# Ag(I) –C–H Activation Enables Near-Room-Temperature Direct α-Arylation of Benzo[*b*]thiophenes

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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 μL). $AgNO_3$ impregnated silica gel was prepared by absorbing a solution of $AgNO_3$ in MeCN (10% wt of $AgNO_3$ to silica) on silica. The MeCN was removed under reduced pressure on a rotary evaporator and the silica was further dried at 90 °C and < 1 mbar for 1-2 h. 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 analysis was carried out using an AGILENT 7820A-GC and 5975-MS. Melting points were obtained using a SMP 11 Stuart Scientific apparatus. NMR spectra were recorded in $CDCl_3$ on Bruker AV–400/AV–500 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 7.26/7.26/77.16, $^{1}H/^{2}H/^{13}C$ NMR; DMSO: δ 2.50/39.52, $^{1}H/^{13}C$ 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, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. 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. High performance liquid chromatography was performed on Agilent Technologies chromatographs (Series 1260; G1315D-1260 DAD VL) using Chiralpak OD-H column. Optical rotations were measured using a Rudolph Research Analytical Autopol I Polarimeter.

## II. Optimization of Reaction Conditions

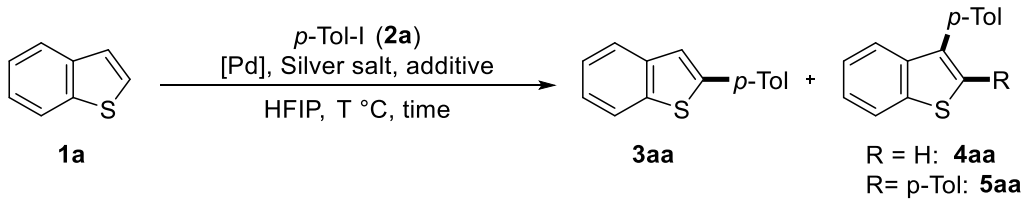



***Table S.1:*** Screening of Catalyst Loading at 80 °C.

| Entry[a,b] | [Pd] (x mol%) | time | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|---|
| 1 | 2.5 | 1 h | *Nd* | 21 | *traces* | 91 | *traces* |
| 2 | 1.0 | 16 h | 6 | 15 | ~3 | 67 | ~20 |
| 3 | 0.5 | 16 h | 17 | 31 | 14 | 47 | 18 |
| 4 | 0.2 | 16 h | 40 | 68 | 34 | 12 | 9 |
| 5 | 0.05 | 16 h | 56 | 95 | 26 | 6 | 2 |
| 6 | 0.05 | 3 days | 52 | 94 | 27 | 5 | 2 |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] **1a** (0.5 mmol), **2a** (0.75 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (x mol %), $Ag_2CO_3$ (0.375 mmol), HFIP (0.5 mL).

***Table S.2:*** Screening of Silver Salts at 30 °C.

| Entry[a,b] | [Ag] | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|
| 1[c] | $Ag_2CO_3$ | 65 | 94 | - | 21 | - |
| 2[d] | AgOPiv | 75 | 107 | 6 | 3 | - |
| 3[c] | $Ag_2O$ | 45 | 66 | 26 | 10 | 4 |
| 4[d] | AgOAc | 85 | 122 | *traces* | 5 | - |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] **1a** (0.25 mmol), **2a** (0.375 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.2 mol %), HFIP (0.25 mL), 16 h. [c] Ag salt (0.188 mmol). [d] Ag salt (0.375 mmol).

***Table S.3:*** Screening of Additives at 30 °C.

| Entry[a,b] | Additive | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|
| 1[c] | XantPhos | 83 | 104 | 9 | 3 | - |
| 2[d] | $PPh_3$ | 48 | 43 | 17 | 22 | 5 |
| 3[c] | BINAP | 79 | 106 | 10 | 5 | *traces* |
| 4[c] | dppe | 78 | 99 | - | - | - |
| 5[d] | $PCy_3$ | 33 | 42 | 16 | 12 | 3 |
| 6[c] | 2,2'-Bipyridine | 86 | 112 | - | - | - |
| 7[d] | TMP | 52 | 74 | 27 | 12 | 5 |
| 8[d] | NaOAc | 39 | 74 | 45 | 1 | 1 |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] **1a** (0.25 mmol), **2a** (0.375 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.2 mol %), $Ag_2O$ (0.188 mmol), HFIP (0.25 mL), 16 h. [c] Additive (0.063 mmol). [d] Additive (0.125 mmol).

***Table S.4:*** Screening of Equivalents of NaOAc at 30 °C.

| Entry[a,b] | Additive (equiv) | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|
| 1 | 0.25 | 42 | 76 | 41 | 1 | 1 |
| 2 | 0.5 | 39 | 74 | 45 | 1 | 1 |
| 3 | 0.75 | 44 | 80 | 42 | 2 | 1 |
| 4 | 1 | 48 | 82 | 38 | 2 | 1 |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] **1a** (0.25 mmol), **2a** (0.375 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.2 mol %), $Ag_2O$ (0.188 mmol), NaOAc (x equiv), HFIP (0.25 mL), 16 h.

***Table S.5:*** Screening of Acetate Salts at 30 °C.

| Entry[a,b] | Additive | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|
| 1 | NaOAc | 39 | 74 | 45 | 1 | 1 |
| 2 | KOAc | 45 | 84 | 39 | 1 | 1 |
| 3 | LiOAc | 46 | 80 | 38 | 1 | 1 |
| 4 | CsOAc | 56 | 93 | 29 | 3 | 1 |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] **1a** (0.25 mmol), **2a** (0.375 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.2 mol %), $Ag_2O$ (0.188 mmol), MOAc (0.125 mmol), HFIP (0.25 mL), 16 h.

***Table S.6:*** Screening of Palladium Catalysts at 30 °C.

| Entry[a,b] | [Pd] catalyst | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|
| 1 | $Pd_2dba_3{\cdot}CHCl_3$ | 39 | 74 | 45 | 1 | 1 |
| 2 | $PdI_2$ | 24 | 36 | 54 | 6 | 5 |
| 3 | $PdCl_2$ | 80 | 113 | 8 | *traces* | *traces* |
| 4 | $Pd(TFA)_2$ | 20 | 34 | 52 | 6 | 4 |
| 5 | $Pd(PPh_3)_4$ | 28 | 48 | 47 | 6 | 4 |
| 6 | $Pd(OAc)_2$ | 26 | 36 | 54 | 6 | 5 |
| 7 | Pd/C | 88 | 117 | - | - | - |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] **1a** (0.25 mmol), **2a** (0.375 mmol), [Pd] (0.4 mol %), $Ag_2O$ (0.188 mmol), NaOAc (0.125 mmol), HFIP (0.25 mL), 16 h.

***Table S.7:*** Screening of Different Stoichiometry at 30 °C.

| Entry[a,b] | mmol 1a : mmol 2a | 1a (%) | 2a (%) | 3aa (%) | 4aa (%) | 5aa (%) |
|---|---|---|---|---|---|---|
| 1 | 0.25 : 0.375 | 26 | 36 | 54 | 6 | 5 |
| 2 | 0.25 : 0.75 | 42 | 133 | 32 | 15 | 4 |
| 3 | 0.5 : 0.25 | 92 | 10 | 73 | 5 | 2 |
| 4[c] | 0.5 : 0.25 | 83 | 5 | 83 | 3 | 2 |
| 5[c,d] | 0.5 : 0.25 | 123 | 41 | 57 | 2 | 1 |

[a] Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] $Pd(OAc)_2$ (0.4 mol %), $Ag_2O$ (0.188 mmol), NaOAc (0.125 mmol), HFIP (0.25 mL), 16 h. [c] $Ag_2O$ (0.25 mmol). [d] $Pd(OAc)_2$ (0.2 mol %).

## III. Experimental Details, Spectroscopic and Analytical Data

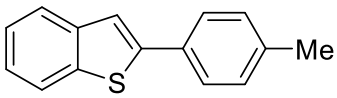
### III-1. Experimental Details

***General procedure A.*** $Pd(OAc)_2$ (0.4 mol %), silver oxide (1.0 equiv), NaOAc (0.5 equiv), aryl iodide (1.0 equiv) and (substituted) benzo[*b*]thiophene (2.0 equiv) were stirred in 1,1,1,3,3,3-hexafluoro-2-propanol [1 M] at 30 °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.

***General procedure B.*** $Pd(OAc)_2$ (0.8 mol %), silver oxide (1.0 equiv), NaOAc (0.5 equiv), aryl iodide (1.0 equiv) and substituted thiophene (2.0 equiv) were stirred in 1,1,1,3,3,3-hexafluoro-2-propanol [1 M] at 50 °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.

***General procedure C.*** $Pd(OAc)_2$ (0.8 mol %), silver oxide (1.0 equiv), NaOAc (0.5 equiv), aryl iodide (2.0 equiv) and substituted thiophene (1.0 equiv) were stirred in 1,1,1,3,3,3-hexafluoro-2-propanol [1 M] at 50 °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.

## III-2. Spectroscopic and Analytical Data



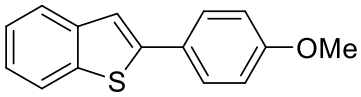

**2-(*p*-tolyl)benzo[*b*]thiophene (3aa)**

The product **3aa** was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 84% yield (141 mg, 0.63 mmol).

The same reaction on a 20 mmol scale afforded 71% yield of product **3aa** (3.18 g, 14.2 mmol).

**$R_f$** (hexane): 0.47. **$^1$H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.37-7.27 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.7, 141.1, 140.0, 138.6, 131.8, 130.0, 126.7,

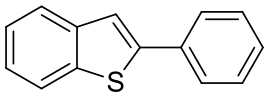
124.8, 124.4, 123.7, 122.6, 119.2, 21.6. **HRMS**: calcd for $C_{15}H_{12}S$ ($M^+$), 224.0654; found, 224.0654. **Mp**: 166-168 °C. Data is in accordance with the literature.[1]




**2-(4-methoxyphenyl)benzo[*b*]thiophene (3ab)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4-iodoanisole **2b** (180 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:$CH_2Cl_2$ = 4:1) as a white solid in 81% yield (146 mg, 0.61 mmol).

**$R_f$** (hexane:$CH_2Cl_2$ = 4:1): 0.30. **$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.43 (s, 1H), 7.34-7.26 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 160.1, 144.5, 141.2, 139.5, 128.1, 127.4, 124.8, 124.3, 123.6, 122.5, 118.5, 114.7, 55.7. **HRMS**: calcd for $C_{15}H_{12}OS$, 241.0682 ($MH^+$); found, 241.0681. **Mp**: 180-190 °C. Data is in accordance with the literature.[1]

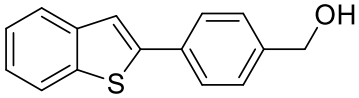



**2-phenylbenzo[*b*]thiophene (3ac)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and iodobenzene **2c** (87 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 84% yield (132 mg, 0.63 mmol).

**$R_f$** (hexane): 0.43. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.75-7.72 (m, 2H), 7.56 (s, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.39-7.31 (m, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.6, 141.0, 139.8, 134.6, 129.3, 128.6, 126.8, 124.8, 124.7, 123.9,

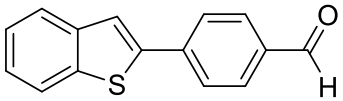
122.6, 119.8. **HRMS**: calcd for $C_{14}H_{10}S$ ($M^+$), 210.0498; found, 210.0498. **Mp**: 170-172 °C. Data is in accordance with the literature.[1]




**4-(benzo[*b*]thiophen-2-yl)benzyl alcohol (3ad)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4-iodobenzyl alcohol **2d** (181 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 7:3) as a white solid in 84% yield (151 mg, 0.63 mmol).

**$R_f$** (hexane:EtOAc = 7:3): 0.29. **$^1$H-NMR** (400 MHz, DMSO-$d_6$): δ (ppm) 7.96 (d, *J* = 7.7 Hz, 1H), 7.84-7.82 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.40-7.33 (m, 2H), 5.31 (t, *J* = 5.7 Hz, 1H), 4.55 (d, *J* = 5.7 Hz, 2H). **$^{13}$C-NMR** (101 MHz, DMSO-$d_6$): δ (ppm) 143.3, 143.2, 140.6, 138.5, 131.9, 127.2, 125.9, 124.8, 124.6, 123.7, 122.5, 119.7, 62.5. **IR**: ν = 3923, 3056, 3024, 2913, 2860, 1456, 1432, 1362, 1301, 1179, 1070, 1006, 937, 824, 808, 740, 725 $cm^{-1}$. **HRMS**: calcd for $C_{15}H_{12}OS$, 240.0603 ($M^+$); found, 240.0600. **Mp**: 206-208°C.

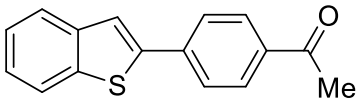



**4-(benzo[b]thiophen-2-yl)benzaldehyde (3ae)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4-iodobenzaldehyde **2e** (181 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 92:8) as a white solid in 80% yield (142 mg, 0.60 mmol).

**$R_f$** (hexane:EtOAc = 92:8): 0.30. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 10.03 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.87-7.84 (m, 3H), 7.82-7.80 (m, 1H), 7.69 (s, 1H), 7.41-7.34 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 191.8, 142.7, 140.7, 140.4, 140.4, 136.0, 130.7, 127.1, 125.5, 125.2,

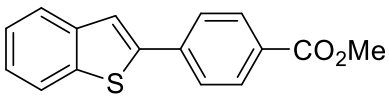
124.4, 122.7, 122.0. **HRMS**: calcd for $C_{15}H_{10}OS$ ($M^+$), 238.0447; found, 238.0447. **Mp**: 174-176 °C. Data is in accordance with the literature.[2]




**2-(4-acetophenone)benzo[*b*]thiophene (3af)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (68 mg, 0.5 mmol, 2.0 equiv) and 4'-iodoacetophenone **2f** (65 mg, 0.25 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 9:1) as a white solid in 84% yield (53 mg, 0.21 mmol).

**$R_f$** (hexane:EtOAc = 9:1): 0.34. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.02 (d, *J* = 8.4 Hz, 2H), 7.82-7.79 (m, 4H), 7.67 (s, 1H), 7.37-7.35 (m, 2H), 2.64 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 197.6, 142.9, 140.7, 140.1, 139.0, 136.6, 129.3, 126.6, 125.3, 125.0, 124.2, 122.6, 121.4, 26.9. **HRMS**: calcd for $C_{16}H_{12}OS$, 252.0603 ($M^+$); found, 252.0601. **Mp**: 208-210°C. Data is in accordance with the literature.[3]

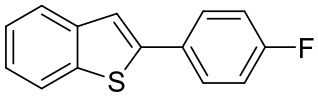



**Methyl 4-(benzo[*b*]thiophene-2-yl)benzoate (3ag)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (68 mg, 0.5 mmol, 2.0 equiv) and methyl-4-iodobenzoate **2g** (67 mg, 0.25 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 95:5) as a pale yellow solid in 70% yield (47 mg, 0.18 mmol).

**$R_f$** (hexane:EtOAc = 95:5): 0.26. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, *J* = 8.0 Hz, 2H), 7.84-7.77 (m, 4H), 7.66 (s, 1H), 7.40-7.33 (m, 2H), 3.95 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 166.8, 142.9, 140.6, 140.0, 138.7, 130.4, 129.7, 126.3, 125.1, 124.9, 124.1, 122.5, 121.2,

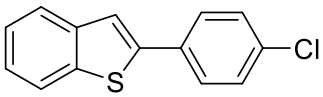
52.4. **HRMS** calcd for $C_{16}H_{12}O_2S$, 268.0553 ($M^+$); found, 268.0551. **Mp**: > 250°C. Data is in accordance with the literature.[4]



**2-(4-fluorophenyl)benzo[*b*]thiophene (3ah)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-fluoro-4-iodobenzene **2h** (87 µl, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 80% yield (137 mg, 0.60 mmol).

**$R_f$** (hexane): 0.45. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.67 (dd, *J* = 8.7 and 5.2 Hz, 2H), 7.47 (s, 1H), 7.38-7.31 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 162.8 (d, *J* = 250.1 Hz), 143.4, 141.0, 139.8, 130.9 (d, *J* = 3.4 Hz), 128.5 (d, *J* = 8.3 Hz), 125.0, 124.7, 123.9, 122.6, 119.8 (d, *J* = 1.2 Hz), 116.3 (d, *J* = 22.0 Hz). **$^{19}$F-NMR** (376 MHz, $CDCl_3$): δ (ppm) -113.3. **HRMS**: calcd for $C_{14}H_9FS$ ($M^+$), 228.0404; found, 228.0404. **Mp**: 180-182 °C. Data is in accordance with the literature.[5]

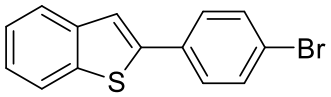


**2-(4-chlorophenyl)benzo[*b*]thiophene (3ai)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-chloro-4-iodobenzene **2i** (181 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 82% yield (150 mg, 0.61 mmol).

**$R_f$** (hexane): 0.48. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.52 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.40-7.31 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 143.2, 140.9, 139.8, 134.4, 133.2, 129.5, 128.0, 125.0,

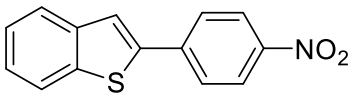
124.9, 124.0, 122.6, 120.2. **HRMS**: calcd for $C_{14}H_9ClS$ ($M^+$), 244.0107; found, 244.0108. **Mp**: 196-198 °C. Data is in accordance with the literature.[5]




**2-(4-bromophenyl)benzo[*b*]thiophene (3aj)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-bromo-4-iodobenzene **2j** (216 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 83% yield (180 mg, 0.62 mmol).

**$R_f$** (hexane): 0.50. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.59-7.53 (m, 5H), 7.39-7.31 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 143.2, 140.9, 139.8, 133.6, 132.4, 128.3, 125.0, 125.0, 124.0, 122.6, 122.6, 120.3. **HRMS**: calcd for $C_{14}H_9BrS$ ($M^+$), 287.9603; found, 287.9601. **Mp**: 210-212 °C. Data is in accordance with the literature.[6]

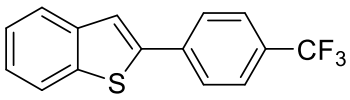



**2-(4-nitrophenyl)benzo[*b*]thiophene (3ak)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-iodo-4-nitrobenzene **2k** (191 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:$CH_2Cl_2$ = 75:25) as a yellow solid in 48% yield (91 mg, 0.36 mmol).

**$R_f$** (hexane:$CH_2Cl_2$ = 75:25): 0.33. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.28 (d, *J* = 8.8 Hz, 2H), 7.88-7.82 (m, 4H), 7.71 (s, 1H), 7.41-7.38 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 147.3, 141.3, 140.7, 140.4, 140.3, 126.9, 125.7, 125.2, 124.5, 124.4, 122.6, 122.6. **HRMS**: calcd

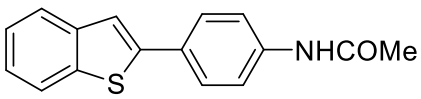
for $C_{14}H_9NO_2S$, 255.0349 ($M^+$); found, 255.0348. **Mp**: 212-214°C. Data is in accordance with the literature.[7]



**2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (3al)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4-iodobenzotrifluoride **2l** (111 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 79% yield (164 mg, 0.59 mmol).

**$R_f$** (hexane): 0.51. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.87-7.80 (m, 4H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.64 (s, 1H), 7.42-7.33 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 142.4, 140.6, 140.0, 137.9, 129.9 (q, *J* = 32.8 Hz), 126.7, 126.1 (q, *J* = 3.9 Hz), 125.1, 125.0, 124.9 (q, *J* = 272.0 Hz), 124.1, 122.8, 121.2. **$^{19}$F-NMR** (376 MHz, $CDCl_3$) δ (ppm) -62.6. **HRMS**: calcd for $C_{15}H_9F_3S$, 278.0372 ($M^+$); found, 278.0371. **Mp**: 214-216°C. Data is in accordance with the literature.[8]

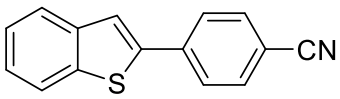


**2-(4-phenylacetamide)benzo[*b*]thiophene (3an)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4'-iodoacetanilide **2n** (196 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 1:1) as a white solid in 38% yield (76 mg, 0.28 mmol).

**$R_f$** (hexane:EtOAc = 1:1): 0.29. **$^1$H-NMR** (400 MHz, DMSO-$d_6$): δ (ppm) 10.13 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.76 (s, 1H), 7.74-7.67 (m, 4H), 7.37-7.32 (m, 2H), 2.07 (s, 3H). **$^{13}$C-NMR** (101 MHz, DMSO-$d_6$): δ (ppm) 168.5, 143.2, 140.6, 139.7, 138.3, 128.1, 126.6, 124.8, 124.4, 123.5, 122.4, 119.3, 118.9, 24.1. **IR**: ν = 3305, 2914, 2850, 1736, 1659,

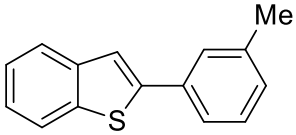
1598, 1542, 1433, 1408, 1368, 1323, 817, 739, 727 $cm^{-1}$. **HRMS**: calcd for $C_{16}H_{13}NOS$, 268.0791 ($MH^+$); found, 268.0789. **Mp**: 136-138°C.




**4-(benzo[*b*]thiophen-2-yl)benzonitrile (3ao)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 4-iodobenzonitrile **2o** (174 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:$Et_2O$ = 9:1) as a white solid in 63% yield (111 mg, 0.47 mmol).

**$R_f$** (hexane:$Et_2O$ = 9:1): 0.18. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.85-7.77 (m, 4H), 7.70-7.68 (d, *J* = 8.6 Hz, 2H), 7.65 (s, 1H), 7.41-7.36 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 141.8, 140.4, 140.1, 138.7, 132.9, 126.9, 125.5, 125.1, 124.3, 122.5, 121.9, 118.8, 111.4. **HRMS**: calcd for $C_{15}H_9NS$, 235.0450 ($M^+$); found, 235.0449. **Mp**: 182-184°C. Data is in accordance with the literature.[2]



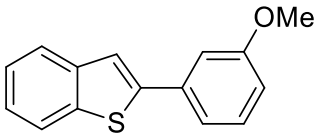

**2-(*m*-tolyl)benzo[*b*]thiophene (3ap)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 3-iodotoluene **2p** (99 µl, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 86% yield (145 mg, 0.65 mmol).

**$R_f$** (hexane): 0.47. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.85 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.56-7.54 (m, 3H), 7.39-7.30 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 2.44 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.8, 141.0, 139.8, 139.0, 134.5, 129.4, 129.2, 127.5, 124.8,

124.6, 124.0, 123.8, 122.6, 119.7, 21.8. **HRMS**: calcd for $C_{15}H_{12}S$ ($M^+$), 224.0654; found, 224.0654. **Mp**: 114-116 °C. Data is in accordance with the literature.[1]

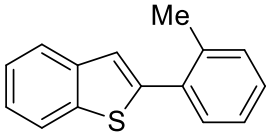
**2-(3-methoxyphenyl)benzo[*b*]thiophene (3aq)**




The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 3-iodoanisole **2q** (90 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EOAc = 98:2) as a white solid in 78% yield (140 mg, 0.58 mmol).

**$R_f$** (hexane:EtOAc = 98:2): 0.25. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.38-7.30 (m, 4H), 7.27-7.25 (m, 1H), 6.90 (dt, *J* = 7.2 and 2.1 Hz, 1H), 3.88 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 160.1, 144.2, 140.7, 139.6, 135.8, 130.1, 124.7, 124.5, 123.7, 122.4, 119.8, 119.2, 113.9, 112.2, 55.5. **HRMS**: calcd for $C_{15}H_{12}OS$, 241.0682 ($MH^+$); found, 241.0680. **Mp**: 62-64°C. Data is in accordance with the literature.[5]

**2-(*o*-tolyl)benzo[*b*]thiophene (3ar)**

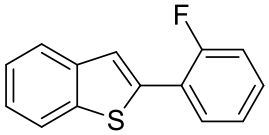



The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 2-iodotoluene **2r** (98 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as an inseparable mixture C2:C3 = 4:1 in overall yield of 71% yield (120 mg, 0.53 mmol).

**$R_f$** (hexane): 0.48. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.57-7.55 (m, 1H), 7.46-7.30 (m, 6H), 2.55 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 143.6, 140.3, 140.2, 136.5, 134.3, 130.9, 130.8, 128.4, 126.0, 124.5, 124.2, 123.6, 123.1,

122.1, 21.2. **HRMS**: calcd for $C_{15}H_{12}S$, 225.0729 ($MH^+$); found, 225.0732. Data is in accordance with the literature.[2]

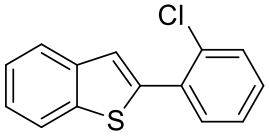
**2-(2-fluorophenyl)benzo[*b*]thiophene (3as)**




The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-fluoro-2-iodobenzene **2s** (87 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 81% yield (139 mg, 0.61 mmol).

**$R_f$** (hexane): 0.34. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89-7.81 (m, 2H), 7.76 (s, 1H), 7.72 (dt, *J* = 7.7 and 1.8 Hz, 1H), 7.43-7.29 (m, 3H), 7.25-7.17 (m, 2H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 159.4 (d, *J* = 251.3 Hz), 140.5, 139.6 (d, *J* = 2.7 Hz), 137.4 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 8.6 Hz), 124.8, 124.7 (d, *J* = 3.6 Hz), 124.6, 124.0, 123.5 (d, *J* = 8.6 Hz), 122.3 (d, *J* = 12.3 Hz), 122.1, 116.5 (d, *J* = 22.5 Hz). **$^{19}$F-NMR** (376 MHz, $CDCl_3$) δ (ppm) -113.0. **HRMS**: calcd for $C_{14}H_9FS$, 228.0404 ($M^+$); found, 228.0403. **Mp**: 60-62°C. Data is in accordance with the literature.[9]

**2-(2-chlorophenyl)benzo[*b*]thiophene (3at)**

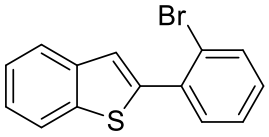



The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-chloro-2-iodobenzene **2t** (92 µL, 0.75 mmol, 1.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a white solid in 70% yield (129 mg, 0.53 mmol).

**$R_f$** (hexane): 0.30. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.86 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.83 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.60 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.59 (s, 1H), 7.52 (dd, *J* = 7.4, 1.8 Hz, 1H),

7.41-7.28 (m, 4H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) 140.4, 140.3, 140.0, 133.4, 133.0, 132.0, 130.7, 129.4, 127.1, 124.7, 124.6, 124.6, 124.0, 122.2..**HRMS**: calcd for $C_{14}H_9ClS$, 244.0113 ($M^+$); found, 244.0109. **Mp**: 56-58°C. Data is in accordance with the literature.[9]

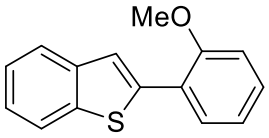
**2-(2-bromophenyl)benzo[*b*]thiophene (3au)**




The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-bromo-2-iodobenzene **2u** (96 µL, 0.75 mmol, 1.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a white solid in 75% yield (162 mg, 0.56 mmol).

**$R_f$** (hexane): 0.30. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.86 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.50 (s, 1H), 7.42-7.33 (m, 3H), 7.26-7.23 (m, 1H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) 142.1, 140.4, 139.9, 135.5, 133.8, 132.4, 129.7, 127.6, 124.7, 124.6, 124.6, 124.0, 123.2, 122.2. **HRMS**: calcd for $C_{14}H_9BrS$, 287.9608 ($M^+$); found, 287.9600. **Mp**: 64-67°C. Data is in accordance with the literature.[9]

**2-(2-methoxyphenyl)benzo[*b*]thiophene (3av)**

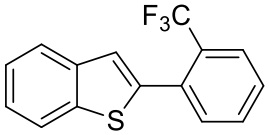



The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 2-iodoanisole **2v** (98 µL, 0.75 mmol, 1.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane:$Et_2O$ = 98:2) as a colorless oil in 80% yield (144 mg, 0.60 mmol).

**$R_f$** (hexane:$Et_2O$ = 96:4): 0.4. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.76 (s, 1H), 7.72 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.36-7.30 (m, 3H), 7.06-7.02 (m, 2H), 3.98 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) 156.5, 140.3, 140.1, 139.9, 129.7,

129.4, 124.3, 124.2, 123.6, 123.3, 122.6, 122.0, 121.1, 111.8, 55.8. **HRMS**: calcd for $C_{15}H_{13}OS$, 241.0687 ($MH^+$); found, 241.0676. Data is in accordance with the literature.[10]

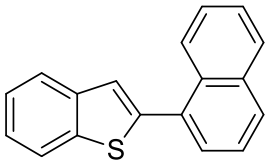
**2-(2-(trifluoromethyl)phenyl)benzo[*b*]thiophene (3aw)**




The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 2-iodobenzotrifluoride **2w** (105 µL, 0.75 mmol, 1.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a colorless oil in 48% yield (75 mg, 0.36 mmol).

**$R_f$** (hexane): 0.35. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.86 (d, *J* = 7.9 Hz, 1H), 7.84-7.78 (m, 2H), 7.59 (d, *J* = 4.1 Hz, 2H), 7.54-7.49 (m, 1H), 7.42-7.35 (m, 2H), 7.34 (s, 1H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) δ 140.5, 139.9, 139.8, 133.6 (q, *J* = 2.0 Hz), 133.3, 131.5, 129.4 (q, *J* = 30.1 Hz), 128.6, 126.6 (q, *J* = 5.5 Hz), 124.8 (q, *J* = 2.6 Hz), 124.7, 124.7, 124.0 (q, *J* = 274.0 Hz), 124.0, 122.1. **$^{19}$F-NMR** (376 MHz, $CDCl_3$) δ (ppm) -57. 6. **IR**: ν = 3059, 2361, 1603, 1576, 1487, 1446, 1432, 1312, 1267, 1170, 1126, 1110, 1061, 1035, 766, 745 $cm^{-1}$. **HRMS**: calcd for $C_{15}H_{10}F_3S$, 279.0455 ($MH^+$); found, 279.0462.

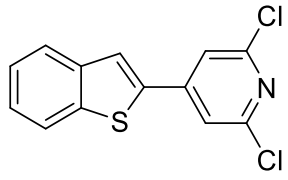
**2-(naphthalen-1-yl)benzo[*b*]thiophene (3ax)**




The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 1-iodonaphthalene **2x** (114 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography on 10% $AgNO_3$ impregnated silica (hexane) as a white solid in 77% yield (150 mg, 0.58 mmol).

**$R_f$** (hexane): 0.34. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.34 (d, *J* = 8.1 Hz, 1H), 7.96-7.87 (m, 4H), 7.70 (d, *J* = 6.9 Hz, 1H), 7.58-7.52 (m, 3H), 7.49 (s, 1H), 7.47-7.39 (m, 2H). **$^{13}$C-NMR** (101

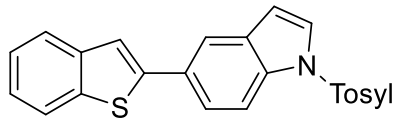
MHz, $CDCl_3$): δ (ppm) 142.2, 140.4, 140.3, 133.9, 132.5, 131.9, 129.0, 128.6, 128.5, 126.7, 126.3, 125.9, 125.3, 124.6, 124.4, 124.2, 123.7, 122.2. **HRMS**: calcd for $C_{18}H_{12}S$, 260.0654 ($M^+$); found, 260.0654. **Mp**: 100-102°C. Data is in accordance with the literature.[2]




**4-(benzo[*b*]thiophen-2-yl)-2,6-dichloropyridine (3ay)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 2,6-dichloro-4-iodopyridine **2y** (212 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 9:1) as a white solid in 28% yield (58 mg, 0.21 mmol).

**$R_f$** (hexane:EtOAc = 9:1): 0.32. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.87-7.83 (m, 2H), 7.76 (s, 1H), 7.52 (s, 2H), 7.43-7.41 (m, 2H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 151.4, 146.9, 140.3, 139.8, 138.0, 126.5, 125.4, 124.8, 124.1, 122.7, 119.5. **IR**: ν = 3097, 3061, 3038, 1576, 1533, 1516, 1408, 1372, 1337, 1165, 1109, 1020, 981, 815, 738, 721 $cm^{-1}$. **HRMS**: calcd for $C_{13}H_7NCl_2S$, 279.9749 ($MH^+$); found, 279.9747. **Mp**: 154-156°C.

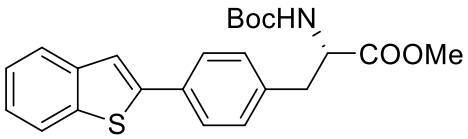



**5-(benzo[*b*]thiophen-3-yl)-1-tosyl-1*H*-indole (3az)**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and 5-iodo-1-tosyl-1*H*-indole **2z** (297 mg, 0.75 mmol, 1.0 equiv), previously synthesized in 95% yield according to the procedure reported in *Chem. Pharm. Bull.* **2009**, *57*, 591. The product was isolated by column chromatography (hexane) as a white solid in 67% yield (203 mg, 0.50 mmol).

**$R_f$** (hexane): 0.12. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 8.6 Hz, 1H), 7.84-7.70 (m, 5H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.57 (d, *J* = 3.1 Hz, 1H), 7.48 (s, 1H), 7.34-7.25 (m, 2H), 7.23-7.19

(m, 2H), 6.67 (d, *J* = 3.0 Hz, 1H), 2.30 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 145.3, 144.4, 140.9, 139.5, 135.2, 134.7, 131.4, 130.1, 129.9, 127.4, 126.9, 124.7, 124.3, 123.6, 123.5, 122.3, 119.5, 119.4, 114.1, 109.3, 21.7. **IR**: ν = 3126, 3054, 2925, 1594, 1460, 1360, 1274, 1189, 1168, 1154, 1122, 994, 884, 810, 763, 726, 705 $cm^{-1}$. **HRMS**: calcd for $C_{23}H_{17}NO_2S_2$ 403.0695 ($M^+$); found, 403.0695. **Mp**: 204-206°C.



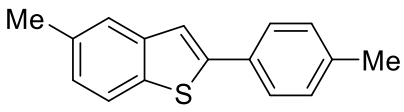

**Methyl (*S*)-3-(4-(benzo[*b*]thiophen-2-yl)phenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (3aa')**

The product was obtained via the general procedure A using benzo[*b*]thiophene **1a** (205 mg, 1.5 mmol, 2.0 equiv) and methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate **(*S*)-2a'** (304 mg, 0.75 mmol, 1.0 equiv), previously synthesized enantiomerically pure in 90% yield according to the procedure reported in *Org. Lett.* **2002**, *4*, 4171. Product **(*S*)-3aa'** was isolated by column chromatography (hexane:EtOAc = 80:20) as a white solid in 83% yield (255 mg, 0.62 mmol).

**Rf** (hexane:EtOAc = 80:20): 0.26. **$^{1}$H-NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J*= 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (s, 1H), 7.32-7.23 (m, 2H), 7.13 (d, *J*= 8.0 Hz, 2H), 5.04 (d, *J*= 8.0 Hz, 0.9 H, conformer 1), 4.82 (br, 0.1 H, conformer 2), 4.59 (m, 0.9 H, conformer 1), 4.38 (br, 0.1 H, conformer 2), 3.7 (s, 3H), 3.18-2.84 (m, 2H), 1.39 (s, 9H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 172.3, 155.2, 143.9, 140.7, 139.5, 136.4, 133.1, 130.0, 126.6, 124.6, 124.4, 123.6, 122.3, 119.4, 80.1, 54.4, 52.4, 38.1, 28.4. **IR**: ν = 3369, 1734, 1695, 1509, 1435, 1365, 1338, 1290, 1246, 1166, 1013, 818, 746 $cm^{-1}$. **HRMS**: calcd for $C_{23}H_{25}NO_4S$, 412.1577 ($MH^+$); found, 412.1579. **Mp**: 130-132°C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ : +38 (*c* = 0.5, $CHCl_3$).

The enantiomeric excess of compound **(*S*)-3aa'** was determined by **HPLC** with a Chiralcel OD-H column, hexane-isopropanol 92:8, 0.8 $mL \cdot min^{-1}$, 310-280-254-210 nm: $t_R$ = 14.88 min

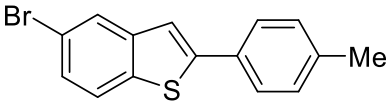
[enatiomerically pure]. As reference, compound **(*R*)-3aa'** presented $[\alpha]_D^{25}$ : -35 (*c* = 0.5, $CHCl_3$) and $t_R$ = 13.68 min.




**5-methyl-2-(*p*-tolyl)benzo[*b*]thiophene (3ba)**

The product was obtained via the general procedure A using 5-methylbenzo[*b*]thiophene **1b** (222 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 86% yield (153 mg, 0.64 mmol).

**$R_f$** (hexane): 0.26. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.58 (s, 1H), 7.45 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.6, 141.3, 138.3, 136.7, 134.3, 131.8, 129.7, 126.5, 126.0, 123.5, 122.0, 118.7, 21.6, 21.4. **IR**: ν = 3014, 2911, 2855, 2722, 1422, 1407, 1121, 1015, 889, 809, 796, 727 $cm^{-1}$. **HRMS**: calcd for $C_{16}H_{14}S$, 238.0811 ($M^+$); found, 238.0810. **Mp**: 160-162°C.

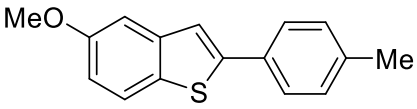



**5-bromo-2-(*p*-tolyl)benzo[*b*]thiophene (3ca)**

The product was obtained via the general procedure A using 5-bromobenzo[*b*]thiophene **1c** (320 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 66% yield (150 mg, 0.49 mmol).

**$R_f$** (hexane): 0.35. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 1.4 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.40 (d, *J* = 8.5 and 1.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 146.5, 142.5, 138.9, 138.0, 131.1, 129.9, 127.2, 126.6, 126.1, 123.7, 118.6, 118.1, 21.4. **IR**: ν = 2912, 2853, 1735, 1574,

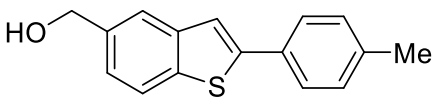
1511, 1432, 1414, 1168, 1120, 1069, 883, 808, 799, 720 $cm^{-1}$. **HRMS**: calcd for $C_{15}H_{11}BrS$, 302.9838 ($MH^+$); found, 302.9836. **Mp**: 202-204°C.




**5-methoxy-2-(*p*-tolyl)benzo[*b*]thiophene (3da)**

The product was obtained via the general procedure A using 5-methoxybenzo[*b*]thiophene **1d** (246 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:$CH_2Cl_2$ = 92:8) as a white solid in 90% yield (171 mg, 0.67 mmol).

**$R_f$** (hexane: $CH_2Cl_2$ = 92:8): 0.23. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.66 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.42 (s, 1H), 7.22 (m, 3H), 6.95 (m, 1H), 3.86 (s, 3H), 2.38 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 157.7, 145.8, 141.9, 138.4, 131.8, 131.7, 129.7, 126.4, 123.0, 118.8, 114.4, 105.7, 55.6, 21.4. **IR**: ν = 3014, 2968, 2913, 2855, 1593, 1452, 1421, 1331, 1214, 1157, 1120, 1025, 1017, 948, 856, 825, 803, 766, 721, 703 $cm^{-1}$. **HRMS**: calcd for $C_{16}H_{14}OS$, 255.0838 ($MH^+$); found, 255.0828. **Mp**: 142-144°C.



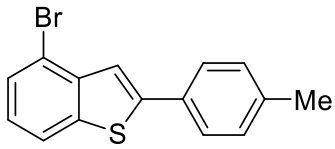

**(2-(*p*-tolyl)benzo[*b*]thiophen-5-yl)methanol (3ea)**

The product was obtained via the general procedure A using benzo[*b*]thiophen-5-ylmethanol **1e** (246 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:EtOAc = 7:3) as a white solid in 75% yield (144 mg, 0.57 mmol).

**$R_f$** (hexane:EtOAc = 7:3): 0.26. **$^1$H-NMR** (400 MHz, DMSO-$d_6$): δ (ppm) 7.88 (d, *J* = 8.2 Hz, 1H), 7.79 (s, 1H), 7.76 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.31-7.27 (m, 3H), 5.29 (t, *J* = 5.7 Hz, 1H), 4.60 (d , *J* = 5.7 Hz, 2H), 2.34 (s, 3H). **$^{13}$C-NMR** (125 MHz, DMSO-$d_6$): δ (ppm) 143.5,

140.6, 139.4, 138.1, 136.8, 130.9, 129.8, 125.9, 123.6, 122.0, 121.2, 119.4, 62.9, 20.8. **IR**: ν = 3308, 2912, 2854, 1501, 1441, 1360, 1306, 1259, 1121, 1068, 1024, 947, 892, 808, 772, 729, 687 $cm^{-1}$. **HRMS**: calcd for $C_{16}H_{14}OS$, 255.0838 ($MH^+$); found, 255.0838. **Mp**: 182-184°C.

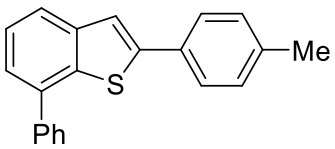
**4-bromo-2-(*p*-tolyl)benzo[*b*]thiophene (3fa)**




The product was obtained via the general procedure A using 4-bromobenzo[*b*]thiophene **1f** (320 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 86% yield (196 mg, 0.65 mmol).

**$R_f$** (hexane): 0.33. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 2.42 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 145.5, 140.6, 140.0, 138.9, 131.1, 129.8, 127.8, 126.5, 125.0, 121.4, 119.1, 117.2, 21.4. **IR**: ν = 3044, 3018, 2909, 2852, 1498, 1446, 1408, 1325, 1178, 1083, 945, 880, 802, 755 $cm^{-1}$. **HRMS**: calcd for $C_{15}H_{11}BrS$, 302.9838 ($MH^+$); found, 302.9845. **Mp**: 80-82°C.

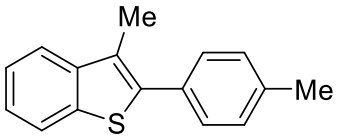
**7-phenyl-2-(*p*-tolyl)benzo[*b*]thiophene (3ga)**




The product was obtained via the general procedure A using 7-phenylbenzo[*b*]thiophene **1g** (315 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as an inseparable mixture C2:C3 = 6:1 in overall yield of 78% (176 mg, 0.59 mmol).

**$R_f$** (hexane): 0.19. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.66-7.61 (m, 3H), 7.56-7.52 (m, 2H), 7.46-7.44 (m, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 144.7, 141.6,

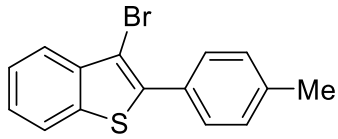
140.7, 138.4, 138.3, 136.6, 131.5, 129.7, 128.9, 128.3, 128.0, 126.4, 125.3, 124.3, 122.6, 119.3, 21.3. **IR**: ν = 3054, 3024, 2917, 1573, 1505, 1493, 1461, 1445, 1388, 1181, 1029, 953, 838, 811, 785, 754, 726, 698 $cm^{-1}$. **HRMS**: calcd for $C_{21}H_{16}S$, 301.1038 ($MH^+$); found, 301.1045.




**3-methyl-2-(*p*-tolyl)benzo[*b*]thiophene (5ba)**

The product was obtained via the general procedure A using 3-methylbenzo[*b*]thiophene **4a** (210 µL, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 92% yield (164 mg, 0.69 mmol).

**$R_f$** (hexane): 0.26. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (dt, *J* = 7.0 and 1.0 Hz, 1H), 7.34 (dt, *J* = 7.0 and 1.0 Hz, 1H), 7.27 (d, *J* = 8.0, 2H), 2.47 (s, 3H), 2.42 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 141.4, 139.0, 138.3, 137.8, 132.0, 129.7, 129.4, 127.2, 124.3, 124.2, 122.2, 122.2, 21.4, 12.8. **HRMS**: calcd for $C_{16}H_{14}S$, 238.0811 ($M^+$); found, 238.0810. **Mp**: 78-80°C. Data is in accordance with the literature.[11]

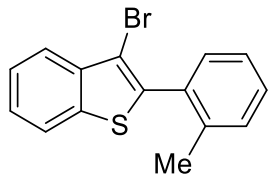



**3-bromo-2-(*p*-tolyl)benzo[*b*]thiophene (5ca)**

The product was obtained via the general procedure A using 3-bromobenzo[*b*]thiophene **4c** (207 µl, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 92% yield (208 mg, 0.69 mmol).

**$R_f$** (hexane:): 0.34. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.51 (dt, *J* = 8.1 and 1.1 Hz, 1H), 7.43 (dt, *J* = 8.1 and 1.2

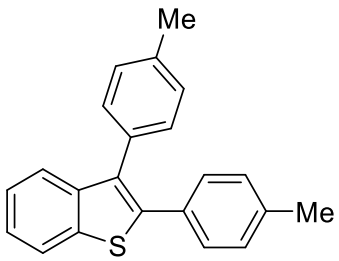
Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H). **$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ (ppm) 139.3, 139.0, 138.5, 137.7, 130.2, 129.6, 129.4, 125.4, 125.3, 123.6, 122.2, 104.7, 21.5. **HRMS**: calcd for $C_{15}H_{11}BrS$, 301.9759 ($M^+$); found, 301.9758. **Mp**: 62-64°C. Data is in accordance with the literature.[12]




**3-bromo-2-(*o*-tolyl)benzo[*b*]thiophene (5cr)**

The product was obtained via the general procedure A using 3-bromobenzo[*b*]thiophene **4c** (207 µL, 1.5 mmol, 2.0 equiv) and 2-iodotoluene **2r** (98 µL, 0.75 mmol, 1.0 equiv) and isolated by column chromatography on 10% $AgNO_3$ impregnated silica (hexane) as a colorless oil in 87% yield (197 mg, 0.65 mmol).

**$R_f$** (hexane): 0.28. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.43-7.29 (m, 4H), 2.34 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 138.5, 138.4, 138.3, 138.0, 132.5, 131.0, 130.4, 129.4, 125.8, 125.5, 125.3, 123.5, 122.4, 107.8, 20.3. **IR**: ν = 3059, 2920, 1480, 1456, 1432, 1250, 1069, 1018, 974, 891, 810, 742 $cm^{-1}$. **HRMS**: calcd for $C_{15}H_{11}BrS$, 301.9759 ($M^+$); found, 301.9759.

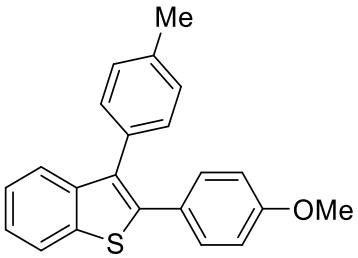



**2,3-di-*p*-tolylbenzo[*b*]thiophene (5aa)**

The product was obtained via the general procedure A using 3-*p*-tolylbenzo[*b*]thiophene **4a** (336 mg, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a white solid in 93% yield (219 mg, 0.70 mmol).

**$R_f$** (hexane): 0.19. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.75-7.73 (m, 1H), 7.50-7.47 (m, 1H), 7.24-7.18 (m, 2H), 7.16-7.07 (m, 6H), 7.70 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H), 2.20 (s, 3H). **$^{13}$C-**

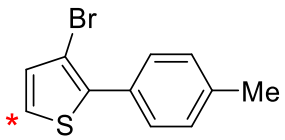
**NMR** (101 MHz, $CDCl_3$): δ (ppm) 141.3, 139.5, 138.8, 137.6, 137.1, 132.9, 132.8, 131.6, 130.4, 129.6, 129.5, 129.2, 124.4, 124.4, 123.4, 122.1, 21.5, 21.3. **IR**: ν = 3028, 2919, 2858, 1514, 1433, 1231, 1182, 1070, 1022, 892, 845, 822, 761, 733 $cm^{-1}$. **HRMS**: calcd for $C_{22}H_{18}S$, 315.1202 ($MH^+$); found, 315.1200. **Mp**: 130-132°C.




**2-(4-methoxyphenyl)-3-(*p*-tolyl)benzo[b]thiophene (5ab)**

The product was obtained via the general procedure A using 3-(*p*-tolyl)benzo[*b*]thiophene **4a** (336 mg, 1.5 mmol, 2.0 equiv) and 4-iodoanisole **2b** (180 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane:$Et_2O$ = 98:2) as a white solid in 78% yield (193 mg, 0.58 mmol).

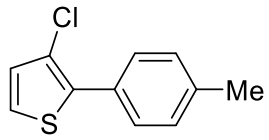
**$R_f$** (hexane:$Et_2O$ = 98:2): 0.28. **$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.87-7.85 (m, 1H), 7.61-7.59 (m, 1H), 7.38-7.19 (m, 8H), 6.80 (d, *J* = 7.8 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H). **$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ (ppm) 159.3, 141.3, 139.3, 138.7, 137.0, 132.8, 132.4, 130.9, 130.4, 129.5, 126.9, 124.4, 124.3, 123.3, 122.1, 113.9, 55.3, 21.5. **HRMS**: calcd for $C_{22}H_{18}OS$, 331.1151 ($MH^+$); found, 311.1148. **Mp**: 104-106°C. Data in accordance with the literature.[13]




**3-bromo-2-(*p*-tolyl)thiophene (7aa)**

The product was obtained via the general procedure B using 3-bromothiophene **7a** (141 µL, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated by column chromatography (hexane) as a colorless oil in 62% yield in a mixture with the corresponding bis-arylated product ($^1$H NMR ratio mono:bis = 71:29).

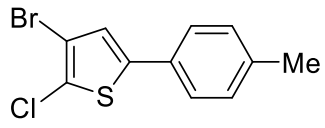
**$R_f$** (hexane): 0.35. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.57 (d, *J* = 7.8 Hz, 2H), 7.31-7.22 (m, 3H), 7.07 (d, *J* = 5.2 Hz, 1H), 2.42 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) 138.5, 138.4, 131.7, 130.1, 129.4, 129.1, 124.8, 107.4, 21.5. **HRMS**: calcd for $C_{11}H_9BrS$, 251.9608 ($M^+$); found, 251.9602. Data in accordance with the literature.[14]




**3-chloro-2-(*p*-tolyl)thiophene (7ba)**

The product was obtained via the general procedure B using 3-chlorothiophene **7b** (139 µL, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a colorless oil in 60% yield (94mg, 0.45mmol).

**$R_f$** (hexane): 0.41. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 8.1 Hz, 2H), 7.33-7.19 (m, 3H), 7.01 (d, *J* = 5.4 Hz, 1H), 2.42 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) δ 138.2, 136.4, 129.4, 129.4, 129.3, 128.7, 123.6, 121.1, 21.4. **HRMS**: calcd for $C_{11}H_9ClS$, 208.0113 ($M^+$); found, 208.0110. Data in accordance with the literature.[14]

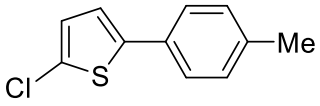



**3-bromo-2-chloro-5-(*p*-tolyl)thiophene (7ca)**

The product was obtained via the general procedure B using 3-bromo-2-chlorothiophene **7e** (164 µL, 1.5 mmol, 2.0 equiv) and 4-iodotoluene **2a** (165 mg, 0.75 mmol, 1.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a white solid in 50% yield (108 mg, 0.38 mmol).

**$R_f$** (hexane): 0.49. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.37 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.05 (s, 1H), 2.37 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) 142.5, 138.8, 130.1, 129.9, 125.5, 125.1, 124.5, 111.2, 21.4. **IR**: ν = 3019, 2913, 2851, 1500, 1439, 1377, 1325,

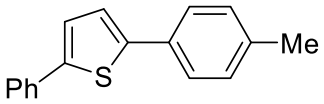
1309, 1119, 1103, 1015, 954, 821, 797 $cm^{-1}$. **HRMS**: calcd for $C_{11}H_8BrClS$, 285.9218 ($M^+$); found, 285.9222. **Mp**: 85-87°C.




**2-chloro-5-(*p*-tolyl)thiophene (7da)**

The product was obtained via the general procedure C using 2-chlorothiophene **7c** (69 µL, 0.75 mmol, 1.0 equiv) and 4-iodotoluene **2a** (330 mg, 1.5 mmol, 2.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a white solid in 50% yield (78 mg, 0.37 mmol).

**$R_f$** (hexane): 0.44. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.40 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 3.8 Hz, 1H), 6.87 (d, *J* = 3.9 Hz, 1H), 2.37 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) 143.2, 137.9, 131.1, 129.8, 128.6, 127.1, 125.6, 121.8, 21.3. **HRMS**: calcd for $C_{11}H_{10}ClS$, 209.0191 ($MH^+$); found, 209.0184. **Mp**: 86-88°C. Data in accordance with the literature.[15]




**2-phenyl-5-(*p*-tolyl)thiophene (7ea)**

The product was obtained via the general procedure C using 2-phenylthiophene **7d** (120 mg, 0.75 mmol, 1.0 equiv) and 4-iodotoluene **2a** (330 mg, 1.5 mmol, 2.0 equiv) and isolated on 10% $AgNO_3$ impregnated silica (hexane) as a white solid in 45% yield (85 mg, 0.34 mmol).

**$R_f$** (hexane): 0.5. **$^1$H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.65 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.41 (app.t, *J* = 7.8 Hz, 2H), 7.33-7.25 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.39 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$): δ (ppm) δ 144.0, 143.2, 137.6, 134.5, 131.7, 129.7, 129.0,

127.5, 125.7, 125.7, 124.1, 123.6, 21.4. **HRMS**: calcd for $C_{17}H_{15}S$, 251.0894 ($MH^+$); found, 251.0888. **Mp**: 138-140°C. Data in accordance with the literature.[16]

## IV. Application to Other Heterocycles

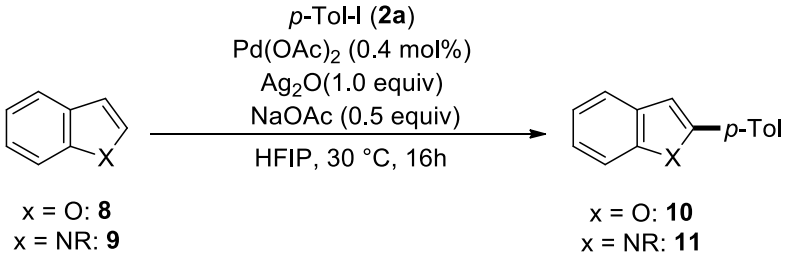
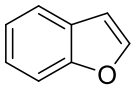
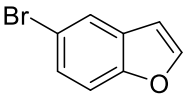
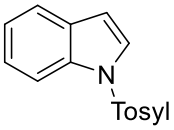
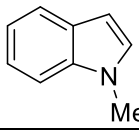


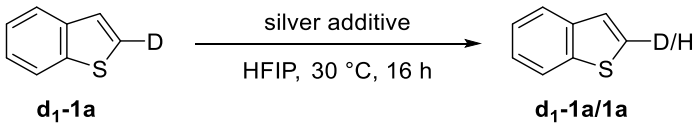

***Table S.8:*** Heterocycles screening

| Entry[a,b] | Heterocycles | 10 / 11[c] |
|---|---|---|
| 1 |  | 25 |
| 2 |  | - |
| 3 |  | - |
| 4 |  | *traces* |

[a] Yield determined by quantitative $^1H$ NMR using 1,3,5-trimethoxybenzene as internal standard. [b] **8/9** (0.25 mmol), HFIP (0.25 mL). [c] No relevant side products formed with complete recovery of the starting materials.

## V. Mechanistic Studies

### V-1. D/H Scrambling Experiments




**$d_1$-1a** **$d_1$-1a/1a**

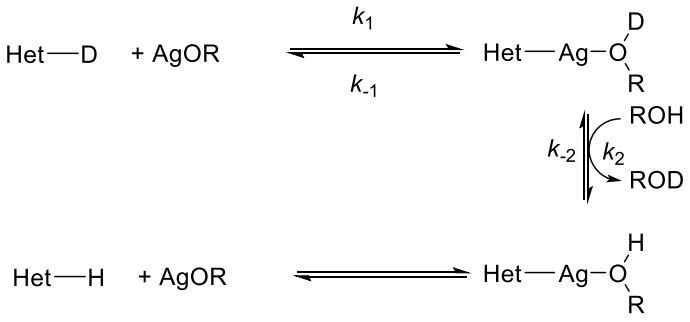
***Table S.9:*** D/H scrambling with different Ag additives

| Entry[a,b] | Additive | ratio $d_1$-1a : 1a |
|---|---|---|
| 1[c] | $Ag_2CO_3$ | >99:1 |
| 2[d] | AgOPiv | >99:1 |
| 3[d] | AgOAc | >99:1 |
| 4[c] | $Ag_2O$ | 90:10 |
| 5[e] | $Ag_2O$ + NaOAc | 66:34 |

[a] Yield determined by quantitative $^1$H NMR using 1,3,5-trimethoxybenzene as internal standard. [b] **1a** (0.25 mmol), HFIP (0.25 mL). [c] Ag salt (0.188 mmol). [d] Ag salt (0.375 mmol). [e] $Ag_2O$ (0.188 mmol), NaOAc (0.125 mmol).

#### *Role of NaOAc in D/H Scrambling experiment*

D/H exchange experiments do not necessarily measure the rate of C–H activation, if a slower step is involved in the D/H exchange itself. As outlined in the scheme below, after initial C–D activation of benzo[*b*]thiophene (Het), the deuterated 'base' (ROD) remains bound to Het–Ag (*R would be $CH(CF_3)_2$ in our case*). This can either go back to the original Het–D or can exchange with ROH in the medium, which would subsequently form the Het–H. If *step 2* is slow (ie $k_2 << k_{-1}$), we will observe a D/H exchange rate much slower than the actual C–H activation itself. We hypothesised that the effect of NaOAc in our D/H exchange experiments could be to accelerate the exchange of ROD with ROH (*step 2*), thus providing an overall faster D/H exchange rate in those experiments, without affecting the rate of Ag C–H activation.

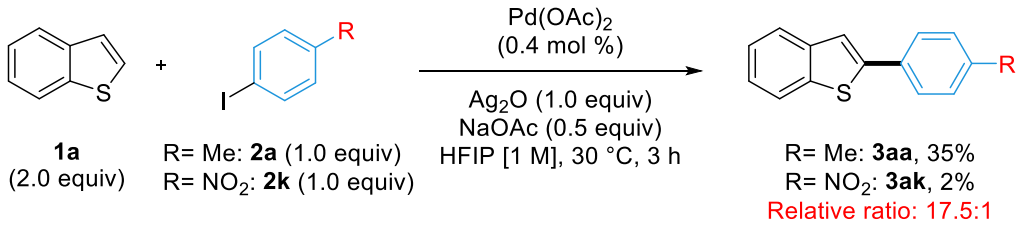



***Scheme 1:*** D/H scrambling with $Ag_2O$

## V-2. Competition Experiments

### *Competition Experiment Between 4-Iodotoluene 2a and 1-Iodo-4-nitrobenzene 2k*

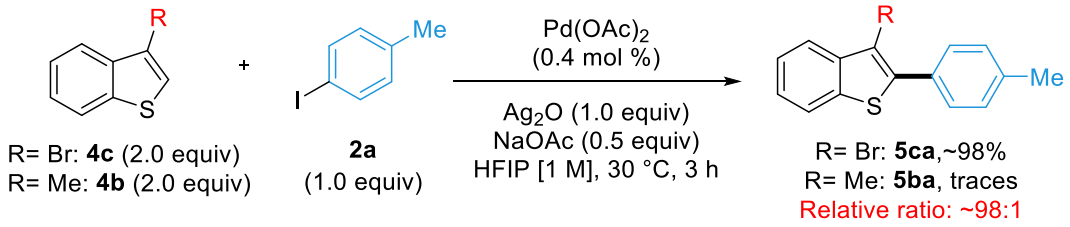
$Pd(OAc)_2$ (0.4 mol %), silver oxide (57.9 mg, 0.25 mmol, 1.0 equiv), NaOAc (10.2 mg, 0.12 mmol, 0.5 equiv), 4-iodotoluene **2a** (55 mg, 0.25 mmol, 1.0 equiv), 1-iodo-4-nitrobenzene **2k** (63 mg, 0.25 mmol, 1.0 equiv) and benzo[*b*]thiophene (68 mg, 0.50 mmol, 2.0 equiv) were stirred in hexafluoro-2-propanol (0.25 mL) at 30 °C for 3 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 (5 mL) and the filtrate was evaporated to dryness under reduced pressure. Yields were calculated by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.




The higher reactivity of iodoarenes **2a** suggests that the oxidative addition is reversible and happening before the rate-limiting step.[17]

### *Competition Experiment Between 3-Bromobenzo[b]thiophene 4c and 3-Methylbenzo[b]thiophene 4b*

$Pd(OAc)_2$ (0.4 mol %), silver oxide (57.9 mg, 0.25 mmol, 1.0 equiv), NaOAc (10.2 mg, 0.12 mmol, 0.5 equiv), 4-iodotoluene **2a** (55 mg, 0.25 mmol, 1.0 equiv), 3-bromobenzo[*b*]thiophene **4c** (69 µL, 0.5 mmol, 2.0 equiv) and 3-methylbenzo[*b*]thiophene **4b** (70 µL, 0.5 mmol, 2.0 equiv) were stirred in hexafluoro-2-propanol (0.25 mL) at 30 °C for 3 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 (5 mL) and the filtrate was evaporated to dryness under reduced pressure. Yields were calculated by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.

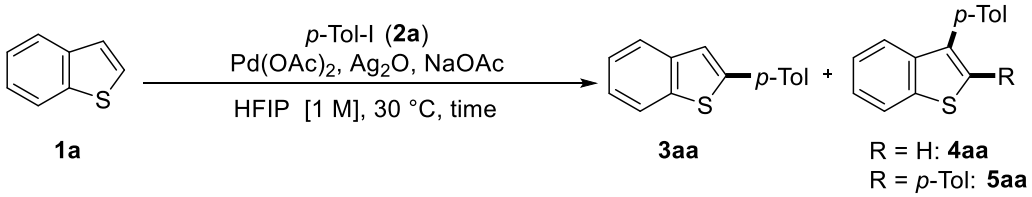



The higher reactivity of the most acidic **4c** suggests that the C–H activation is rate-limiting and proceeding via a concerted metalation-deprotonation step.[18]

## V-3. Kinetic Experiments

### V-3.1. Kinetic Experiments Employing Benzo[*b*]thiophene 1a

#### *General procedure*




Silver oxide, 4-iodotoluene **2a**, benzo[*b*]thiophene **1a**, NaOAc, 1,3,5-trimethoxybenzene were weighed in the glovebox into a microwave vial. The vial was sealed, transferred out of the glovebox and $Pd(OAc)_2$ was added as solution in hexafluoro-2-propanol. The vial was placed in an oil bath at 30 °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 internal standard.

#### *General consideration*

The temporal reaction profiles were determined using two different methods:

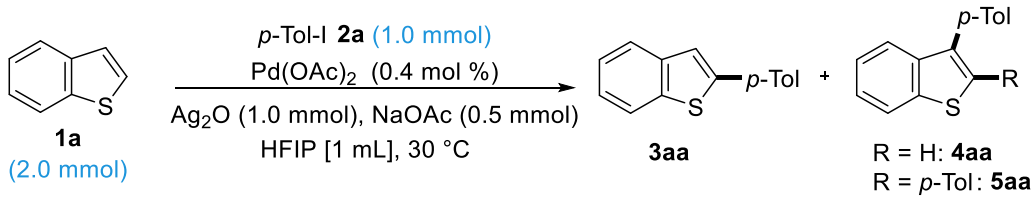
**Method 1)** Assuming that **5aa** is coming only from a C-2 arylation of **4aa**, we compared the reaction profiles considering only the C-2 arylated product **3aa**.

**Method 2)** Assuming that **5aa** is coming only from a C-3 arylation of **3aa**, we compared the reaction profiles considering the sum of C-2 arylated product **3aa** and bis-arylated product **5aa**.

The situation that corresponds to the 'real' kinetic is intermediate between the ones described in method 1 and 2. Nonetheless, these two extremes led to the same conclusions (*vide infra*) and they can therefore fully represent the 'real' catalytic system.

### V-3.1.1. Reproducibility of Kinetic Data

#### *Standard condition*



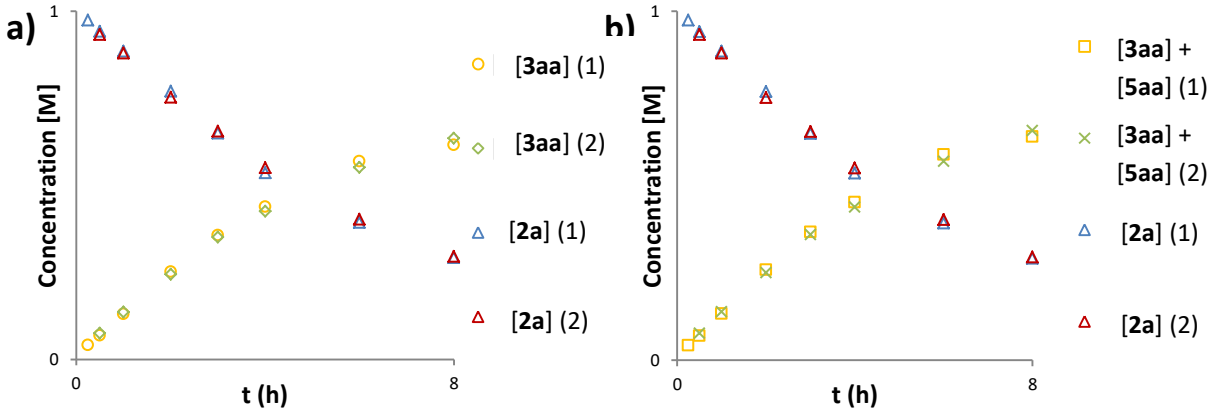



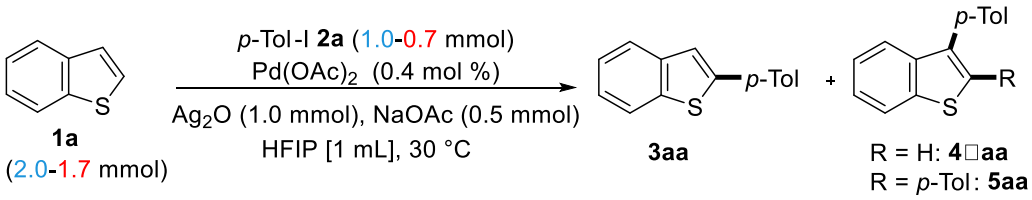

***Figure S.1:*** Reproducibility of temporal reaction profiles carried out under the standard condition applying method 1 (**a**) and method 2 (**b**).

The overlap between the two reaction profiles assessed the reproducibility of the kinetics.

### V-3.1.2. Same [“Excess”] Reaction

In Reaction Progress Kinetic Analysis (RPKA), the term [“excess”] indicates the difference between the initial concentration of the substrates of the reaction (in our case [**1a**]-[**2a**]).[19] The same [“excess”] reaction has been obtained keeping the [“excess”] constant but varying the initial concentration of **1a** and **2a**.

***Standard condition* vs *Same [“excess”]***



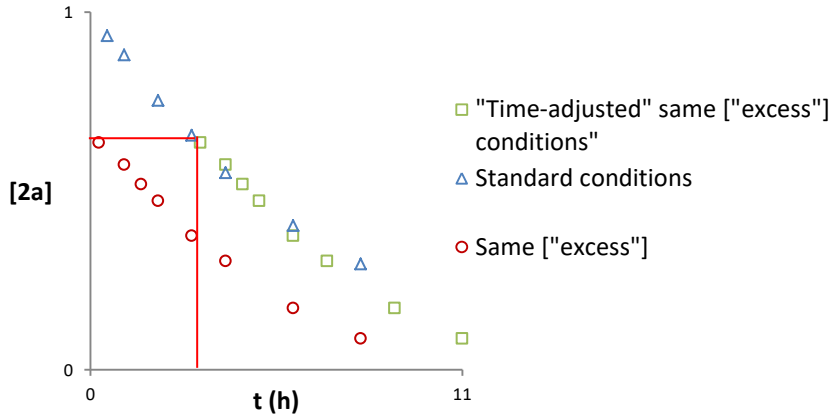




***Figure S.2:*** Same [“excess”] reaction.

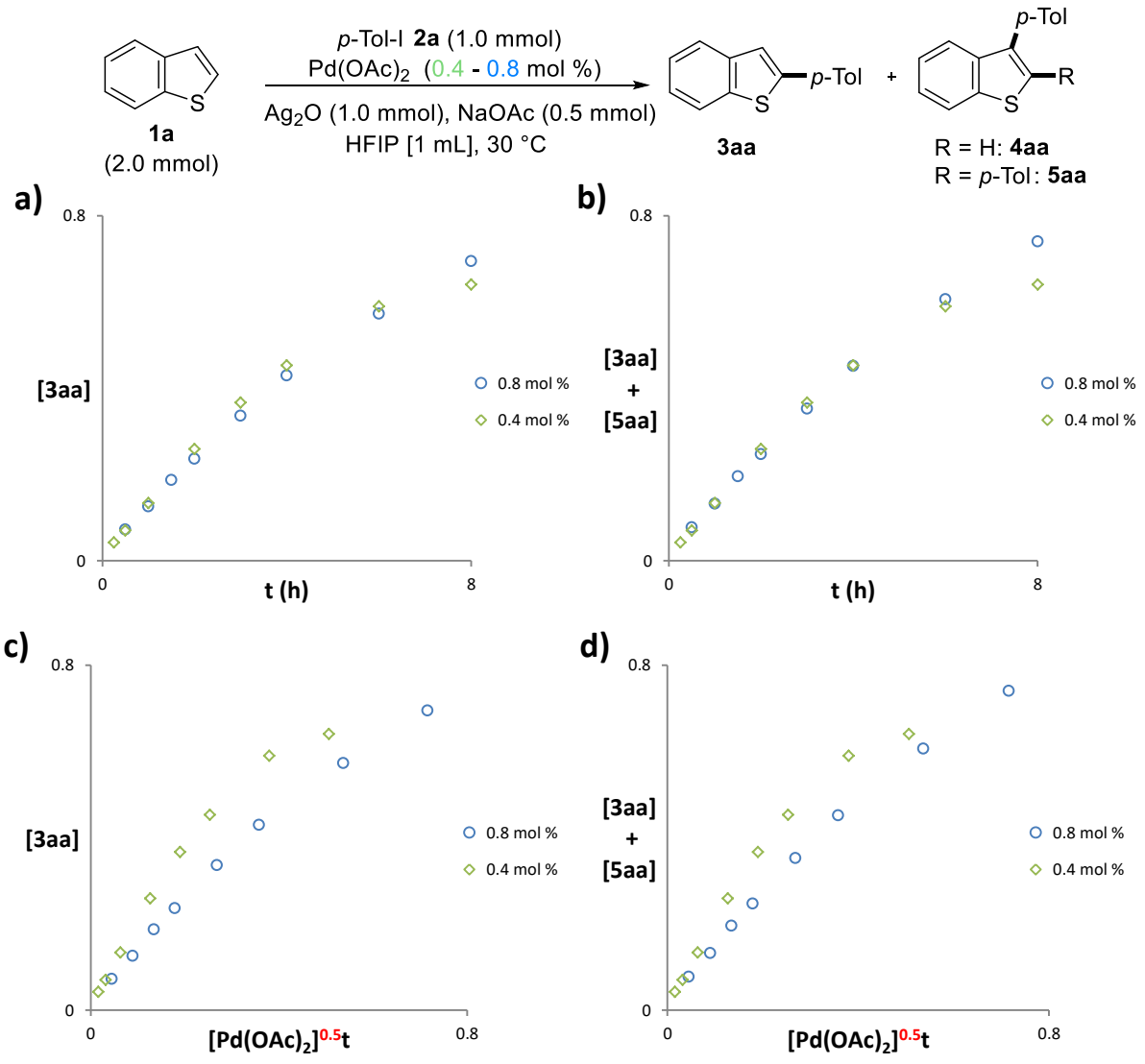
The overlap between the standard conditions and the “time-adjusted” same [“excess”] conditions indicates that neither significant catalyst decomposition or product inhibition occur during the reaction.[19]

### V-3.1.3. Determination of the Order in Catalyst

#### *General consideration*

The order in catalyst has been determined using normalized time scale analysis.[20] Reactions were carried out with different concentrations of catalyst and their temporal profiles were normalized according to the catalyst loading raised to the power of the order in the catalyst. All the resulting curves were plotted together and the correct order in catalyst corresponds to the one that causes all the curves to overlay.

#### *Determination of order in $Pd(OAc)_2$*



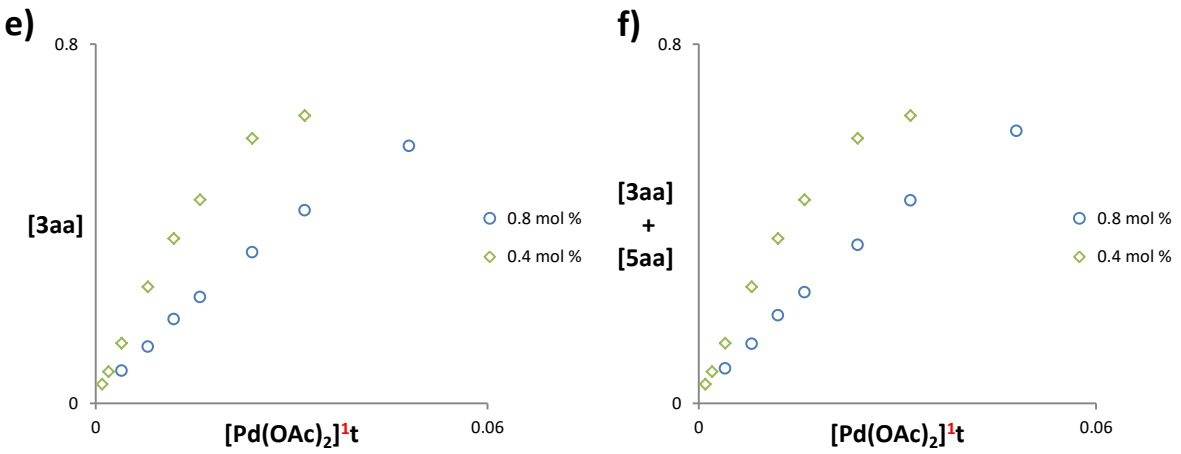



***Figure S.3:*** Temporal reaction profiles of reactions carried out with 0.4-0.8 mol % of $Pd(OAc)_2$ applying method 1 (**a**) and 2 (**b**). Normalized time scale profiles for order 0.5 in $Pd(OAc)_2$ applying method 1 (**c**) and 2 (**d**). Normalized time scale profiles for order 1 in $Pd(OAc)_2$ applying method 1 (**e**) and 2 (**f**).

The overlap between the temporal reaction profiles with catalyst loadings of 0.4 and 0.8 mol % suggests that the order in $Pd(OAc)_2$ is 0 at these concentrations, which implies that an external process to the catalytic cycle is rate-limiting.[21]

### V-3.1.4. Determination of the Orders of Reactants

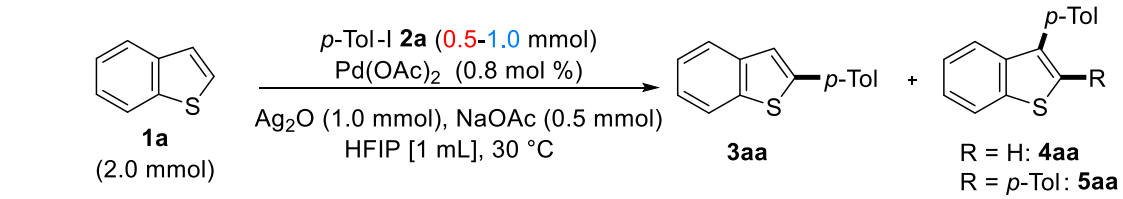
#### *General considerations*

The order in reactants has been determined with a catalyst loading of 0.8 mol % using the variable time normalisation analysis.[22] The method compares reactions carried out with different concentrations of one reactant and normalises the time between each pair of data points with the average of the concentration of the reactant at these points raised to the power of the order in the reactant itself.

$$\int_{t=0}^{t=n} [A]^{\alpha} dt = \sum_{i=1}^{n} \left( \frac{[A]_i + [A]_{i-1}}{2} \right)^{\alpha} (t_i - t_{i-1})$$

All the resulting curves were plotted together and the correct order in the reactant corresponds to the one that causes all the curves to overlay.

## *Determination of order in ArI 2a*



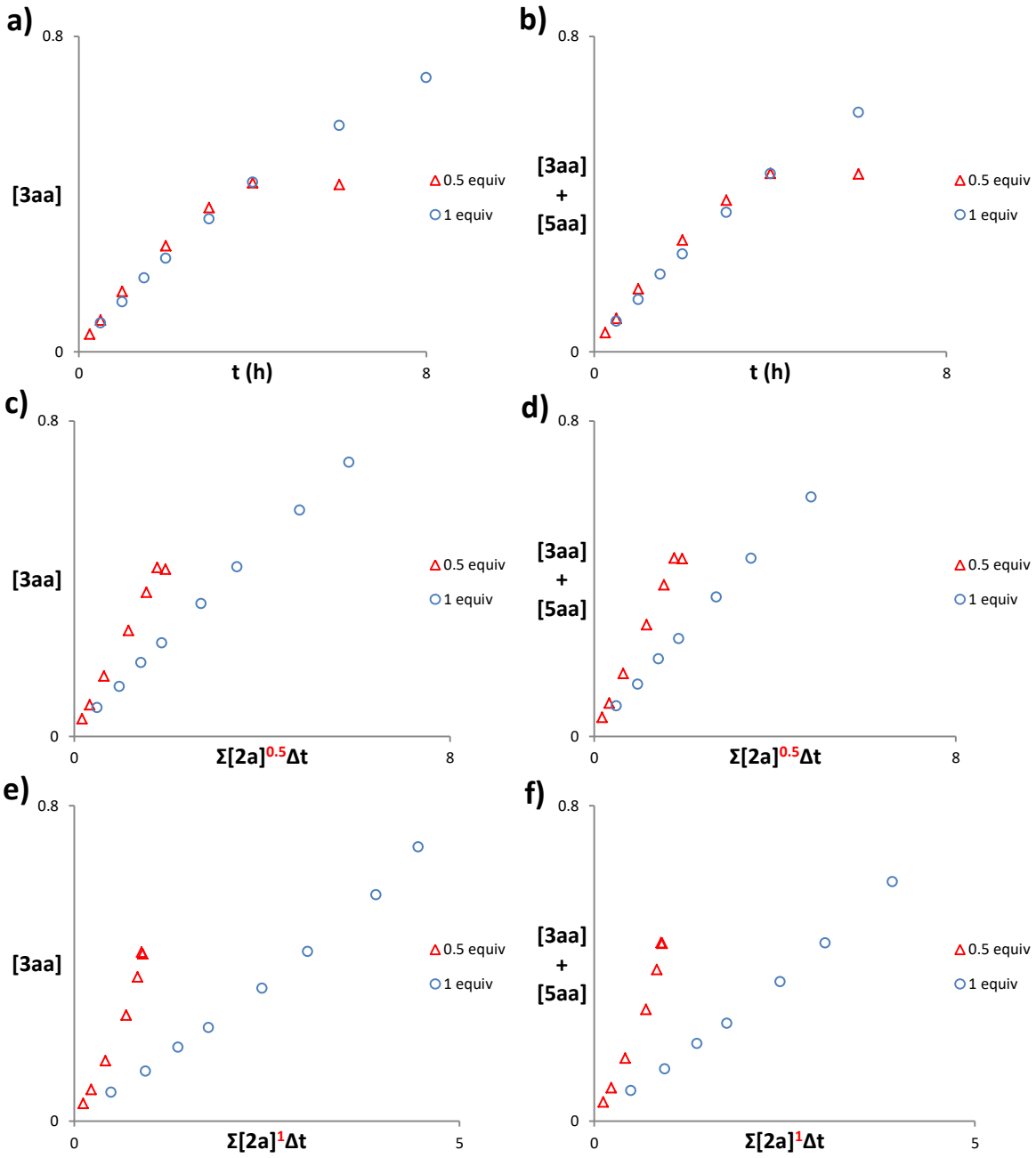
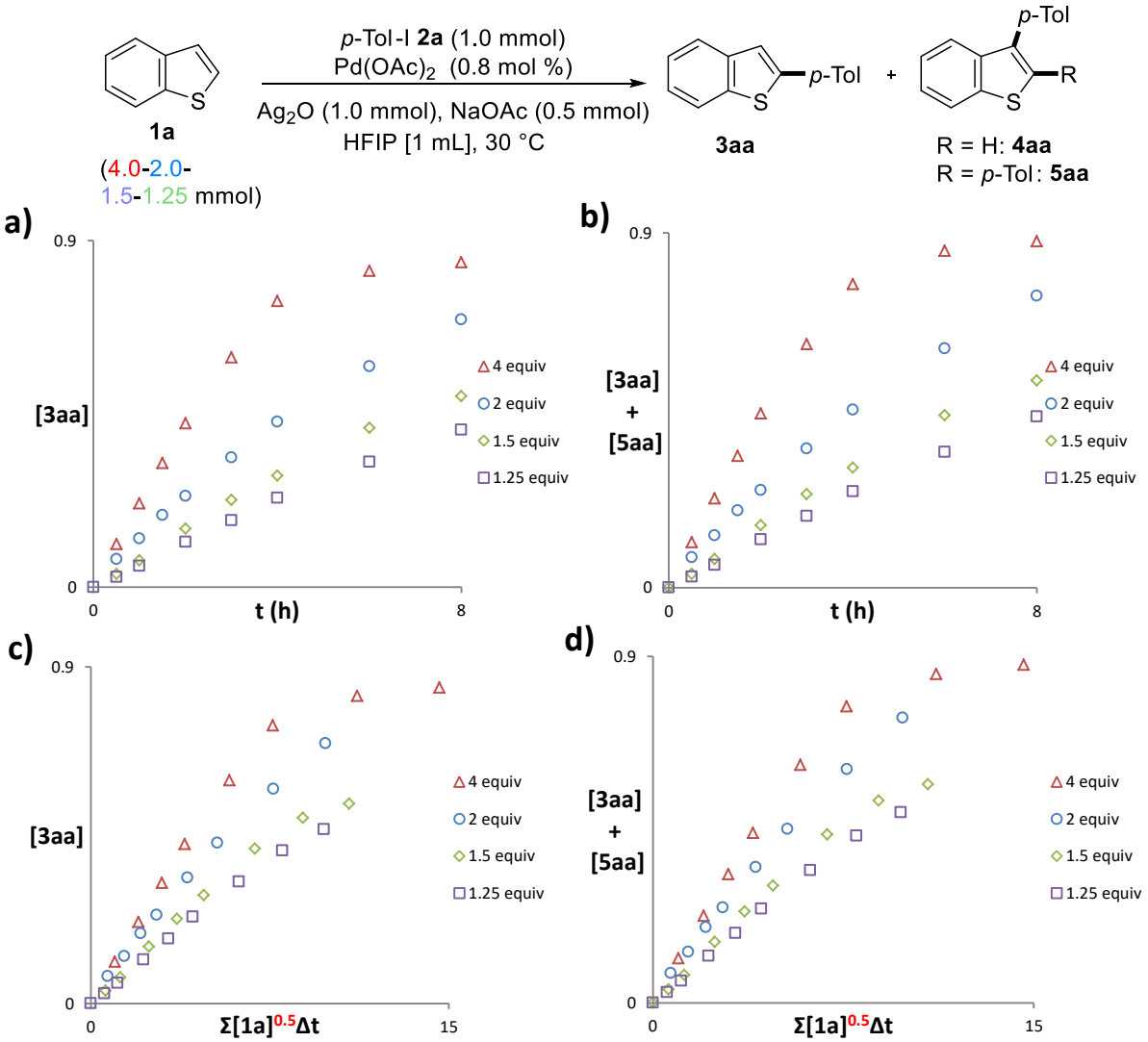




***Figure S.4:*** Temporal reaction profiles for reactions carried out with 0.5-1.0 equiv of **2a** applying method 1 (**a**) and 2 (**b**). Normalized time scale profiles for order 0.5 in **2a** applying method 1 (**c**) and 2 (**d**). Normalized time scale profiles for order 1 in **2a** applying method 1 (**e**) and 2 (**f**).

The overlap between the temporal reaction profiles of reactions using 0.5 and 1 equiv of **2a** indicates an order 0 in this reagent, which therefore doesn't appear in the rate equation. In agreement with the 0 order in Pd and the competition experiment between electronically different iodoarenes, this ruled out the oxidative addition as rate-limiting step. The points at 6 h don't overlay due to the fact that the reaction with 0.5 equiv reached full conversion ~4 h.

### *Determination of order in Benzo[b]thiophene 1a*



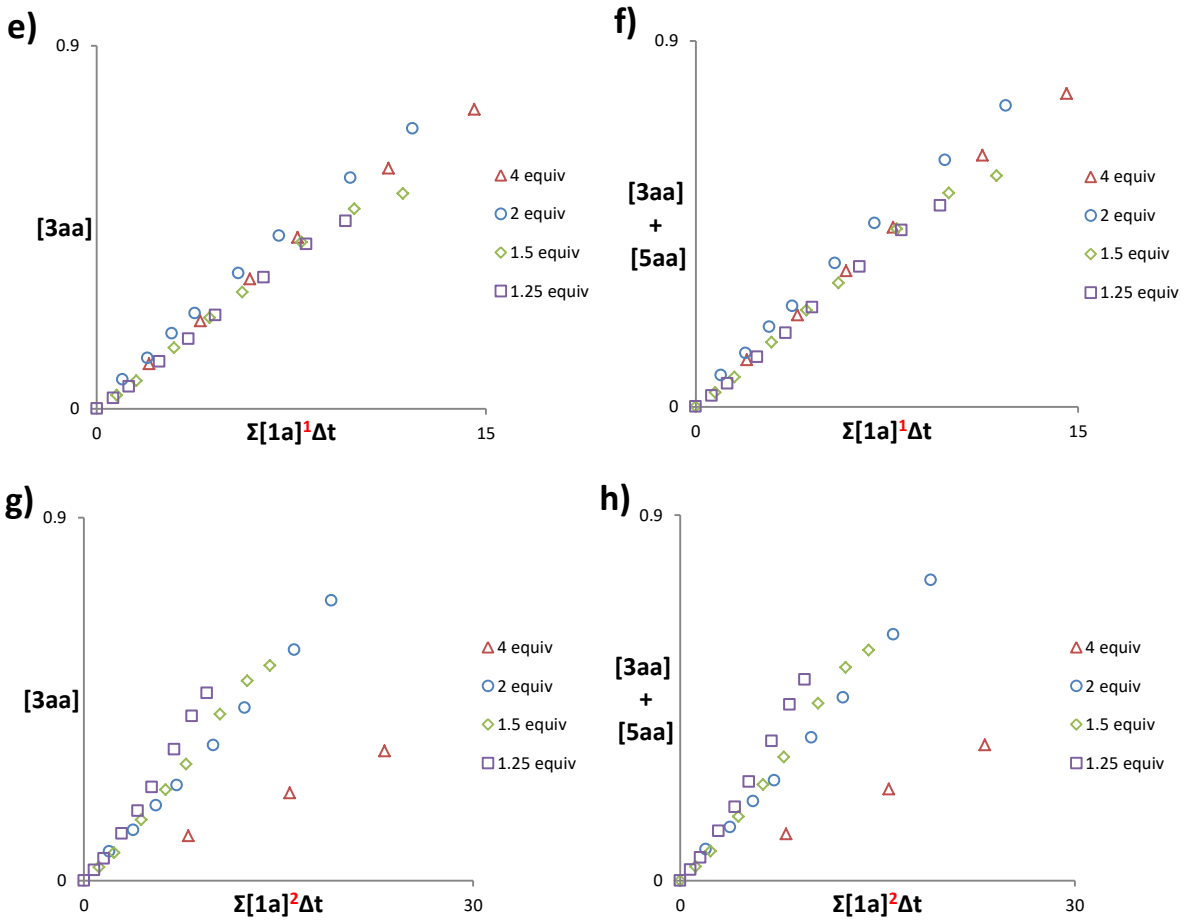



***Figure S.5:*** Temporal reaction profiles for reactions carried out with 4.0-2.0-1.5-1.25 equiv of **1a** applying method 1 (**a**) and 2 (**b**). Normalized time scale profiles for order 0.5 in **1a** applying method 1 (**c**) and 2 (**d**). Normalized time scale profiles for order 1 in **1a** applying method 1 (**e**) and 2 (**f**). Normalized time scale profiles for order 2 in **1a** applying method 1 (**g**) and 2 (**h**).

Applying the variable time normalization analysis, significant overlap between the curves was obtained for an order of **1a** equal to 1, which suggests that this reagent is involved in the rate-limiting step. Considering the high solubility of $Pd(OAc)_2$ in HFIP and the 0 order seen on this catalyst, this experiment points towards a Ag mediated C–H activation of benzo[*b*]thiophene **1a**.

### *Kinetic profiles with different loading of $Ag_2O$*

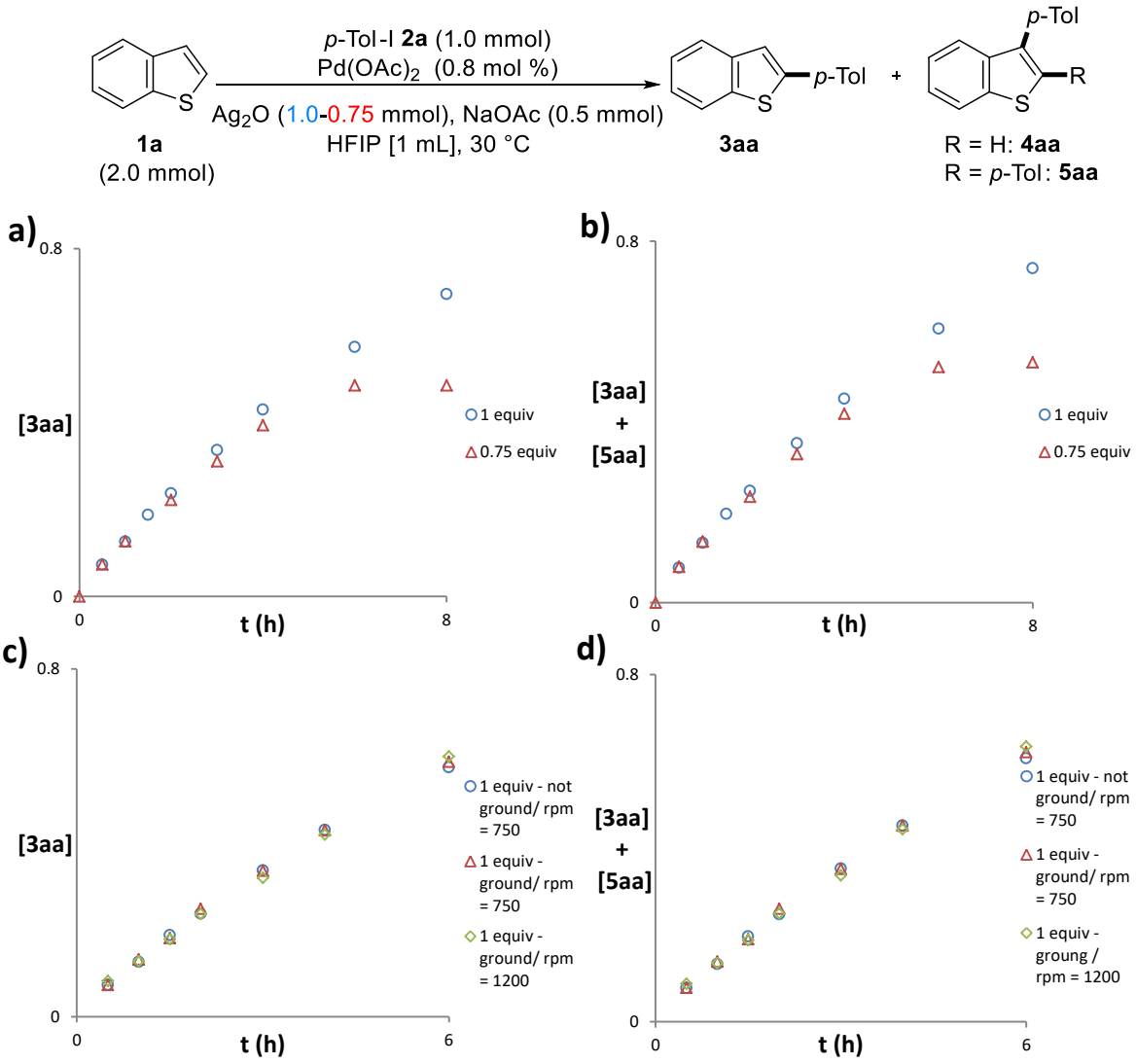



***Figure S.6:*** Temporal reaction profiles for reactions carried out with 1.0-0.75 equiv of $Ag_2O$ applying method 1 (**a**) and 2 (**b**). Effect of grinding $Ag_2O$ into fine nanoparticles and stirring rate have been investigated (**c**-**d**).

The poor solubility of $Ag_2O$ in HFIP prevents determination of the order in this reagent with any accuracy at these concentrations. Indeed, reactions carrying out with 0.75 and 1.0 equiv of $Ag_2O$ overlay. Nonetheless, higher loadings in $Ag_2O$ led to higher formation of product **3aa** over time. Additionally, reactions run with different stirring rates and with different particle sizes of $Ag_2O$ gave identical temporal concentration profiles, suggesting that there is no kinetic dependency on this reagent within this range. On the other hand, lowering the

amount to $Ag_2O$ to 0.5 equiv, produced a mixture of C2 and C3 product (**3aa** and **4aa** respectively).

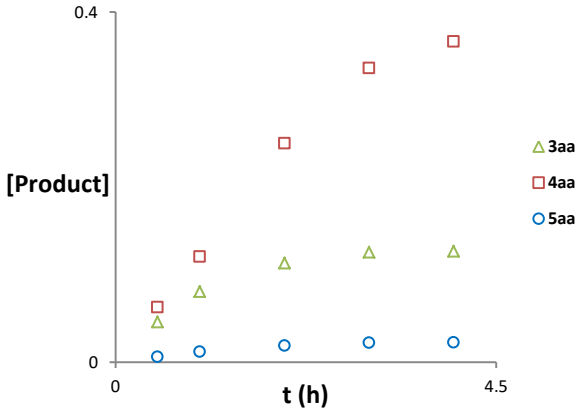
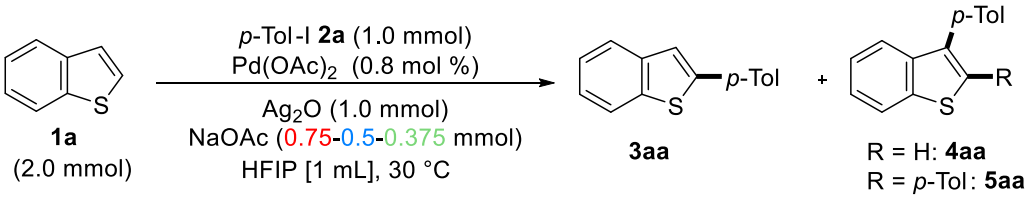
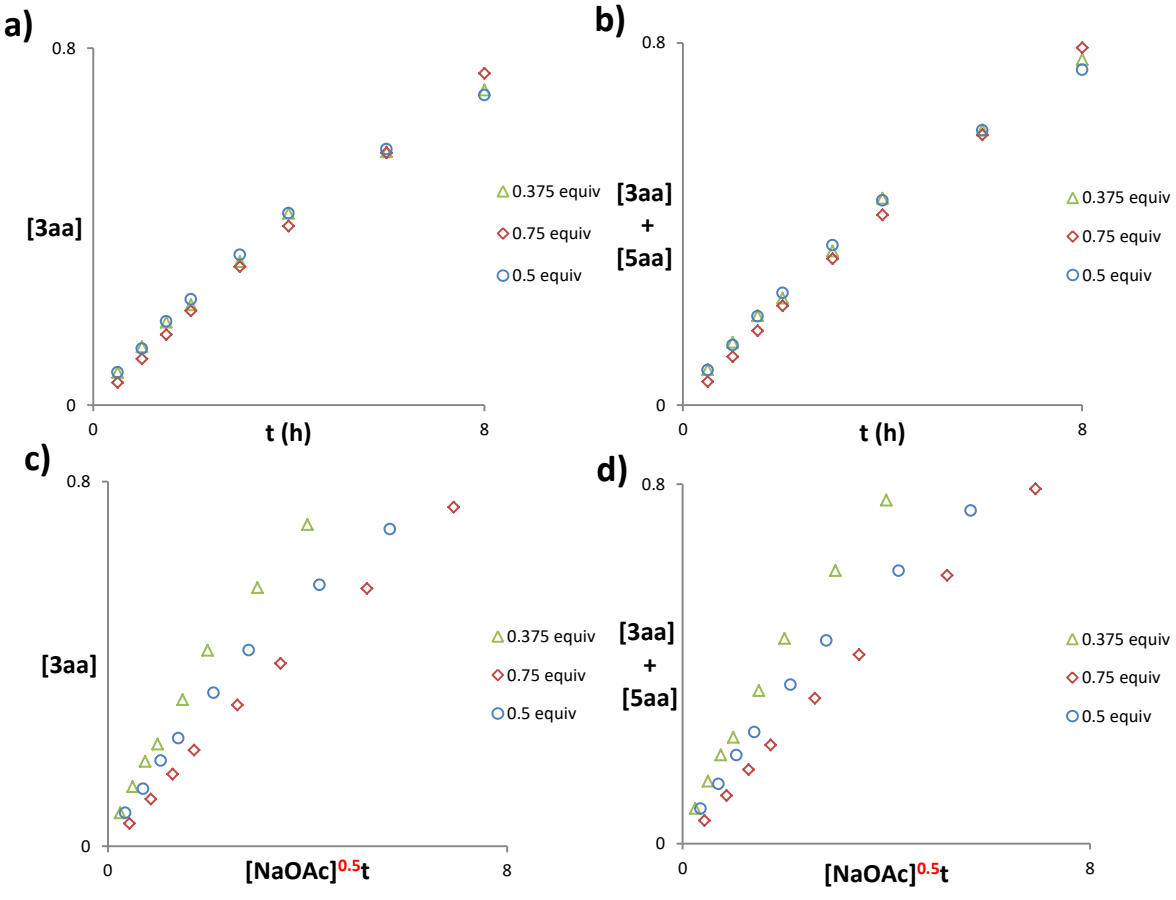



***Figure S.7:*** Temporal reaction profile of reaction carried out with 0.5 equiv of $Ag_2O$

## *Determination order in NaOAc*



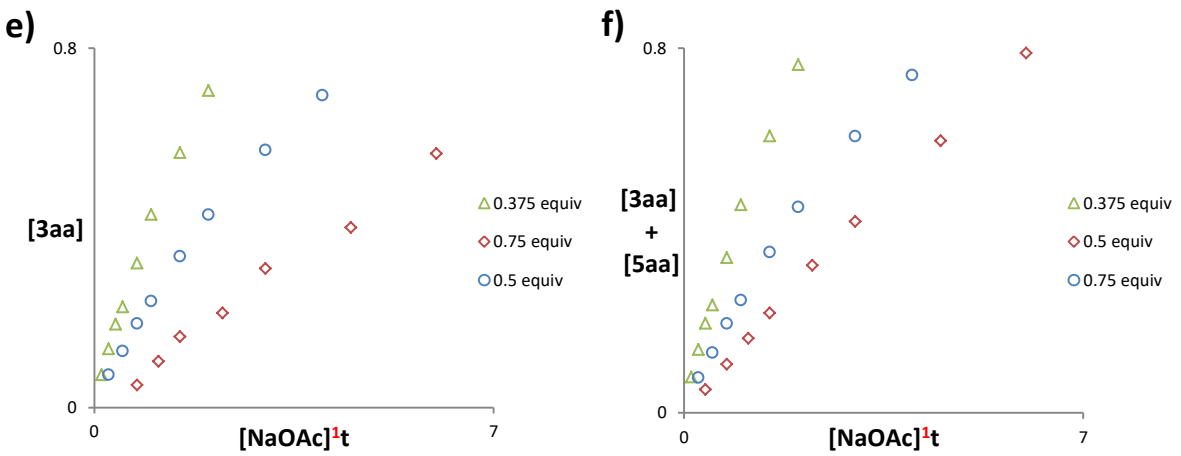
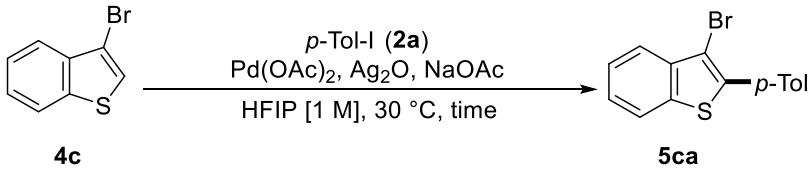



***Figure S.8:*** Temporal reaction profiles for reaction carried out with different loadings of NaOAc applying method 1 (**a**) and 2 (**b**). Normalized time scale profiles for order 0.5 in NaOAc applying method 1 (**c**) and 2 (**d**). Normalized time scale profiles for order 1 in NaOAc applying method 1 (**e**) and 2 (**f**).

The overlap between the temporal reaction profiles of reactions using 0.375, 0.5 and 0.75 equiv of NaOAc indicates an order 0 in this reagent.

## V-3.2. Kinetic Experiments Employing 3-Bromobenzo[*b*]thiophene 4c

### *General procedure*




Silver oxide, 4-iodotoluene **2a**, NaOAc, 1,3,5-trimethoxybenzene were weighed in the glovebox into a microwave vial. The vial was sealed, transferred out of the glovebox and 3-bromobenzo[*b*]thiophene **5c** and $Pd(OAc)_2$ (as solution in hexafluoro-2-propanol) were added. The vial was placed in an oil bath at 30 °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 internal standard.

## V-3.2.1. Determination of the Order in Catalyst

### *Determination of order in $Pd(OAc)_2$*

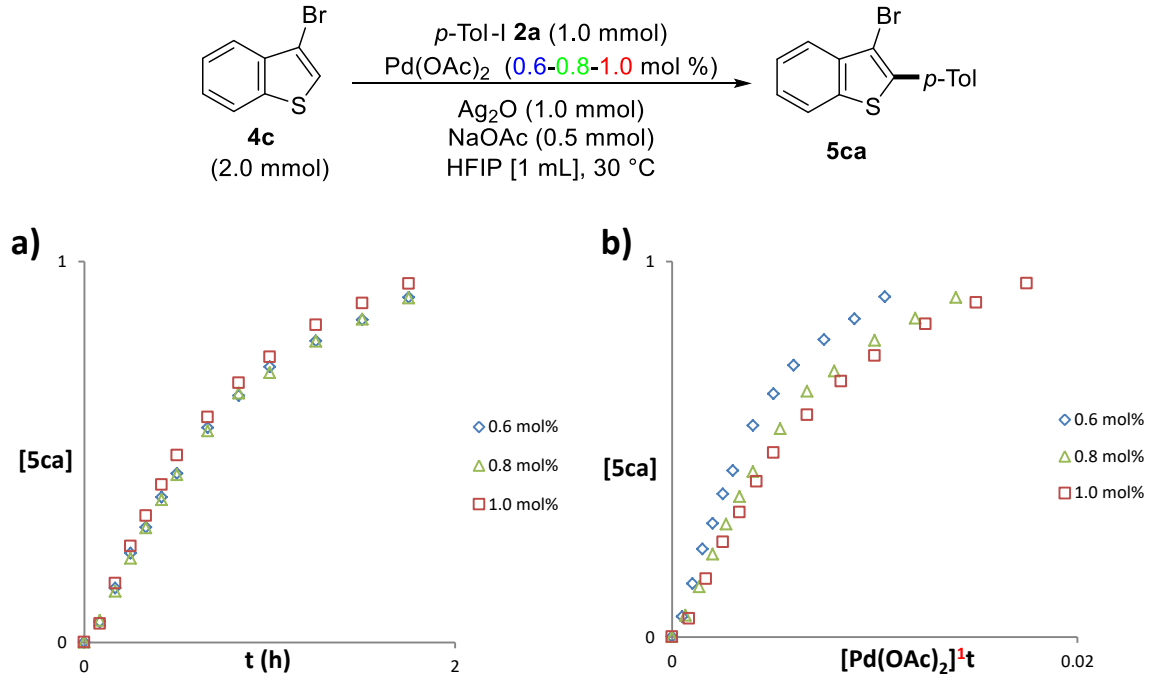
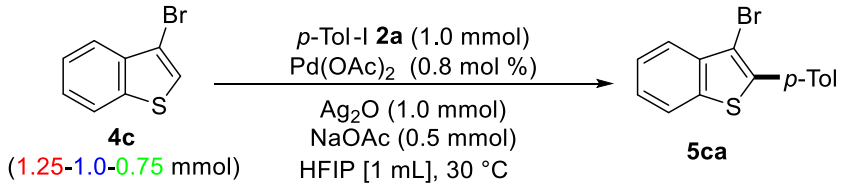



***Figure S.9:*** Temporal reaction profiles for reaction carried out with different loadings of $Pd(OAc)_2$ (**a**). Normalized time scale profiles for order 1 in $Pd(OAc)_2$ (**b**).

The overlap between the temporal reaction profiles with catalyst loadings of 0.6, 0.8 and 1.0 mol % suggests that the order in $Pd(OAc)_2$ is 0 at these concentrations, which implies that an external process to the catalytic cycle is rate-limiting.[21]

## V-3.2.2. Determination of the Order in Reactants

### *Determination of order in 3-bromo[b]benzothiophene 4c*



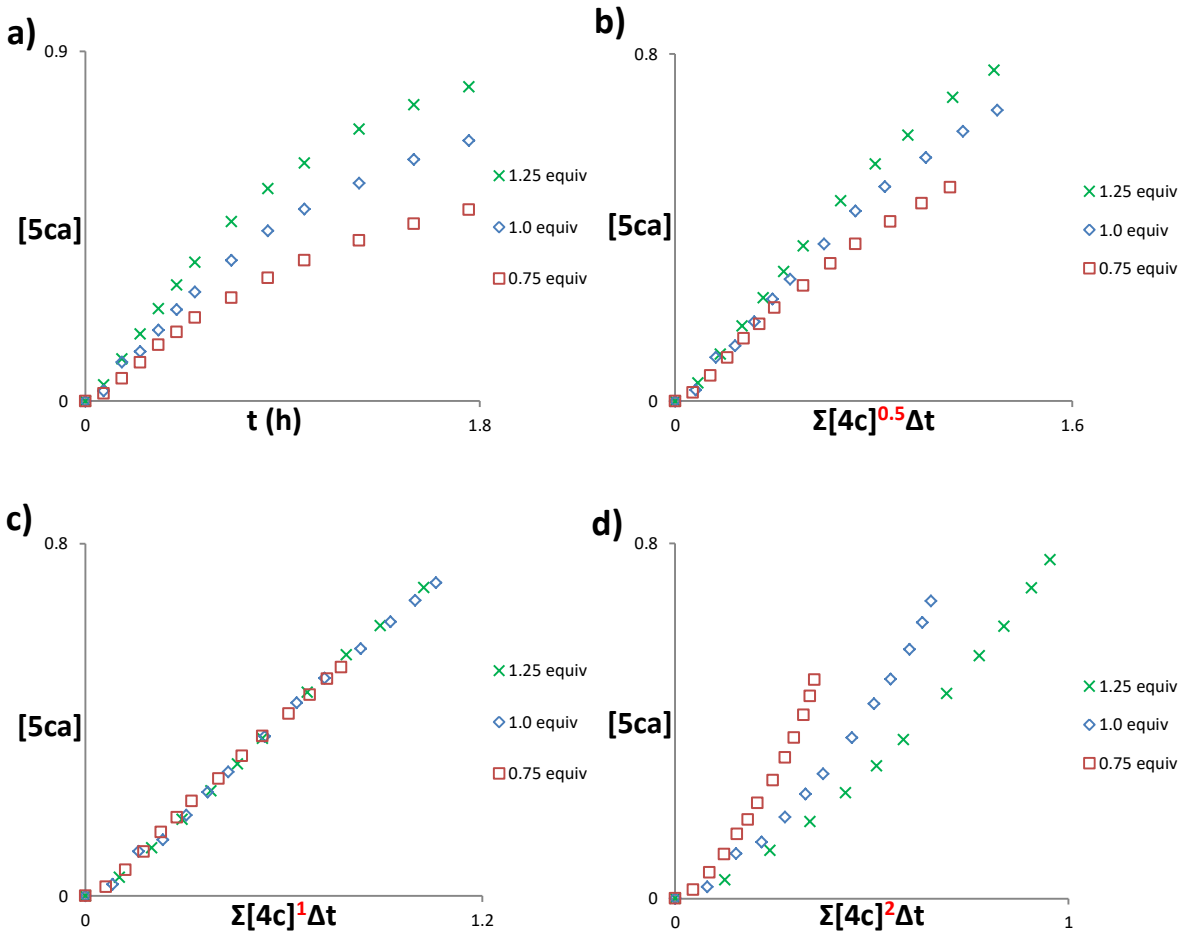




***Figure S.10:*** Temporal reaction profiles for reaction carried out with different loadings of $Ag_2O$ (**a**). Normalized time scale profiles for order 0.5 in **4c** (**b**). Normalized time scale profiles for order 1 in **4c** (**c**). Normalized time scale profiles for order 2 in **4c** (**d**).

Applying the variable time normalization analysis, significant overlap between the curves was obtained for an order of **4c** equal to 1, which suggests that this reagent is involved in the rate-limiting step. Considering the high solubility of $Pd(OAc)_2$ in HFIP and the 0 order seen

on this catalyst, this experiment points towards a Ag mediated C–H activation of 3-bromothianaphthene **4c**.

### *Determination of order in $Ag_2O$*

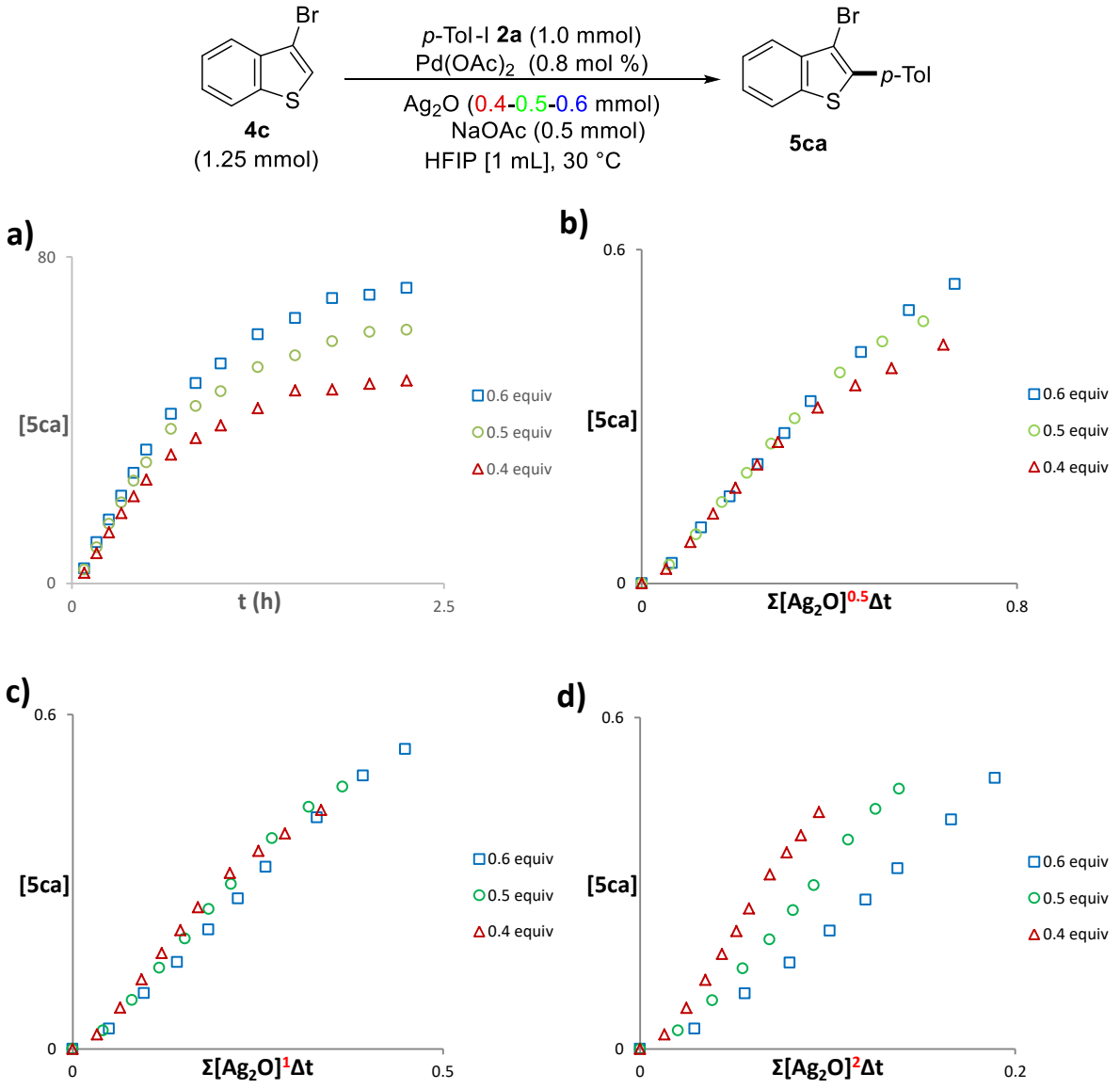


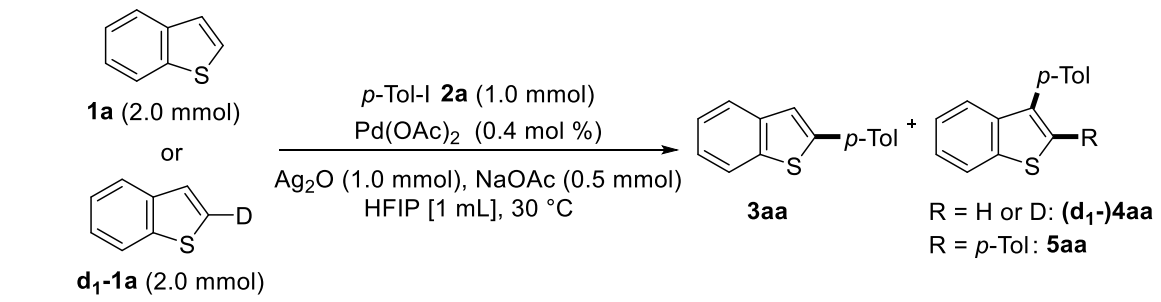

***Figure S.11:*** Temporal reaction profiles for reaction carried out with different loadings of $Ag_2O$ (**a**). Normalized time scale profiles for order 0.5 in $Ag_2O$ (**b**). Normalized time scale profiles for order 1 in $Ag_2O$ (**c**). Normalized time scale profiles for order 2 in $Ag_2O$ (**d**).

Applying the variable time normalization analysis, significant overlap between the curves was obtained for an order of $Ag_2O$ equal to 0.5, which suggests that this reagent is present as an inactive dimeric resting state of the type $[Ag_2X_n]$ in equilibrium with the active

monomeric species AgX. Moreover, we speculate that a plausible monomeric $AgOCH(CF_3)_2$ species, formed in situ by acid-base reaction with HFIP could be responsible for the observed reactivity and is present in a low concentration.

## V-4. Determination of $^2$H KIE

KIE at the α-position of benzo[*b*]thiophene was calculated as ratio of the rate constants ($k_H/k_D$) determined by kinetic analysis.[23] $k_H$ and $k_D$ have been obtained with the linearisation method reported by Burés.[22]



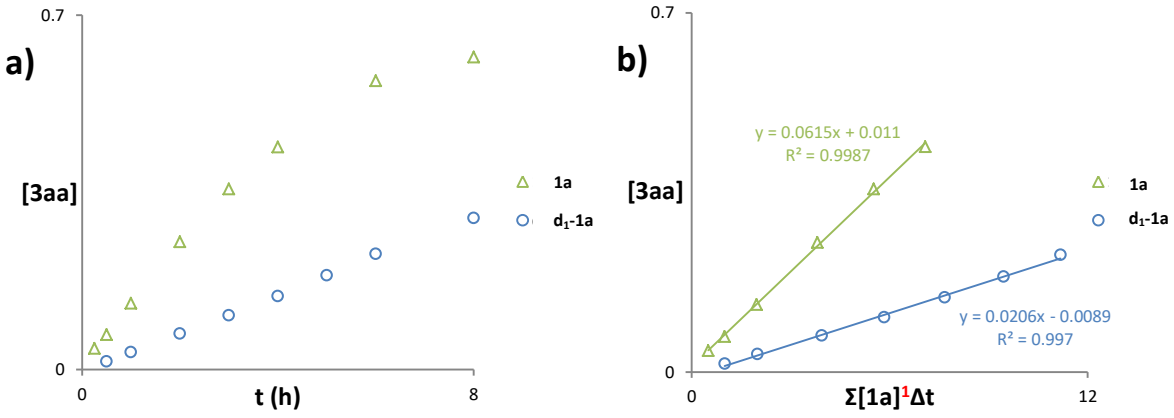




***Figure S.12:*** Temporal reaction profiles for reaction carried out with **1a** and **$d_1$-1a** (a). Normalized time scales enable the determination of $k_H$ and $k_D$ (b)**.**

$k_H = 0.062$

$k_D = 0.021$

KIE = $k_H/k_D = 0.0615/0.0206 = 3.0$

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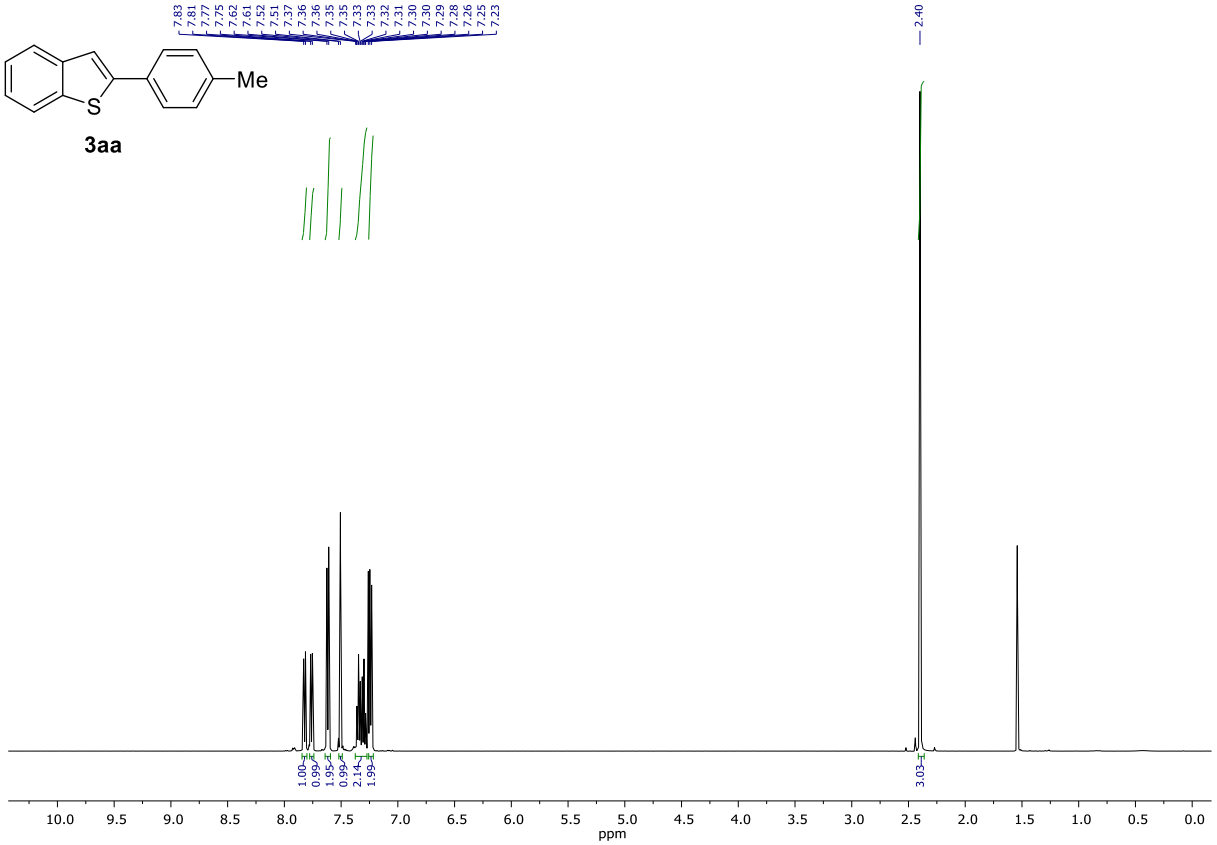
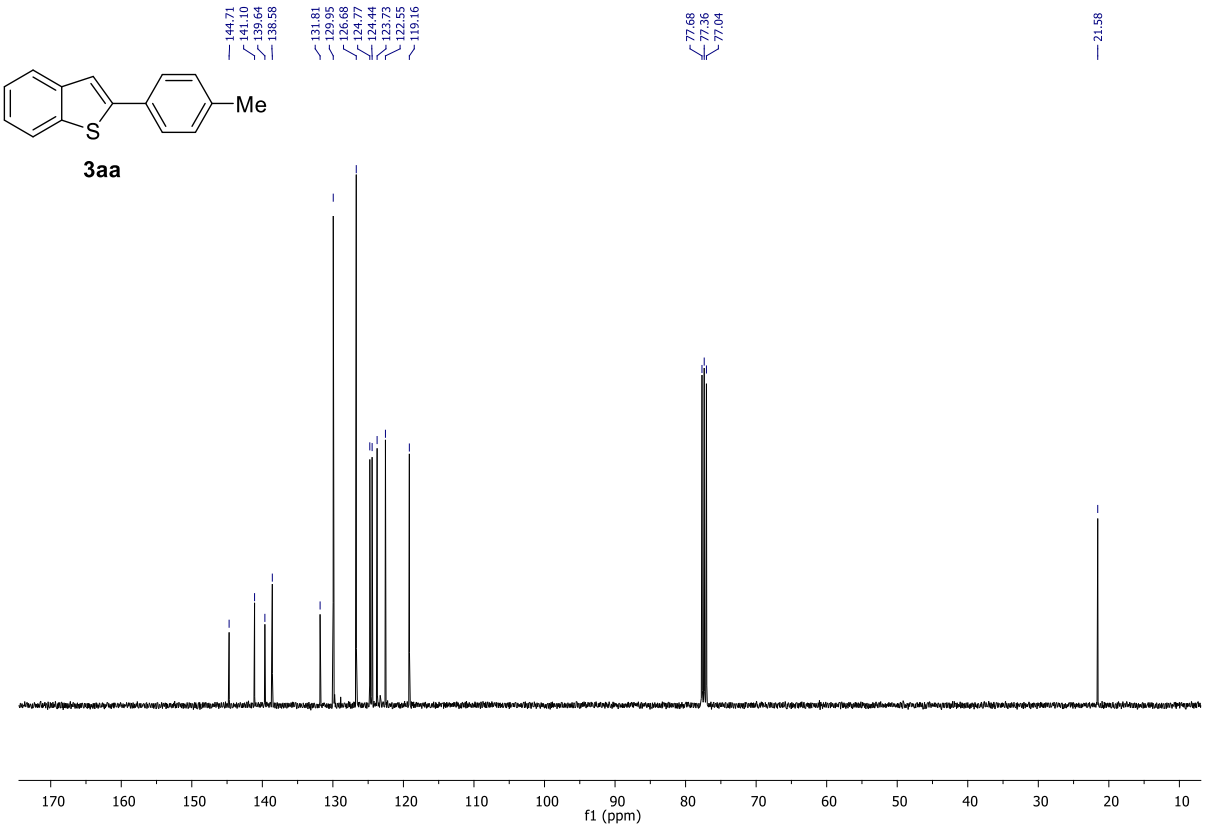
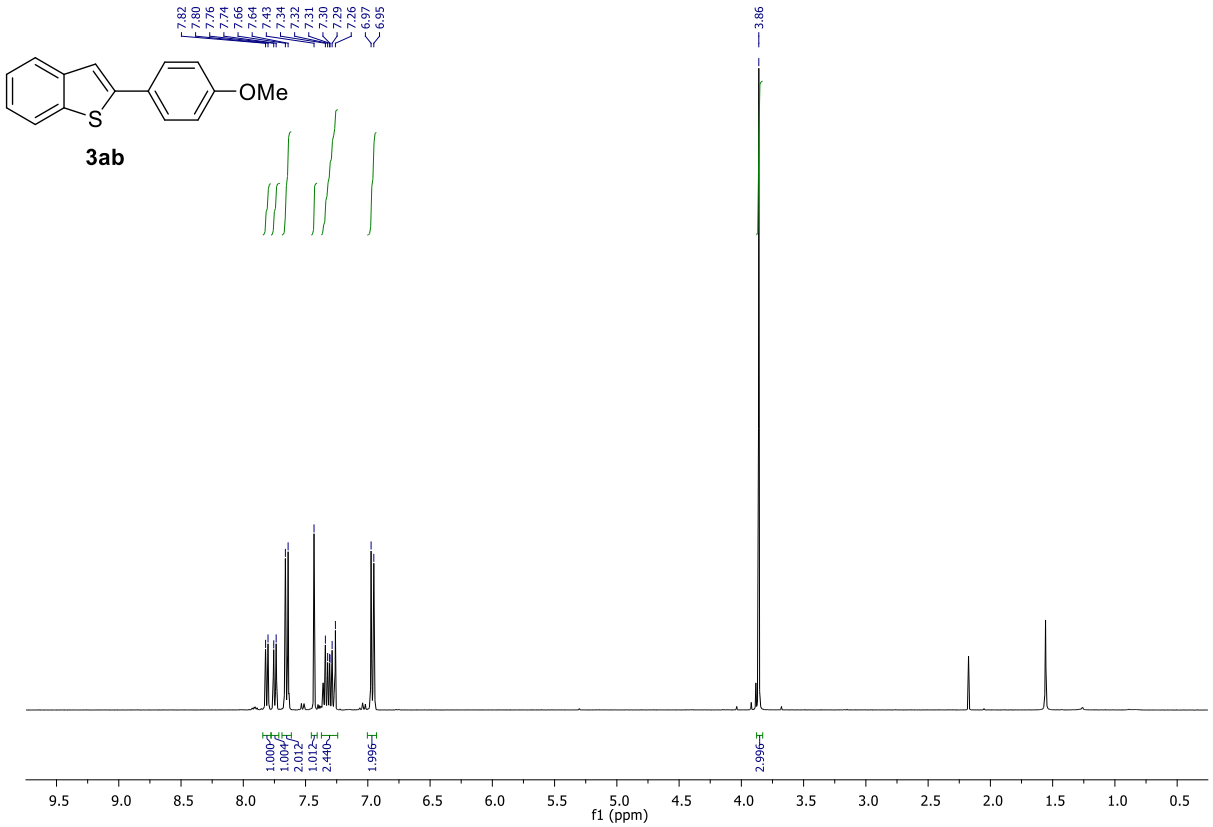
## VII. $^{1}$H-NMR and $^{13}$C-NMR spectra

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6.95
3.86
OMe
S
3ab
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1.004
2.012
1.012
2.440
1.996
2.996
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8.0
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6.0
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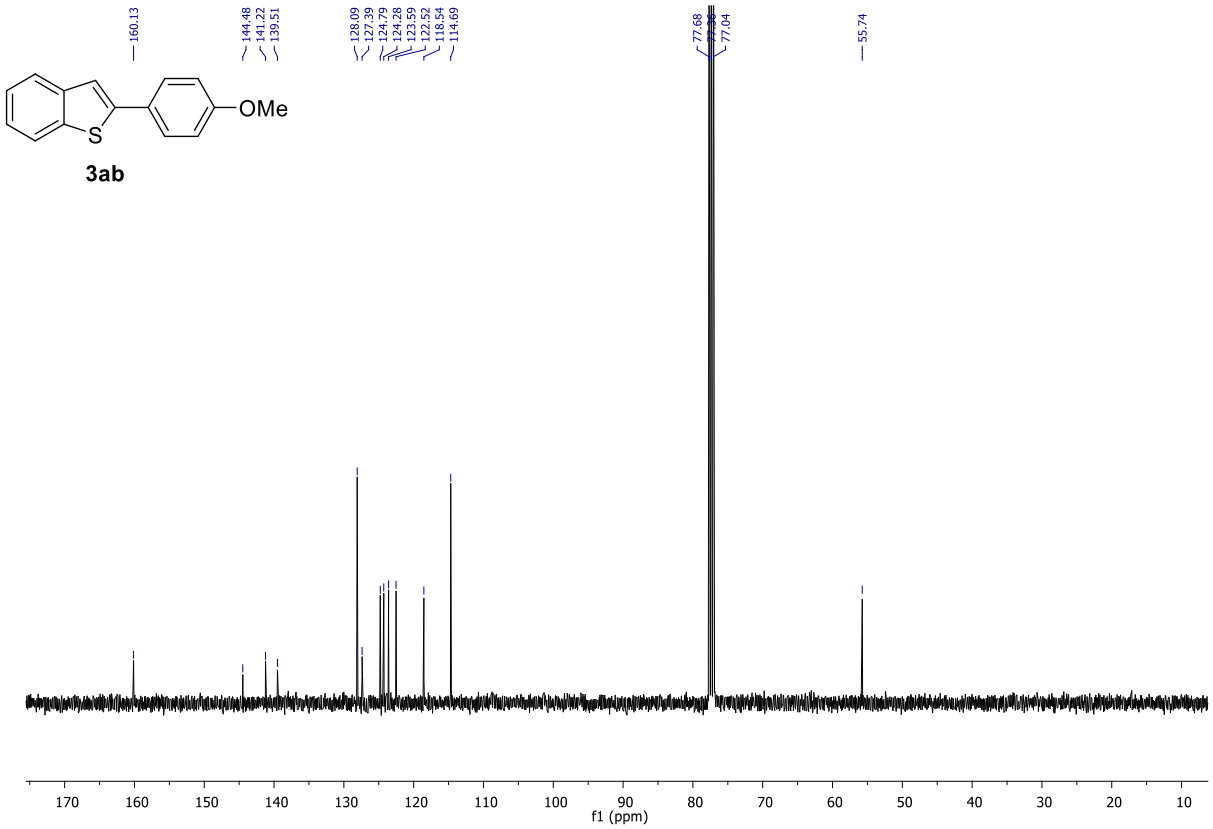
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55.74
OMe
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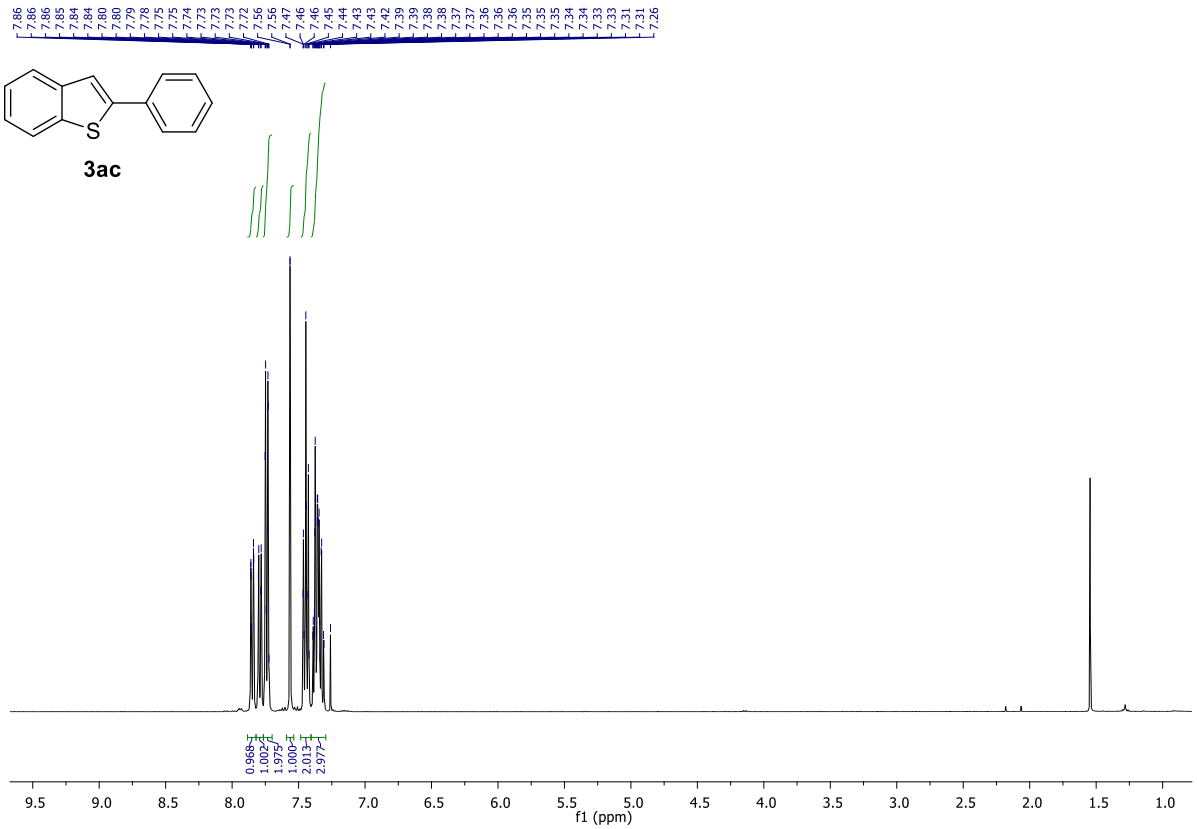
f1 (ppm)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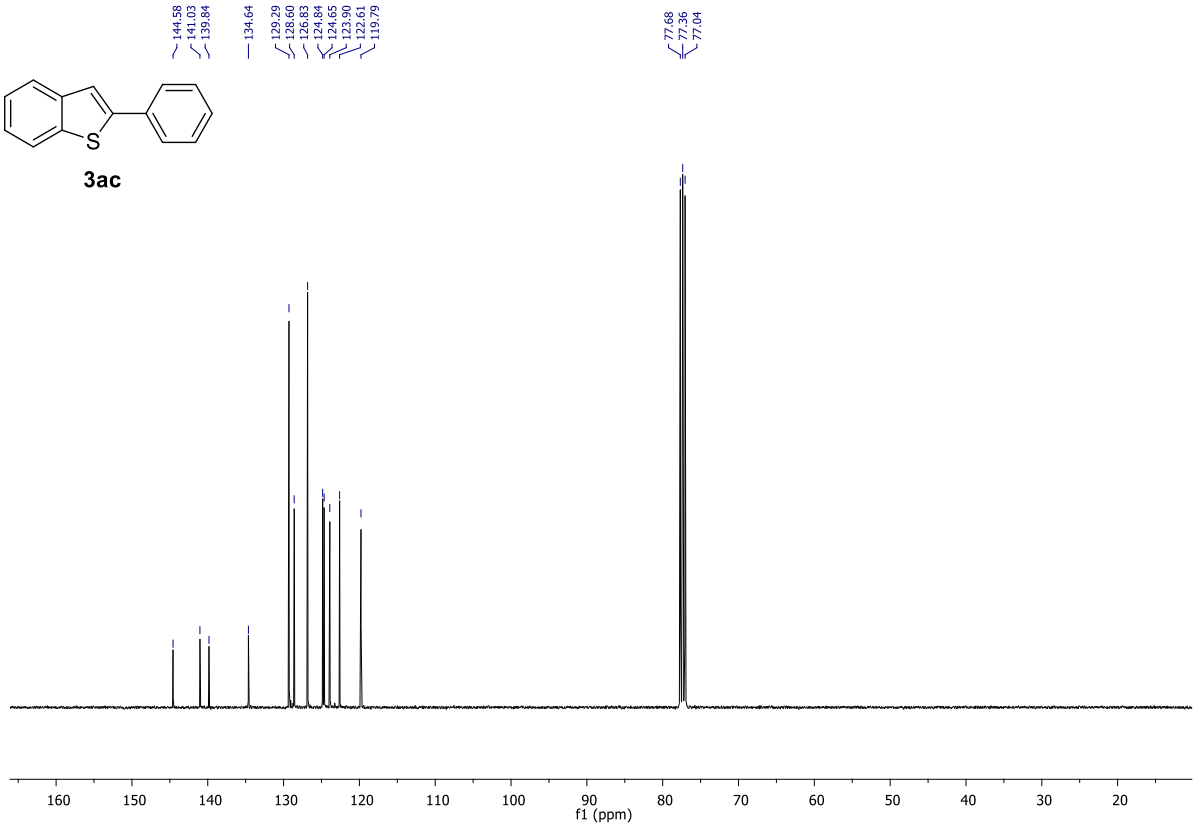
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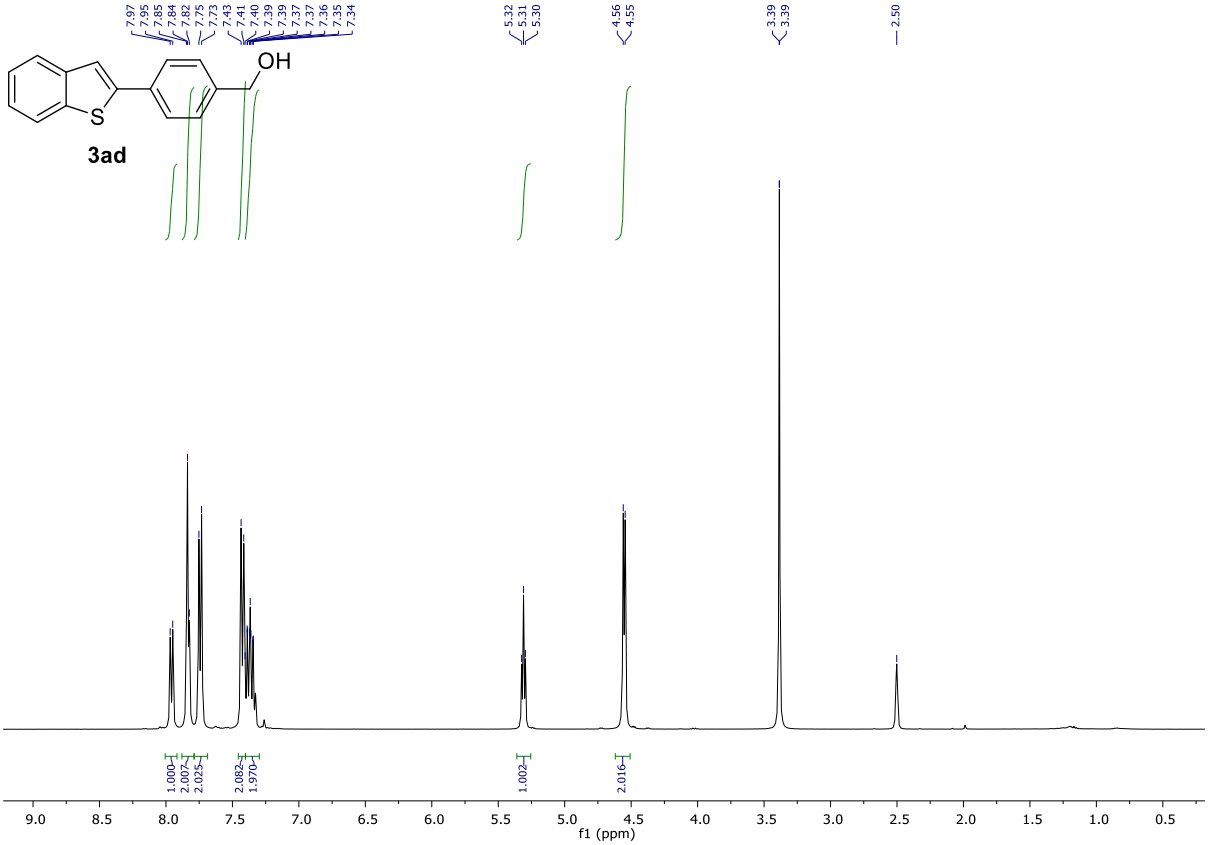
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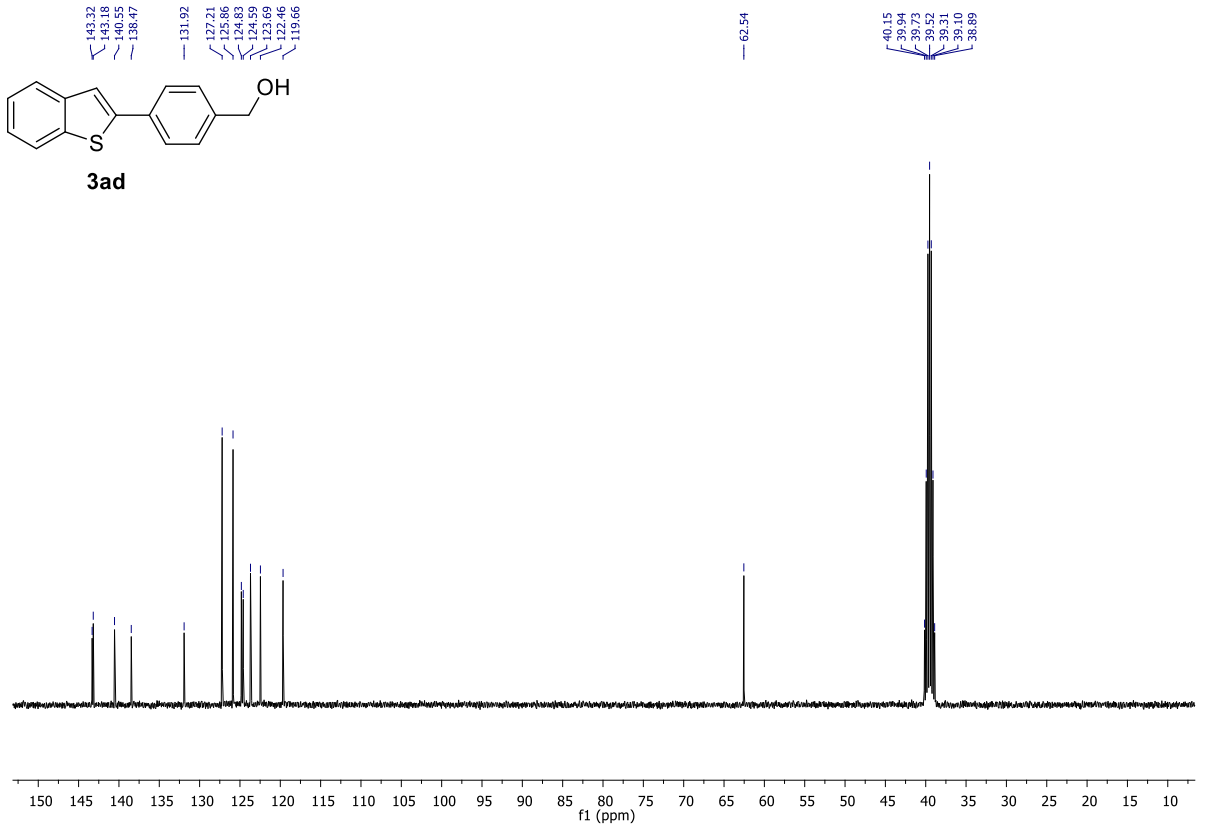
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105
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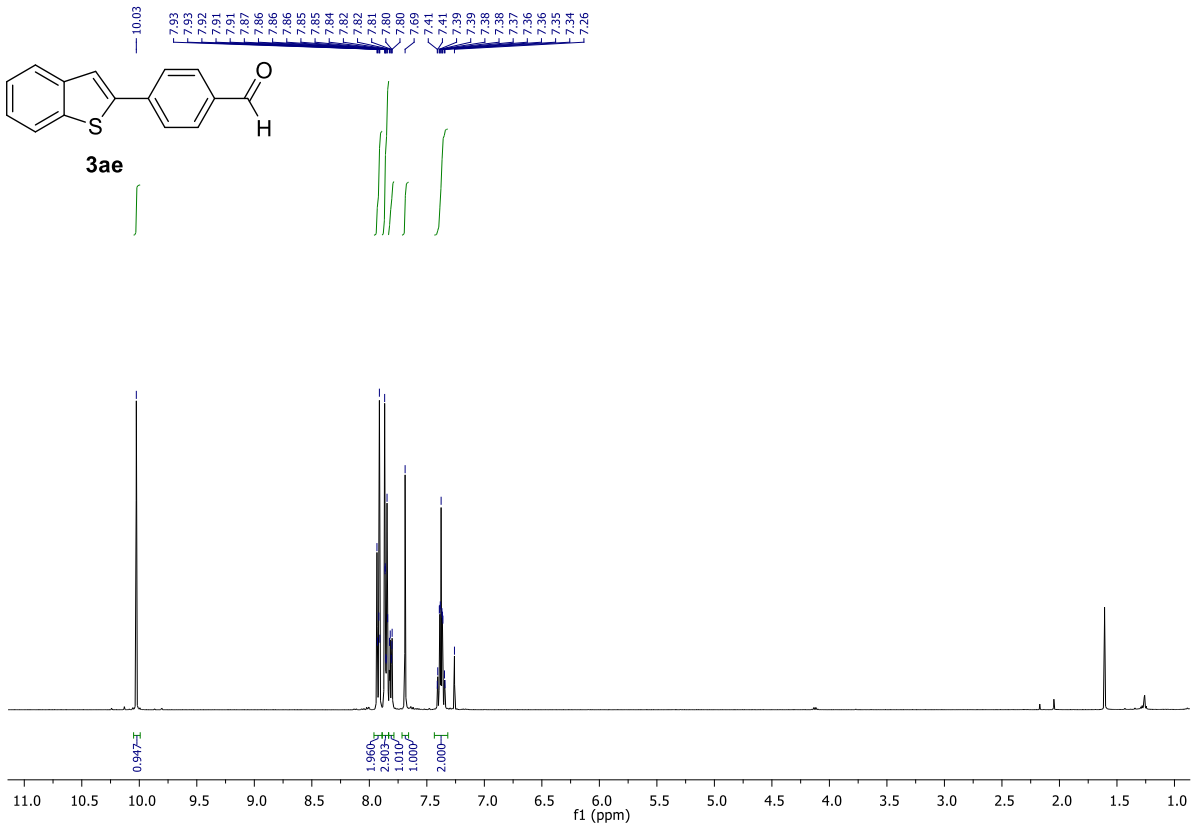
f1 (ppm)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H
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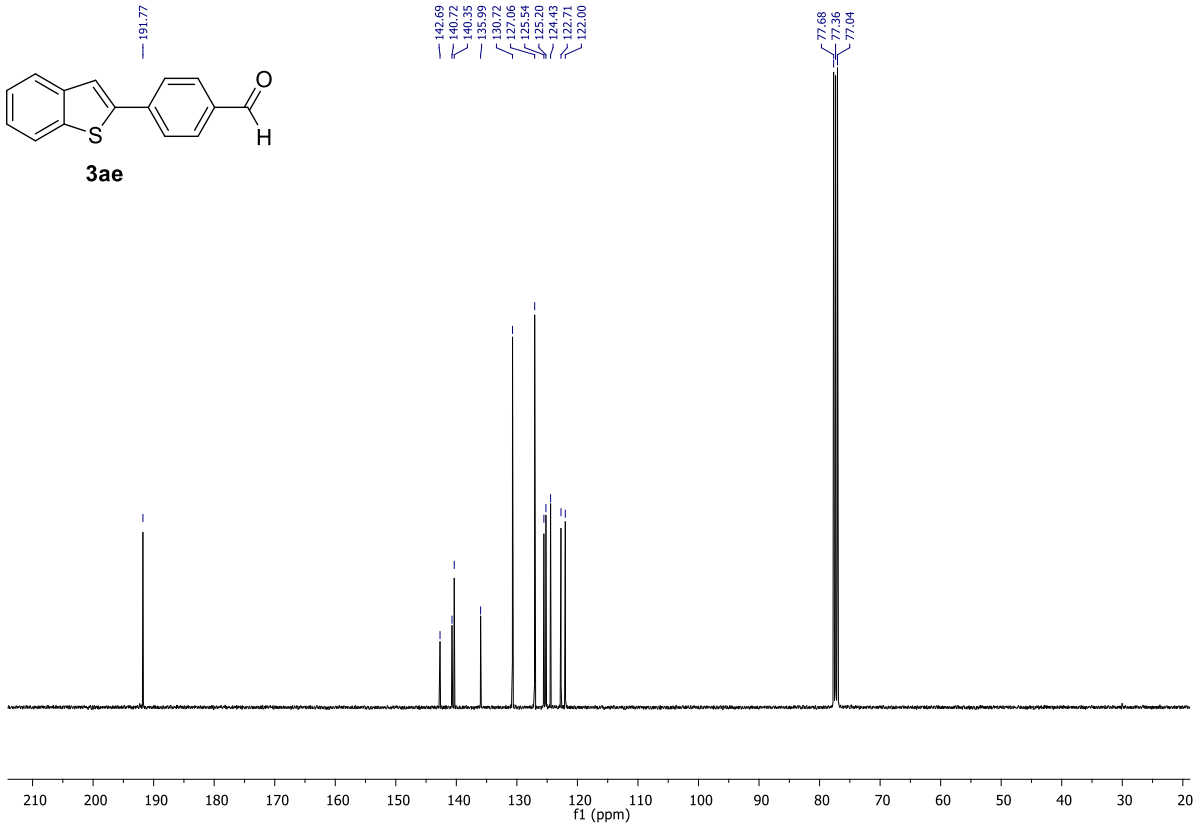
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110
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90
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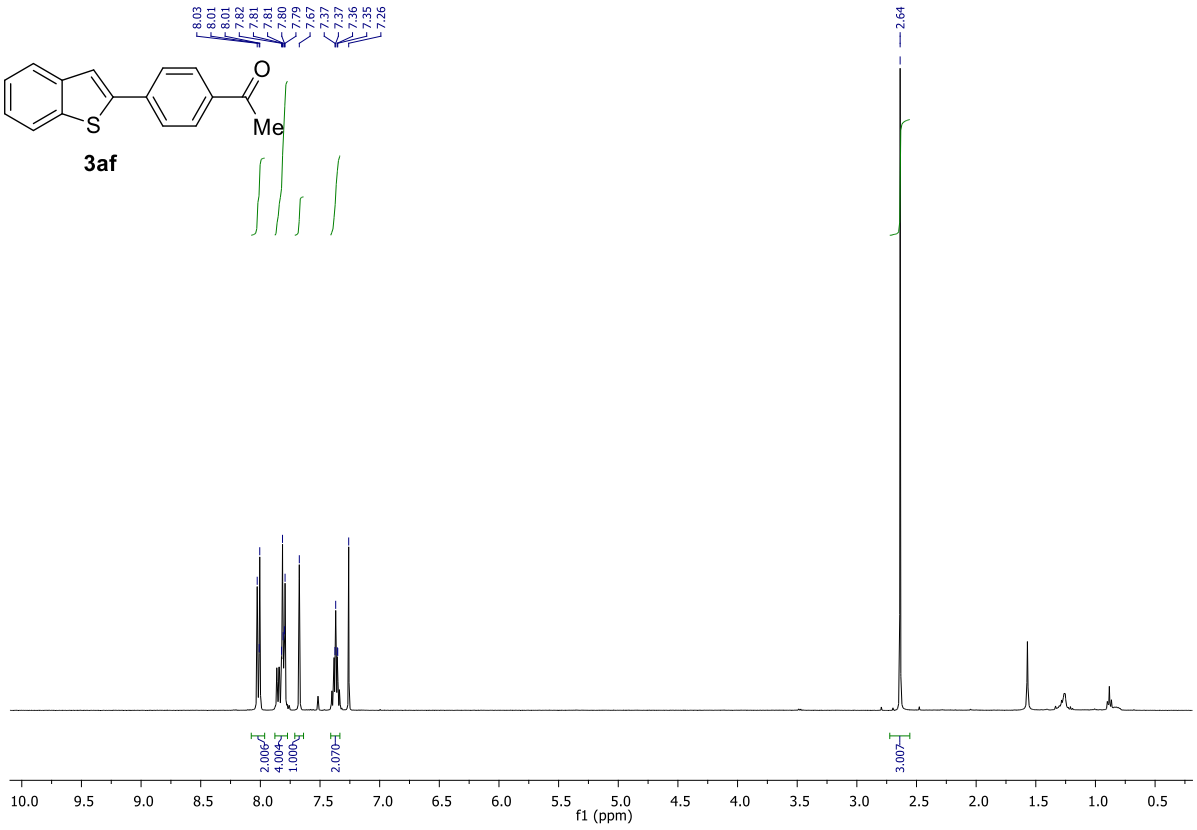
70
60
50
40
30
20
f1 (ppm)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8.01
8.01
7.82
7.81
7.81
7.80
7.79
7.67
7.37
7.37
7.36
7.35
7.26
2.64
O
S
Me
3af
2.006
4.004
1.000
2.070
3.007
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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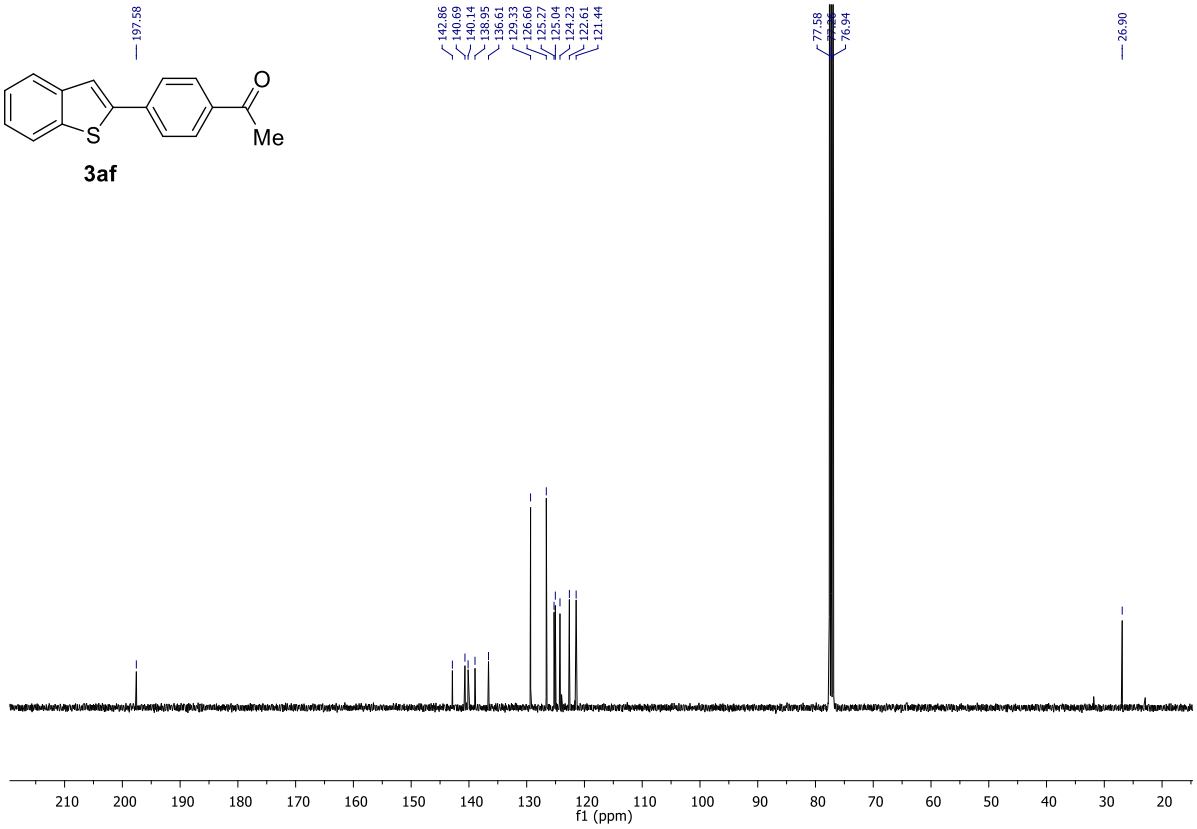
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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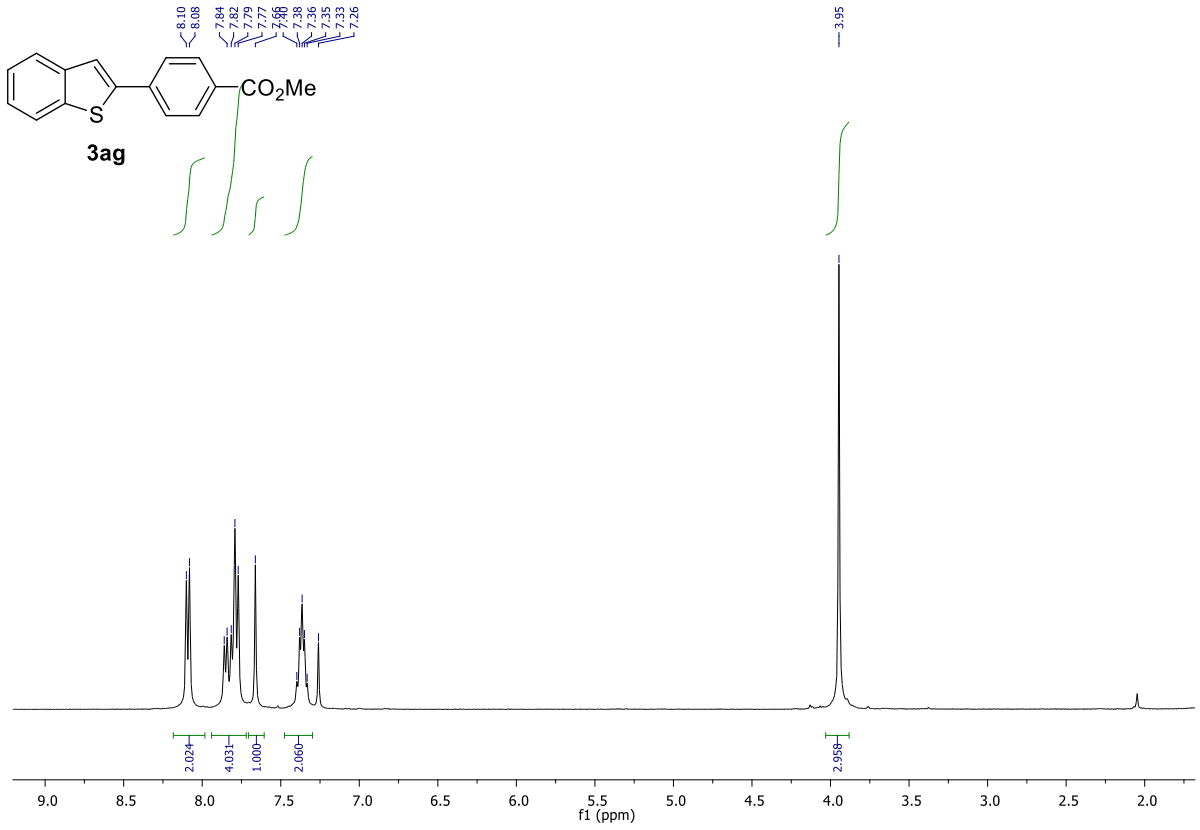
140.69
140.14
138.95
136.61
129.33
126.60
125.27
125.04
124.23
122.61
121.44
77.58
76.94
26.90
O
S
Me
3af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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8.08
7.84
7.82
7.79
7.77
7.38
7.36
7.35
7.33
7.26
3.95
CO2Me
S
3ag
2.024
4.031
1.000
2.060
2.958
9.0
8.5
8.0
7.5
7.0
6.5
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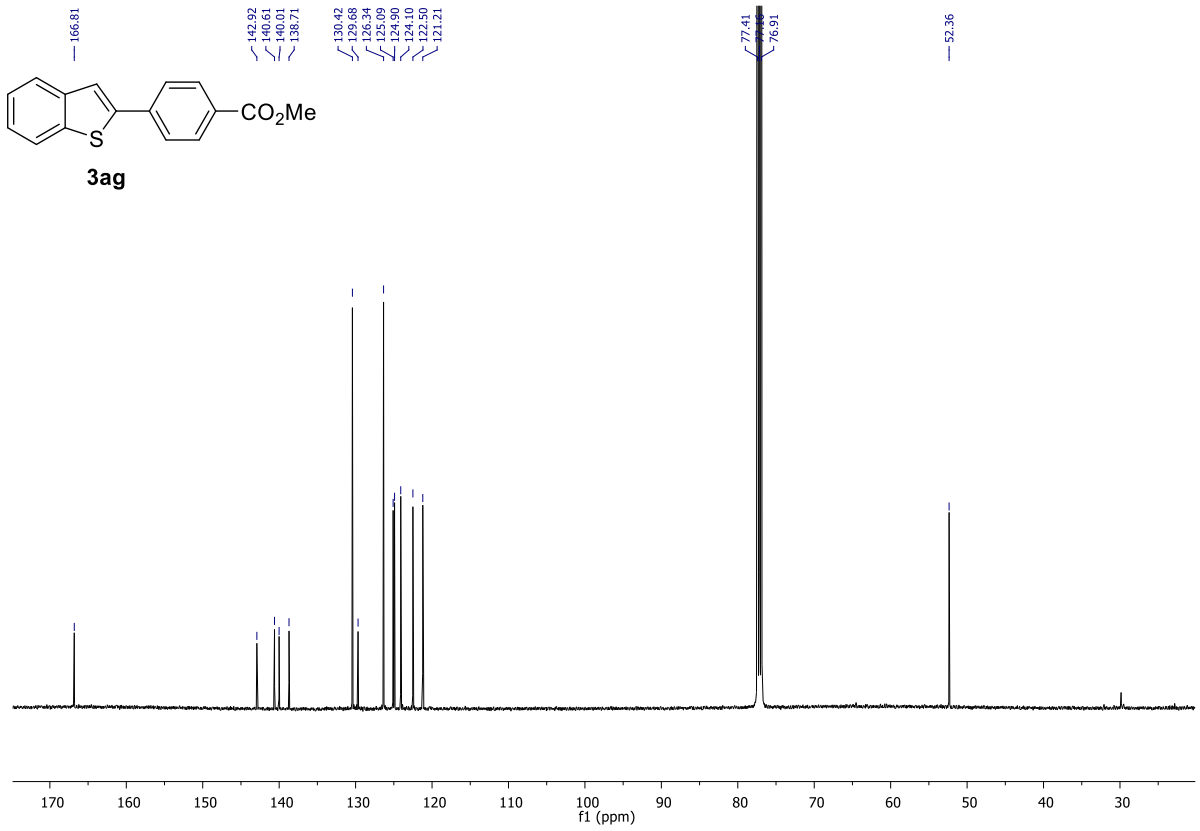
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)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142.92
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138.71
130.42
129.68
126.34
125.09
124.90
124.10
122.50
121.21
77.41
76.91
52.36
CO2Me
S
3ag
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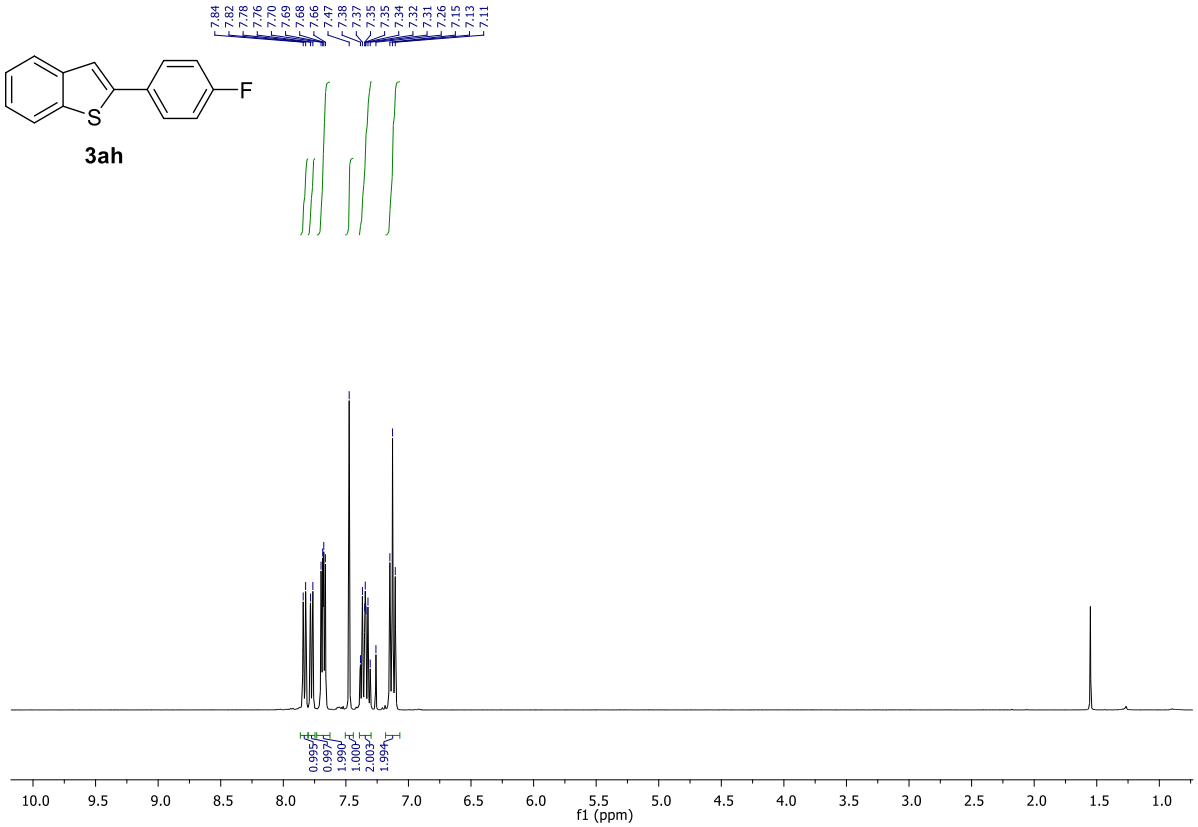
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)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7.82
7.78
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7.69
7.68
7.66
7.47
7.38
7.37
7.35
7.35
7.34
7.32
7.31
7.26
7.15
7.13
7.11
F
S
3ah
0.995
0.997
1.990
1.000
2.003
1.994
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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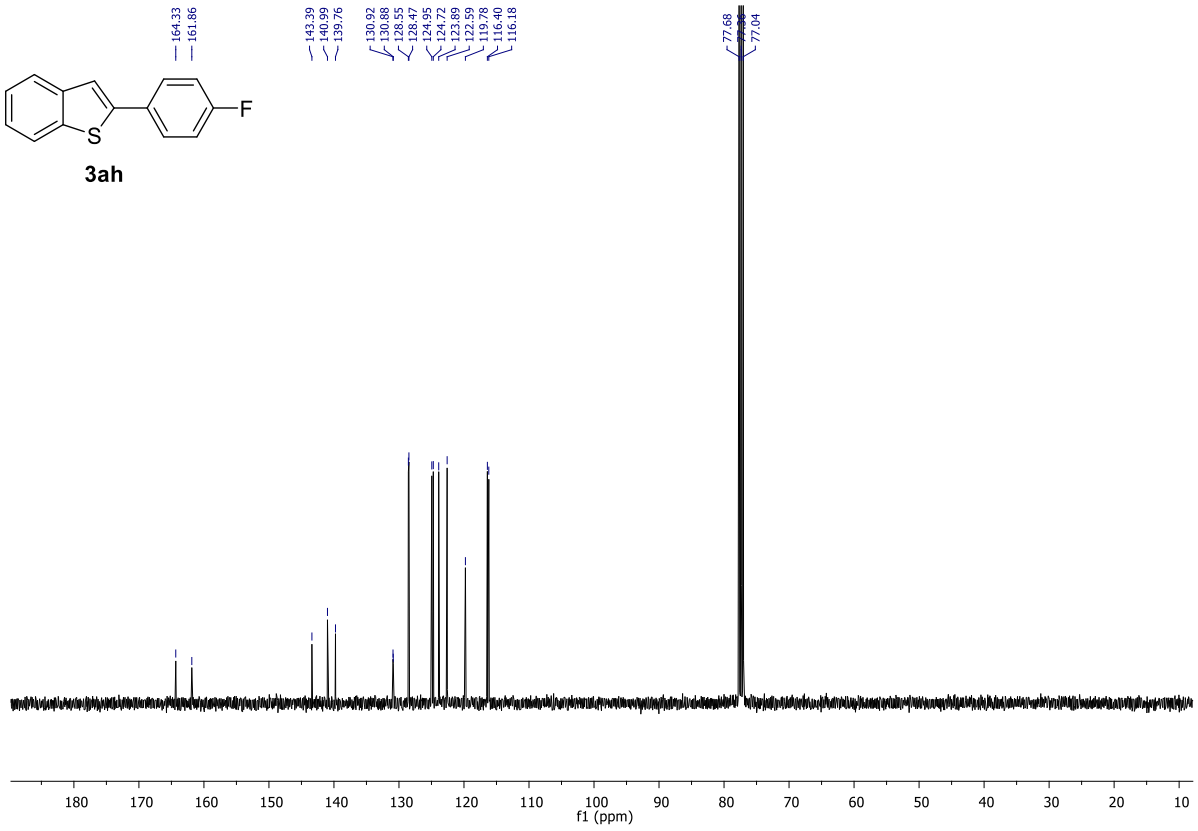
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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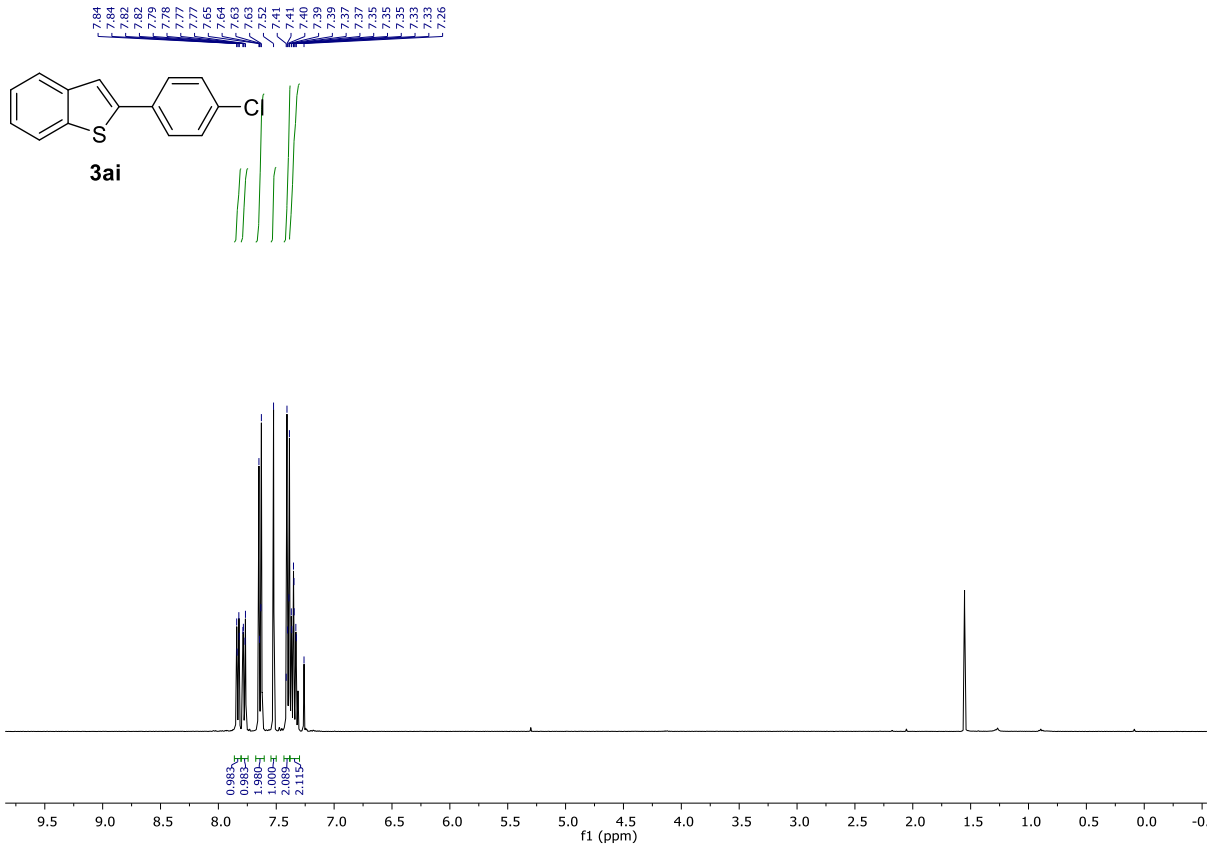
161.86
143.39
140.99
139.76
130.92
130.88
128.55
128.47
124.95
124.72
123.89
122.59
119.78
116.40
116.18
77.68
77.04
F
S
3ah
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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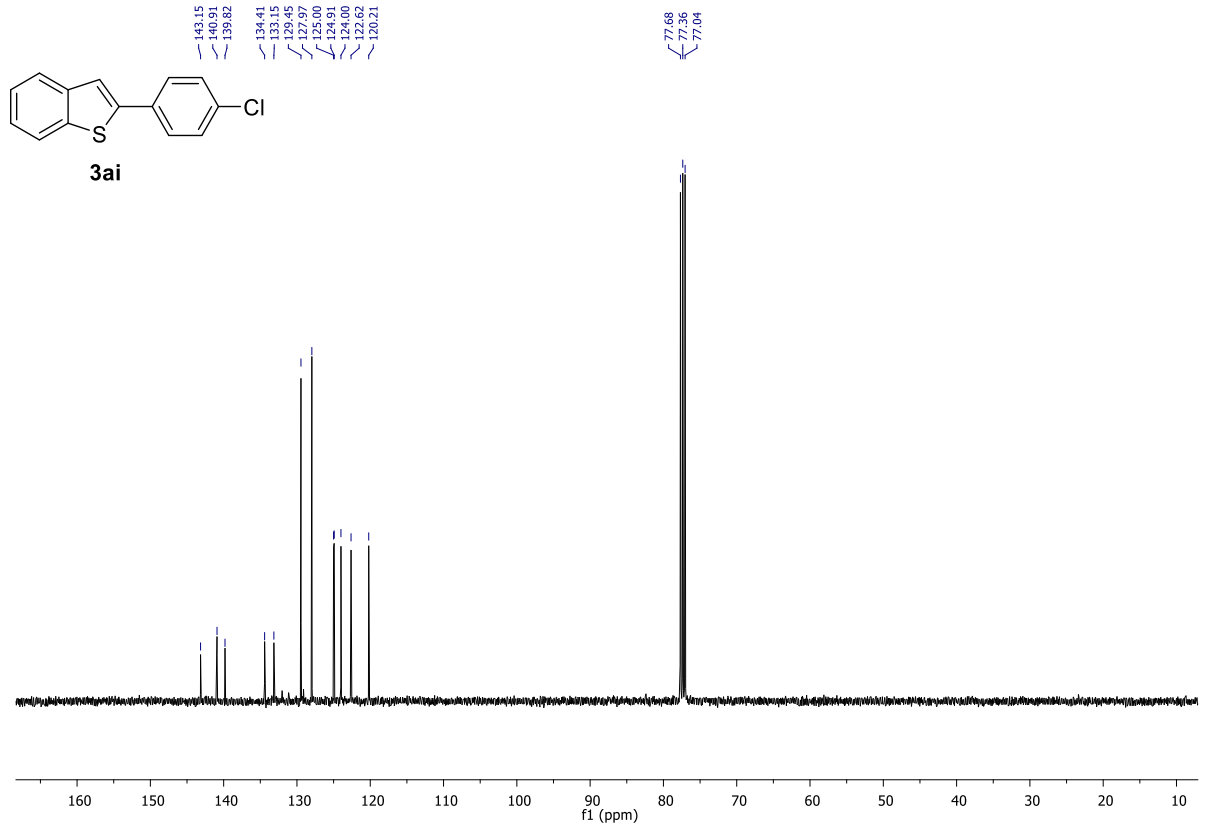
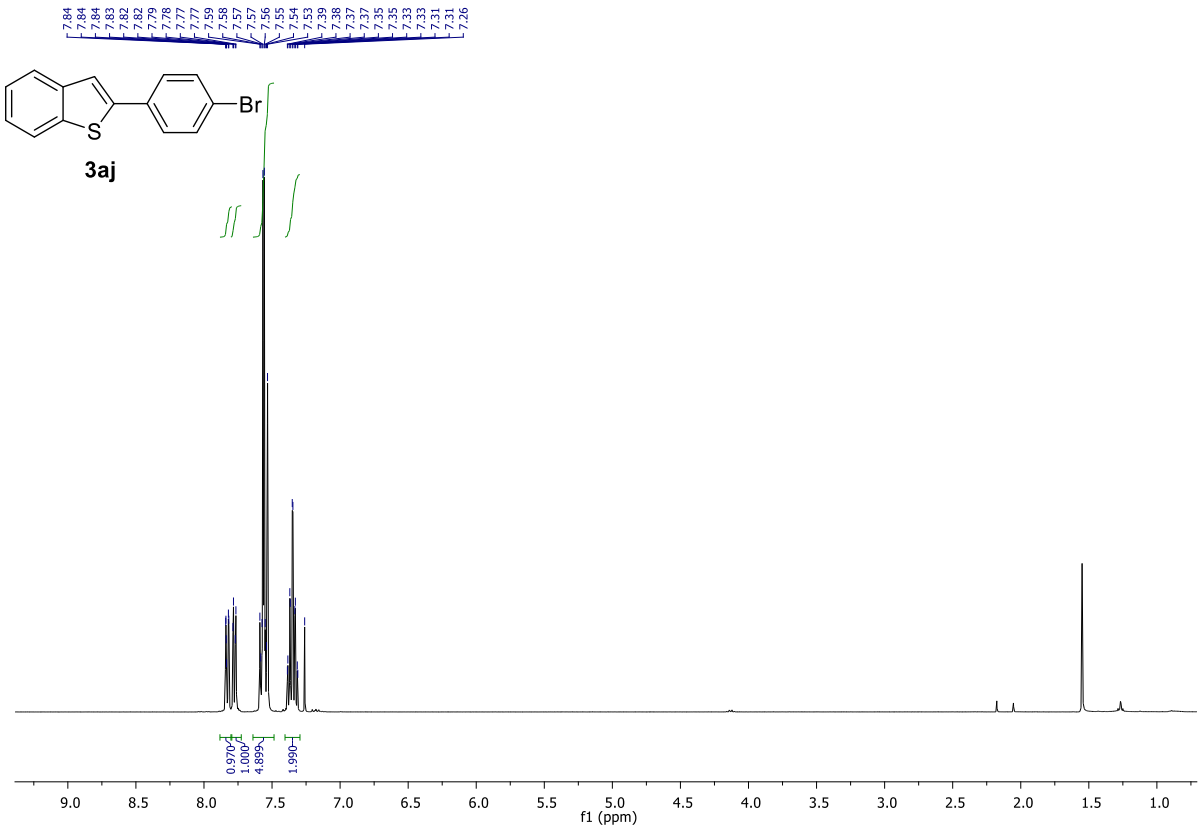
7.84
7.82
7.82
7.79
7.78
7.77
7.77
7.65
7.64
7.63
7.63
7.52
7.41
7.40
7.39
7.39
7.37
7.37
7.35
7.35
7.33
7.33
7.26
Cl
S
3ai
0.983
0.983
1.980
1.000
2.089
2.115
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.15
140.91
139.82
134.41
133.15
129.45
127.97
125.00
124.91
124.60
122.62
120.21
77.68
77.36
77.04
Cl
S
3ai
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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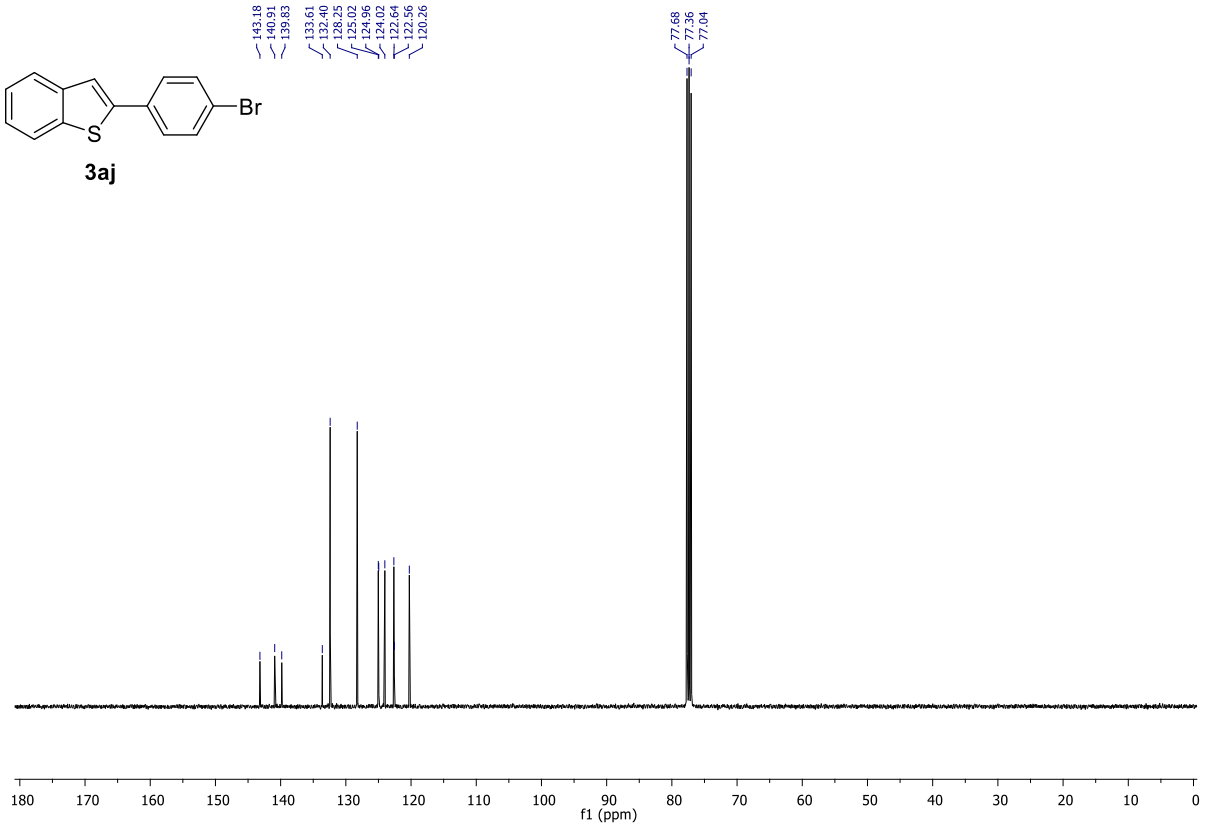
7.84
7.84
7.83
7.82
7.82
7.79
7.78
7.77
7.77
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.53
7.39
7.38
7.37
7.37
7.35
7.35
7.33
7.33
7.31
7.31
7.26
Br
S
3aj
0.970
1.000
4.899
1.990
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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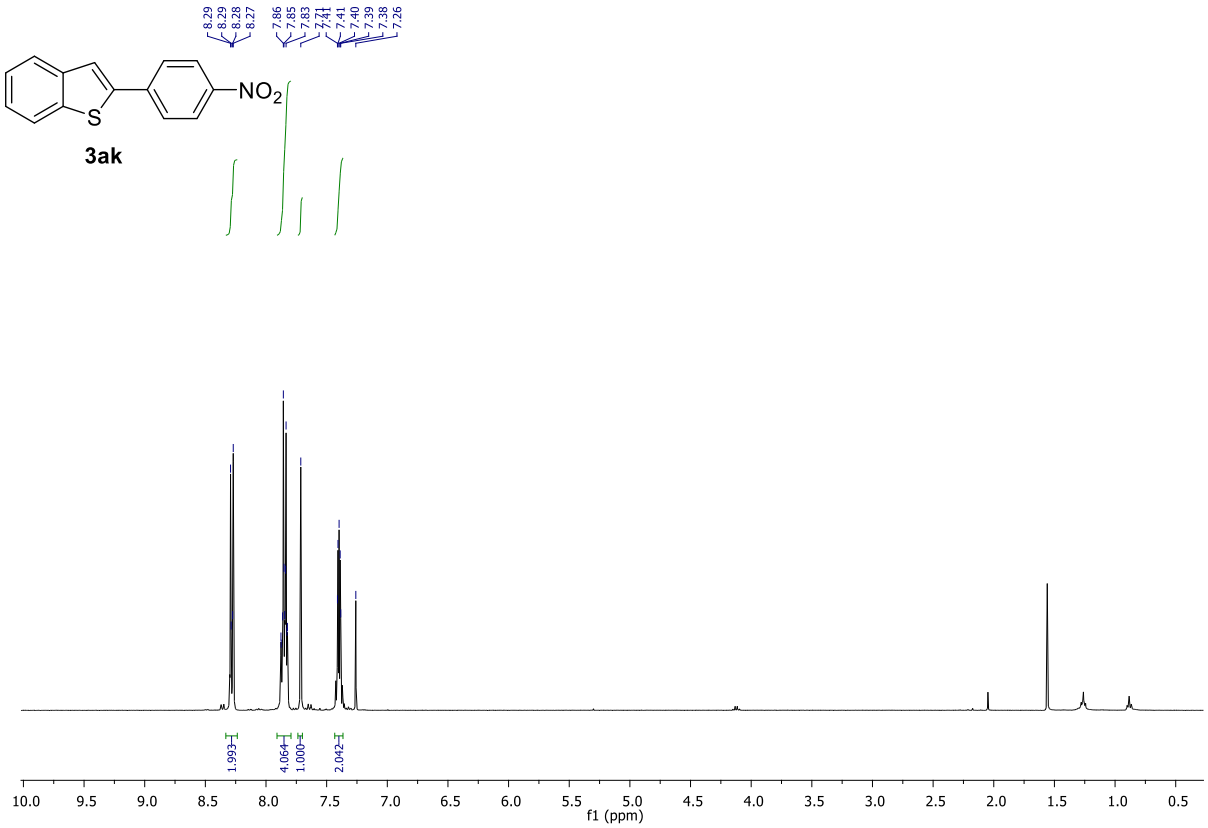
140.91
139.83
133.61
132.40
128.25
125.02
124.96
124.02
122.64
122.56
120.26
77.68
77.36
77.04
Br
S
3aj
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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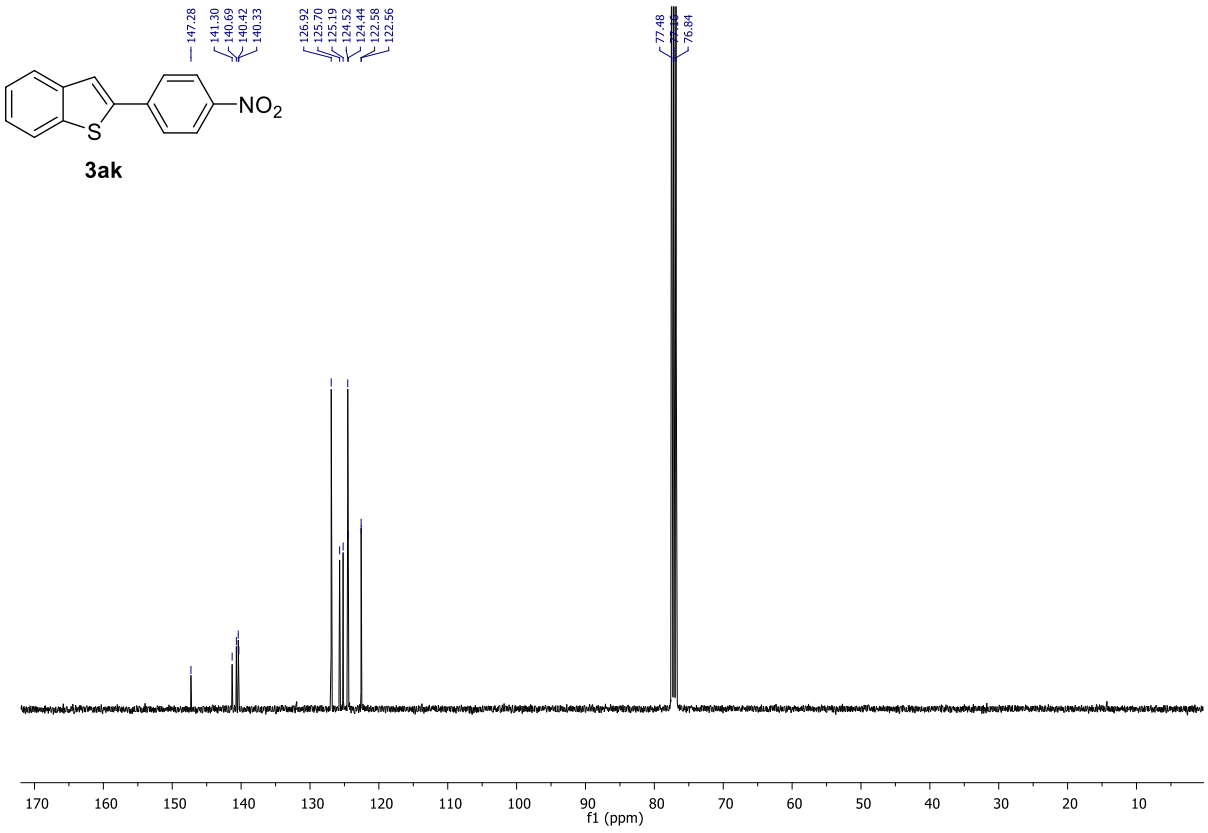
8.29
8.28
8.27
7.86
7.85
7.83
7.71
7.41
7.41
7.40
7.39
7.38
7.26
NO2
S
3ak
1.993
4.064
1.000
2.042
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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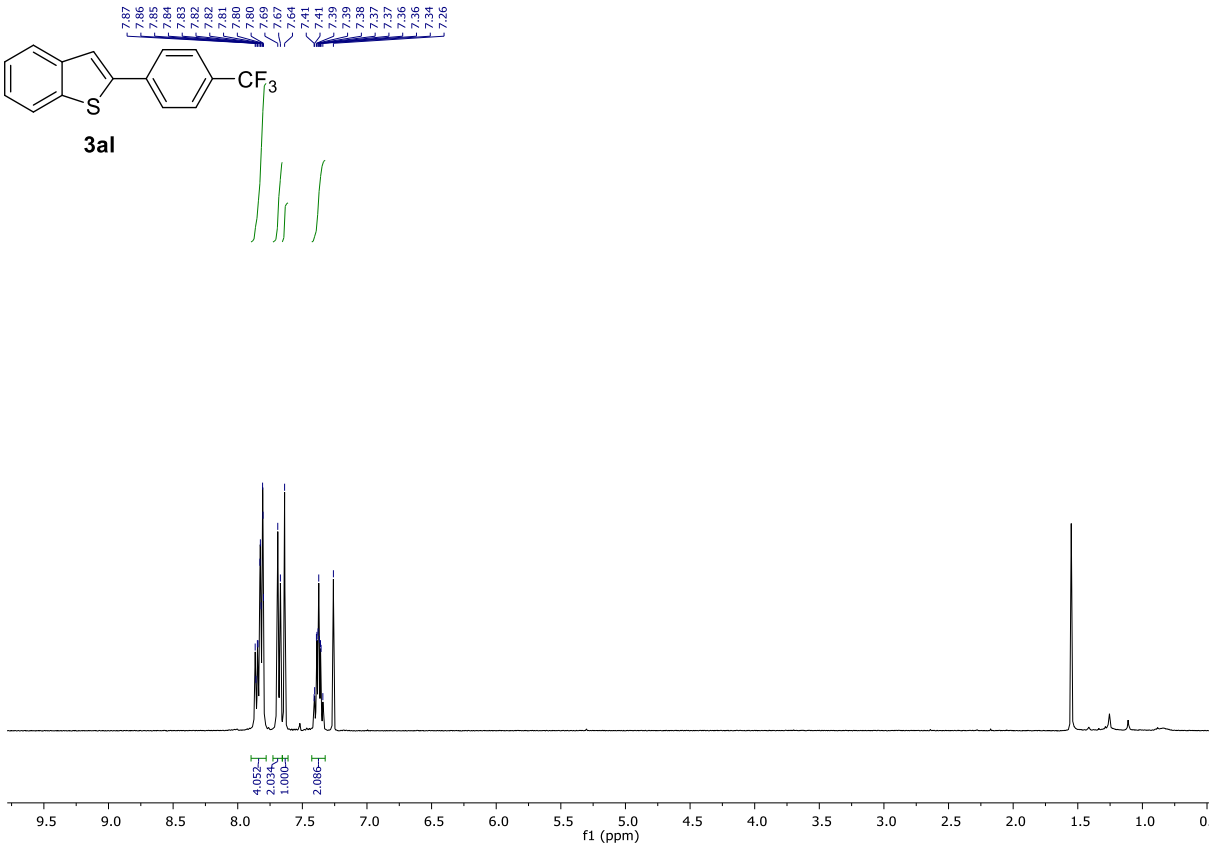
140.69
140.42
140.33
126.92
125.70
125.19
124.52
124.44
122.58
122.56
77.48
77.16
76.84
NO2
S
3ak
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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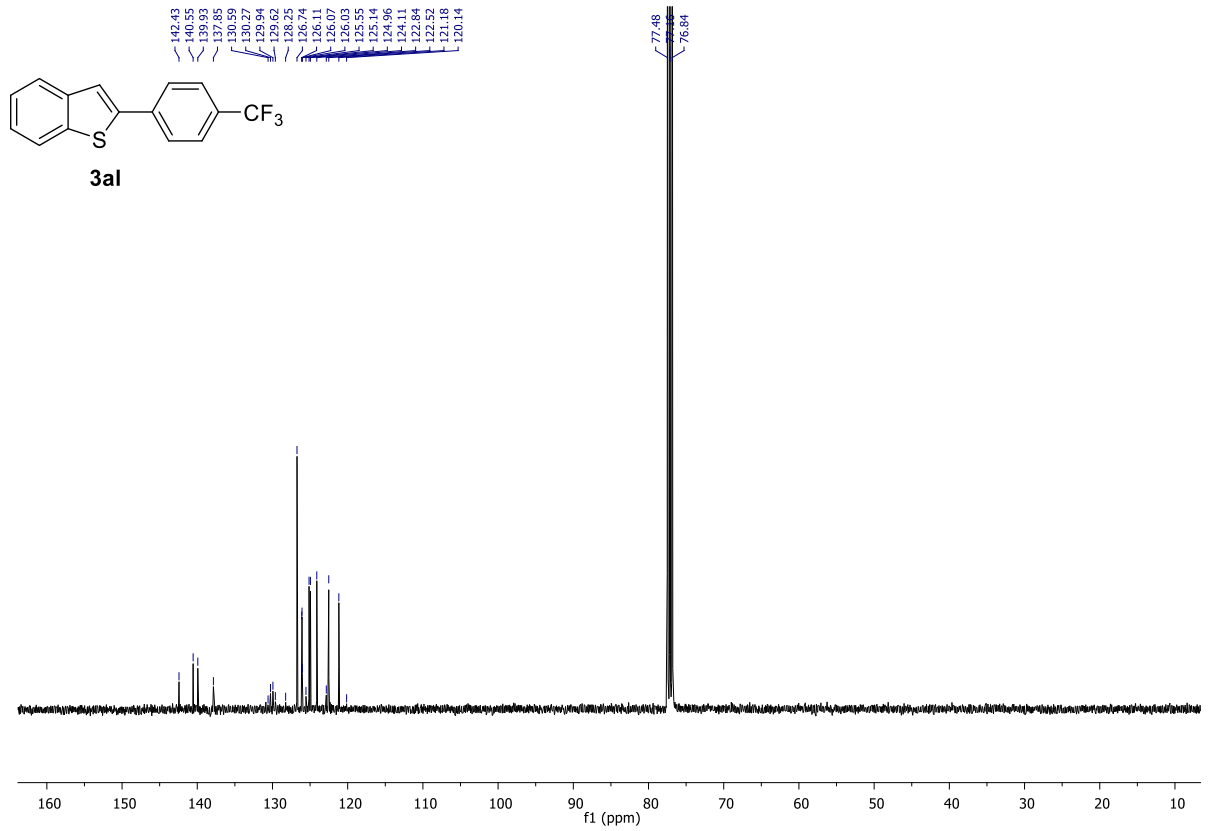
7.82
7.82
7.81
7.80
7.80
7.69
7.67
7.64
7.41
7.41
7.39
7.38
7.37
7.36
7.36
7.34
7.26
CF3
S
3al
4.052
2.034
1.000
2.086
f1 (ppm)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137.85
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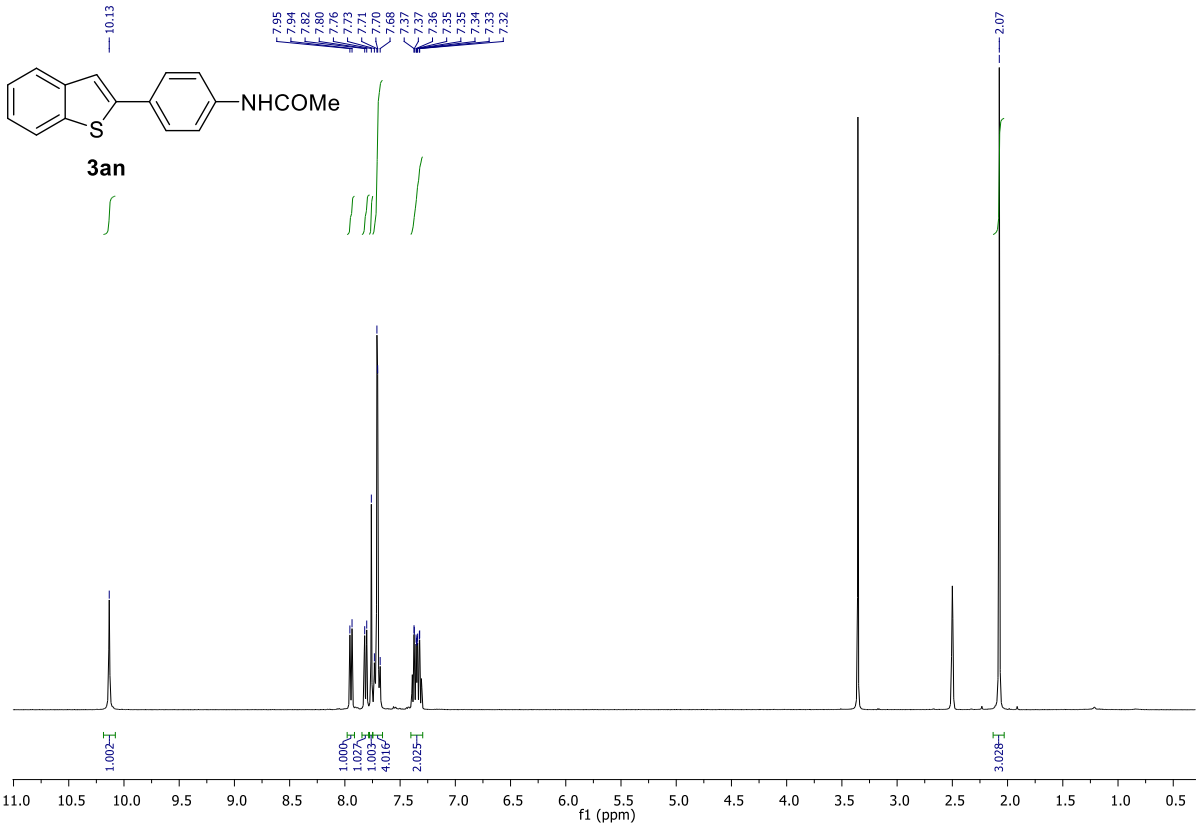
130.27
129.94
129.62
128.25
126.74
126.11
126.07
126.03
125.55
125.14
124.96
124.11
122.84
122.52
121.18
120.14
77.48
77.16
76.84
CF3
S
3al
f1 (ppm)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7.94
7.82
7.80
7.76
7.73
7.71
7.70
7.68
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
2.07
NHCOMe
S
3an
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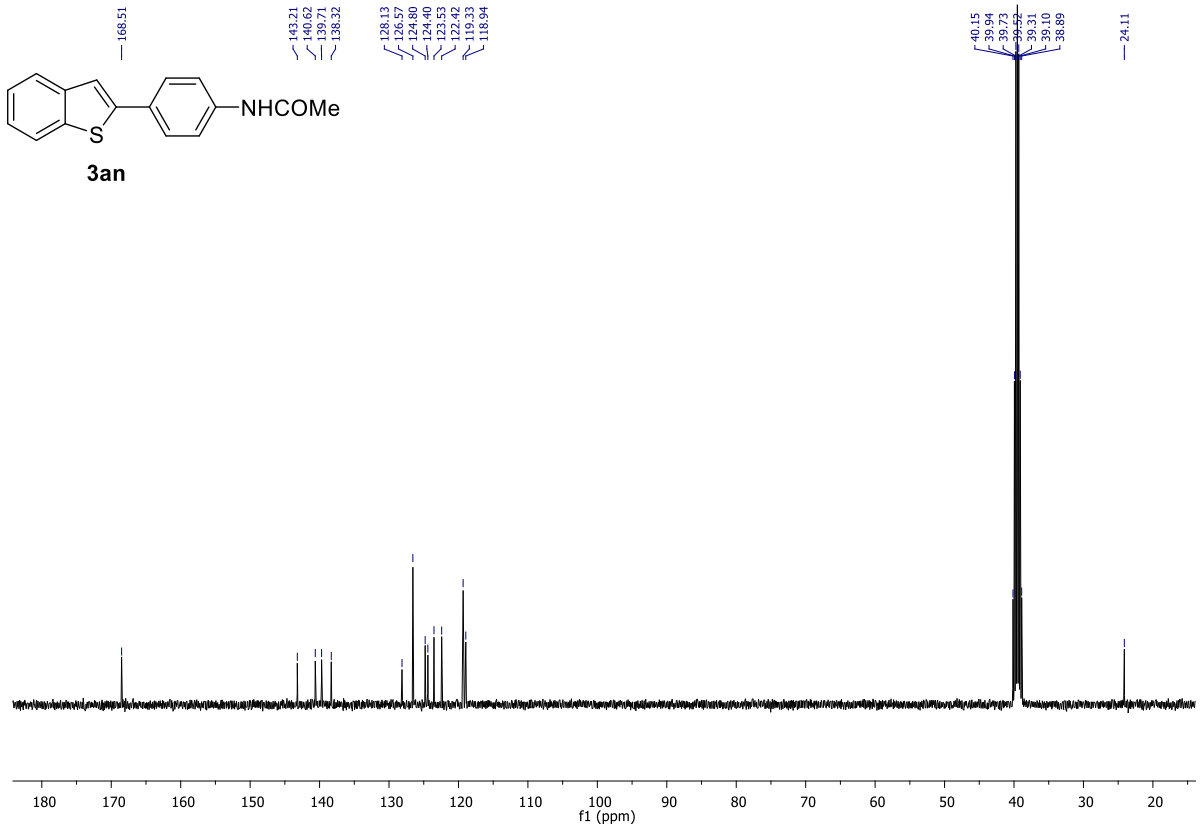
1.000
1.027
1.003
4.016
2.025
3.028
f1 (ppm)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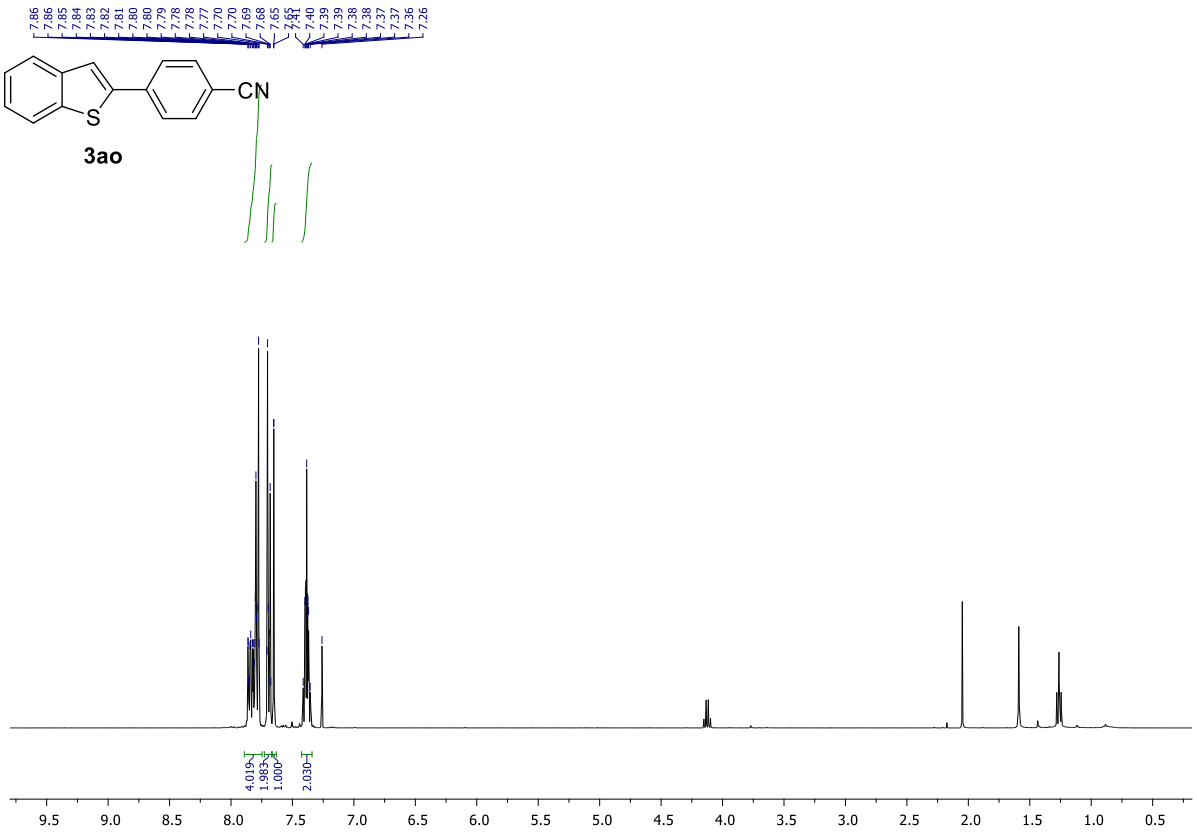
139.71
138.32
128.13
126.57
124.80
124.40
123.53
122.42
119.33
118.94
40.15
39.94
39.73
39.52
39.31
39.10
38.89
24.11
NHCOMe
S
3an
f1 (ppm)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7.86
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7.82
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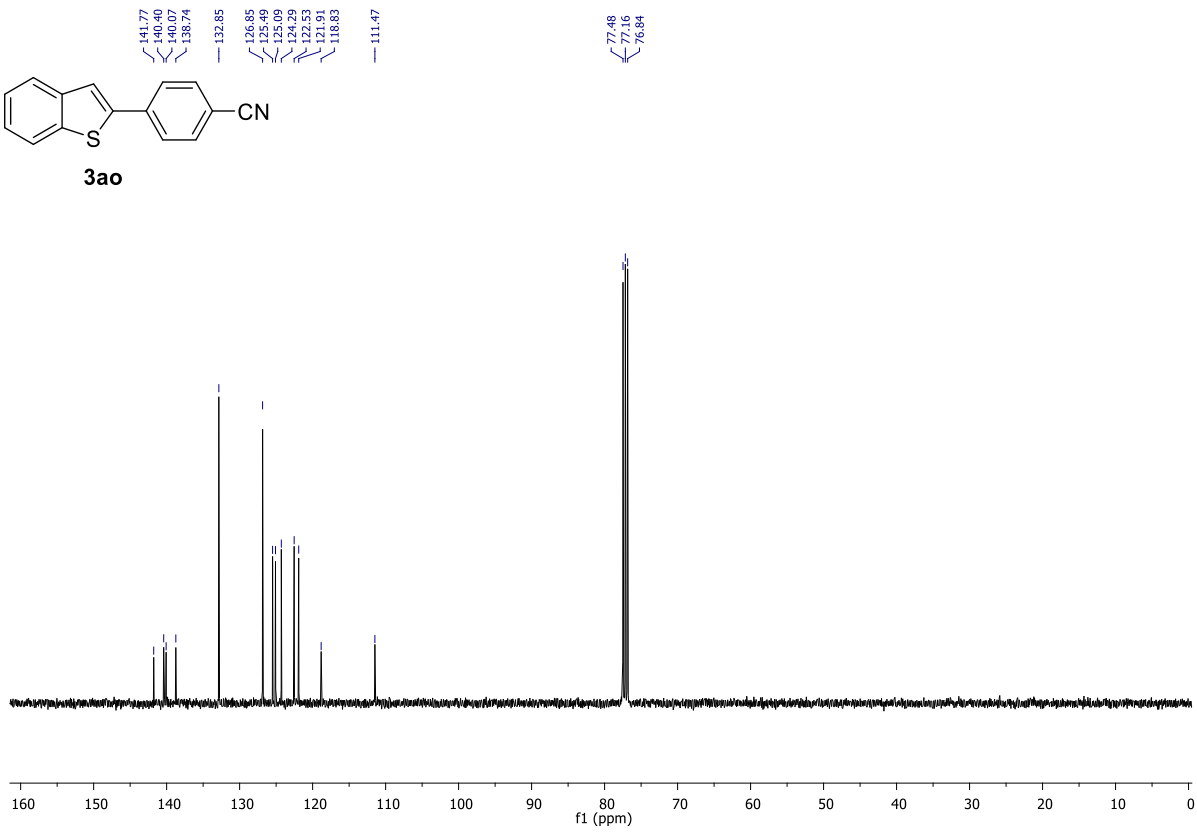
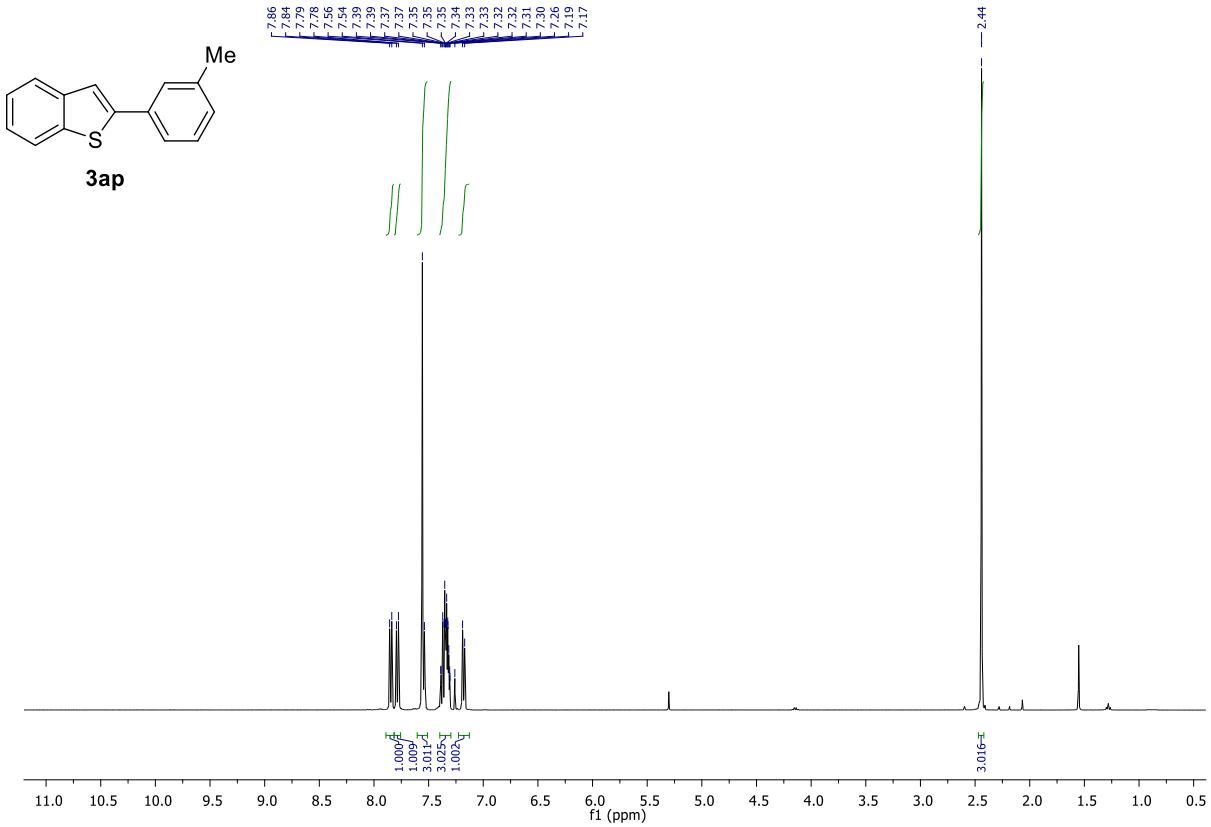
7.80
7.80
7.79
7.78
7.78
7.77
7.70
7.70
7.69
7.68
7.65
7.65
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.26
CN
S
3ao
4.019
1.983
1.000
2.030
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


141.77
140.40
140.07
138.74
132.85
126.85
125.49
125.09
124.29
122.53
121.91
118.83
111.47
77.48
77.16
76.84
CN
S
3ao
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
S
3ap
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7.84
7.79
7.78
7.56
7.54
7.39
7.39
7.37
7.37
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.26
7.19
7.17
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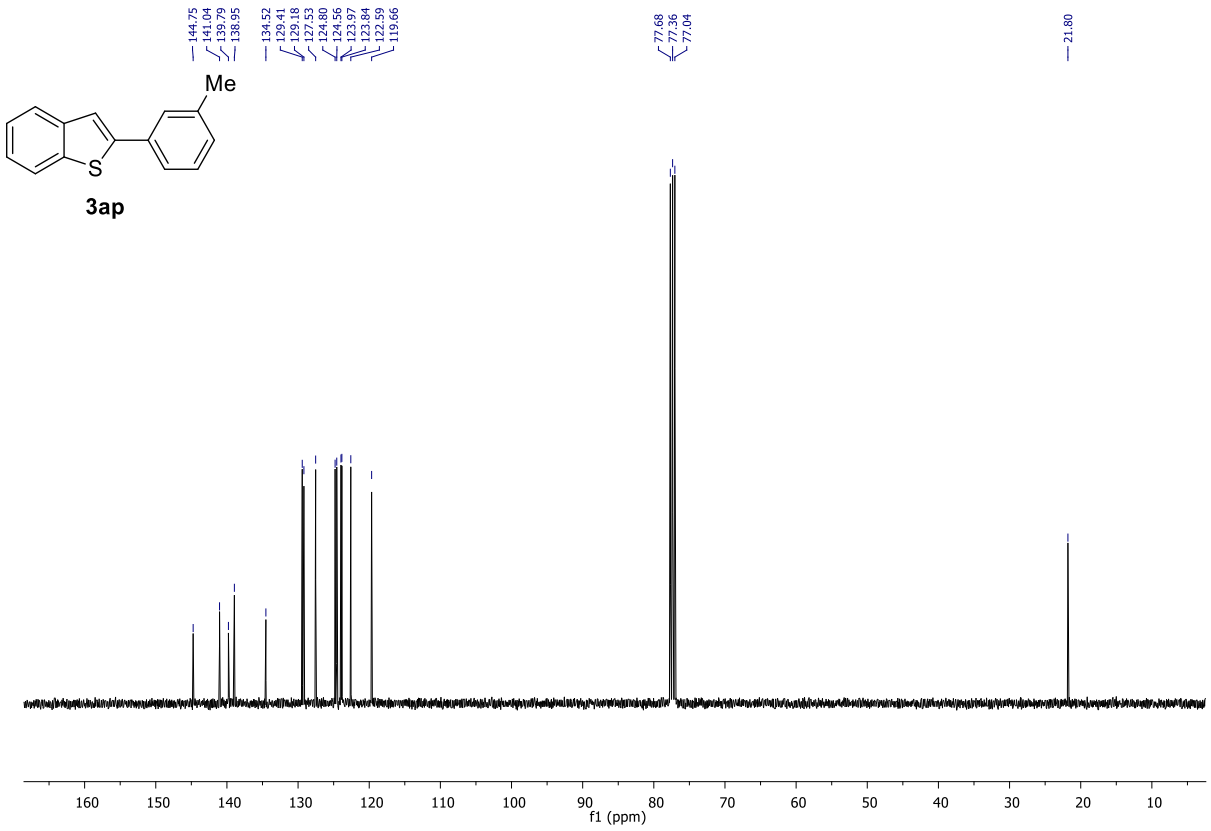
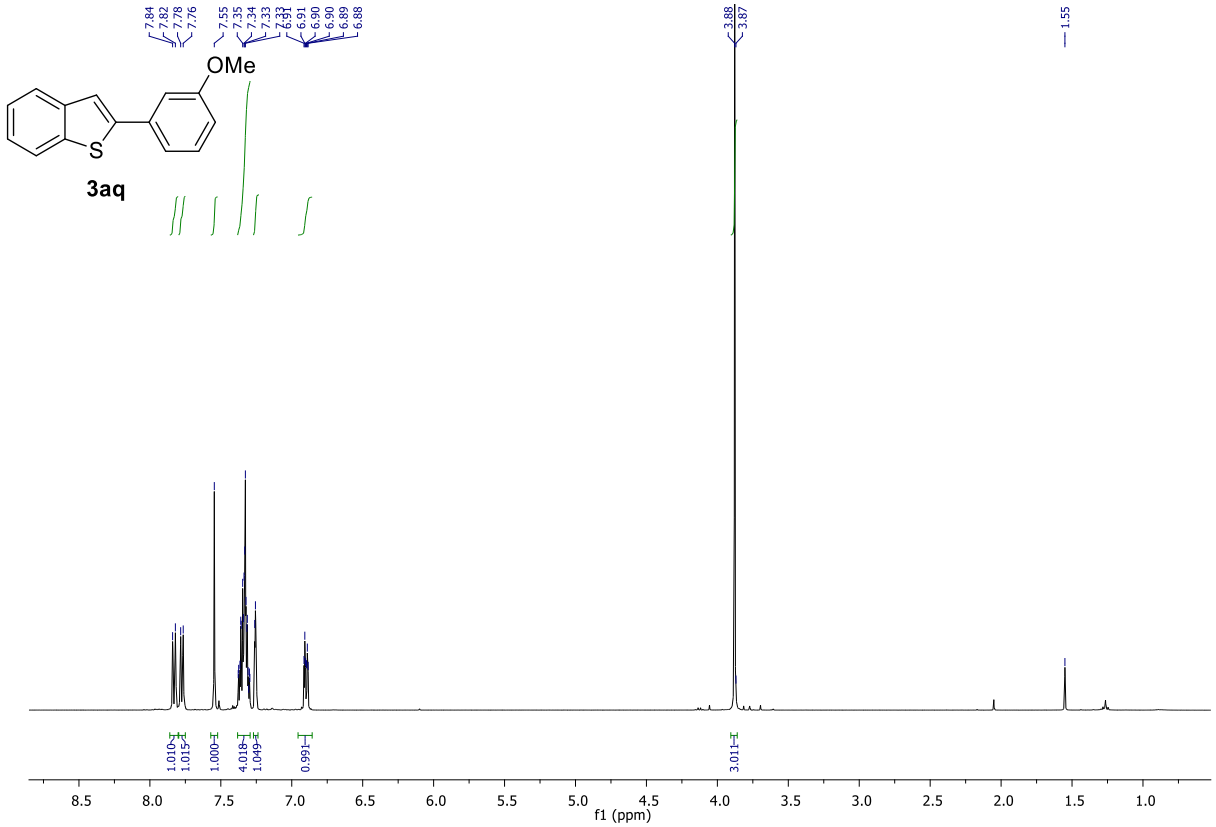
1.000
1.009
3.011
3.025
1.002
3.016
f1 (ppm)


Me
S
3ap
144.75
141.04
139.79
138.95
134.52
129.41
129.18
127.53
124.80
124.56
123.97
123.84
122.59
119.66
77.68
77.36
77.04
21.80
f1 (ppm)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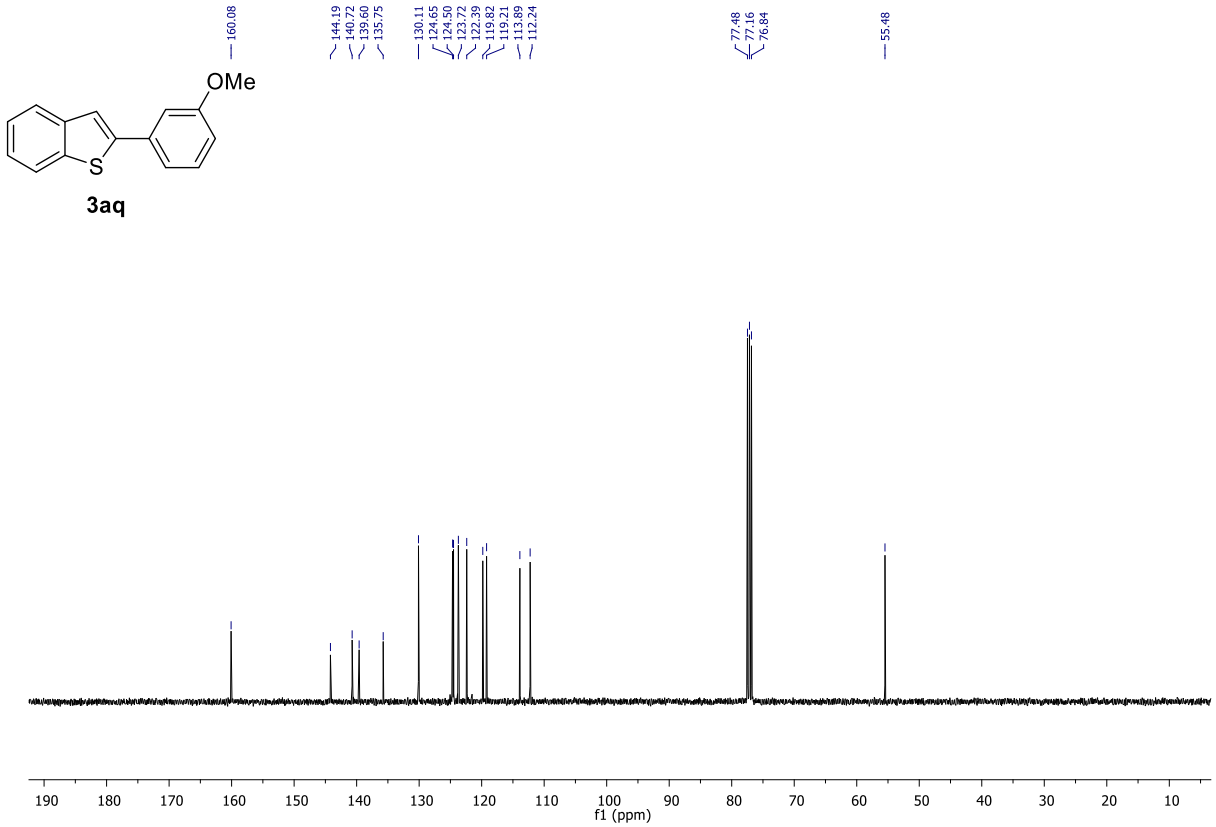
7.82
7.78
7.76
7.55
7.35
7.34
7.33
7.33
6.91
6.90
6.90
6.89
6.88
3.88
3.87
1.55
OMe
S
3aq
1.010
1.015
1.000
4.018
1.049
0.991
3.011
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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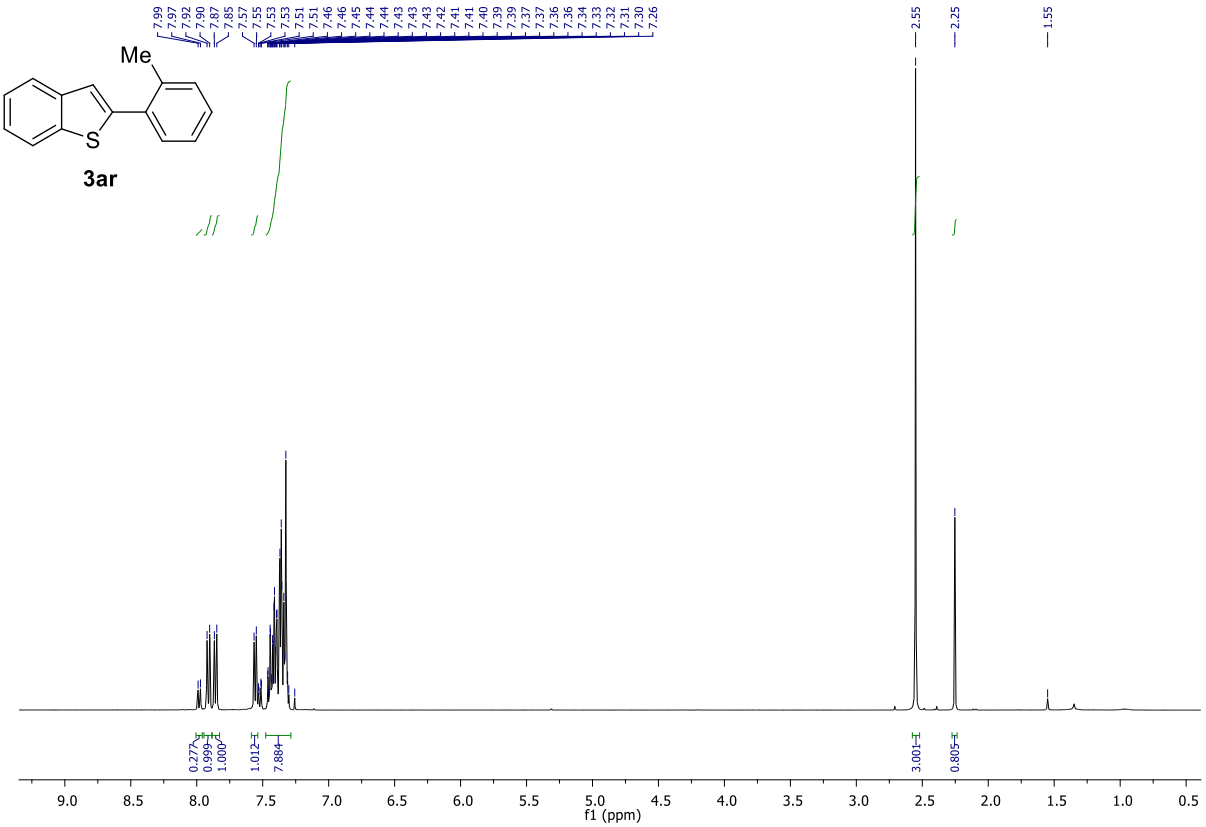
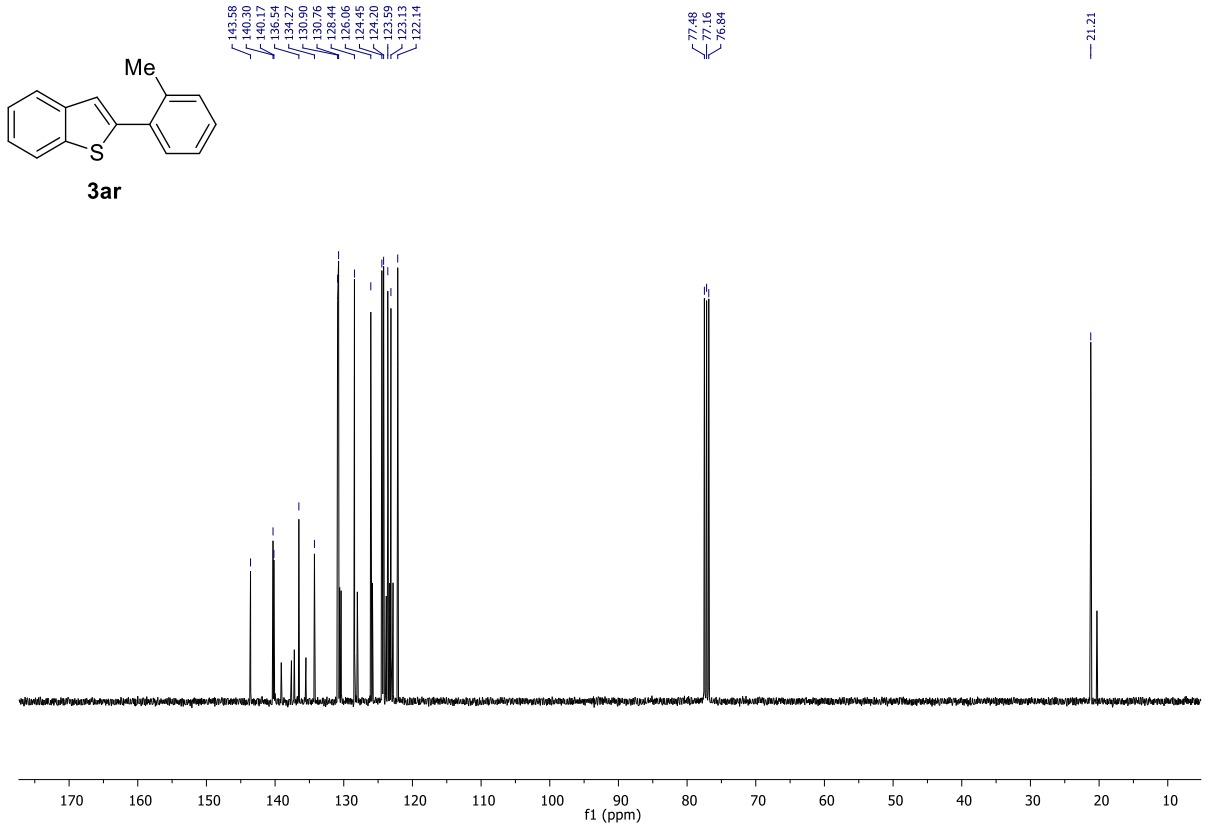
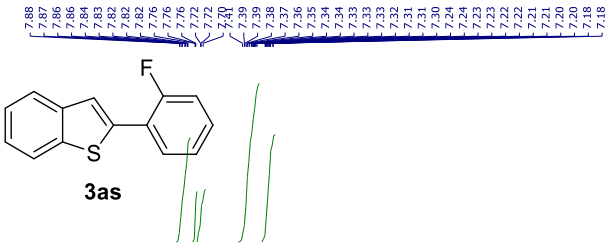
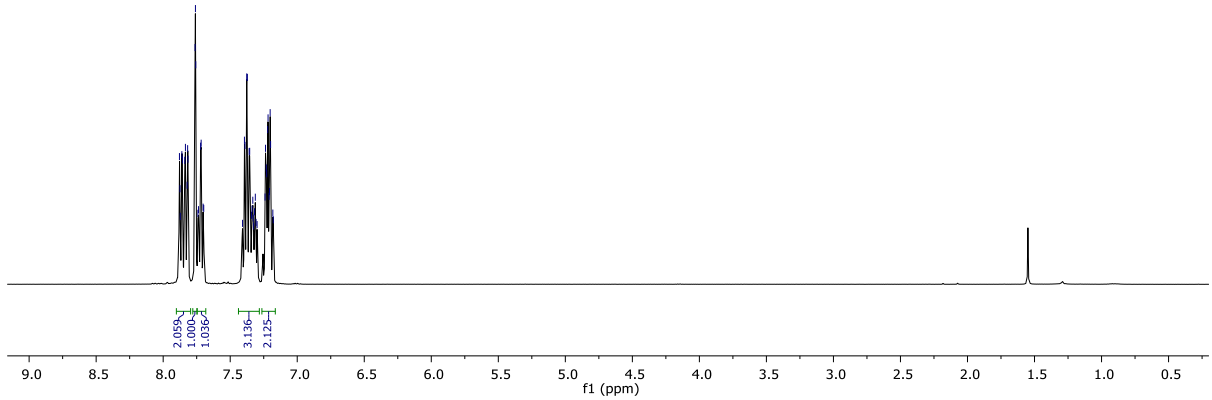
139.60
135.75
130.11
124.65
124.50
123.72
122.39
119.82
119.21
113.89
112.24
77.48
77.16
76.84
55.48
OMe
S
3aq
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

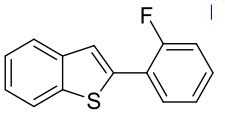

Me
S
3ar
7.99
7.97
7.92
7.90
7.87
7.85
7.57
7.55
7.53
7.53
7.51
7.51
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.37
7.37
7.36
7.36
7.34
7.33
7.32
7.31
7.30
7.26
2.55
2.25
1.55
0.277
0.999
1.000
1.012
7.884
3.001
0.805
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Me
S
3ar
143.58
140.30
140.17
136.54
134.27
130.90
130.76
128.44
126.06
124.45
124.20
123.59
123.13
122.14
77.48
77.16
76.84
21.21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

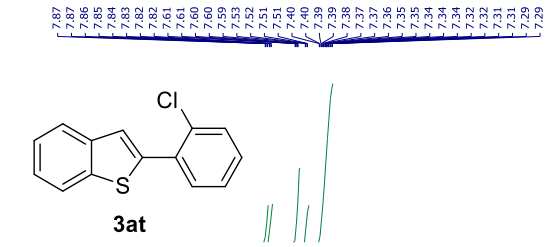



**3as**




**3as**


7.87
7.87
7.86
7.85
7.84
7.83
7.82
7.82
7.61
7.61
7.60
7.60
7.59
7.53
7.52
7.51
7.51
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7.37
7.37
7.36
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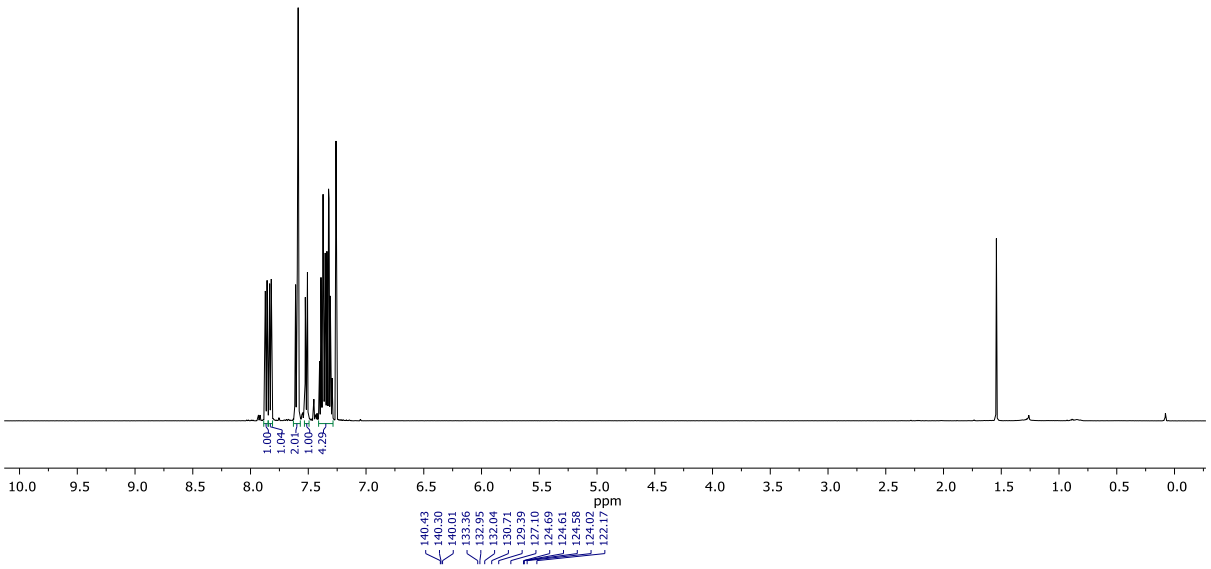
7.29
7.29
Cl
S

**3at**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6.0
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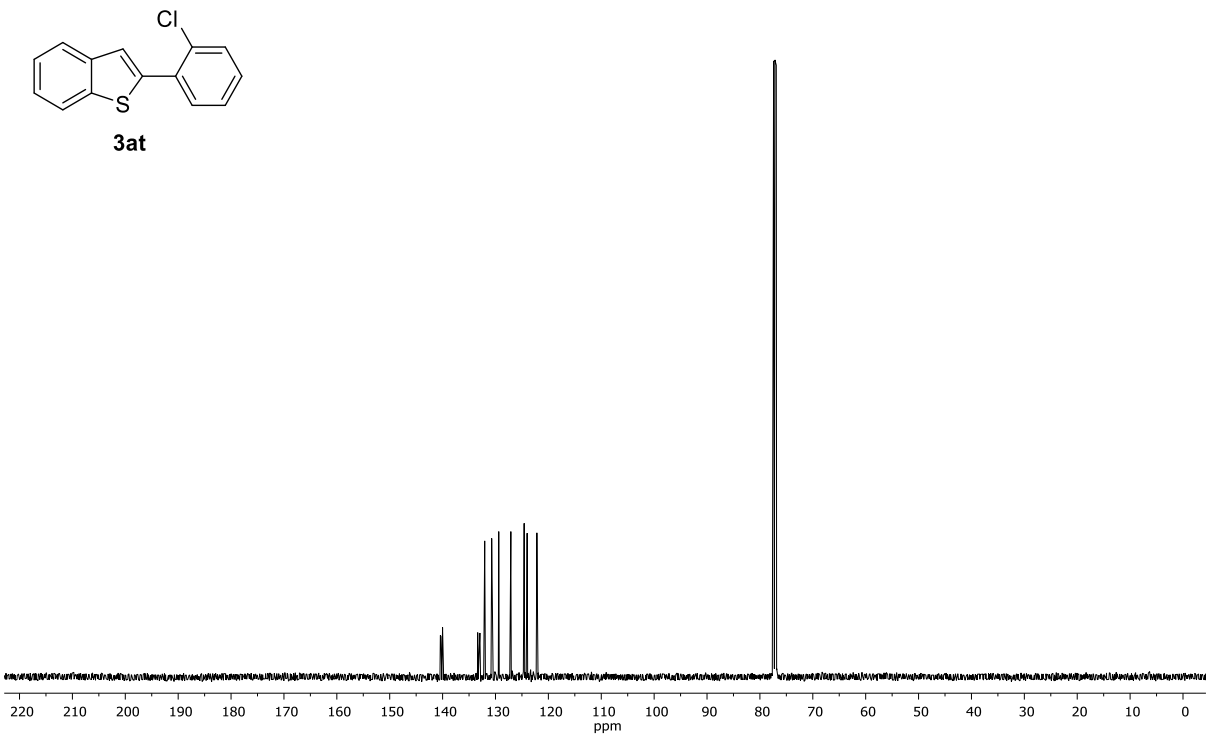
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132.04
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129.39
127.10
124.69
124.61
124.58
124.02
122.17
Cl
S
220
210
200
190
180
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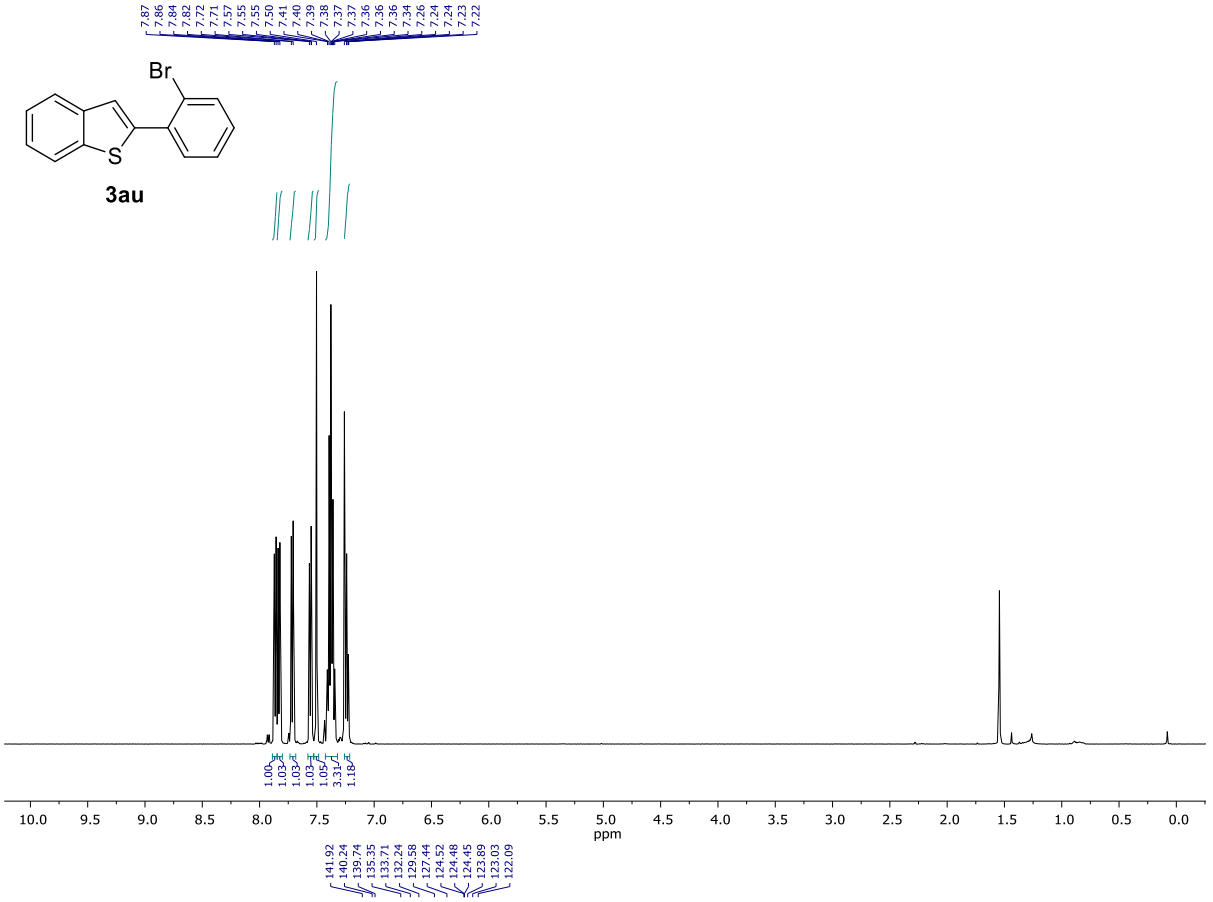
**3at**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7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.34
7.26
7.24
7.24
7.23
7.22
Br
S
3au
1.00
1.03
1.03
1.03
1.05
3.31
1.18
10.0
9.5
9.0
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8.0
7.5
7.0
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6.0
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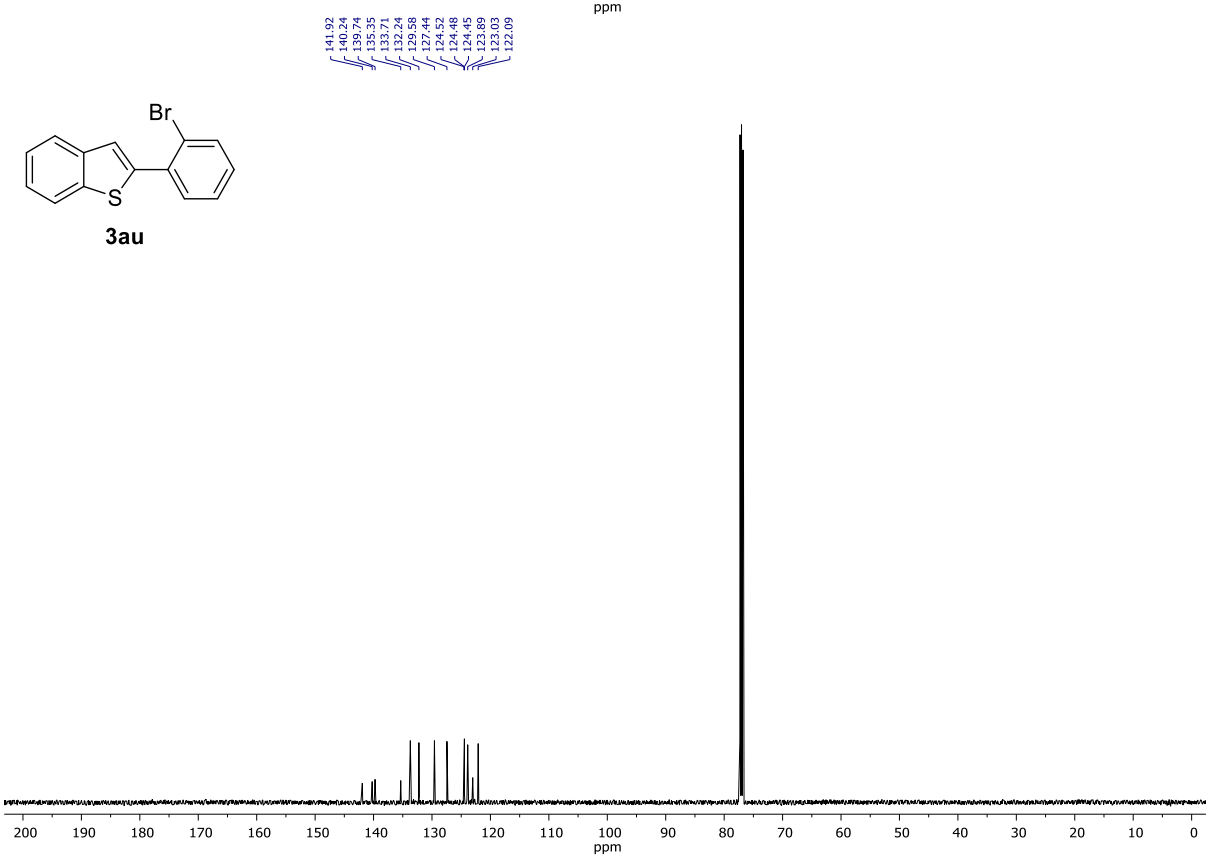
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124.45
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123.03
122.09
Br
S
3au
200
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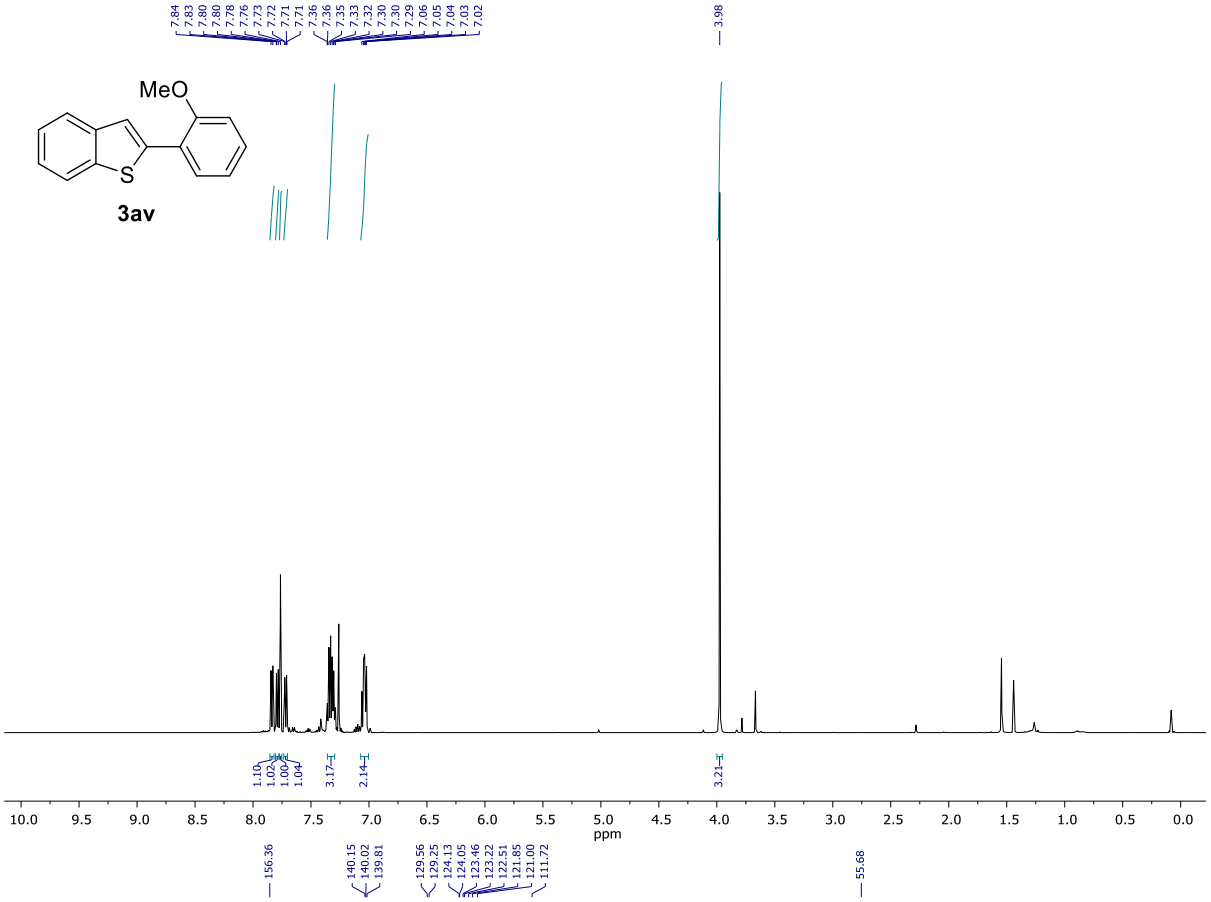
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7.72
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7.32
7.30
7.30
7.29
7.06
7.05
7.04
7.03
7.02
3.98
MeO
S
3av
1.10
1.02
1.00
1.04
3.17
2.14
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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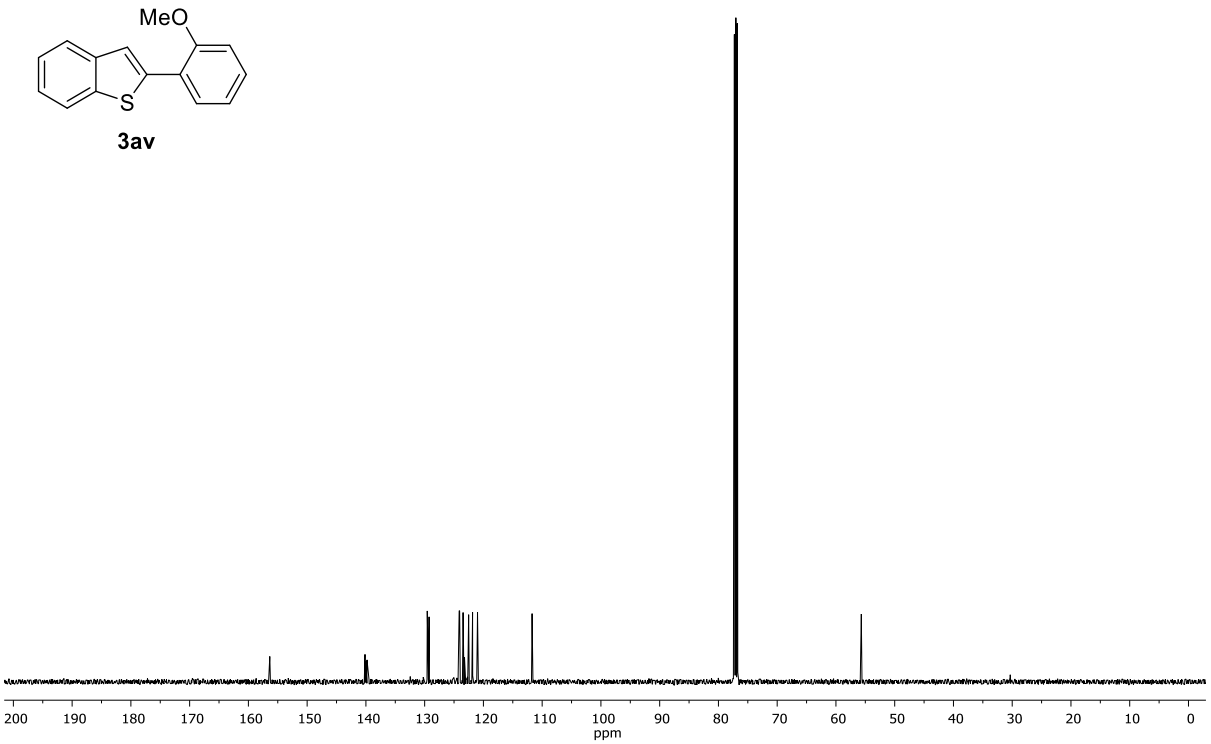
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129.25
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124.05
123.46
123.22
122.51
121.85
121.00
111.72
55.68
MeO
S
3av
200
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140
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120
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100
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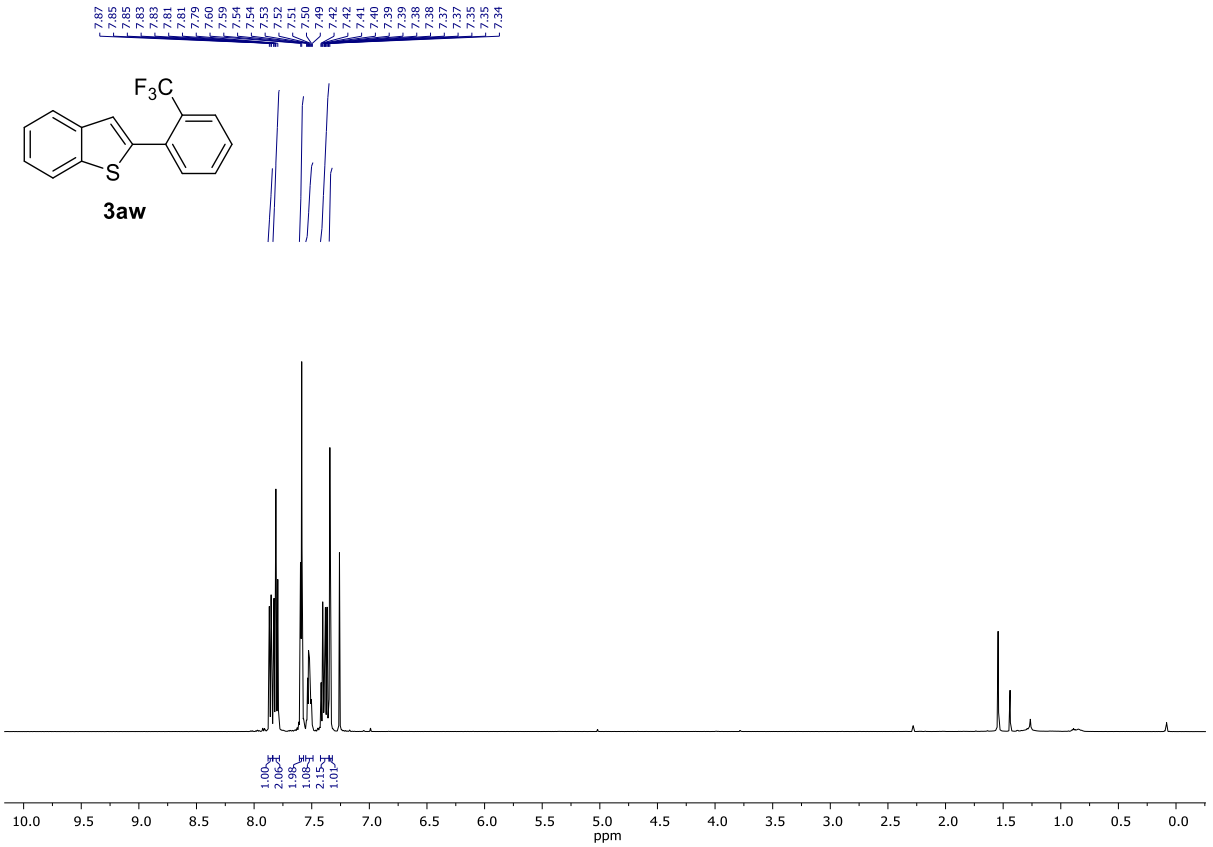
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7.54
7.53
7.52
7.51
7.50
7.49
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.35
7.35
7.34
F3C
S
3aw
1.00
2.06
1.98
1.08
2.15
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
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3.0
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0.5
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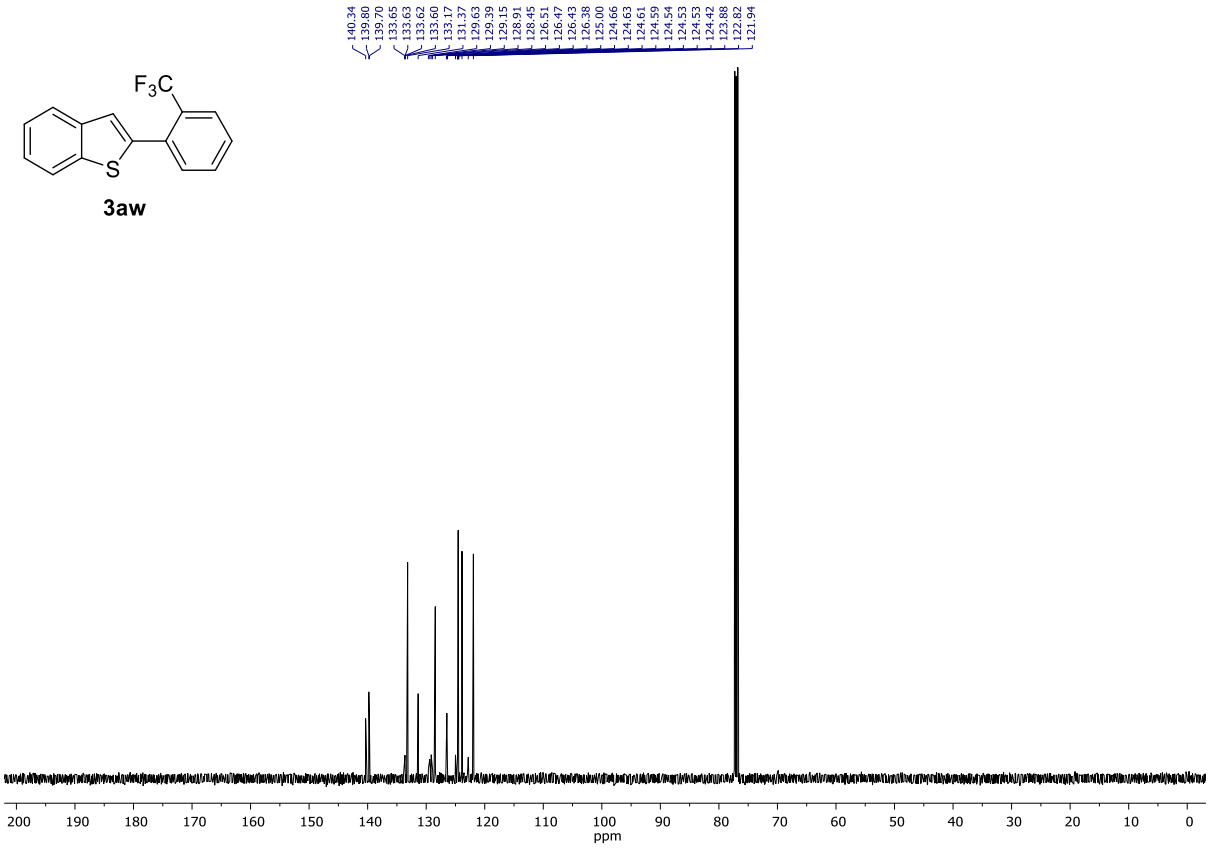
ppm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129.63
129.39
129.15
128.91
128.45
126.51
126.47
126.43
126.38
125.00
124.66
124.63
124.61
124.59
124.54
124.53
124.53
124.42
123.88
122.82
121.94
F3C
S
3aw
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
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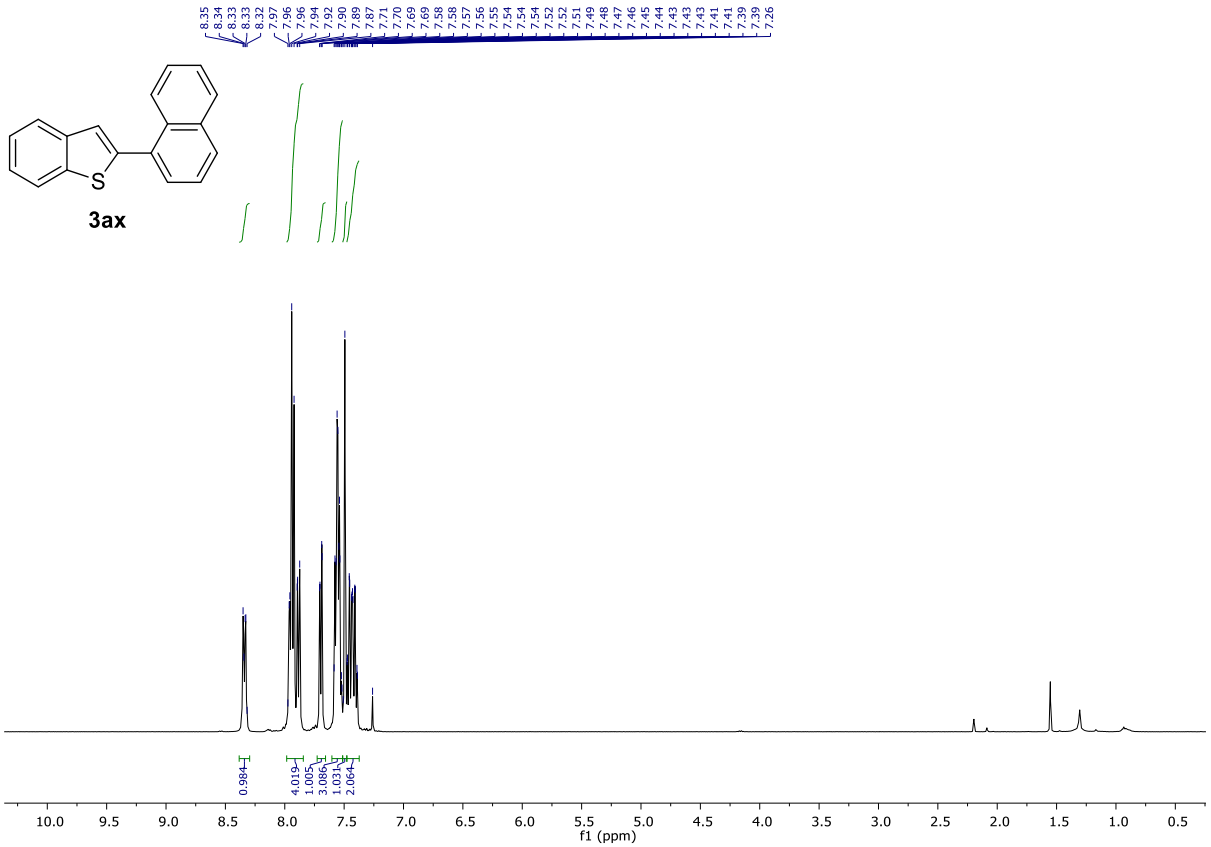
30
20
10
0
ppm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7.58
7.57
7.56
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7.54
7.54
7.54
7.52
7.52
7.51
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.43
7.43
7.41
7.41
7.39
7.39
7.26
S
3ax
0.984
4.019
1.005
3.086
1.031
2.064
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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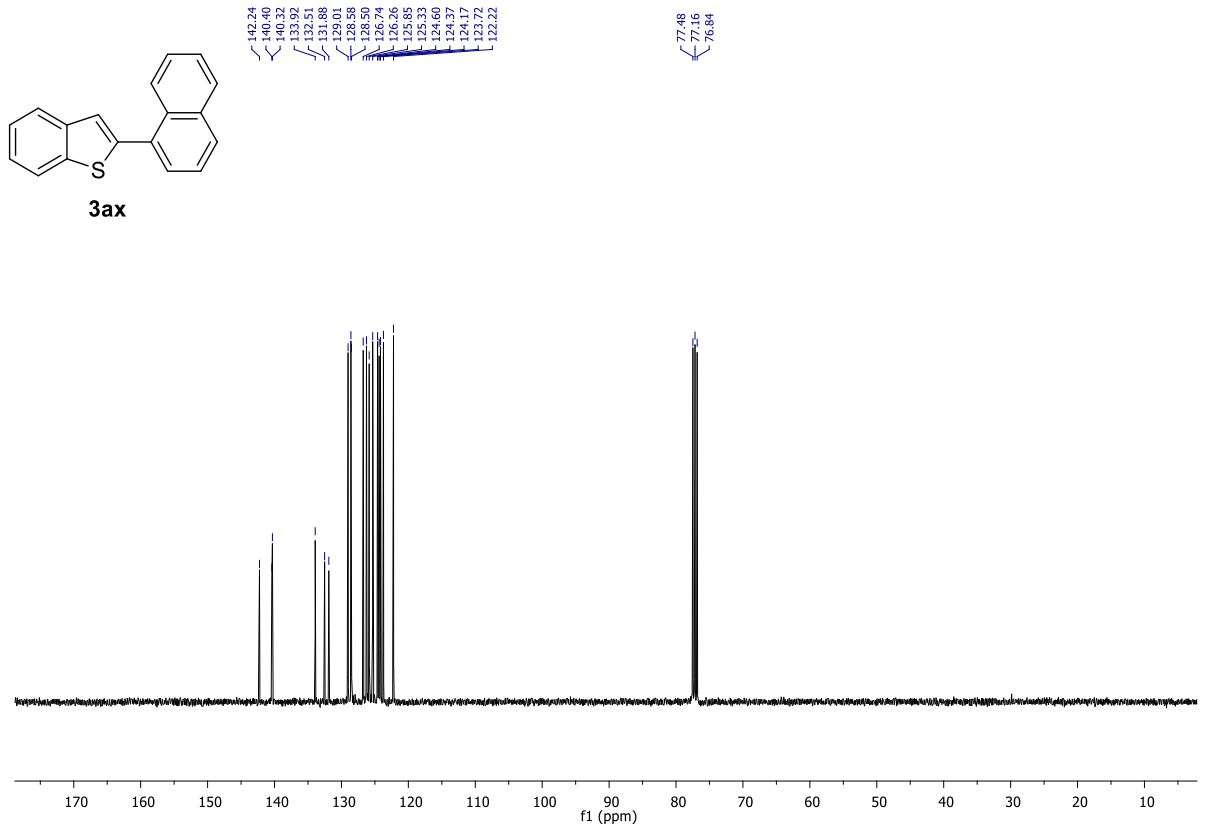
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


142.24
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133.92
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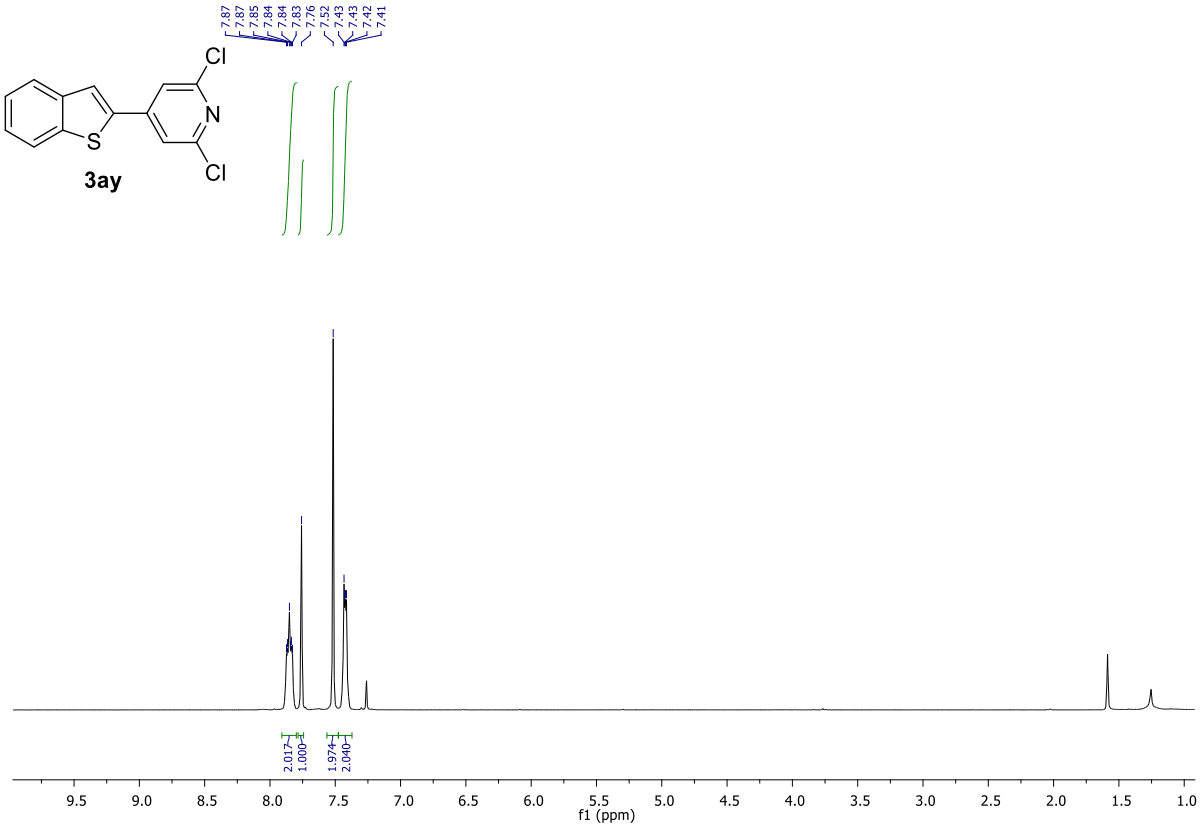
131.88
129.01
128.58
128.50
126.74
126.26
125.85
125.33
124.60
124.37
124.17
123.72
122.22
77.48
77.16
76.84
S
3ax
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.87
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7.84
7.84
7.83
7.76
7.52
7.43
7.42
7.41
Cl
N
S
Cl
3ay
2.017
1.000
1.974
2.040
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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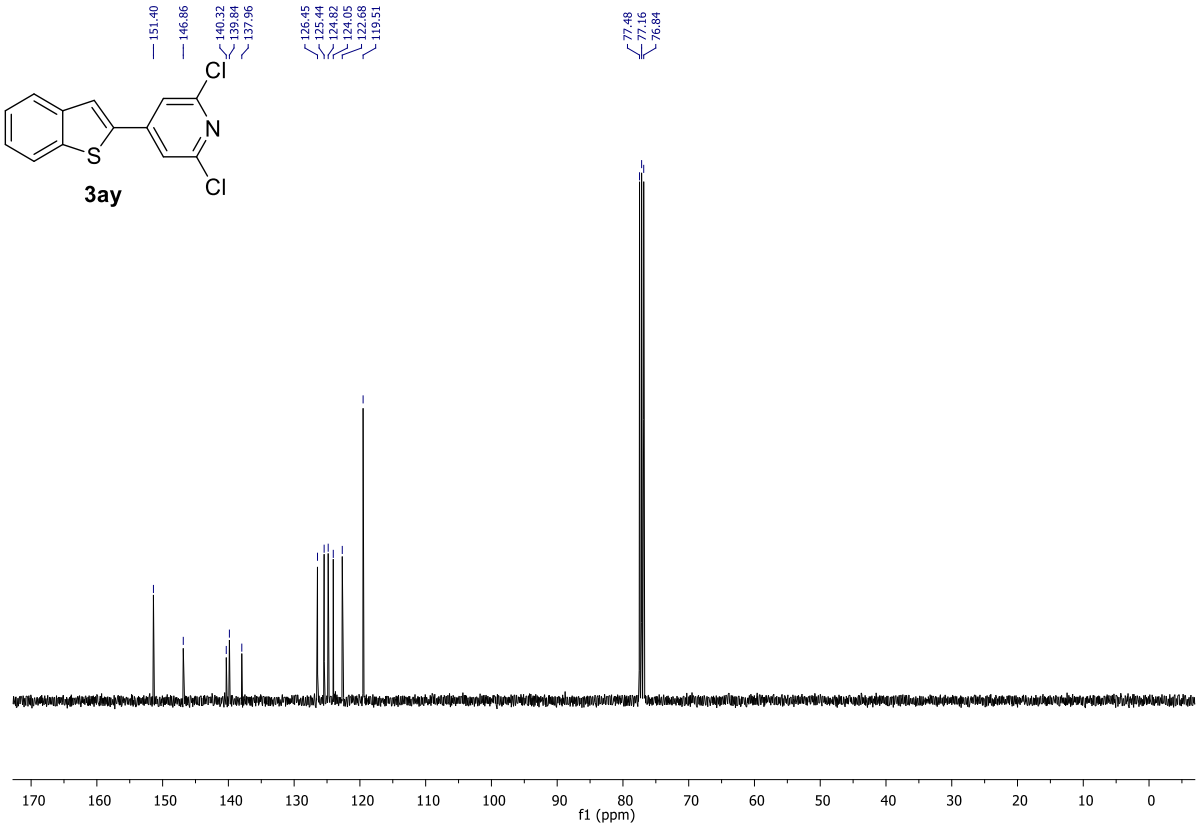
1.0
f1 (ppm)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124.82
124.05
122.68
119.51
77.48
77.16
76.84
Cl
N
S
Cl
3ay
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160
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140
130
120
110
100
90
80
70
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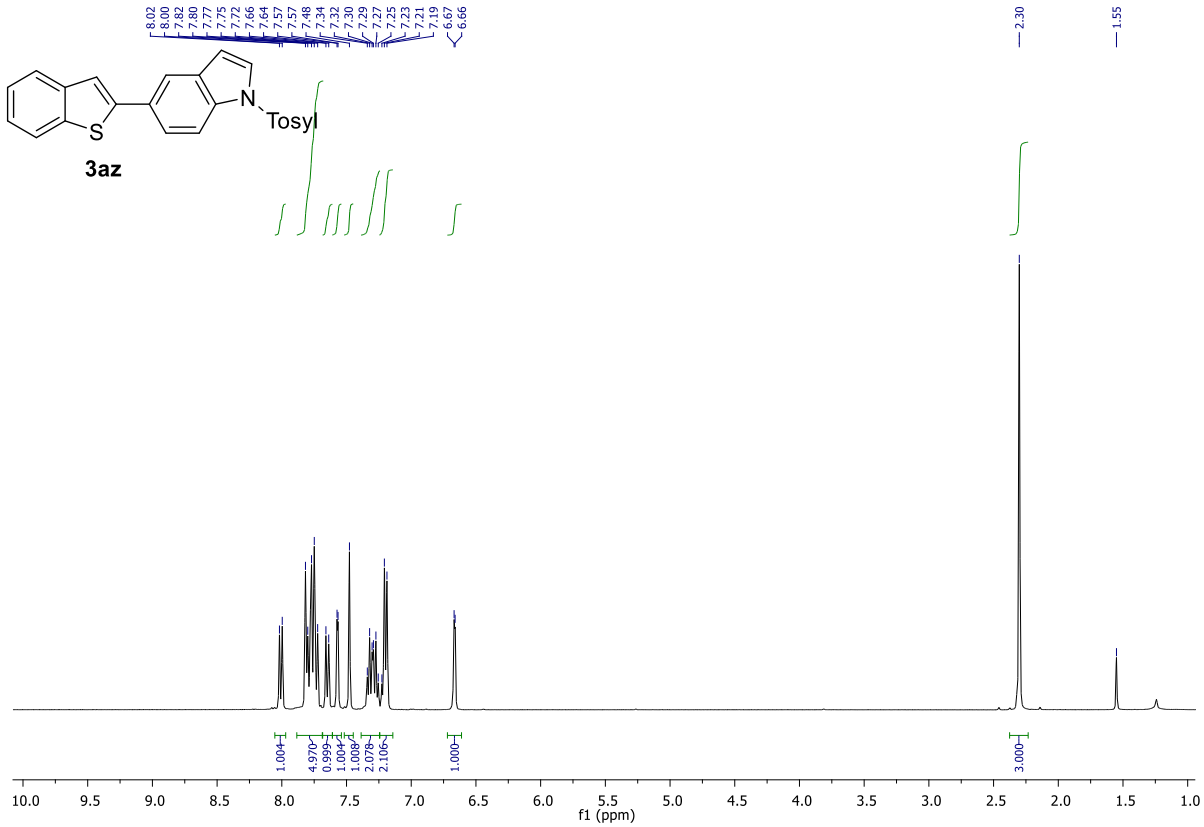
50
40
30
20
10
0
f1 (ppm)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7.66
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7.57
7.57
7.48
7.34
7.32
7.30
7.29
7.27
7.25
7.23
7.21
7.19
6.67
6.66
2.30
1.55
N
Tosyl
S
3az
1.004
4.970
0.999
1.004
1.008
2.078
2.106
1.000
3.000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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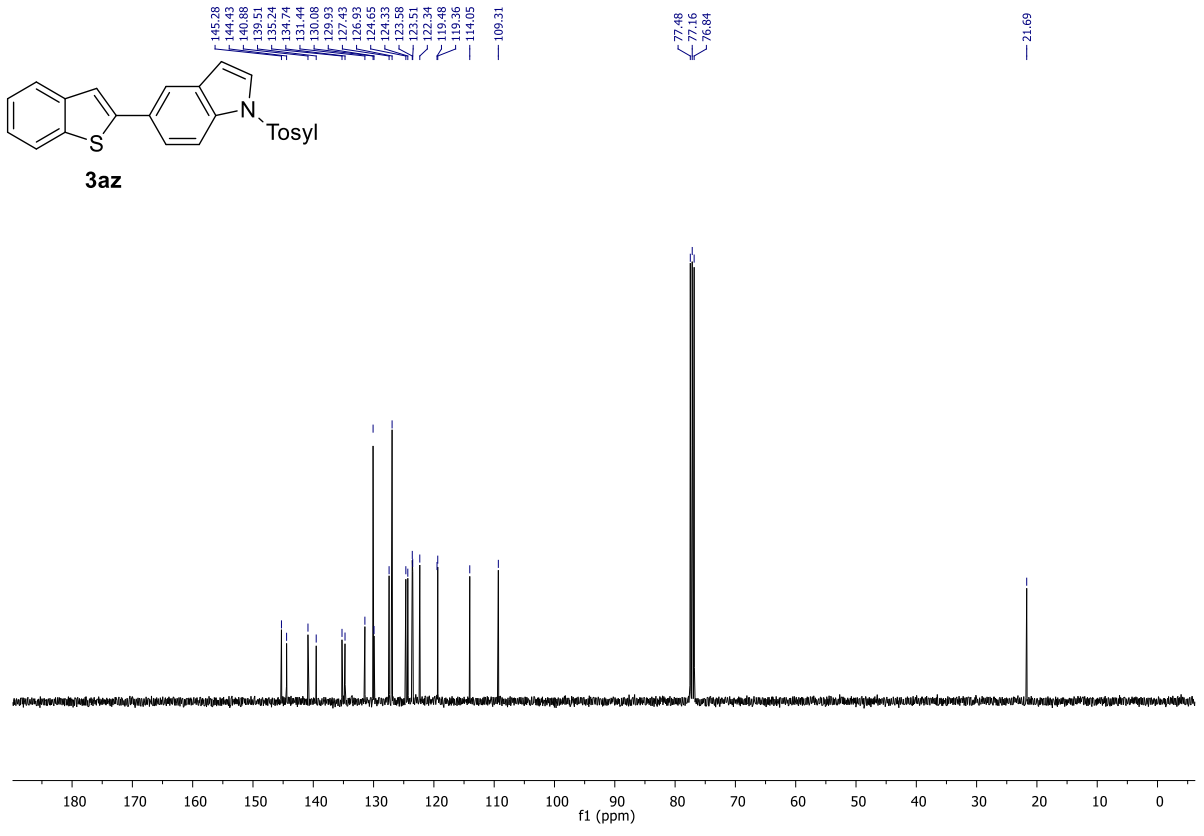
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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130.08
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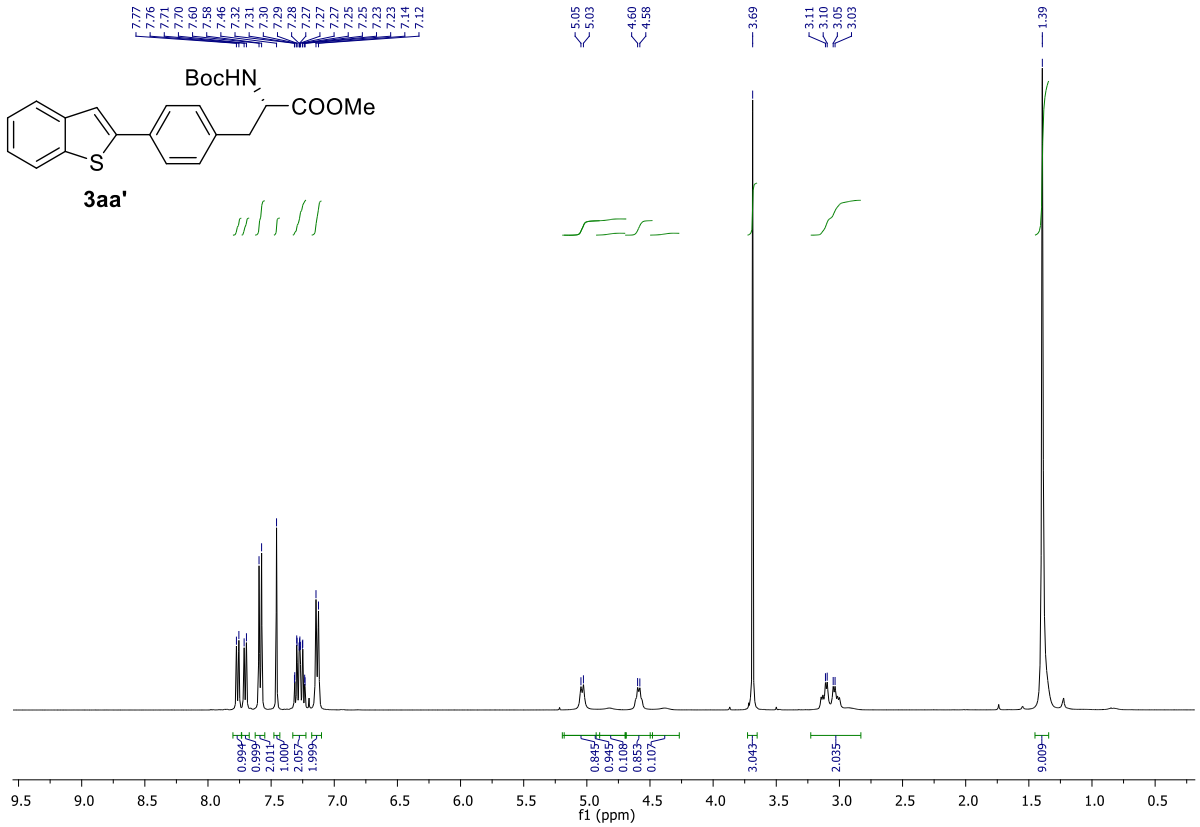
127.43
126.93
124.65
124.33
123.58
123.51
122.34
119.48
119.36
114.05
109.31
77.48
77.16
76.84
21.69
N
Tosyl
S
3az
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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COOMe
S
3aa'
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7.58
7.46
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.25
7.25
7.23
7.23
7.14
7.12
5.05
5.03
4.60
4.58
3.69
3.11
3.10
3.05
3.03
1.39
0.994
0.999
2.011
1.000
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0.945
0.168
0.853
0.107
3.043
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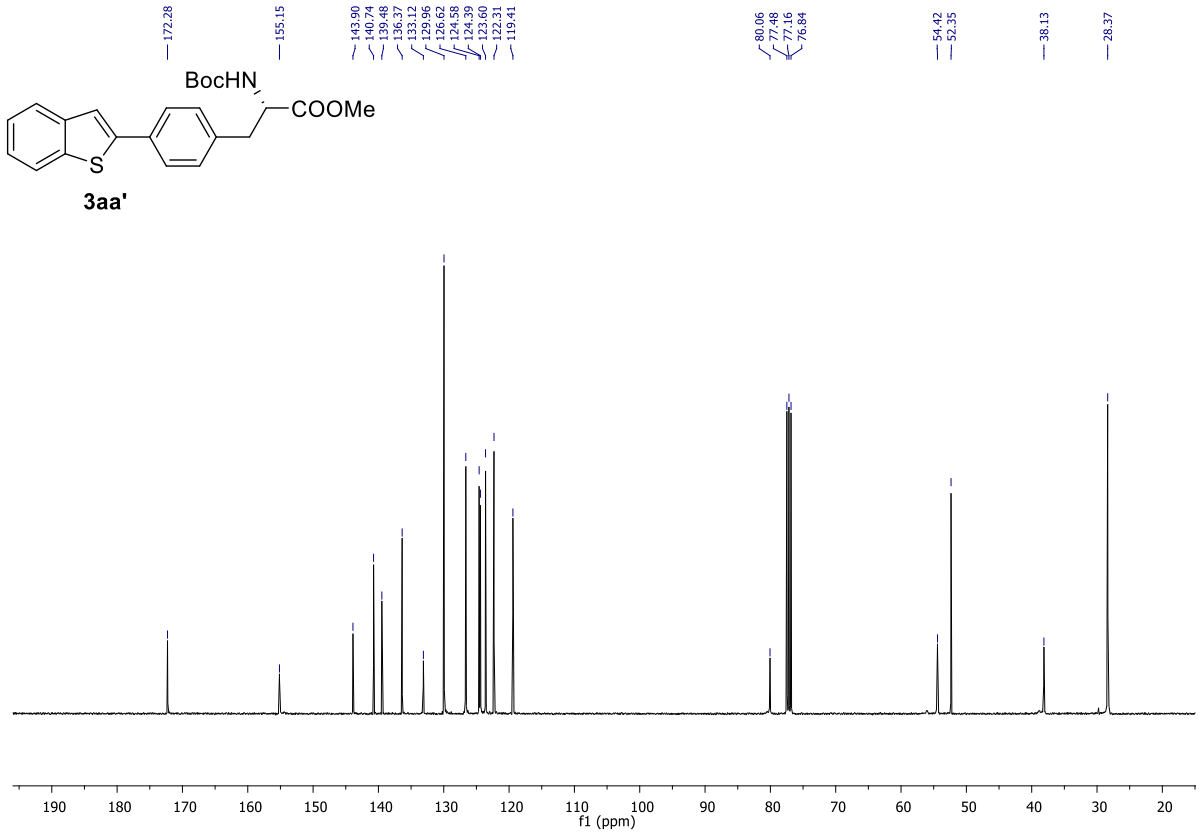
9.009
f1 (ppm)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COOMe
S
3aa'
172.28
155.15
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140.74
139.48
136.37
133.12
129.96
126.62
124.58
124.39
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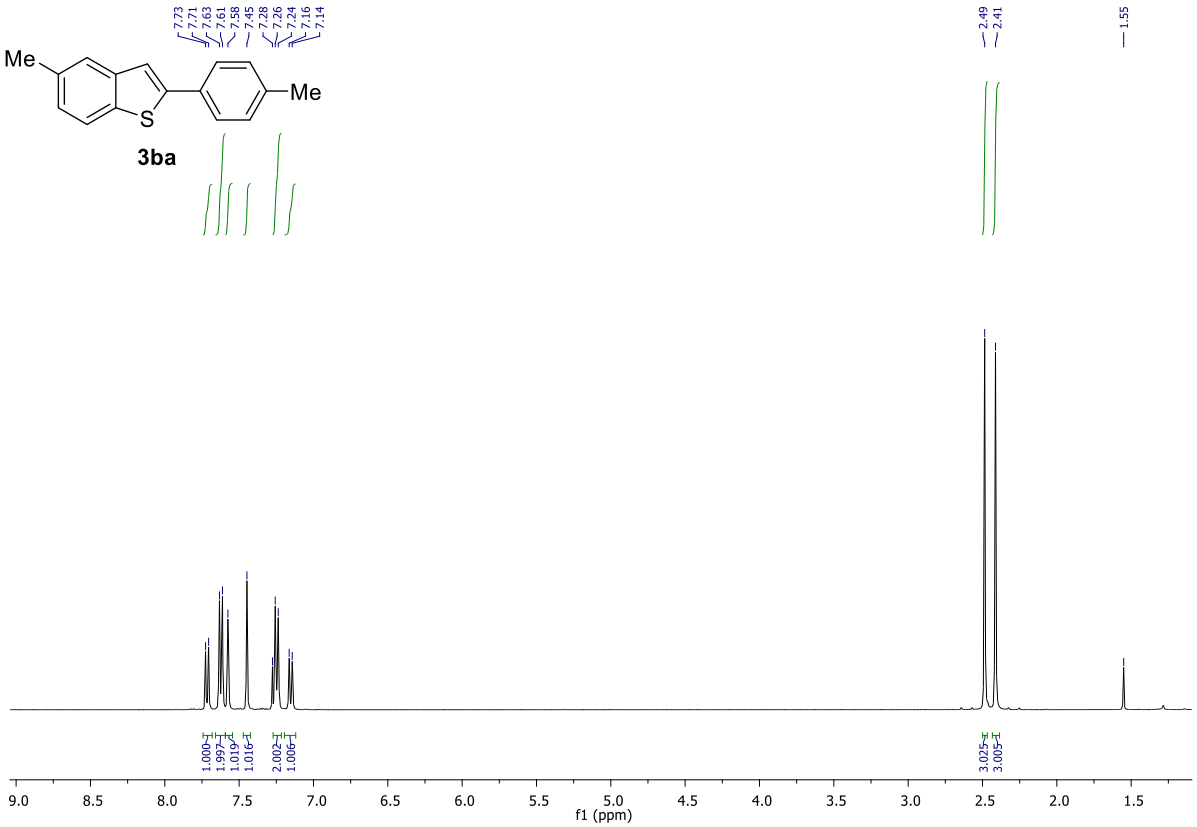
122.31
119.41
80.06
77.48
77.16
76.84
54.42
52.35
38.13
28.37
f1 (ppm)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7.63
7.61
7.58
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7.26
7.24
7.16
7.14
2.49
2.41
1.55
Me
Me
S
3ba
1.000
1.997
1.019
1.016
2.002
1.006
3.025
3.005
9.0
8.5
8.0
7.5
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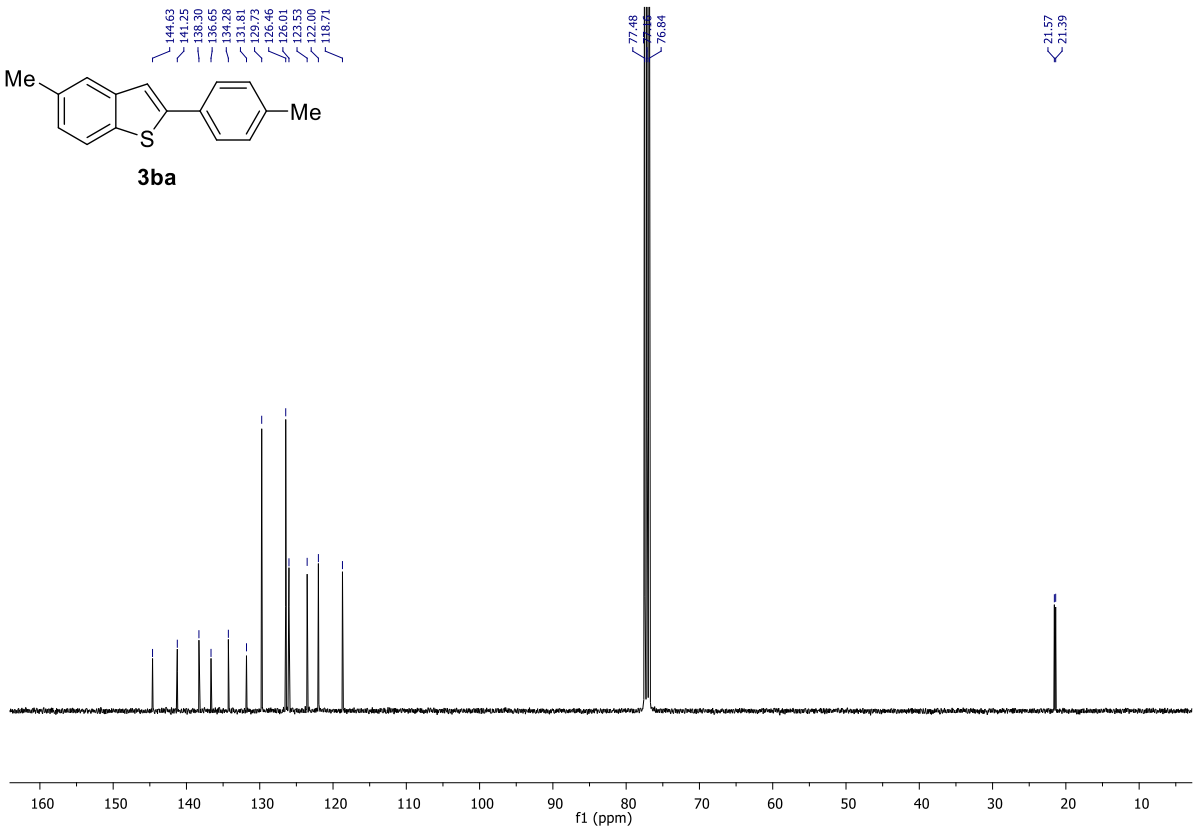
3.0
2.5
2.0
1.5
f1 (ppm)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129.73
126.46
126.01
123.53
122.00
118.71
77.48
77.16
76.84
21.57
21.39
Me
Me
S
3ba
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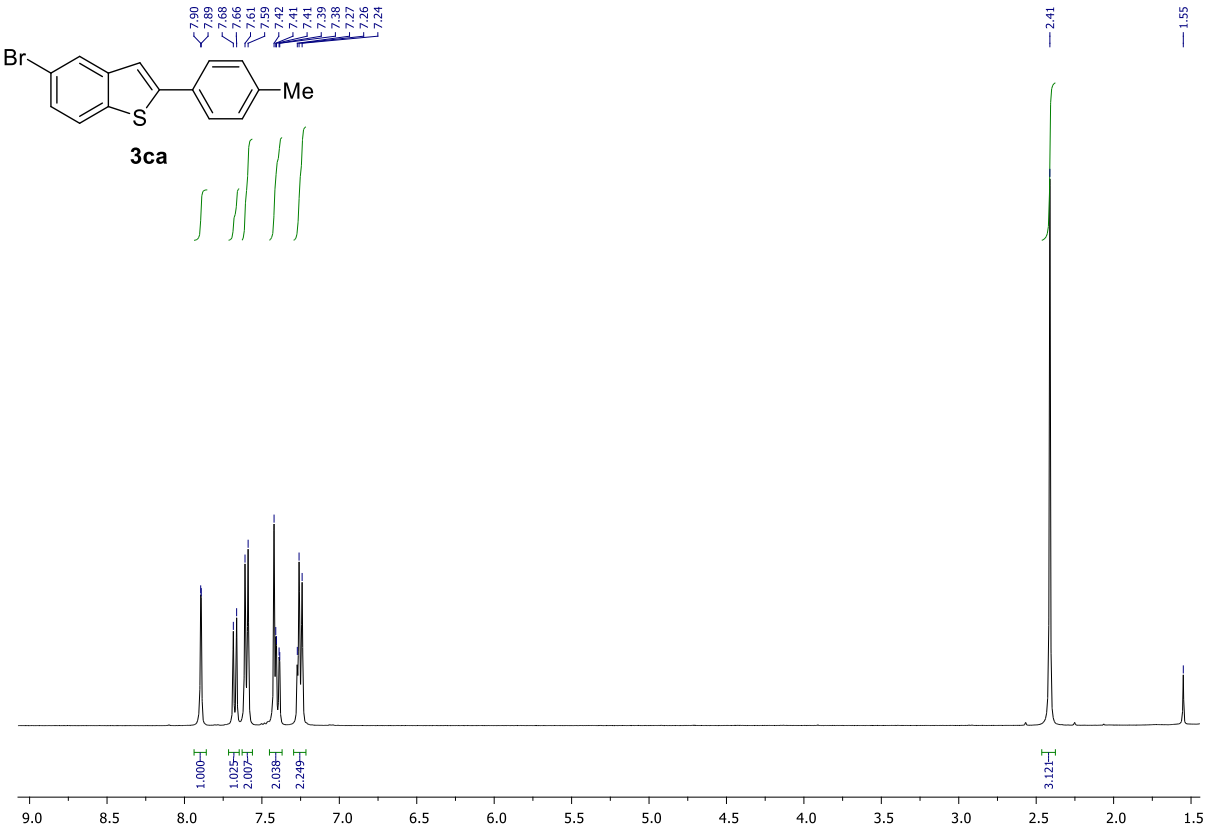
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.66
7.61
7.59
7.42
7.41
7.41
7.39
7.38
7.27
7.26
7.24
2.41
1.55
Br
Me
S
3ca
1.000
1.025
2.007
2.038
2.249
3.121
9.0
8.5
8.0
7.5
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3.5
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2.5
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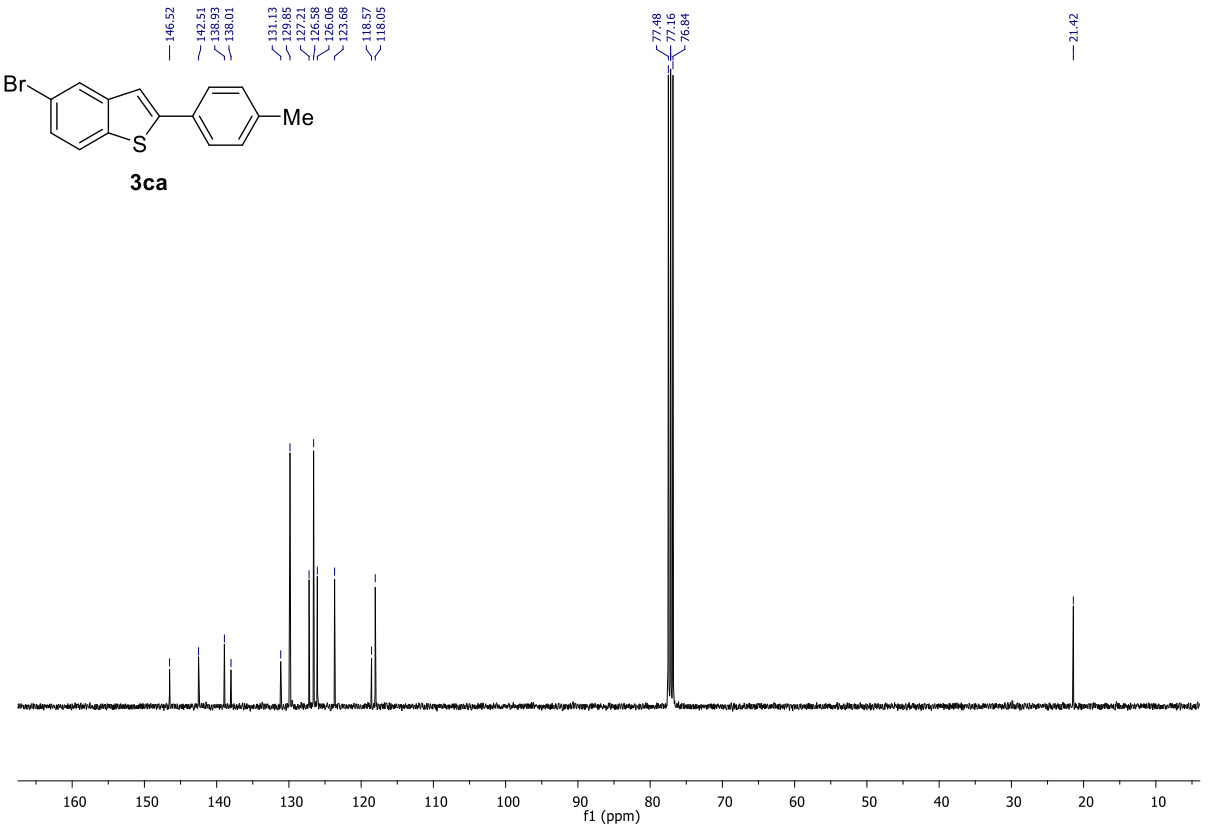
1.5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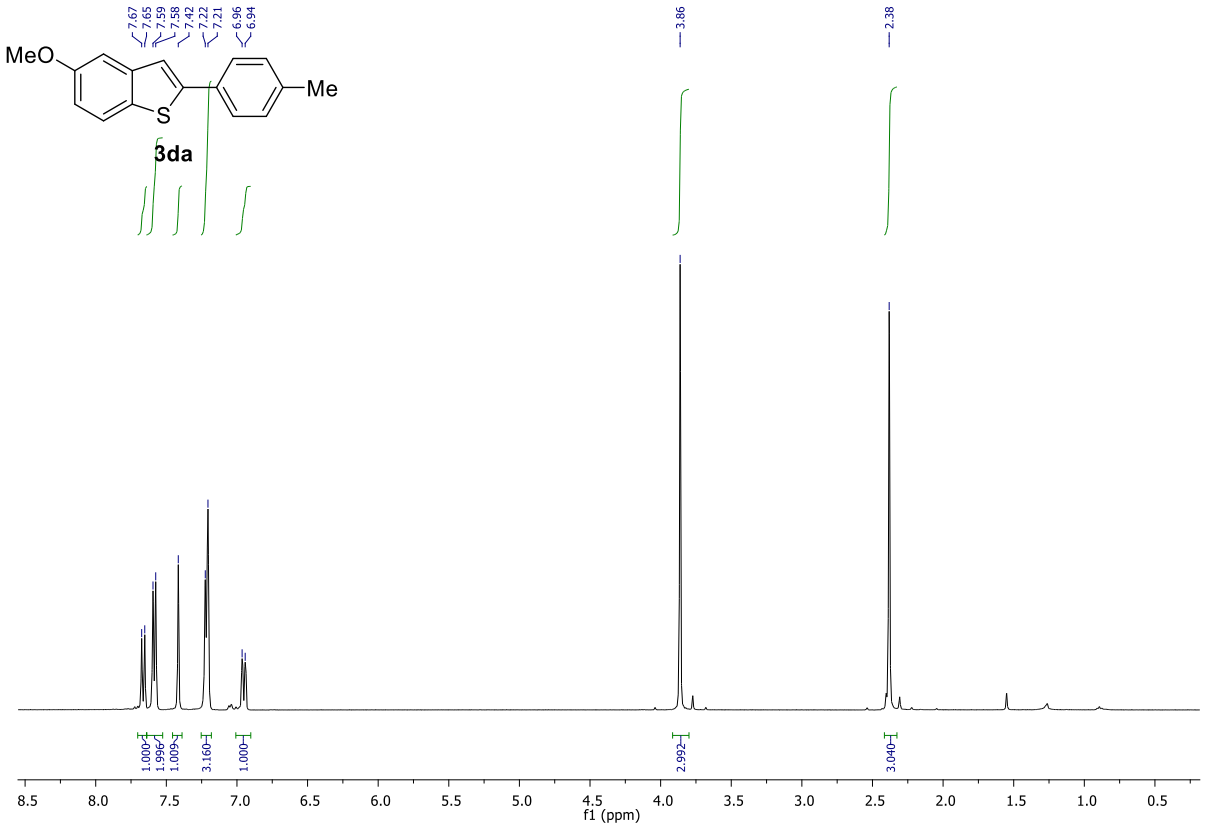
129.85
127.21
126.58
126.06
123.68
118.57
118.05
77.48
77.16
76.84
21.42
Br
Me
S
3ca
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.58
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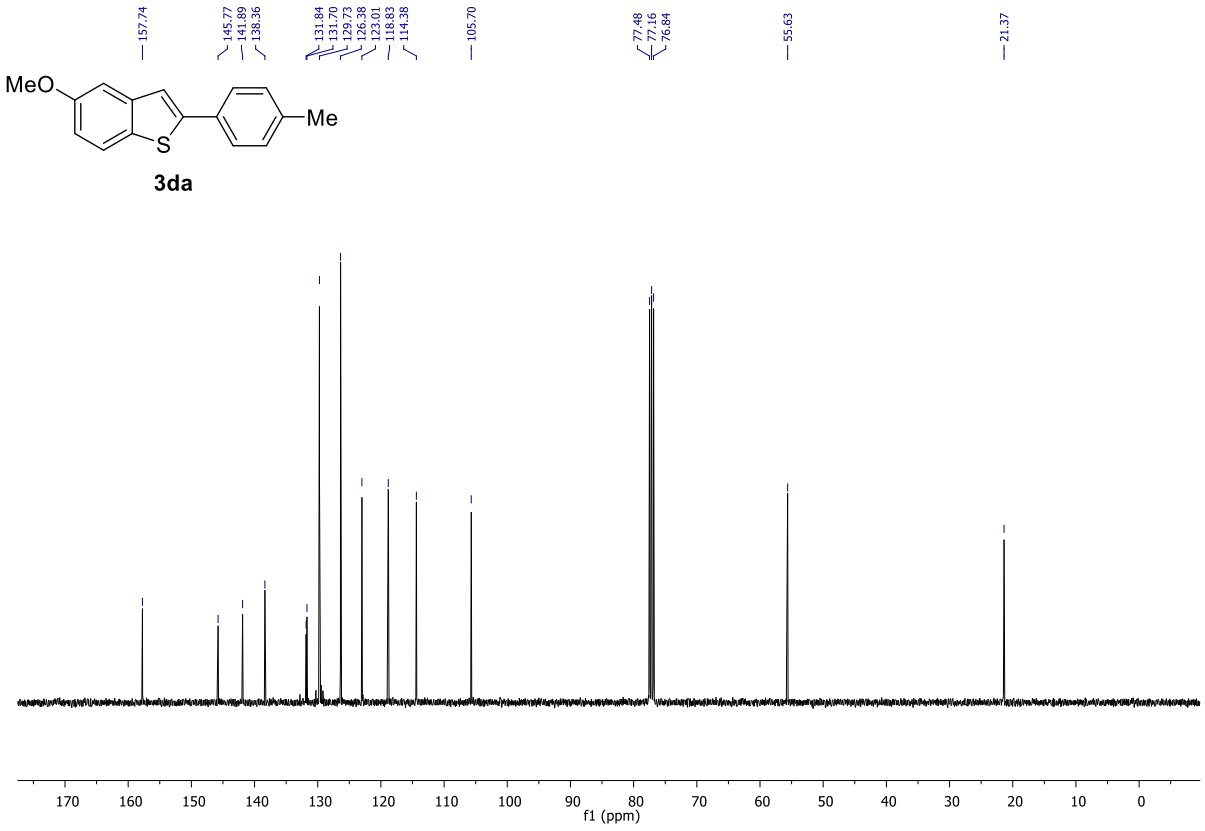
7.21
6.96
6.94
3.86
2.38
MeO
Me
S
3da
1.000
1.996
1.009
3.160
1.000
2.992
3.040
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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126.38
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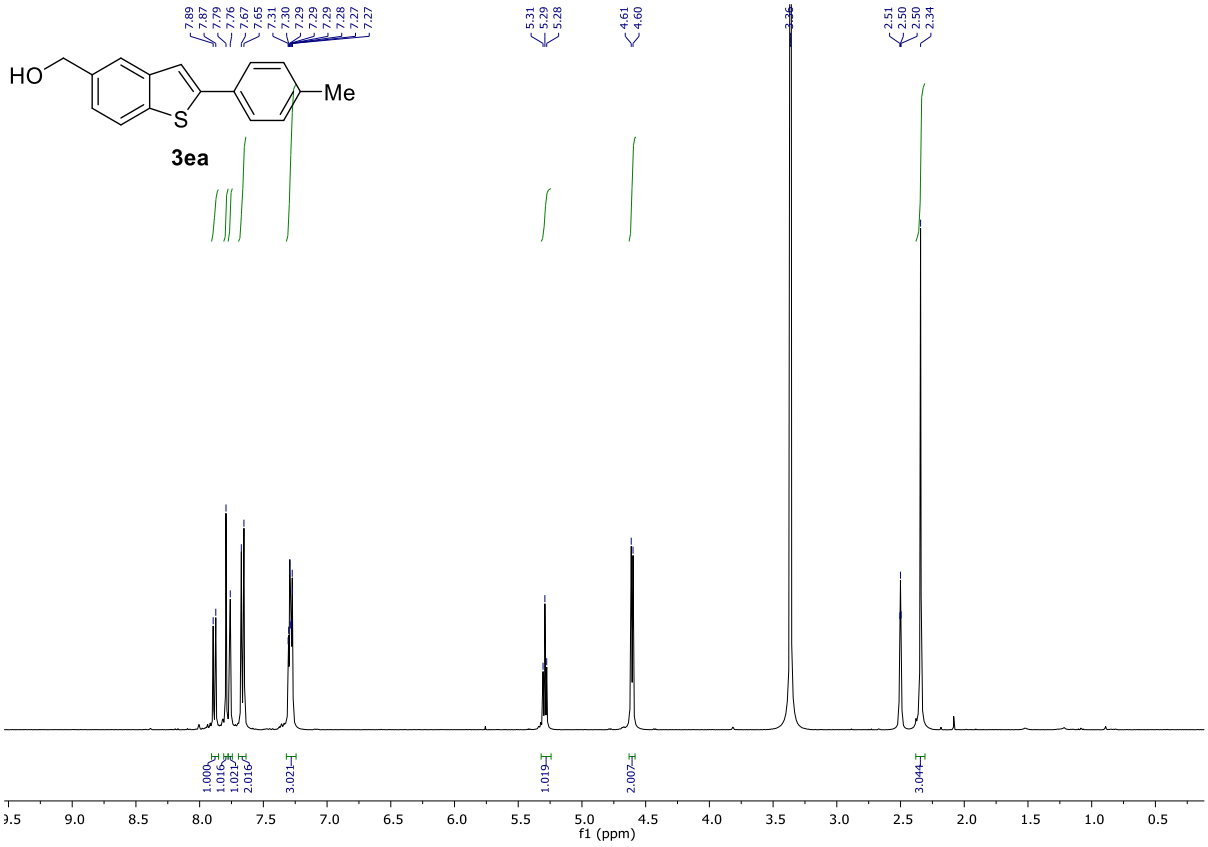
118.83
114.38
105.70
77.48
77.16
76.84
55.63
21.37
MeO
Me
S
3da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.76
7.67
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7.31
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7.29
7.29
7.28
7.27
7.27
5.31
5.29
5.28
4.61
4.60
3.36
2.51
2.50
2.50
2.34
HO
S
Me
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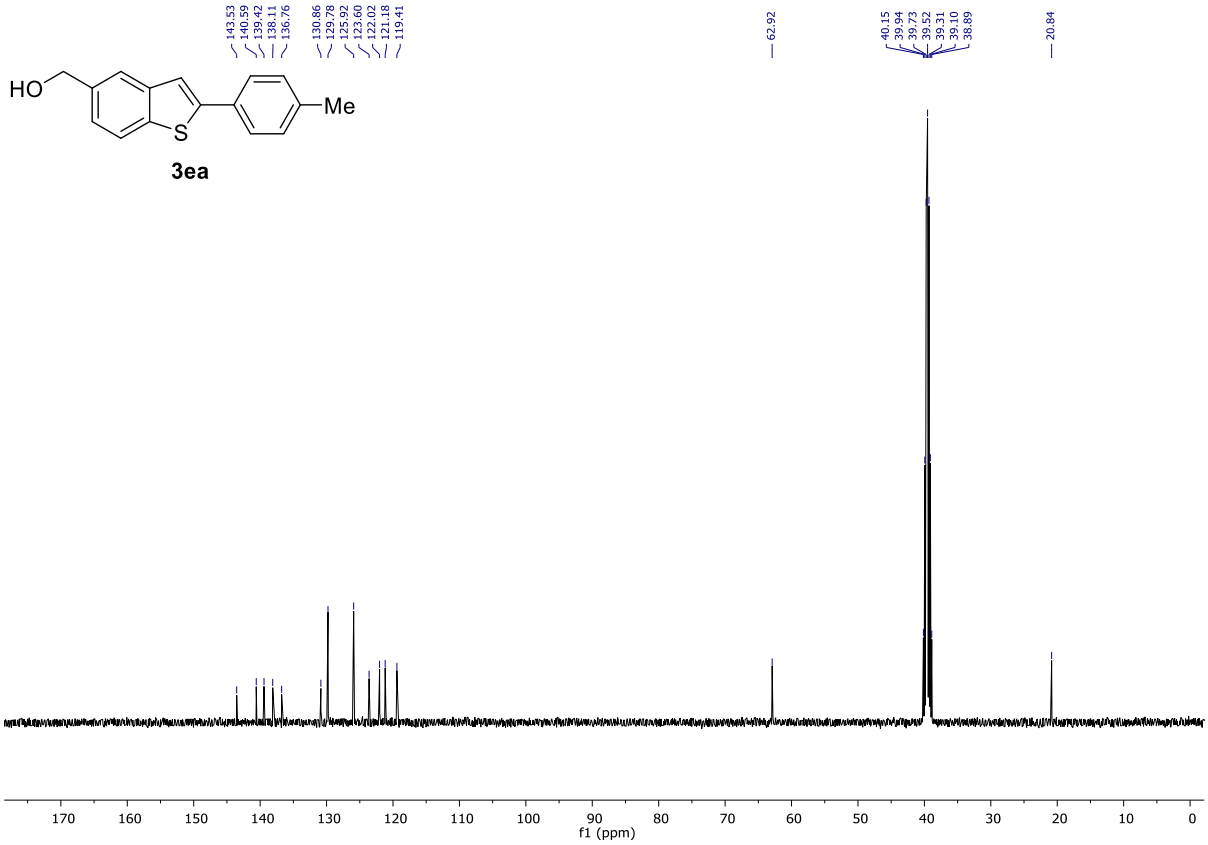
1.016
1.021
2.016
3.021
1.019
2.007
3.044
f1 (ppm)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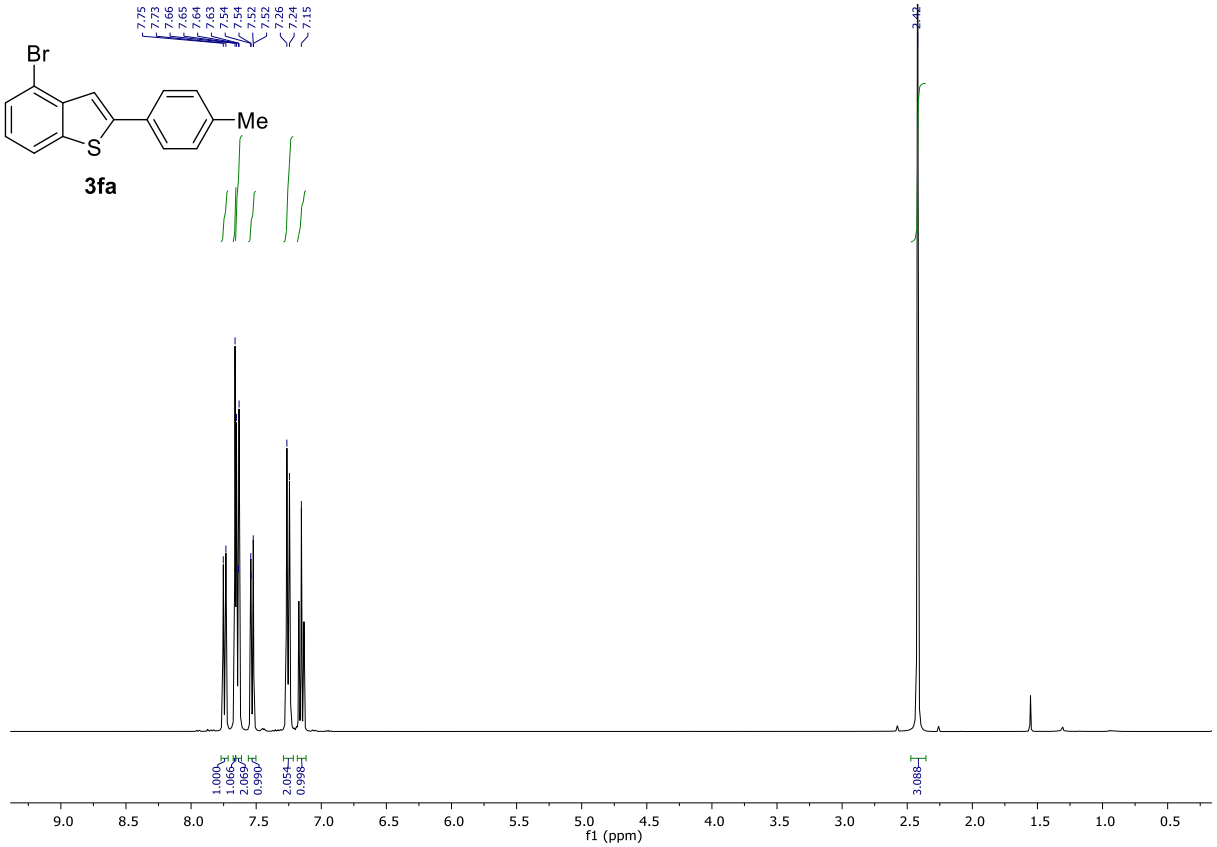
123.60
122.02
121.18
119.41
62.92
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.84
HO
S
Me
3ea
f1 (ppm)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7.73
7.66
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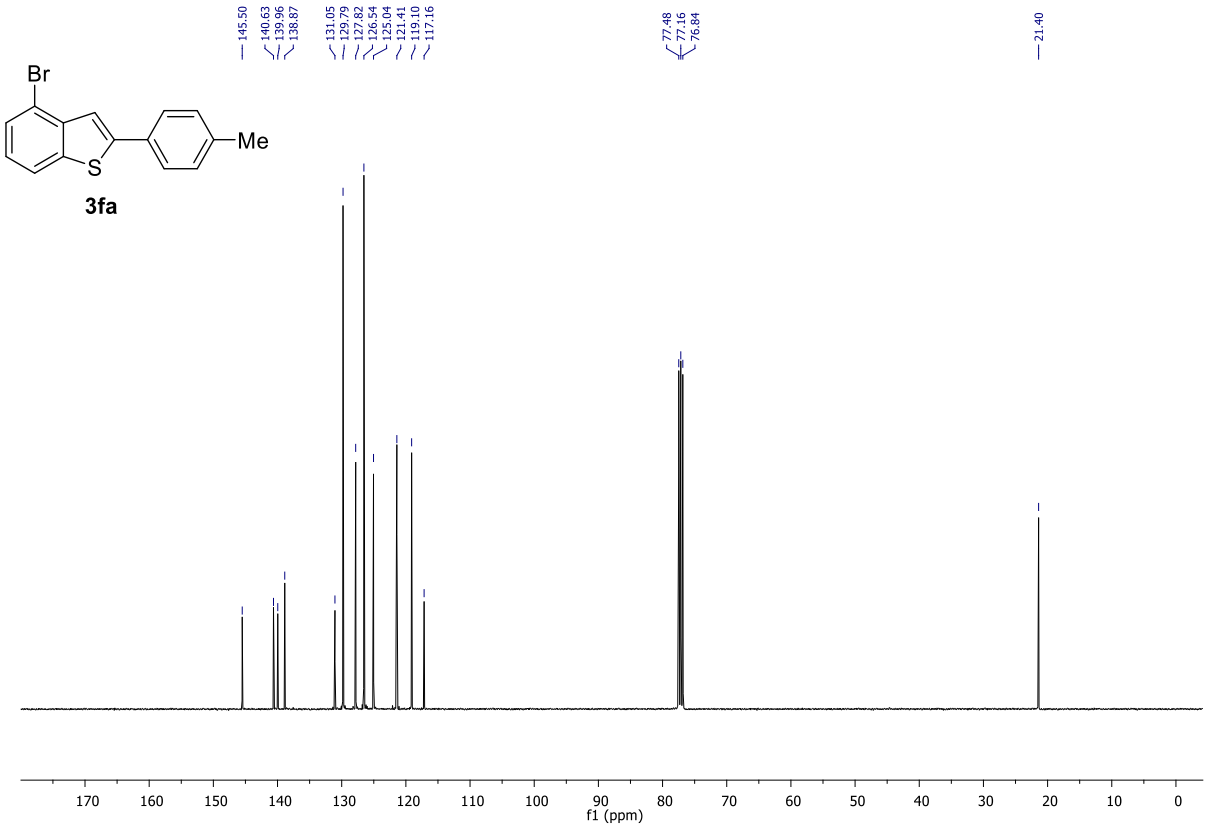
7.63
7.54
7.54
7.52
7.26
7.24
7.15
2.42
Br
Me
S
3fa
1.000
1.066
2.069
0.990
2.054
0.998
3.088
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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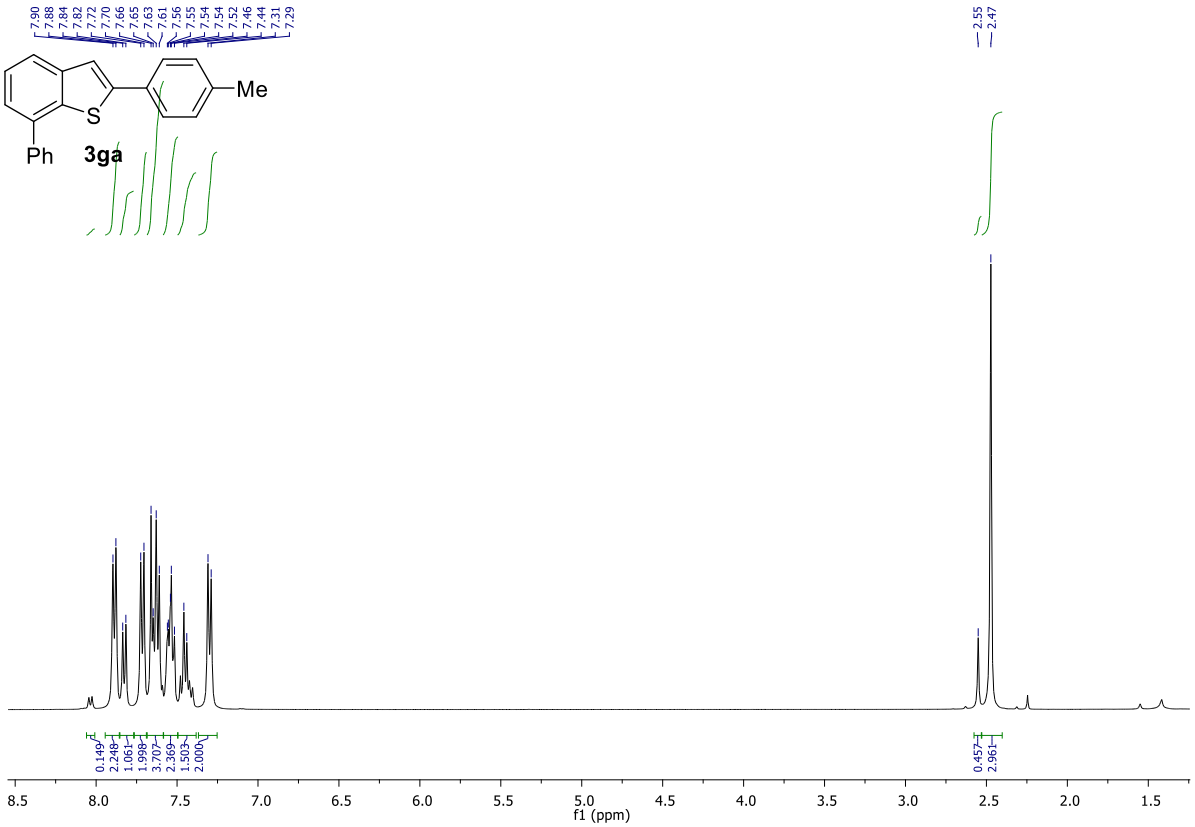
140.63
139.96
138.87
131.05
129.79
127.82
126.54
125.04
121.41
119.10
117.16
77.48
77.16
76.84
21.40
Br
Me
S
3fa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.88
7.84
7.82
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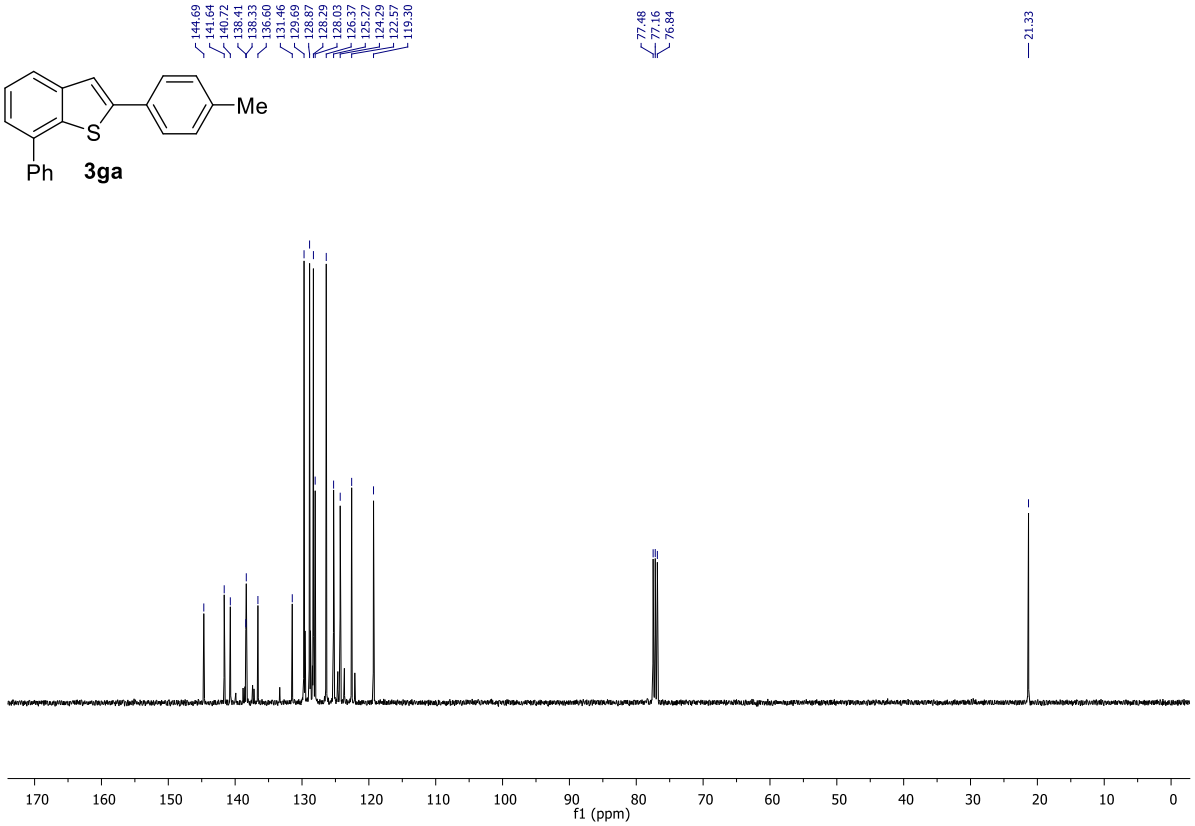
7.70
7.66
7.65
7.63
7.61
7.56
7.55
7.54
7.54
7.52
7.46
7.44
7.31
7.29
2.55
2.47
Me
S
Ph
3ga
0.149
2.248
1.061
1.998
3.707
2.369
1.503
2.000
0.457
2.961
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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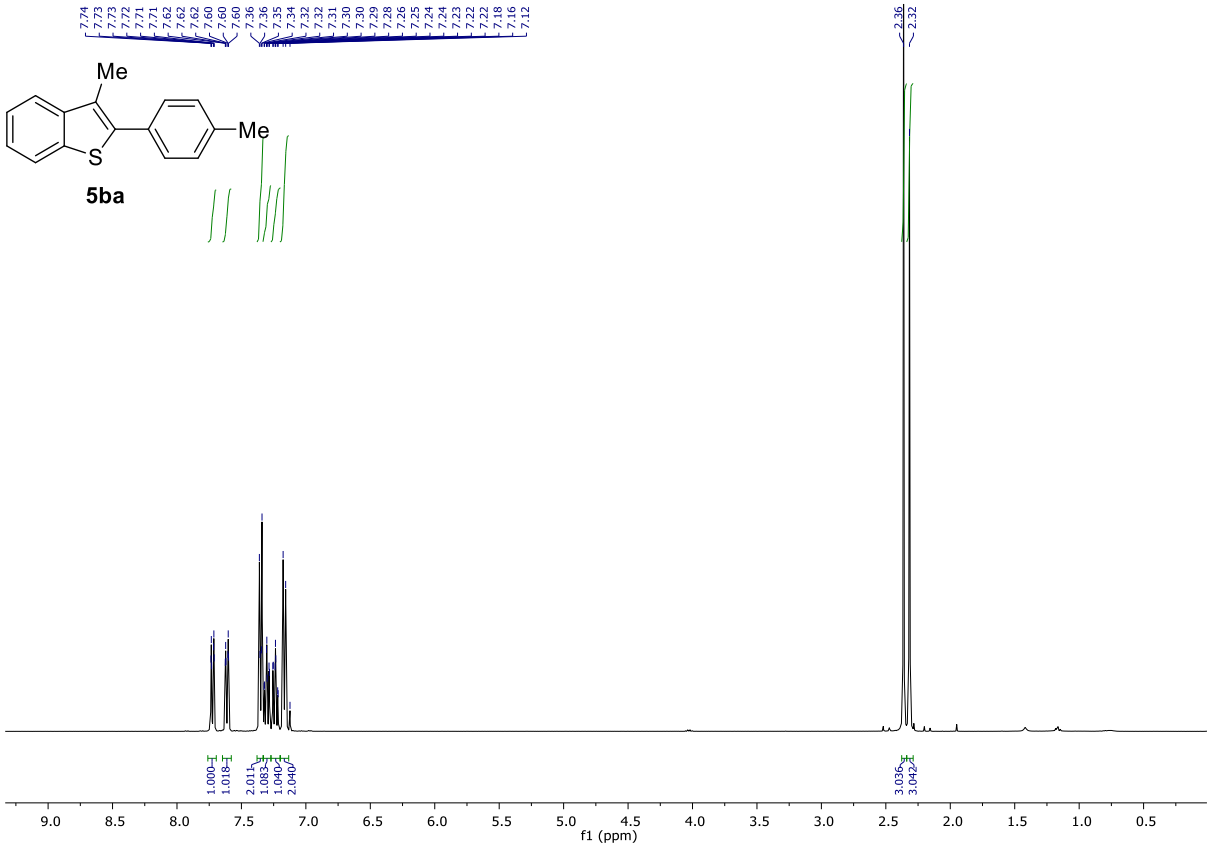
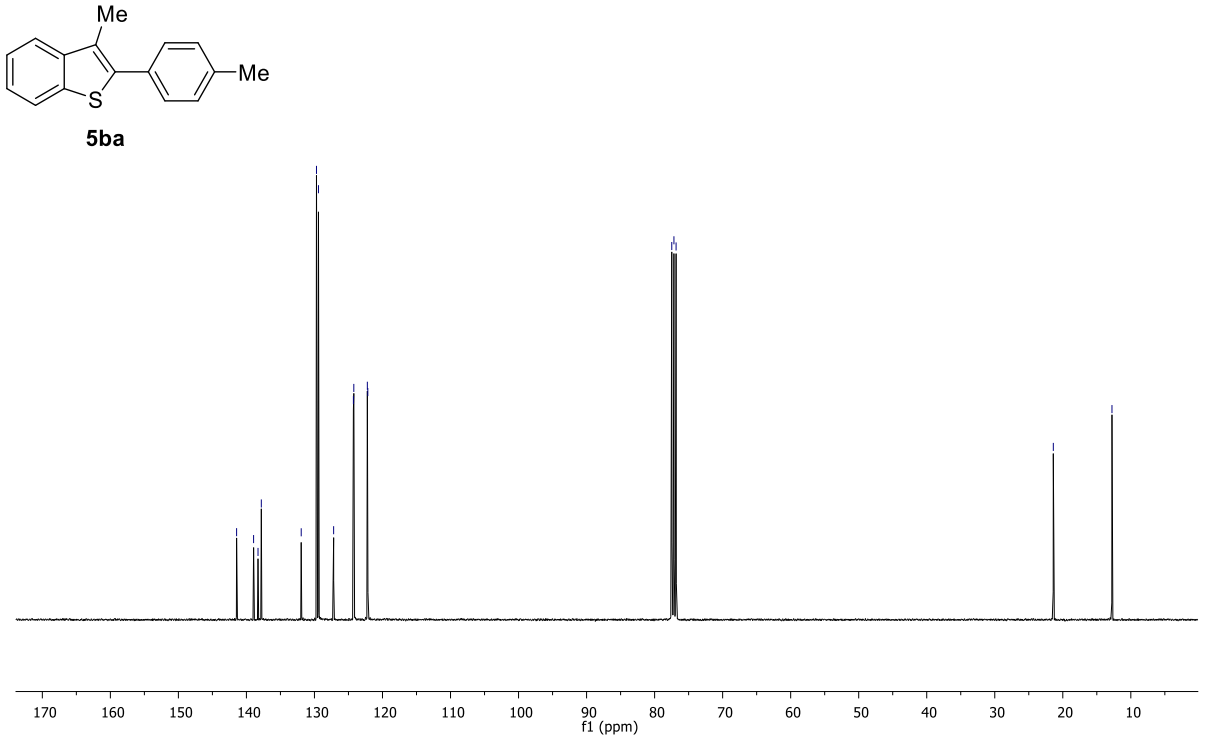
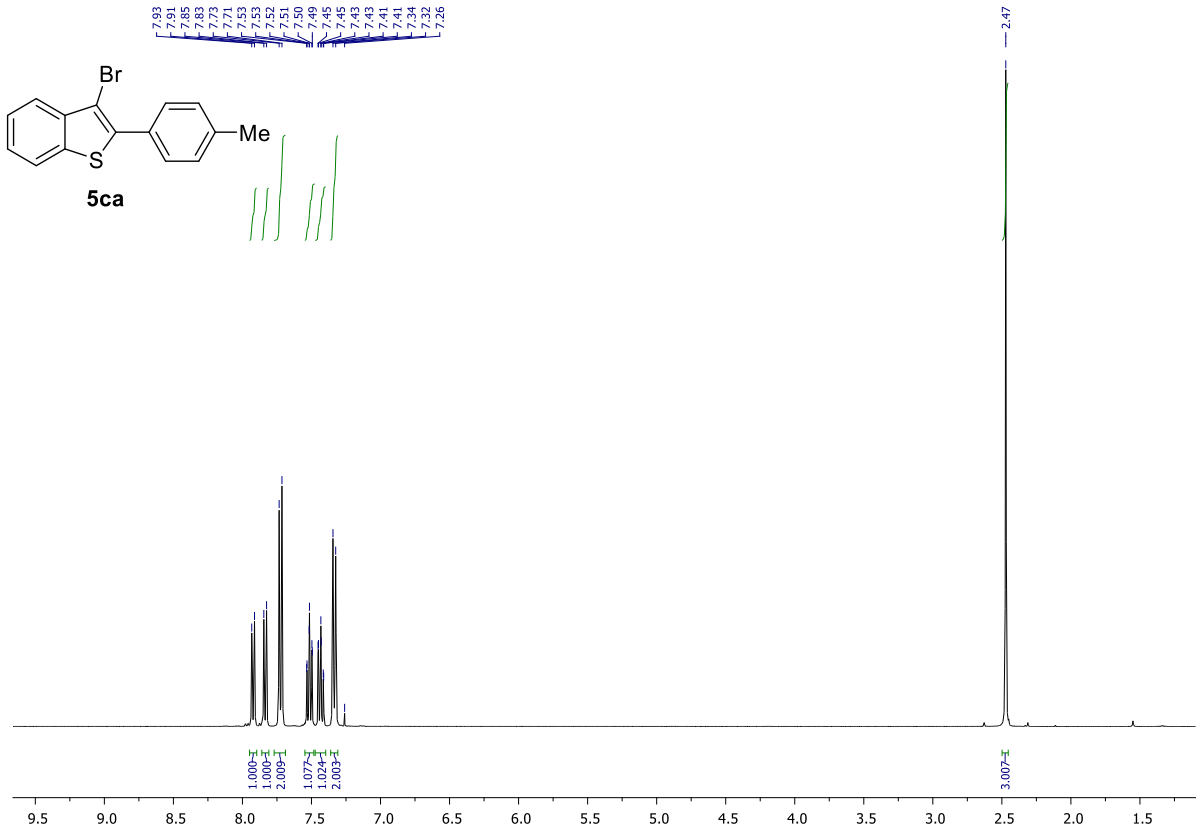
131.46
129.69
128.87
128.29
128.03
126.37
125.27
124.29
122.57
119.30
77.48
77.16
76.84
21.33
Me
S
Ph
3ga
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
S
5ba
f1 (ppm)


Me
Me
S
5ba
f1 (ppm)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7.85
7.83
7.73
7.71
7.53
7.53
7.52
7.51
7.50
7.49
7.45
7.45
7.43
7.43
7.41
7.41
7.34
7.32
7.26
2.47
Br
Me
S
5ca
1.000
1.000
2.009
1.077
1.024
2.003
3.007
9.5
9.0
8.5
8.0
7.5
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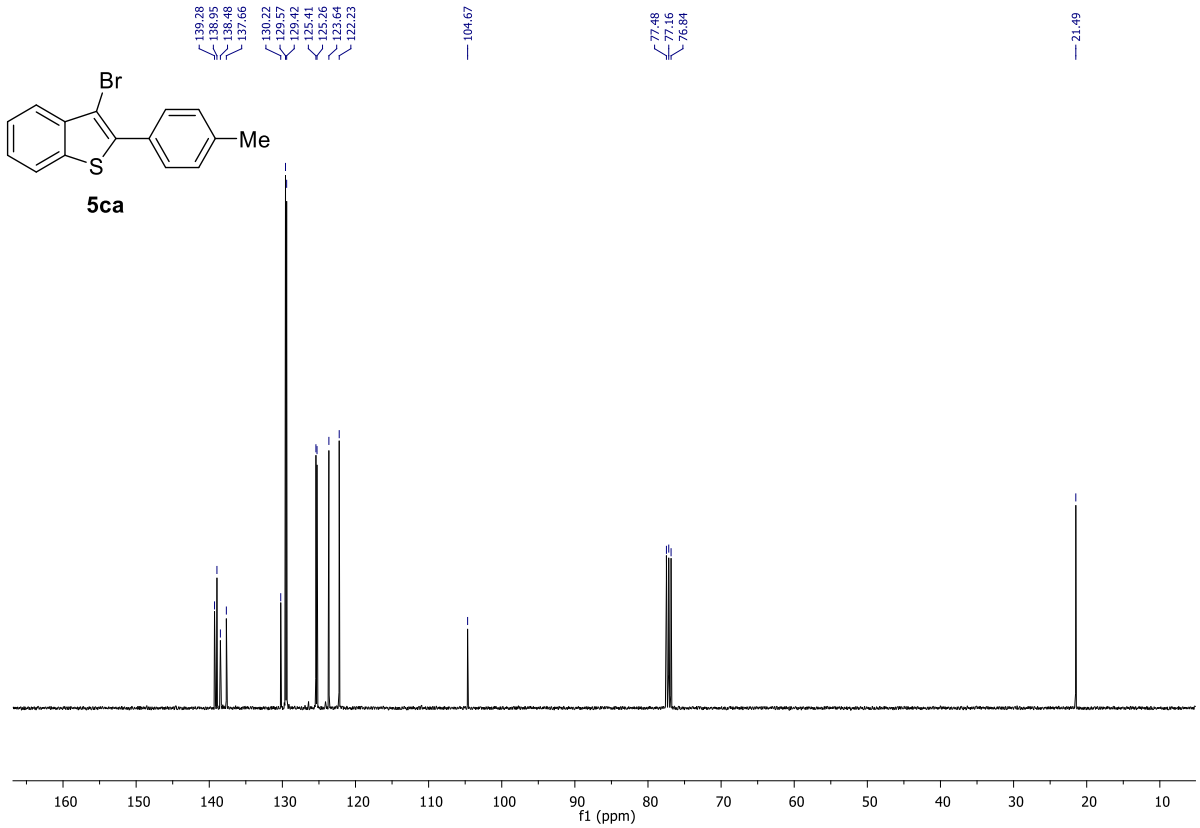
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5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138.95
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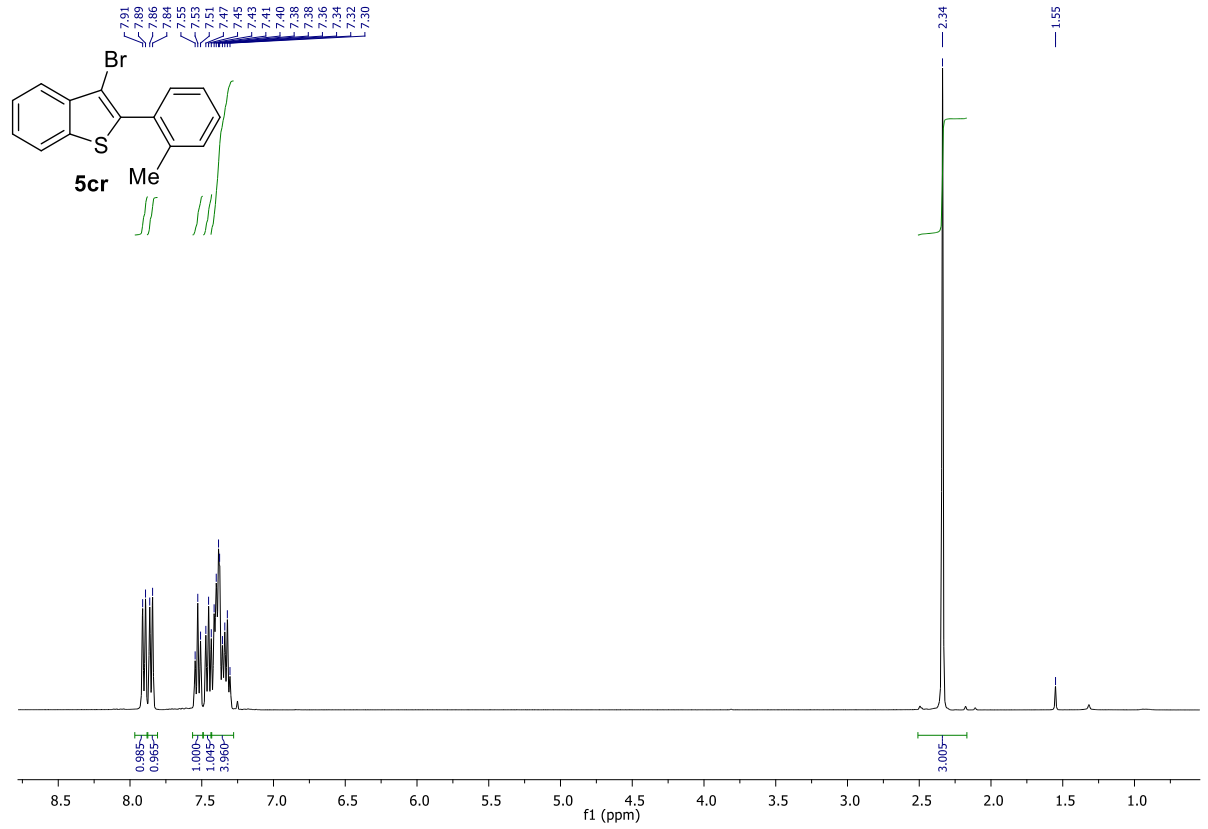
129.57
129.42
125.41
125.26
123.64
122.23
104.67
77.48
77.16
76.84
21.49
Br
Me
S
5ca
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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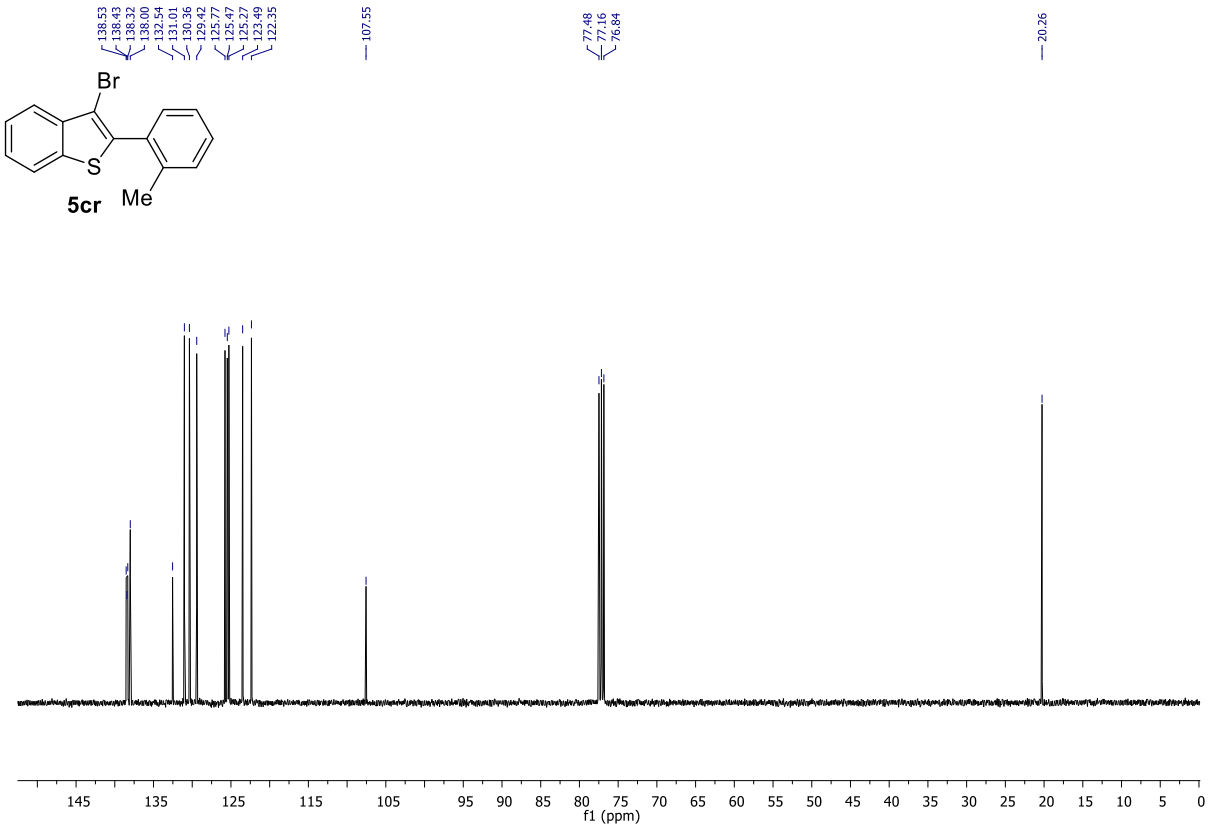
7.89
7.86
7.84
7.55
7.53
7.51
7.47
7.45
7.43
7.41
7.40
7.38
7.38
7.36
7.34
7.32
7.30
2.34
1.55
Br
S
Me
5cr
0.985
0.965
1.000
1.045
3.960
3.005
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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138.32
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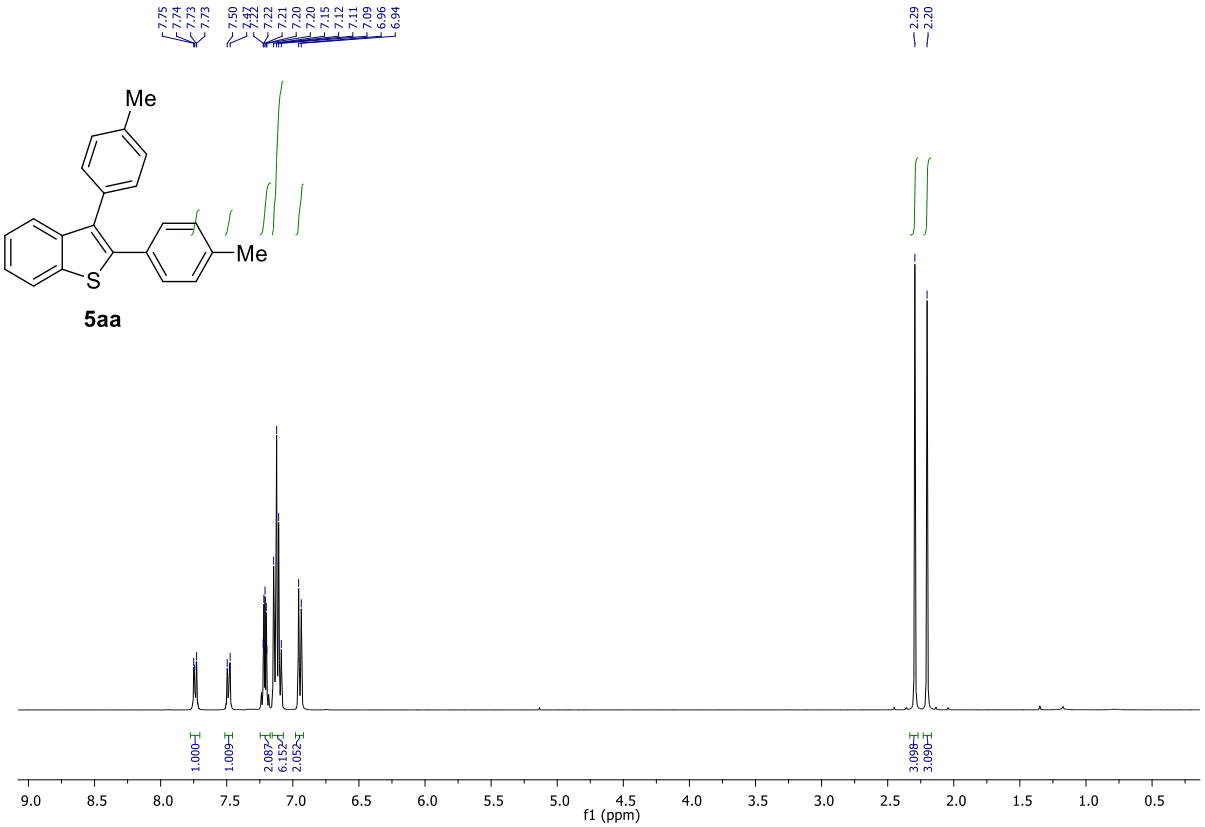
132.54
131.01
130.36
129.42
125.77
125.47
125.27
123.49
122.35
107.55
77.48
77.16
76.84
20.26
Br
S
Me
5cr
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)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7.73
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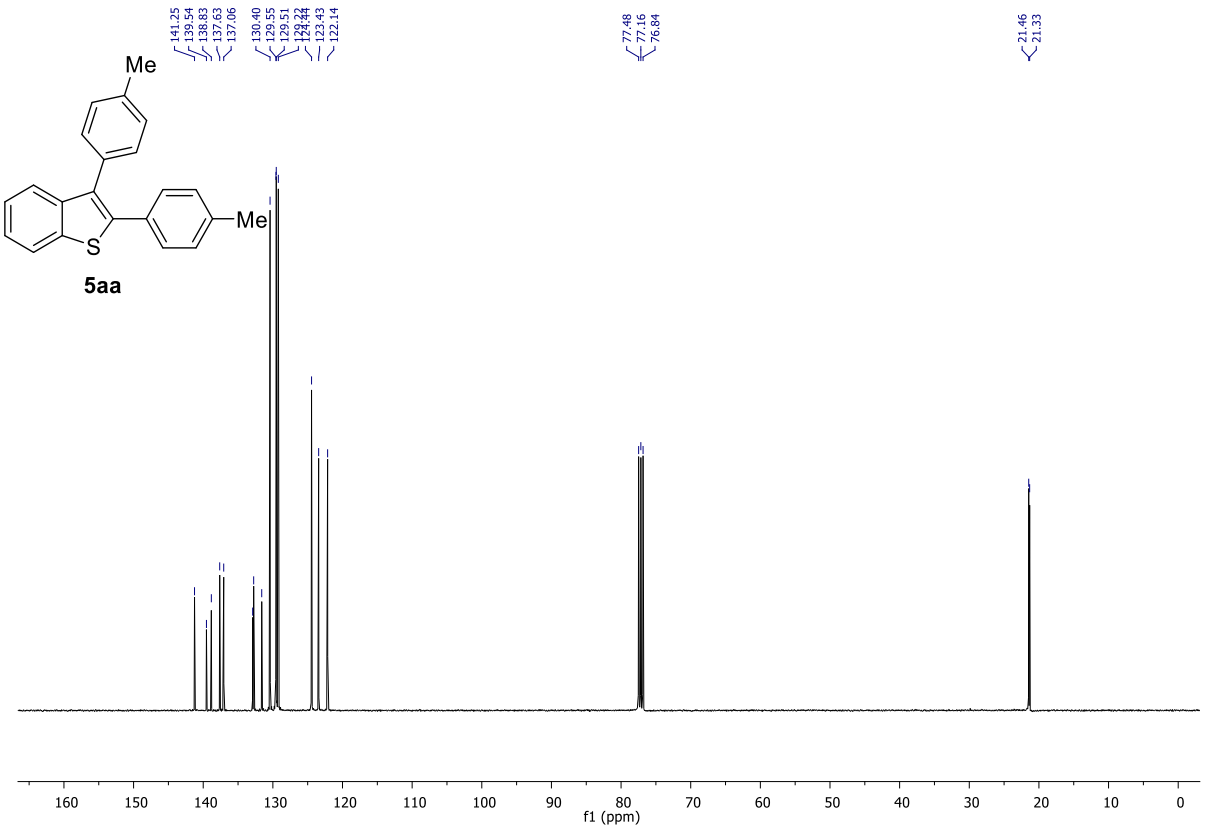
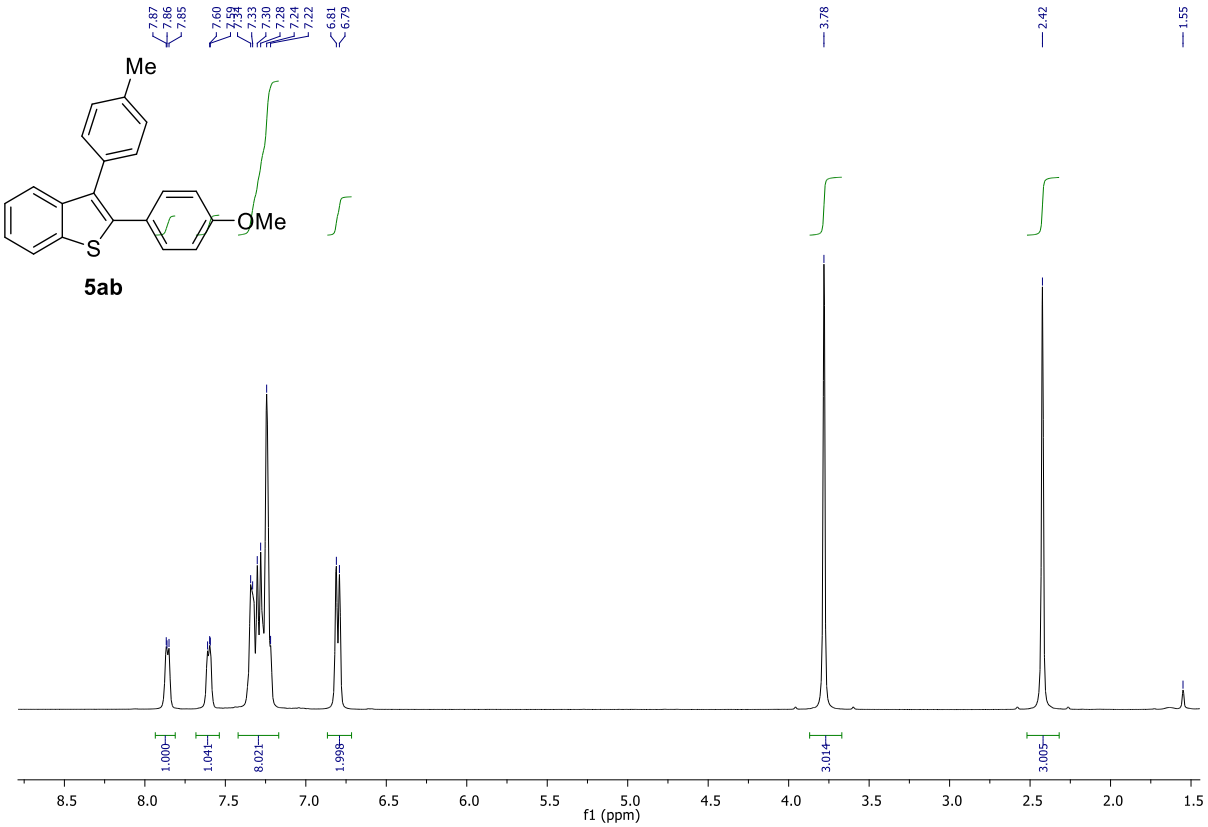
7.50
7.42
7.42
7.22
7.21
7.20
7.20
7.15
7.12
7.11
7.09
6.96
6.94
2.29
2.20
Me
Me
S
1.000
1.009
2.087
6.152
2.052
3.098
3.090
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

**5aa**


141.25
139.54
138.83
137.63
137.06
130.40
129.55
129.51
123.43
122.14
77.48
77.16
76.84
21.46
21.33
Me
Me
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**5aa**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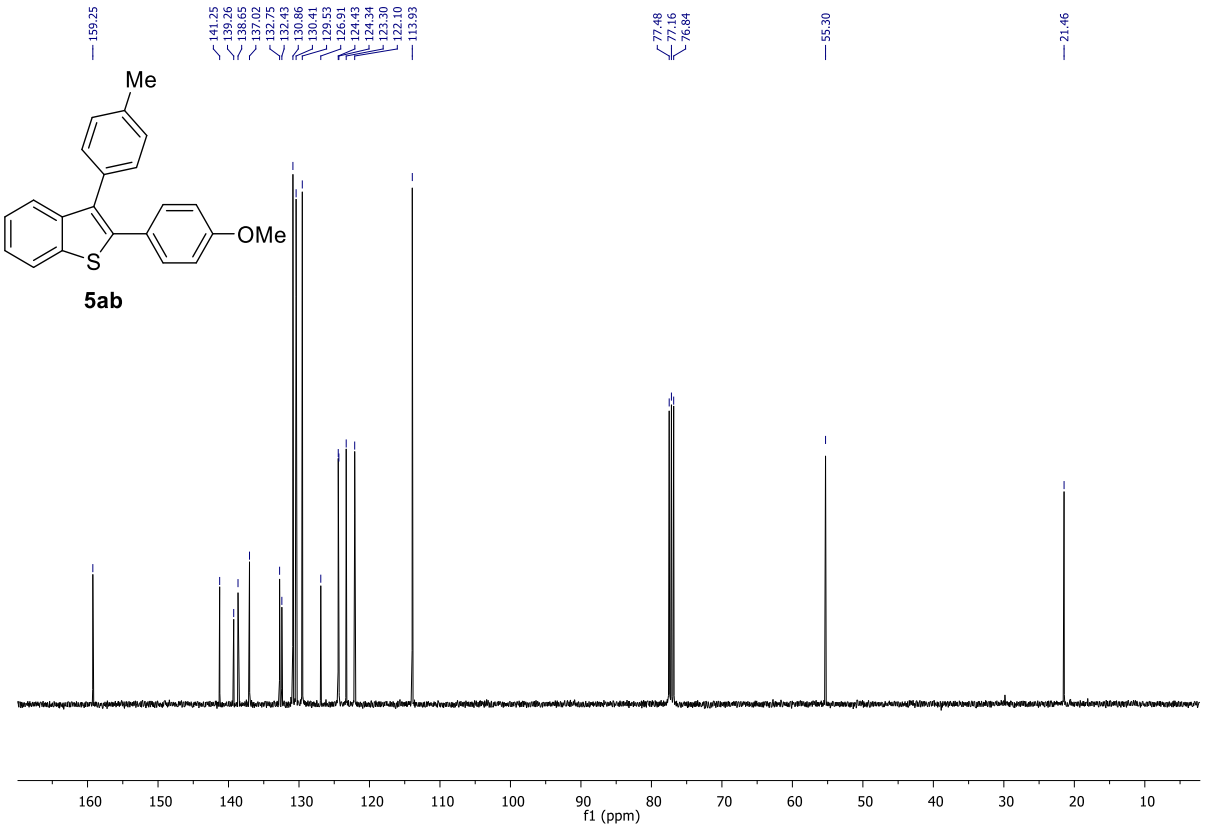
7.85
7.60
7.59
7.34
7.33
7.30
7.28
7.24
7.22
6.81
6.79
3.78
2.42
1.55
Me
OMe
S
5ab
1.000
1.041
8.021
1.998
3.014
3.005
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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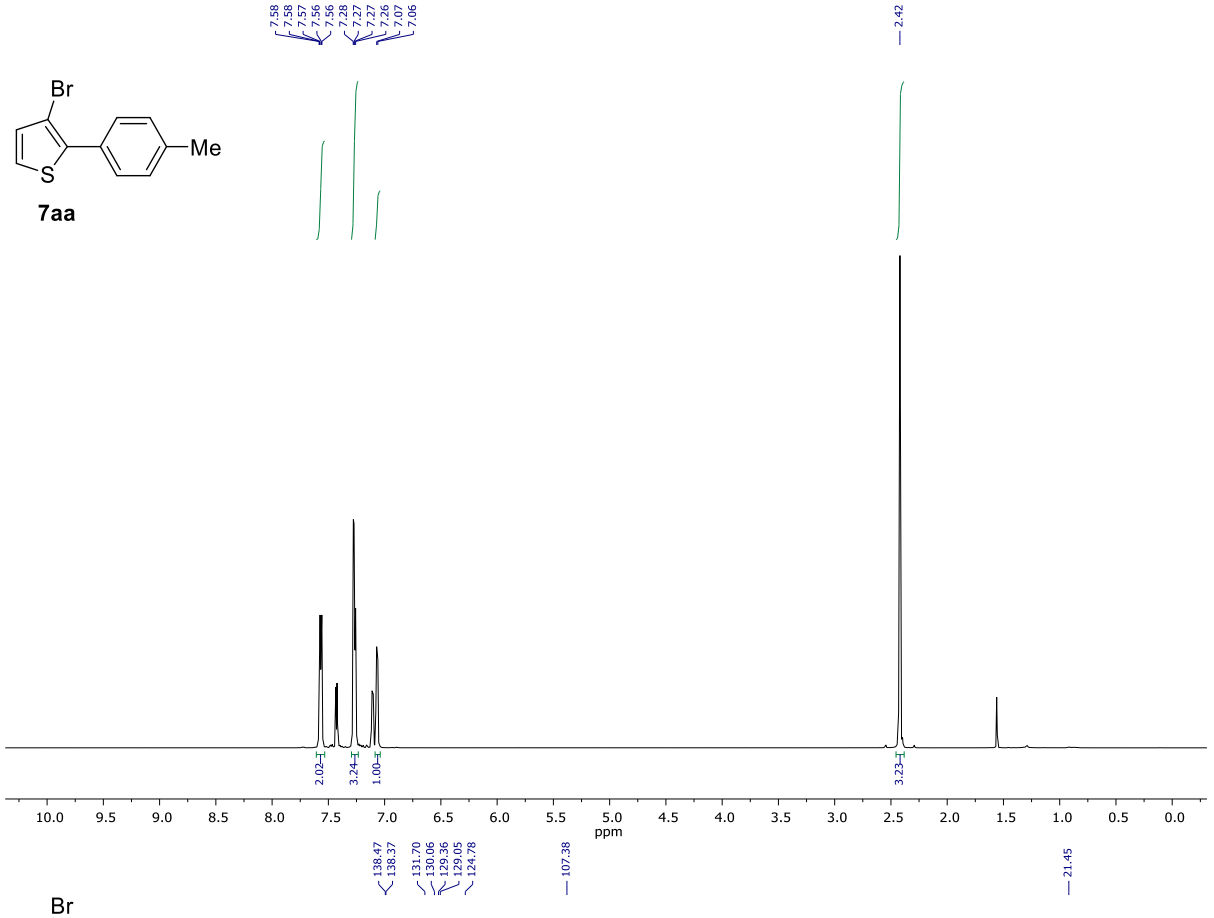
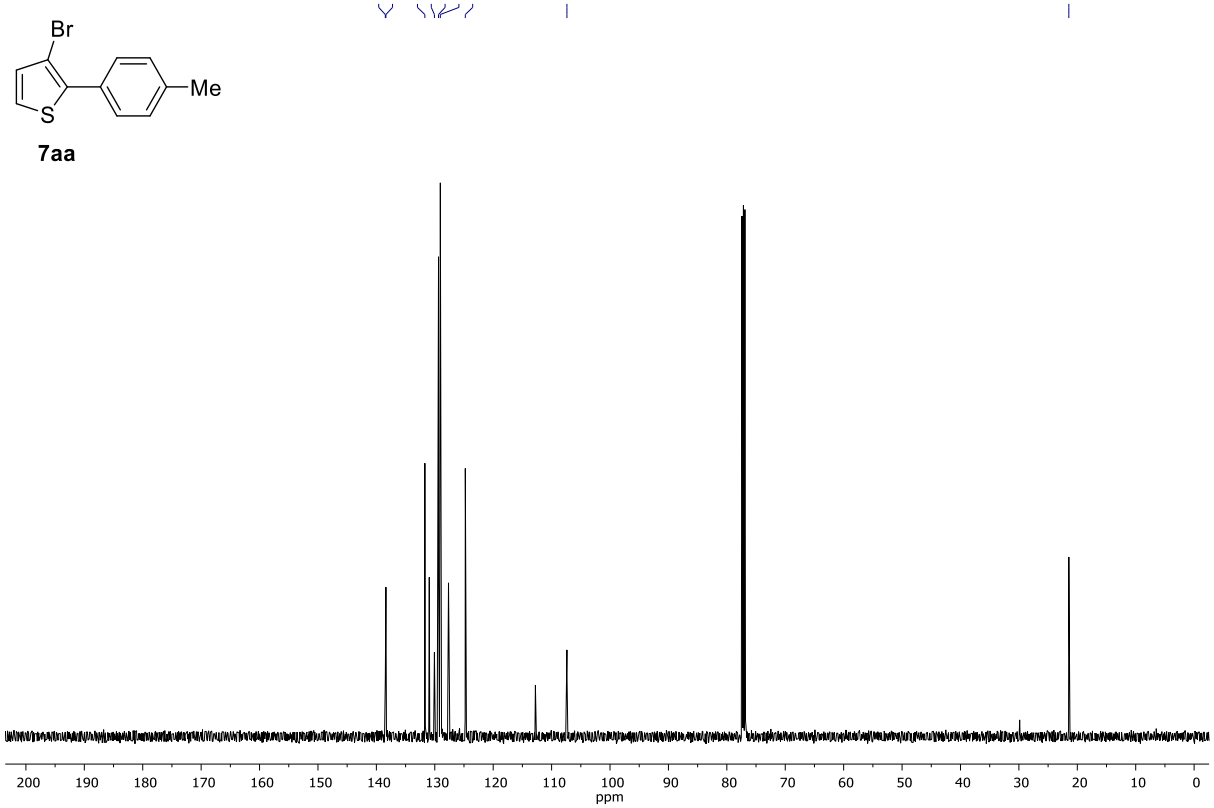
132.75
132.43
130.86
130.41
129.53
126.91
124.43
124.34
123.30
122.10
113.93
77.48
77.16
76.84
55.30
21.46
Me
OMe
S
5ab
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Br
Me
S
7aa
7.58
7.58
7.57
7.56
7.56
7.28
7.27
7.27
7.26
7.07
7.06
2.42
2.02
3.24
1.00
3.23
ppm


Br
Me
S
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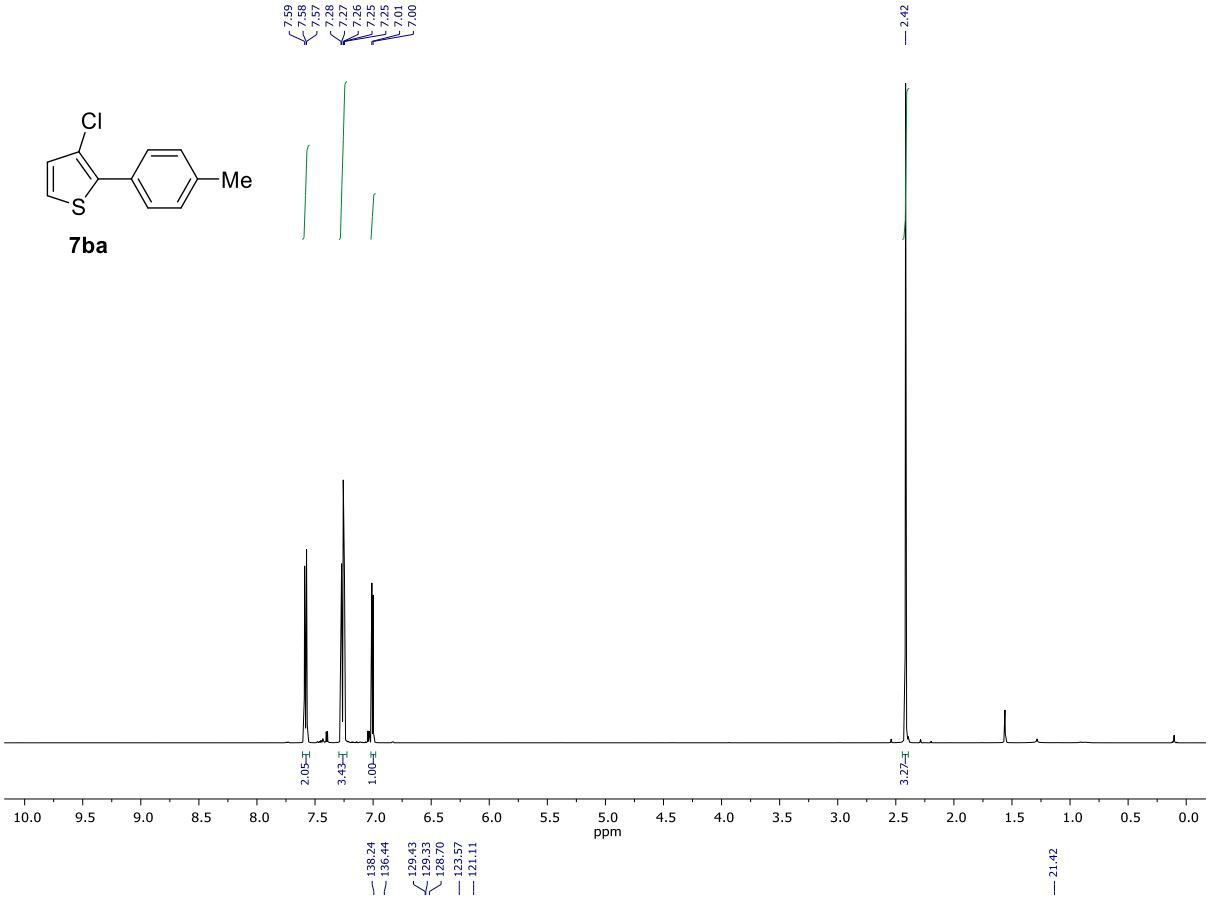
131.70
130.06
129.36
129.05
124.78
107.38
21.45
ppm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7.57
7.28
7.27
7.26
7.25
7.25
7.01
7.00
2.42
Cl
Me
S
7ba
2.05
3.43
1.00
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
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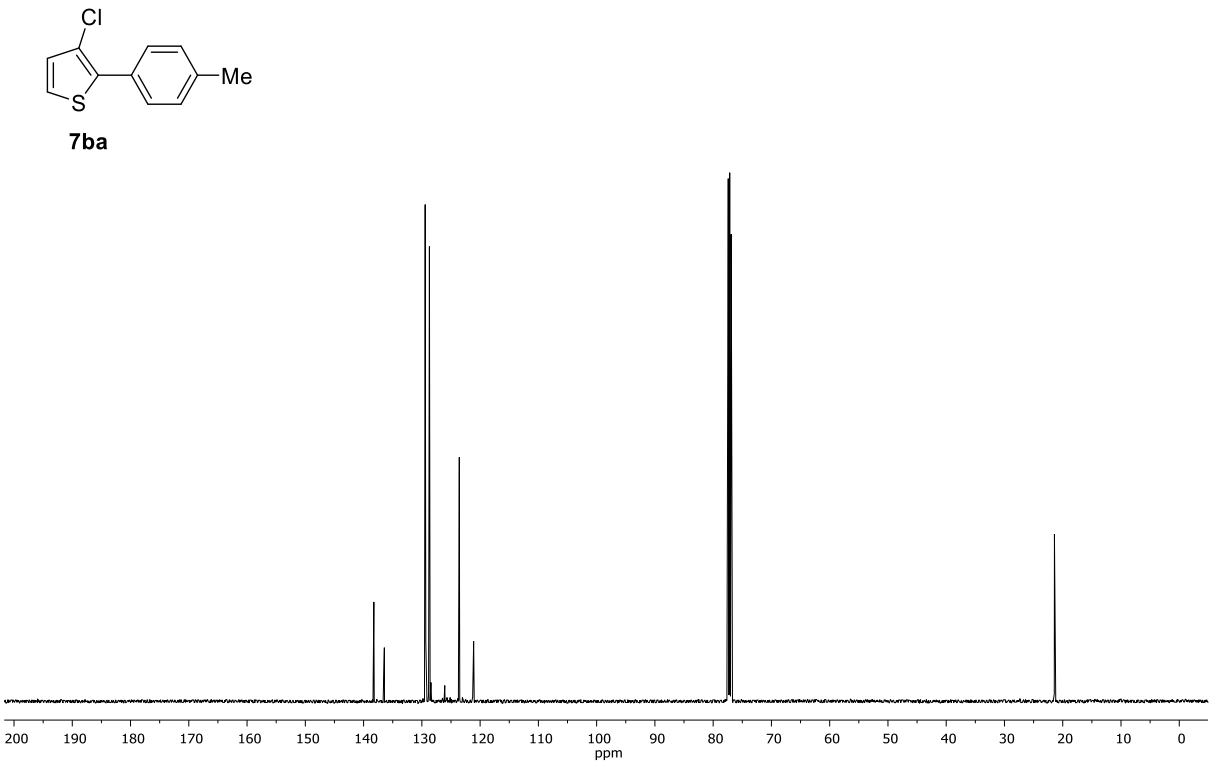
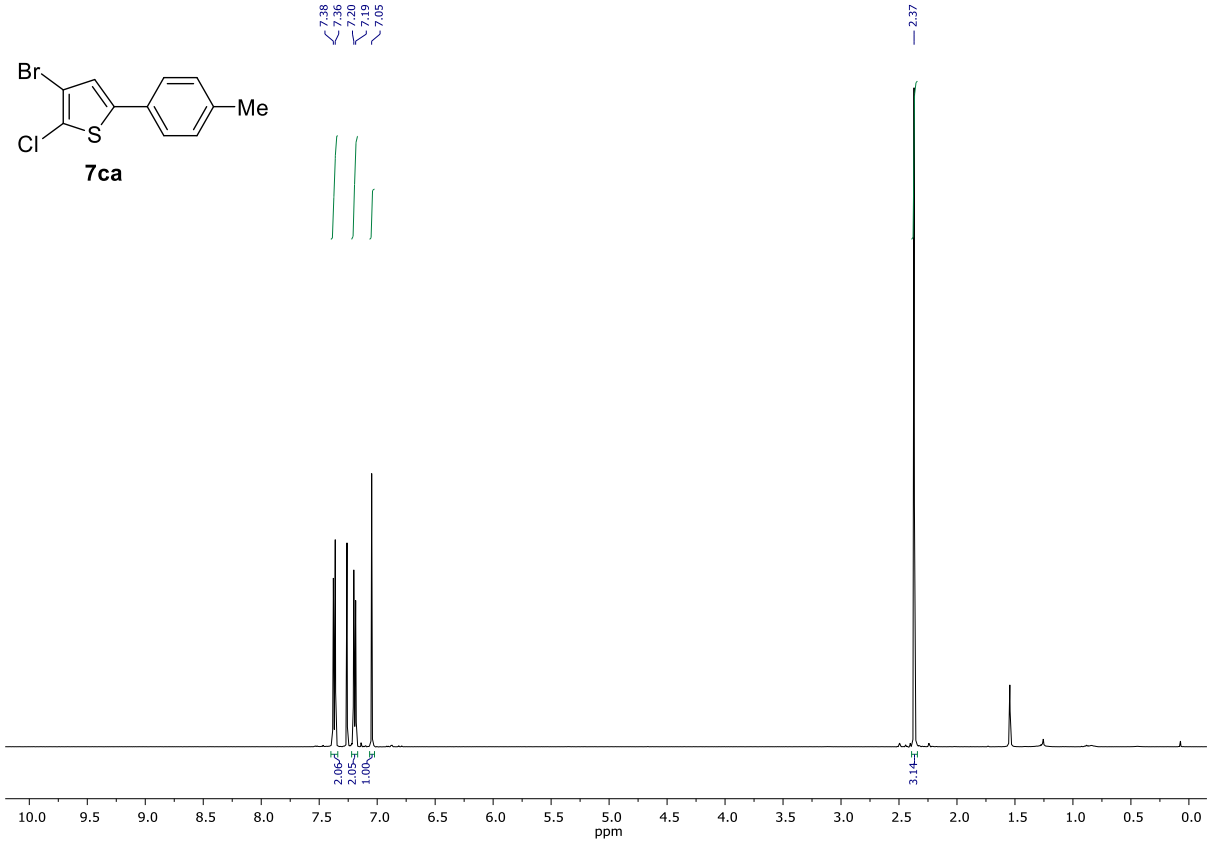
136.44
129.43
129.33
128.70
123.57
121.11
21.42


Cl
Me
S
7ba
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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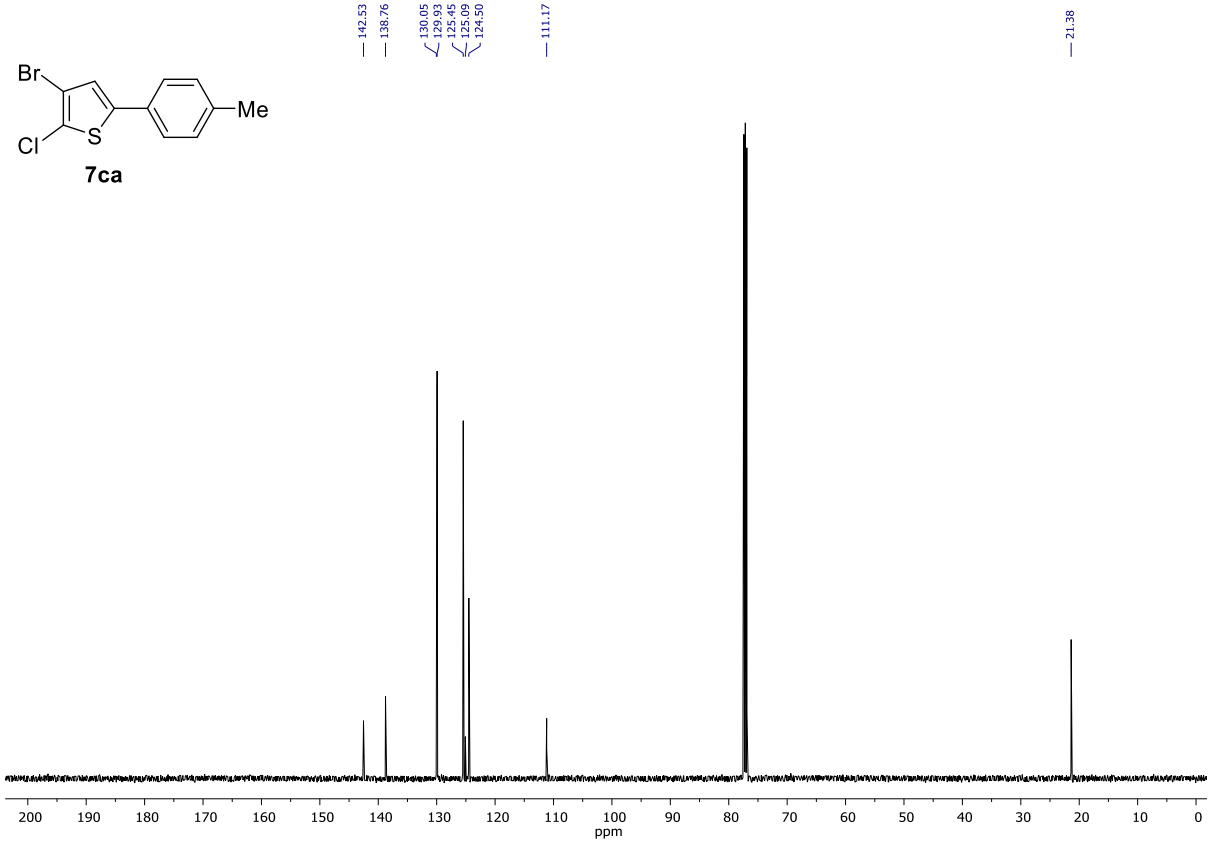
Cl
S
Me
7ca
7.38
7.36
7.20
7.19
7.05
2.37
2.06
2.05
1.00
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


Br
Cl
S
Me
7ca
142.53
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130.05
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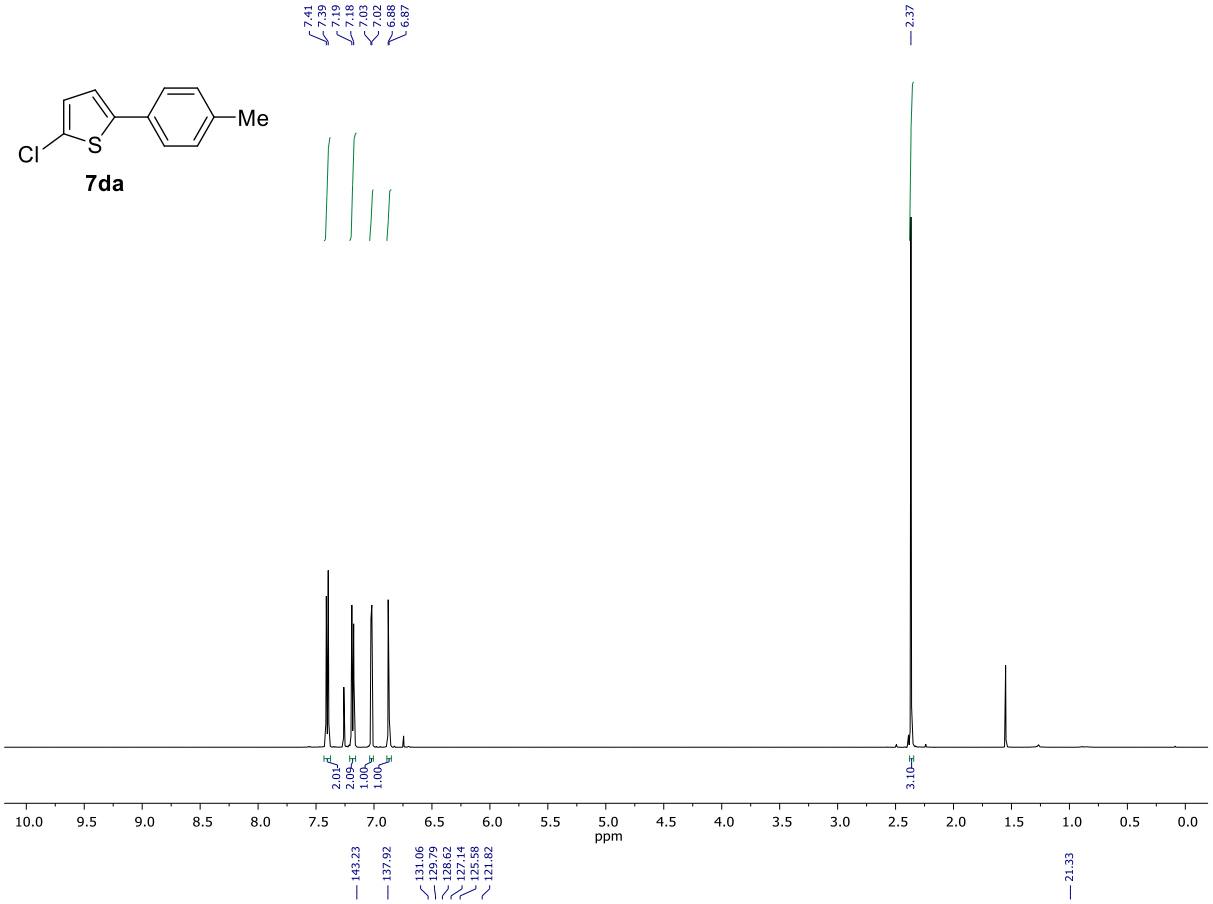
125.45
125.09
124.50
111.17
21.38
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.19
7.18
7.03
7.02
6.88
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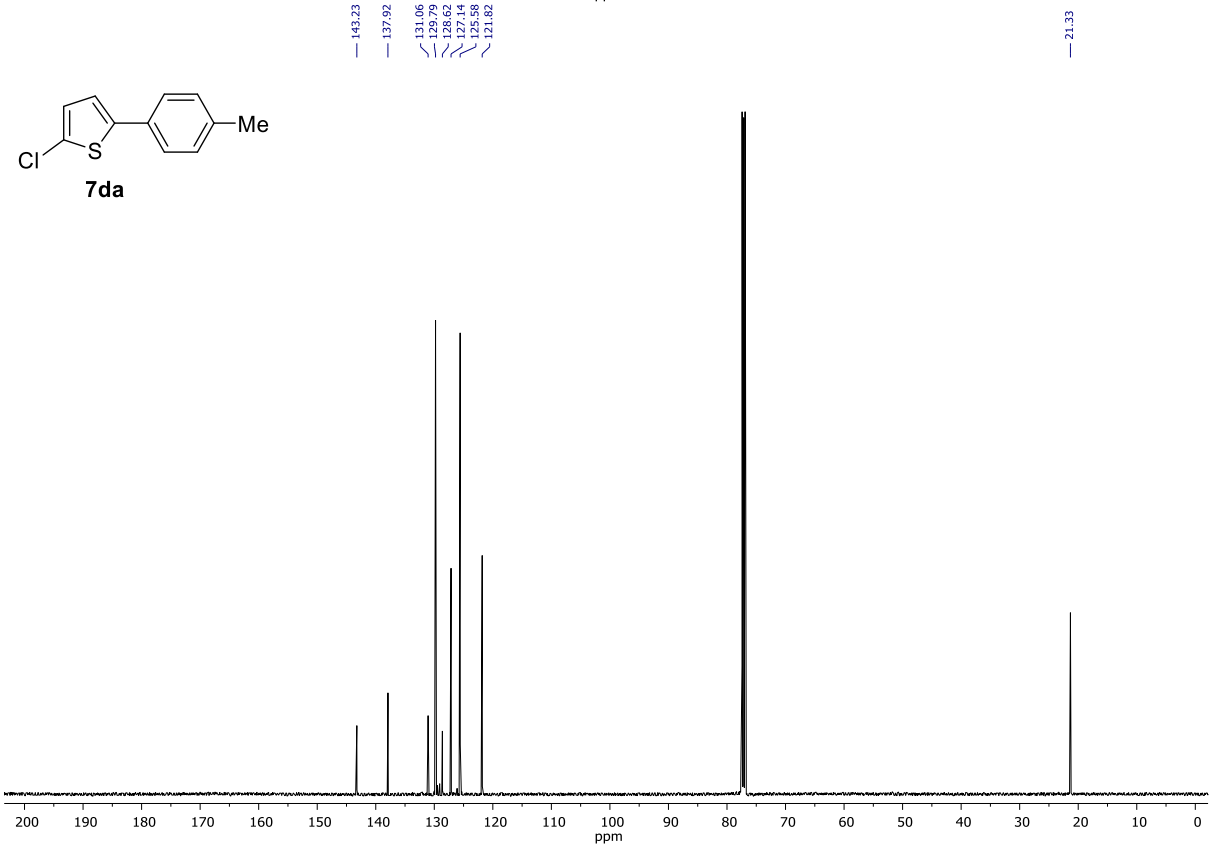
2.37
Cl
S
Me
7da
2.01
2.09
1.00
1.00
3.10
ppm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129.79
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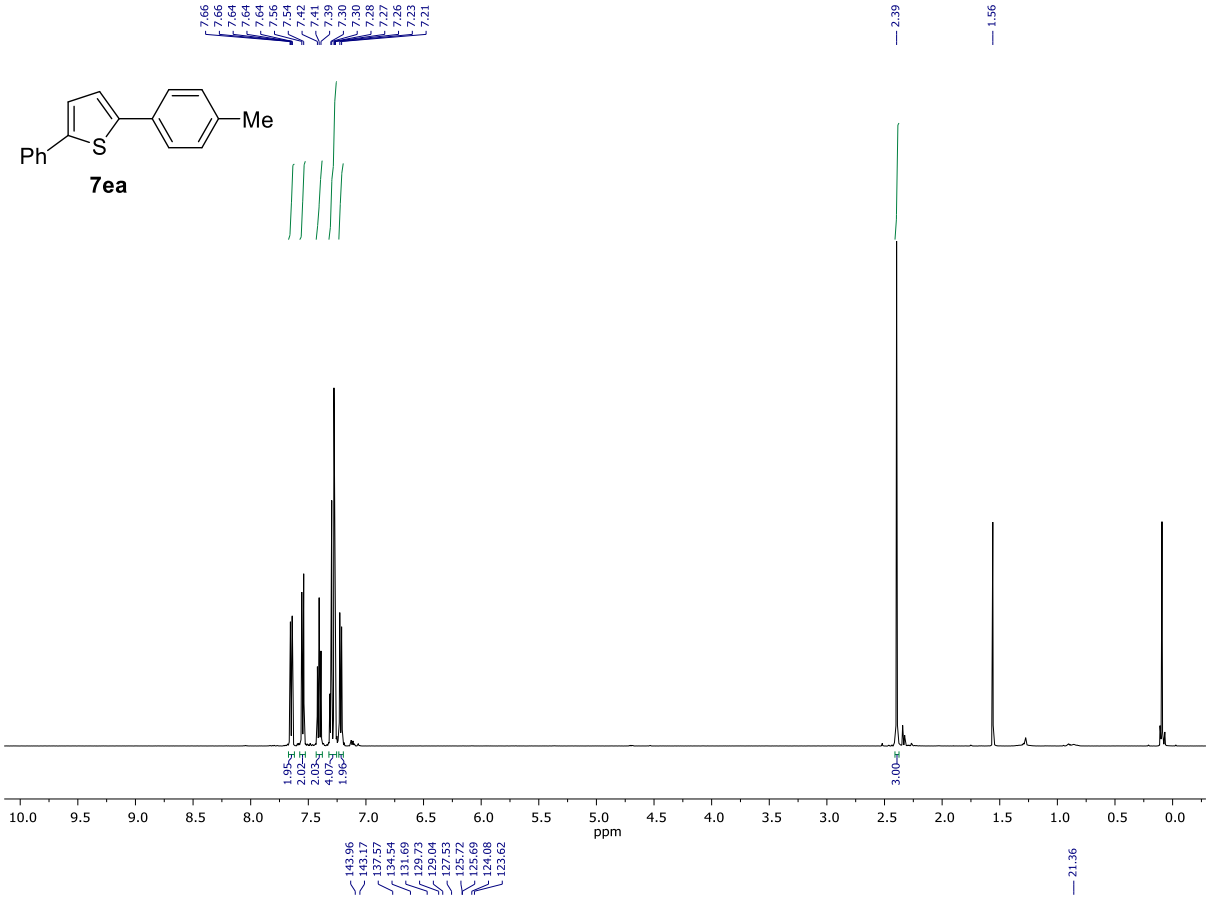
127.14
125.58
121.82
21.33
Cl
S
Me
7da
ppm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7.64
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7.42
7.41
7.39
7.30
7.30
7.28
7.27
7.26
7.23
7.21
2.39
1.56
Me
Ph
S
7ea
1.95
2.02
2.03
4.07
1.96
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
2.0
1.5
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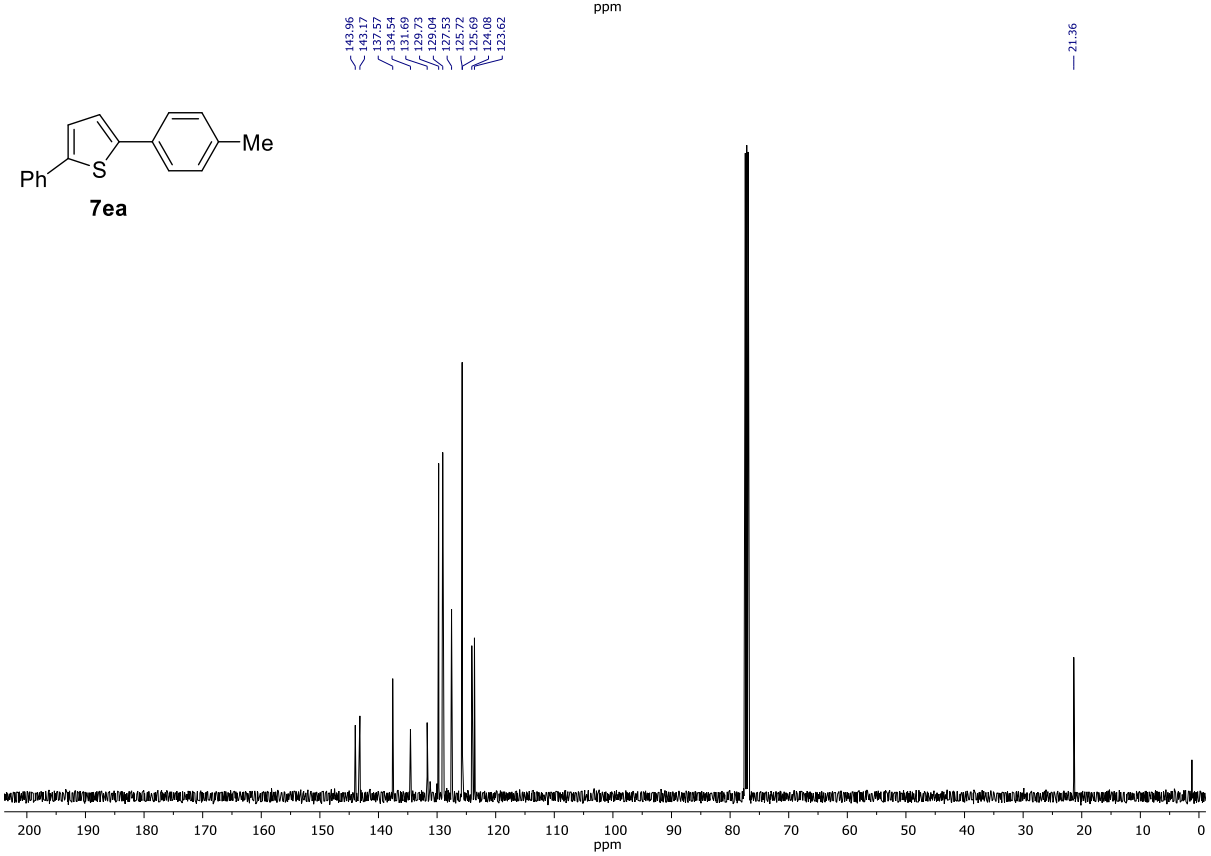
ppm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127.53
125.72
125.69
124.08
123.62
21.36
Me
Ph
S
7ea
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm