Reaction monitoring reveals poisoning mechanism of $Pd_2(dba)_3$ and guides catalyst selection

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I. Experimental

General Information. Reagents were purchased from commercial sources and used without further purification. Column chromatography was performed on silica gel (40–63 μm) or on a Biotage Isolera Four purification system using Biotage ZIP cartridges. Analytical thin layer chromatography was performed on pre-coated aluminium-backed silica gel F_{254} plates with visualization under UV light (λ = 254 nm). GC-MS analyses were carried out using an AGILENT 7820A-GC and 5975-MS. Melting points were obtained using an SMP 11 Stuart Scientific apparatus. NMR spectra were recorded in $CDCl_3$ on Bruker AV–400 instrument at a constant temperature of 300 K (unless otherwise specified). Chemical shifts (δ) are reported in parts per million from low to high field and referenced to residual solvent ($CDCl_3$: δ 7.26/77.16, $^1H/^{13}C$ NMR); ^{19}F-NMR are referred to C_6F_6 (δ -164.9). Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, sep = septet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad, app = apparent. ATR-IR spectra were recorded using a Thermo-Scientific Nicolet iS5 machine and are quoted in cm^{-1}. High Resolution Mass Spectroscopy (HRMS) were recorded on Thermo Finnigan MAT95XP or Thermo Scientific Exactive Plus EMR.

II. Procedures for Kinetic Experiments

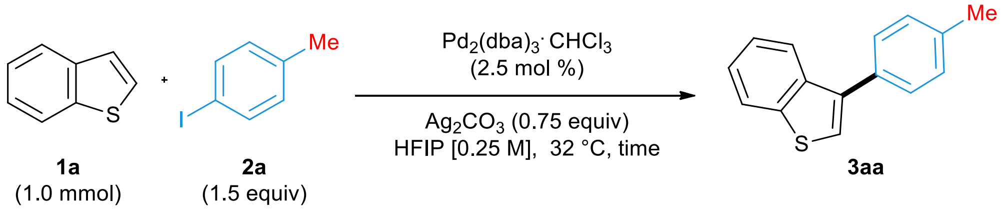
Synthesis of $Pd_2(dba)_3 \cdot CHCl_3$

$Pd_2(dba)_3 \cdot CHCl_3$ was synthesized according to the procedure of Ananikov *et al.*[1] $Pd(OAc)_2$ (200 mg, 0.89 mmol, 1 equiv), sodium acetate (731 mg, 8.9 mmol, 10 equiv), dibenzylideneacetone (417 mg, 1.78 mmol, 2 equiv) were weighed in a 100 mL round-bottom flask followed by the addition of 20 mL of MeOH. The reaction mixture was stirred at 40 °C for 3 hours. After completion of the reaction a brown solid was formed. The solid was filtered off and washed with MeOH (2 x 3 mL) and water (3 x 3 mL). The residue was washed with $CHCl_3$ and the solution was evaporated. The solid obtained was redissolved in a minimum amount of $CHCl_3$ and acetone

(~ 20 mL) was slowly added to the solution. The mixture was kept overnight in the refrigerator. The crystals of $Pd_2(dba)_3{\cdot}CHCl_3$ were filtered off, washed with cold acetone (~3 mL) and dried under vacuum at 40 °C. $Pd_2(dba)_3{\cdot}CHCl_3$ was obtained in 72% yield (331 mg, 0.32 mmol).

II-1. Coupling Between Benzo[*b*]thiophene 1a and 4-Iodotoluene 2a

General procedure



$Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 2.5 mol %), silver carbonate (207 mg, 0.75 equiv), 4-iodotoluene **2a** (330 mg, 1.5 equiv), benzo[*b*]thiophene **1a** (137 mg, 1.0 equiv), 1,3,5-trimethoxybenzene (168 mg, 1.0 equiv) were weighed into an oven-dried 25 mL microwave vial. The vial was sealed and hexafluoro-2-propanol (4 mL) was added. The vial was placed in an oil bath at 32 °C and aliquots of approximately 40 µL were taken. Each aliquot was diluted in EtOAc (400 µL), passed through a plug of silica into a GC-MS vial, and washed with additional EtOAc (400 µL). The reaction was monitored by GC analysis, using 1,3,5-trimethoxybenzene as an internal standard.

Kinetic reaction profile

The graphs represent the course of the reaction in relation to the consumption of starting materials (reacted **1a** = [**1a**]$_0$-[**1a**]; reacted **2a** = [**2a**]$_0$-[**2a**]) and formation of product **3aa**. The curve of '**2a** consumed in the arylation of dba' has been obtained by subtracting the reacted ArI **2a** with the amount of product **3aa** formed (([**2a**]$_0$-[**2a**])-**3aa**). Isolation of the functionalized dba **4a** (*vide infra*) by column chromatography gain further evidence for the background reaction.

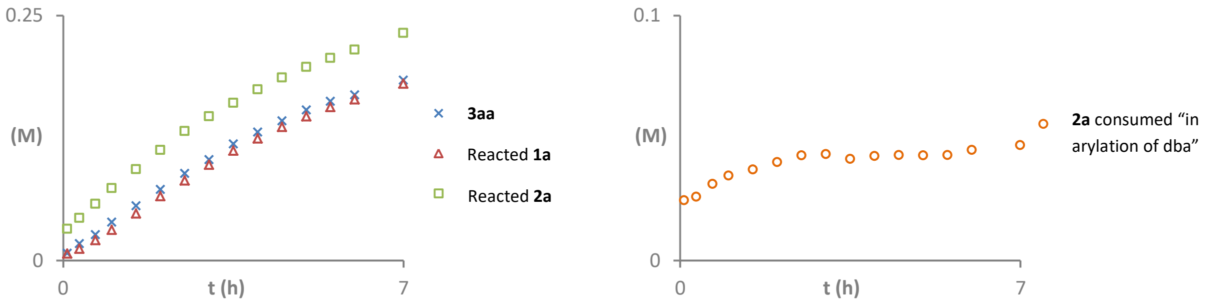
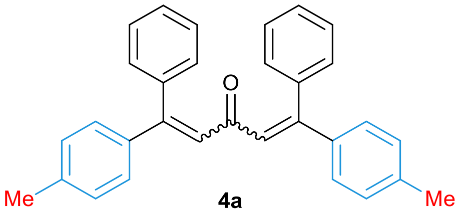


Figure 1: Kinetic reaction profile of coupling between benzo[*b*]thiophene **1a** and ArI **2a**

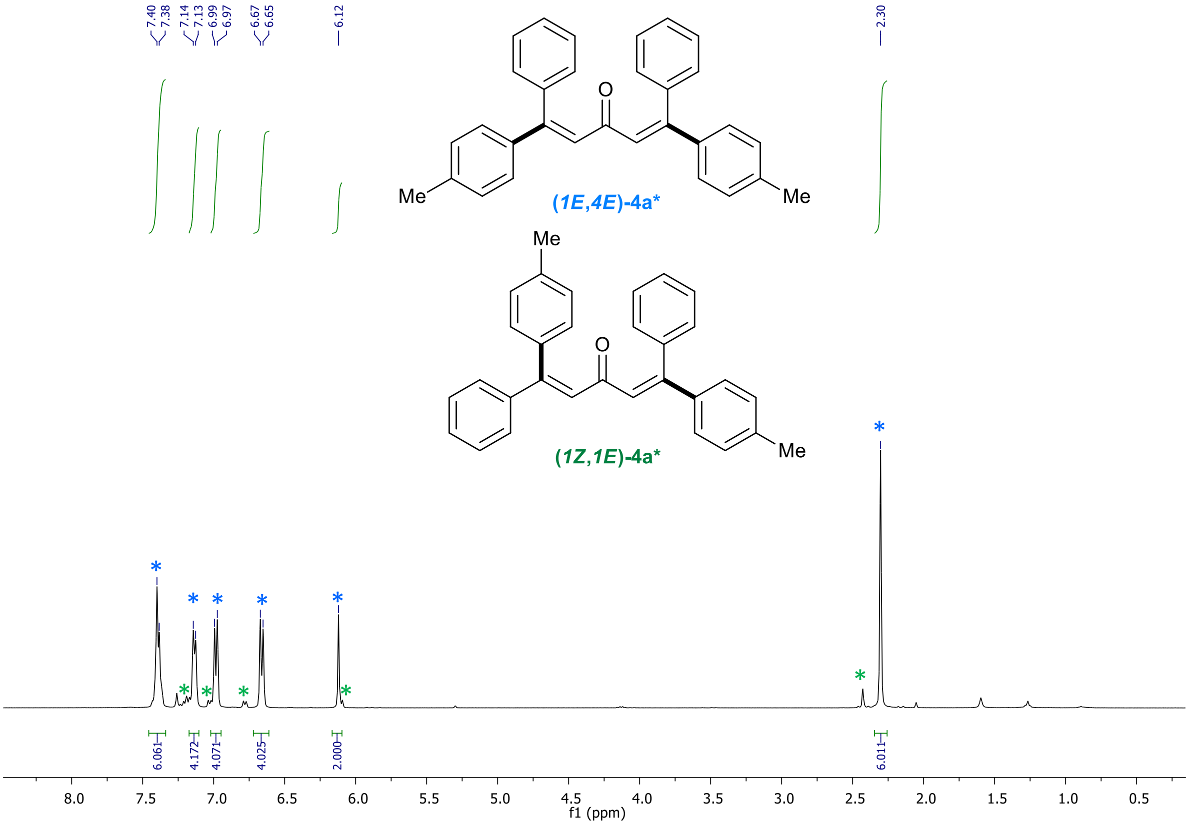
Spectroscopic and Analytical data of 1,5-diphenyl-1,5-di-p-tolylpenta-1,4-dien-3-one (4a)

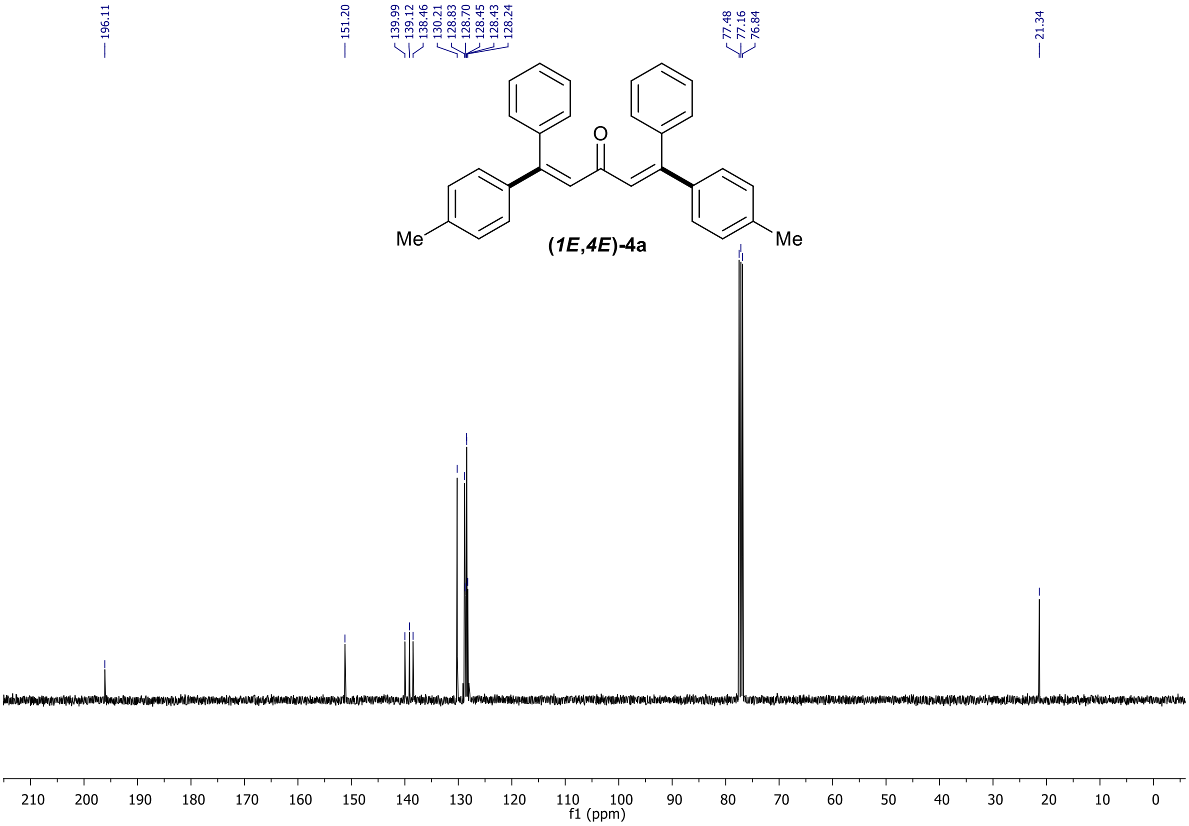


4a

Compound **4a** was isolated by column chromatography from the reaction crude (0-100% CH_2Cl_2 in hexane) as a yellow solid and in mixture 6:1:*traces* of (*1E,4E*):(*1Z,4E*):(*1Z,4Z*) isomers.

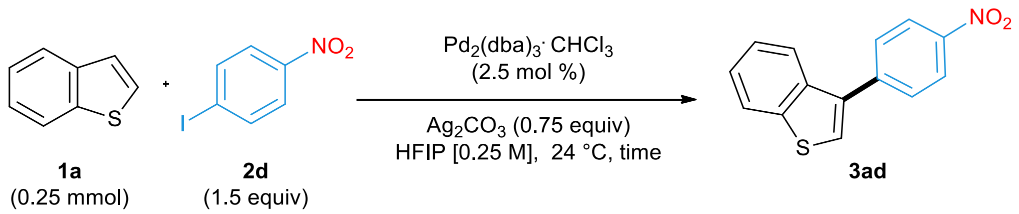
R_f (CH_2Cl_2): 0.60; **NMR characterization of major isomer (*1E,4E*)-4a: ^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.43-7.35 (m, 6H), 7.13 (d, *J* = 6.6 Hz, 4H), 6.98 (d, *J* = 7.7 Hz, 4H), 6.66 (d, *J* = 7.7 Hz, 4H), 6.12 (s, 2H), 2.30 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 196.1, 151.2, 140.0, 139.1, 138.5, 130.2, 128.8, 128.7, 128.5, 128.4, 128.2, 21.3; **IR**: ν = 3025, 2918, 1620, 1604, 1509, 1442, 1346, 1261, 1145, 1115, 1075, 1027 952, 865, 852, 825, 812, 747, 695 cm^{-1}; **HRMS**: calcd for $C_{31}H_{26}O$, 415.2056 (MH^+); found, 415.2043; **Mp**: 162-164°C.


7.40
7.38
7.14
7.13
6.99
6.97
6.67
6.65
6.12
2.30
O
Me
Me
(1E,4E)-4a*
Me
O
Me
(1Z,1E)-4a*
*
6.061
4.172
4.071
4.025
2.000
6.011
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


196.11
151.20
139.99
139.12
138.46
130.21
128.83
128.70
128.45
128.43
128.24
77.48
77.16
76.84
21.34
O
Me
Me
(1E,4E)-4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

II-2. Coupling Between Benzo[*b*]thiophene 1a and 1-Iodo-4-nitrobenzene 2d

General procedure



$Pd_2(dba)_3 \cdot CHCl_3$ (6.5 mg, 2.5 mol %), silver carbonate (52 mg, 0.75 equiv), 1-iodo-4-nitrobenzene **2d** (95 mg, 1.5 equiv), were weighed in the glovebox into microwave vials. The vials were sealed and transferred out of the glovebox. Hexadecane (40 µL) and benzo[*b*]thiophene **1a** (34 mg, 1.0 equiv) were added as solutions in HFIP (1 mL). The vials were placed in an oil bath at 24 °C and stopped at different times for the analysis. Each vial was diluted with EtOAc (5 mL) and filtered through a plug of silica. The silica plug was flushed with EtOAc (30 mL) and the filtrate was evaporated to dryness under reduced pressure. The crude was dissolved in 1 mL of EtOAc and analyzed by GC techniques using hexadecane as an internal standard.

Kinetic reaction profile

The graphs represent the course of the reaction in relation to the consumption of starting materials (reacted **1a** = [**1a**]$_0$-[**1a**]; reacted **2d** = [**2d**]$_0$-[**2d**]) and formation of product **3ad**. The curve of '**2d** consumed in the arylation of dba' has been obtained by subtracting the reacted ArI **2d** with the amount of product **3ad** formed (([**2d**]$_0$-[**2d**])-**3ad**). Isolation of the functionalized dba **4d** (*vide infra*) by column chromatography gain further evidence for the background reaction.

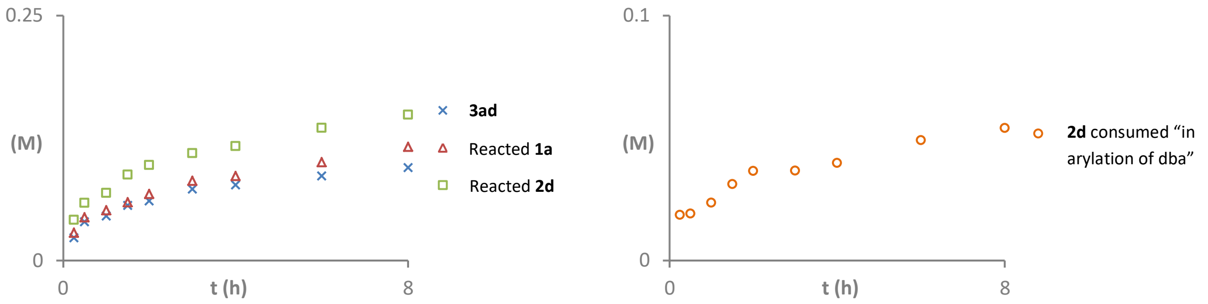
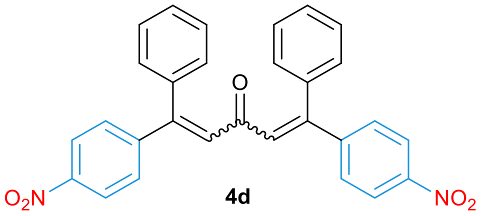


Figure 2: Kinetic reaction profile of coupling between benzo[*b*]thiophene **1a** and ArI **2d**

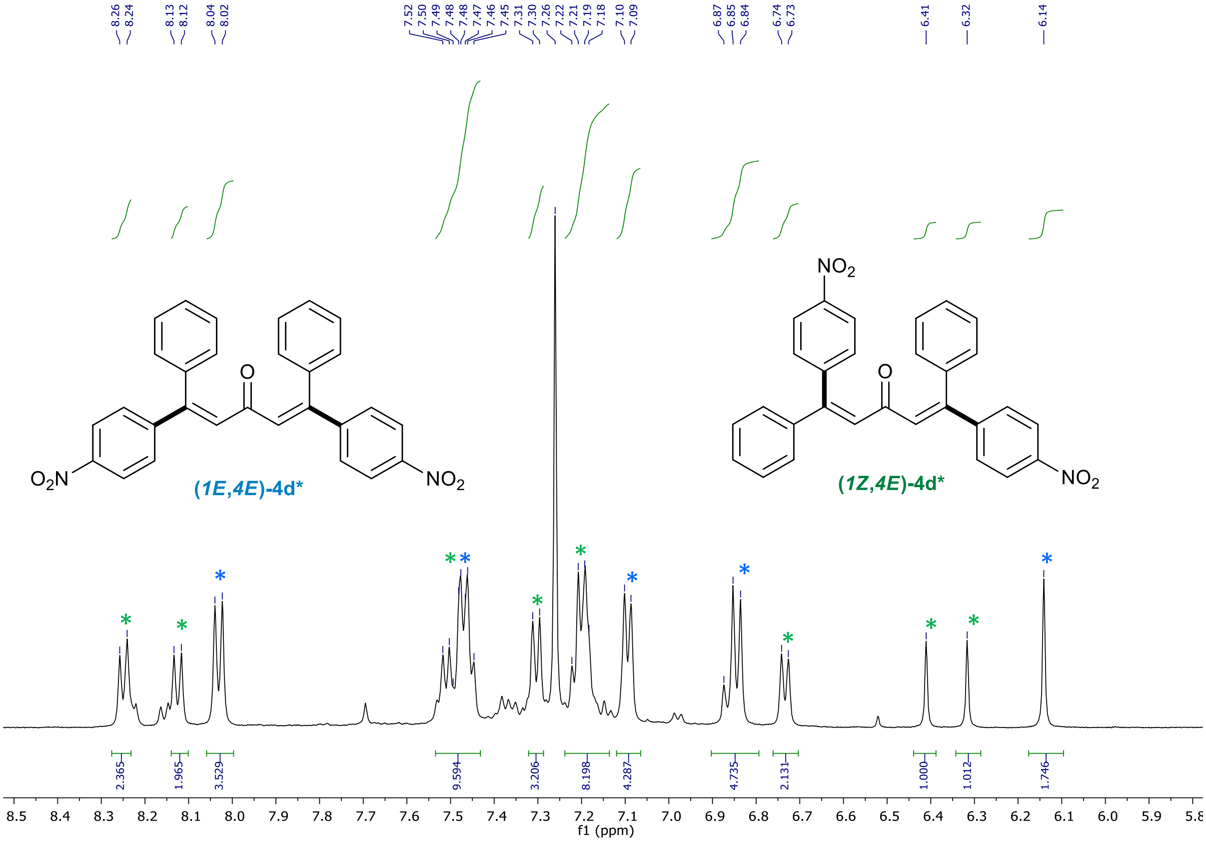
Spectroscopic and Analytical data of 1,5-bis-(4-nitrophenyl)-1,5-diphenylpenta-1,4-dien-3-one (4d)



4d

Compound **4d** was isolated by column chromatography from the reaction crude (0-10% EtOAc in hexane) as a yellow solid and in mixture 0.9:1:<0.1 of (*1E,4E*):(*1Z,4E*):(*1Z,4Z*) isomers.

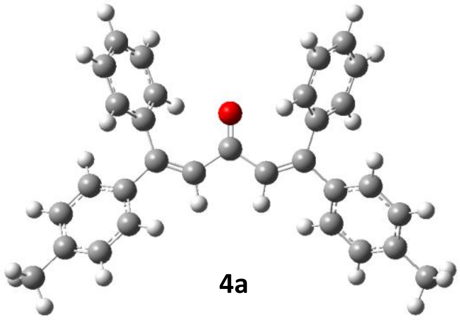
R$_f$ (hexane:EtOAc = 9:1): 0.17; **NMR characterization of major isomers (*1E,4E*)-4d and (*1Z,4E*)-4d: ^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.25 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 3.5H), 7.55-7.43 (m, 5.25H + 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23-7.16 (m, 6H), 7.10 (d, *J* = 7.4 Hz, 3.5H), 6.88-6.82 (m, 3.5H), 6.73 (d, *J* = 7.8 Hz, 2H), 6.41 (s, 1H), 6.32 (s, 1H), 6.14 (s, 1.8 H); **IR**: ν = 3054, 2916, 2849, 1730, 1615, 1592, 1502, 1466, 1435, 1264, 1091, 781, 732, 703 cm^{-1}; **HRMS**: calcd for $C_{29}H_{20}N_2O_5$, 499.1264 (MNa^+); found, 499.1258; **Mp**: decomp. > 220 °C.



III. Computational studies

General Information. Density functional theory calculations were performed using Gaussian 09.[2]. All optimisations and single point calculations were performed using the B3LYP functional with the 6-311G(d,p) basis set for all the atoms (C, H, N and O).

III-1. Optimized Parameters: Cartesian Coordinates

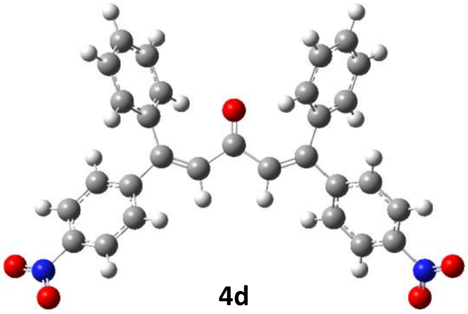


4a

	Symbol	X	Y	Z
1	C	-4.44405	-3.48046	0.91456

2	C	-3.44821	-2.51125	0.85273
3	C	-3.60552	-1.36445	0.0578
4	C	-4.80433	-1.21324	-0.65752
5	C	-5.79433	-2.18888	-0.60458
6	C	-5.61901	-3.32635	0.18114
7	H	-4.30679	-4.35201	1.54488
8	H	-2.54975	-2.6266	1.44744
9	H	-4.94981	-0.33099	-1.26873
10	H	-6.70578	-2.05949	-1.17745
11	C	3.60847	-1.36174	-0.05926
12	C	3.45801	-2.50889	-0.85508
13	C	4.80255	-1.20857	0.66352
14	C	4.45578	-3.47646	-0.91062
15	H	2.5635	-2.62573	-1.45543
16	C	5.79451	-2.18254	0.61673
17	H	4.9428	-0.3261	1.27562
18	C	5.62595	-3.32033	-0.16998
19	H	4.32386	-4.34827	-1.54171
20	H	6.70217	-2.05159	1.19522
21	C	0.00071	0.07278	-0.01445
22	O	0.00154	1.2956	-0.02207
23	C	2.53096	-0.33616	0.0354
24	C	1.23876	-0.74941	0.05734
25	H	1.07362	-1.82133	0.06879
26	C	-1.23779	-0.74935	-0.07673
27	C	-2.53016	-0.33715	-0.04421
28	H	-1.07235	-1.82123	-0.08871
29	C	2.98147	1.0811	0.11556
30	C	3.88297	1.57727	-0.83675
31	C	2.57366	1.92472	1.15605
32	C	4.34091	2.88966	-0.7675
33	H	4.21658	0.93278	-1.6421
34	C	3.05259	3.227	1.2404
35	H	1.87754	1.55617	1.89773
36	C	3.93109	3.71709	0.27529
37	H	5.0226	3.26229	-1.52391
38	H	2.72994	3.86474	2.05564
39	H	4.29477	4.73674	0.33723
40	C	-2.98375	1.07944	-0.1175
41	C	-3.88087	1.57042	0.84179
42	C	-2.58363	1.92767	-1.15726
43	C	-4.34204	2.882	0.77984
44	H	-4.20849	0.92238	1.64675
45	C	-3.06605	3.22916	-1.2343
46	H	-1.89068	1.56347	-1.90389
47	C	-3.94005	3.71391	-0.26248

48	H	-5.02014	3.25051	1.54148
49	H	-2.74948	3.87046	-2.04911
50	H	-4.30632	4.73297	-0.31877
51	C	6.73082	-4.39136	-0.23132
52	H	7.3963	-4.17139	-1.03981
53	H	7.27645	-4.39404	0.68911
54	H	6.28738	-5.3528	-0.38587
55	C	-6.7217	-4.39921	0.24933
56	H	-7.39185	-4.17138	1.05176
57	H	-7.26256	-4.41395	-0.67379
58	H	-6.27683	-5.35772	0.4174

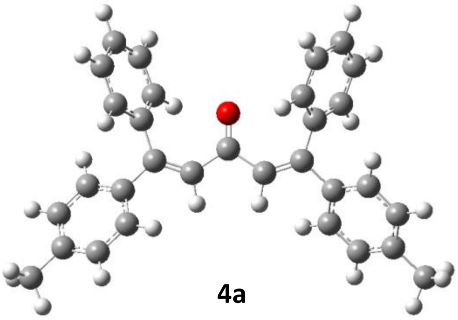


4d

	Symbol	X	Y	Z
1	C	-4.44405	-3.48046	0.91456
2	C	-3.44821	-2.51125	0.85273
3	C	-3.60552	-1.36445	0.0578
4	C	-4.80433	-1.21324	-0.65752
5	C	-5.79433	-2.18888	-0.60458
6	C	-5.61901	-3.32635	0.18114
7	H	-4.30679	-4.35201	1.54488
8	H	-2.54975	-2.6266	1.44744
9	H	-4.94981	-0.33099	-1.26873
10	H	-6.70578	-2.05949	-1.17745
11	C	3.60847	-1.36174	-0.05926
12	C	3.45801	-2.50889	-0.85508
13	C	4.80255	-1.20857	0.66352
14	C	4.45578	-3.47646	-0.91062
15	H	2.5635	-2.62573	-1.45543
16	C	5.79451	-2.18254	0.61673
17	H	4.9428	-0.3261	1.27562
18	C	5.62595	-3.32033	-0.16998
19	H	4.32386	-4.34827	-1.54171
20	H	6.70217	-2.05159	1.19522
21	C	0.00071	0.07278	-0.01445
22	O	0.00154	1.2956	-0.02207
23	C	2.53096	-0.33616	0.0354
24	C	1.23876	-0.74941	0.05734

25	H	1.07362	-1.82133	0.06879
26	C	-1.23779	-0.74935	-0.07673
27	C	-2.53016	-0.33715	-0.04421
28	H	-1.07235	-1.82123	-0.08871
29	C	2.98147	1.0811	0.11556
30	C	3.88297	1.57727	-0.83675
31	C	2.57366	1.92472	1.15605
32	C	4.34091	2.88966	-0.7675
33	H	4.21658	0.93278	-1.6421
34	C	3.05259	3.227	1.2404
35	H	1.87754	1.55617	1.89773
36	C	3.93109	3.71709	0.27529
37	H	5.0226	3.26229	-1.52391
38	H	2.72994	3.86474	2.05564
39	H	4.29477	4.73674	0.33723
40	C	-2.98375	1.07944	-0.1175
41	C	-3.88087	1.57042	0.84179
42	C	-2.58363	1.92767	-1.15726
43	C	-4.34204	2.882	0.77984
44	H	-4.20849	0.92238	1.64675
45	C	-3.06605	3.22916	-1.2343
46	H	-1.89068	1.56347	-1.90389
47	C	-3.94005	3.71391	-0.26248
48	H	-5.02014	3.25051	1.54148
49	H	-2.74948	3.87046	-2.04911
50	H	-4.30632	4.73297	-0.31877
51	N	-6.67158	-4.35044	0.24623
52	O	-7.66931	-4.18457	-0.3983
53	O	-6.49055	-5.31094	0.94128
54	N	6.6806	-4.34268	-0.22853
55	O	7.67408	-4.17511	0.42212
56	O	6.50545	-5.30351	-0.92461

III-2. Optimized Parameters: Mulliken Charges



4a

	Symbol	Charge
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2	C	-0.065225
3	C	-0.097156
4	C	-0.047248
5	C	-0.071016
6	C	-0.105449
7	H	0.086367
8	H	0.097786
9	H	0.106789
10	H	0.087445
11	C	-0.096530
12	C	-0.065093
13	C	-0.047542
14	C	-0.071529
15	H	0.097807
16	C	-0.070808
17	H	0.106816
18	C	-0.105420
19	H	0.086363
20	H	0.087445
21	C	0.236522
22	O	-0.330097
23	C	0.077742
24	C	-0.153396
25	H	0.095763
26	C	-0.153143
27	C	0.077588
28	H	0.095939
29	C	-0.143425
30	C	-0.045325
31	C	0.007243
32	C	-0.093984
33	H	0.093981
34	C	-0.098239
35	H	0.092135
36	C	-0.087186
37	H	0.091469
38	H	0.093267
39	H	0.092768
40	C	-0.144120
41	C	-0.045439
42	C	0.008113
43	C	-0.094121
44	H	0.094113

45	C	-0.098607
46	H	0.092348
47	C	-0.087094
48	H	0.091458
49	H	0.093328
50	H	0.092784
51	C	-0.255280
52	H	0.130049
53	H	0.113676
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57	H	0.114059
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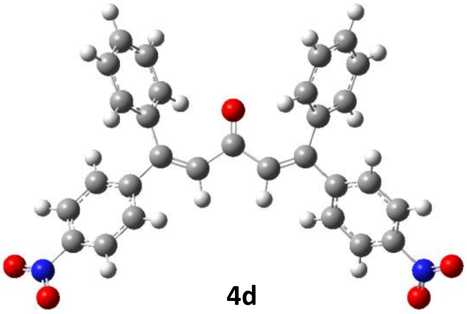

4d

	Symbol	Charge
1	C	-0.055404
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3	C	-0.095416
4	C	-0.042306
5	C	-0.056504
6	C	0.128615
7	H	0.135531
8	H	0.111285
9	H	0.121525
10	H	0.136563
11	C	-0.094764
12	C	-0.061256
13	C	-0.042582
14	C	-0.055450
15	H	0.111295
16	C	-0.056512
17	H	0.121559
18	C	0.128645
19	H	0.135529

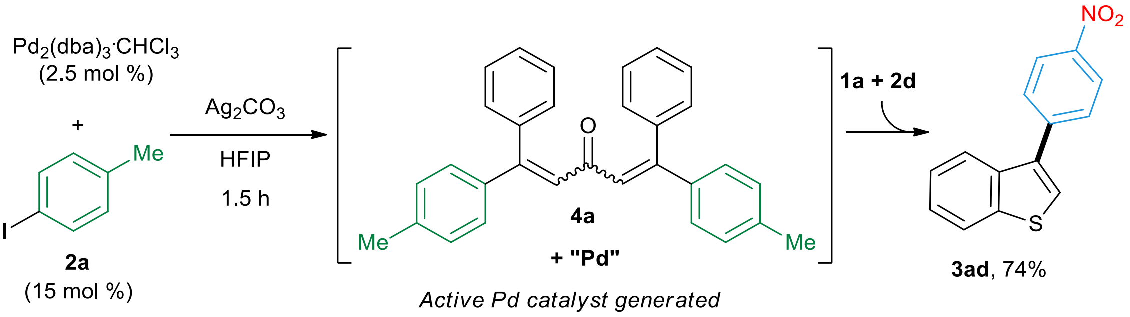
20	H	0.136552
21	C	0.239029
22	O	-0.317003
23	C	0.084019
24	C	-0.147089
25	H	0.101797
26	C	-0.146825
27	C	0.083850
28	H	0.101969
29	C	-0.148652
30	C	-0.047163
31	C	0.005889
32	C	-0.091449
33	H	0.096618
34	C	-0.096166
35	H	0.094543
36	C	-0.083583
37	H	0.098390
38	H	0.099023
39	H	0.099642
40	C	-0.149309
41	C	-0.047279
42	C	0.006769
43	C	-0.091582
44	H	0.096719
45	C	-0.096528
46	H	0.094779
47	C	-0.083488
48	H	0.098383
49	H	0.099093
50	H	0.099663
51	N	0.177448
52	O	-0.263248
53	O	-0.264013
54	N	0.177444
55	O	-0.263251
56	O	-0.264013

IV. Addition protocol

The addition protocol has been tested at concentration of 0.25 M in agreement with the kinetic studies, in which was observed complete arylation of dba with both iodoarenes **2a** and **2d** after 1-2 h of reaction. An average timeframe of 1.5 h was therefore applied in the addition protocol for the studies of the effect of the pre-arylation of dba on the coupling between benzo[*b*]thiophene **1a** and 1-iodo-4-nitrobenzene **2d**.

As comparison, the standard room temperature conditions reported in our previous publication[3] referred to a concentration of 0.25 M gave 41% of β-arylated product **3ad**, instead of 30% obtained at 1 M.

IV-1. Effect of pre-arylating dba in the coupling between 1a and 2d



$Pd_2(dba)_3{\cdot}CHCl_3$ (6.5 mg, 2.5 mol %), silver carbonate (52 mg, 0.75 equiv), 4-iodotoluene **2a** (8.4 mg, 15 mol %) were weighed into a microwave vial. The vial was sealed followed by the addition of hexafluoro-2-propanol (1 mL) and placed in an oil bath at 24 °C for 1.5 h. After this time, benzo[*b*]thiophene **1a** (34 mg, 1.0 equiv) and 1-iodo-4-nitrobenzene **2d** (95 mg, 1.5 equiv) were added and the reaction mixture was kept stirring for 16 h at 24 °C. The vial was diluted with EtOAc (5 mL) and filtered through a plug of silica. The silica plug was flushed with EtOAc (30 mL) and the filtrate was evaporated to dryness under reduced pressure. The crude was dissolved in 1 mL of EtOAc and analyzed by ^{1}H-NMR techniques using 1,3,5-trimethoxybenzene as an internal standard. This protocol led to **3ad** in 74% yield.

Control experiments using 15 mol% of selected electron-deficient iodoarenes **2g** (5-iodo-1,2,3-trimethoxybenzene, 11.4 mg), **2i** (3-iodobenzaldehyde, 8.9 mg) and **2j** (3-iodoanisole, 4.5 µL, 8.9 mg) for the pre-arylation of dba led to the formation of product **3ad** in yields of 12%, 21% and 5% respectively. These experiments confirm the importance of the undesired arylation of dba on the coupling yields.

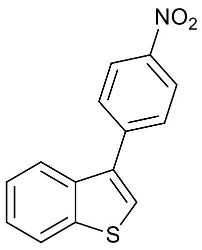
At last, premixing of $Pd_2dba_3 \cdot CHCl_3$ and Ag_2CO_3 in HFIP for 1.5 h, followed by the addition of **1a** and **2d**, didn't improve the formation of compound **3ad**, which was obtained in 41% yield. This excludes any modification of the catalyst in the pre-heating step as the key element for the increased reactivity observed when dba was pre-arylated with the electron-rich iodoarene **2a**.

V. Experimental Details, Spectroscopic and Analytical Data

V-1. Experimental Details

General procedure. PdI_2 (5 mol %), silver carbonate (0.75 equiv), aryl iodide (1.5 equiv) and benzo[*b*]thiophene **1a** (1.0 equiv) were stirred in hexafluoro-2-propanol at 24 °C for 16 h. After this time, the resultant mixture was diluted with EtOAc (5 mL) and filtered through a plug of silica. The silica plug was flushed with EtOAc (30 mL) and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography using the specified eluent to afford the product.

V-2. Spectroscopic and Analytical Data

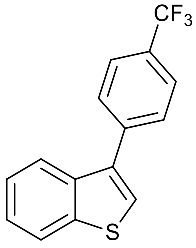


3-(4-nitrophenyl)benzo[*b*]thiophene (3ad)

The product **3ad** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 1-iodo-4-nitrobenzene **2d** (286 mg, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:DCM = 80:20) as a yellow solid in 86% yield (164 mg, 0.64 mmol).

The same reaction using 1.0 equiv of 1-iodo-4-nitrobenzene **2d** (191 mg) afforded product **3ad** in 82% yield (the yield was determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as an internal standard).

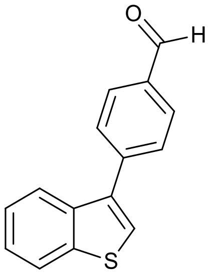
R$_f$ (hexane:DCM = 80:20): 0.21; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 8.32 (d, *J* = 8.2 Hz, 2H), 7.95 (m, 1H), 7.89 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.54 (s, 1H), 7.47-7.42 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 147.0, 142.5, 140.8, 137.0, 135.8, 129.2, 125.9, 125.0, 125.0, 124.1, 123.2, 122.4; **HRMS**: calcd for $C_{14}H_9O_2NS$, 256.0427 (MH$^+$); found, 256.0425; **Mp**: 106-108 °C. Data is in accordance with the literature.[3]



3-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (3ae)

The product **3ae** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 4-iodobenzotrifluoride **2e** (165 µL, 1.12 mmol, 1.5 equiv) and isolated by automated column chromatography (hexane) as a white solid in 89% yield (186 mg, 0.67 mmol).

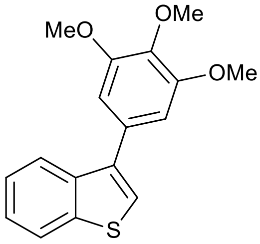
R$_f$ (hexane): 0.52; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 8.00-7.96 (m, 1H), 7.94-7.92 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.46 (s, 1H), 7.46-7.43 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 140.9, 139.7, 137.5, 136.7, 129.7 (q, *J* = 32.4 Hz), 129.0, 125.8 (q, *J* = 3.8 Hz), 124.9, 124.8, 124.8, 124.4 (q, *J* = 272.5 Hz), 123.2, 122.7; **^{19}F-NMR** (376 MHz, CDCl$_3$) δ (ppm) -62.3; **HRMS**: calcd for $C_{15}H_9F_3S$, 278.0372 (M$^+$); found, 278.0369; **Mp**: 38-40 °C. Data is in accordance with the literature.[3]



4-(benzo[*b*]thiophen-3-yl)benzaldehyde (3af)

The product **3af** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 4-iodobenzaldehyde **2f** (261 mg, 1.12 mmol, 1.5 equiv) and isolated by automated column chromatography (hexane:EtOAc = 95:5) as a colorless oil in 91% yield (163 mg, 0.68 mmol).

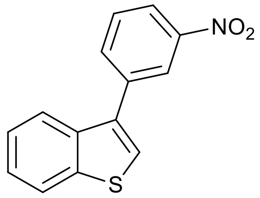
R$_f$ (hexane:EtOAc = 95:5): 0.15; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 10.09 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.96-7.92 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.51 (s, 1H), 7.45-7.43 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 191.8, 142.1, 140.8, 137.2, 136.7, 135.3, 130.2, 129.1, 125.2, 124.8, 124.8, 123.1, 122.6; **HRMS**: calcd for $C_{15}H_{10}OS$, 239.0525 (MH$^+$); found, 239.0523. Data is in accordance with the literature.[3]



3-(3,4,5-trimethoxyphenyl)benzo[*b*]thiophene (3ag)

The product **3ag** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 5-iodo-1,2,3-trimethoxybenzene **2g** (341 mg, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:EtOAc = 90:10) as white solid in 85% yield (192 mg, 0.64 mmol).

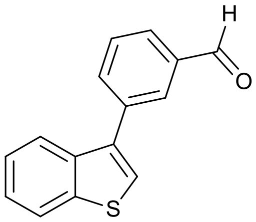
R$_f$ (hexane:EtOAc = 90:10): 0.23; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 7.98-7.90 (m, 2H), 7.44-7.38 (m, 3H), 6.81 (s, 2H), 3.96 (s, 3H), 3.92 (s, 6H); **^{13}C-NMR** (101 MHz, CDCl$_3$): 153.5, 140.7, 138.1, 137.9, 137.6, 131.7, 124.5, 124.5, 123.3, 123.0, 122.9, 105.9, 61.0, 56.2; **IR**: ν = 3088, 2993, 2928, 2833, 1582, 1556, 1522, 1458, 1413, 1354, 1307, 1235, 1124, 998, 823, 770, 761, 732, 690 cm^{-1}; **HRMS**: $C_{17}H_{16}O_3S$, 301.0893 (MH$^+$); found, 301.0889; **Mp**: 108-110 °C.



3-(3-nitrophenyl)benzo[*b*]thiophene (3ah)

The product **3ah** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 1-iodo-3-nitrobenzene **2h** (283 mg, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:DCM = 80:20) as a yellow solid in 87% yield (167 mg, 0.65 mmol).

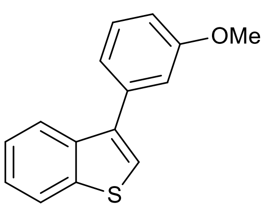
R$_f$ (hexane:DCM = 80:20): 0.23; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 8.44 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.95-7.86 (m, 3H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.46-7.42 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 148.6, 140.7, 137.5, 137.1, 135.4, 134.6, 129.7, 125.3, 124.9, 124.9, 123.3, 123.2, 122.3, 122.2; **HRMS**: calcd for $C_{14}H_9O_2NS$, 256.0427 (MH$^+$); found, 256.0422; **Mp**: 68-70 °C. Data is in accordance with the literature.[4]



3-(benzo[*b*]thiophen-3-yl)benzaldehyde (3ai)

The product **3ai** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 3-iodobenzaldehyde **2i** (266 mg, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:EtOAc = 98:2) as a colorless oil in 94% yield (168 mg, 0.70 mmol).

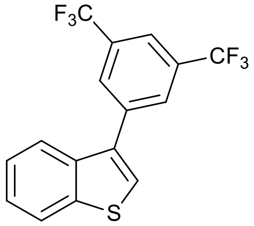
R$_f$ (hexane:EtOAc = 98:2): 0.20; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 10.08 (s, 1H), 8.07 (s, 1H), 7.93-7.82 (m, 4H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.45 (s, 1H), 7.41-7.39 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 192.3, 140.8, 137.5, 137.0, 137.0, 136.6, 134.6, 129.8, 129.6, 128.9, 124.8, 124.7, 124.6, 123.2, 122.6; **IR**: ν = 3058, 2915, 2847, 2731, 1697, 1232, 1159, 782, 759, 739, 692 cm^{-1}; **HRMS**: calcd for $C_{15}H_{10}OS$, 239.0525 (MH$^+$); found, 239.0528.



3-(3-methoxyphenyl)benzo[*b*]thiophene (3aj)

The product **3aj** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 3-iodoanisole **2j** (135 µL, 1.12 mmol, 1.5 equiv) and isolated by automated column chromatography (hexane) as colorless oil in 89% yield (160 mg, 0.67 mmol).

R$_f$ (hexane): 0.19; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 8.03-7.97 (m, 1H), 7.97-7.91 (m, 1H), 7.48-7.39 (m, 4H), 7.23-2.16 (m, 2H), 7.01-6.98 (m, 1H), 3.88 (s, 3H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 159.9, 140.8, 138.0, 137.9, 137.4, 129.8, 124.5, 124.5, 123.6, 123.1, 123.0, 121.3, 114.4, 113.2, 55.4; **HRMS**: calcd for $C_{15}H_{12}OS$, 241.0682 (MH$^+$); found, 241.0677. Data is in accordance with the literature.[3]

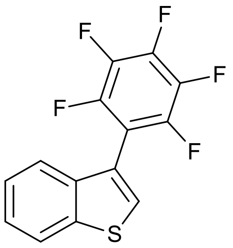


3-(3,5-bis(trifluoromethyl)phenyl)benzo[*b*]thiophene (3ak)

The product **3ak** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 1-iodo-3,5-bis(trifluoromethyl)benzene **2k** (199 µL, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 90% yield (235 mg, 0.68 mmol).

R$_f$ (hexane): 0.62; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 8.07 (s, 2H), 7.96 (m, 2H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.50-7.44 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 140.9, 138.2, 137.1, 135.1, 132.1 (q, *J* = 33.3 Hz), 128.8 (q, *J* = 2.9 Hz), 125.9, 125.2, 125.2, 123.4, 122.1, 122.1 (q, *J* = 272.5 Hz), 121.4 (sep, *J* = 3.8 Hz); **^{19}F-NMR** (376 MHz, CDCl$_3$) δ (ppm) -62.8; **IR**: ν = 1379, 1328, 1274, 1168, 1124, 1106, 986, 899, 845, 787, 758, 734, 705, 682, 666 cm^{-1}; **HRMS**: calcd for $C_{16}H_8F_6S$, 347.0324 (MH$^+$); found, 347.0309.

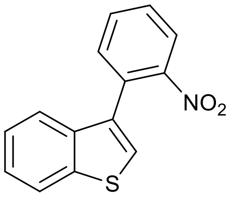
3-(perfluorophenyl)benzo[*b*]thiophene (3al)



The product **3al** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and iodopentafluorobenzene **2l** (152 µL, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as white solid in 49% yield (111 mg, 0.37 mmol).

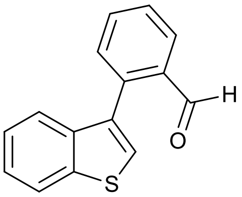
R$_f$ (hexane): 0.38; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 7.98-7.92 (m, 1H), 7.60 (s, 1H), 7.54-7.49 (m, 1H), 7.46-7.41 (m, 2H); **^{13}C-NMR** (126 MHz, CDCl$_3$): 144.7 (dm, *J*= 248.9 Hz), 141.1 (dm, *J*= 254.7 Hz), 139.8, 138.1 (dm, *J*= 253.4 Hz), 137.4, 129.0, 125.1, 125.0, 123.0, 122.6, 121.1 (m), 110.3 (m); **^{19}F-NMR** (376 MHz, CDCl$_3$) δ (ppm) -138.9 (app dd, *J*= 22.7, 7.8 Hz), -154.3 (app t, *J* = 21.0 Hz), -161.6 (app dt, *J* = 22.4, 7.7 Hz); **IR**: ν = 1532, 1509, 1489, 1458, 1438, 1336, 1260, 1118, 1061, 1005, 977, 864, 809, 794, 774, 758, 738, 688 cm^{-1}; **HRMS**: calcd for $C_{14}H_5F_5S$, 300.0027 (M$^+$); found, 300.0023; **Mp**: 122-124 °C.

3-(2-nitrophenyl)benzo[*b*]thiophene (3am)



The product **3am** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 2-iodonitrobenzene **2m** (280 mg, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:DCM = 80:20) as a yellow oil in 86% yield (164 mg, 0.64 mmol).

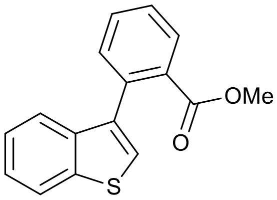
R$_f$ (hexane:DCM = 80:20): 0.25; **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) 8.05 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59-7.53 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.46-7.35 (m, 3H); **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) 149.6, 139.8, 138.0, 132.9, 132.8, 132.8, 130.3, 128.9, 124.8, 124.7, 124.7, 124.4, 123.0, 121.9; **IR**: ν = 3064, 1521, 1345, 854, 783, 759, 729, 677 cm^{-1}; **HRMS**: calcd for $C_{14}H_9O_2NS$, 256.0427 (MH$^+$); found, 256.0425.



2-(benzo[*b*]thiophene-3-yl)benzaldehyde (3an)

The product **3an** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and 2-iodobenzaldehyde **2n** (266 mg, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:EtOAc = 98:2) as a colorless oil in 73% yield (131 mg, 0.55 mmol).

R$_f$ (hexane:EtOAc = 98:2): 0.20; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.77 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49-7.41 (m, 3H), 7.33-7.26 (m, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 192.1, 140.1, 139.4, 139.4, 134.9, 134.1, 133.5, 131.5, 128.6, 127.7, 126.6, 125.0, 125.0, 123.0, 122.8; **HRMS**: calcd for $C_{15}H_{10}OS$, 239.0525 (MH^+); found, 239.0524. Data is in accordance with the literature.[5]



Methyl 2-(benzo[*b*]thiophene-3-yl)benzoate (3ao)

The product **3ao** was obtained via the general procedure using benzo[*b*]thiophene **1a** (102 mg, 0.75 mmol, 1.0 equiv) and methyl 2-iodobenzoate **2o** (174 µL, 1.12 mmol, 1.5 equiv) and isolated by column chromatography (hexane:Et_2O = 96:4) as a colorless oil in 66% yield (133 mg, 0.50 mmol).

R$_f$ (hexane:Et_2O = 96:4): 0.29; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.96 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.50-7.42 (m, 3H), 7.37-7.27 (m, 3H), 3.45 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 168.4, 139.7, 139.0, 137.3, 136.2, 131.9, 131.7, 131.7, 130.3, 128.0, 124.4, 124.4, 123.4, 122.9, 122.4, 52.1; **IR**: ν = 3059, 2947, 1715, 1427, 1291, 1251, 1123, 1081, 760, 733, 715 cm^{-1}; **HRMS**: calcd for $C_{16}H_{12}O_2S$, 269.0631 (MH^+); found, 269.0622.

VI. References

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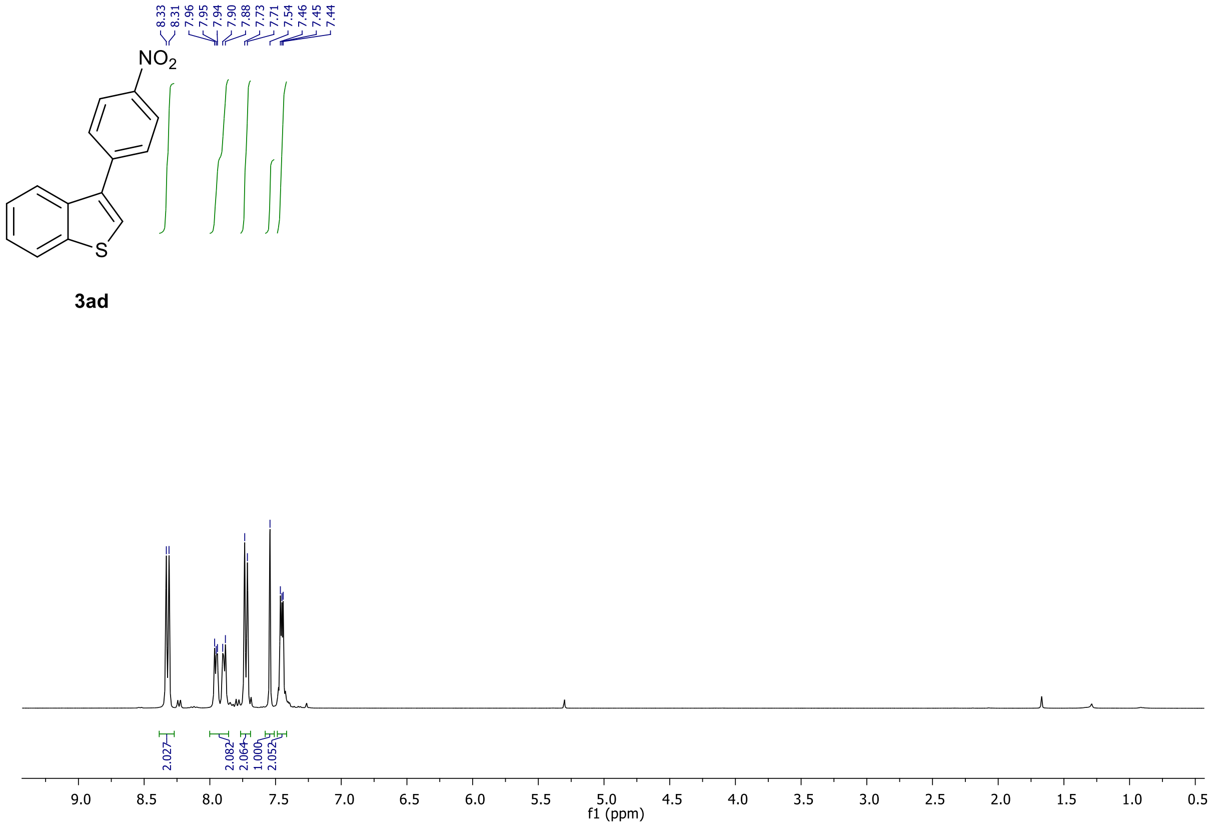
VII. ^{1}H-NMR and ^{13}C-NMR spectra



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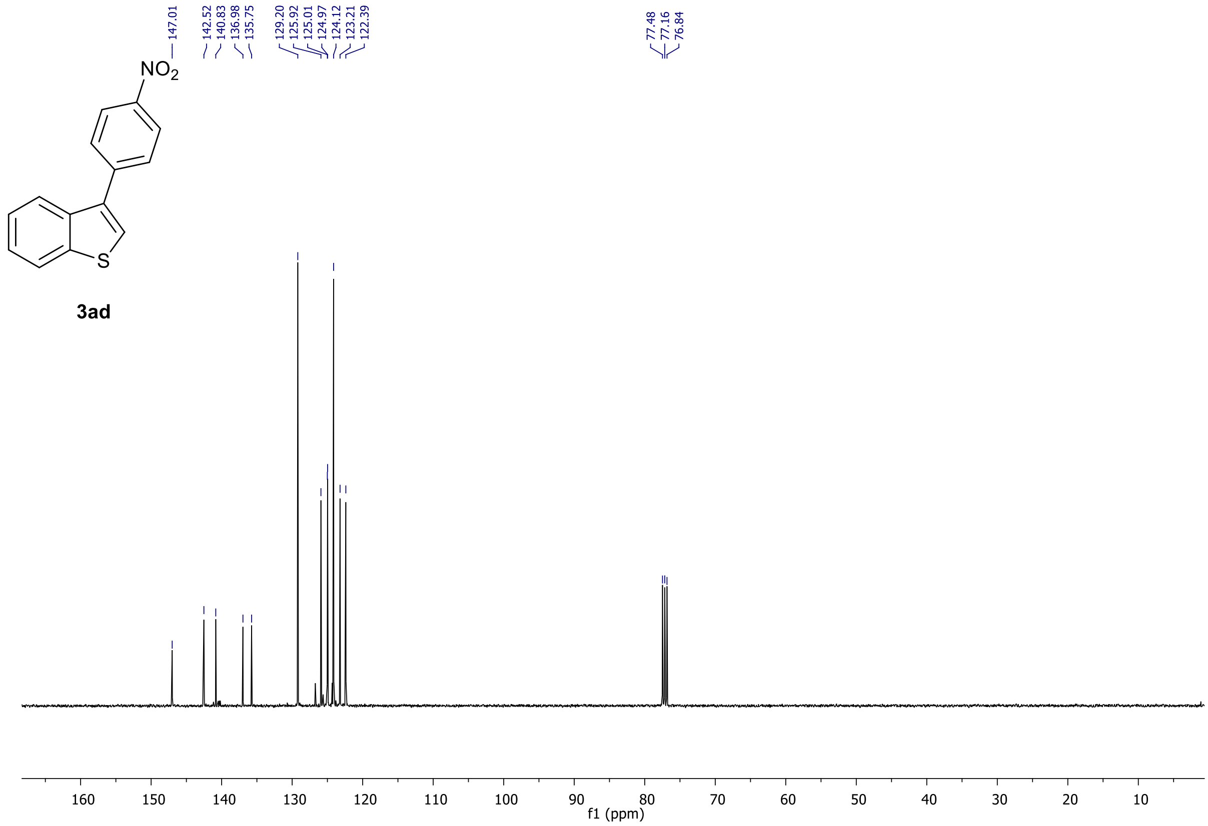

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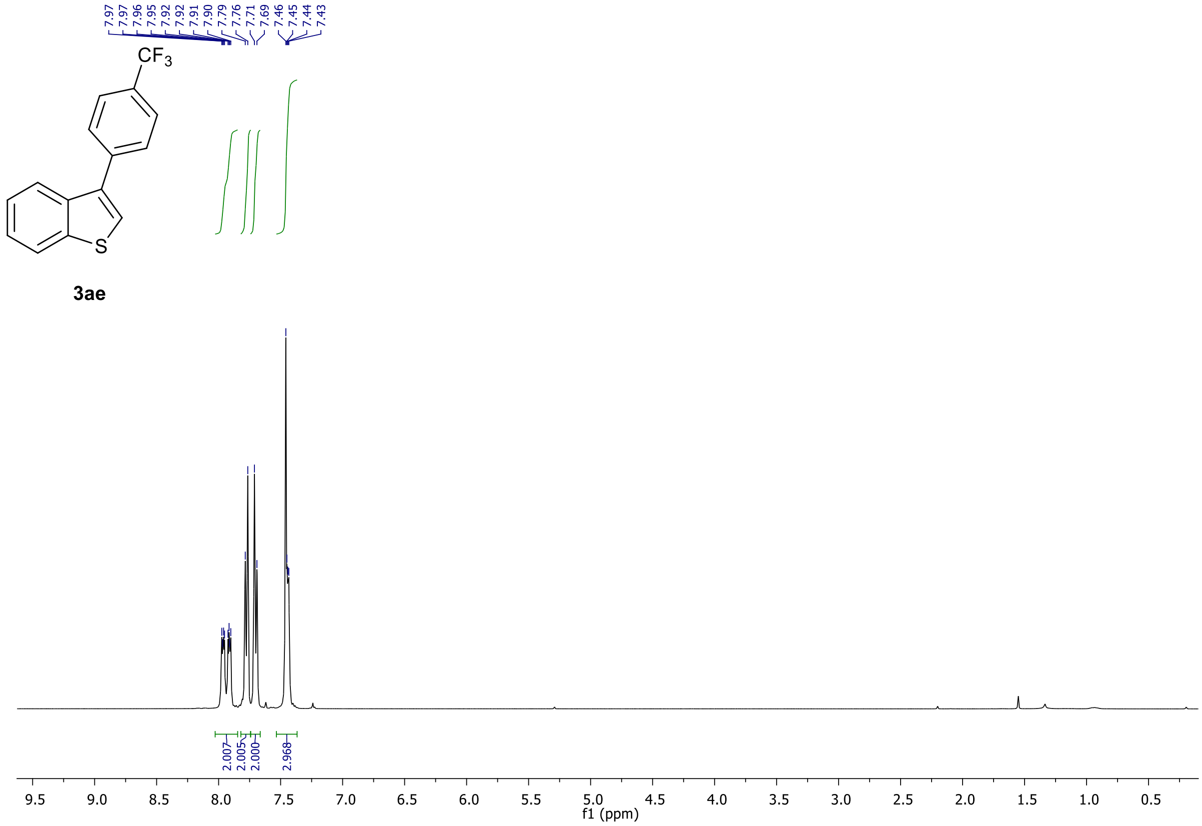
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7.97
7.96
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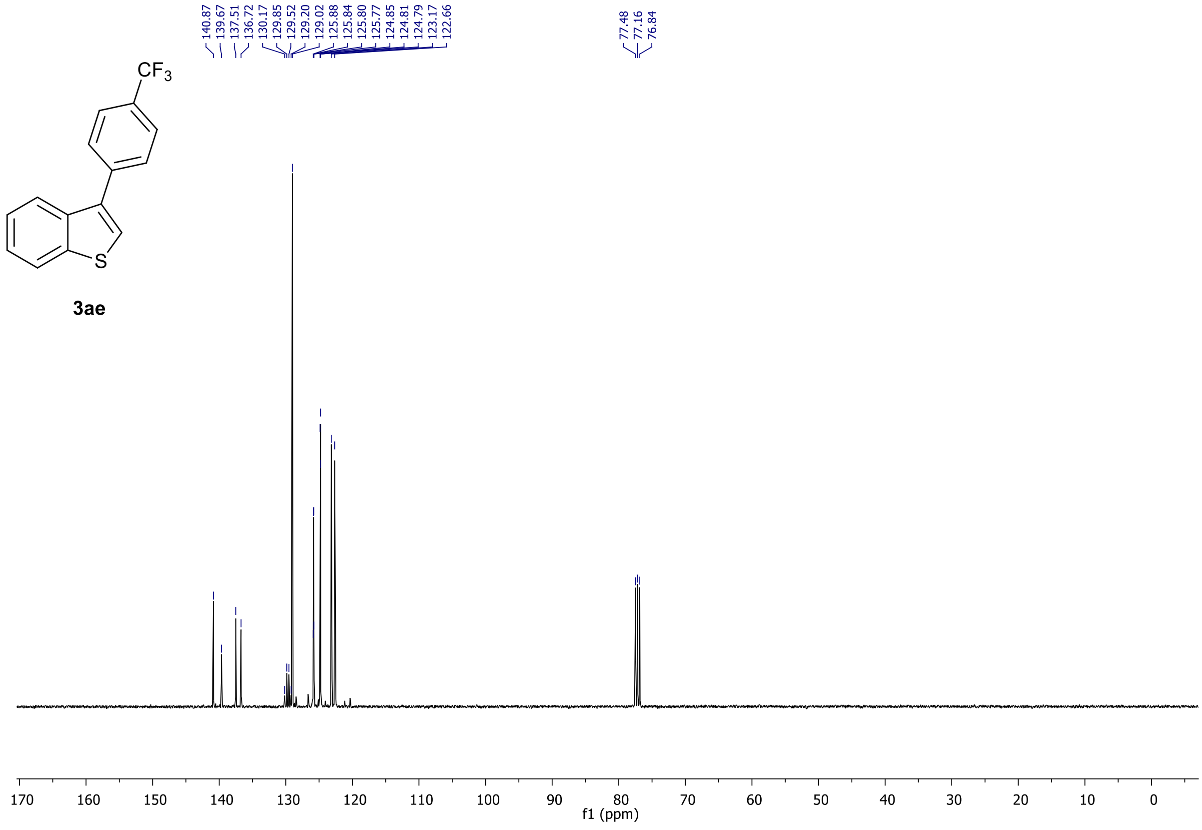
7.92
7.92
7.91
7.90
7.79
7.76
7.71
7.69
7.46
7.45
7.44
7.43
CF3
S
3ae
2.007
2.005
2.000
2.968
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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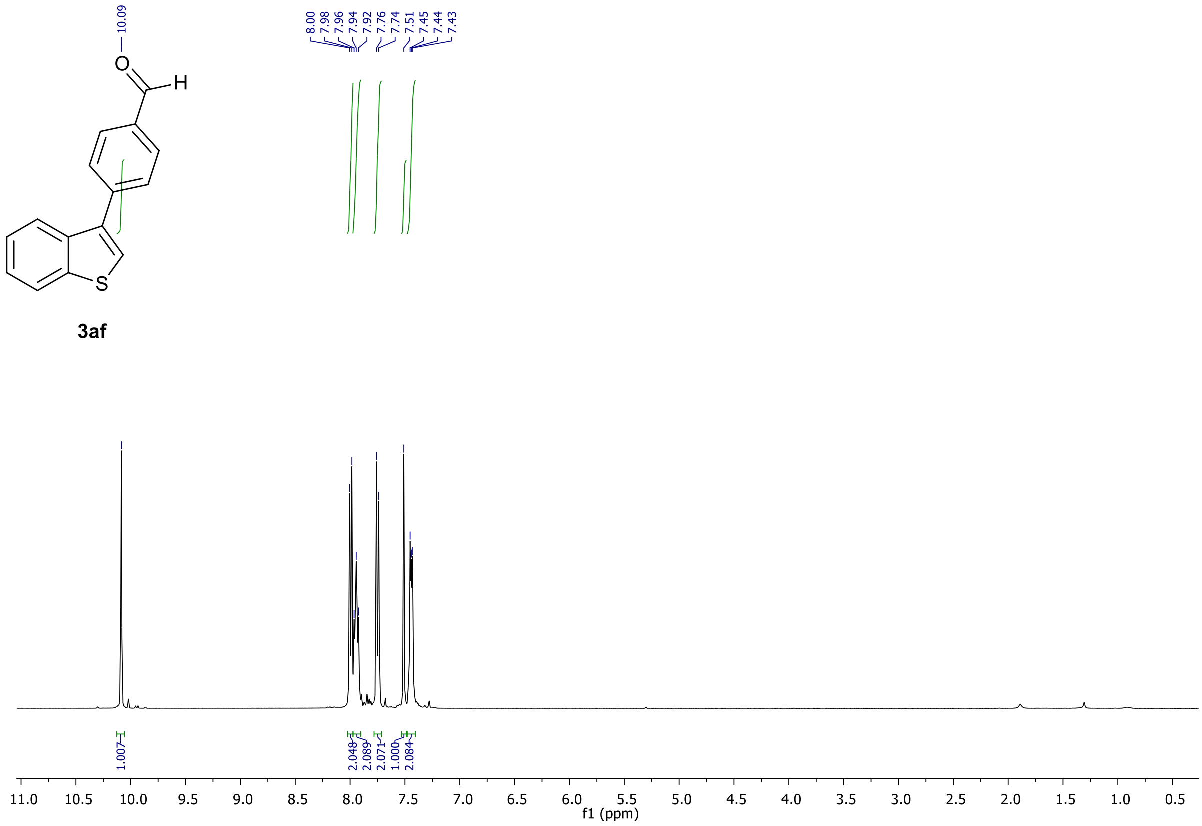
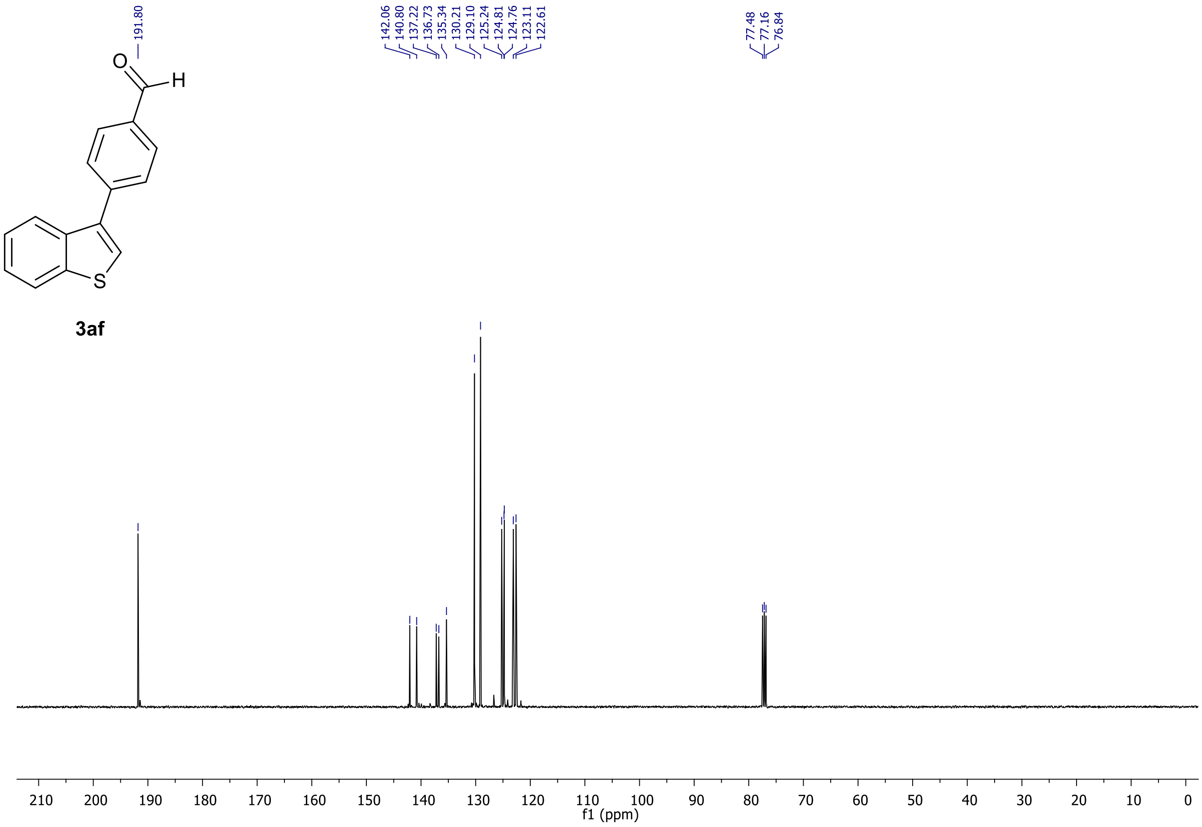
139.67
137.51
136.72
130.17
129.85
129.52
129.20
129.02
125.88
125.84
125.80
125.77
124.85
124.81
124.79
123.17
122.66
77.48
77.16
76.84
CF3
S
3ae
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



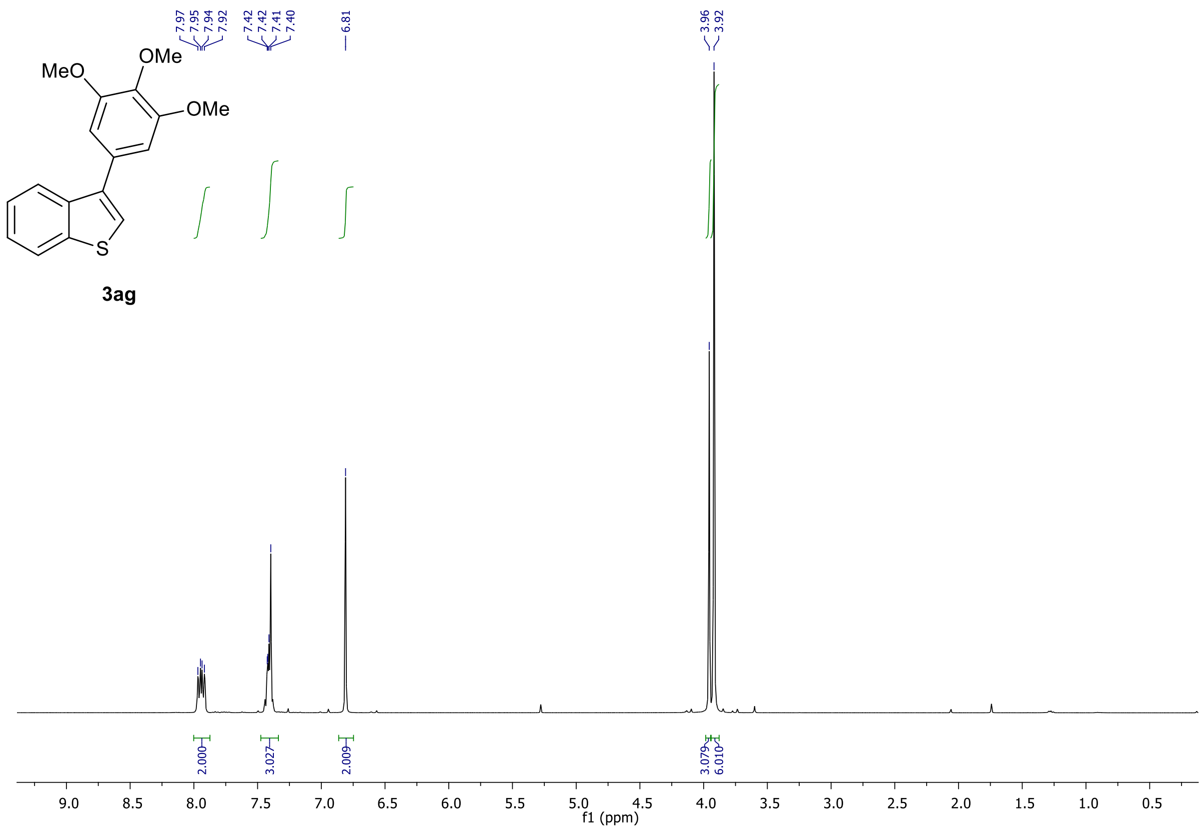
3af

10.09
8.00
7.98
7.96
7.94
7.92
7.76
7.74
7.51
7.45
7.44
7.43
O
H
S
1.007
2.048
2.089
2.071
1.000
2.084
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



3af

191.80
142.06
140.80
137.22
136.73
135.34
130.21
129.10
125.24
124.81
124.76
123.11
122.61
77.48
77.16
76.84
O
H
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.95
7.94
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7.42
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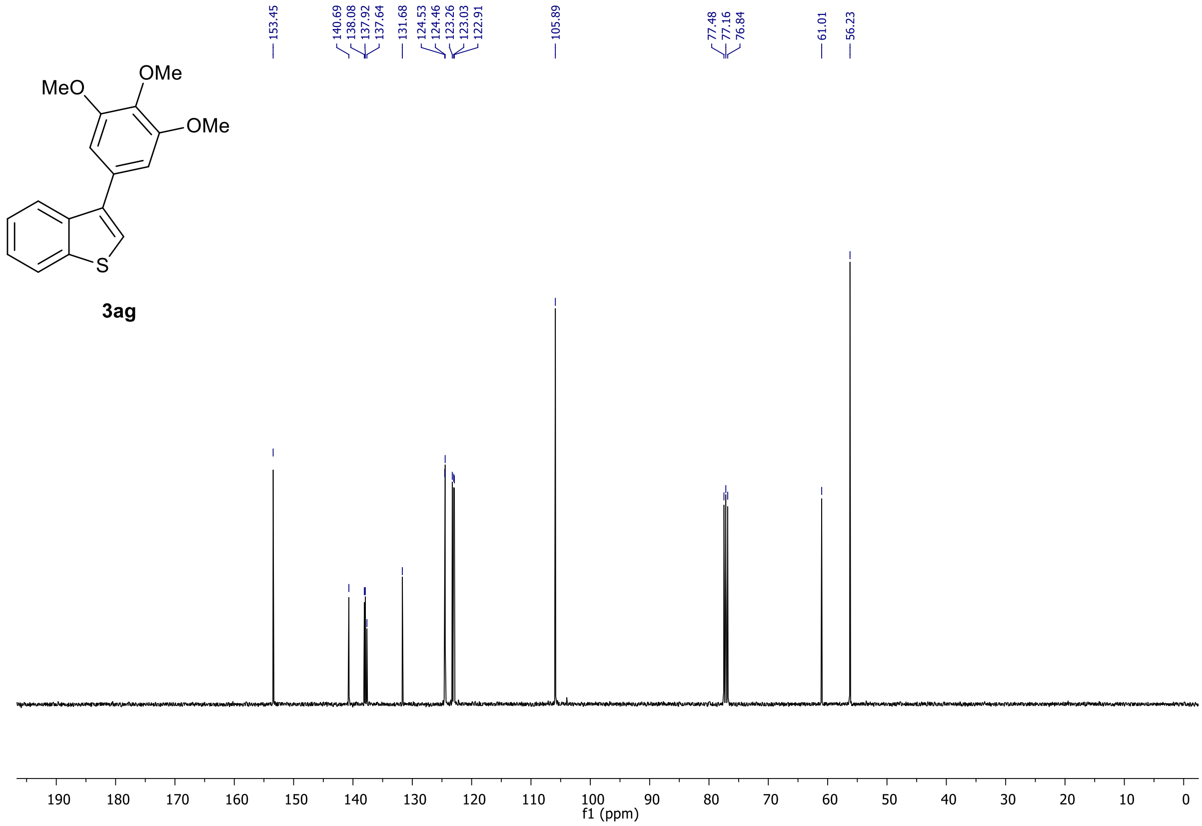
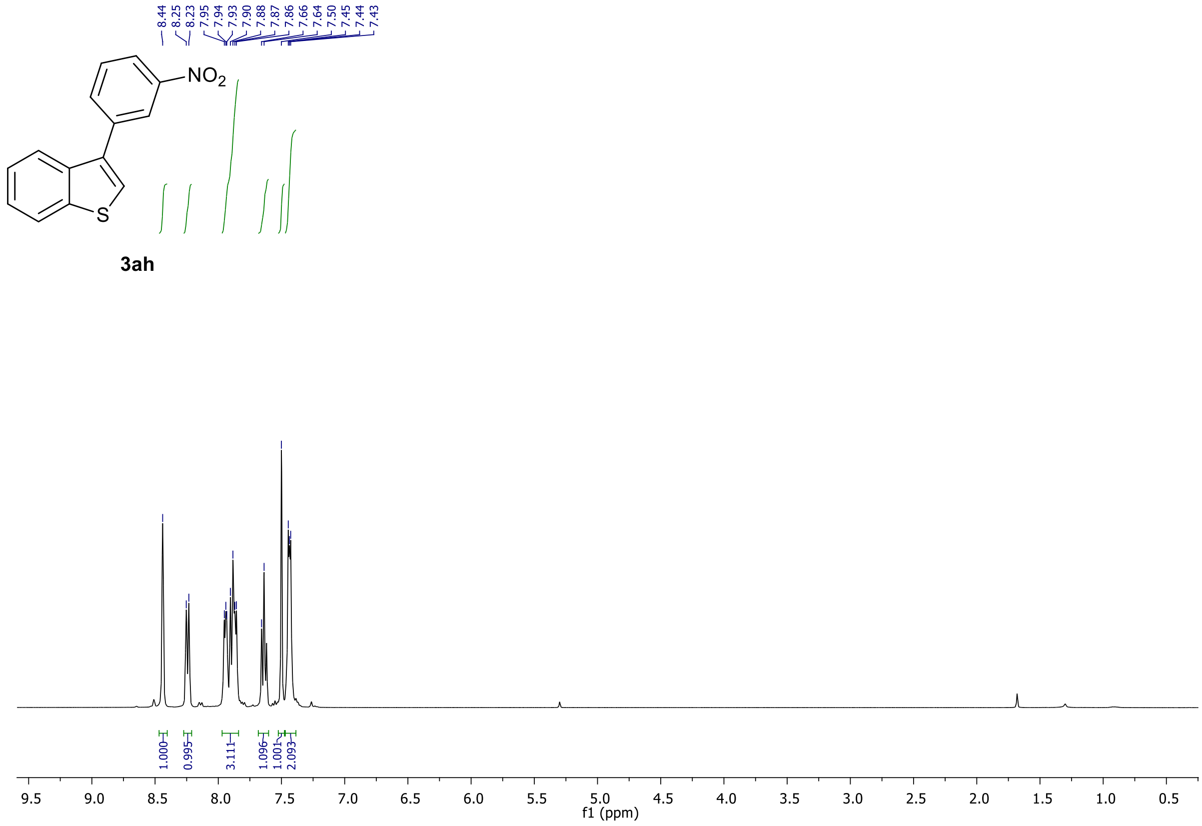
7.40
6.81
3.96
3.92
MeO
OMe
OMe
S
2.000
3.027
2.009
3.079
6.010
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3ag

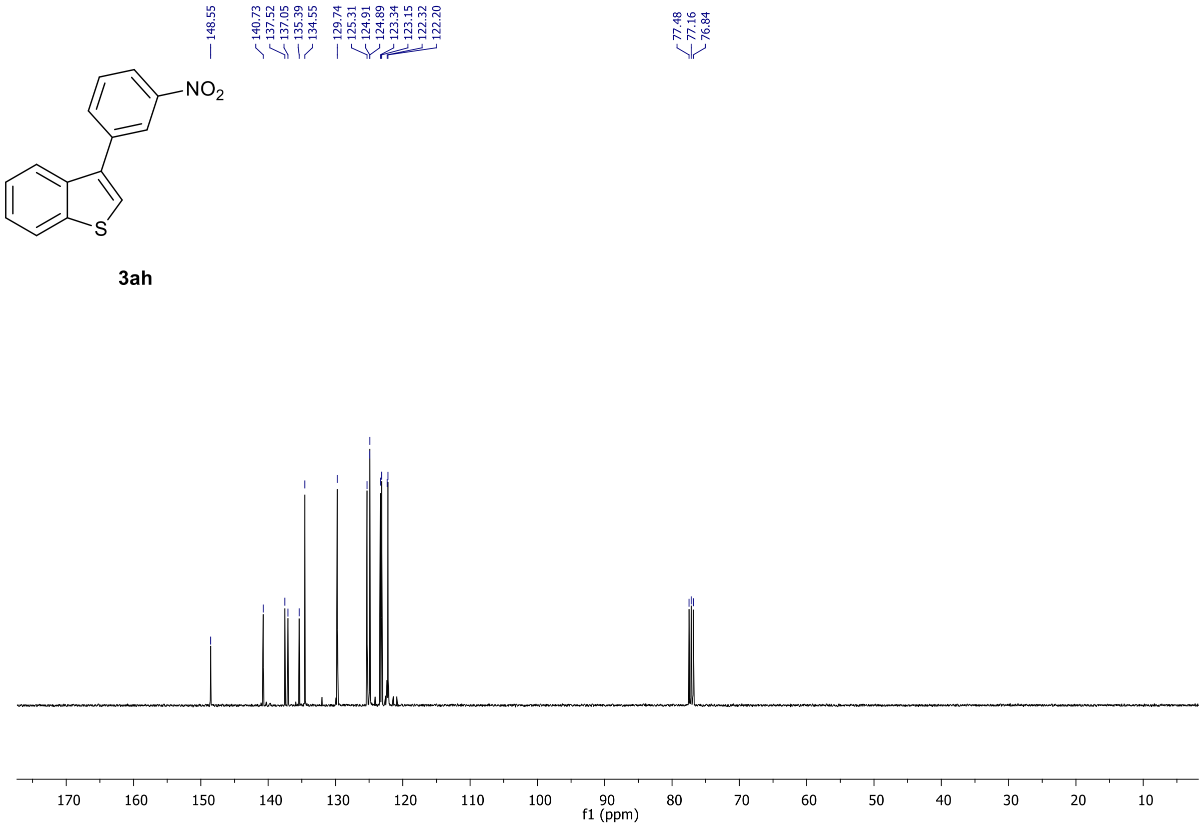

153.45
140.69
138.08
137.92
137.64
131.68
124.53
124.46
123.26
123.03
122.91
105.89
77.48
77.16
76.84
61.01
56.23
MeO
OMe
OMe
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ag



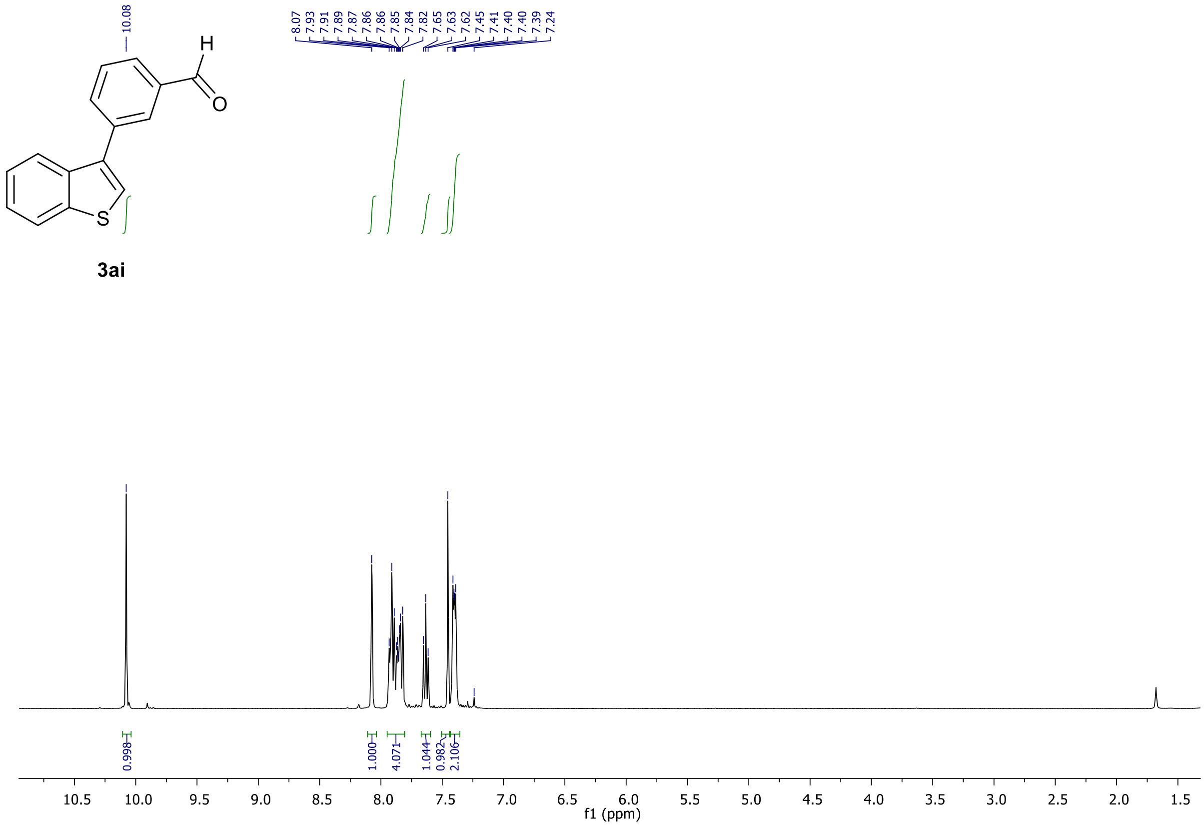
8.44
8.25
8.23
7.95
7.94
7.93
7.90
7.88
7.87
7.86
7.66
7.64
7.50
7.45
7.44
7.43
NO2
S
1.000
0.995
3.111
1.096
1.001
2.093
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3ah

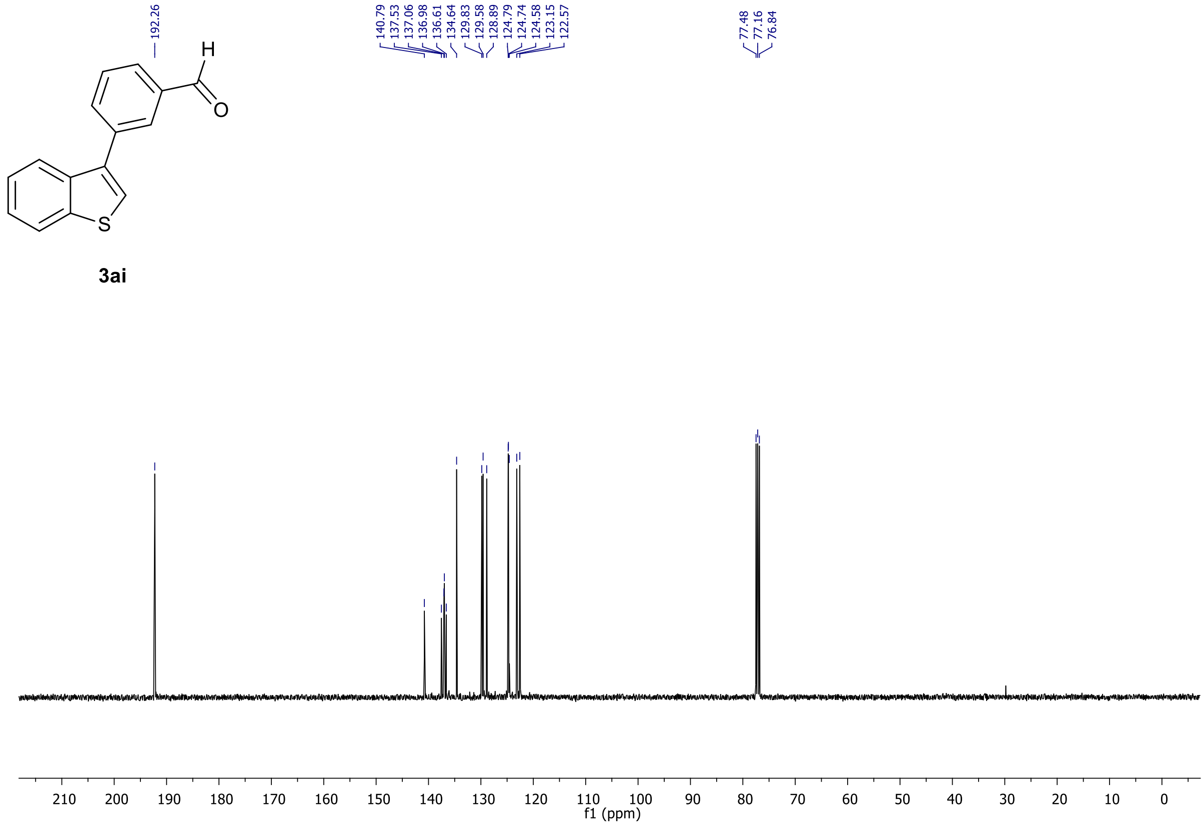


148.55
140.73
137.52
137.05
135.39
134.55
129.74
125.31
124.91
124.89
123.34
123.15
122.32
122.20
77.48
77.16
76.84
NO2
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

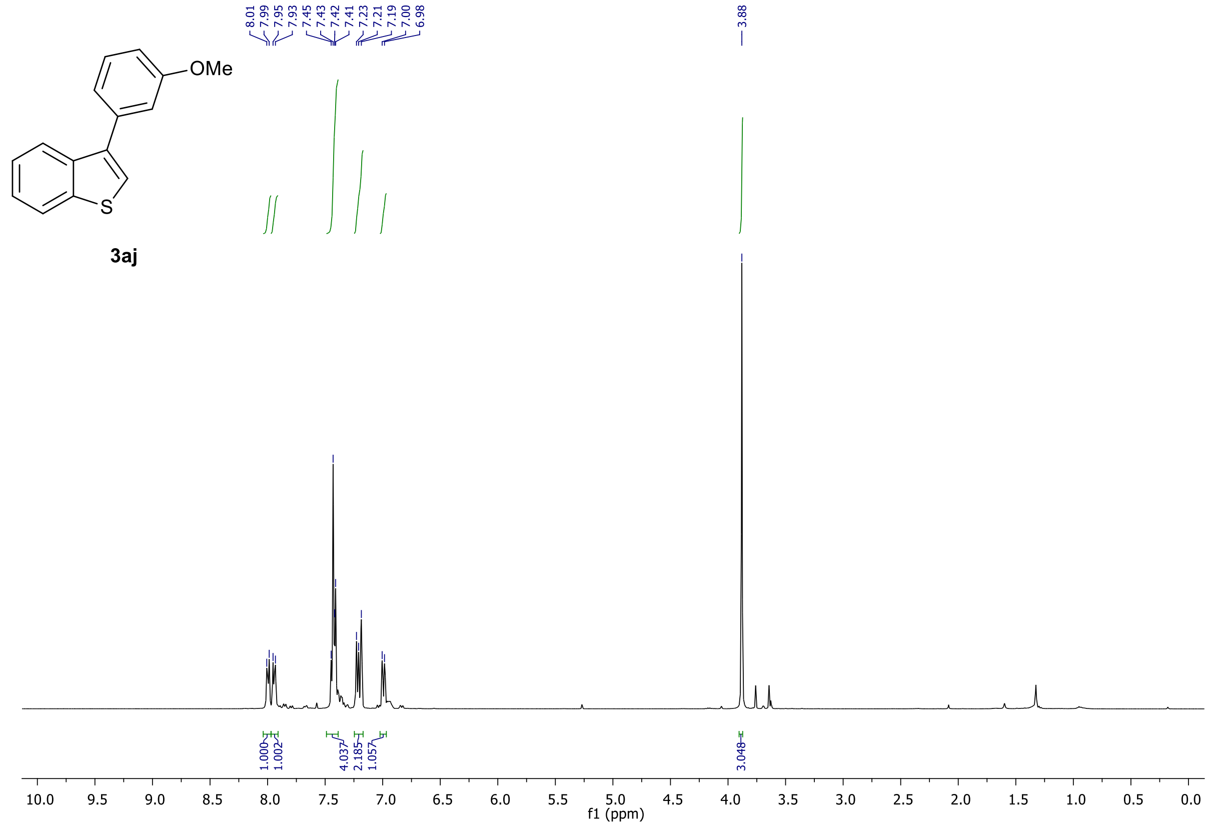
3ah


3ai

10.08
8.07
7.93
7.91
7.89
7.87
7.86
7.86
7.85
7.84
7.82
7.65
7.63
7.62
7.45
7.41
7.40
7.40
7.39
7.24
H
O
S
0.998
1.000
4.071
1.044
0.982
2.106
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

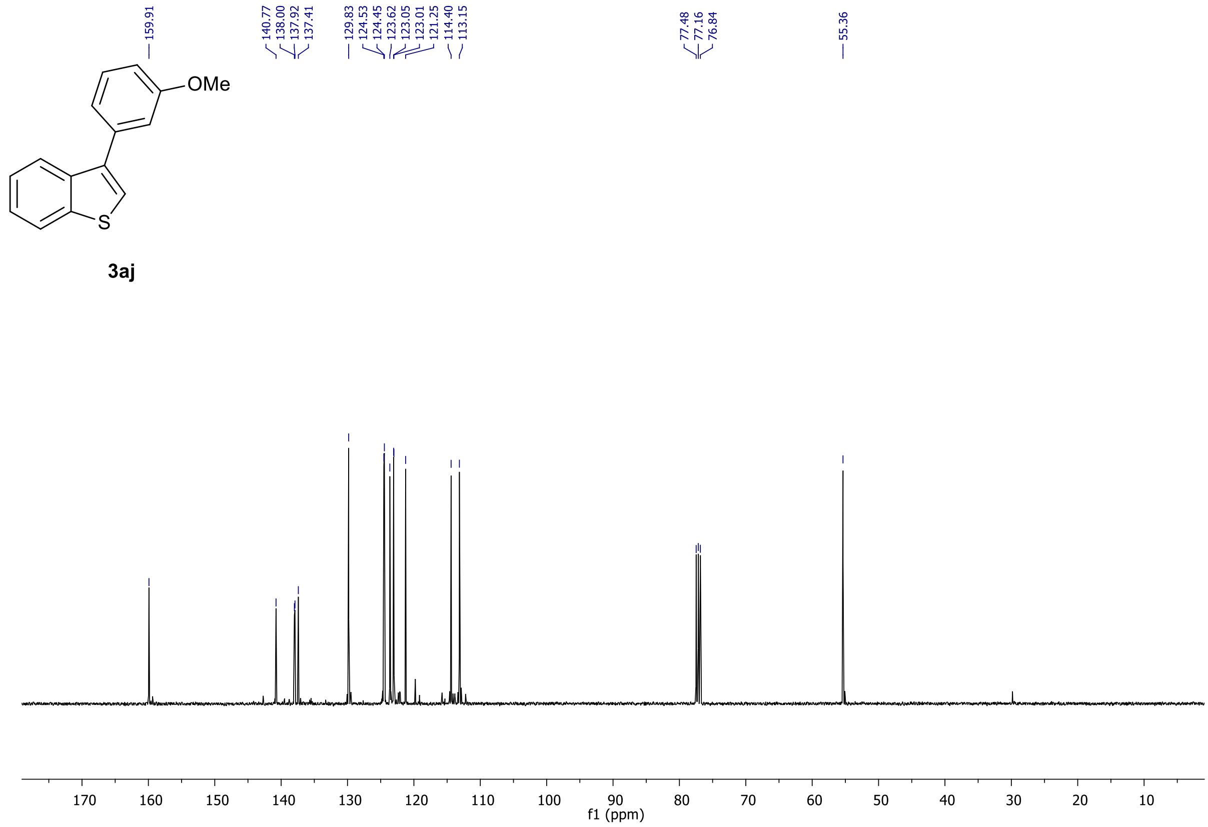

3ai

192.26
140.79
137.53
137.06
136.98
136.61
134.64
129.83
129.58
128.89
124.79
124.74
124.58
123.15
122.57
77.48
77.16
76.84
H
O
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



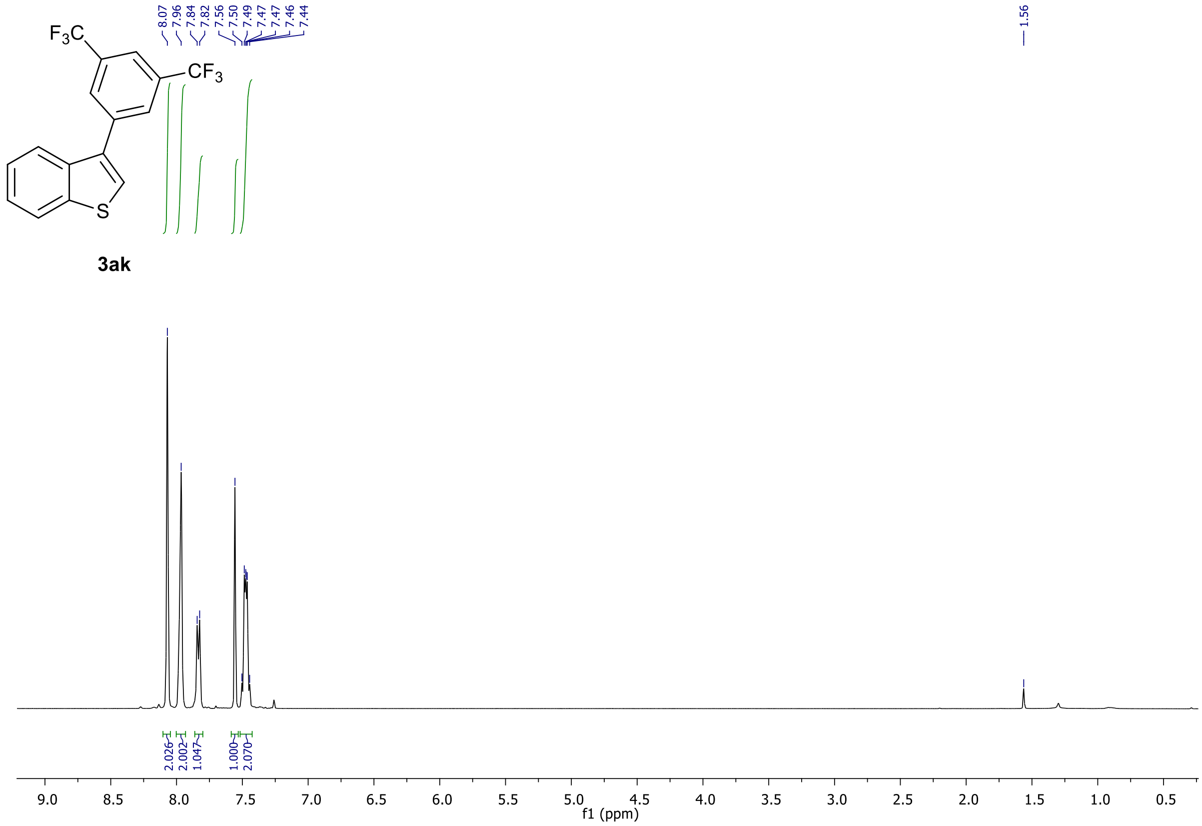
3aj

OMe
S
8.01
7.99
7.95
7.93
7.45
7.43
7.42
7.41
7.23
7.21
7.19
7.00
6.98
3.88
1.000
1.002
4.037
2.185
1.057
3.048
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

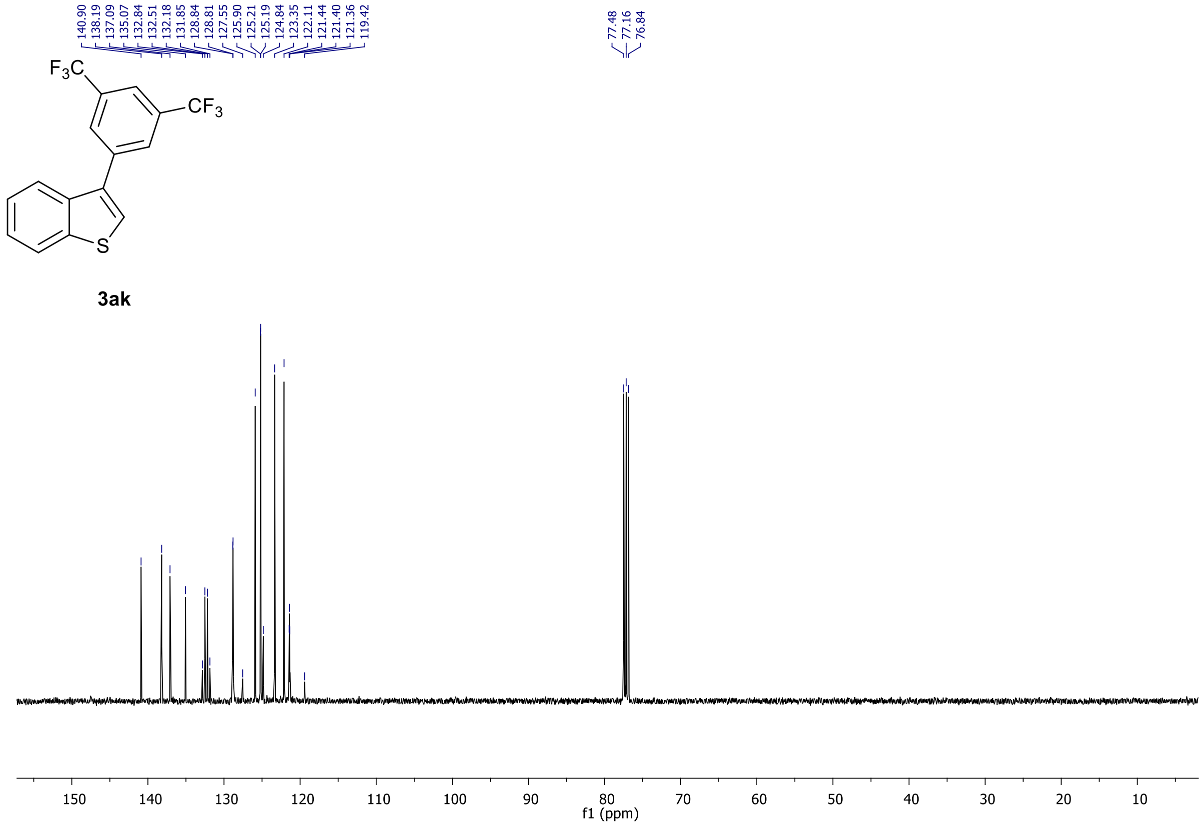


3aj

OMe
S
159.91
140.77
138.00
137.92
137.41
129.83
124.53
124.45
123.62
123.05
123.01
121.25
114.40
113.15
77.48
77.16
76.84
55.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


F$_3$C
CF$_3$
S
8.07
7.96
7.84
7.82
7.56
7.50
7.49
7.47
7.47
7.46
7.44
1.56
2.026
2.002
1.047
1.000
2.070
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3ak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CF$_3$
S
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138.19
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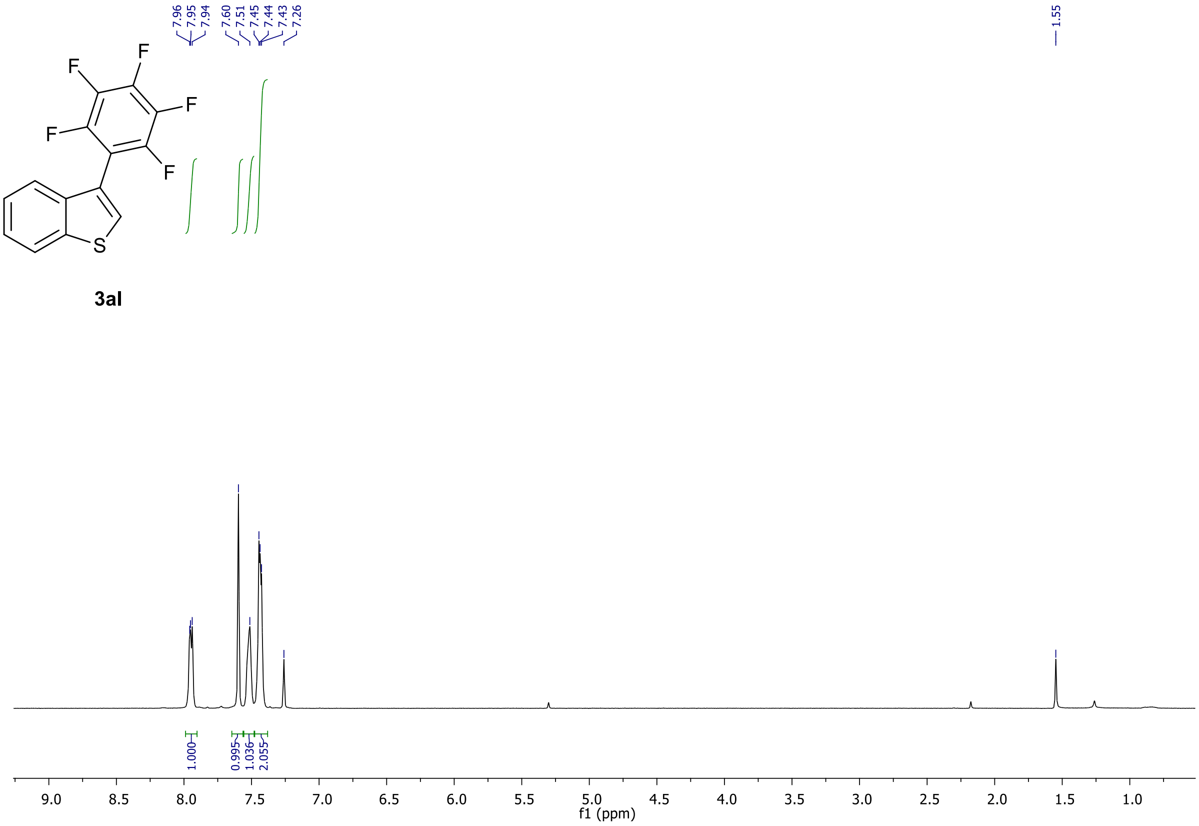
135.07
132.84
132.51
132.18
131.85
128.84
128.81
127.55
125.90
125.21
125.19
124.84
123.35
122.11
121.44
121.40
121.36
119.42
77.48
77.16
76.84
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3ak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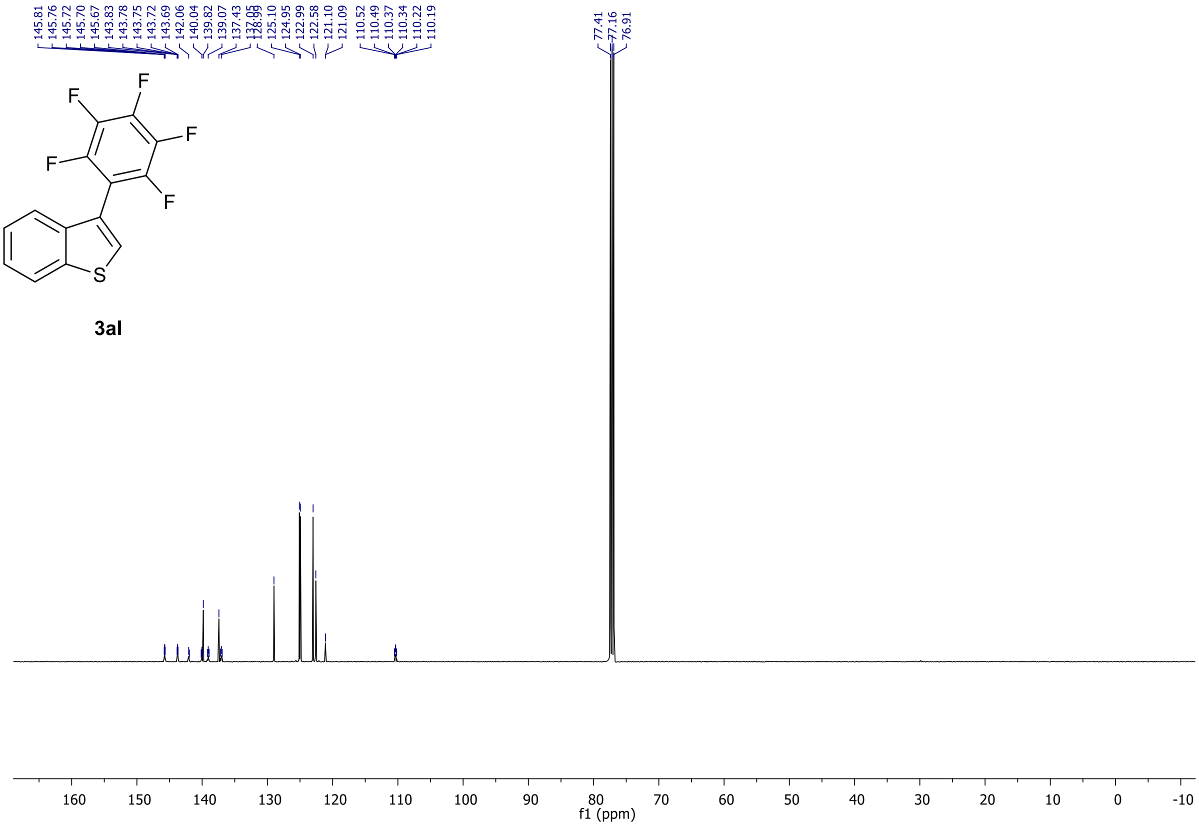
7.95
7.94
7.60
7.51
7.45
7.44
7.43
7.26
1.55
F
F
F
F
F
S
1.000
0.995
1.036
2.055
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

3al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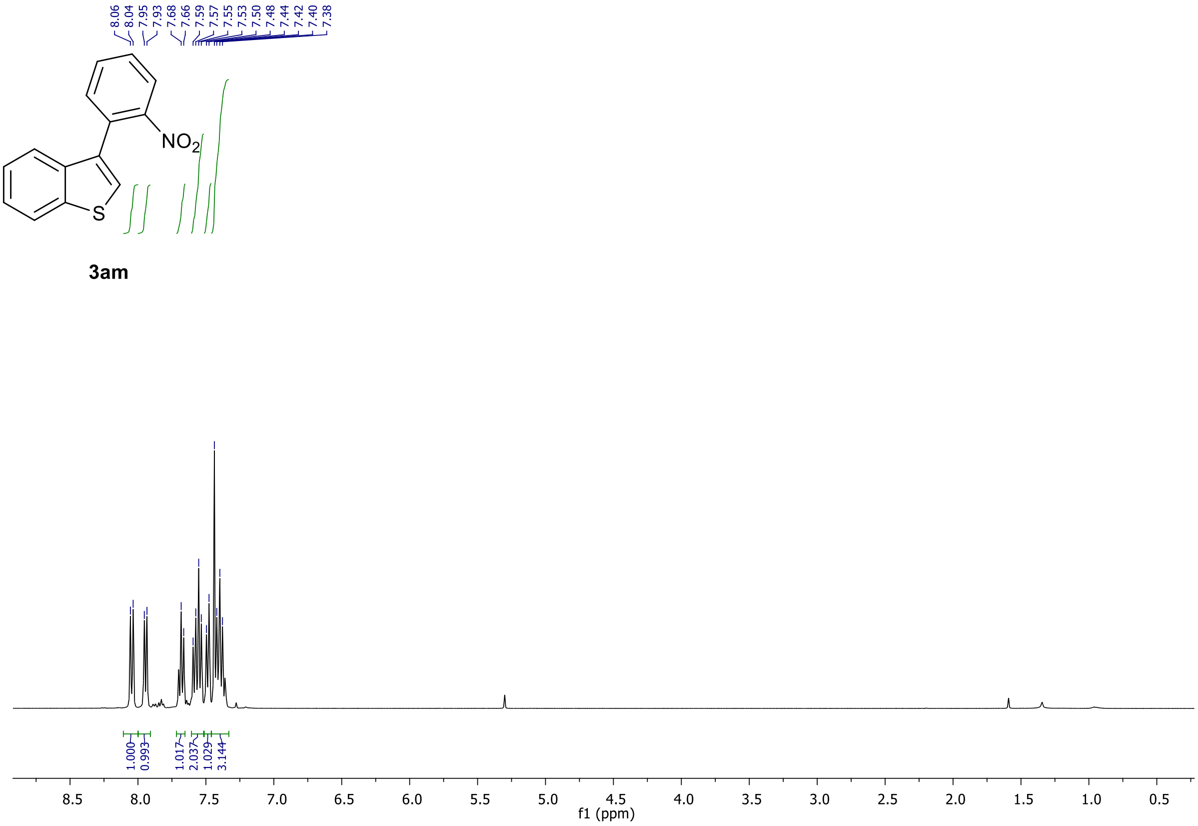
140.04
139.82
139.07
137.43
137.05
128.99
125.10
124.95
122.99
122.58
121.10
121.09
110.52
110.49
110.37
110.34
110.22
110.19
77.41
77.16
76.91
F
F
F
F
F
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3al



3am

8.06
8.04
7.95
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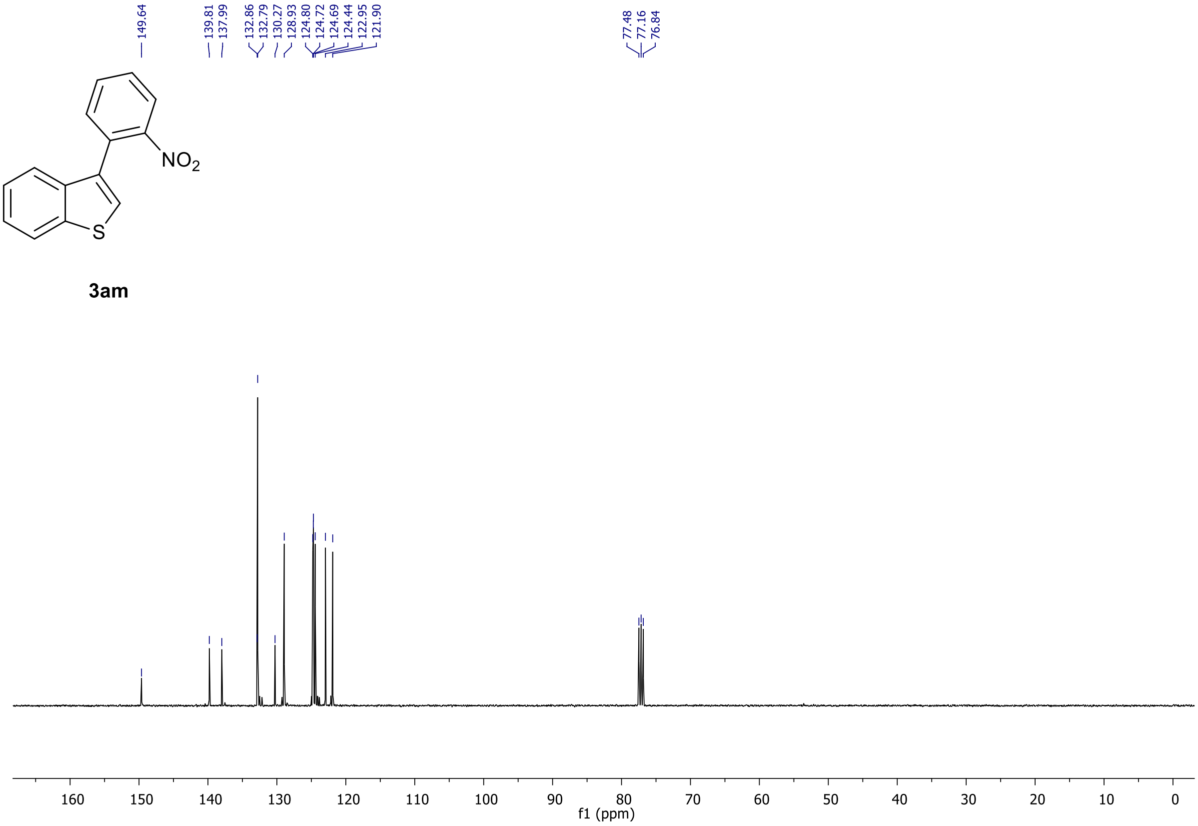
7.68
7.66
7.59
7.57
7.55
7.53
7.50
7.48
7.44
7.42
7.40
7.38
NO2
S
1.000
0.993
1.017
2.037
1.029
3.144
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



3am

149.64
139.81
137.99
132.86
132.79
130.27
128.93
124.80
124.72
124.69
124.44
122.95
121.90
77.48
77.16
76.84
NO2
S
160
150
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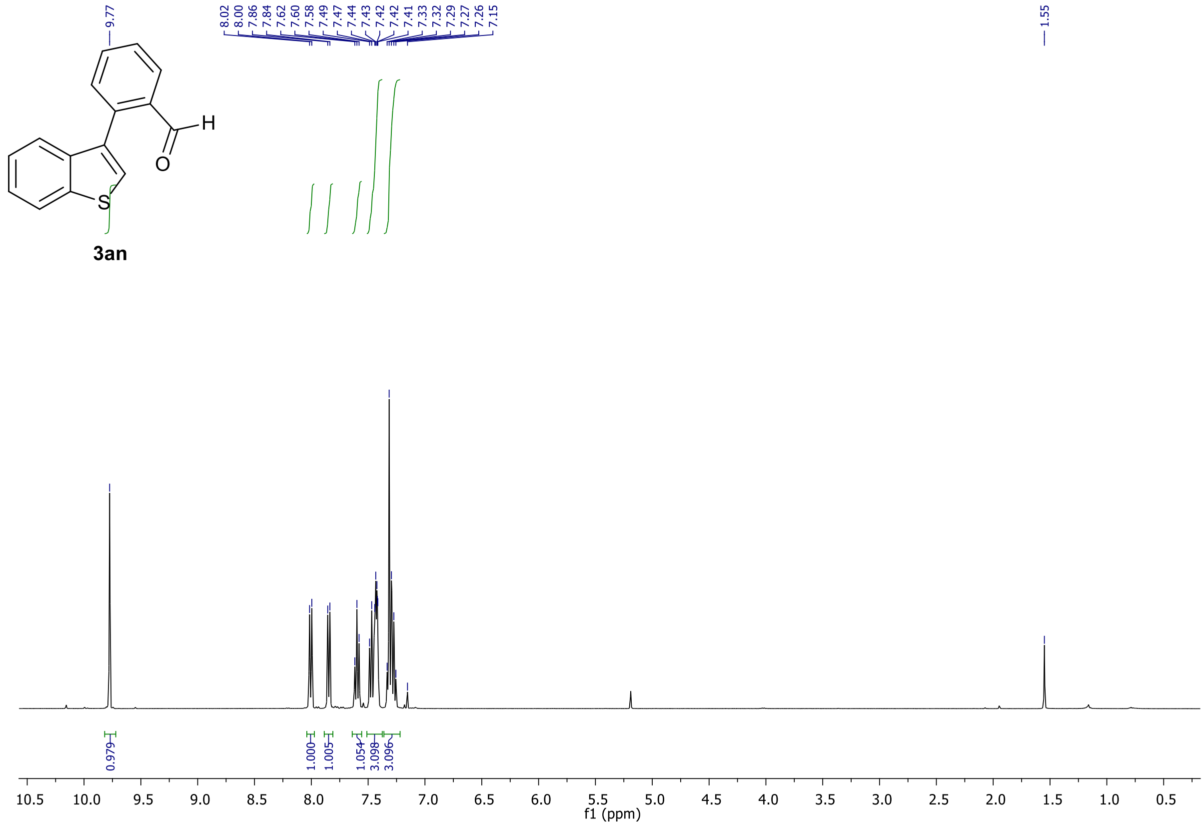
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3an

9.77
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8.00
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7.84
7.62
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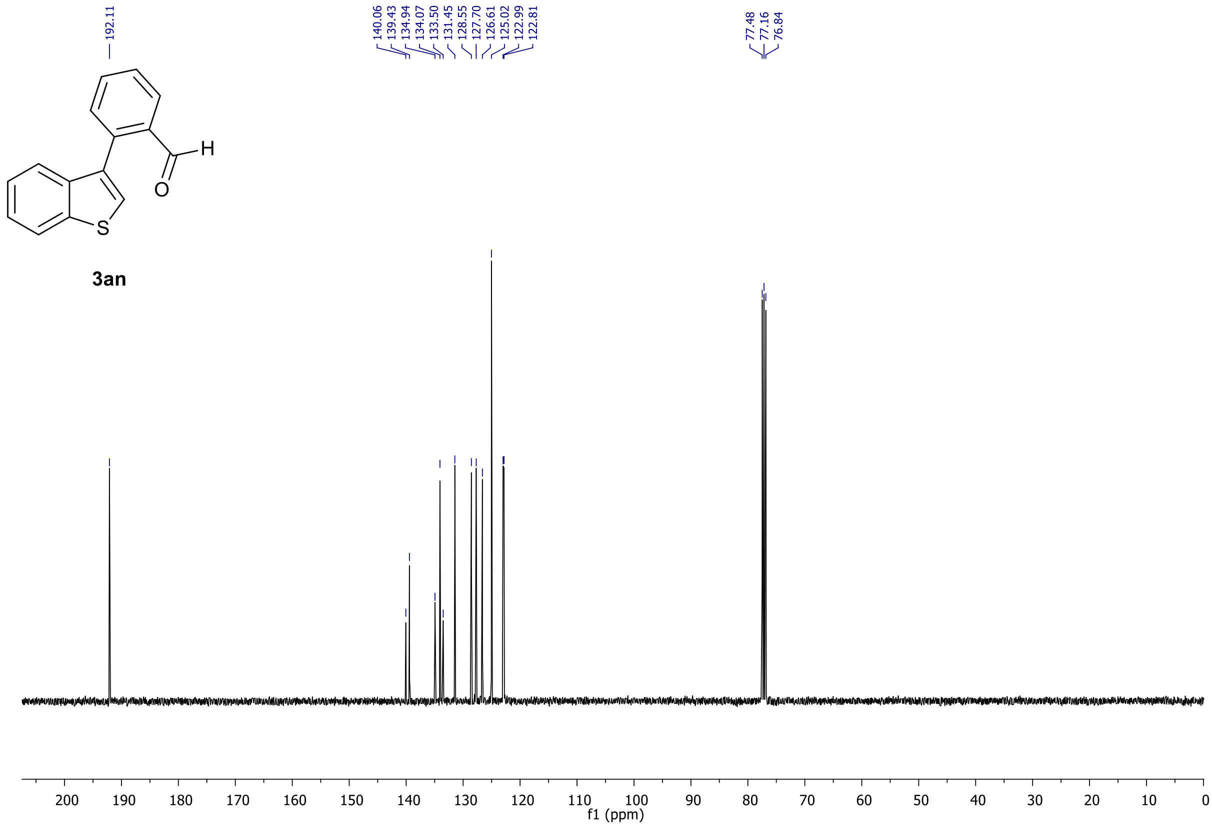
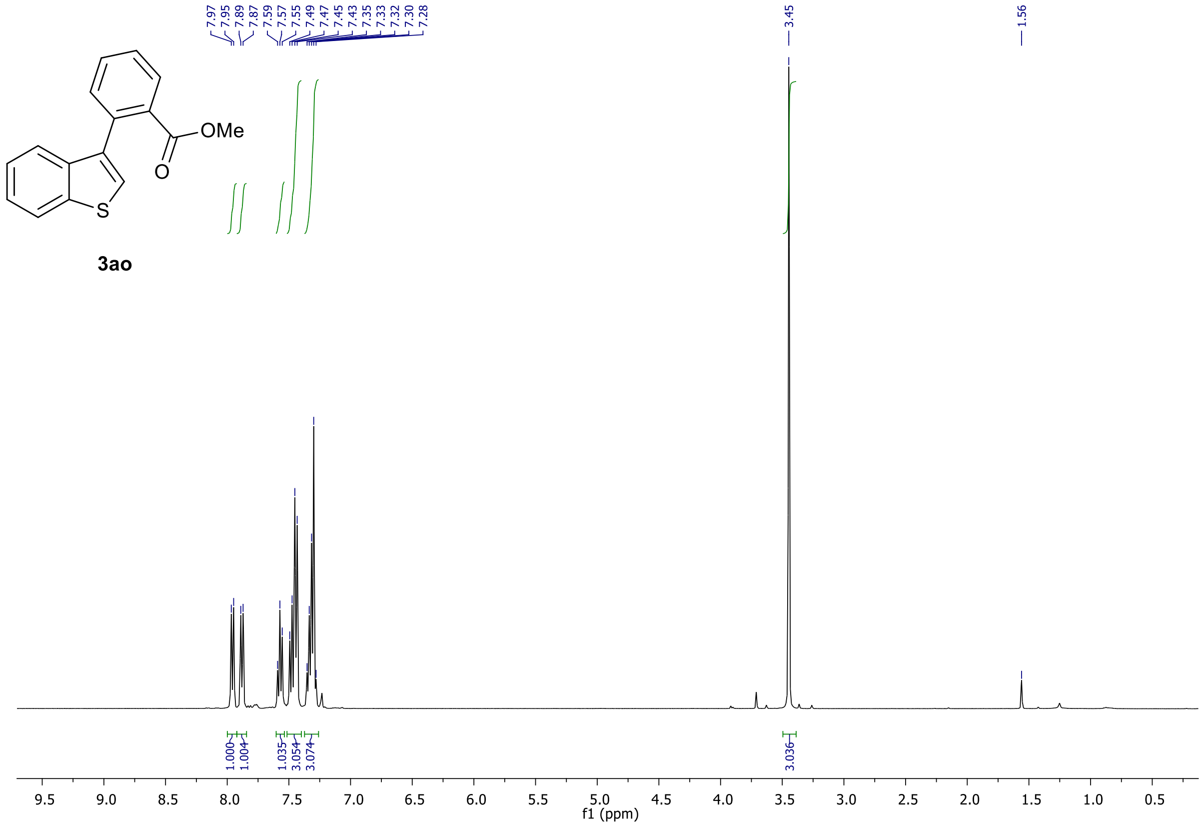
7.58
7.49
7.47
7.44
7.43
7.42
7.42
7.41
7.33
7.32
7.29
7.27
7.26
7.15
1.55
0.979
1.000
1.005
1.054
3.098
3.096
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



3an

192.11
140.06
139.43
134.94
134.07
133.50
131.45
128.55
127.70
126.61
125.02
122.99
122.81
77.48
77.16
76.84
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.97
7.95
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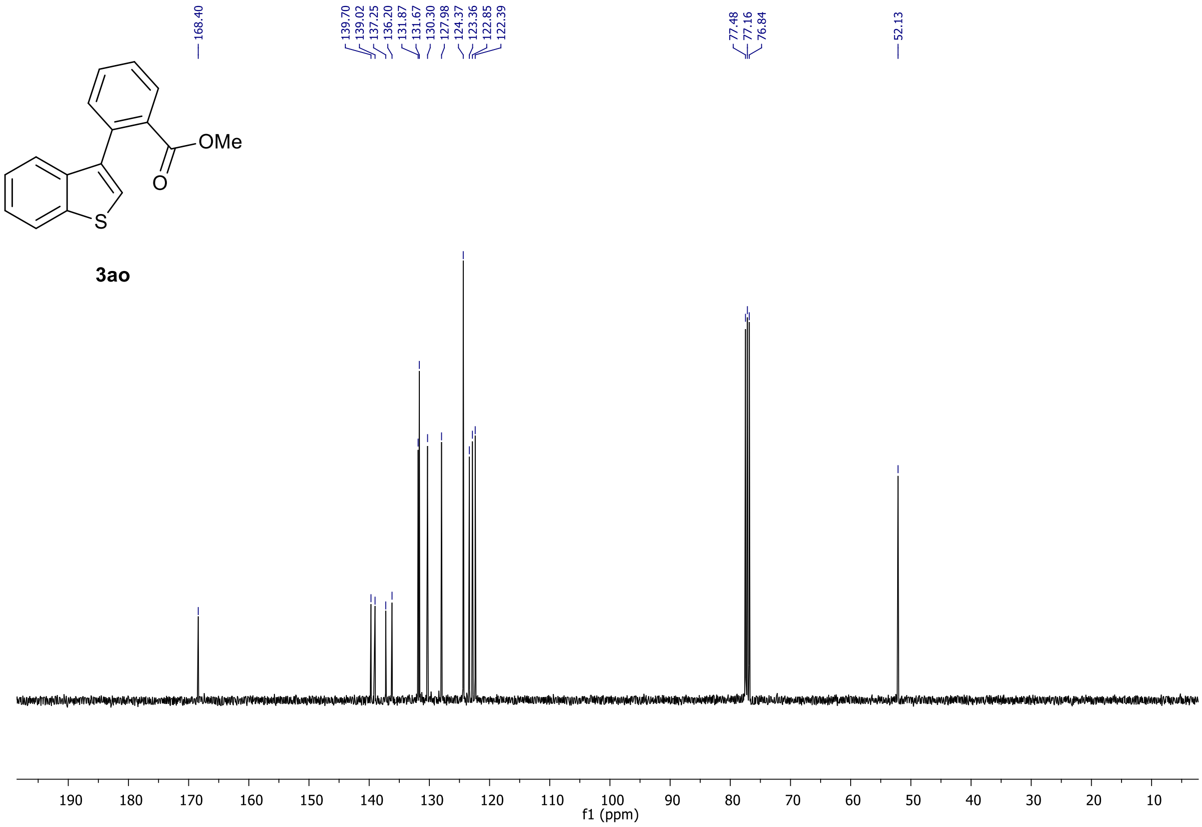
7.87
7.59
7.57
7.55
7.49
7.47
7.45
7.43
7.35
7.33
7.32
7.30
7.28
3.45
1.56
OMe
O
S
3ao
1.000
1.004
1.035
3.054
3.074
3.036
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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137.25
136.20
131.87
131.67
130.30
127.98
124.37
123.36
122.85
122.39
77.48
77.16
76.84
52.13
OMe
O
S
3ao
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)