Supporting Information

Mild Synthesis of Triaryl Sulfonium Salts with Arynes

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1 Preparation of aryne precursor 1 and diarylsulfide 2

Aryne precursors **1a**, **1c**, **1d** and **1f** were prepared following our reported procedures[1].

4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethane-sulfonate (1b).

A mixture of 4,5-dimethyl-2-bromophenol (4.02 g, 20 mmol) and 1,1,1,3,3,3-hexamethyl -disilazane (HMDS, 5.4 mL, 26 mmol) in THF (70 mL) was stirred at 66 °C under nitrogen atmosphere for 4 h. Then, the volatile substances were removed under reduced pressure, affording the crude product as a yellow oil, which was used without further purification.

To a solution of the obtained crude material, (2-bromo-4,5-dimethylphenoxy) trimethylsilane in THF (90 mL) was added *n*-BuLi (8.8 mL, 2.5 M, 22 mmol) at -78 °C. After stirring under the same temperature for 20 min, to the mixture was added Tf_2O (3.67 mL, 22 mmol) in a dropwise manner. Then the mixture was warmed to room temperature and stirred for 20 min. After that, the mixture was quenched with $NaHCO_3$ (aq.). The aqueous layer was extracted with ethyl acetate (3×40 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel to give the title compound **1b** as a colorless oil, 4.05 g, 62% yield. (Rf = 0.60, eluent: petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (s, 1H), 7.09 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 0.35 (s, 9H). The ^{1}H NMR of **1b** is consistent with the reported spectra.[2]

2-bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (1e)

A mixture of Me_3SiCl (1.9 mL, 15 mmol) and Et_3N (2.1 mL, 15 mmol) and 2,6-dibromophenol (2.6 g, 10 mmol) was stirred in THF (50 mL, 0.20 M) for 1 h at room temperature. The reaction mixture was evaporated under reduced pressure and the residue was filtrated through a Celite cake and washed with petroleum ether to provide the 2,6-dibromophenyl trimethylsilyl ether which can be used without further purification.

To a solution of the obtained crude material, 2,6-dibromophenyl trimethylsilyl ether, in THF (35 mL) was added *n*-BuLi (4.8 mL, 2.5 M, 12 mmol) at -78 °C. After stirring under the same temperature for 1 h, aq NH_4Cl (8 mL) was added to the reaction mixture at -78 °C. After the mixture was warmed to room temperature, it was extracted with petroleum ether three times. The combined organic extracts were dried over Na_2SO_4, filtered, and

concentrated under reduced pressure. the residue was purified by flash column chromatography on silica gel to give 2-bromo-6-(trimethylsilyl)phenol as a colorless oil, 2.32 g, 95% yield.

To a solution of the obtained 2-bromo-6-(trimethylsilyl)phenol in THF (65 mL) was added *n*-BuLi (4.6 mL, 2.5 M, 11.4 mmol) at -78 °C. After stirring under the same temperature for 20 min, to the mixture was added Tf_2O (2.39 mL, 14.3 mmol) in a dropwise manner. Then the mixture was warmed to room temperature and stirred for 20 min. After that, the mixture was quenched with $NaHCO_3$ (aq.). The aqueous layer was extracted with ethyl acetate (3×40 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel to give the title compound **1e** as a colorless oil, 2.47 g, 69% yield. (Rf = 0.65, eluent: petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.55 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.25 – 7.22 (m, 1H), 0.45 (s, 9H). The ^{1}H NMR of **1e** is consistent with the reported spectrum.[3]

Preparation of diarylsulfide 2

Diarylsulfides **2a**, **2q**, **2r**, **4** are commercially available. Diarylsulfides **2b**[4-6], **2c**[4-6], **2d**[5], **2e**[6], **2f**[4,6], **2g**[7], **2h**[7,8], **2i**[6], **2j**[6], **2k**[1,8], **2l**[7], **2m**[9], **2o**[10] are known in literatures. Commercially unavailable diaryl sulfoxides **2b**-**2m**, **2n**-**2p** were prepared following the procedures shown below.

Typical procedure A for the synthesis of diarylsulfides 2b, 2c, 2e, 2f, 2i and 2j.

To a solution of 4,4'-sulfinylbis(methylbenzene) (1.25 g, 5.40 mmol) in DCM (32 mL) was added oxalyl dichloride (685 μL, 7.56 mmol) dropwise at 0 °C. After stirring for 30 min, DABCO (1.21 g, 10.08 mmol) was added to the mixture which was stirred for another 10 min at the same temperature. After that, $NaHCO_3$ (cold sat. aqueous solution) and H_2O were sequentially added to the mixture. The aqueous layer was extracted with ethyl acetate (3×30 mL), the combined organic layers were dried over Na_2SO_4, filtrated and

concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel to afford the title compound **2b**.

Typical procedure B for the synthesis of diarylsulfdies 2n, 2o and 2p.

A suspension mixture of 4,4'-thiodiphenol (1.09 g, 5 mmol) and K_2CO_3 (1.38 g, 5 mmol) in anhydrous DMF (20 mL) was stirred at rt for 10 min, and then bromoacetone (840 μL, 6.5 mmol) was added dropwise. The mixture was stirred for 12 h at room temperature, and the resulting mixture was extracted with CH_2Cl_2 (3×20 mL). The organic extracts were combined, then washed with brine, dried over Na_2SO_4, and concentrated. The crude material was purified by flash column chromatography on silica gel to afford the title compound **2n**.

Typical procedure C for the synthesis of diarylsulfdies 2g, 2h, 2l and 2m.

To a solution of 2-bromotoluene (600 μL, 5.0 mmol) in ether (6 mL) was added *t*-BuLi (1.6 M in pentane, 6.26 mL, 10 mmol) at -78 ºC. After stirring for 30 min, a solution of $(PhS)_2$ (1.09 g, 5 mmol) in ether (6 mL) was added dropwise under the same temperature. The mixture was warmed to 0 °C and stirred for 1 h, then warmed to room temperature and stirred for 2.5 h. After that, H_2O (8 mL) was added to the mixture. The aqueous layer was extracted with a 1:1 mixture of Et_2O (3×10 mL) and petroleum ether. The combined organic layer was washed with NaOH (2 M aqueous solution) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography on silica gel to afford **2g**.

di-*p*-tolylsulfane (2b). Following the typical procedure A, the title compound was obtained as a white solid, 1.03 g, 89% yield. (Rf = 0.55, eluent: petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 4H), 7.12 – 7.08 (m, 4H), 2.33 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.9, 132.6, 131.0, 129.9, 21.1. The ^{1}H NMR and ^{13}C NMR of **2b** are consistent with the reported spectra.[4]

bis(4-methoxyphenyl)sulfane (2c). Following the typical procedure A, the title compound was obtained as a white solid, 209.5 mg, 90% yield. (Rf = 0.3, eluent: PE/EtOAc = 20/1) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 4H), 6.87 – 6.83 (m, 4H), 3.79 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.9, 132.6, 127.3, 114.7, 55.3. The ^{1}H NMR and ^{13}C NMR of **2c** are consistent with the reported spectra.[4]

bis(4-(benzyloxy)phenyl)sulfane (2d).To a solution of 4,4'-thiodiphenol (0.50 g, 2.29 mmol) in anhydrous DMF (7 ml), under nitrogen and cooled at 0 °C, was added NaH (330 mg, 13.74 mmol). The reaction mixture was stirred for 15 min at 0 °C and treated with benzyl chloride (0.79 mL, 6.87 mmol). After 12 h at room temperature, the reaction mixture was cooled at 0 °C, quenched by slow addition of water, and extracted with ethyl acetate (3×10 mL), the combined organic layers were washed with H_2O, dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel to afford the title compound **2d** as a white solid, 830 mg, 91% yield. (Rf = 0.4, eluent: PE/EtOAc = 30/1) 1H NMR (600 MHz, $CDCl_3$): δ 7.50 – 7.38 (m, 8H), 7.36 – 7.33 (m, 2H), 7.32 – 7.28 (m, 4H), 6.94 – 6.91 (m, 4H), 5.05 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.1, 136.7, 132.7, 128.6, 128.0, 127.6, 127.4, 115.6, 70.1. The ^1H NMR and ^{13}C NMR of **2d** are consistent with the reported spectra.[5]

di([1,1'-biphenyl]-4-yl)sulfane (2e). Following the typical procedure A, the title compound was obtained as a white solid, 477.5 mg, 71% yield. (Rf = 0.45, eluent: PE/EtOAc =30/1) ^1H NMR (600 MHz, $CDCl_3$): δ 7.60 – 7.54 (m, 8H), 7.48 – 7.42 (m, 8H), 7.39 – 7.33 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.3, 140.1, 134.7, 131.4, 128.8, 127.9, 127.5, 126.9. The ^1H NMR and ^{13}C NMR of **2e** are consistent with the reported spectra.[6]

bis(4-chlorophenyl)sulfane (2f). Following the typical procedure A, the title compound was obtained as a white solid, 321.5 mg, 84% yield. (Rf = 0.75, eluent: PE/EtOAc =30/1) ^1H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.30 (m, 4H), 7.29 – 7.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 133.9, 133.4, 132.3, 129.5. The ^1H NMR and ^{13}C NMR of **2f** are consistent with the reported spectra.[4,6]

phenyl(*o*-tolyl)sulfane (2g). Following the typical procedure C, the title compound was obtained as a colorless oil, 931 mg, 93 % yield. (Rf = 0.4, eluent: petroleum ether). ^1H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 4H), 7.30 – 7.23 (m, 4H), 7.22 – 7.19 (m, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 139.9, 136.1, 133.7, 132.9, 130.6, 129.6, 129.1, 127.9, 126.7, 126.3, 20.56. The ^1H NMR and ^{13}C NMR of **2g** are consistent with the reported spectra.[7]

(2-methoxyphenyl)(phenyl)sulfane (2h). Following the typical procedure C, the title compound was obtained as a colorless oil, 984 mg, 91 % yield. (Rf = 0.4, eluent: PE/EtOAc = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.89 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 157.3, 134.4, 131.6, 131.4, 129.1, 128.3, 127.0, 124.0, 121.2, 110.8, 55.8. The ^{1}H NMR and ^{13}C NMR of **2h** are consistent with the reported spectra.[7]

bis(2,4-dimethylphenyl)sulfane (2i). Following the typical procedure A, the title compound was obtained as a white solid, 387 mg, 80% yield. (Rf = 0.55, eluent: petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 6H), 2.36 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 138.6, 136.7, 131.3, 131.1, 131.0, 127.4, 20.9, 20.3. The ^{1}H NMR and ^{13}C NMR of **2i** are consistent with the reported spectra.[6]

dimesitylsulfane (2j). Following the typical procedure A, the title compound was obtained as a white solid, 345 mg, 76% yield. (Rf = 0.35, eluent: petroleum ether) ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.87 (s, 4H), 2.28 (s, 6H), 2.24 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.2, 136.5, 131.2, 129.3, 21.6, 20.8. The ^{1}H NMR and ^{13}C NMR of **2j** are consistent with the reported spectra.[6]

(4-chlorophenyl)(*p*-tolyl)sulfane (2k). A mixture of p-Toluenethiol (622 mg, 5 mmol), chloro-4-iodobenzene (1.19 g, 5 mmol), n-Bu_4NBr (163 mg, 0.5 mmol), NaOH (400 mg, 10 mmol) and CuI (96 mg, 0.5 mmol) in toluene (4 mL) was stirred under reflux for 4 h. Then, the mixture was cooled to room temperature. Afterwards, a saturated aqueous solution of NH_4Cl was added to the mixture. The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure, the crude material was purified by flash column chromatography on silica gel to afford the title compound **2k** as a white solid, 775 mg, 66% yield. (Rf = 0.2, eluent: PE/EtOAc = 5/1) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 2H), 7.28 – 7.25 (m, 2H), 7.24 – 7.17 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 138.0, 135.9, 132.4, 130.7, 130.2, 129.1, 21.1. The ^{1}H NMR and ^{13}C NMR of **2k** are consistent with the reported spectra.[8]

(4-fluorophenyl)(phenyl)sulfane (2l). Following the typical procedure C, the title compound was obtained as a colorless oil, 663 mg, 65 % yield. (Rf = 0.4, eluent: petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.07 – 7.01 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 162.3 (d, J = 247.6 Hz), 136.6, 134.1, 134.0, 129.9, 129.2, 126.7, 116.4 (d, J = 21.1 Hz). The ^{1}H NMR and ^{13}C NMR of **2l** are consistent with the reported spectra.[7]

(3-methoxyphenyl)(phenyl)sulfane (2m). Following the typical procedure C, the title compound was obtained as a colorless oil, 1.0 g, 93 % yield. (Rf = 0.2, eluent: PE/EtOAc = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.22 (m, 1H), 6.93 (dd, J = 7.7, 0.8 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.82 – 6.79 (m, 1H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.0, 137.2, 135.2, 131.4, 129.9, 129.2, 127.2, 122.9, 115.8, 112.7, 55.2. The ^{1}H NMR and ^{13}C NMR of **2m** are consistent with the reported spectra.[9]

1,1'-((thiobis(4,1-phenylene))bis(oxy))bis(propan-2-one) (2n). Following the typical procedure B, the title compound was obtained as a white solid, m.p. 77-78 ºC, 1.24 g, 75% yield. (Rf = 0.2, eluent: PE/EtOAc = 3/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.21 (m, 4H), 6.79 – 6.76 (m, 4H), 4.49 (s, 4H), 2.22 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.9, 157.0, 132.6, 128.2, 115.2, 72.8, 26.4. IR (neat): 3088, 3064, 2889, 2838, 1727, 1589, 1488, 1429, 1247, 1169, 1070, 828, 806, 746, 679, 653. HRMS: $C_{18}H_{18}O_4SNa^+$(M+Na^+): 353.0823; found: 353.0822.

dimethyl 2,2'-((thiobis(4,1-phenylene))bis(oxy))diacetate (2o). Following the typical procedure B, the title compound was obtained as a white solid, m.p. 100-101 ℃, 1.32 g, 73% yield. (Rf = 0.2, eluent: PE/EtOAc = 3/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.25 (m, 4H), 6.85 – 6.82 (m, 4H), 4.61 (s, 4H), 3.80 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.2, 157.2, 132.7, 128.5, 115.5, 65.3, 52.3. HRMS: $C_{18}H_{18}O_6SNa^+$([M+Na^+]$^+$): 385.0722; found: 385.0724. The **2o** is a known compound.[10]

2,2'-((thiobis(4,1-phenylene))bis(oxy))diacetonitrile (2p). Following the typical procedure B, the title compound was obtained as a white solid, m.p. 132-133 ℃, 1.23 g, 83% yield. (Rf = 0.25, eluent: PE/EtOAc = 3/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 4H), 6.97 – 6.90 (m, 4H), 4.76 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 155.9,

132.9, 130.0, 115.9, 114.8, 53.6. IR (neat): 3093, 3040, 2987, 2940, 2082, 1589, 1488, 1444, 1208, 1180, 1044, 947, 890, 815, 790, 652. HRMS: $C_{16}H_{13}N_2O_2S^+(M+H^+)$: 297.0698; found: 297.0698.

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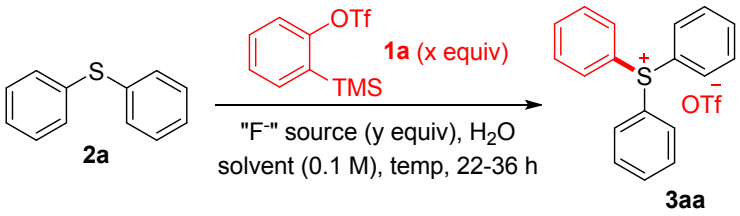
2 Optimization of reaction conditions



entry	"F⁻" source	X/Y	H_2O (equiv)	slovent	temp (°C)	yield(%)[b]
1	CsF	1.0/2.0	0	MeCN	25	33[c]
2	KF/18-crown-6	1.0/2.0	0	THF	25	trace[c]
3	TBAT	1.0/2.0	0	THF	25	trace[c]
4	TBAF·3H_2O	1.0/2.0	0	THF	25	8[c]
5	CsF	1.0/2.0	2.0	MeCN	25	21[c]
6	KF/18-crown-6	1.0/2.0	2.0	THF	25	trace[c]
7	TBAT	1.0/2.0	2.0	THF	25	trace[c]
8	CsF	1.0/2.0	0	MeCN	50	21[c]
9	CsF	1.0/2.0	0	MeCN	0	34[c,d]
10	CsF	1.0/2.0	0	MeCN/toluene (3/1)	25	28[c]
11	CsF	1.0/2.0	0	DME	25	trace[c]
12	CsF	1.0/2.0	0	THF	25	trace[e]
13	CsF	1.5/2.0	0	MeCN	25	35
14	CsF	2.0/2.0	0	MeCN	25	54
15	CsF	2.0/3.0	0	MeCN	25	62
16	CsF	2.5/3.0	0	MeCN	25	55
17	CsF	3.0/3.0	0	MeCN	25	67
18	CsF	3.0/3.0	0	MeCN	25	92 (90)[d,f,g]

[a]Unless otherwise noted, reactions were performed with **1a** (X equiv), diphenyl sulfide **2a** (0.2 mmol), and "F⁻" source (Y equiv) for 22 h. [b]NMR yield (mesitylene as the internal standard); [c]**1a** decomposed after reaction; [d]Reaction time was 36 h. [e]98% of **1a** was recovered. [f]Isolated yield in parentheses. [g]3.0 equiv of CsF was added in three portions. The procedure is shown below.

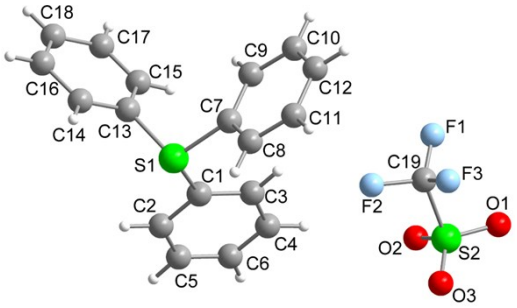
General procedure (for entries 1-17): To a flame-dried reaction tube (25 mL) was added "F" source (Y equiv) under nitrogen atmosphere. (Note: CsF was operated in glove box). Then the solvent (2 mL), H_2O (none or 2.0 equiv), diphenyl sulfide **2a** (37.3 mg, 0.2 mmol) and benzyne precursor **1a** (X equiv) were sequentially added to the reaction tube. The mixture was stirred under the indicated temperature for 22 or 36 h. After that, to the mixture was added mesitylene (0.15

mmol, 21 μL). The obtained mixture was then stirred vigorously for a few seconds. One drop of the mixture was transferred to nmr tube to determine the NMR yields of **3aa**.

Procedure used in entry 18: To a flame-dried reaction tube (25 mL) was added CsF (30.3 mg, 0.2 mmol, 1.0 equiv) under nitrogen atmosphere. Then MeCN (2 mL), diphenyl sulfide **2a** (37.3 mg, 0.2 mmol) and benzyne precursor **1a** (0.6 mmol, 179 mg) were sequentially added to the reaction tube. After stirring under 25 ºC for the first 12 h, another portion of CsF (1.0 equiv) was added to the mixture. It was then stirred for the second 12 h and the last portion of CsF (1.0 equiv) was added to the mixture. After stirring for the last 12 h, to the mixture was added mesitylene (0.15 mmol, 21 μL). The obtained mixture was then stirred vigorously for a few seconds. One drop of the mixture was transferred to nmr tube to determine the NMR yields of **3aa**. After that, the mixture was filtrated through a short plug of silica gel, concentrated and purified by flash column chromatography on silica gel to afford **3aa** in 90% yield (74 mg, white solid).

3 X-ray data for 3aa and 3ac

triphenylsulfonium trifluoromethanesulfonate (3aa):



3aa

Single crystals of product **3aa** was obtained through slow evaporation at room temperature of a solution in ethyl acetate – dichloromethane.

Bond precision:	C-C = 0.0106 A	Wavelength=0.71073	
Cell:	a=8.7640(8)	b=10.0110(8)	c=11.2134(10)
	alpha=99.004(4)	beta=91.663(5)	gamma=98.870(4)
Temperature:	296 K		

	Calculated	Reported
Volume	958.65(15)	958.65(14)
Space group	P -1	P-1

Hall group	-P -1	?
Moiety formula	C18 H15 S, C F3 O3 S	?
Sum formula	C19 H15 F3 O3 S2	C19 H15 F3 O3 S2
Mr	412.43	412.43
Dx,g cm-3	1.429	1.429
Z	2	2
Mu (mm-1)	0.322	0.322
F000	424.0	424.0
F000'	424.75	
h,k,lmax	11, 13, 14	11, 13,14
Nref	4526	4457
Tmin,Tmax	0.926, 0.968	
Tmin'	0.908	

Correction method= Not given

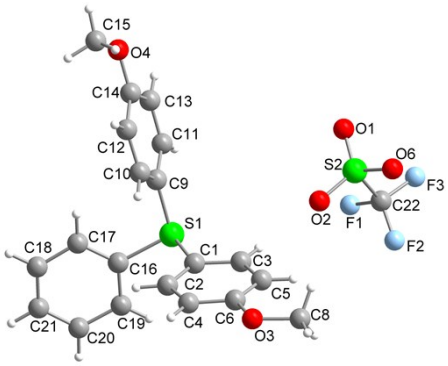
Data completeness= 0.985 Theta(max)= 27.780

R(reflections)= 0.1377 (3508) wR2(reflections)= 0.4205 (4457)

S = 3.083 Npar= 244

For more details please see the CIF file attached with ESI. The crystal data of **3aa** has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is 1550944

bis(4-methoxyphenyl)(phenyl)sulfonium trifluoromethanesulfonate (3ac):



3ac

Single crystals of product **3ac** was obtained through slow evaporation at room temperature of a solution in ethyl acetate – dichloromethane.

Bond precision: C-C = 0.0072 A Wavelength=0.71073

Cell:	a=8.9672(3)	b=22.0738(6)	c=11.2978 (3)
	alpha=90	beta=99.418(2)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2206.15(11)	2206.14(11)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C20 H19 O2 S, C F3 O3 S	?
Sum formula	C21 H19 F3 O5 S2	C21 H19 F3 O5 S2
Mr	472.48	472.48
Dx,g cm-3	1.423	1.423
Z	4	4
Mu (mm-1)	0.296	0.296
F000	976.0	976.0
F000'	977.60	
h,k,lmax	11,28,14	11,28,14
Nref	5118	4457
Tmin,Tmax	0.931,0.971	
Tmin'	0.915	

Correction method= Not given

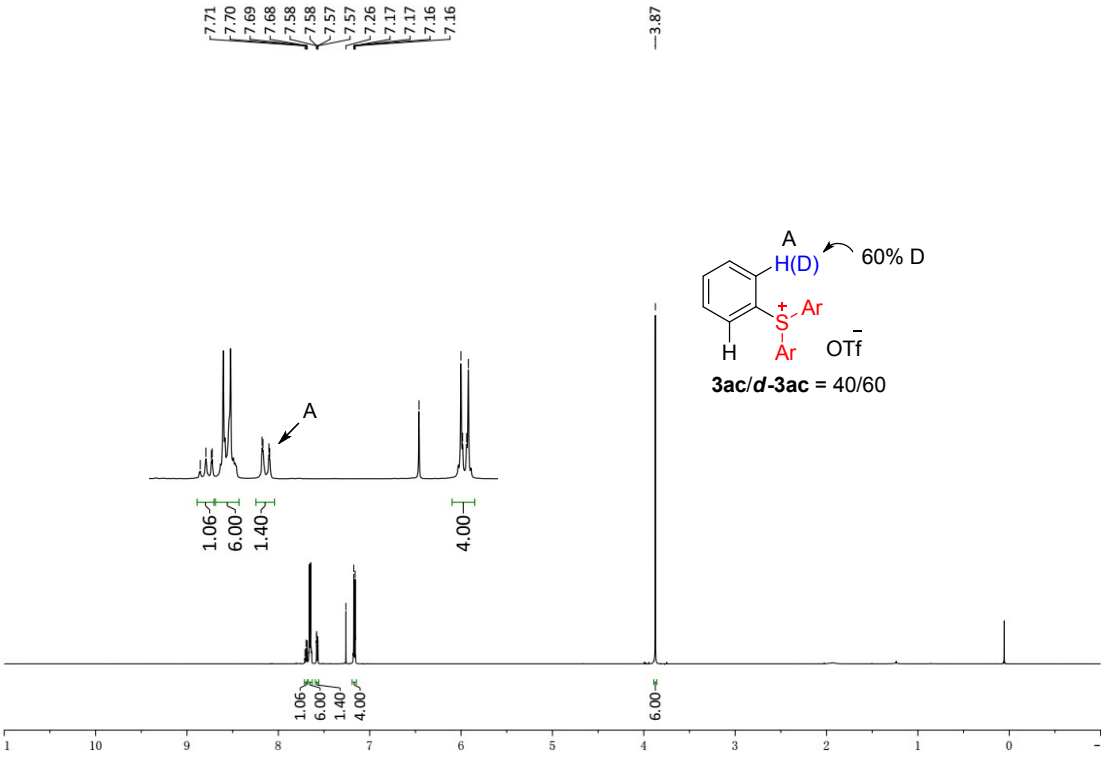
Data completeness= 0.996 Theta(max)= 27.580

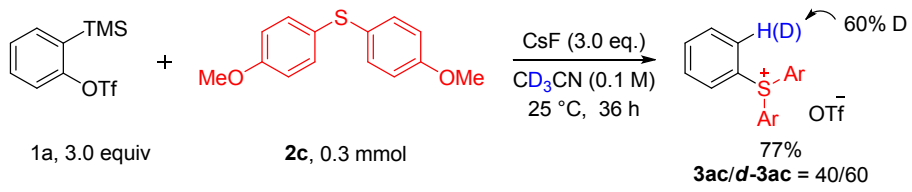
R(reflections)= 0.1026 (3178) wR2(reflections)= 0.3336 (5097)

S = 2.152 Npar= 280

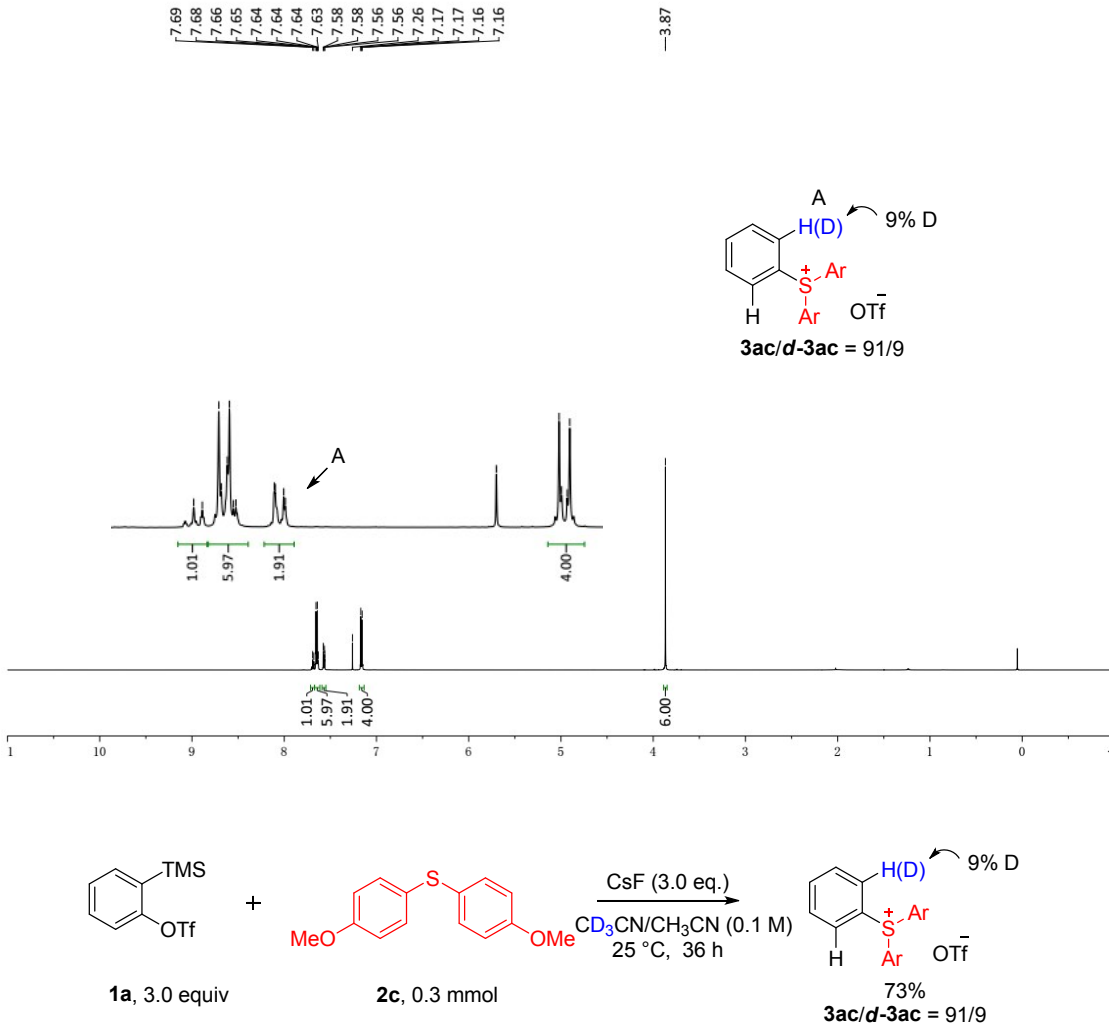
For more details please see the CIF file attached with ESI. The crystal data of **3ac** has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is 1550940

4 Labeling experiment

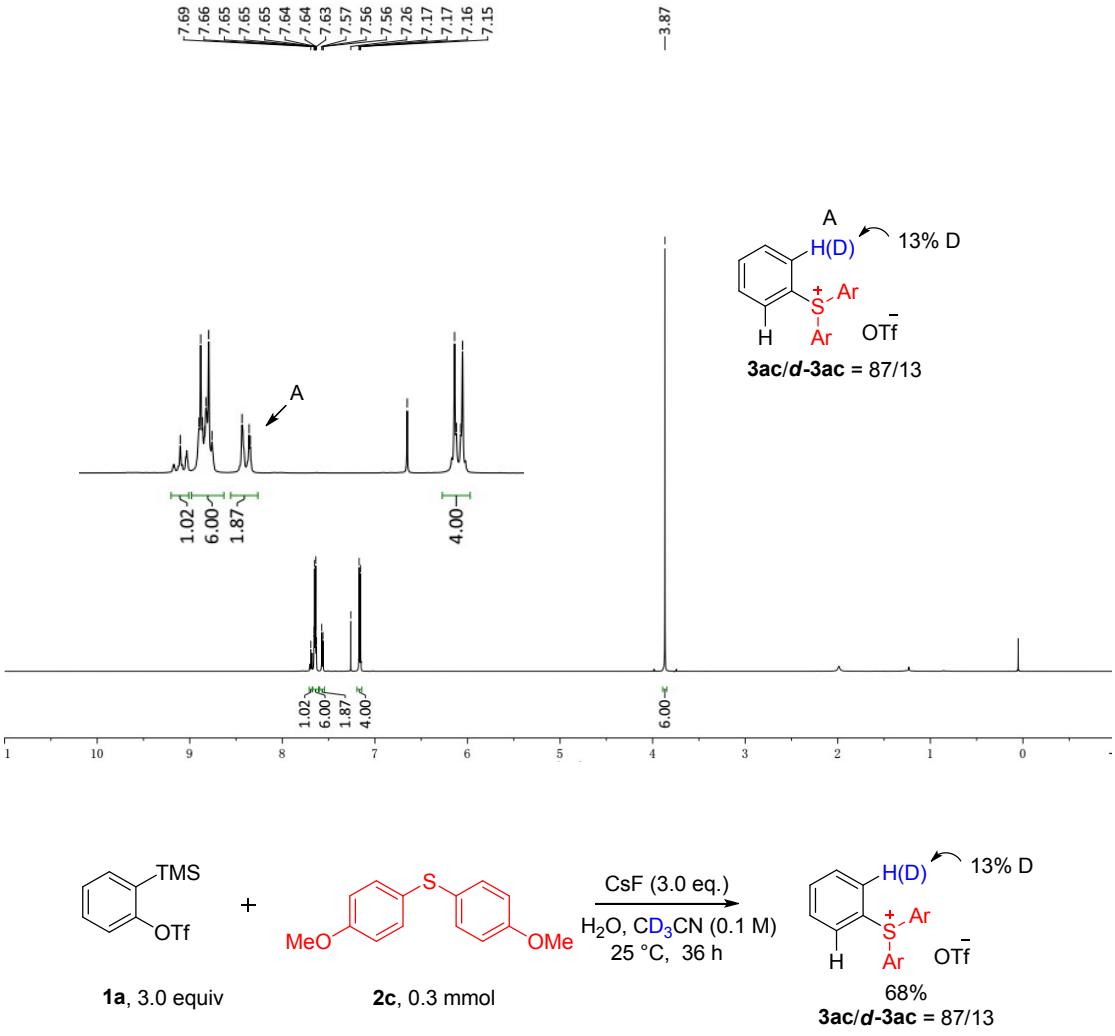




To a flame-dried reaction tube (25 mL) was added CsF (45.5 mg, 1.0 equiv) under nitrogen atmosphere. Then CD_3CN (3 mL), diphenyl sulfide **2c** (73.9 mg, 0.3 mmol) and benzyne precursor **1a** (268 mg, 0.9 mmol) were sequentially added to the reaction tube. After stirring under 25 ºC for the first 12 h, another portion of CsF (1.0 equiv) was added to the mixture. It was then stirred for the second 12 h and the last portion of CsF (1.0 equiv) was added to the mixture. After stirring for the last 12 h, the mixture was filtrated through a short plug of silica gel, concentrated and purified by flash column chromatography on silica gel. A mixture of **3ac** and ***d*-3ac** (**3aa**/***d*-3aa** = 40/60) was obtained as a colorless oil, 109 mg, 77% yield.

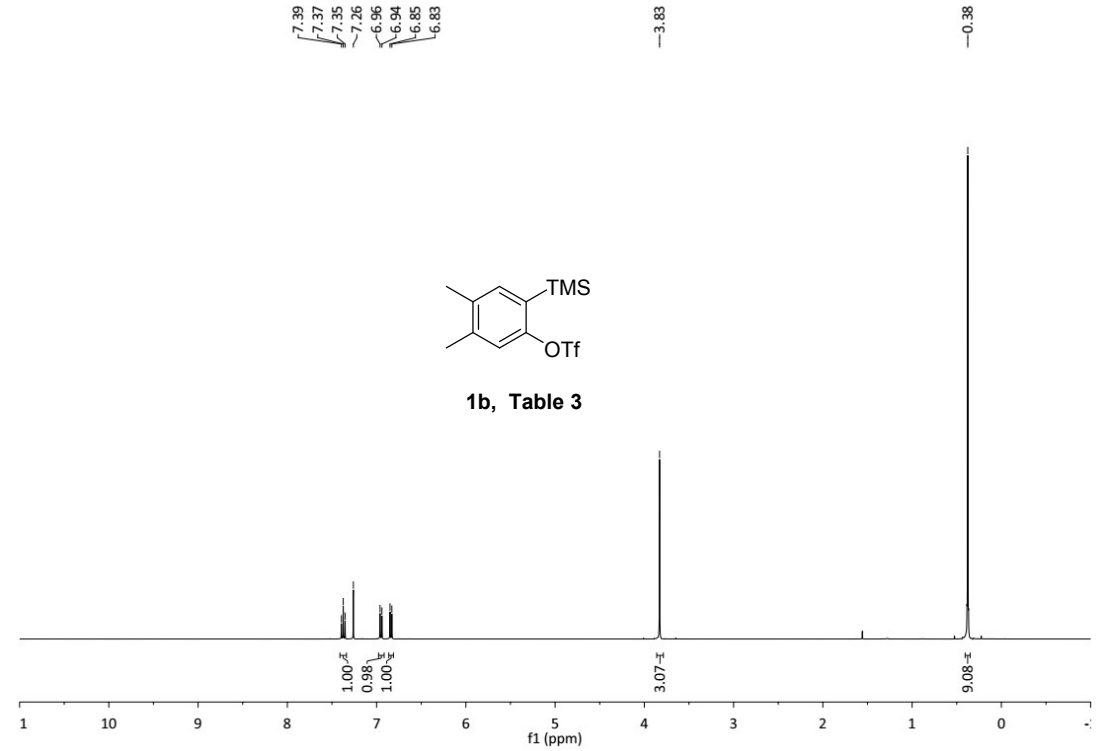


To a flame-dried reaction tube (25 mL) was added CsF (45.5 mg, 1.0 equiv) under nitrogen atmosphere. Then CD_3CN/CH_3CN (3 mL, v/v = 1:1), diphenyl sulfide **2c** (73.9 mg, 0.3 mmol) and benzyne precursor **1a** (268 mg, 0.9 mmol) were sequentially added to the reaction tube. After stirring under 25 ºC for the first 12 h, another portion of CsF (1.0 equiv) was added to the mixture. It was then stirred for the second 12 h and the last portion of CsF (1.0 equiv) was added to the mixture. After stirring for the last 12 h, the mixture was filtrated through a short plug of silica gel, concentrated and purified by flash column chromatography on silica gel. A mixture of **3ac** and ***d*-3ac** (**3aa**/***d*-3aa** = 91/9) was obtained as a colorless oil, 103 mg, 73% yield.

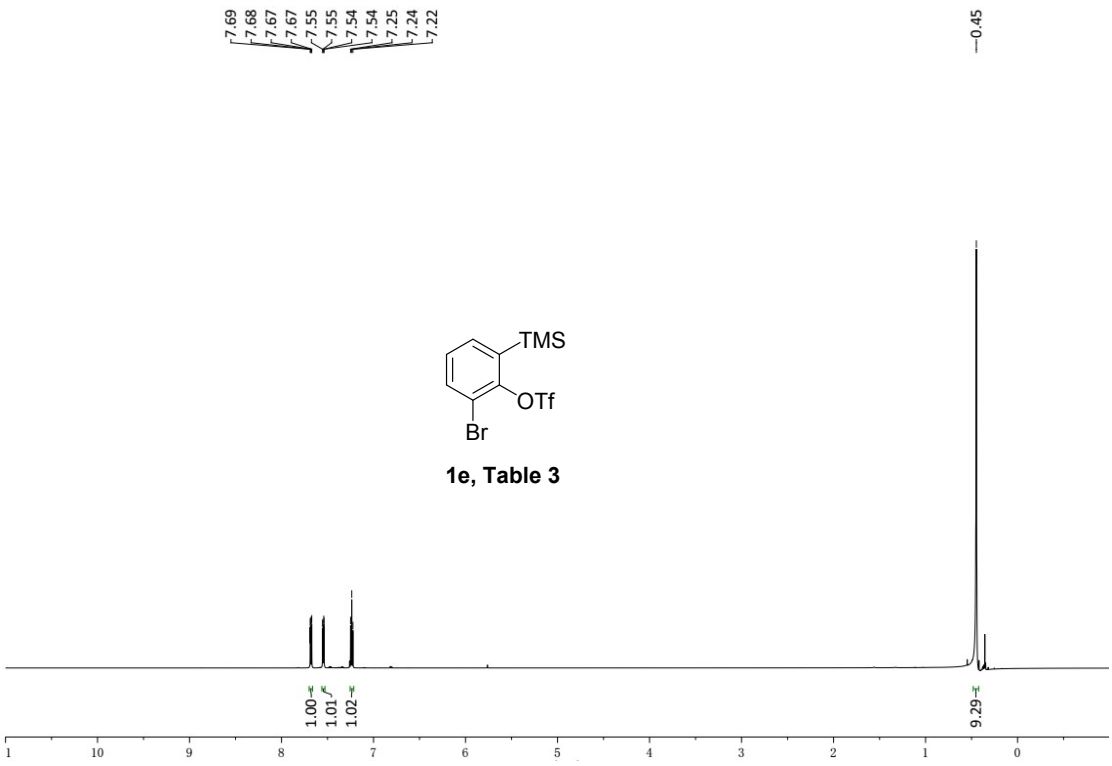


To a flame-dried reaction tube (25 mL) was added CsF (45.5 mg, 1.0 equiv) under nitrogen atmosphere. Then CD_3CN (3 mL), H_2O (1.7 equiv, 9 μL), diphenyl sulfide **2c** (73.9 mg, 0.3 mmol) and benzyne precursor **1a** (268 mg, 0.9 mmol) were sequentially added to the reaction tube. After stirring under 25 ºC for the first 12 h, another portion of CsF (1.0 equiv) was added to the mixture. It was then stirred for the second 12 h and the last portion of CsF (1.0 equiv) was added to the mixture. After stirring for the last 12 h, the mixture was filtrated through a short plug of silica gel, concentrated and purified by flash column chromatography on silica gel. A mixture of **3ac** and ***d*-3ac** (**3aa**/***d*-3aa** = 87/13) was obtained as a colorless oil, 96 mg, 68% yield.

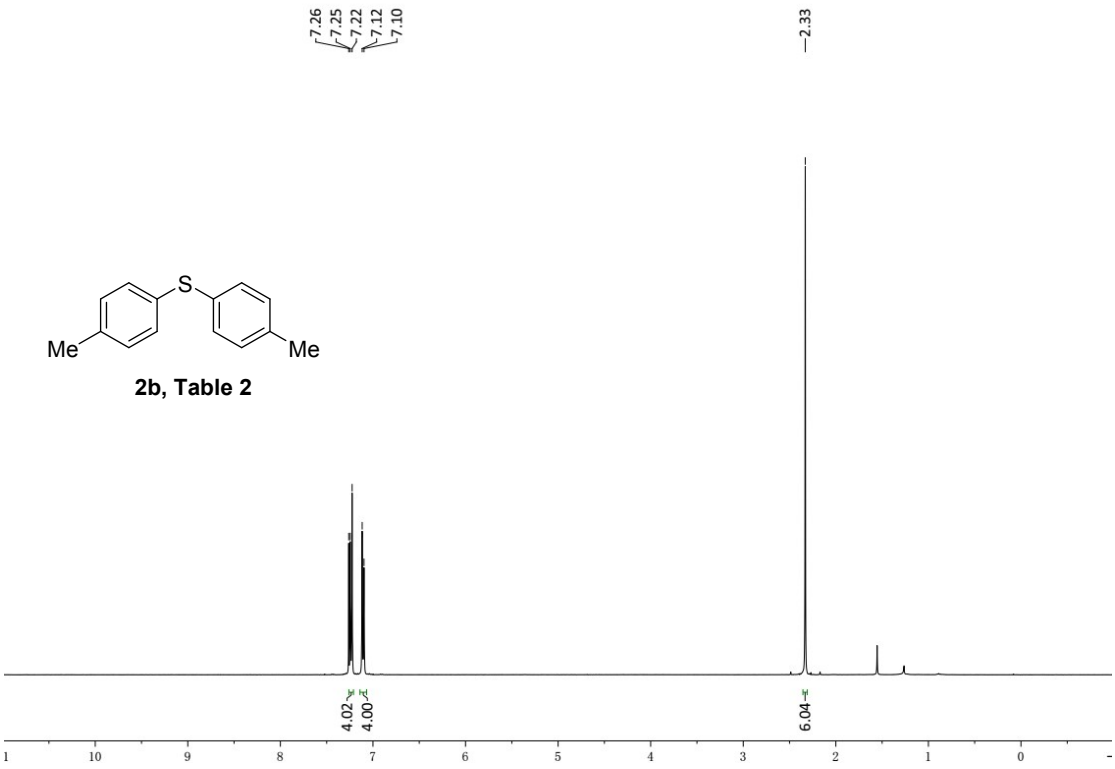
5 NMR spectra



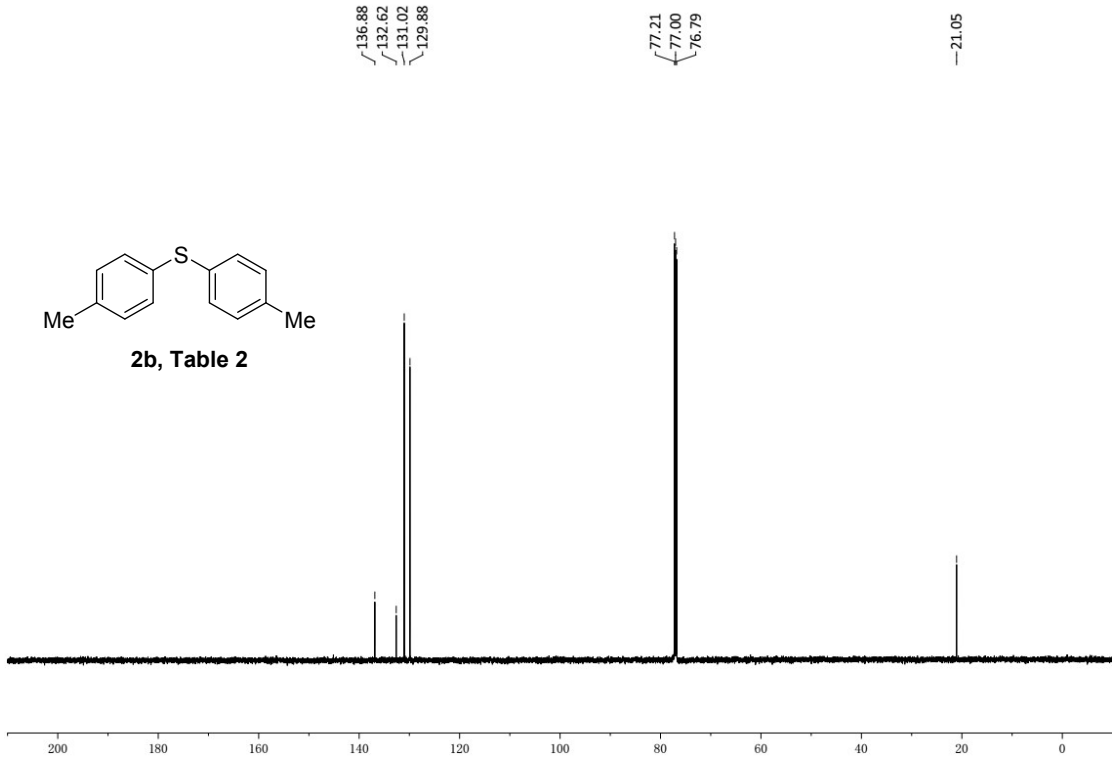
1b, Table 3



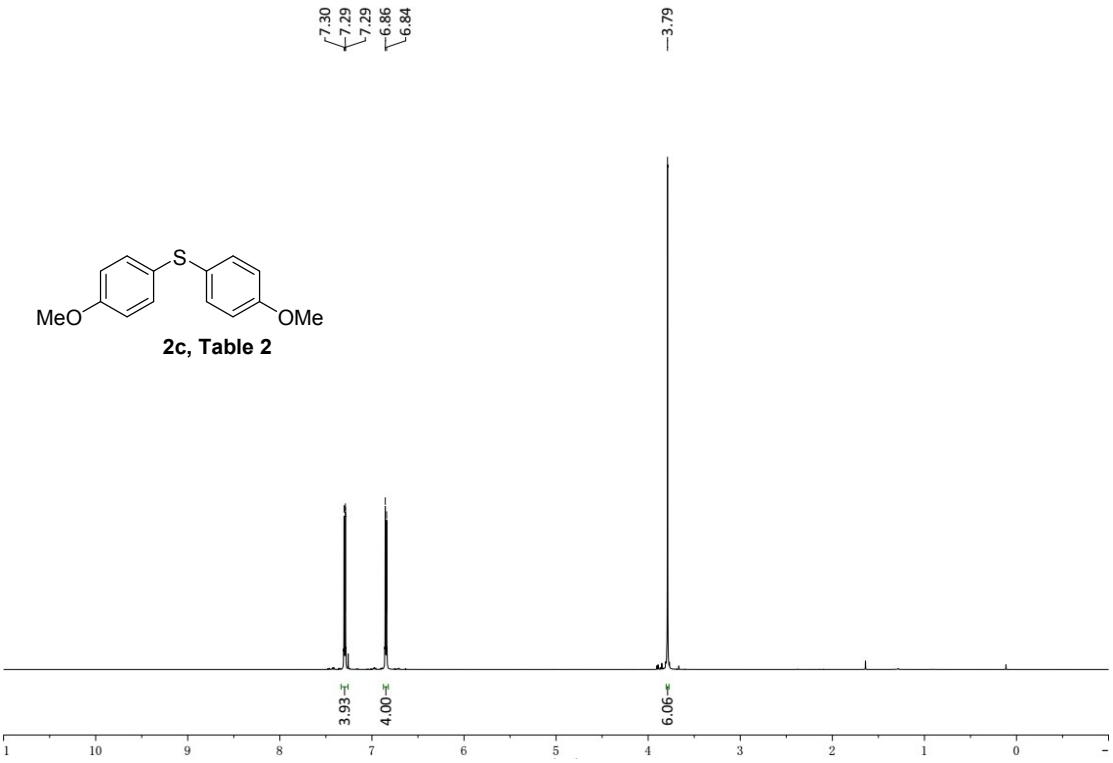
1e, Table 3



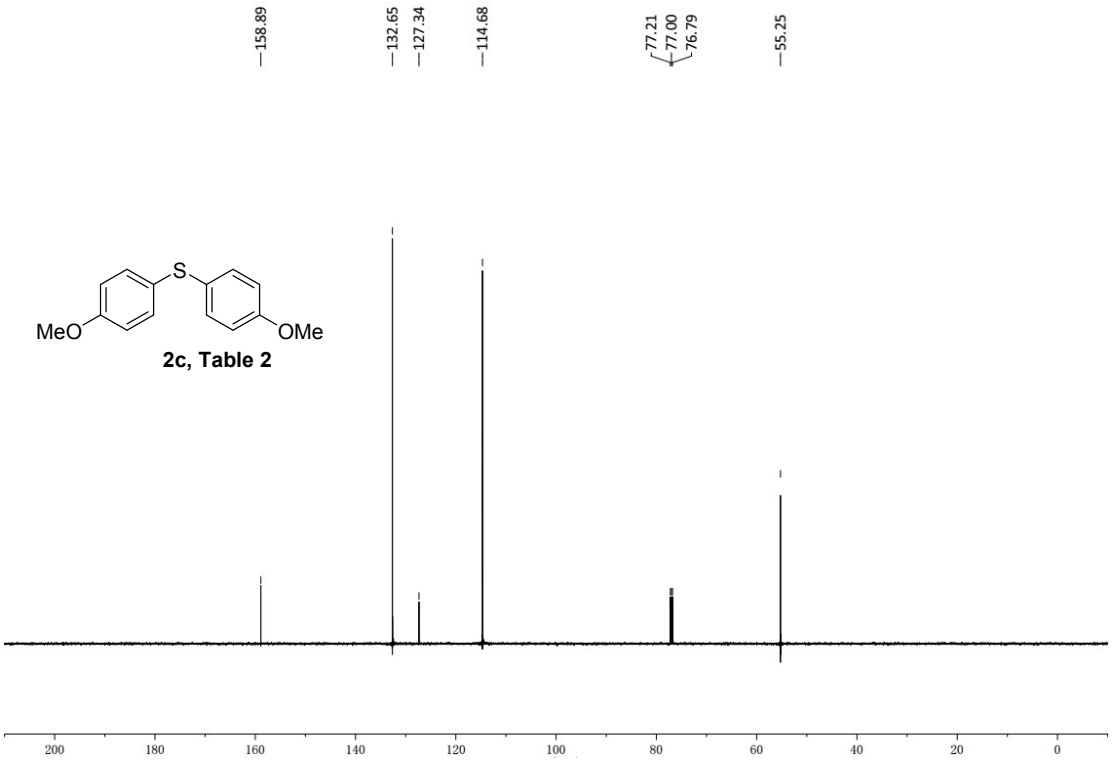
2b, Table 2



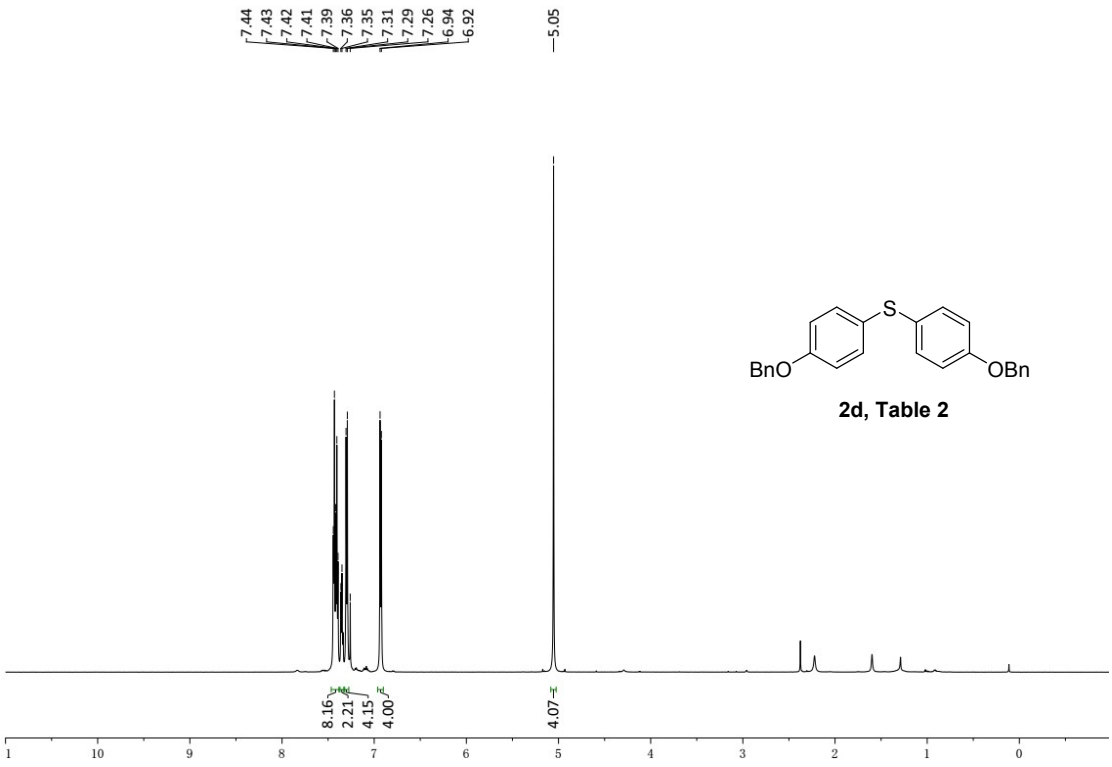
2b, Table 2



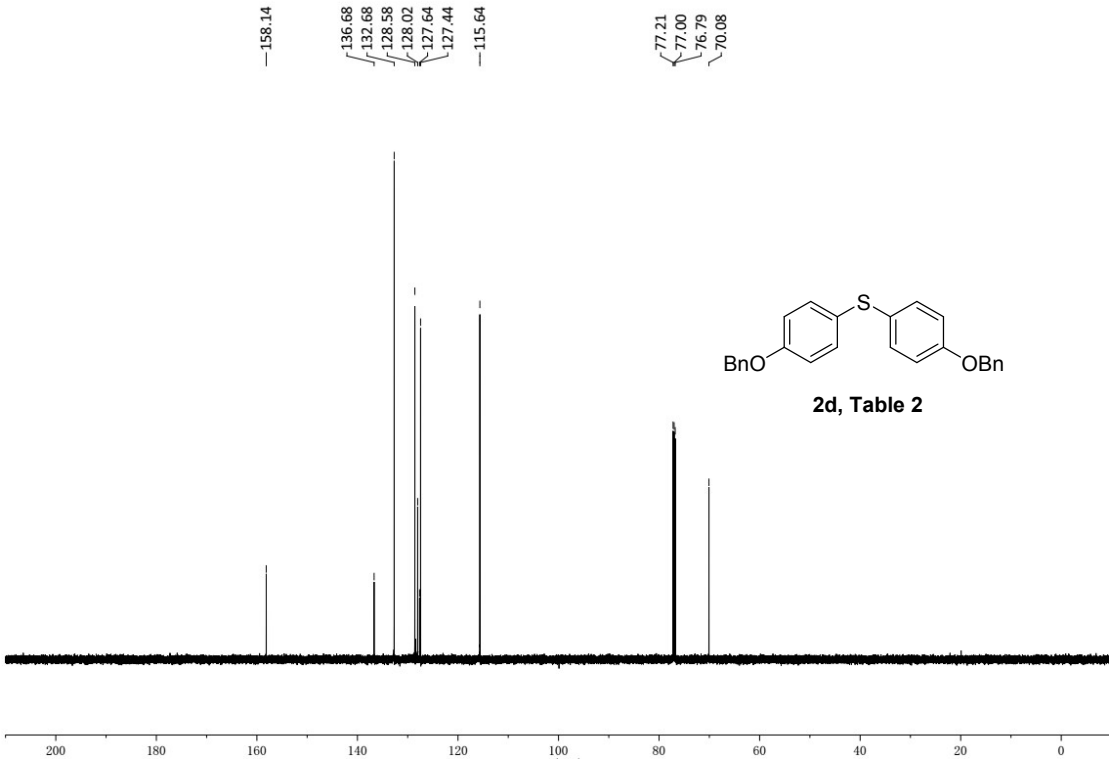
2c, Table 2



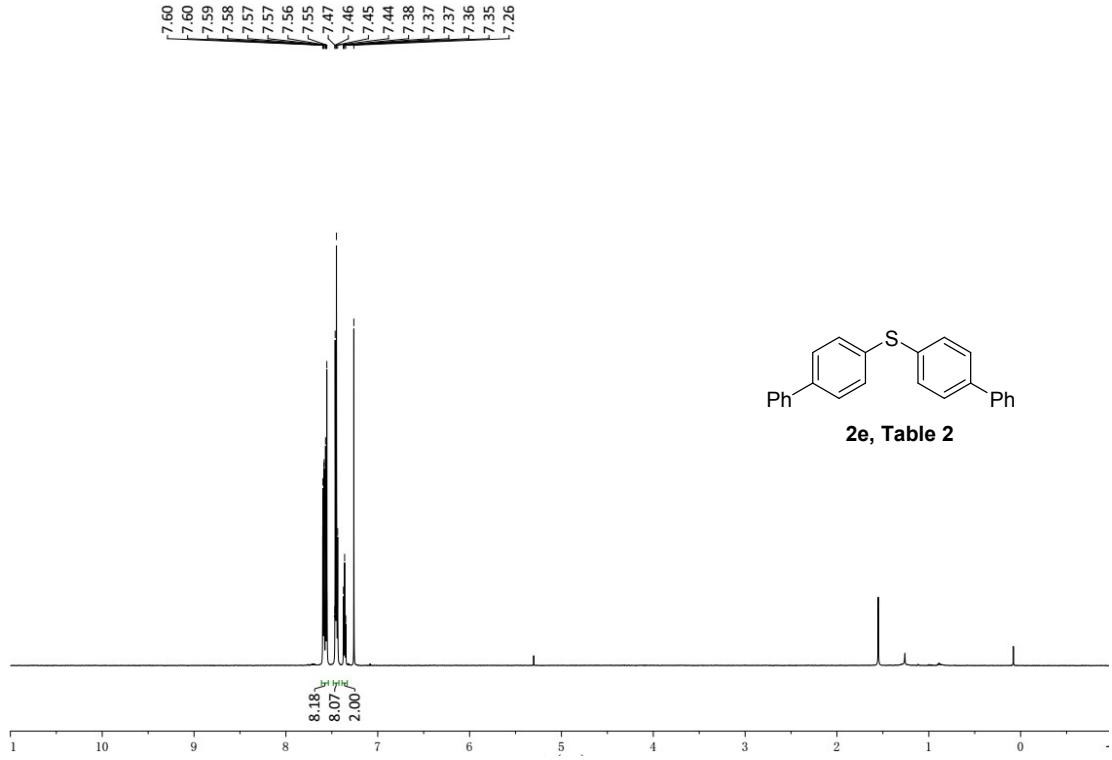
2c, Table 2



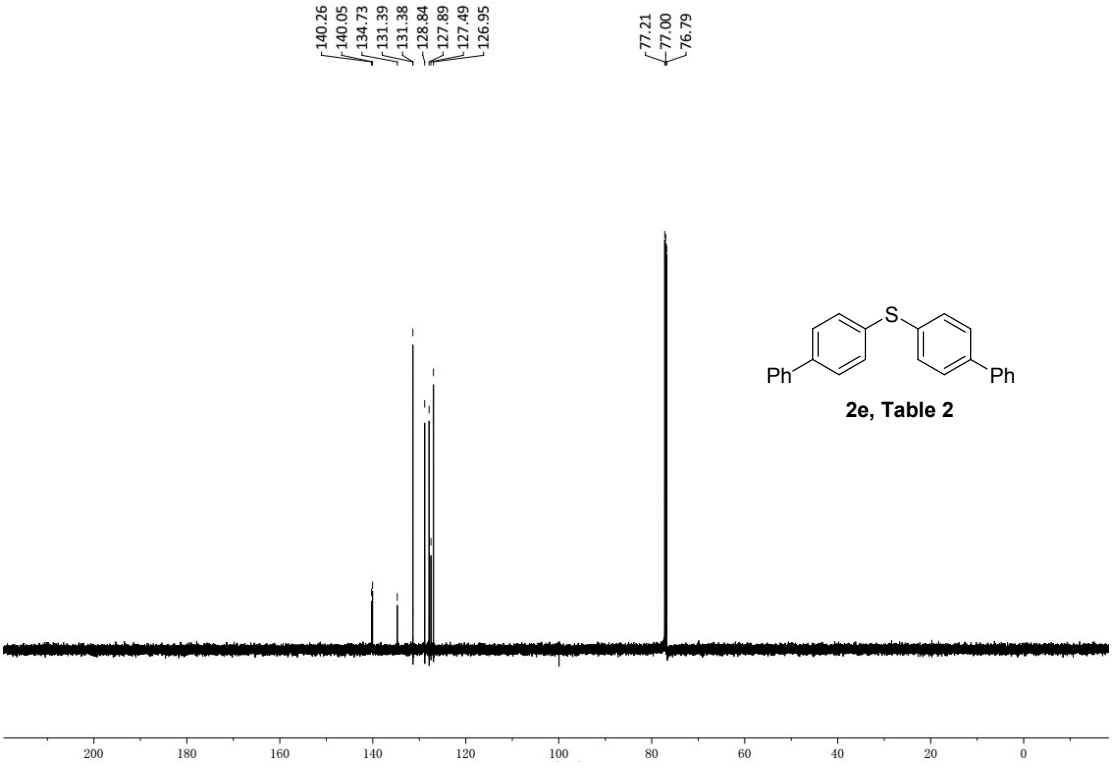
2d, Table 2



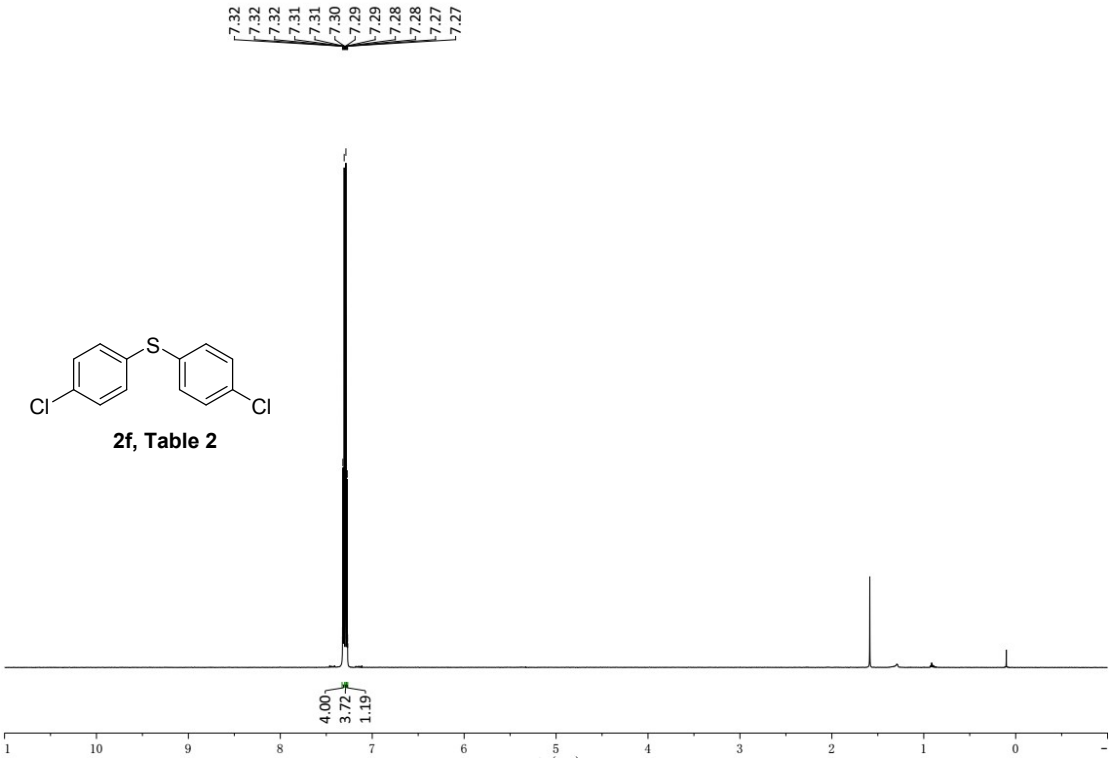
2d, Table 2



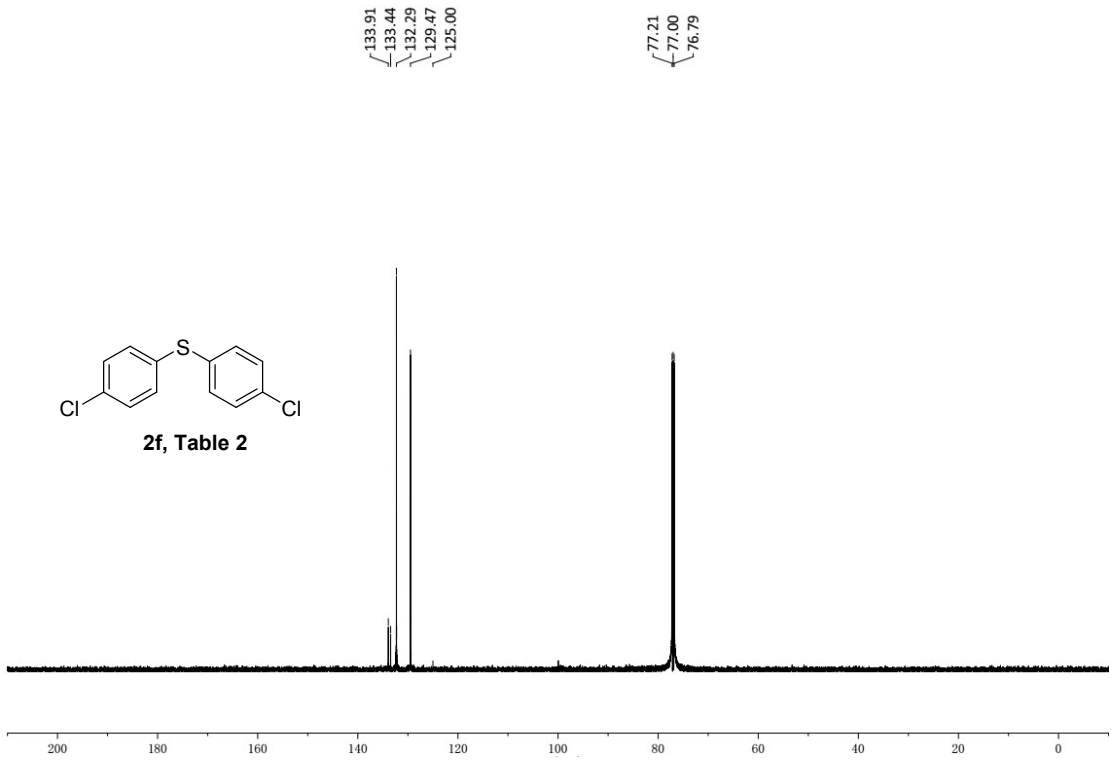
2e, Table 2



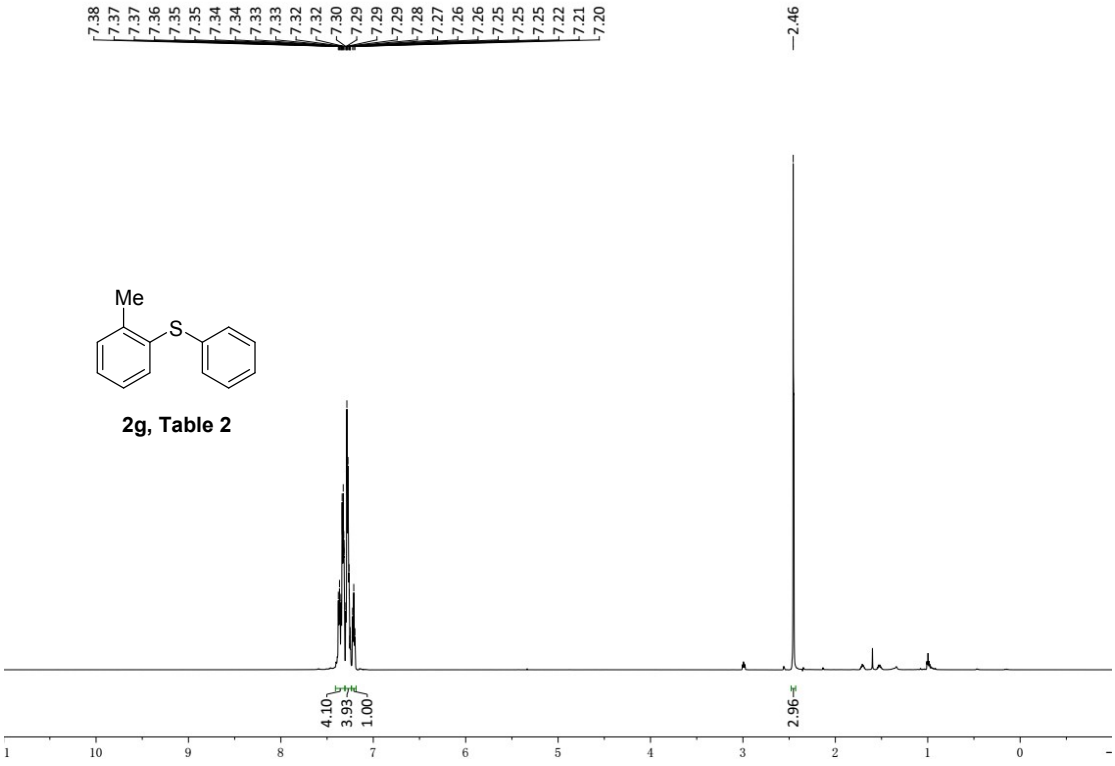
2e, Table 2



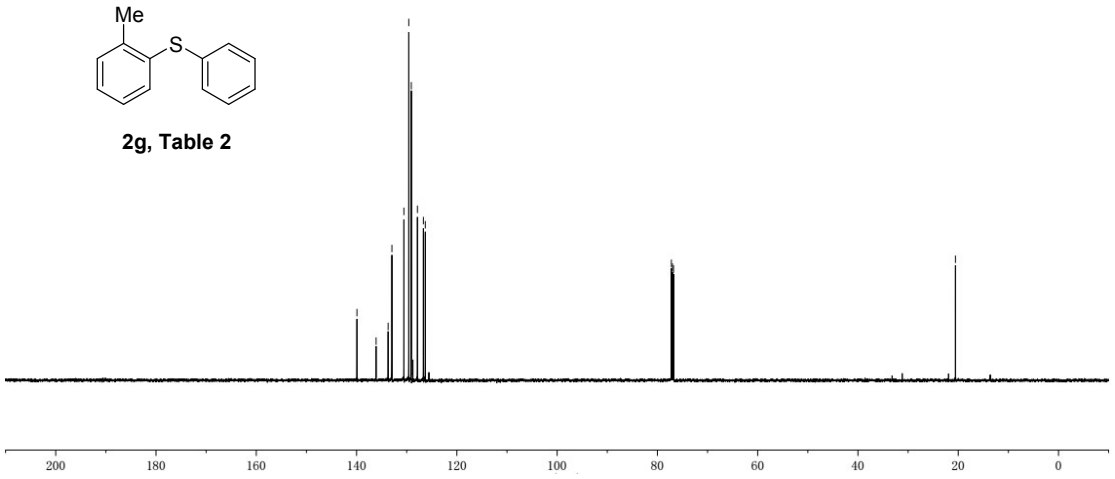
2f, Table 2



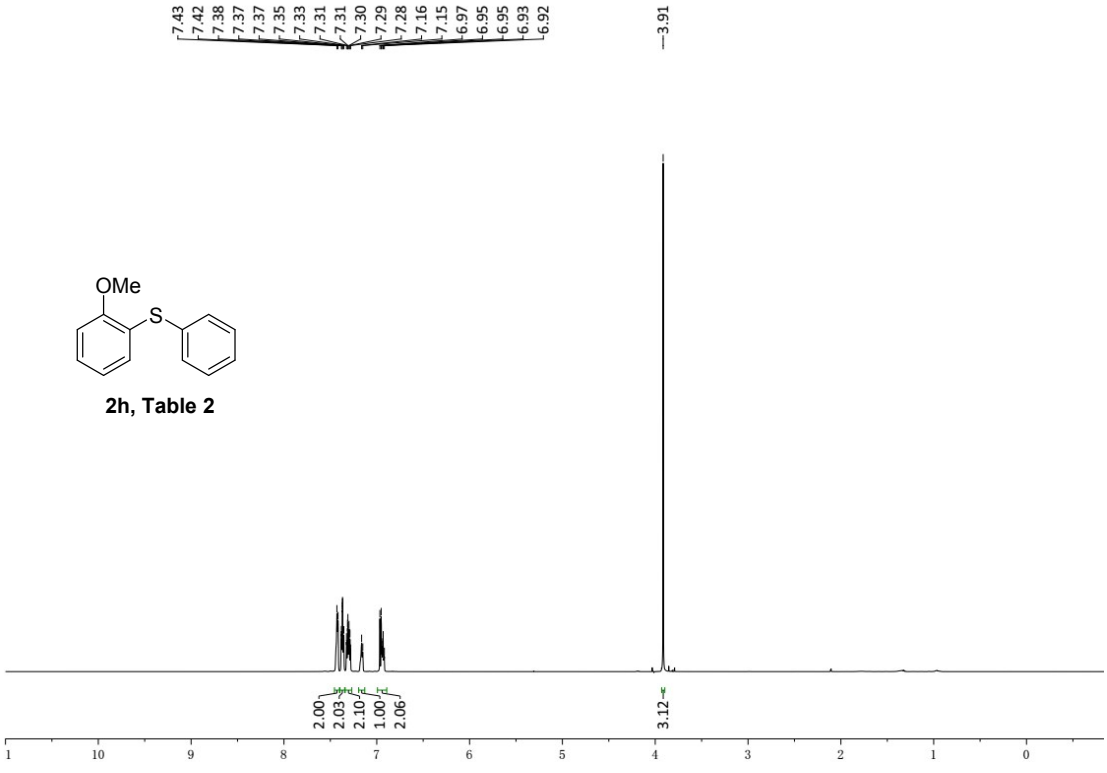
2f, Table 2



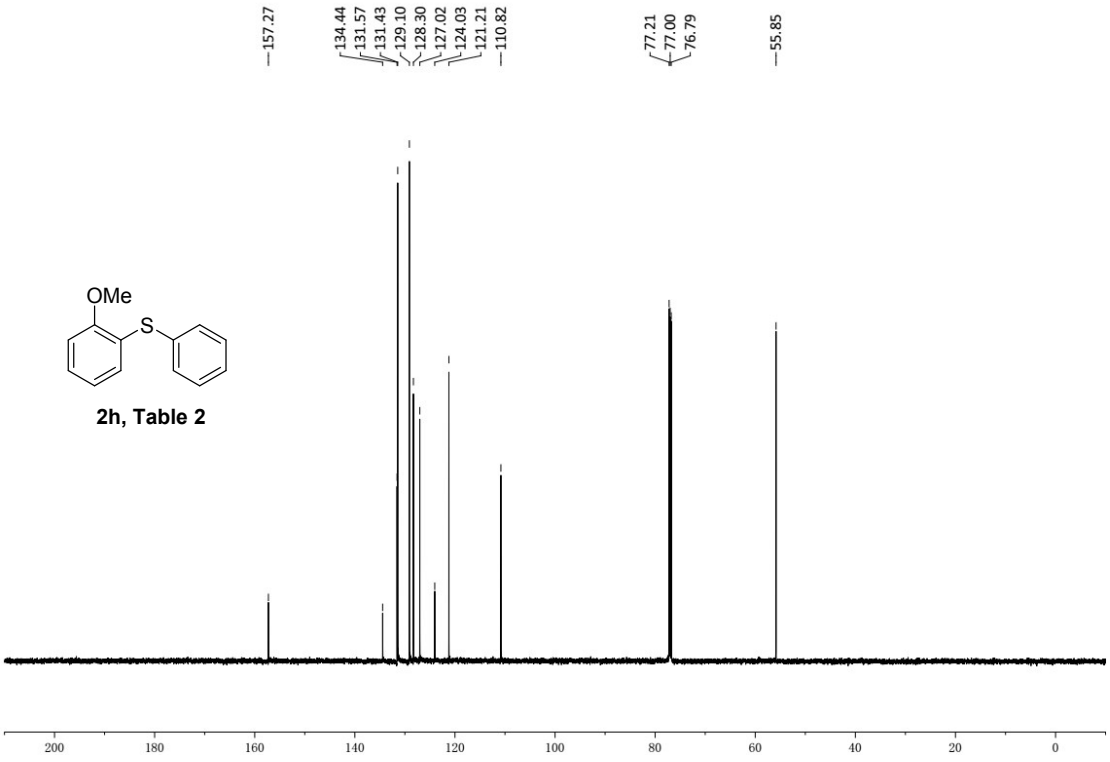
2g, Table 2



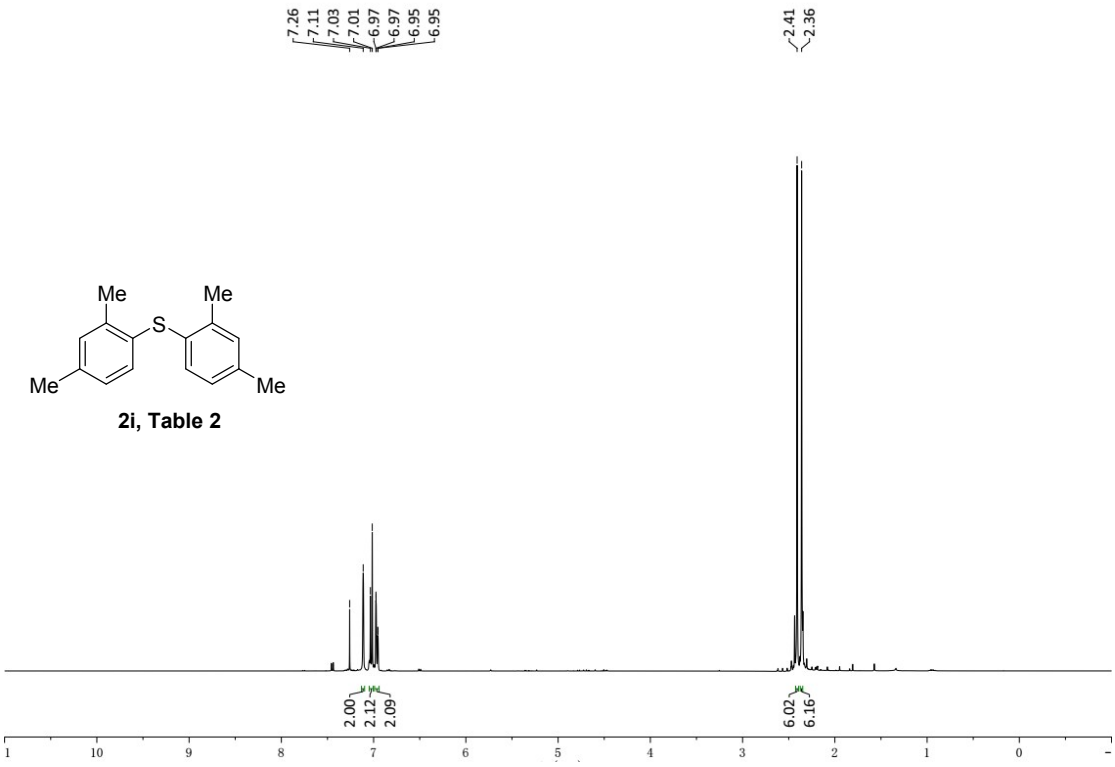
2g, Table 2

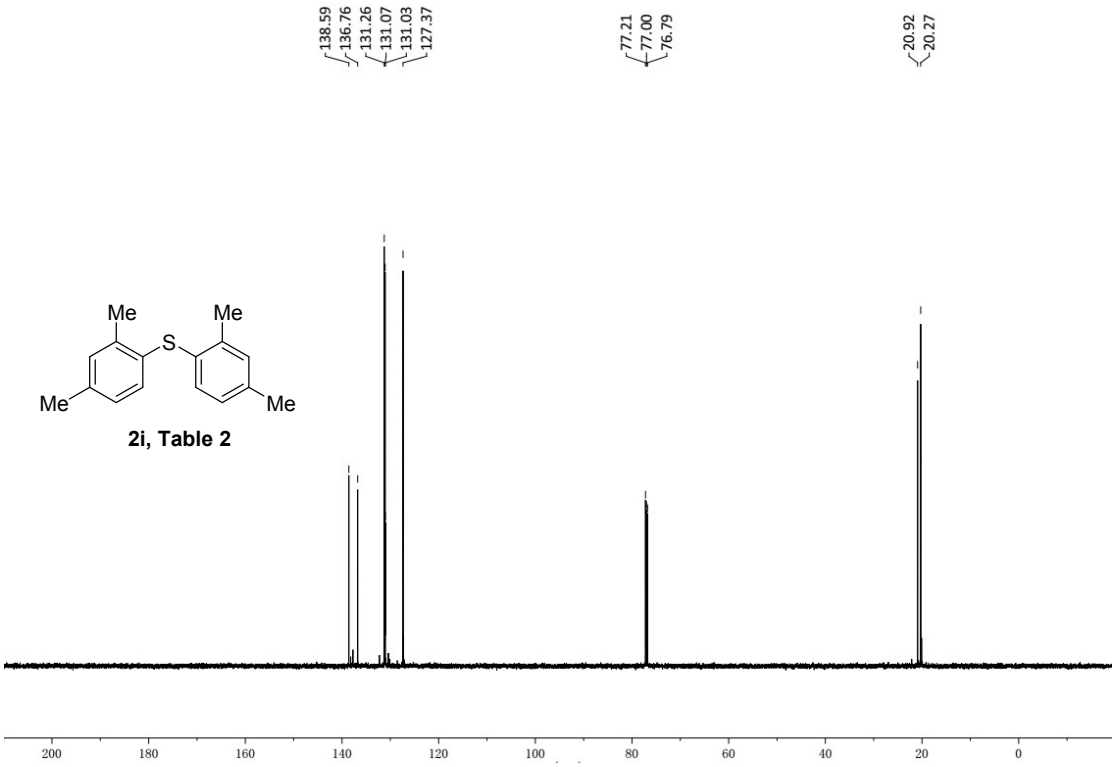


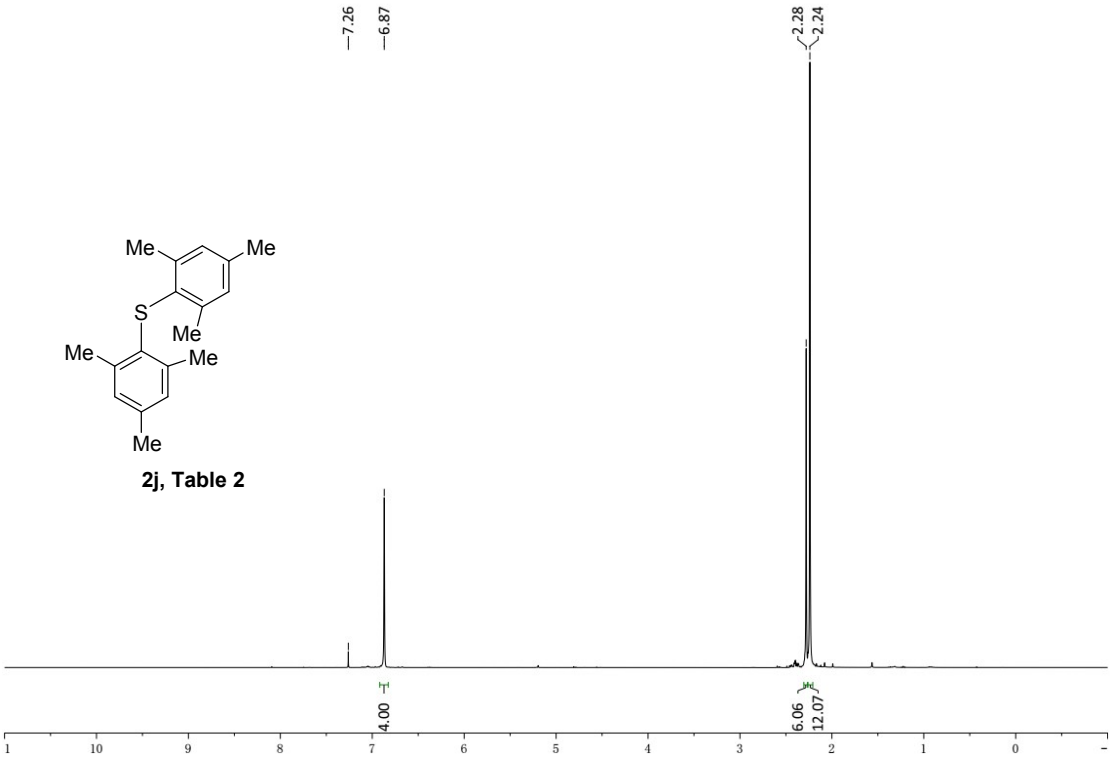
2h, Table 2



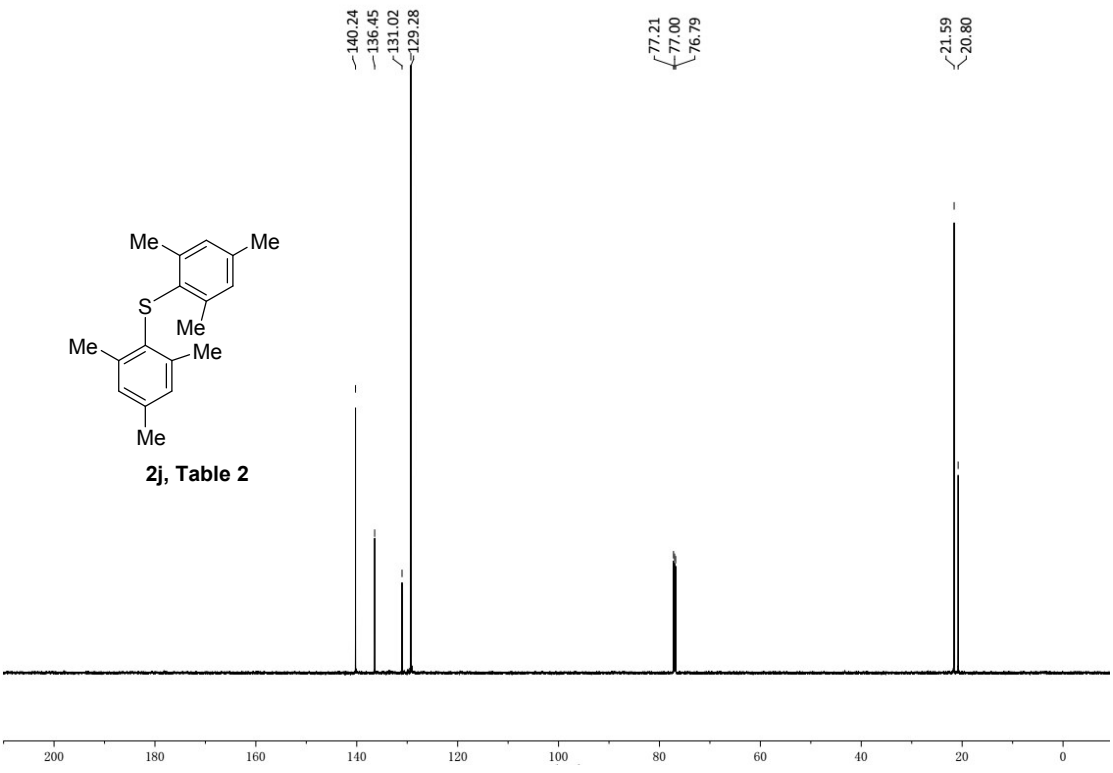
2h, Table 2


7.26
7.11
7.03
7.01
6.97
6.97
6.95
6.95
2.41
2.36
Me
Me
S
Me
Me
2i, Table 2
2.00
2.12
2.09
6.02
6.16
1
10
9
8
7
6
5
4
3
2
1
0

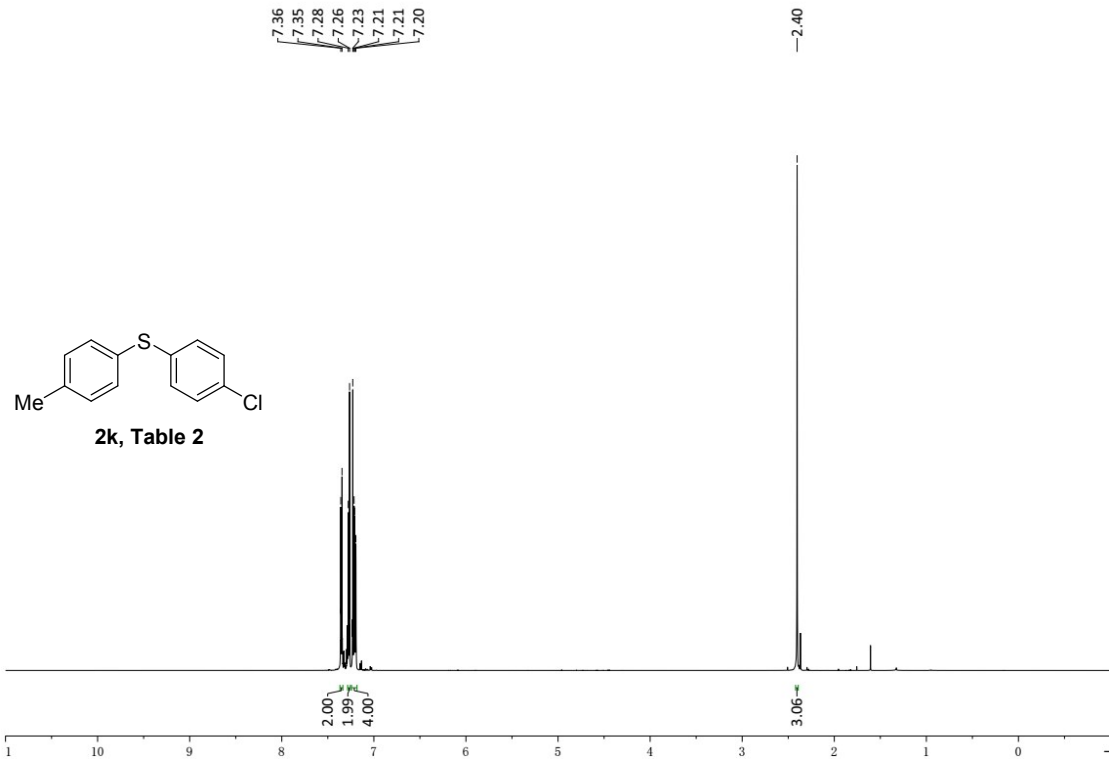

138.59
136.76
131.26
131.07
131.03
127.37
77.21
77.00
76.79
20.92
20.27
Me
Me
S
Me
Me
2i, Table 2
200
180
160
140
120
100
80
60
40
20
0



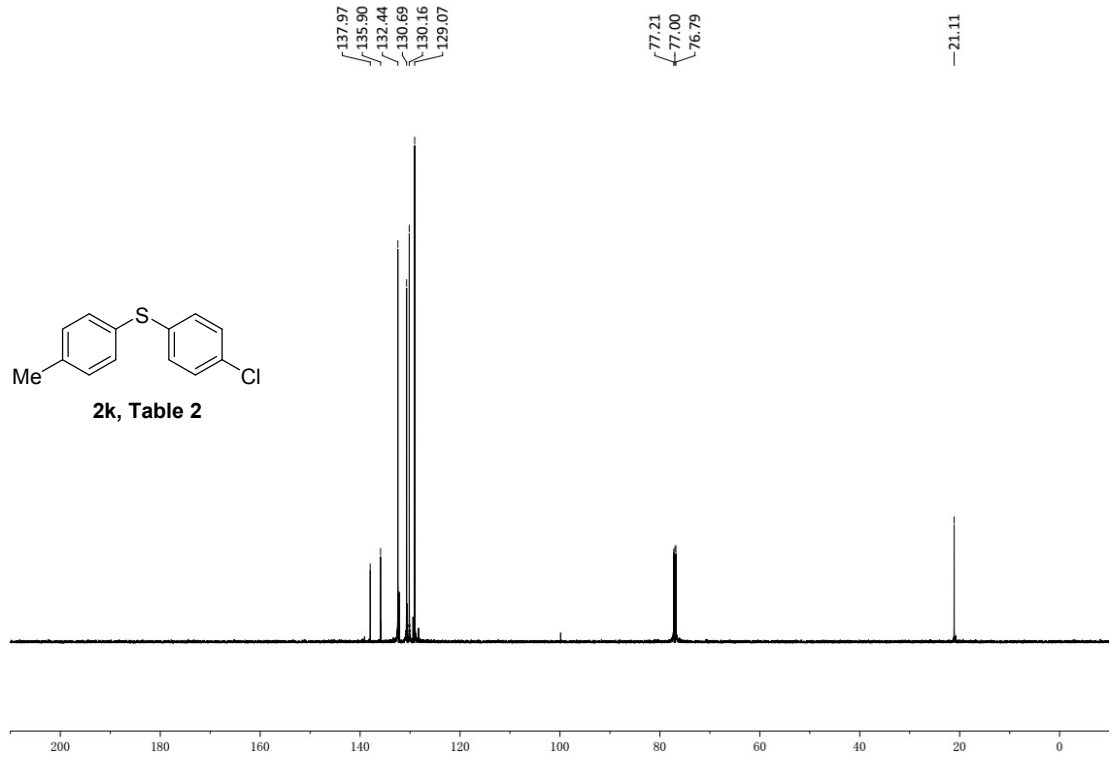
2j, Table 2



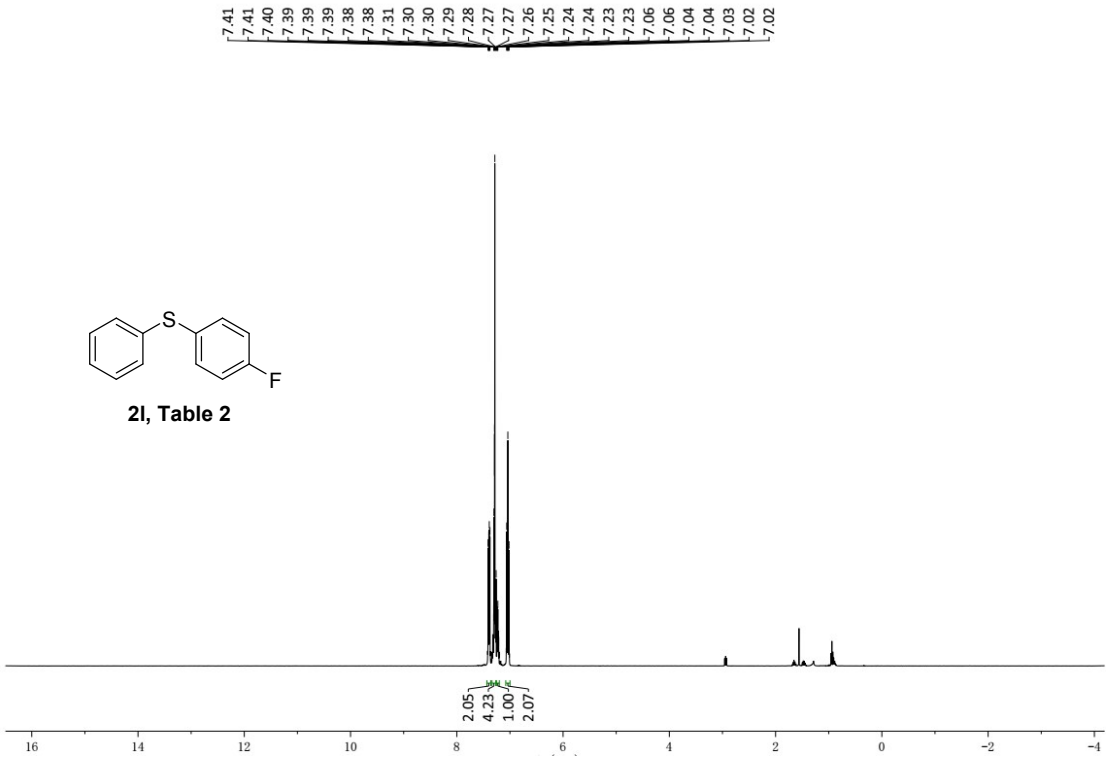
2j, Table 2



2k, Table 2



2k, Table 2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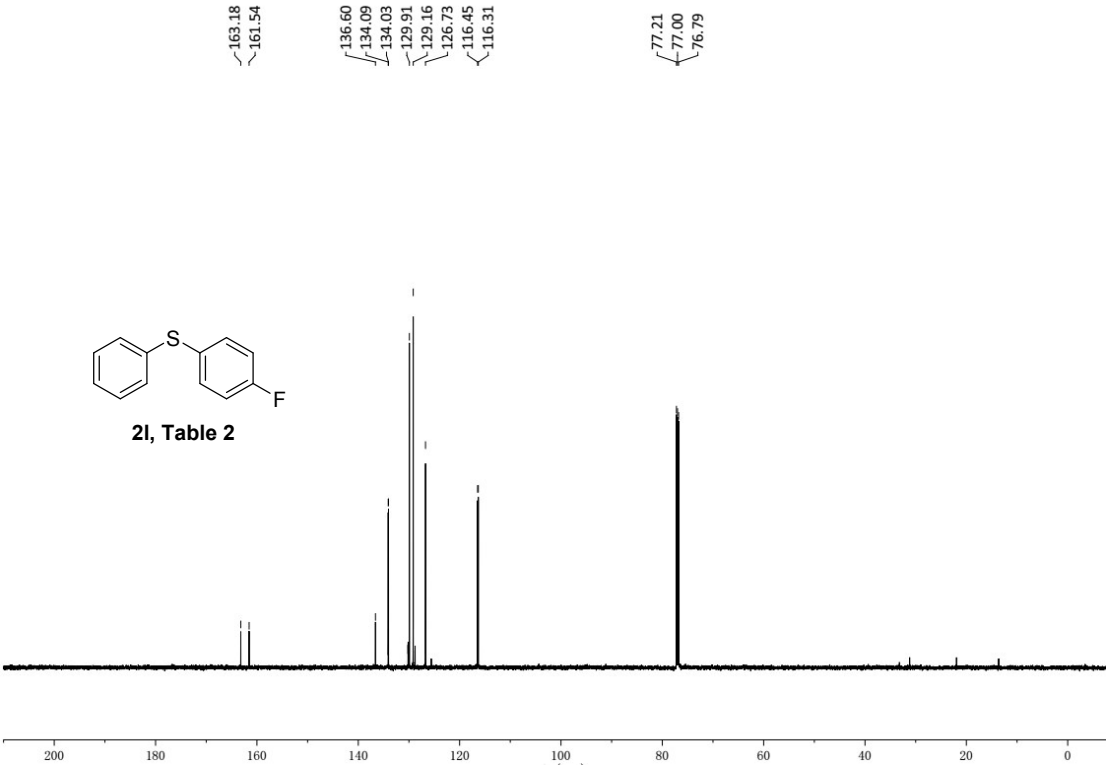
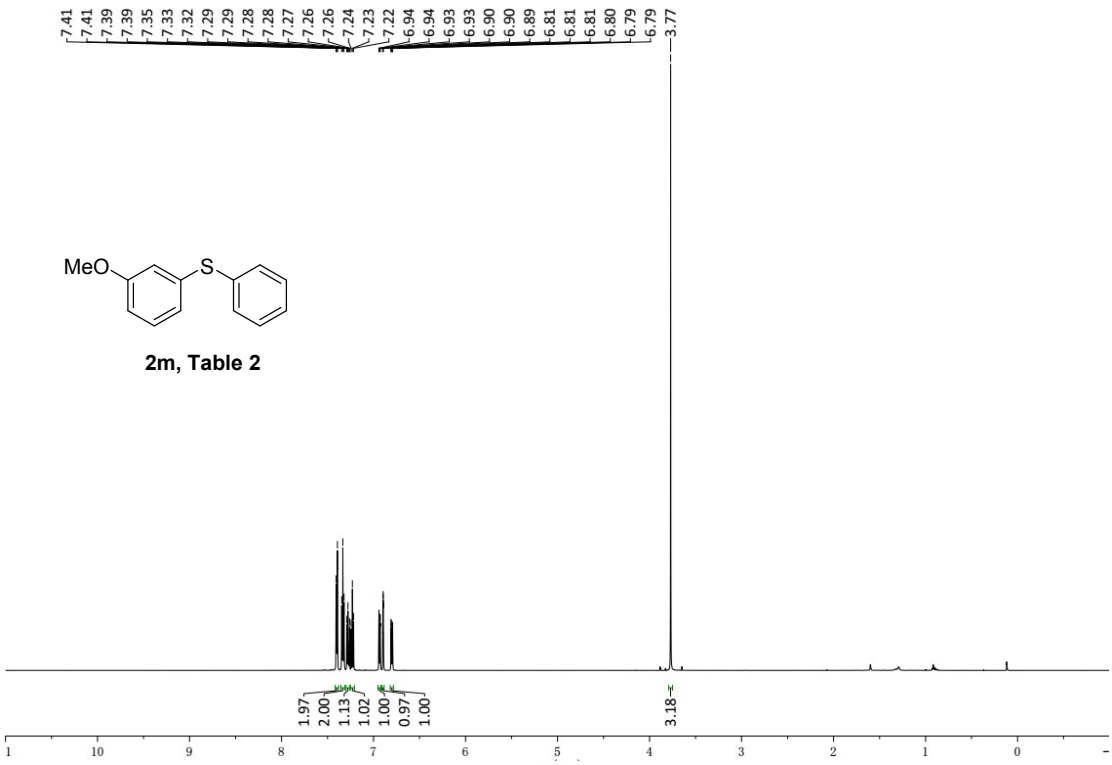
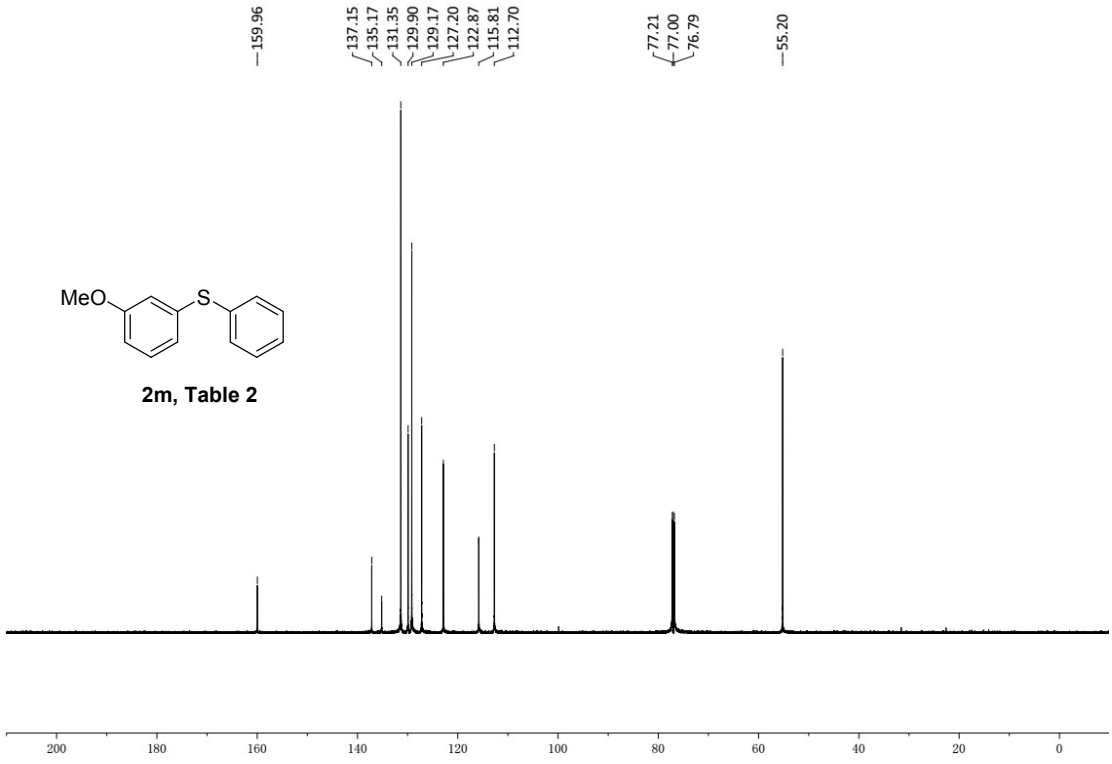
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.06
7.06
7.04
7.04
7.03
7.02
7.02
S
F
2l, Table 2
2.05
4.23
1.00
2.07
16
14
12
10
8
6
4
2
0
−2
−4

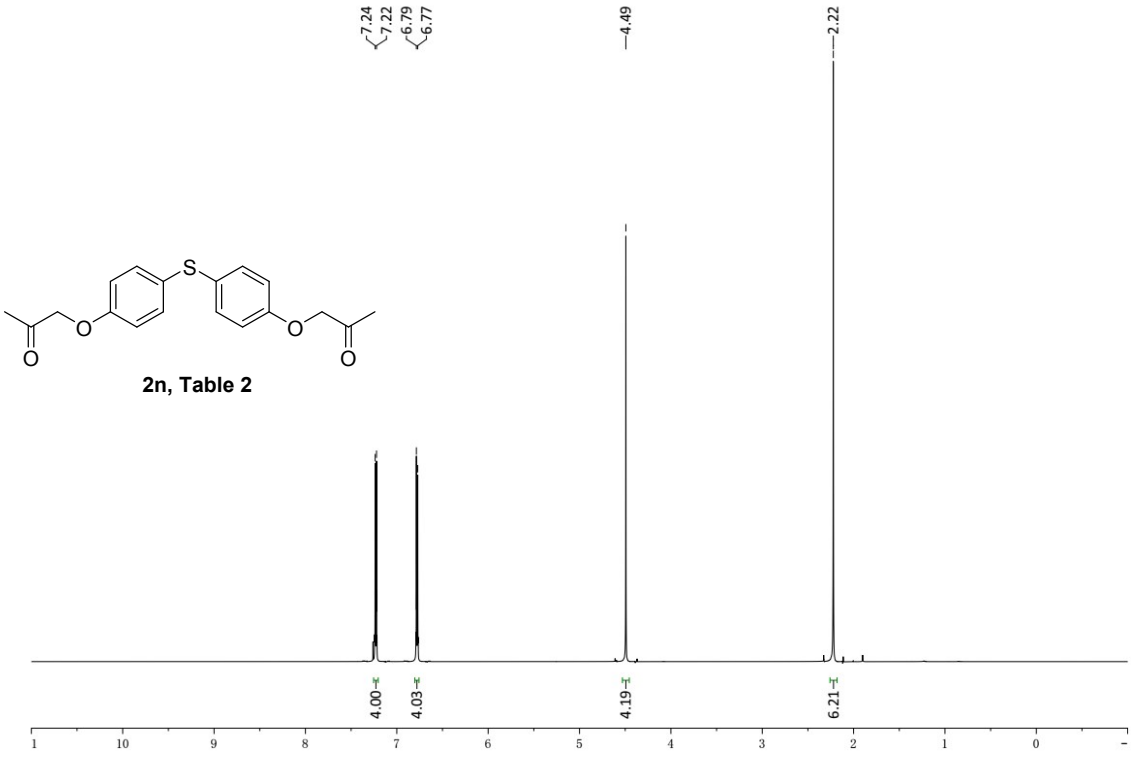

163.18
161.54
136.60
134.09
134.03
129.91
129.16
126.73
116.45
116.31
77.21
77.00
76.79
S
F
2l, Table 2
200
180
160
140
120
100
80
60
40
20
0



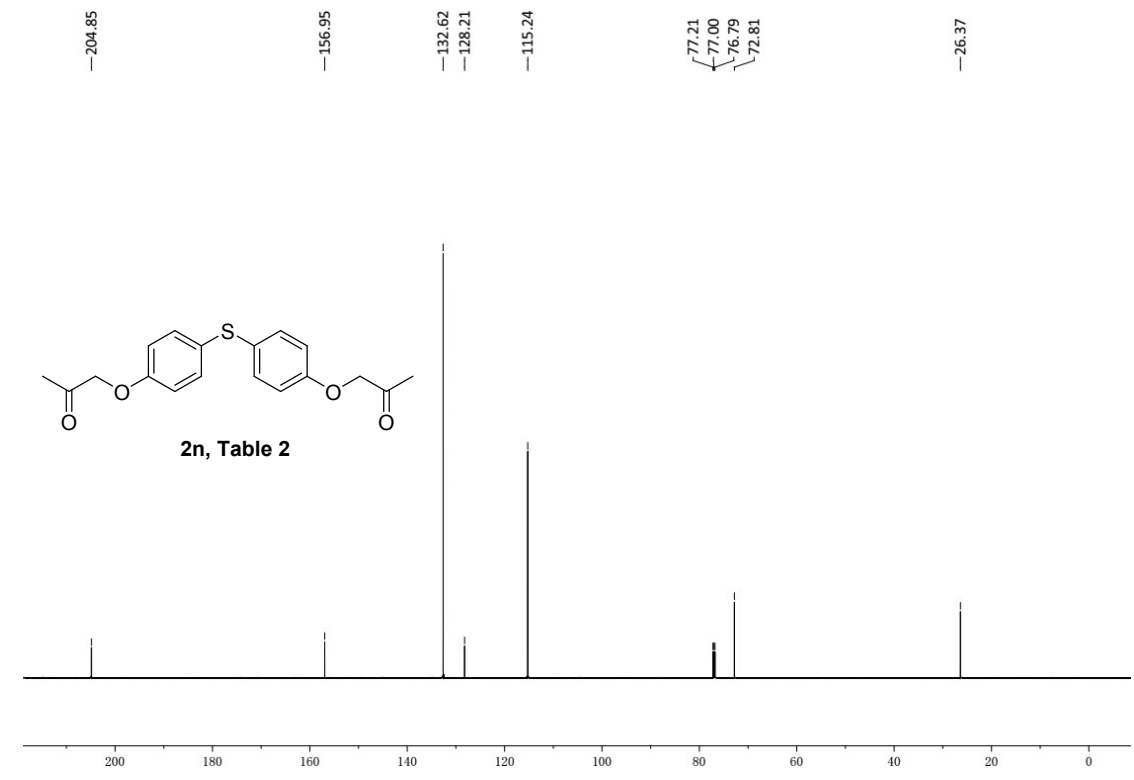
2m, Table 2



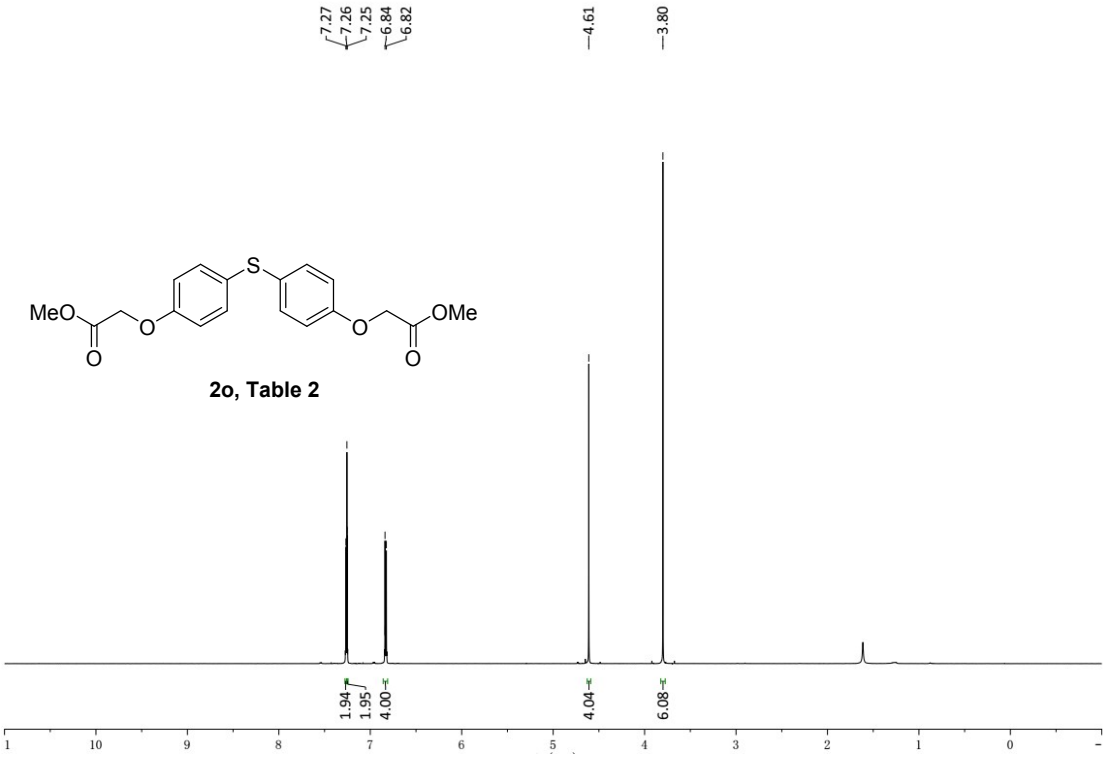
2m, Table 2



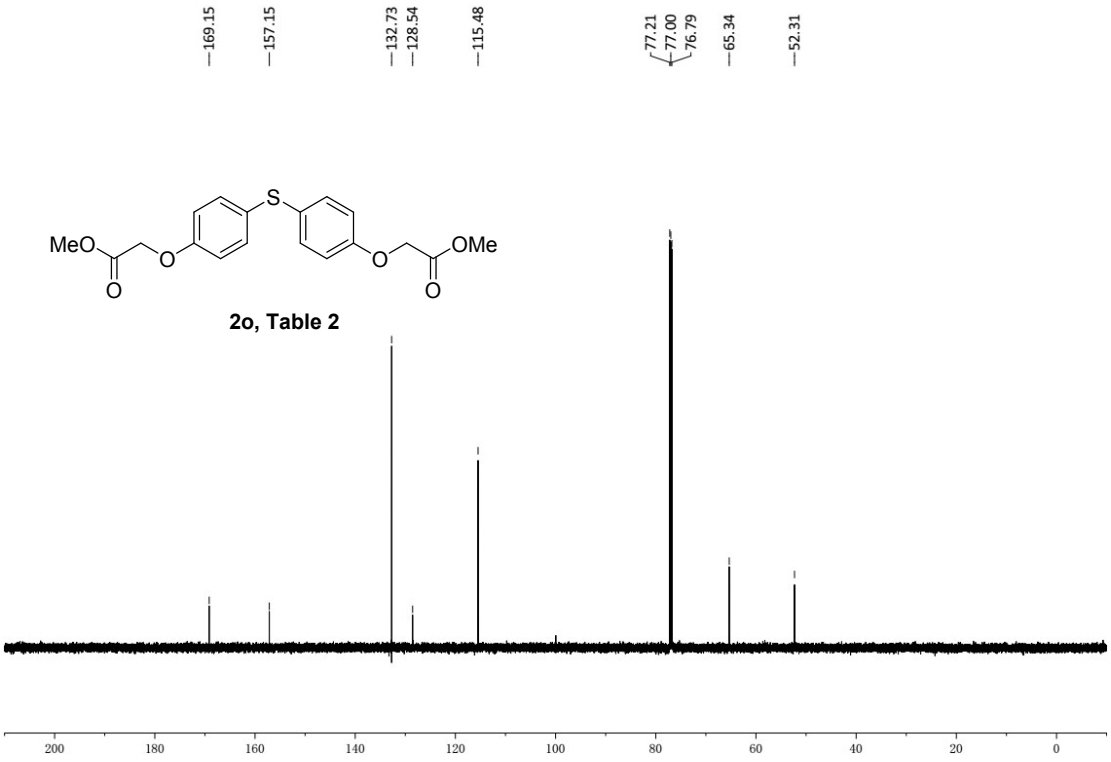
2n, Table 2



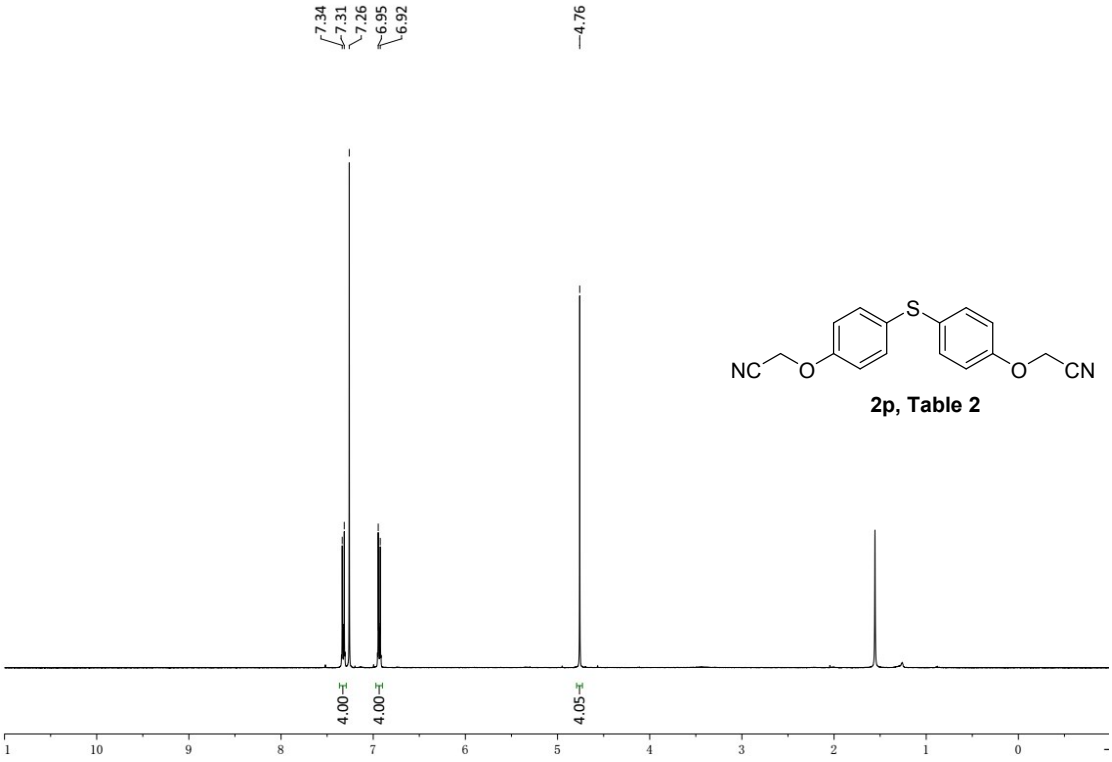
2n, Table 2



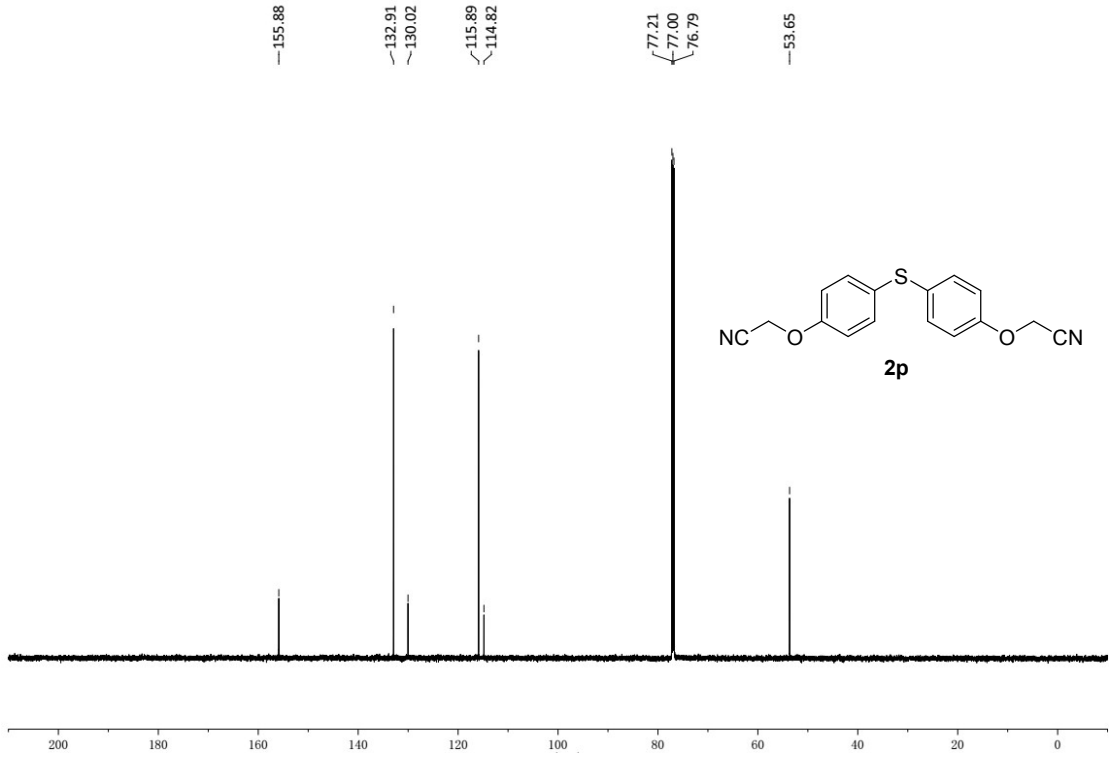
2o, Table 2



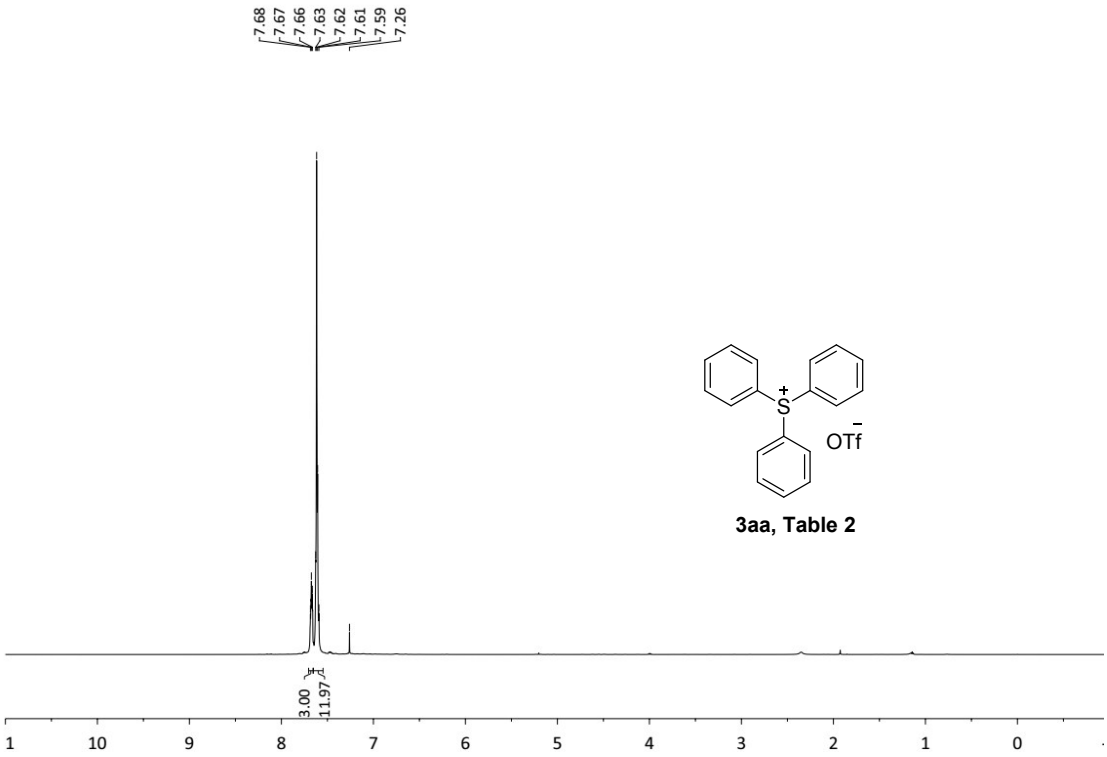
2o, Table 2


7.34
7.31
7.26
6.95
6.92
4.76
4.00
4.00
4.05
NC
O
S
O
CN

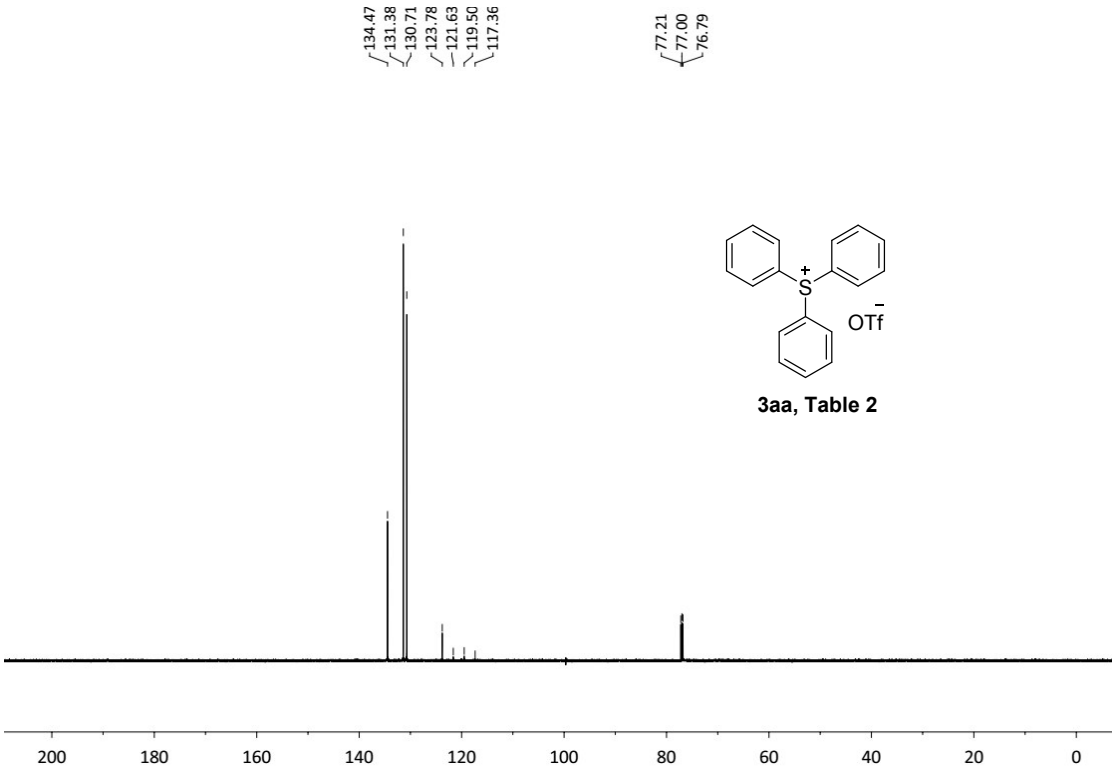
2p, Table 2


155.88
132.91
130.02
115.89
114.82
77.21
77.00
76.79
53.65
NC
O
S
O
CN

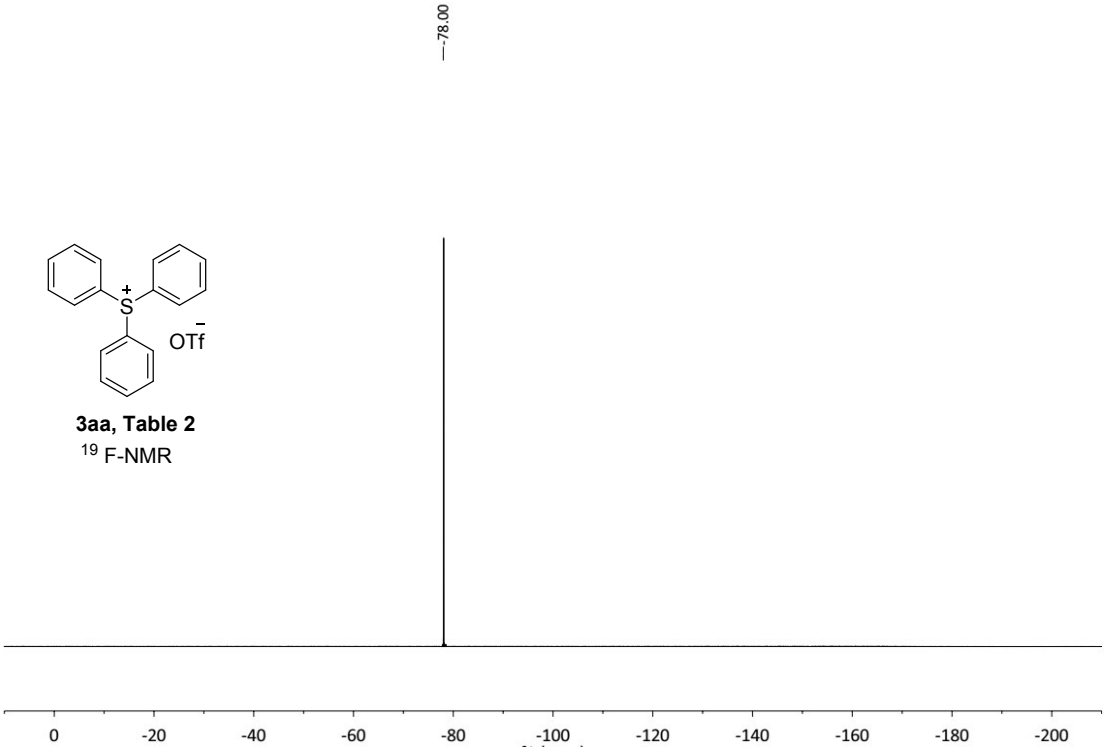
2p



3aa, Table 2

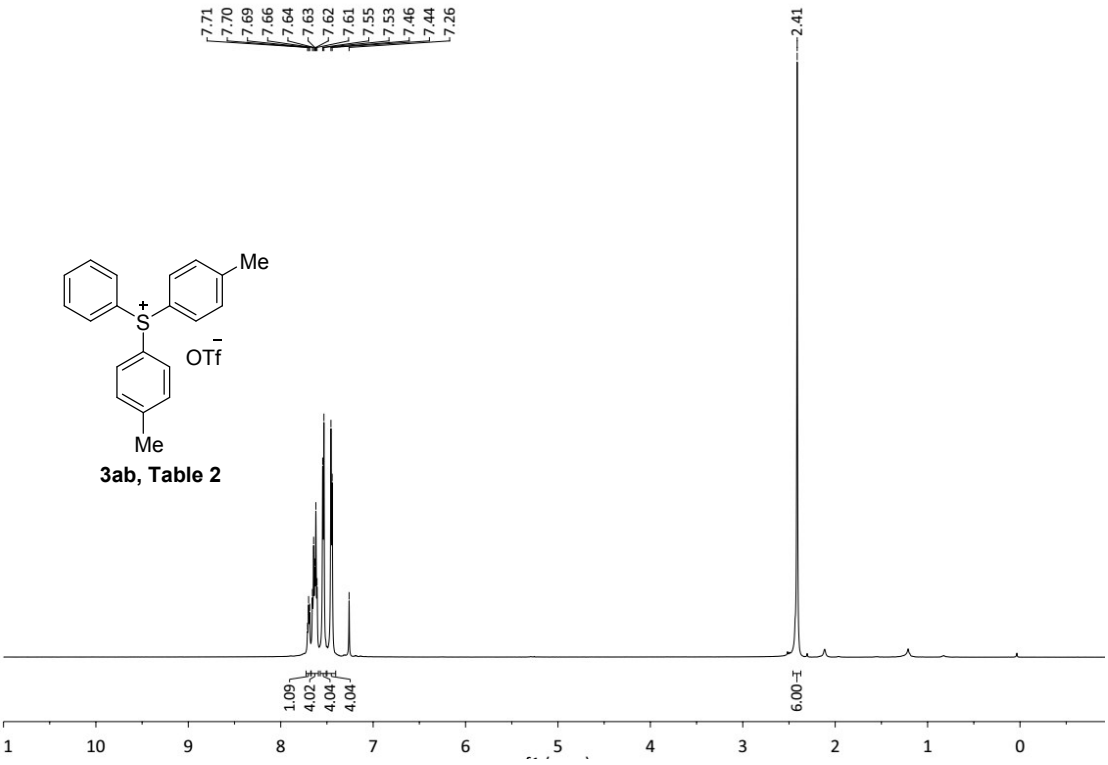


3aa, Table 2

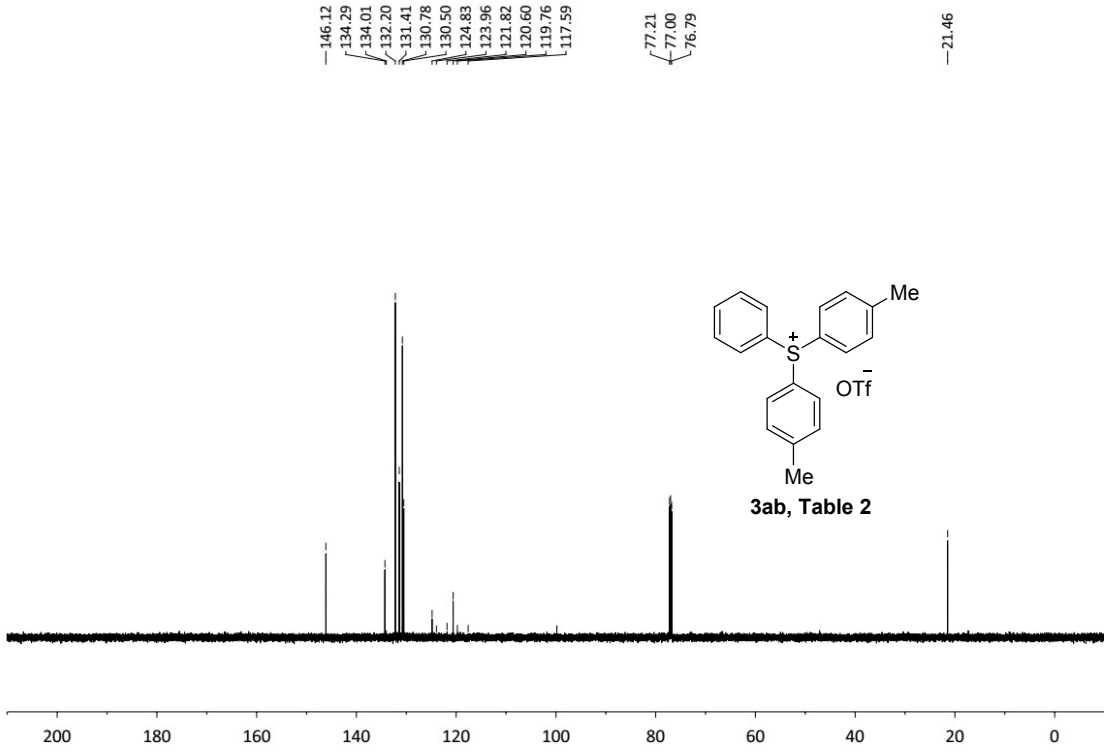


3aa, Table 2

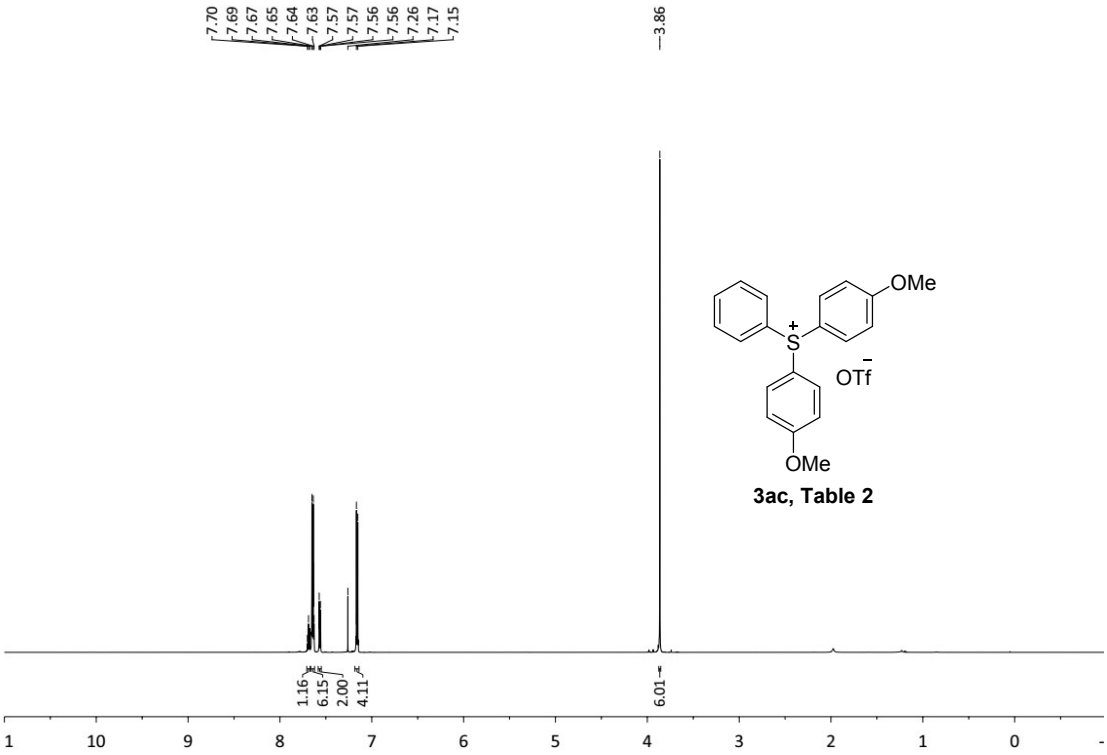
^{19}F-NMR



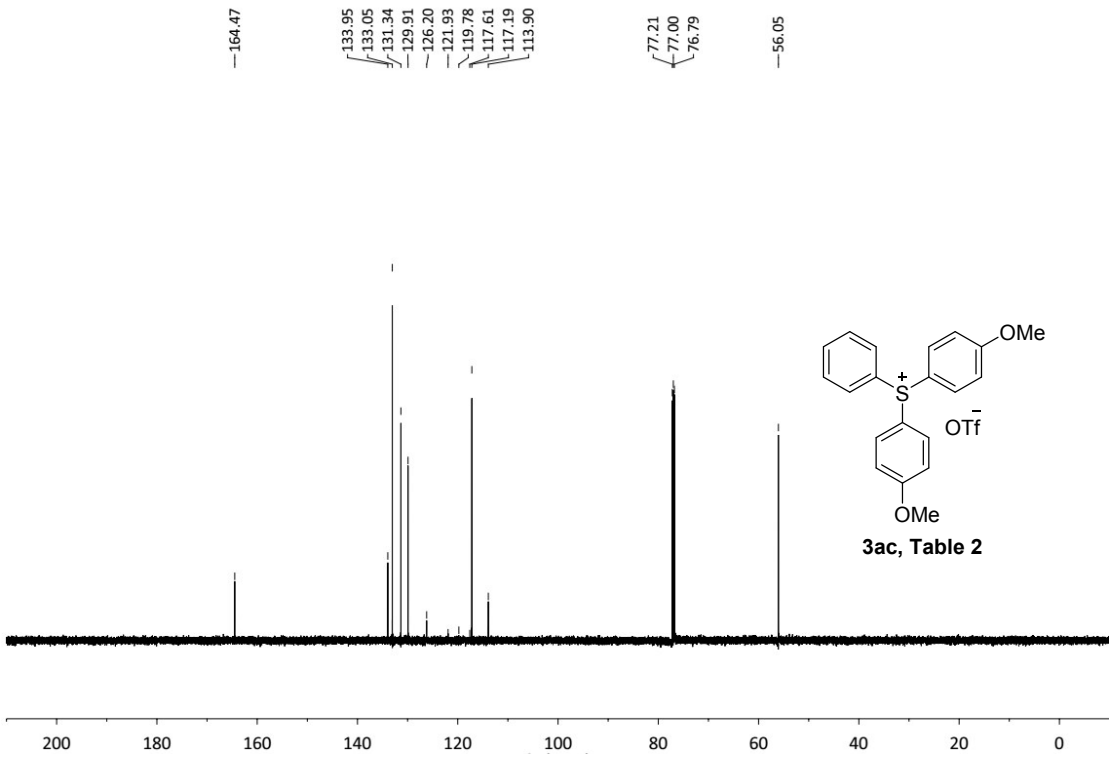
3ab, Table 2



3ab, Table 2



3ac, Table 2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126.20
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117.61
117.19
113.90
77.21
77.00
76.79
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OTf
OMe
3ac, Table 2
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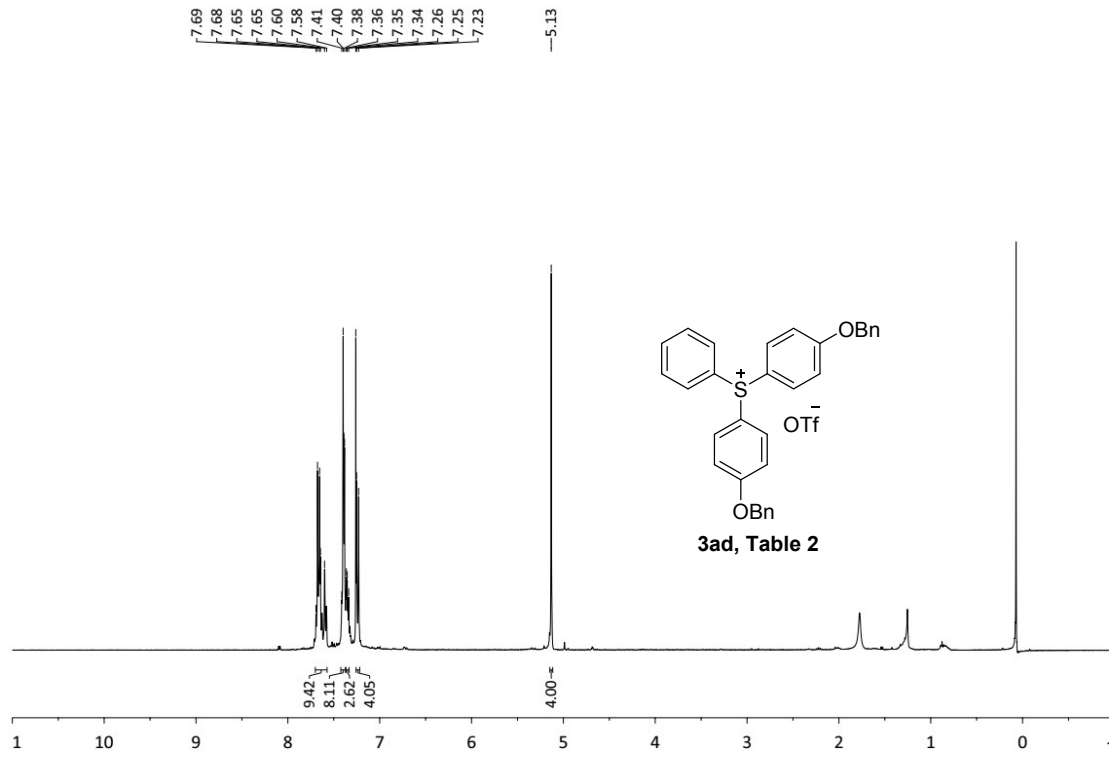
20
0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7.34
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7.25
7.23
5.13
OBn
OTf
OBn
3ad, Table 2
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7
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4
3
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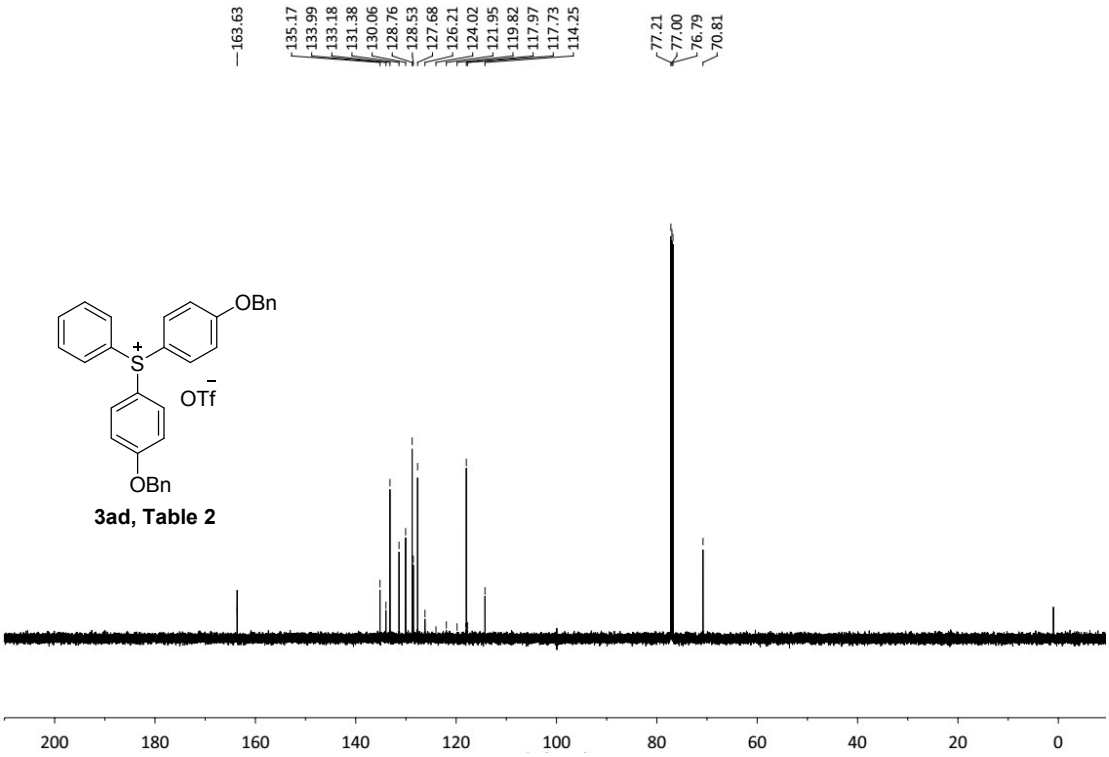
1
0



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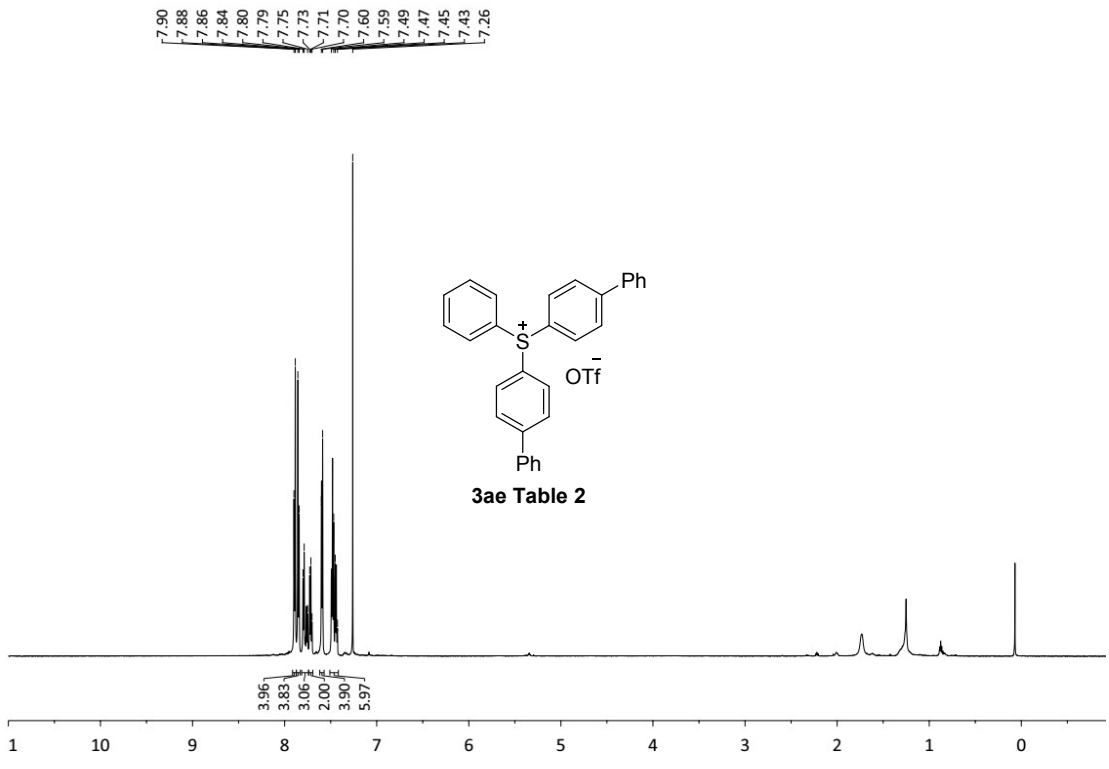
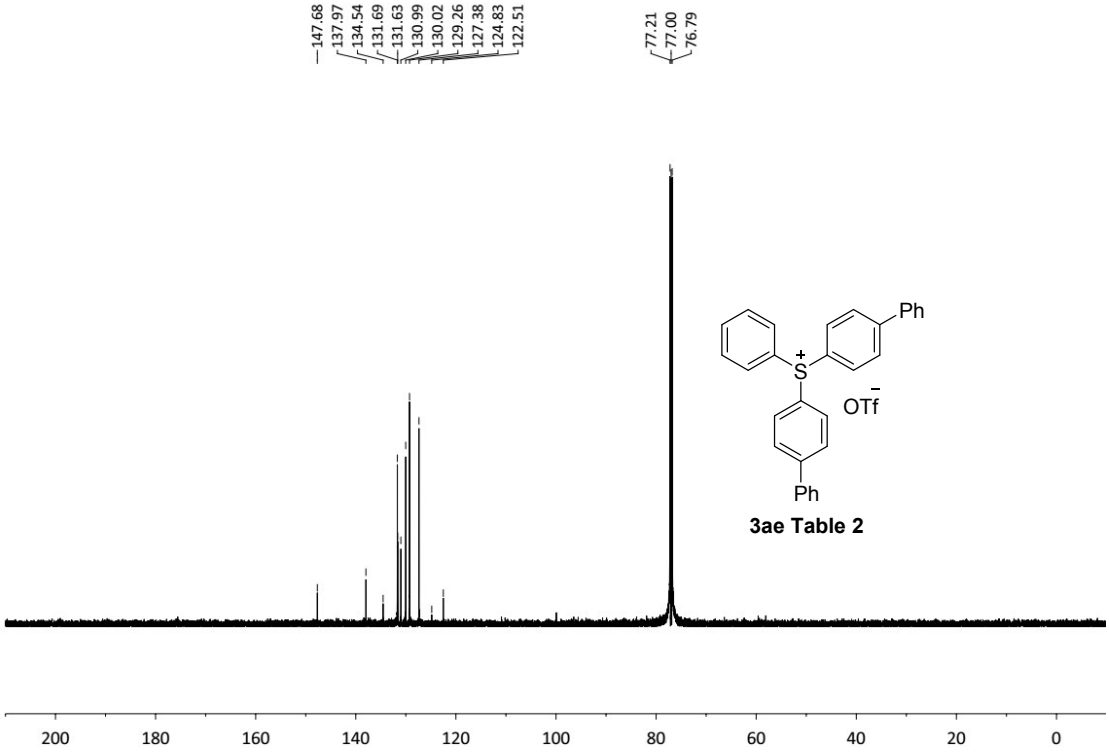
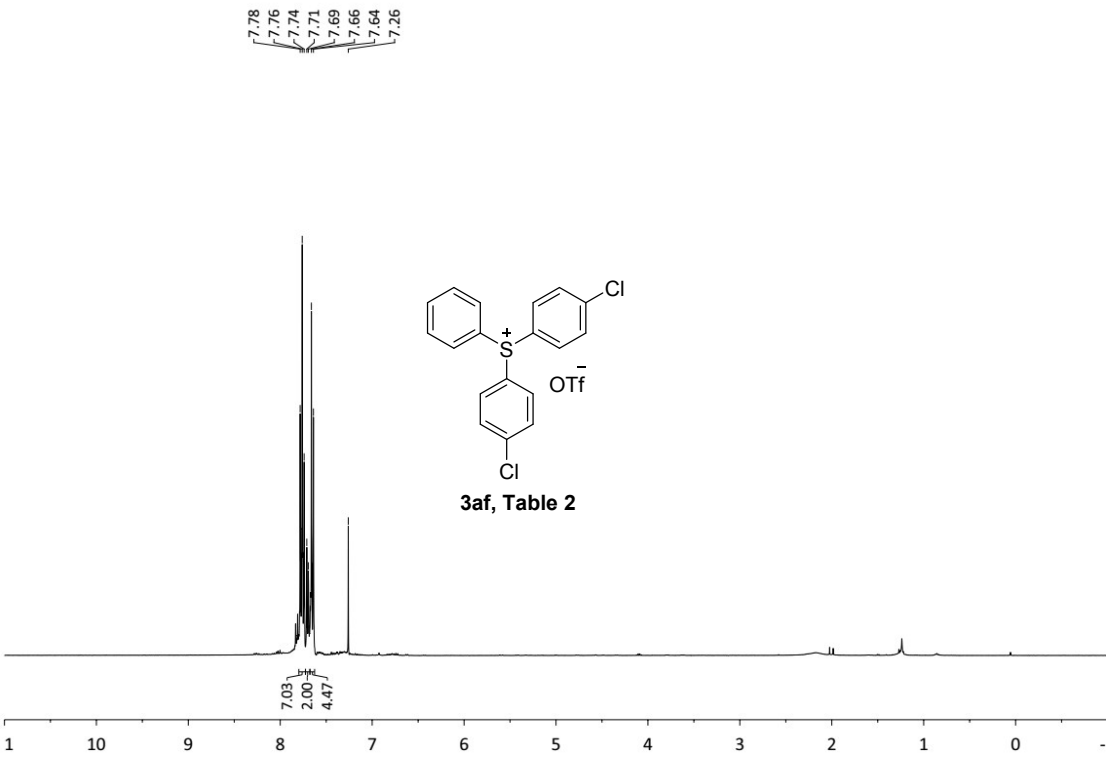


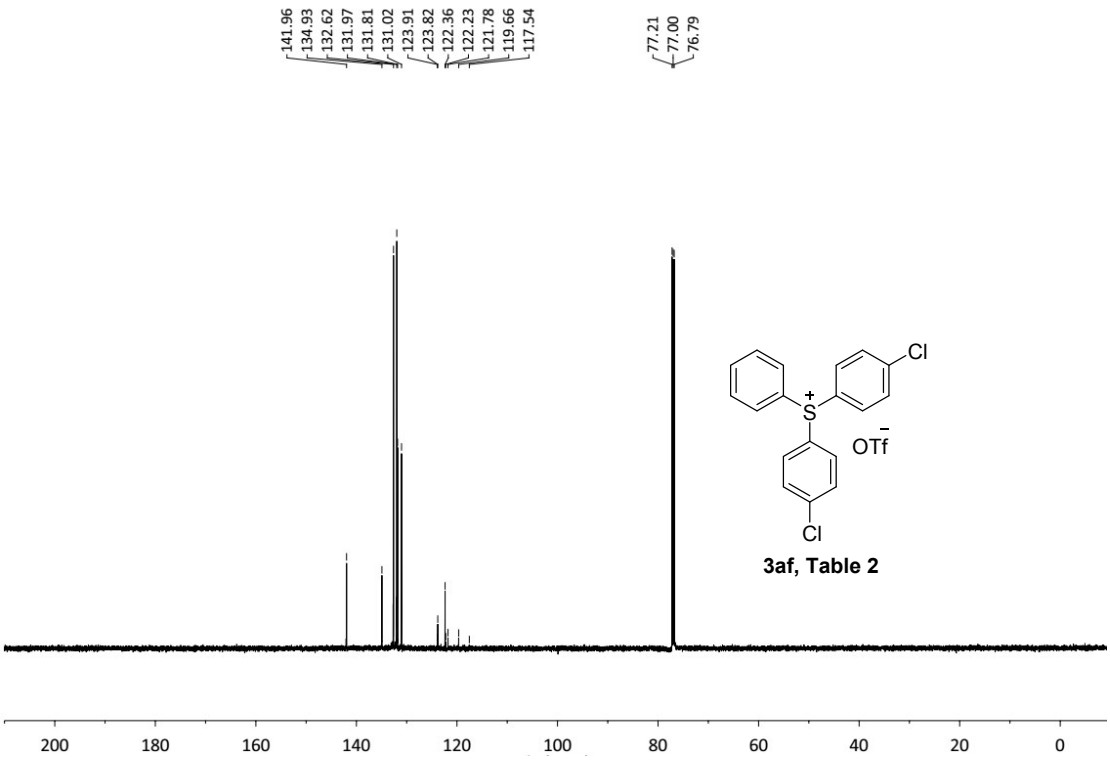
3ae Table 2



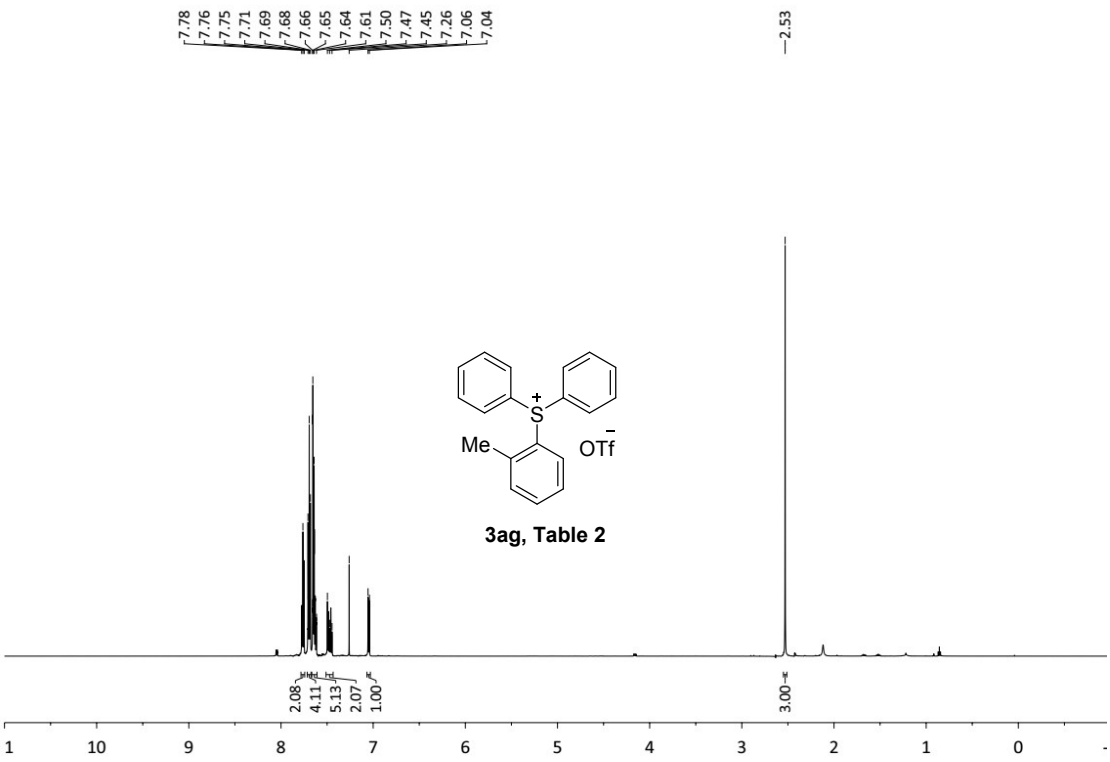
3ae Table 2



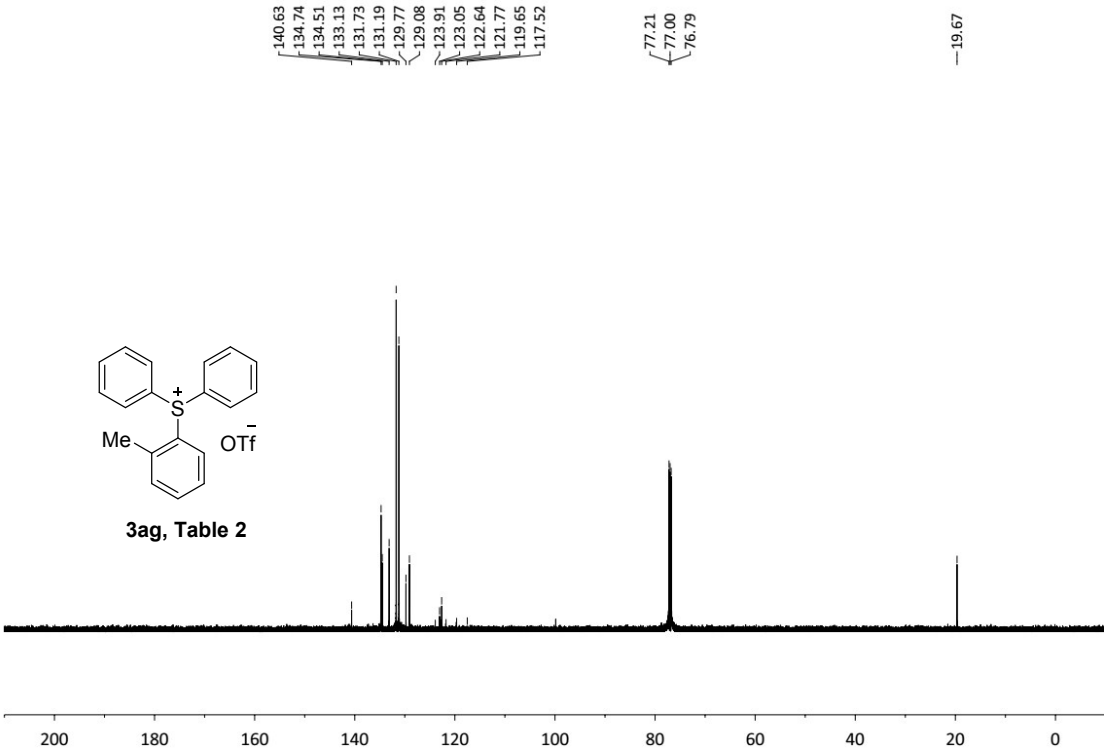
3af, Table 2



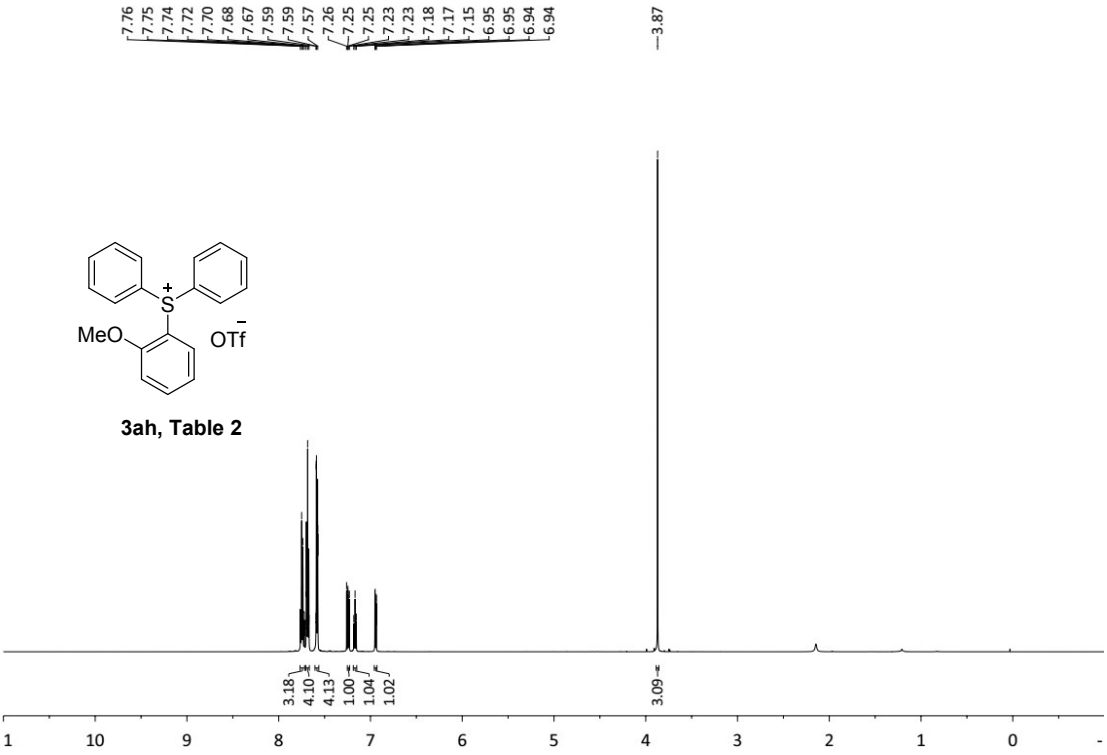
3af, Table 2



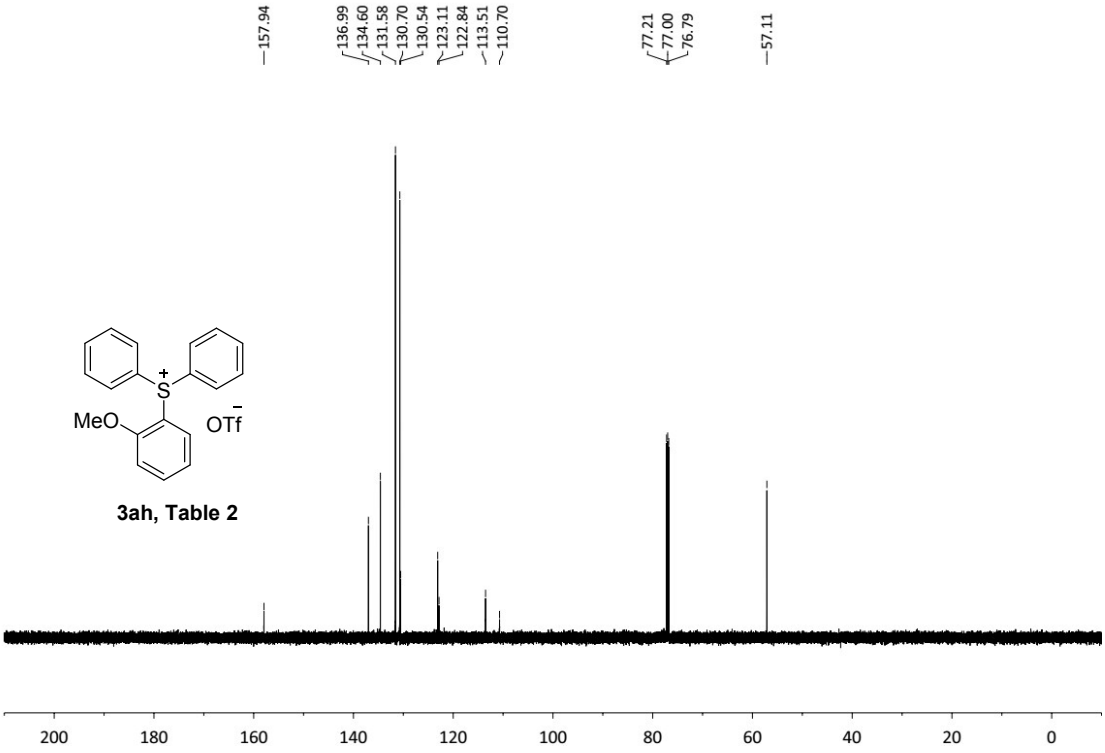
3ag, Table 2



3ag, Table 2



3ah, Table 2



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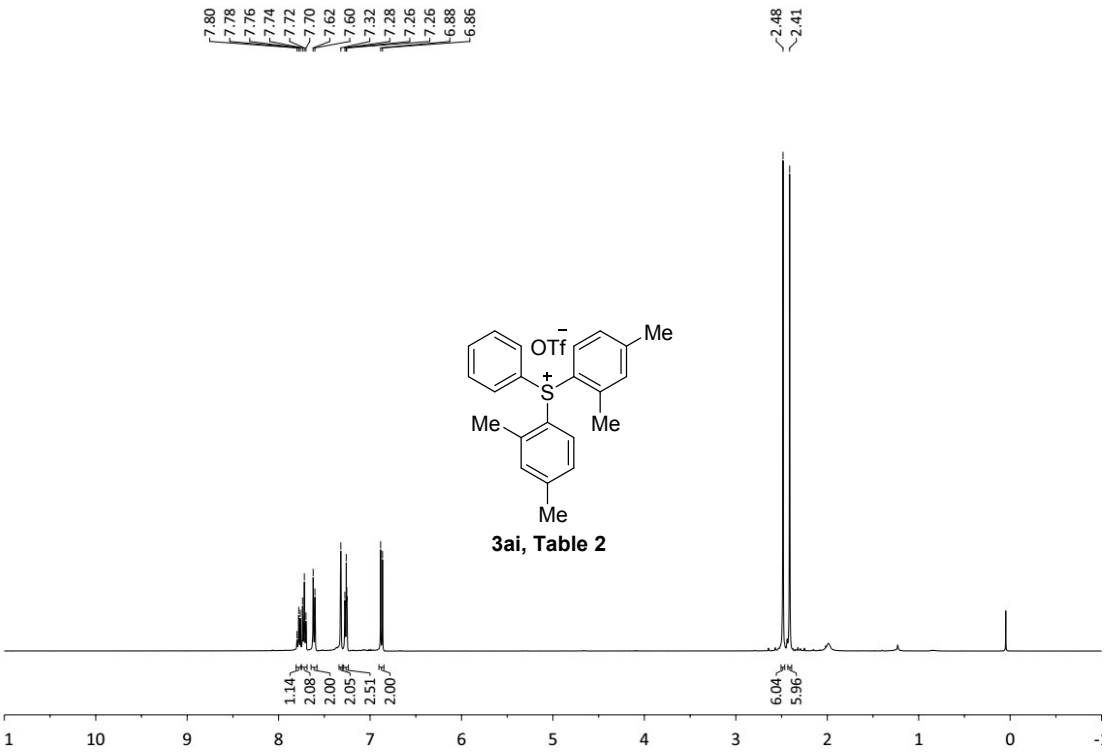
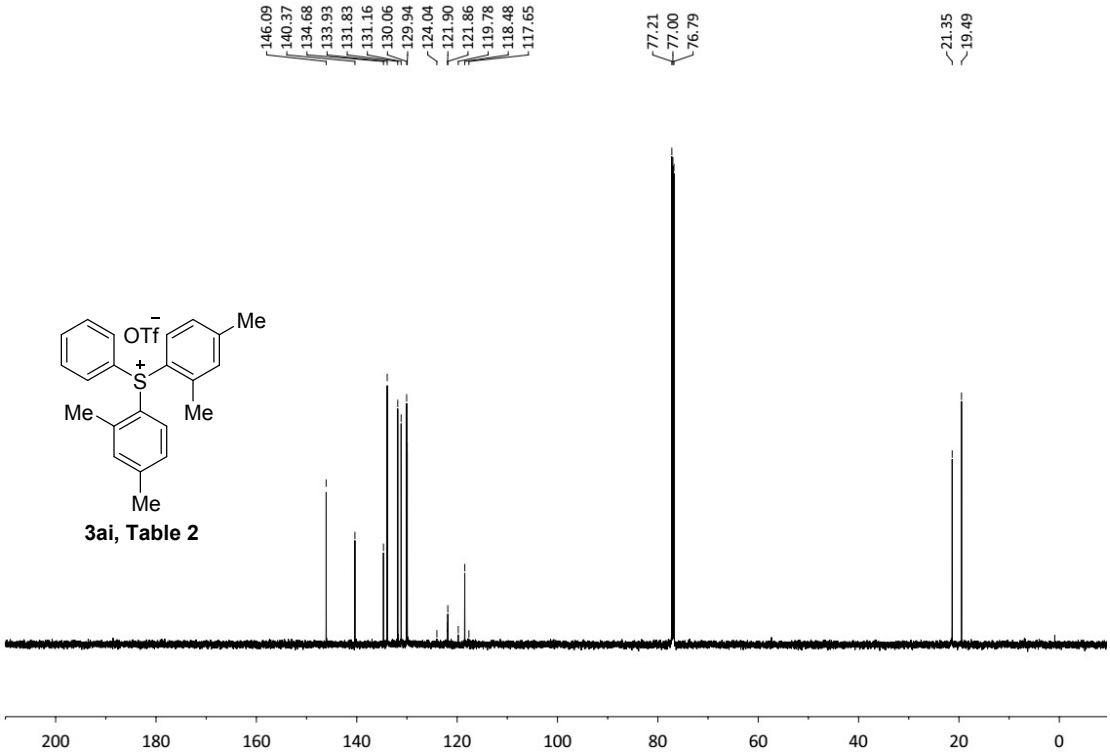


3ai, Table 2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121.86
119.78
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117.65
77.21
77.00
76.79
21.35
19.49
OTf
Me
Me
Me
Me
3ai, Table 2
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180
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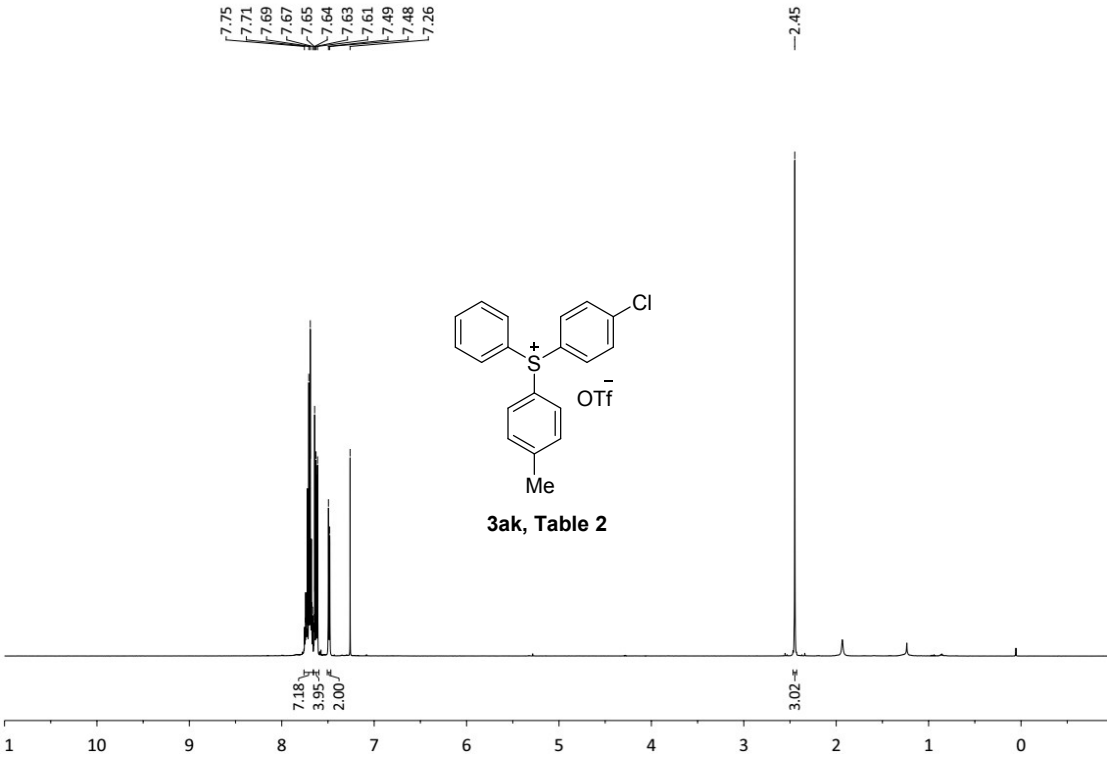
140
120
100
80
60
40
20
0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7.71
7.69
7.67
7.65
7.64
7.63
7.61
7.49
7.48
7.26
2.45
Cl
OTf
Me
3ak, Table 2
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2.00
3.02
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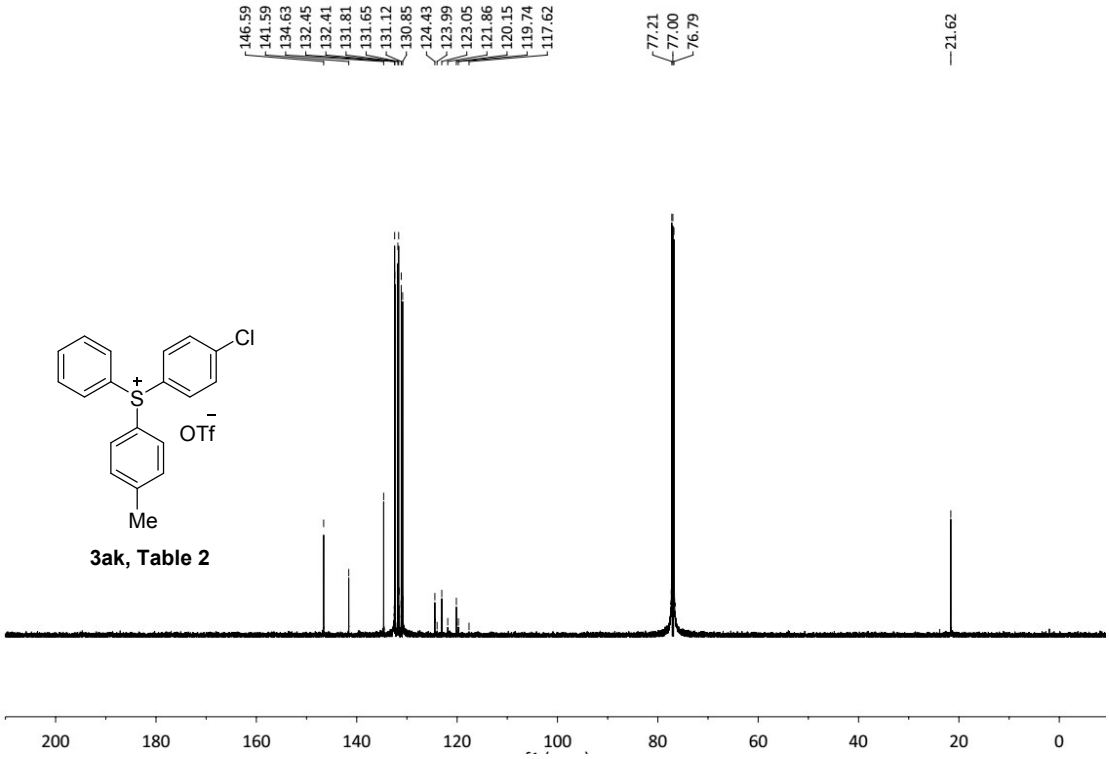
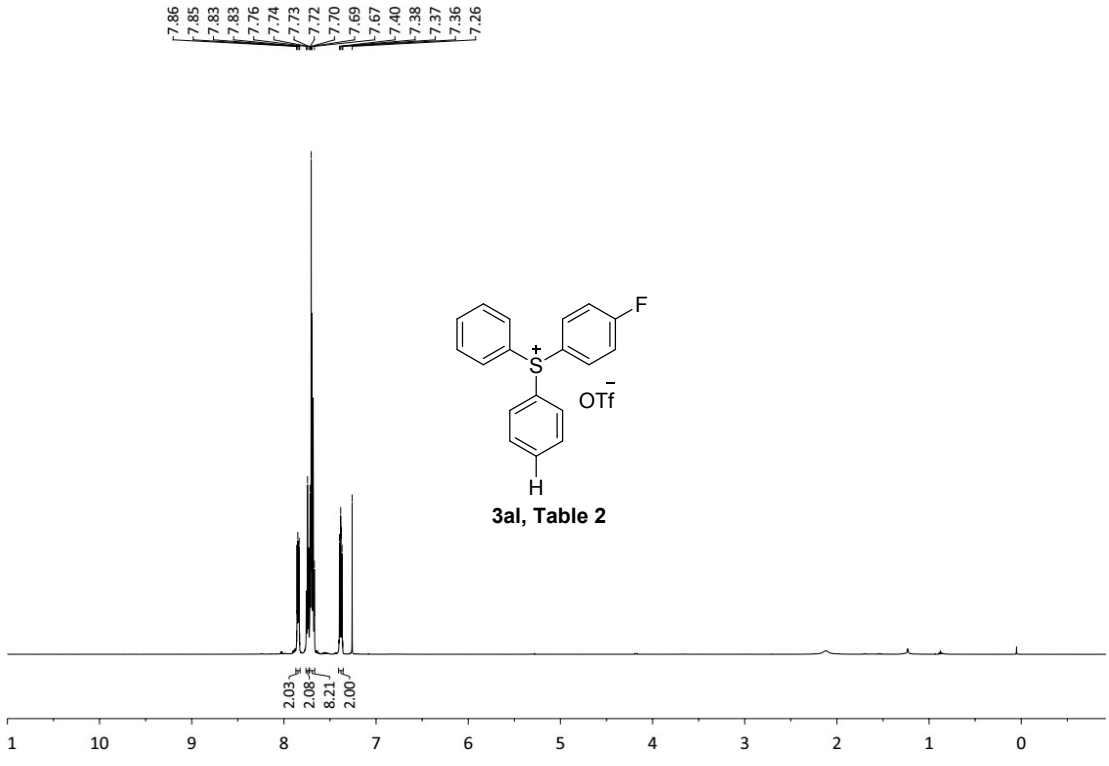
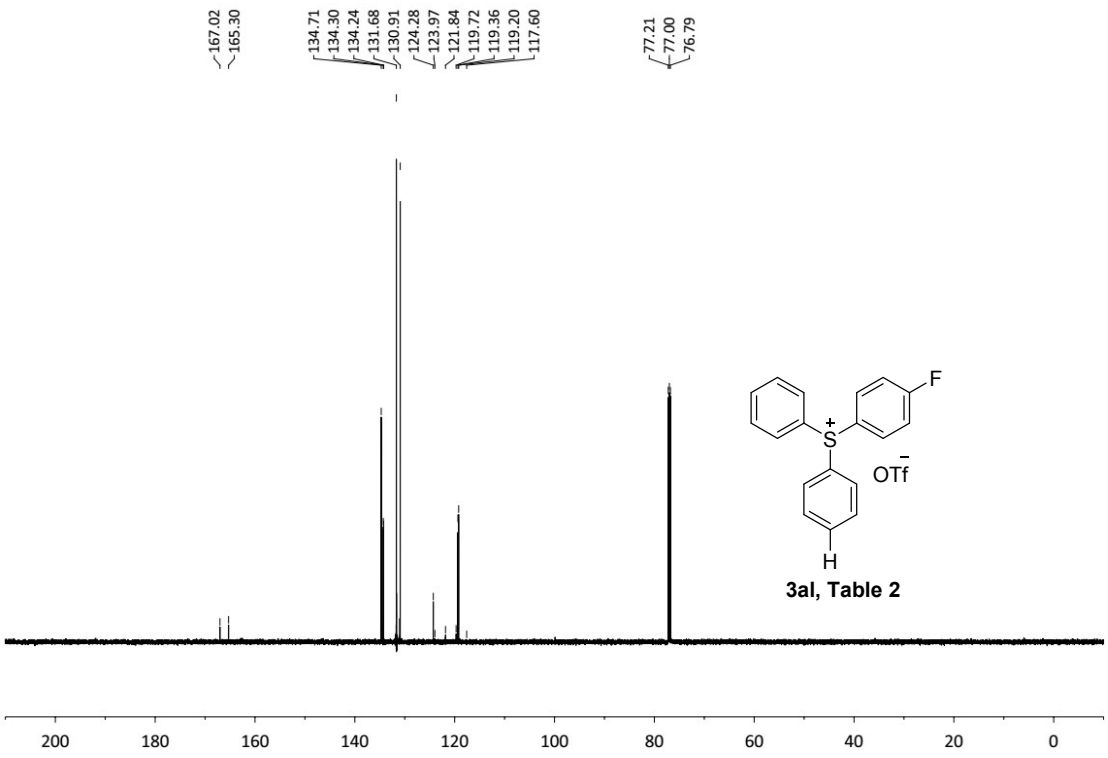
9
8
7
6
5
4
3
2
1
0



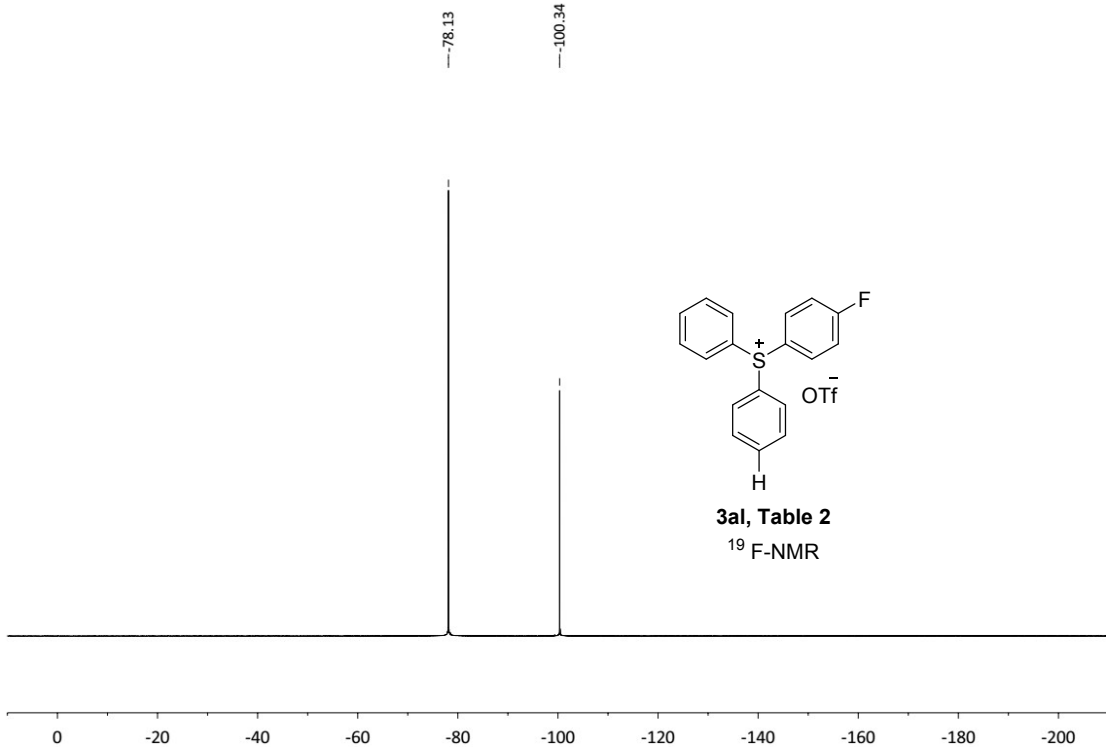
3ak, Table 2



3al, Table 2

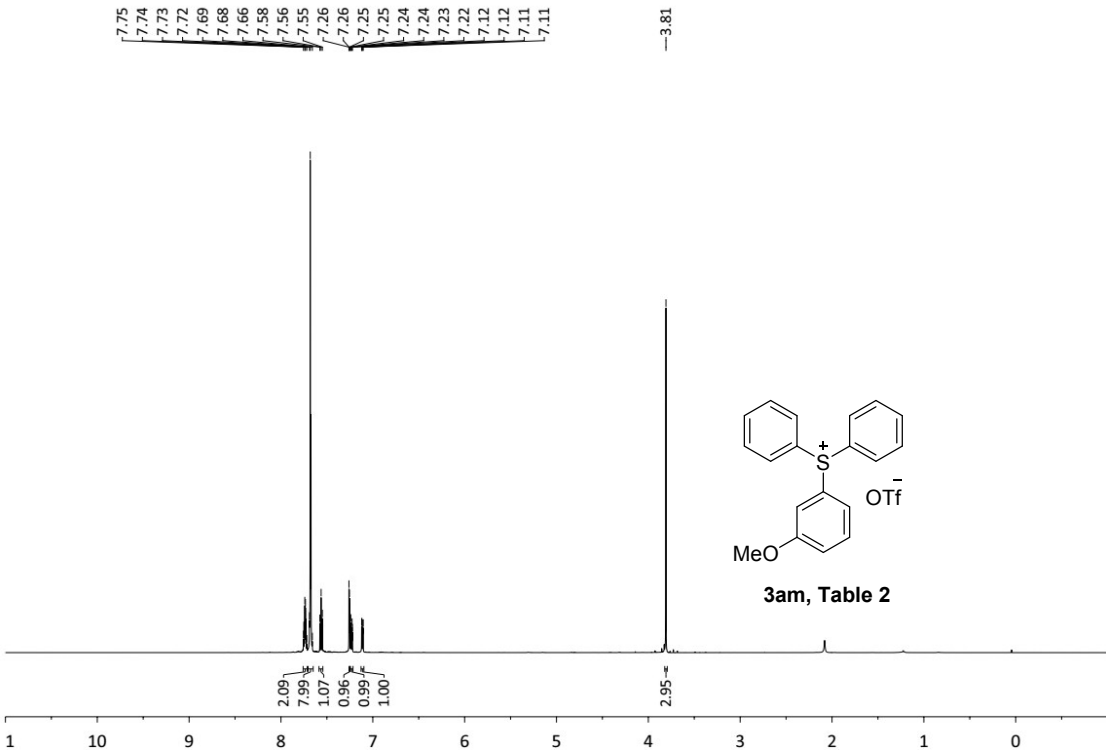


3al, Table 2

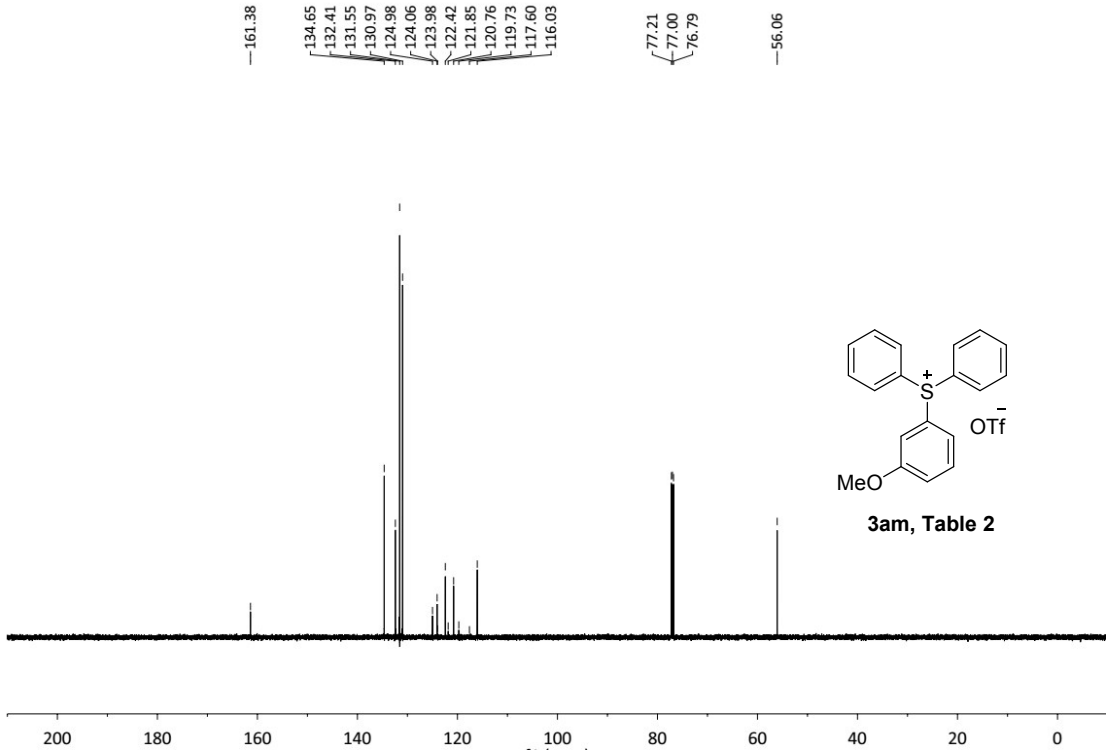


3al, Table 2

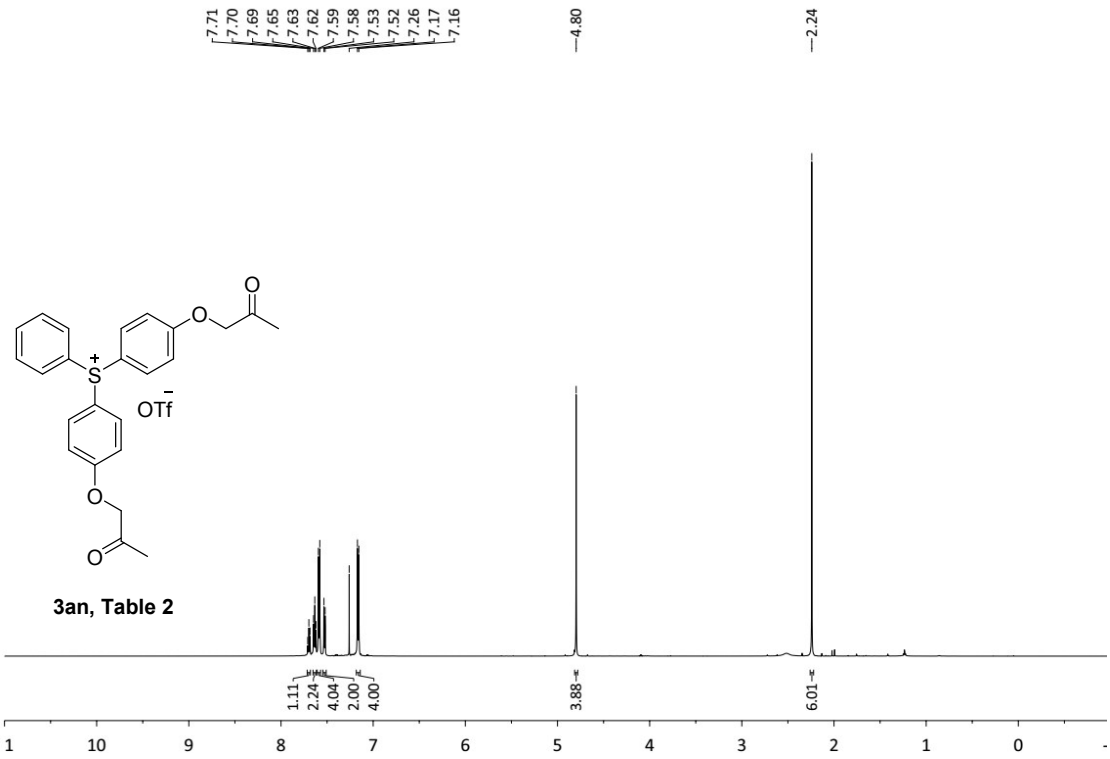
^{19}F-NMR



3am, Table 2



3am, Table 2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7.62
7.59
7.58
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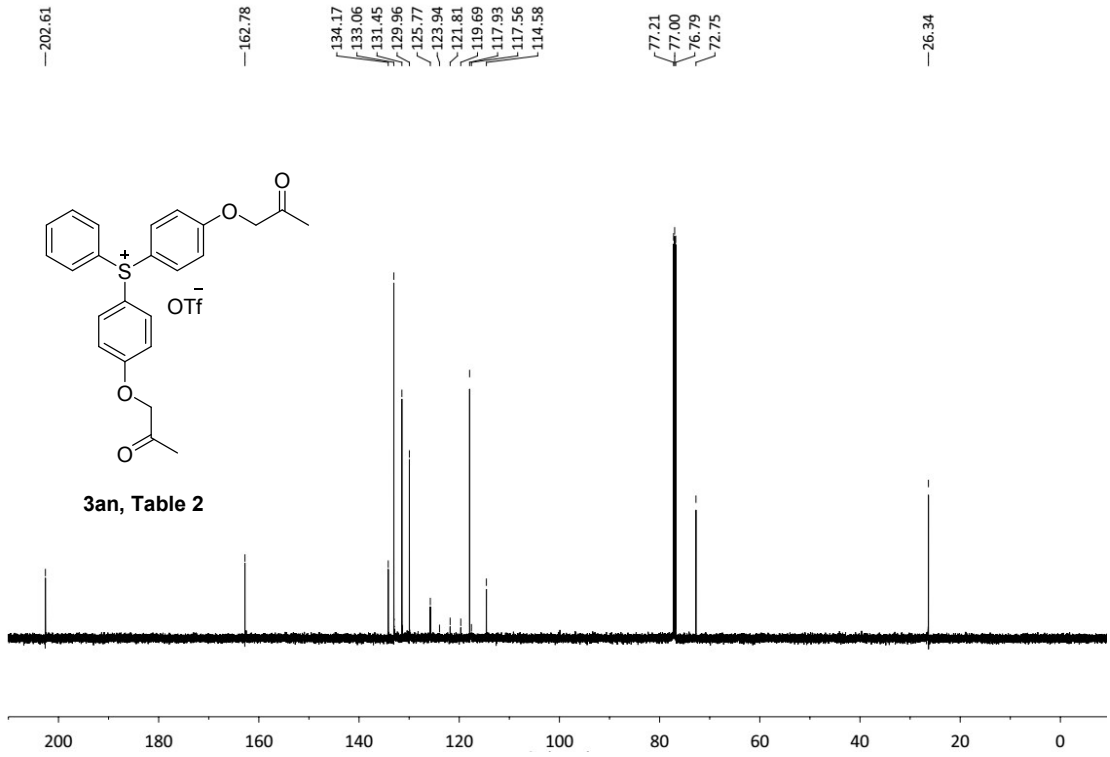
7.52
7.26
7.17
7.16
4.80
2.24
O
O
S
+
OTf
−
O
O
3an, Table 2
1.11
2.24
4.04
2.00
4.00
3.88
6.01
1
10
9
8
7
6
5
4
3
2
1
0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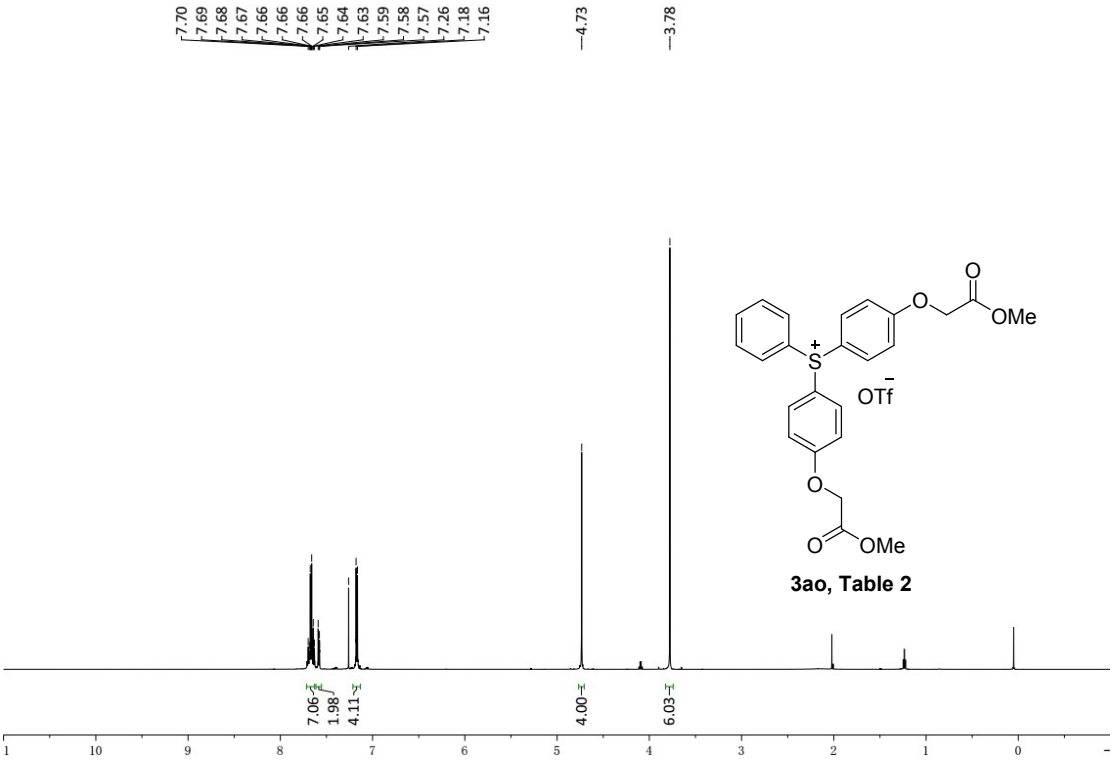
123.94
121.81
119.69
117.93
117.56
114.58
77.21
77.00
76.79
72.75
26.34
O
O
S
+
OTf
−
O
O
3an, Table 2
200
180
160
140
120
100
80
60
40
20
0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7.67
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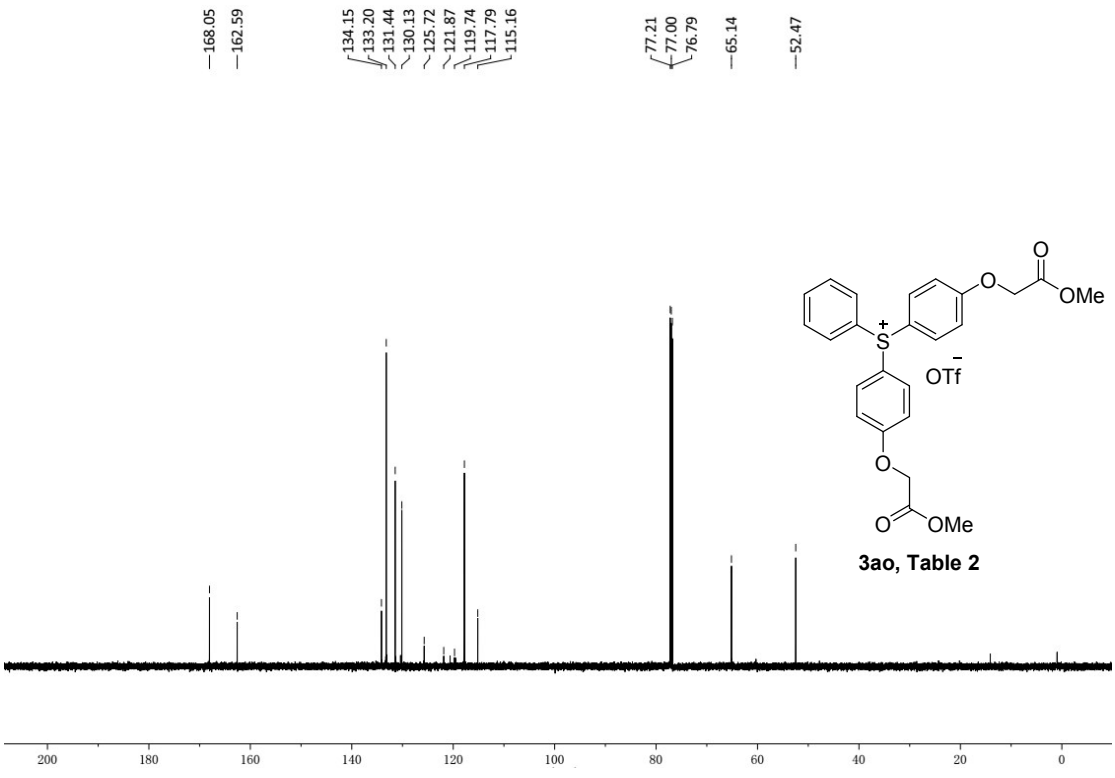
7.66
7.66
7.65
7.64
7.63
7.59
7.58
7.57
7.26
7.18
7.16
4.73
3.78
7.06
1.98
4.11
4.00
6.03
3ao, Table 2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133.20
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117.79
115.16
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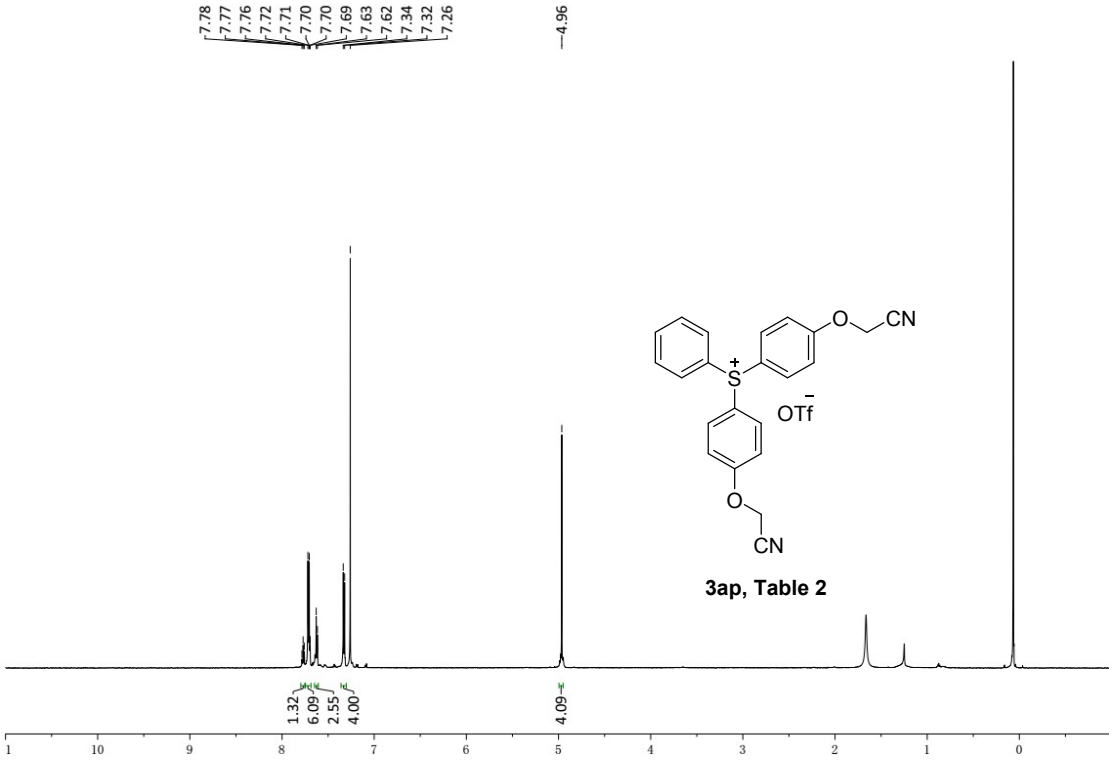
77.00
76.79
65.14
52.47
3ao, Table 2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7.76
7.72
7.71
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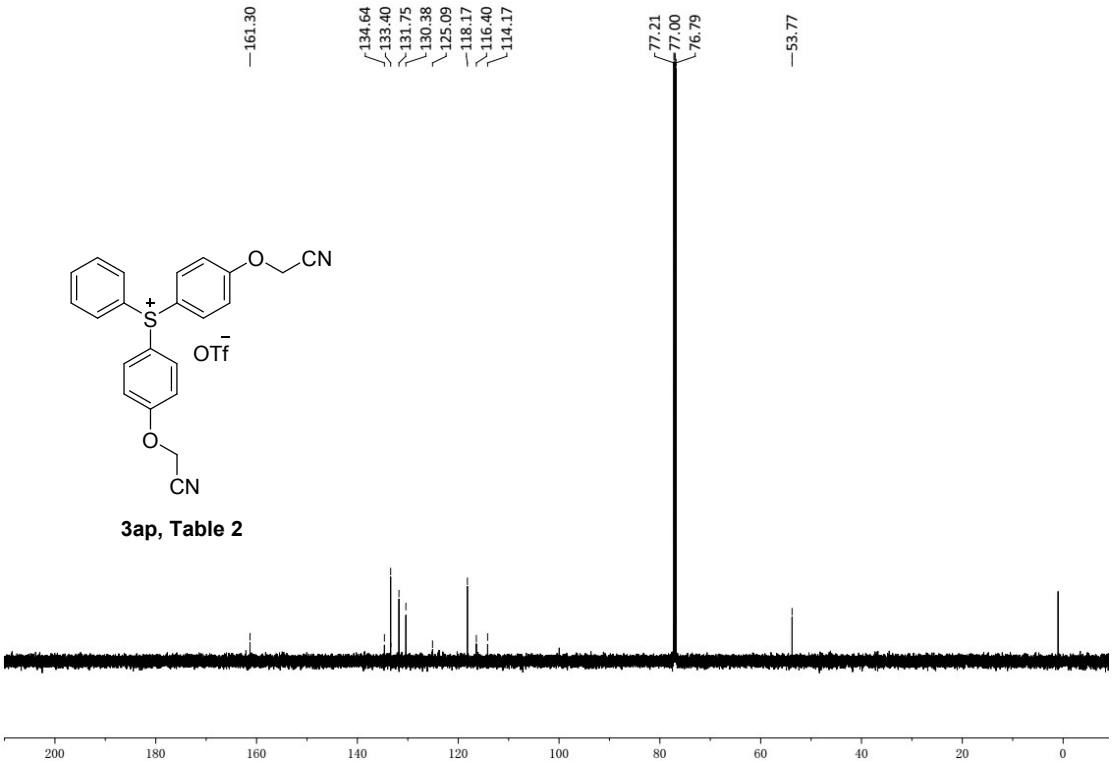
7.70
7.69
7.63
7.62
7.34
7.32
7.26
4.96
1.32
6.09
2.55
4.00
4.09
O
CN
S
OTf
O
CN
3ap, Table 2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125.09
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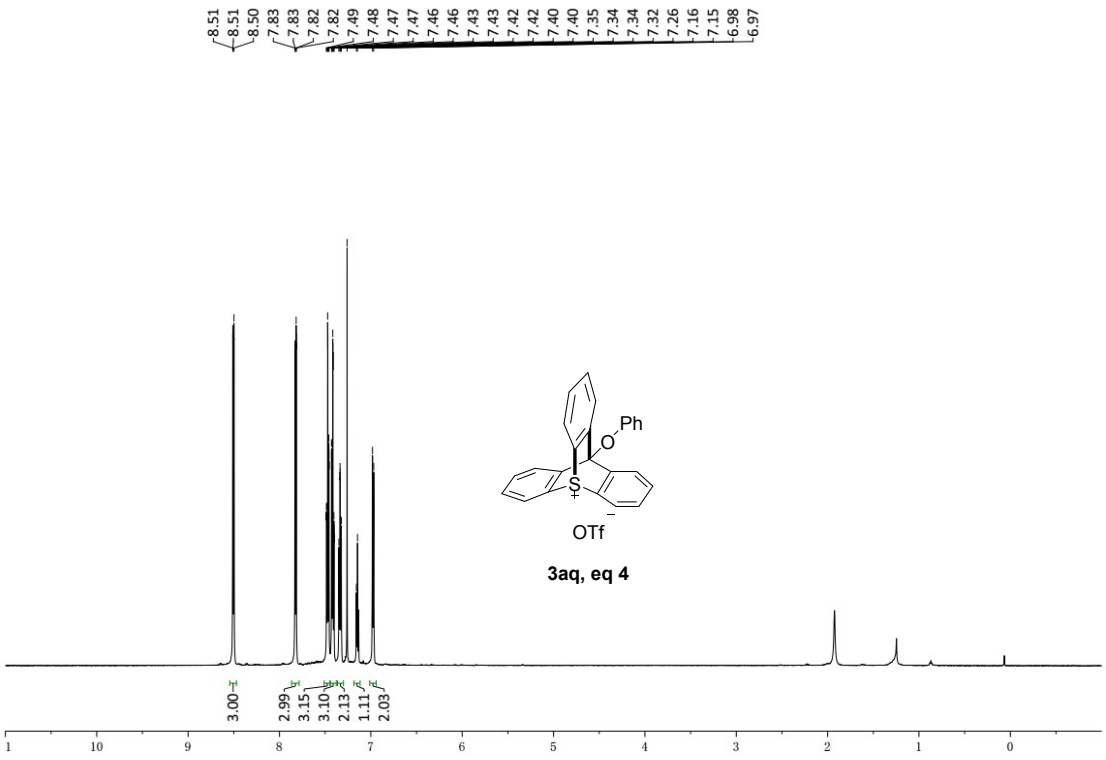
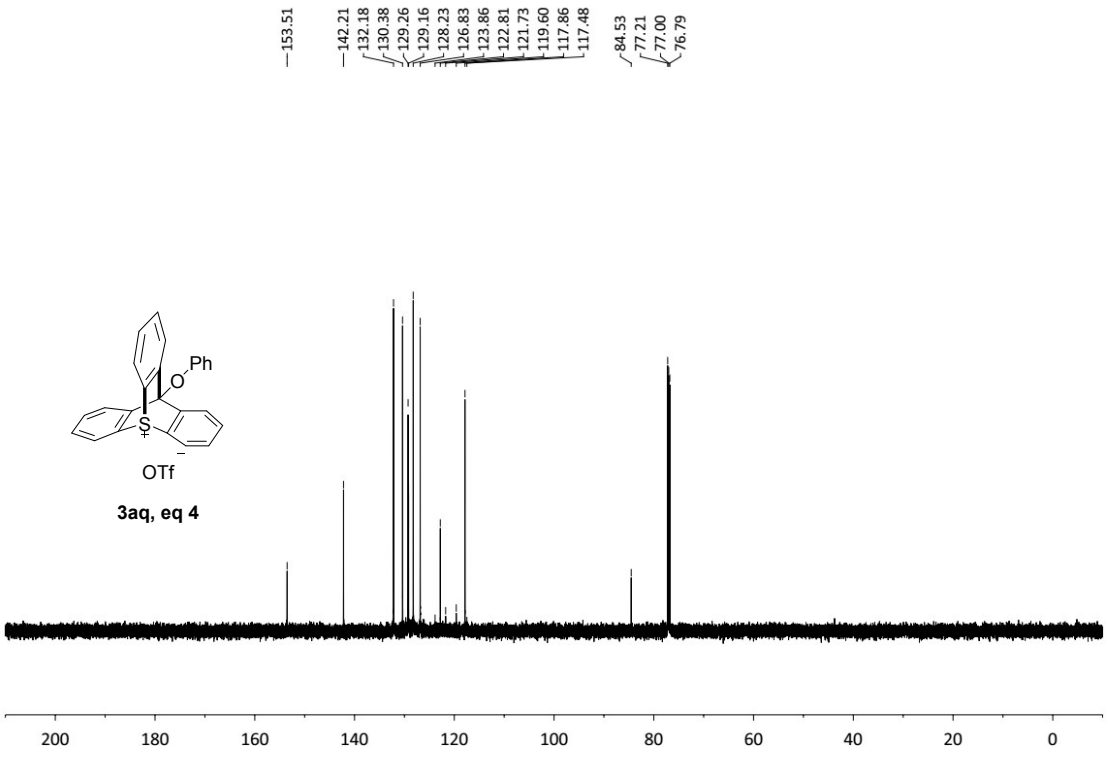
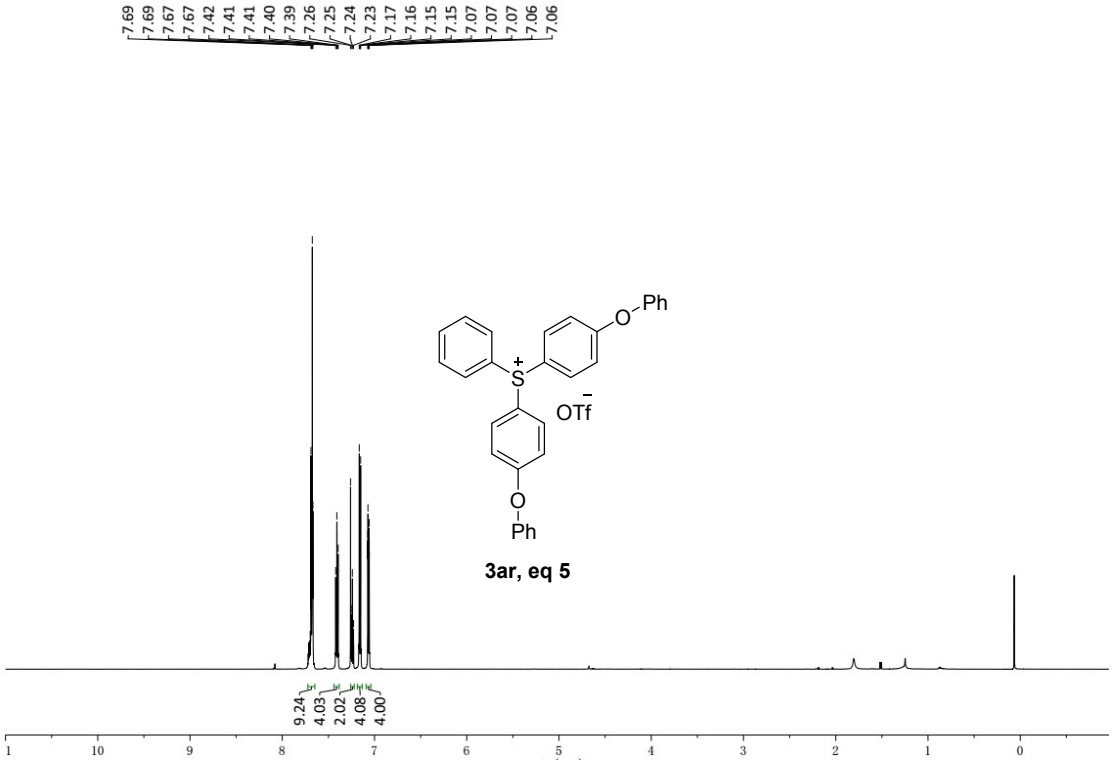
76.79
53.77
O
CN
S
OTf
O
CN
3ap, Table 2



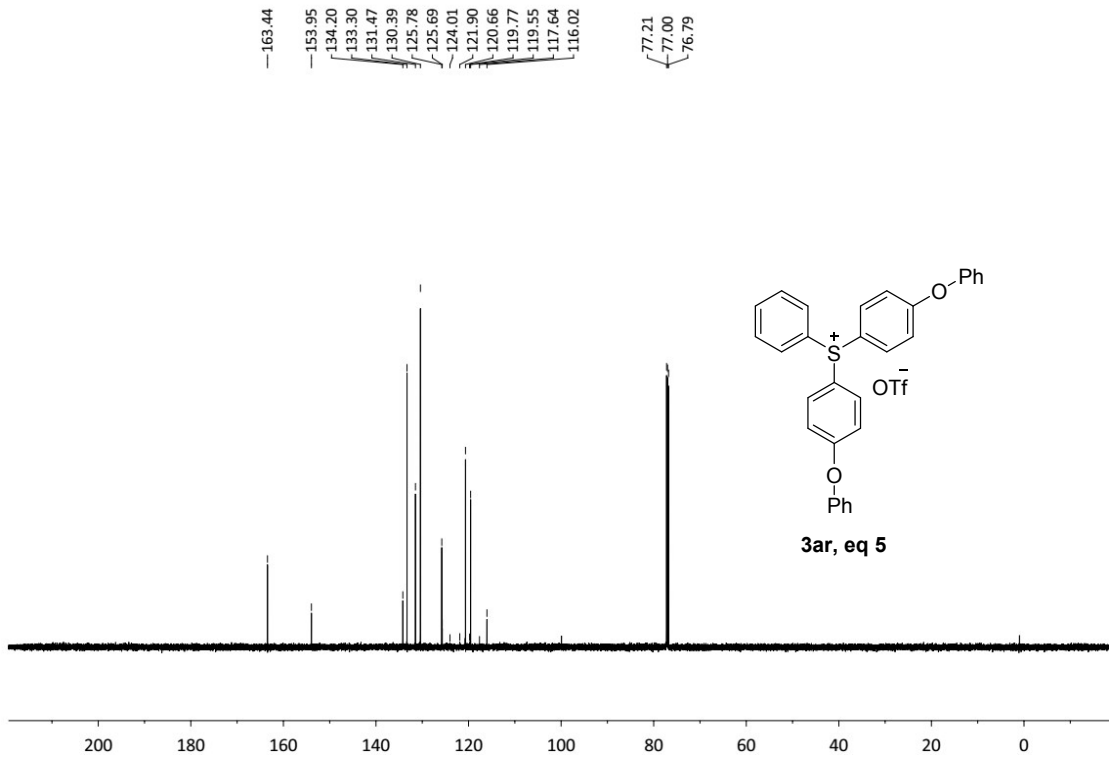
3aq, eq 4



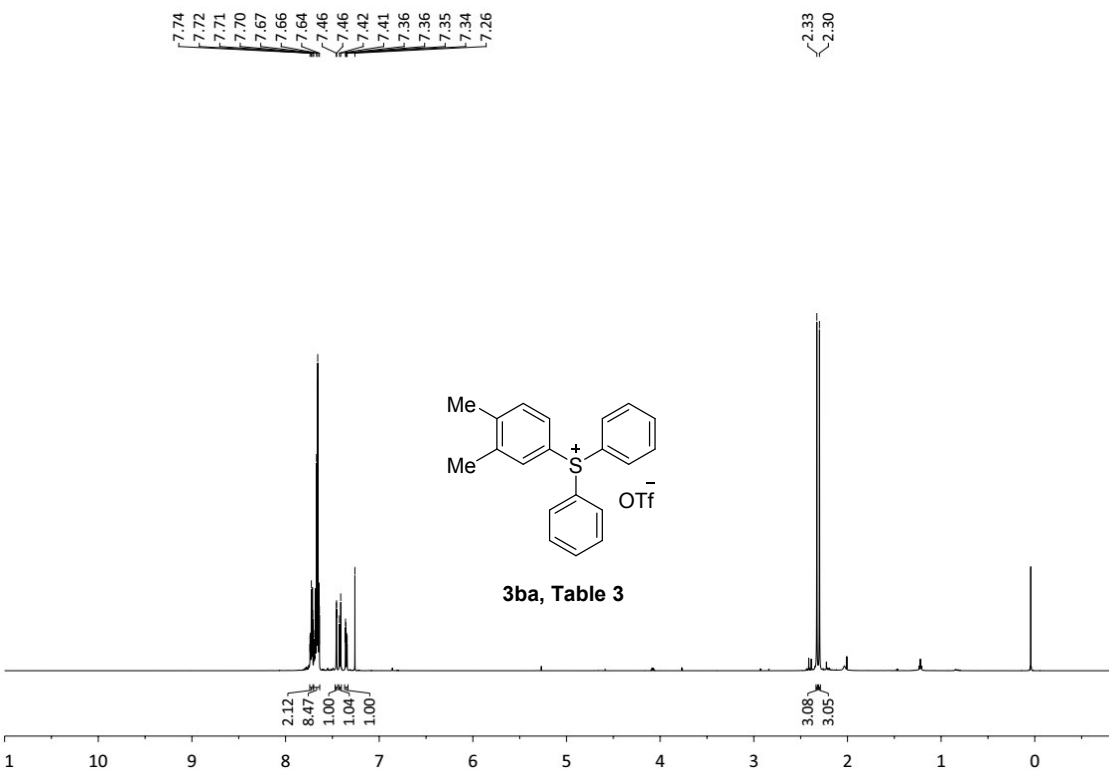
3aq, eq 4



3ar, eq 5



3ar, eq 5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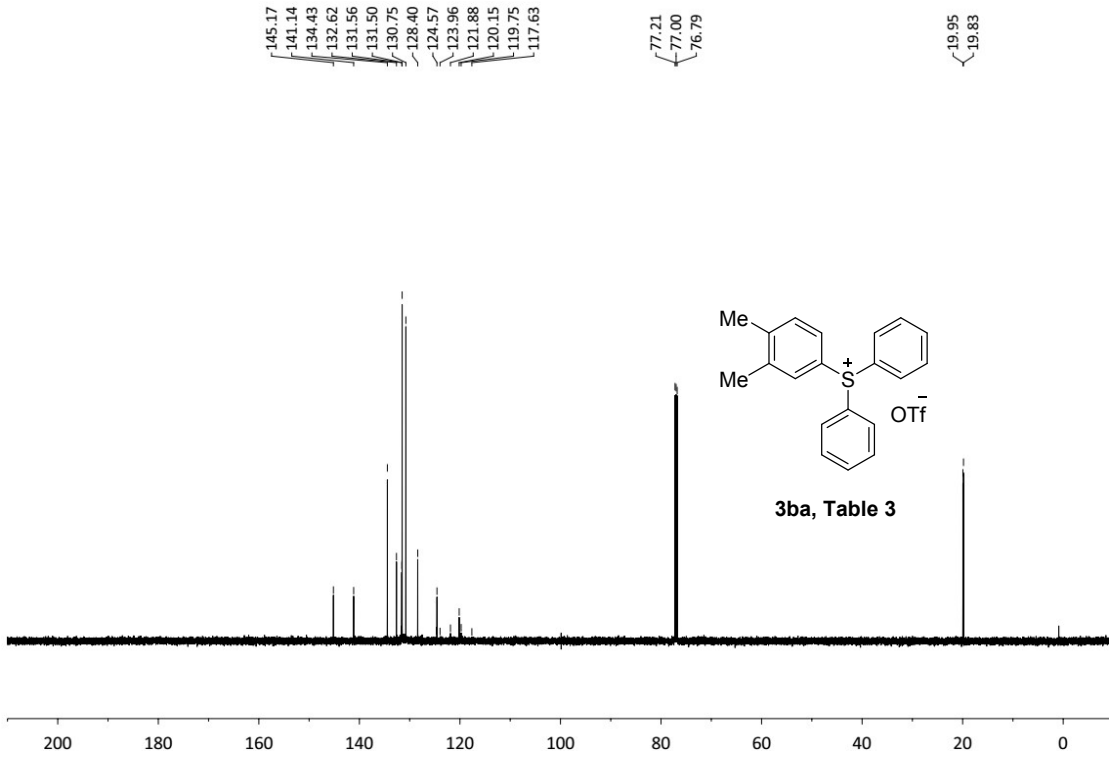
7.42
7.41
7.36
7.36
7.35
7.34
7.26
2.33
2.30
Me
Me
S
OTf
3ba, Table 3
2.12
8.47
1.00
1.04
1.00
3.08
3.05
1
10
9
8
7
6
5
4
3
2
1
0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128.40
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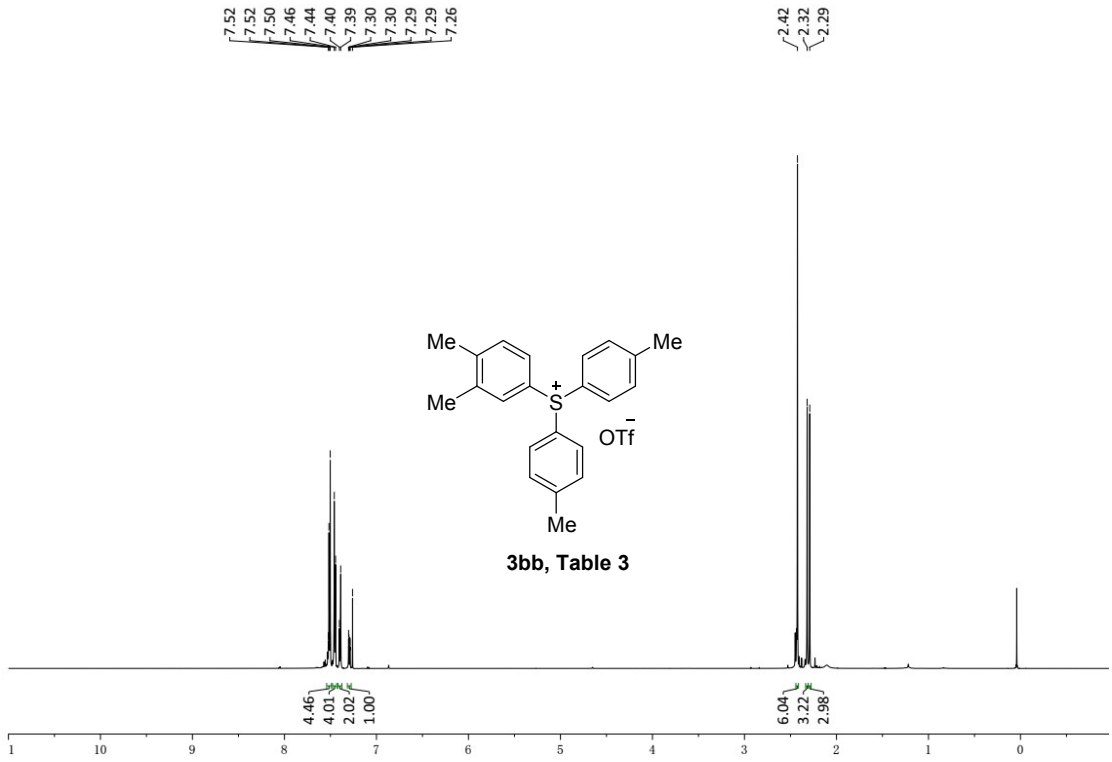
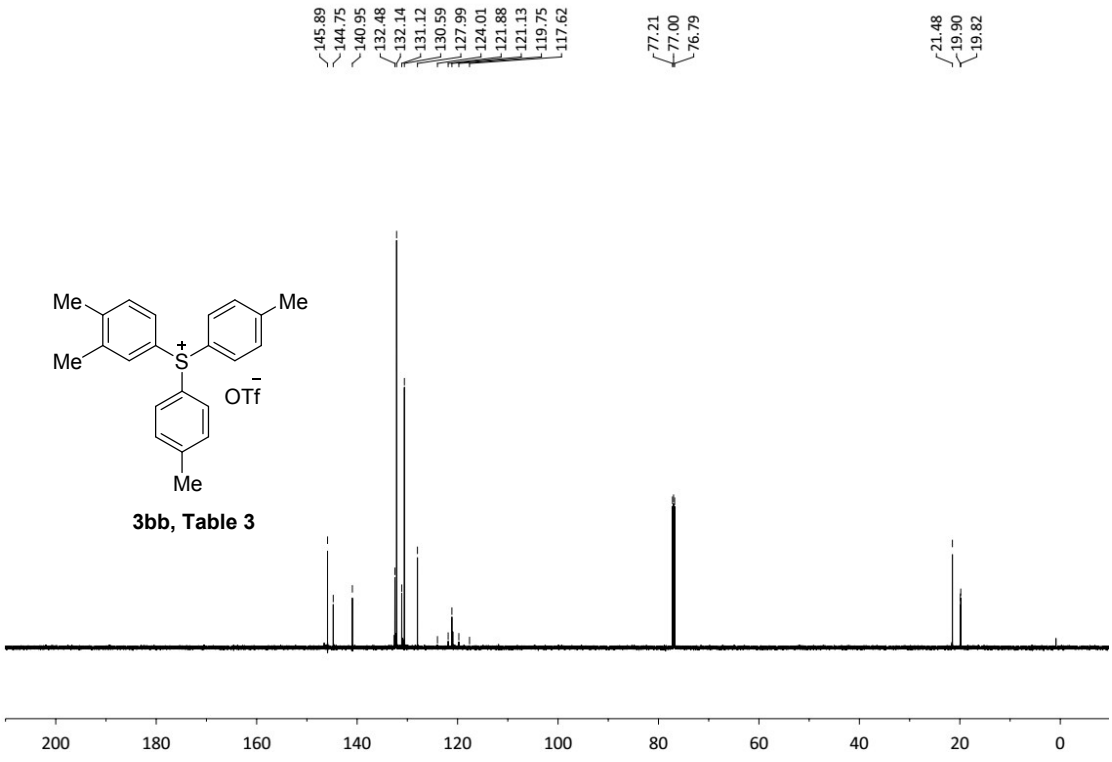
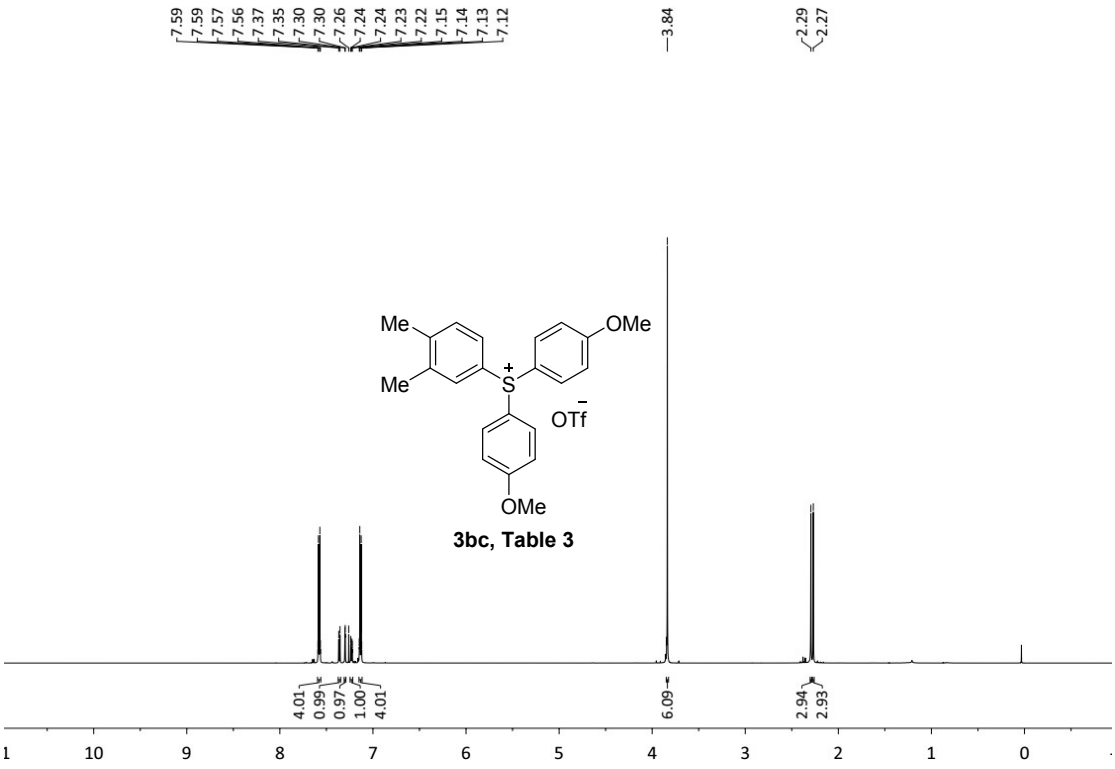
123.96
121.88
120.15
119.75
117.63
77.21
77.00
76.79
19.95
19.83
Me
Me
S
OTf
3ba, Table 3
200
180
160
140
120
100
80
60
40
20
0



3bb, Table 3



3bb, Table 3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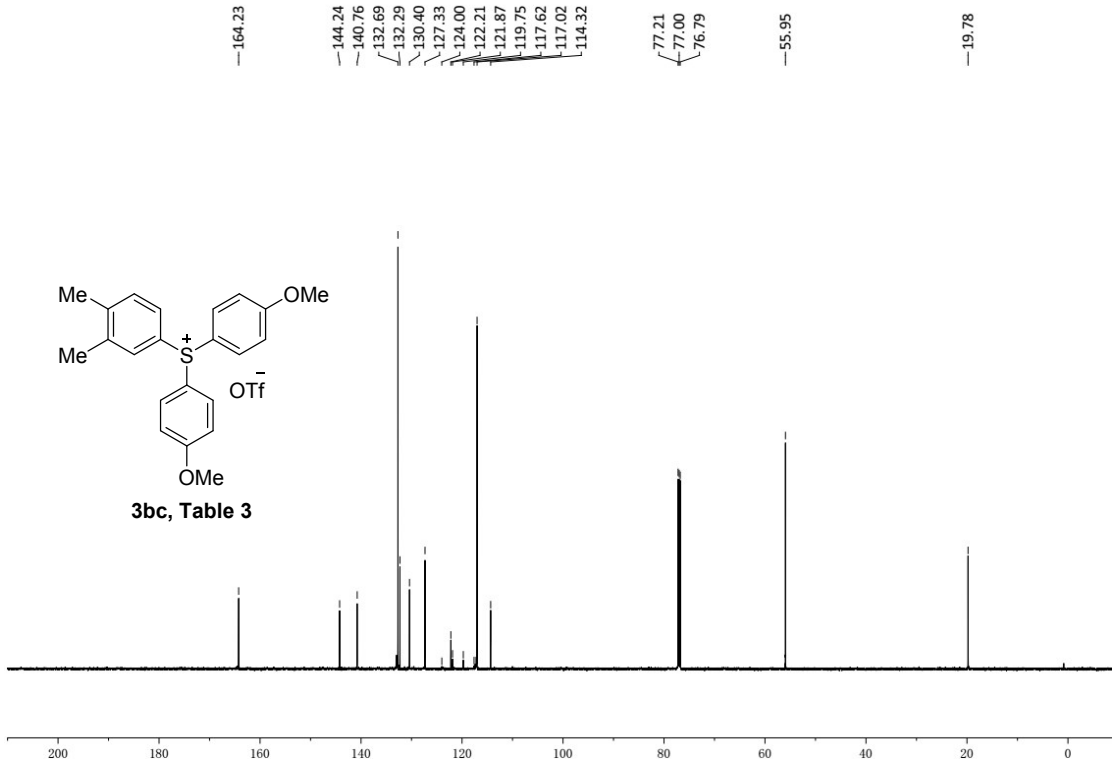
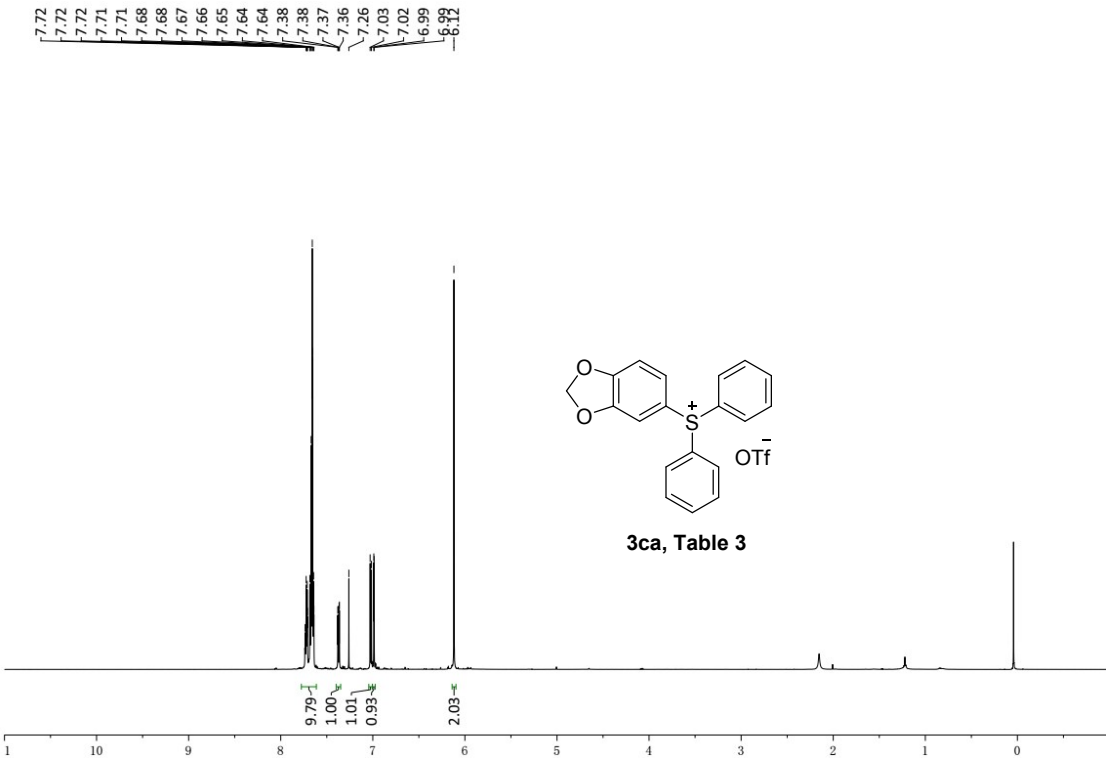
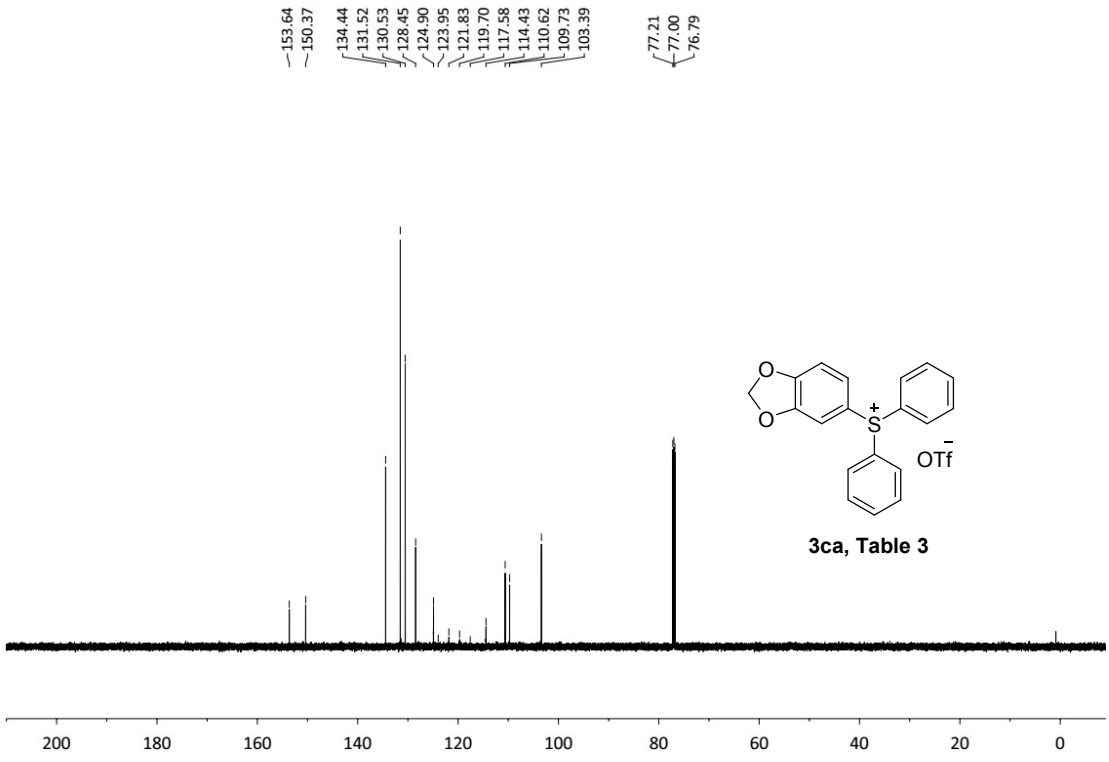
7.23
7.22
7.15
7.14
7.13
7.12
3.84
2.29
2.27
Me
Me
OMe
S
OTf
OMe
3bc, Table 3
4.01
0.99
0.97
1.00
4.01
6.09
2.94
2.93
1
10
9
8
7
6
5
4
3
2
1
0


164.23
144.24
140.76
132.69
132.29
130.40
127.33
124.00
122.21
121.87
119.75
117.62
117.02
114.32
77.21
77.00
76.79
55.95
19.78
Me
Me
OMe
S
OTf
OMe
3bc, Table 3
200
180
160
140
120
100
80
60
40
20
0



3ca, Table 3



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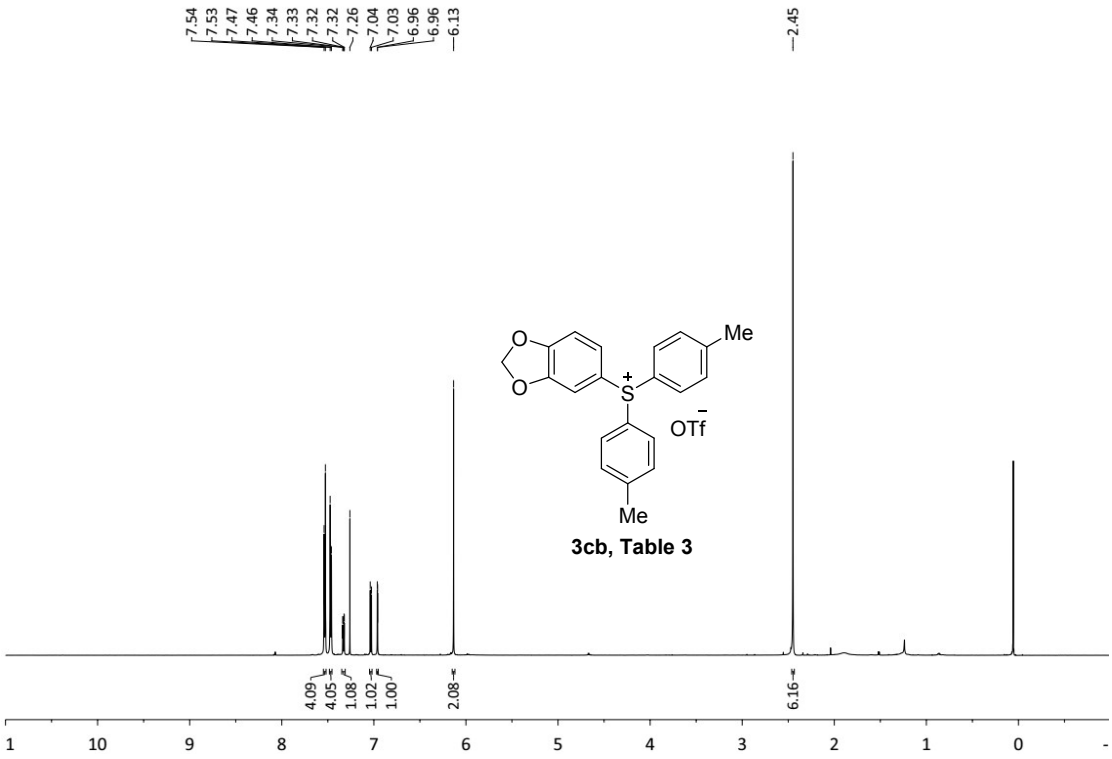

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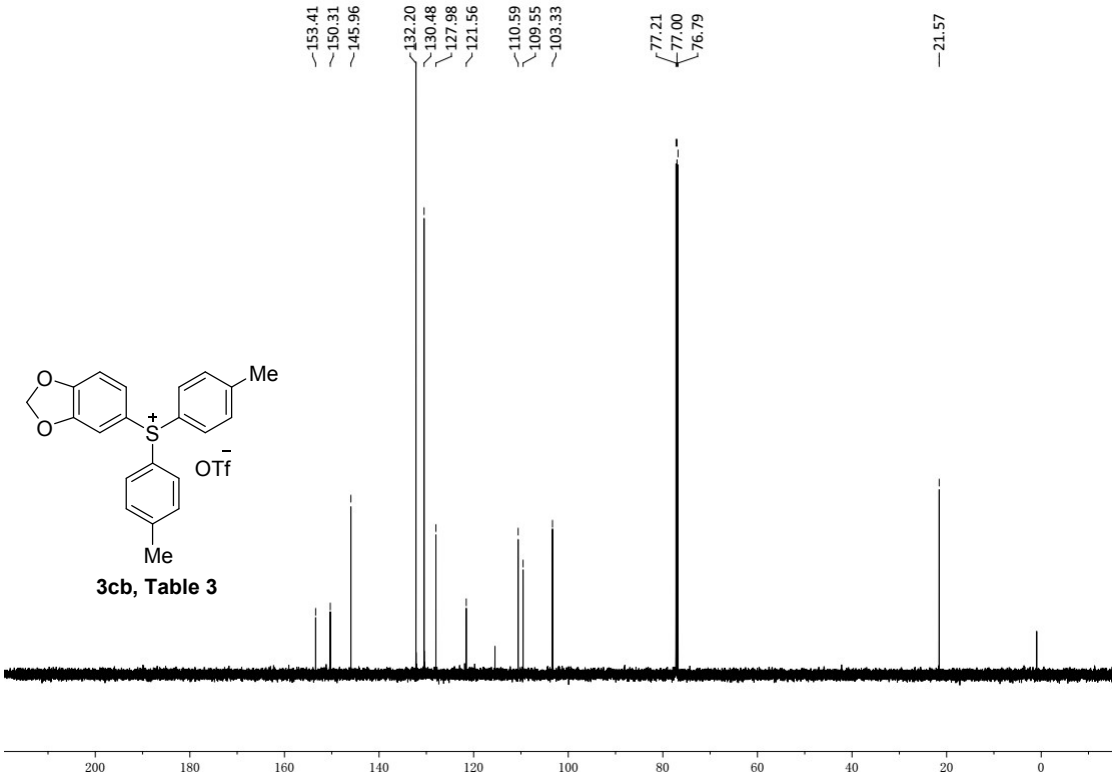

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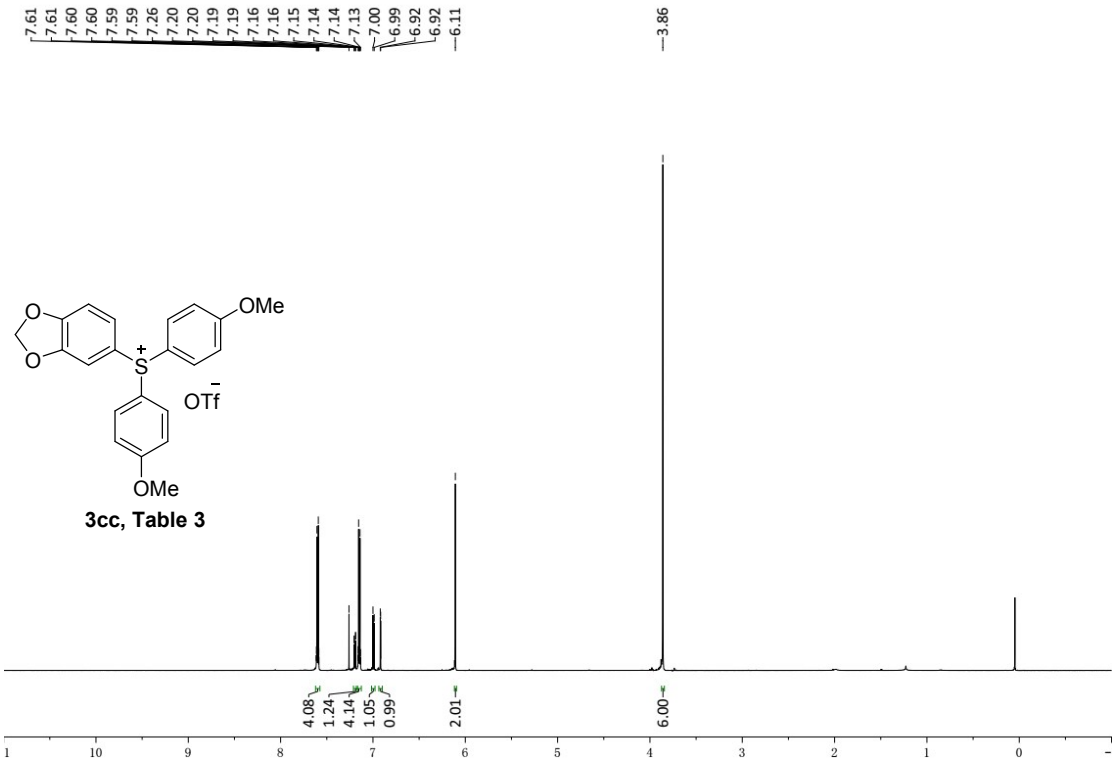

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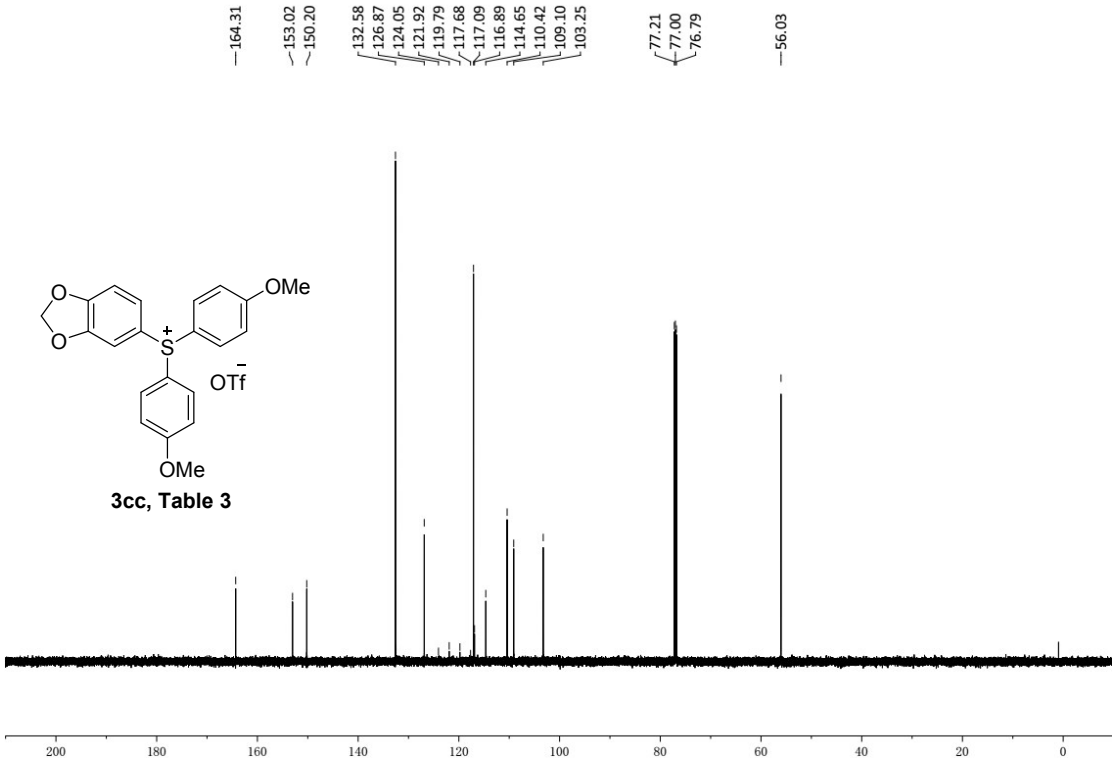

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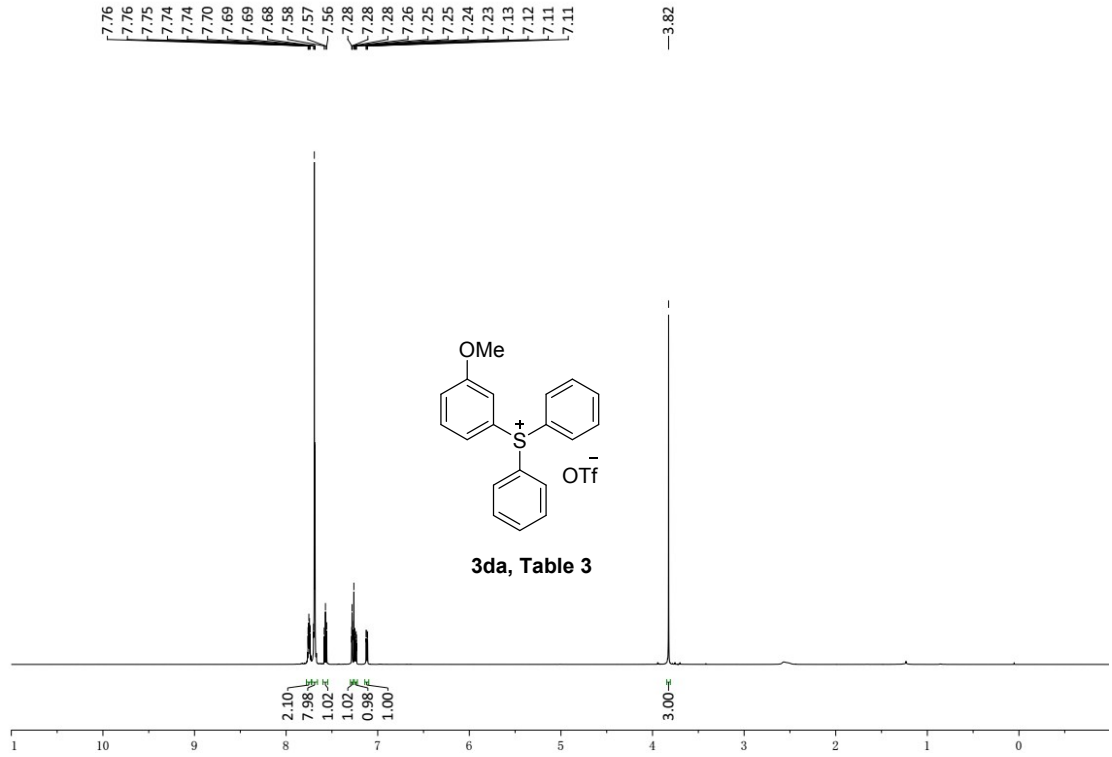

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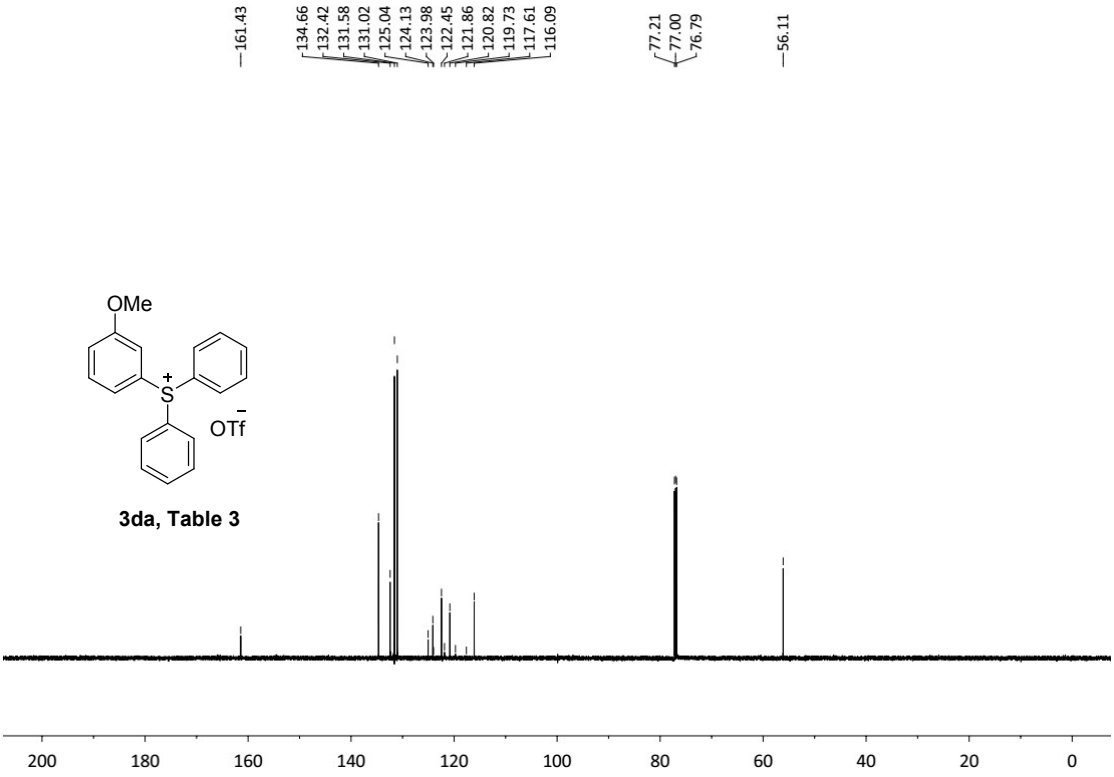

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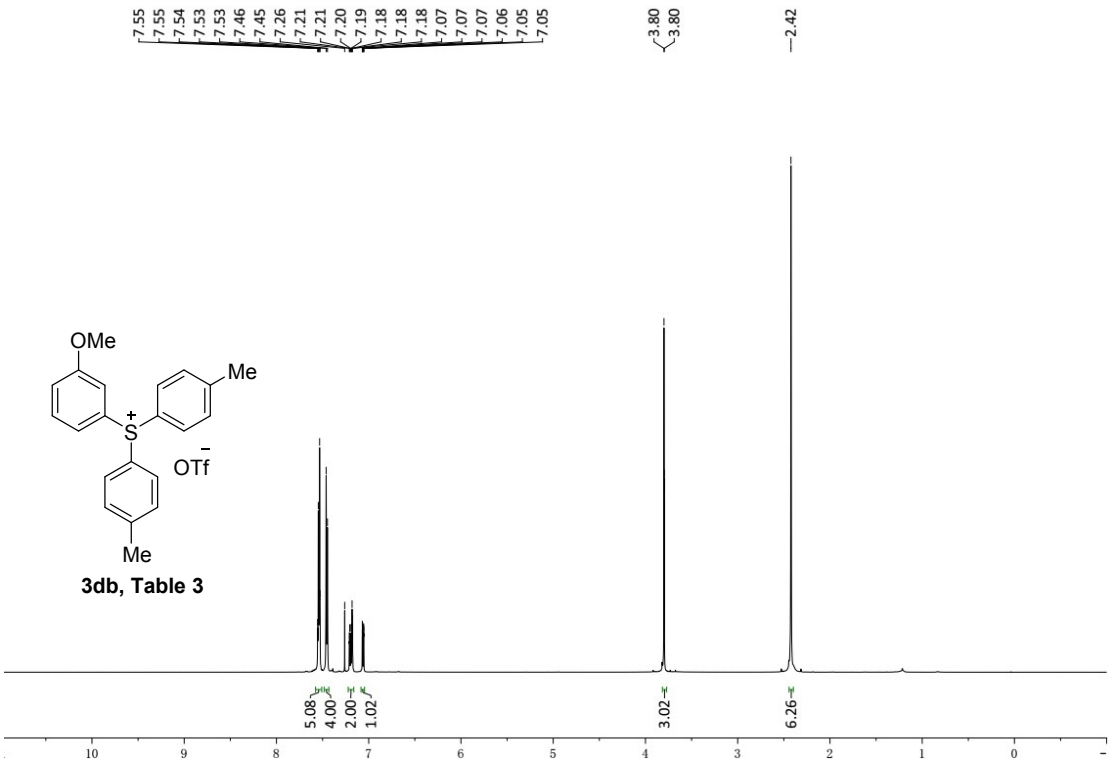

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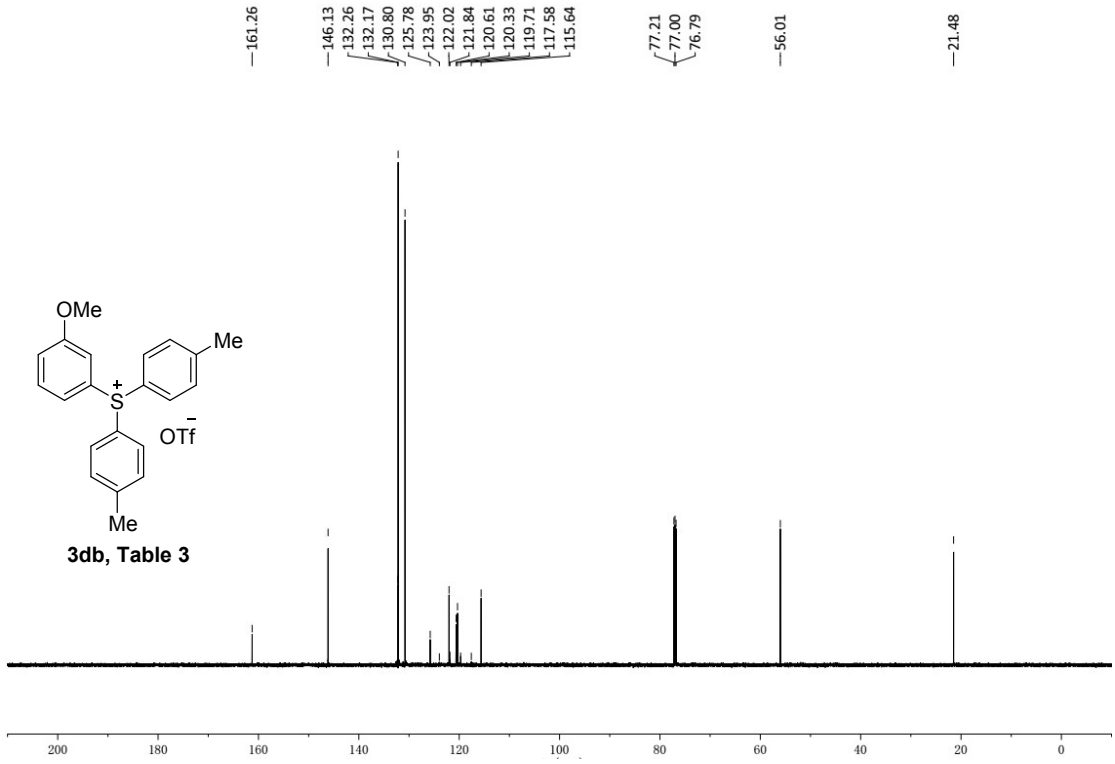

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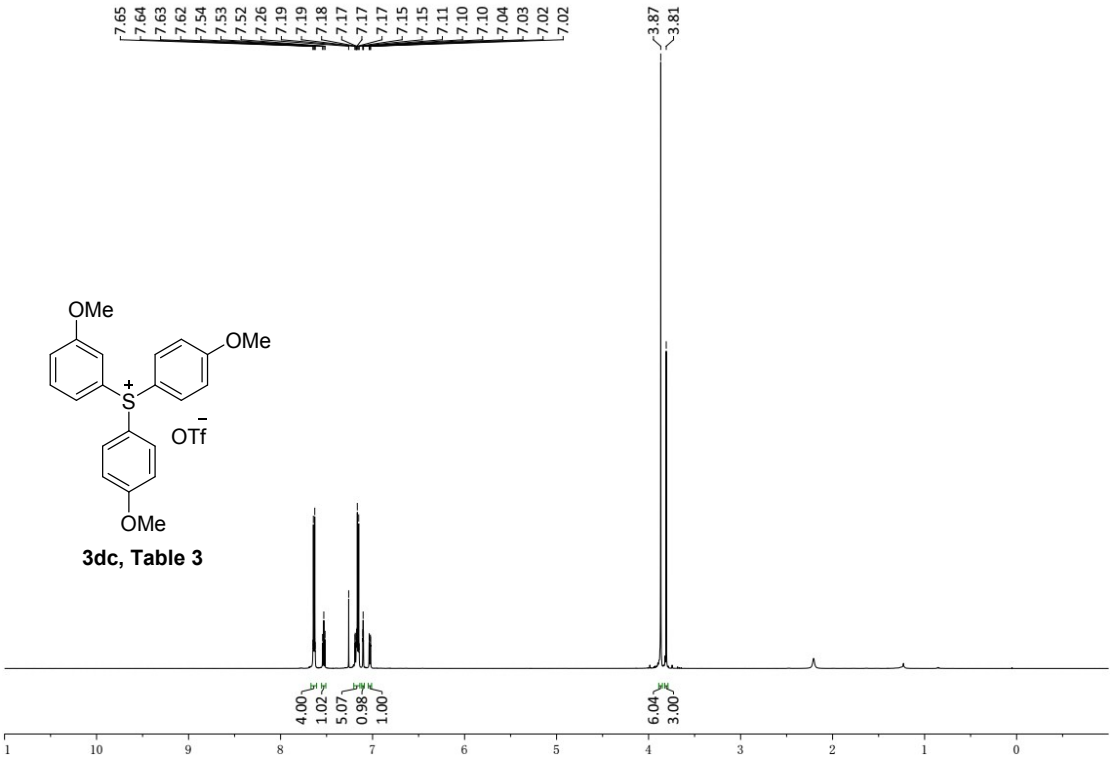

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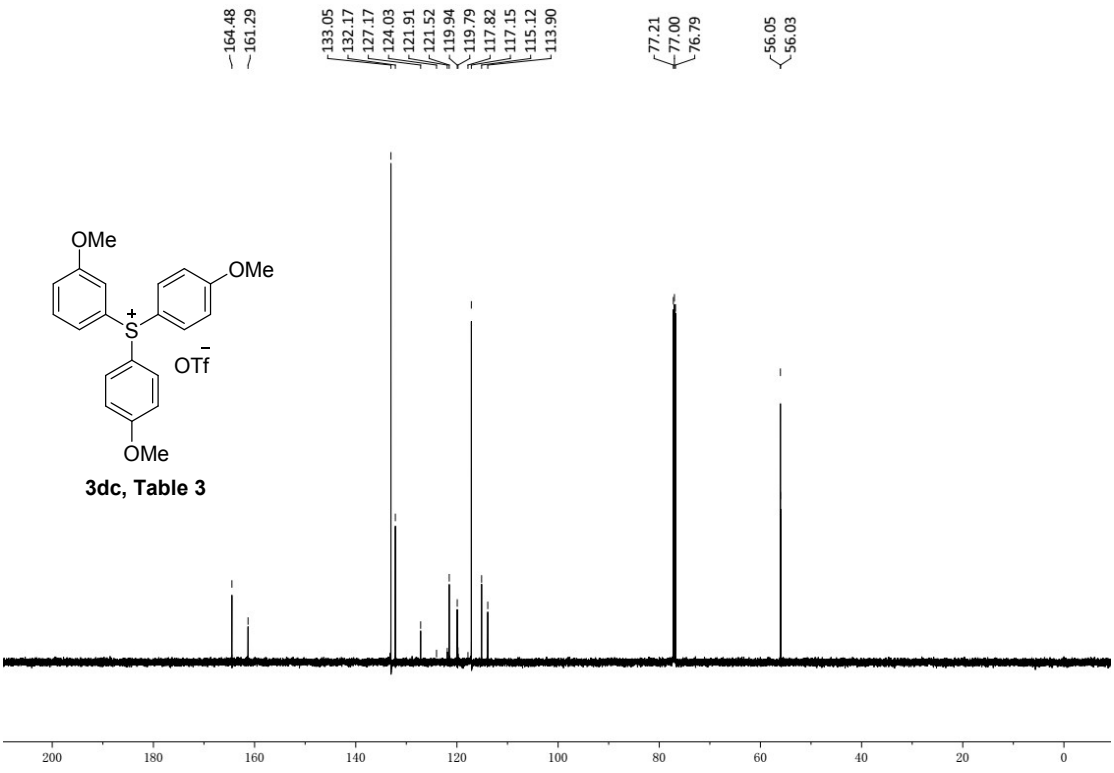

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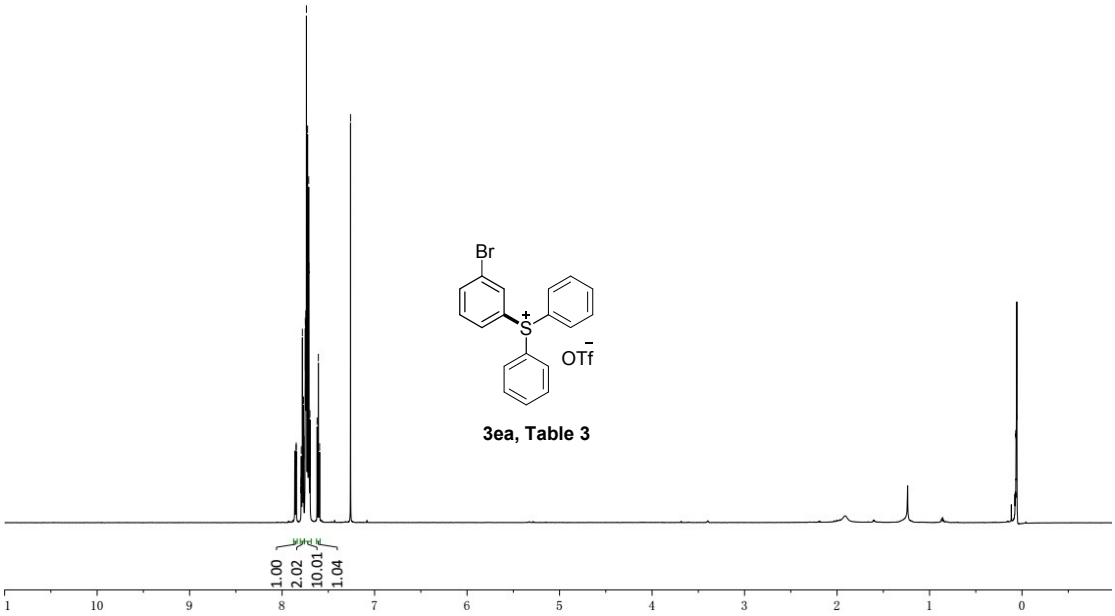

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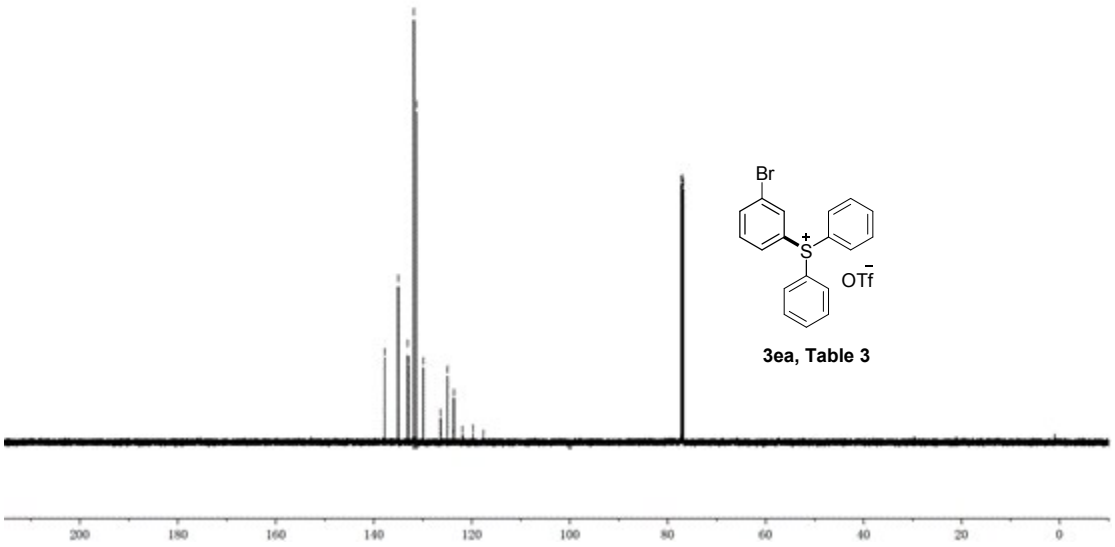

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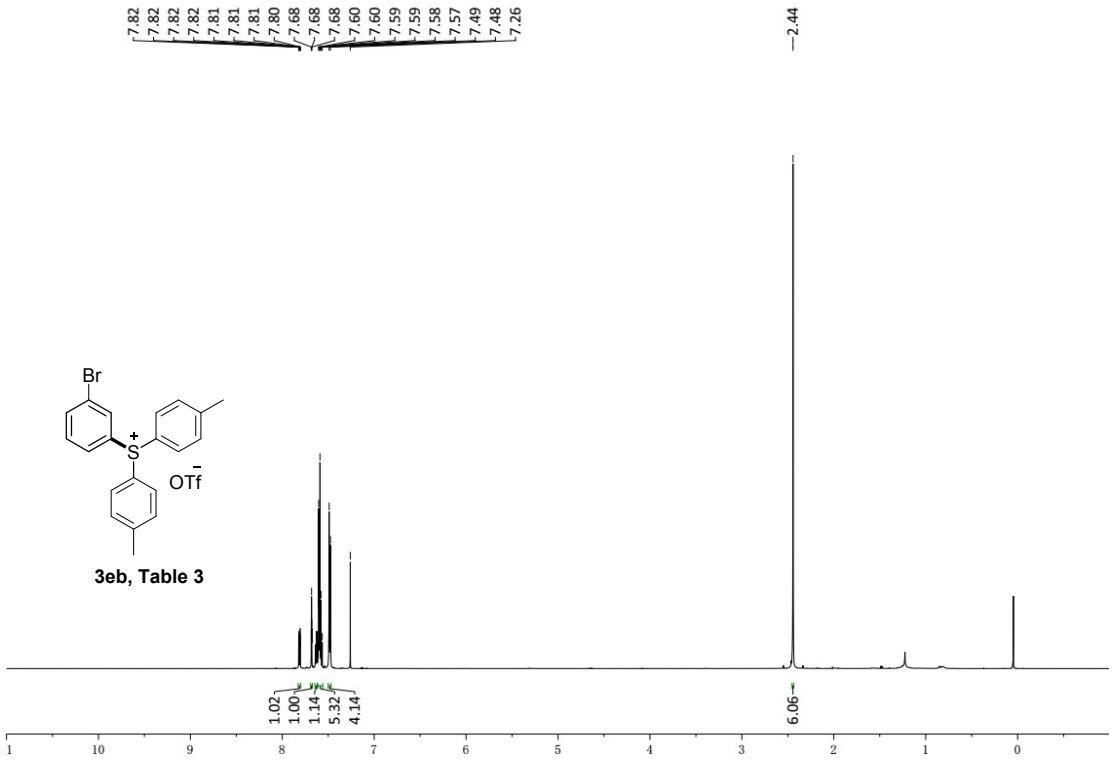

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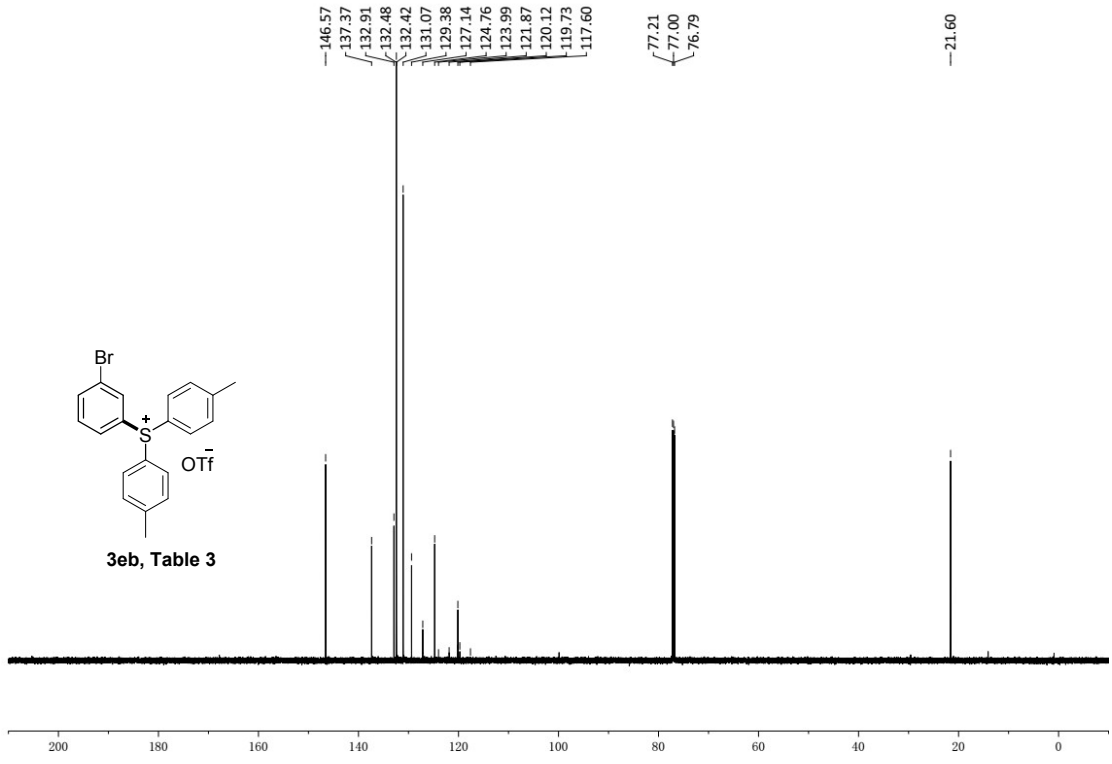

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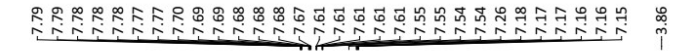

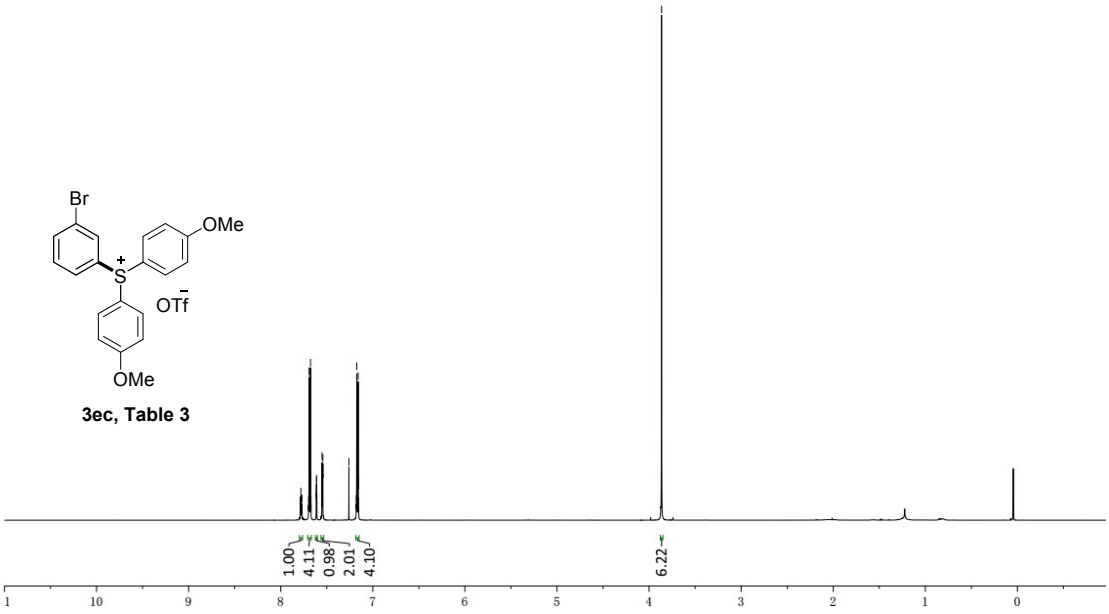

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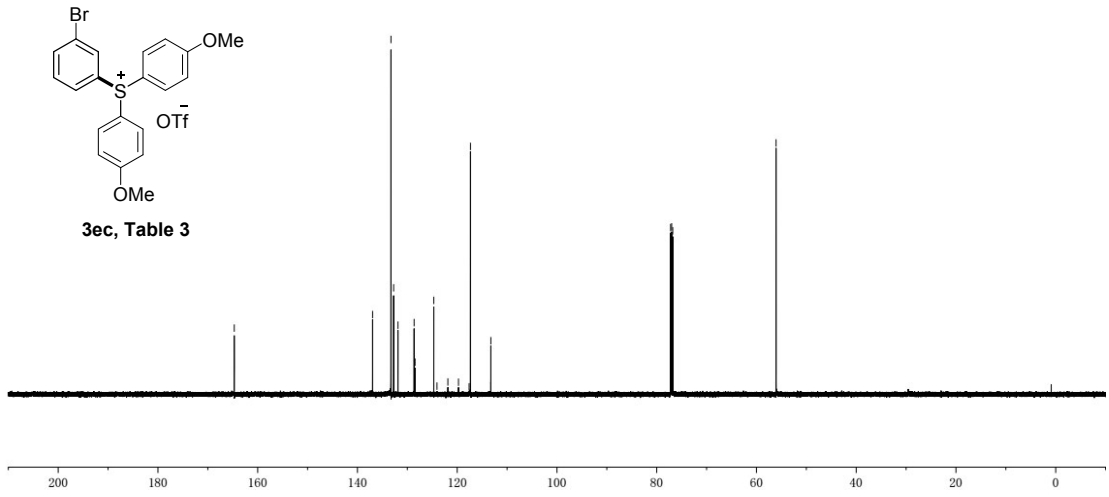

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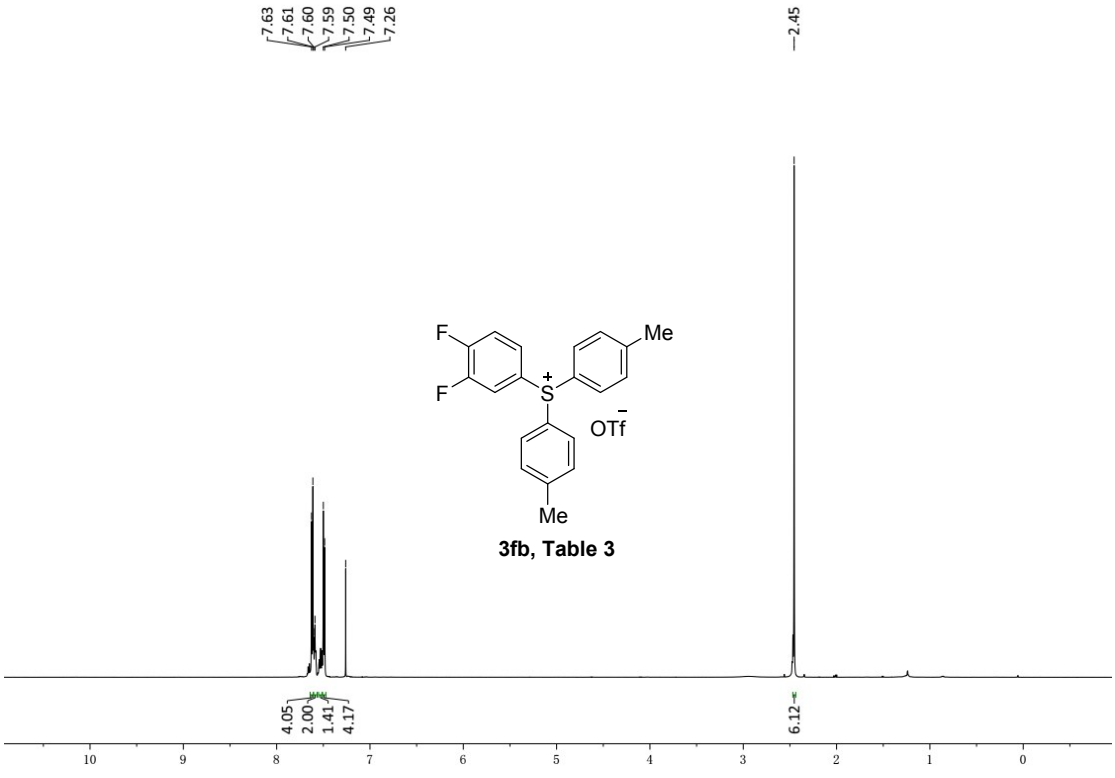

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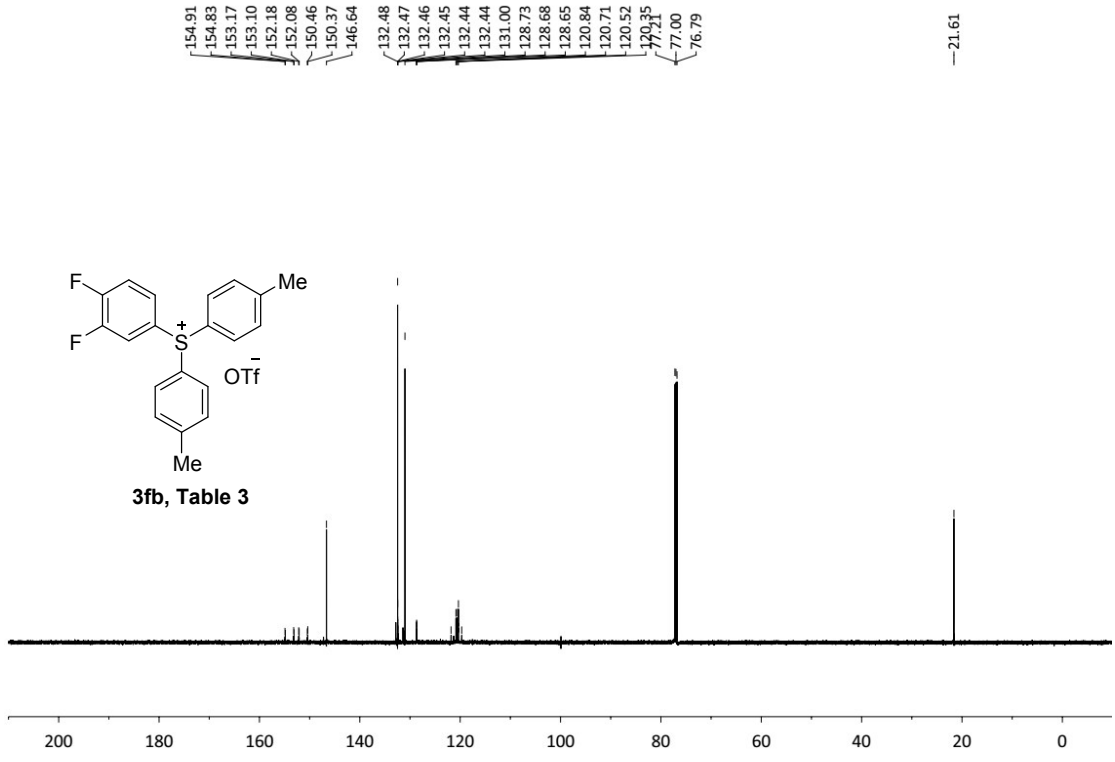

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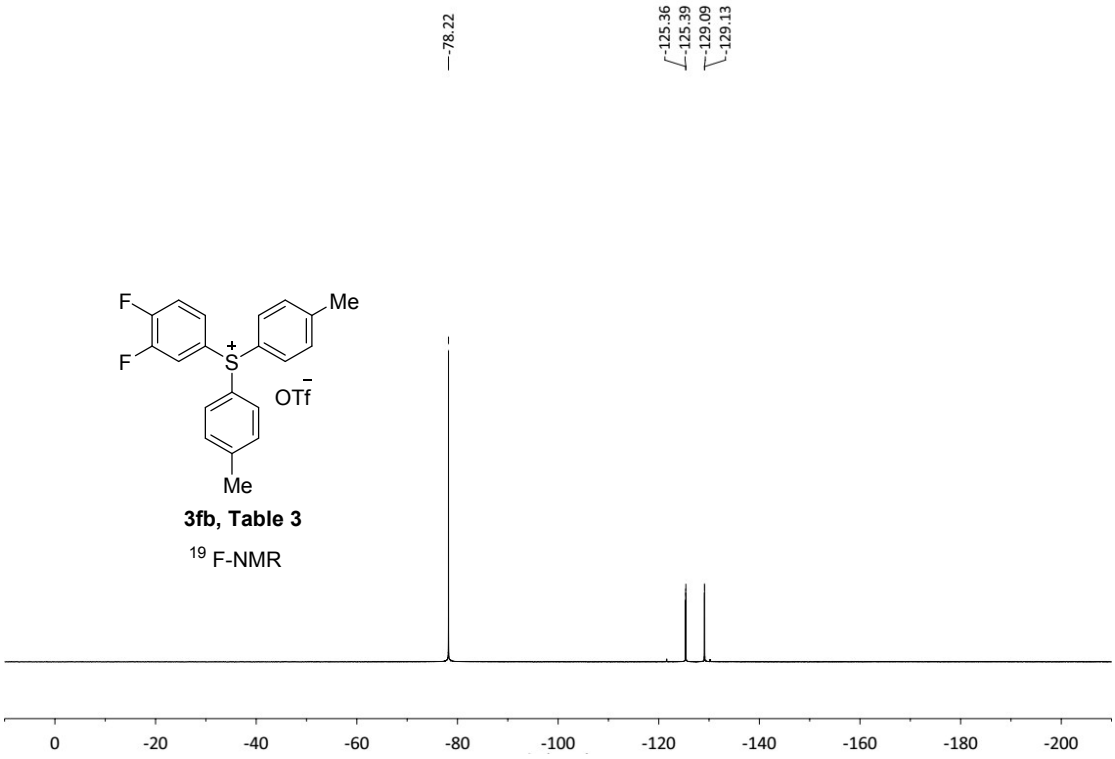

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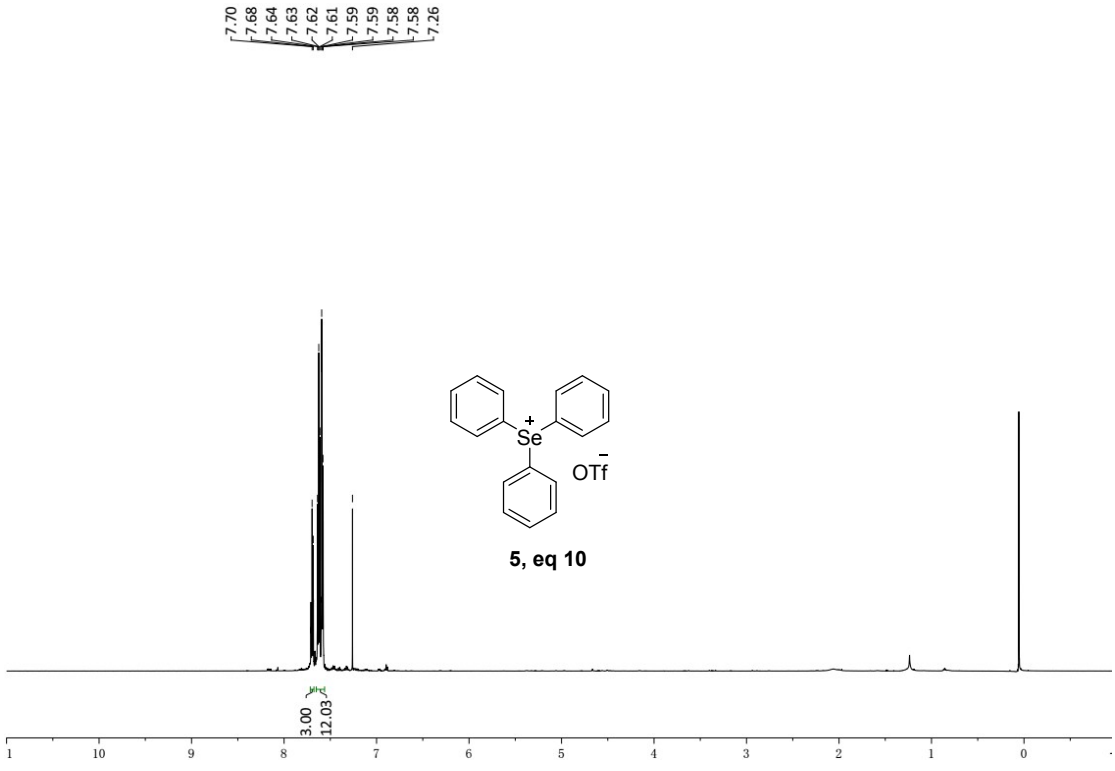

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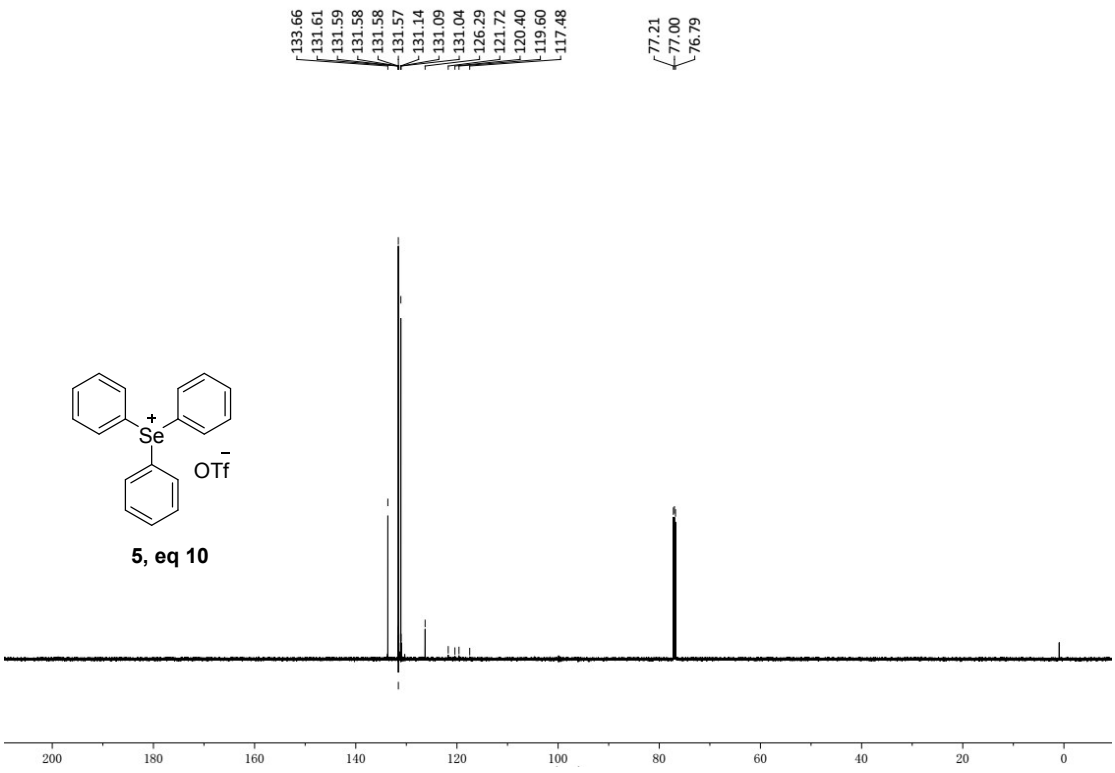
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