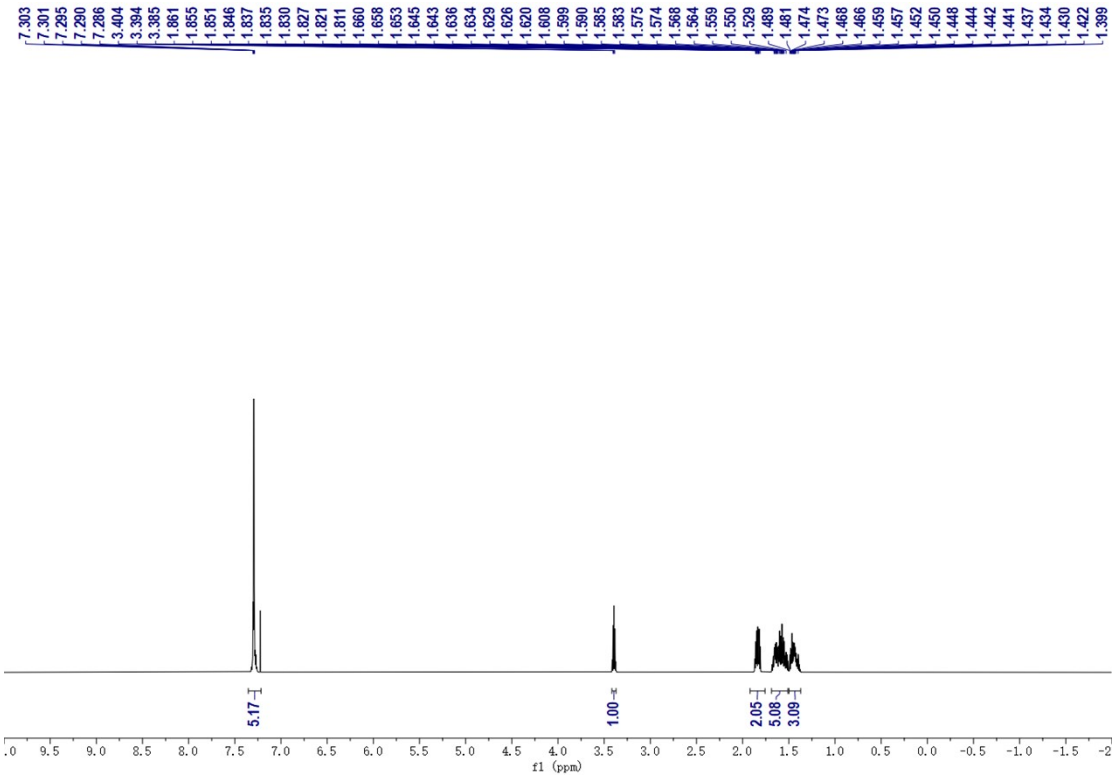
3ha-^{13}C NMR



3ia-^{1}H NMR



3ia-^{13}C NMR



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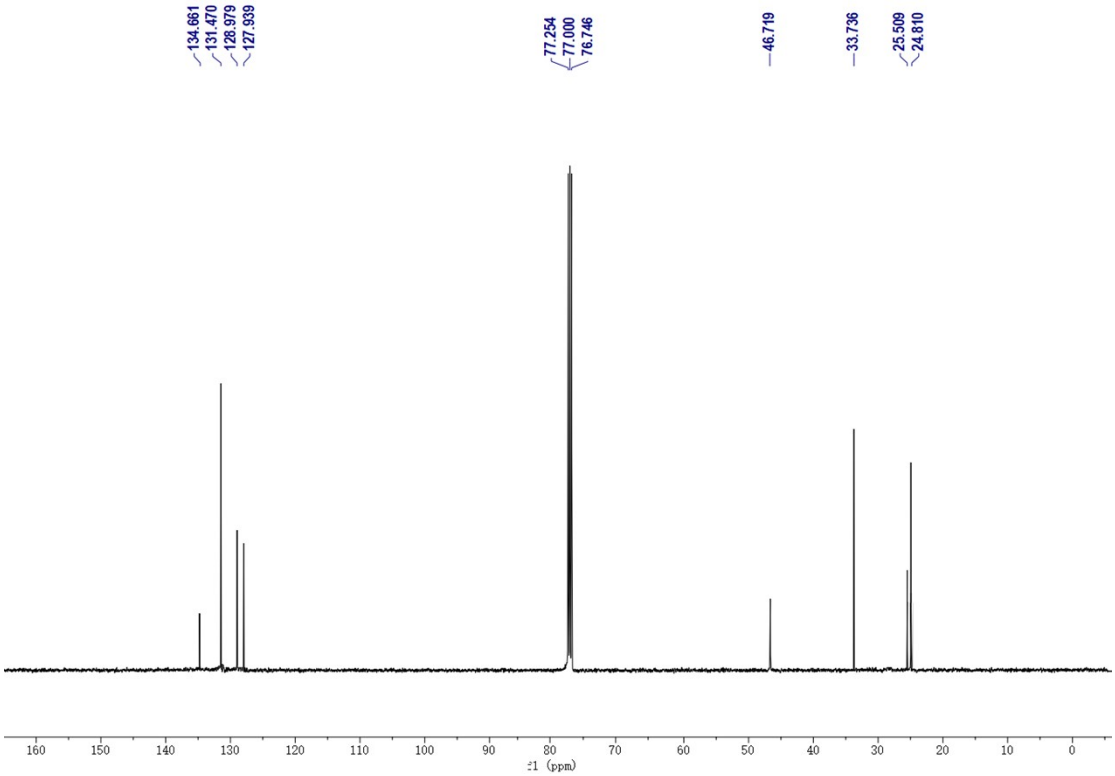

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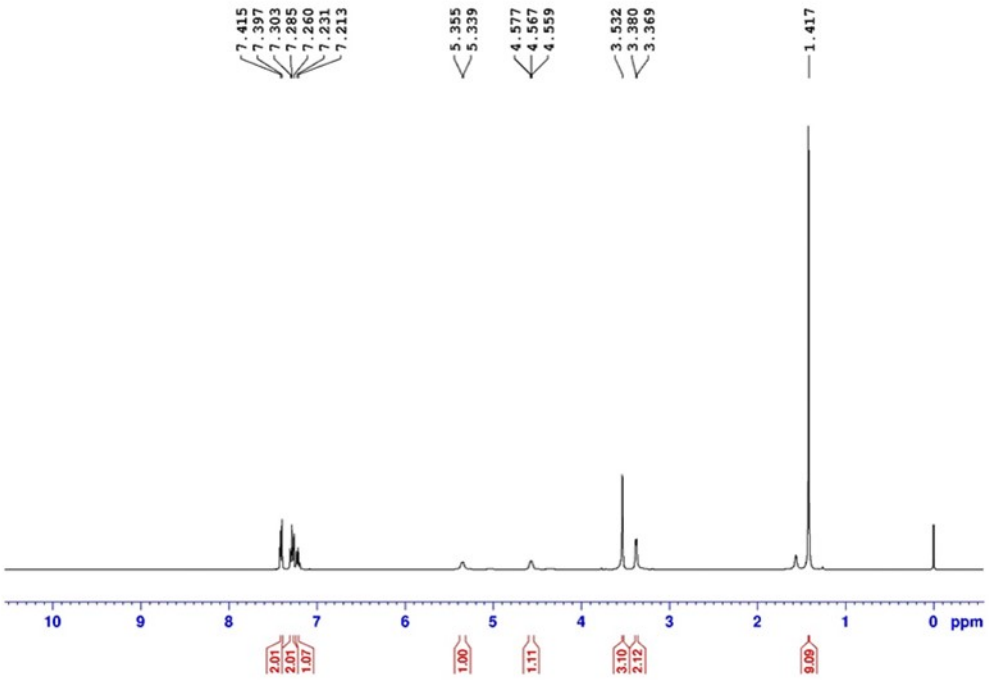
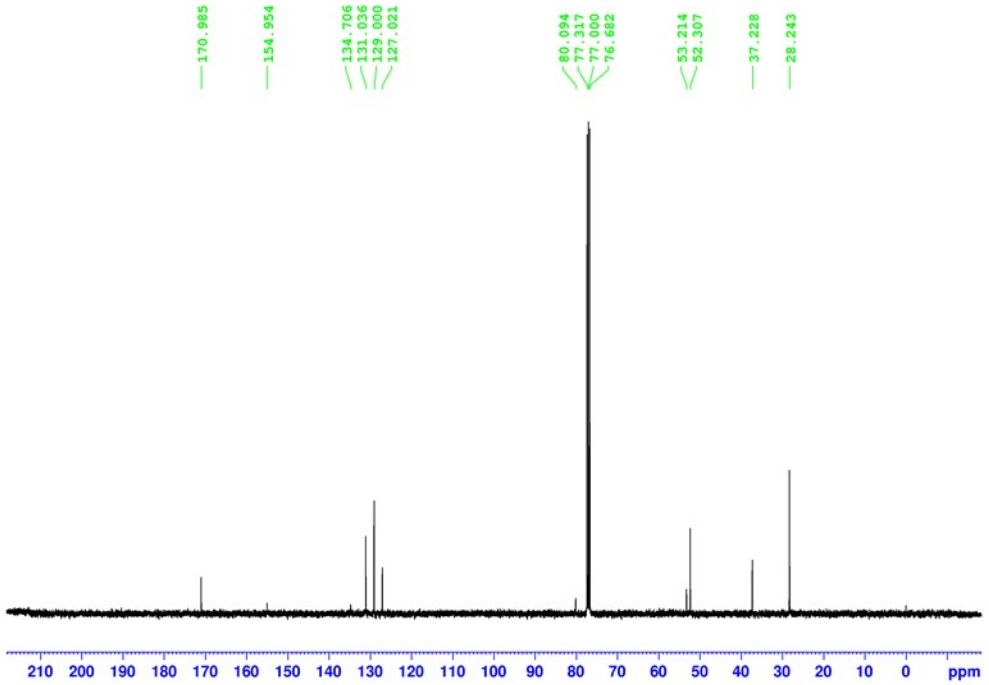
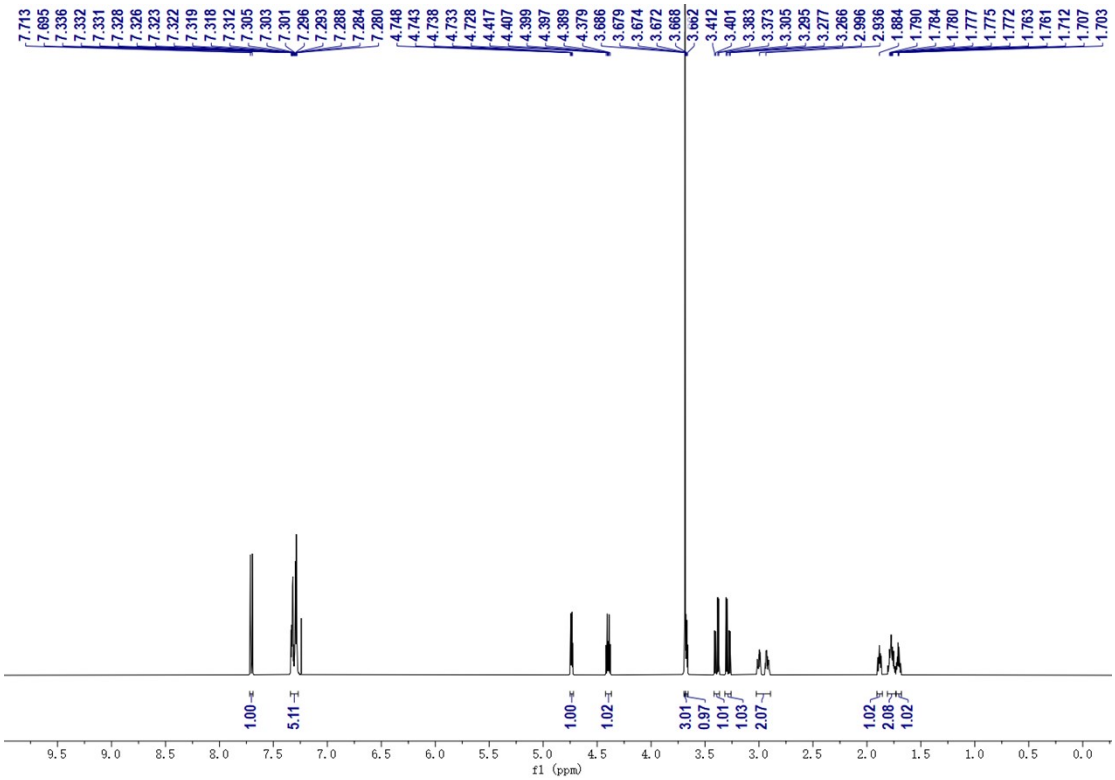


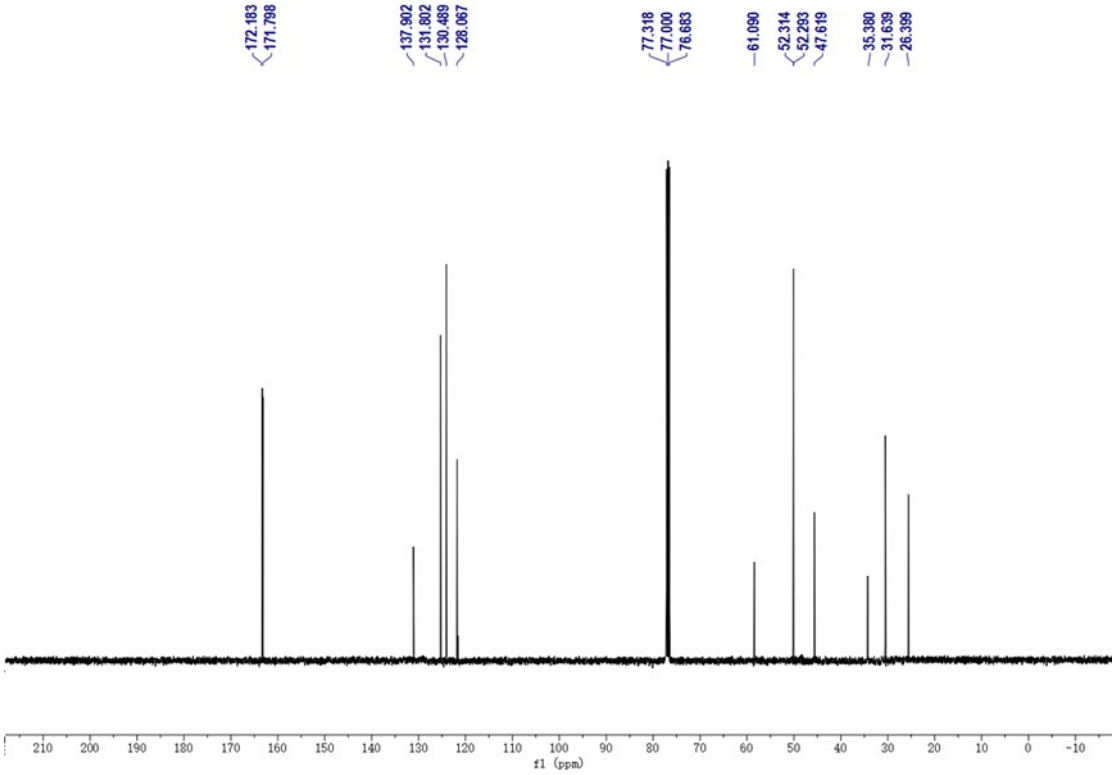
3ka-^{1}H NMR



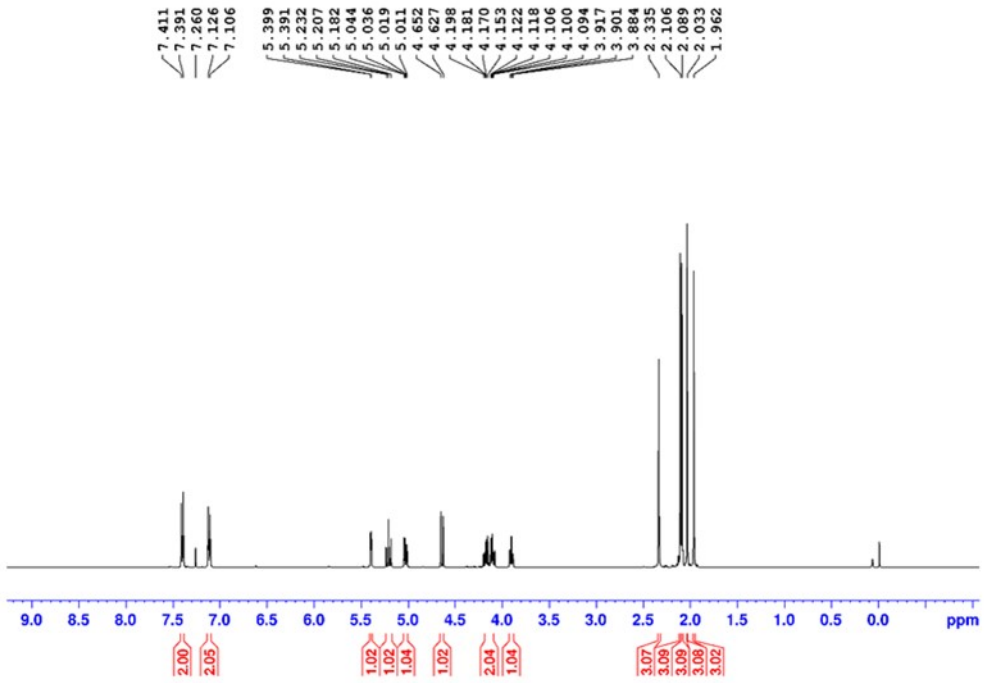
3ka-^{13}C NMR



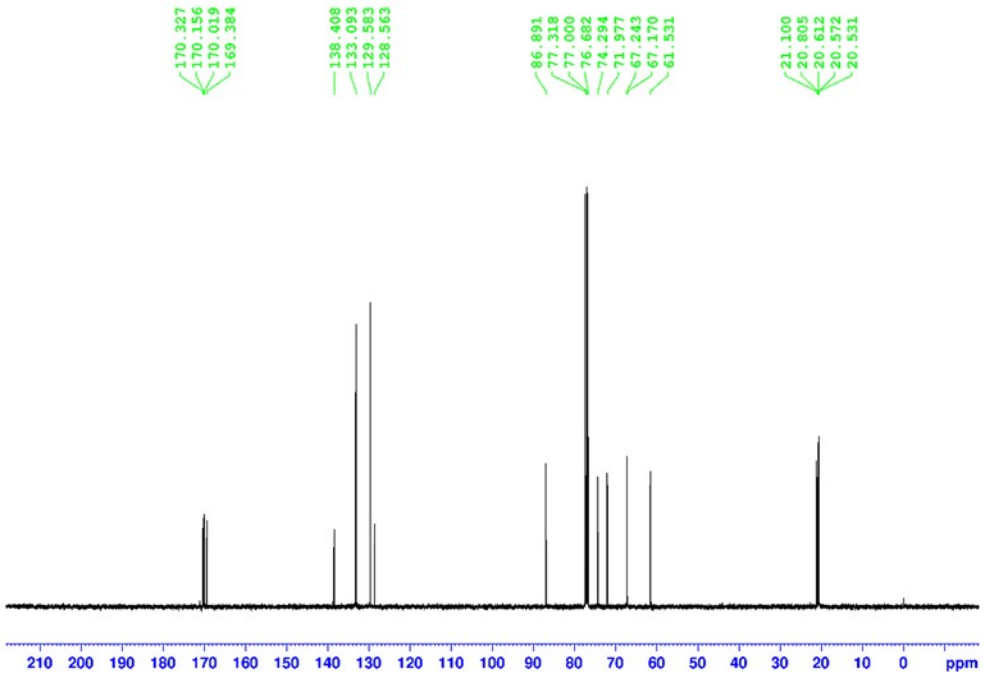
3la-^{1}H NMR



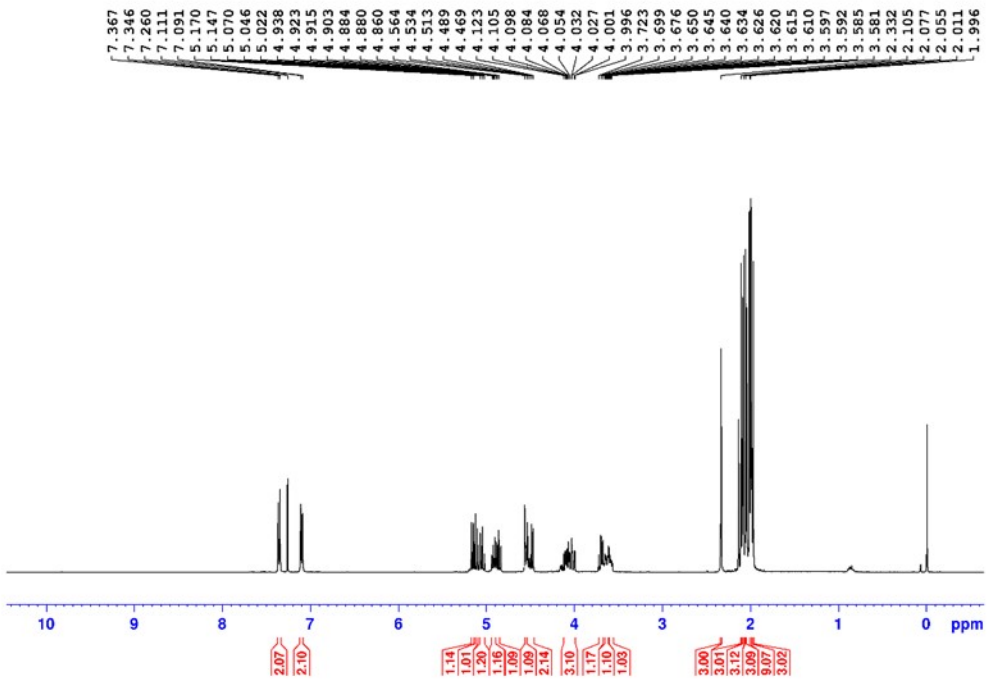
3la-^{13}C NMR



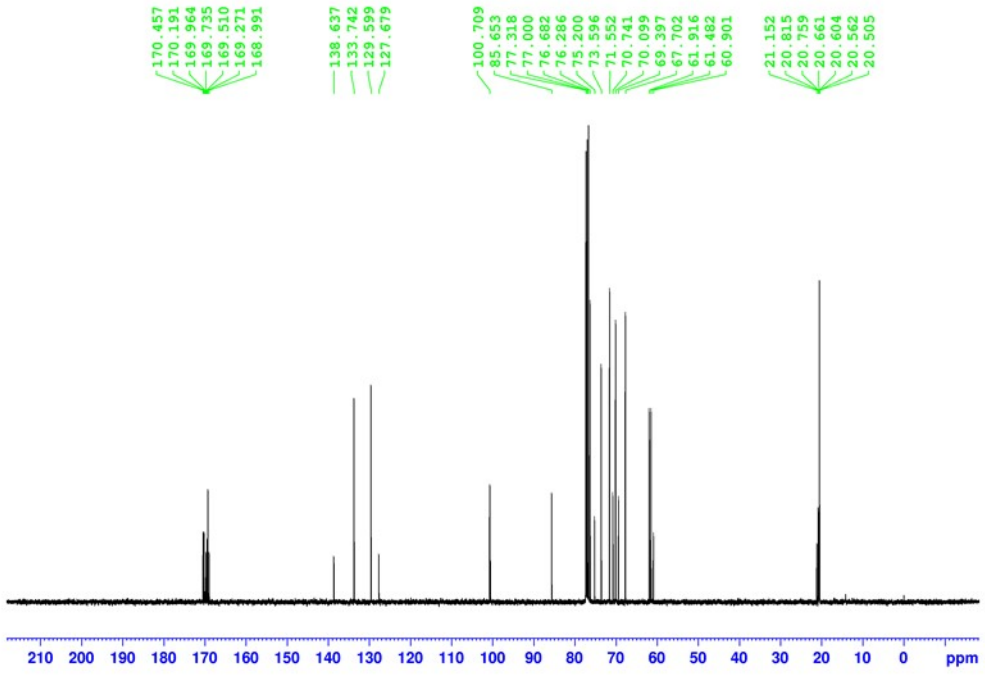
3ma-^{1}H NMR



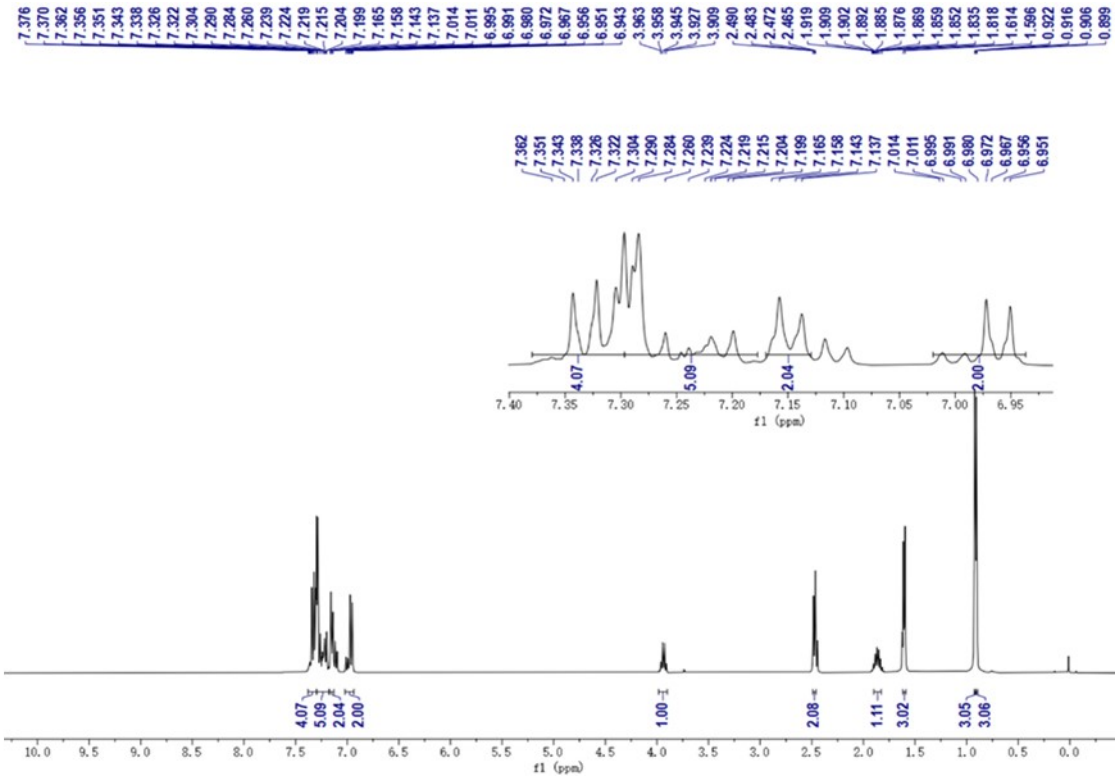
3ma-^{13}C NMR



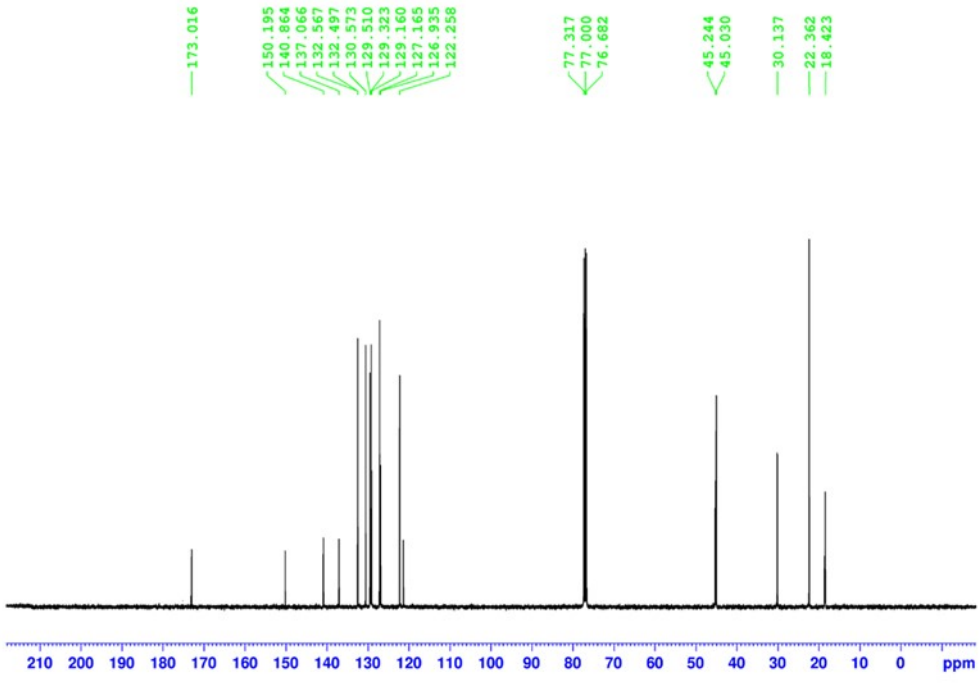
3na-^{1}H NMR



3na-^{13}C NMR



3oa-^{1}H NMR



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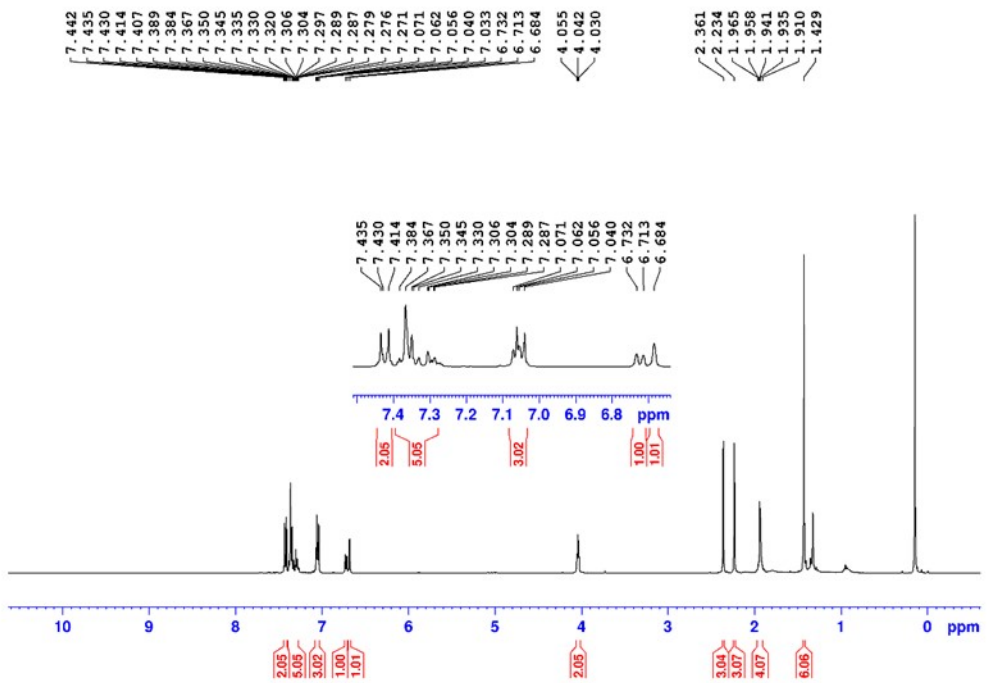

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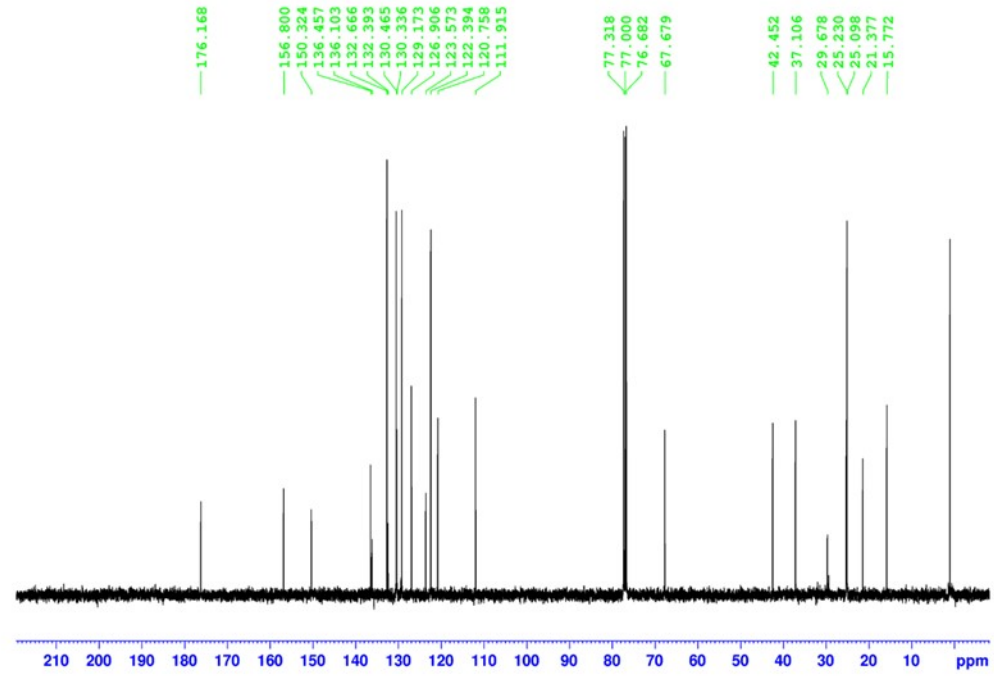

3pa-^{13}C NMR