

Supporting information

Generation of the CF₃ Radical from Trifluoromethyl Sulfonium Salt and Its Trifluoromethylation of Styrenes

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Experimental Details	S2
1. General.....	S2
2. Synthesis of <i>S</i>-(trifluoromethyl)diphenylsulfonium Salt [Ph₂SCF₃]⁺[OTf]⁻.....	S2
3. General Procedure for the Synthesis of Styrenes 1b-i, 1k.....	S2
4. General Procedure for the Synthesis of Styrenes 1j.....	S3
5. General Procedure for the Oxidative-trifluoromethylation of Styrenes 1a-l.....	S3
References.....	S6
The ¹⁹F NMR Analysis of Reaction Mixture.....	S7
Copies of NMR Spectra for 1b-k.....	S13
Copies of NMR Spectra for 2a-k.....	S17

Experimental Details

1. General

Unless otherwise stated, NMR spectra were recorded in CDCl₃ at 300 MHz (¹H NMR), 282 MHz (¹⁹F NMR) and 100 MHz (¹³C NMR). All chemical shifts are reported in ppm relative to TMS or CFCl₃ (positive for downfield shifts) as external standards. MS experiments were performed on an Agilent 5973N instrument for EI-MS and a Waters Micromass GCT Premier instrument for HRMS. DMF (≥99.5%) and Na₂S₂O₄ (≥90.0%) or HOCH₂SO₂Na·2H₂O (≥99.0%) were used without any purification. *S*-(trifluoromethyl)diphenylsulfonium triflate [Ph₂SCF₃]⁺[OTf]⁻ was synthesized according to the literature procedure.¹ Styrenes (**1b-k**) were all prepared according to the literature.² Other reagents used below were all purchased from commercial sources.

2. Synthesis of *S*-(trifluoromethyl)diphenylsulfonium Salt [Ph₂SCF₃]⁺[OTf]⁻¹

Under a nitrogen atmosphere, benzene (20 mL, 0.220 mol) and trifluoromethanesulfonic anhydride (17 mL, 0.100 mol) were added into a suspension of sodium trifluoromethylsulfinate (6.98 g, 44.7 mmol) in dichloromethane (5 mL), which was well cooled by an ice-bath. After vigorously stirring at 0 °C for 1.5 h, the reaction mixture was warmed to room temperature and allowed to react for 34 hours. Then the reaction mixture was diluted with CH₂Cl₂ (150 mL), washed successively with saturated aqueous NaHCO₃ and saturated brine and dried over Na₂SO₄. After concentration under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane / acetonitrile (4:1) as the eluent. 4.53 g of [Ph₂SCF₃]⁺[OTf]⁻ (11.2 mmol, 25%) was obtained as a light yellow solid. ¹H NMR (CD₃COCD₃): δ 8.43 (d, *J* = 8.1 Hz, 4H), 8.13 (t, *J* = 7.5 Hz, 2H), 8.00 (t, *J* = 8.1 Hz, 4H). ¹⁹F NMR: δ -51.0 (s, 3F), -78.5 (s, 3F).

3. General Procedure for the Synthesis of Styrenes **1b-i**, **1k**^{2a}

4-Nitrobenzaldehyde (0.151g, 1.0 mmol) was dissolved in dry THF (10 mL). Methyltriphenylphosphonium iodide (0.448 g, 1.1 mmol) and DBU (0.20 mL, 1.3 mmol) were added. The reaction mixture was then stirred at room temperature overnight. After diluted by ethyl ether (30 mL), the reaction mixture was washed with water (3×20 mL), dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 12:1), providing 1-nitro-4-vinylbenzene **1c** (0.072 g, 0.48 mmol, 48% yield) as yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 6.79 (dd, *J* = 17.6 Hz, *J* = 10.9 Hz, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 5.50 (d, *J* = 10.9 Hz, 1H).

1-nitro-3-vinylbenzene (**1b**): 45% yield, yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ 8.26 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 17.6 Hz, *J* = 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H).

3-vinylbiphenyl (**1d**): 23% yield, colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.61-7.59 (m, 3H), 7.50-7.33 (m, 6H), 6.79 (dd, *J* = 17.5 Hz, *J* = 10.8 Hz, 1H), 5.82 (d, *J* = 17.5 Hz, 1H), 5.30 (d, *J* = 10.8 Hz, 1H).

4-vinylbiphenyl (**1e**): The reaction mixture was refluxed overnight. 27% yield, white solid. ¹H

NMR (300 MHz, CDCl₃): δ 7.58 (m, 4H), 7.49-7.40 (m, 4H), 7.33 (t, $J = 7.4$ Hz, 1H), 6.75 (dd, $J = 17.7$ Hz, $J = 10.9$ Hz, 1H), 5.78 (d, $J = 17.7$ Hz, 1H), 5.26 (d, $J = 10.9$ Hz, 1H).

1-chloro-2-vinylbenzene (**1f**): The reaction mixture was refluxed overnight. 47% yield, colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.56 (dd, $J = 7.3$ Hz, $J = 2.0$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, $J = 1.7$ Hz, 1H), 7.11 (dd, $J = 17.5$ Hz, $J = 11.1$ Hz, 1H), 5.74 (d, $J = 17.5$ Hz, 1H), 5.38 (d, $J = 11.1$ Hz, 1H).

1-chloro-4-vinylbenzene (**1g**): 30% yield, colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.34 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H), 6.67 (dd, $J = 17.5$ Hz, $J = 10.9$ Hz, 1H), 5.72 (d, $J = 17.5$ Hz, 1H), 5.27 (d, $J = 10.9$ Hz, 1H).

1-bromo-4-vinylbenzene (**1h**): The reaction mixture was refluxed overnight. 43% yield, colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.44 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.65 (dd, $J = 17.6$ Hz, $J = 10.8$ Hz, 1H), 5.74 (d, $J = 17.6$ Hz, 1H), 5.28 (d, $J = 10.8$ Hz, 1H).

1-methyl-4-vinylbenzene (**1i**): The reaction mixture was refluxed overnight. 80% yield, colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.31 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 6.69 (dd, $J = 17.6$ Hz, $J = 10.9$ Hz, 1H), 5.69 (d, $J = 17.6$ Hz, 1H), 5.18 (d, $J = 10.9$ Hz, 1H).

1-vinylnaphthalene (**1k**): The reaction mixture was refluxed overnight. 74% yield, colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 8.12 (dm, $J = 8.3$ Hz, 1H), 7.85 (dm, $J = 8.3$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 7.1$ Hz, 1H), 7.54-7.43 (m, 4H), 5.79 (dd, $J = 17.3$ Hz, $J = 1.5$ Hz, 1H), 5.48 (dd, $J = 10.9$ Hz, $J = 1.4$ Hz, 1H).

4. Procedure for the Synthesis of Styrene **1j**^{2b}

Methyltriphenylphosphonium iodide (0.868 g, 2.14 mmol) was dissolved in dry DMF (5 mL) at 0 °C. Sodium hydride (0.334 g, 57.6%, 8.01 mmol) and 4-methoxybenzaldehyde (0.28 mL, 2.26 mmol) were then added. After keeping at 0 °C for 2 h, the reaction mixture was allowed to stir at room temperature for 8 h. EtOH (5 mL) was added and the reaction mixture was diluted with ethyl ether (30 mL). The organic layer was then washed with water (5×20 mL), dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: petroleum ether), yielding 4-methoxystyrene **1j** (0.030 g, 0.224 mmol, 10% yield) in the form of colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.35 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.66 (dd, $J = 17.5$ Hz, $J = 10.9$ Hz, 1H), 5.61 (d, $J = 17.5$ Hz, 1H), 5.12 (d, $J = 10.9$ Hz, 1H), 3.81 (s, 3H).

5. General Procedure for the Oxidative-trifluoromethylation of Styrenes **1a-l**

General procedure for the oxidative-trifluoromethylation of styrenes: The styrene **1e** (27 mg, 0.15 mmol) and [Ph₂SCF₃]⁺[OTf]⁻ (120 mg, 0.30 mmol) were dissolved in DMF (4 mL) in a round-bottom flask (25 mL), cooling to 0 °C. Then HOCH₂SO₂Na·2H₂O (140 mg, 0.90 mmol) was added, and the reaction mixture was stirred at 0 °C for 6 h. After dilution with

diethyl ether, the mixture was washed with H₂O, dried over Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate (15:1)] to give 13 mg of pure **2e** (0.049 mmol, 33%): white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.52-7.42 (m, 3H), 3.83 (q, *J* = 10.0 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.4 (t, *J* = 10.0 Hz, 3F).

3,3,3-trifluoro-1-phenylpropan-1-one (**2a**): white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.1 Hz, 2H), 3.81 (q, *J* = 9.7 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.4 (t, *J* = 9.7 Hz, 3F).

3,3,3-trifluoro-1-(3-nitrophenyl)propan-1-one (**2b**): white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.76 (s, 1H), 8.51 (d, *J* = 7.9 Hz, 1H), 8.30 (t, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 3.88 (q, *J* = 9.9 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.4 (t, *J* = 9.9 Hz, 3F).

3,3,3-trifluoro-1-(4-nitrophenyl)propan-1-one (**2c**): white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.11 (t, *J* = 8.8 Hz, 2H), 3.86 (q, *J* = 9.7 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.4 (t, *J* = 9.7 Hz, 3F).

1-(biphenyl-3-yl)-3,3,3-trifluoropropan-1-one (**2d**): yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ 8.15 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.62-7.56 (m, 3H), 7.51-7.38 (m, 3H), 3.85 (q, *J* = 10.0 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -61.7 (t, *J* = 10.0 Hz, 3F). ¹³C NMR (100 MHz, CDCl₃): 189.7, 142.3, 139.8, 136.4, 132.8, 129.4, 129.1, 128.1, 127.2, 127.1, 127.1, 124.0 (*J* = 276.5 Hz), 42.3 (*J* = 27.9 Hz). EI-MS (*m/z*, %): 264 (39.2), 182 (18.9), 181 (88.9), 155 (10.3), 153 (64.7), 152 (100), 151 (25.3), 76 (16.8). IR (KBr): 3064, 3034, 2933, 2855, 1701, 1599, 1586, 1501, 1480, 1454, 1423, 1371, 1337, 1278, 1217, 1104, 1055, 1032, 999, 936, 909, 854, 801, 757, 698, 616, 550, 532, 504 cm⁻¹. HRMS for C₁₅H₁₁F₃O: 264.0762; Found: 264.0763.

1-(2-chlorophenyl)-3,3,3-trifluoropropan-1-one (**2f**): yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.47-7.44 (m, 2H), 7.40-7.35 (m, 1H), 3.86 (q, *J* = 10.0 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.0 (t, *J* = 10.0 Hz, 3F).

1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one (**2g**): white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.88 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 3.77 (q, *J* = 10.3 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -61.9 (t, *J* = 10.3 Hz, 3F).

1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one (**2h**): white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 3.77 (q, *J* = 10.0 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.4 (t, *J* = 10.0 Hz, 3F).

3,3,3-trifluoro-1-*p*-tolylpropan-1-one (**2i**): white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.76 (q, *J* = 10.0 Hz, 2H), 2.44 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ -62.0 (t, *J* = 10.0 Hz, 3F).

3,3,3-trifluoro-1-(4-methoxyphenyl)propan-1-one (**2j**): yellow liquid. ^1H NMR (300 MHz, CDCl_3): δ 7.92 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.90 (s, 3H), 3.74 (q, $J = 10.0$ Hz, 2H). ^{19}F NMR (282 MHz, CDCl_3): δ -62.4 (t, $J = 10.0$ Hz, 3F).

3,3,3-trifluoro-1-(naphthalen-1-yl)propan-1-one (**2k**): yellow liquid. ^1H NMR (300 MHz, CDCl_3): δ 8.71 (d, $J = 8.7$ Hz, 1H), 8.07 (d, $J = 8.1$ Hz, 1H), 7.89 (t, $J = 7.8$ Hz, 2H), 7.67-7.51 (m, 3H), 3.91 (q, $J = 10.0$ Hz, 2H). ^{19}F NMR (282 MHz, CDCl_3): δ -61.8 (t, $J = 10.0$ Hz, 3F). ^{13}C NMR (100 MHz, CDCl_3): 192.9, 134.2, 134.1, 134.0, 130.2, 128.8, 128.6, 127.0, 125.6, 124.9, 124.2, 124.0 ($J = 276.6$ Hz), 45.0 ($J = 27.8$ Hz). EI-MS (m/z , %): 238 (29.4), 156 (15.7), 155 (100), 128 (15.3), 127 (97.3), 126 (21.1), 77 (11.6), 63 (9.69). IR (KBr): 3053, 2930, 2855, 1690, 1595, 1574, 1508, 1464, 1418, 1397, 1361, 1266, 1235, 1215, 1186, 1139, 1104, 1081, 951, 924, 855, 803, 792, 776, 668, 649, 619, 560, 511, 487 cm^{-1} . HRMS for $\text{C}_{13}\text{H}_9\text{F}_3\text{O}$: 238.0605; Found: 238.0607.

References

- (1) (a) E. Magnier, J. C. Blazejewski, M. Tordeux and C. Wakselman, *Angew. Chem. Int. Ed.* 2006, **45**, 1279. (b) Y. Mace, B. Raymondeau, C. Pradet, J. -C. Blazejewski and E. Magnier, *Eur. J. Org. Chem.* 2009, 1390. (c) C. -P. Zhang, H. -P. Cao, Z. -L. Wang, C. -T. Zhang, Q. -Y. Chen and J. -C. Xiao, *Synlett.* 2010, **7**, 1089.
- (2) (a) D. Simoni, M. Rossi, R. Rondanin, A. Mazzali, R. Baruchello, C. Malagutti, M. Roberti and F. P. Invidiata, *Org. Lett.* 2000, **2**, 3765. (b) K. Ahmad, N. F. Thomas, M. R. Mukhtar, I. Noorbatcha, J. -F. F. Weber, M. A. Nafiah, S. S. Velu, K. Takeya, H. Morita, C. -G. Lim, A. H. A. Hadi and K. Awang, *Tetrahedron* 2009, **65**, 1504.

The ^{19}F NMR Analysis of Reaction Mixture

Table 1, entry 2

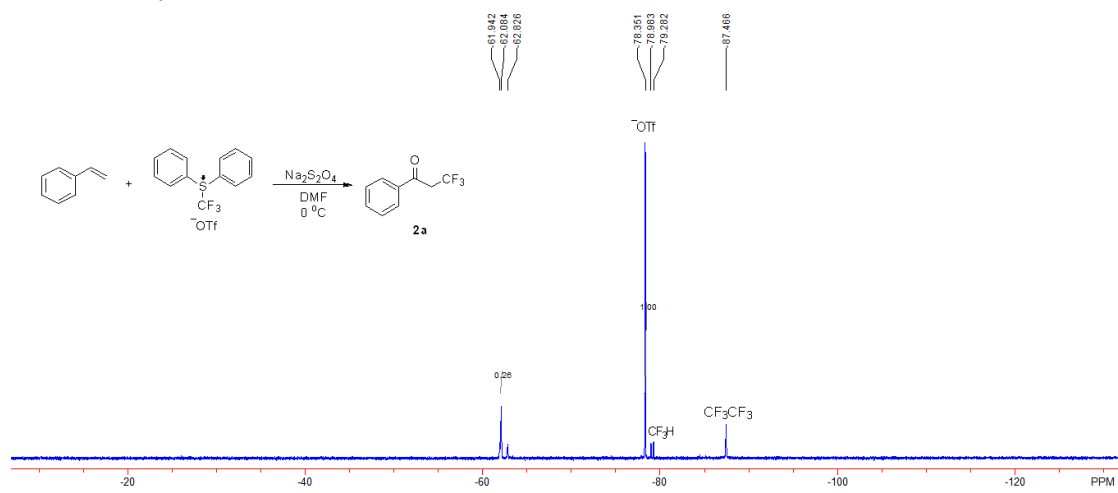


Table 1, entry 5

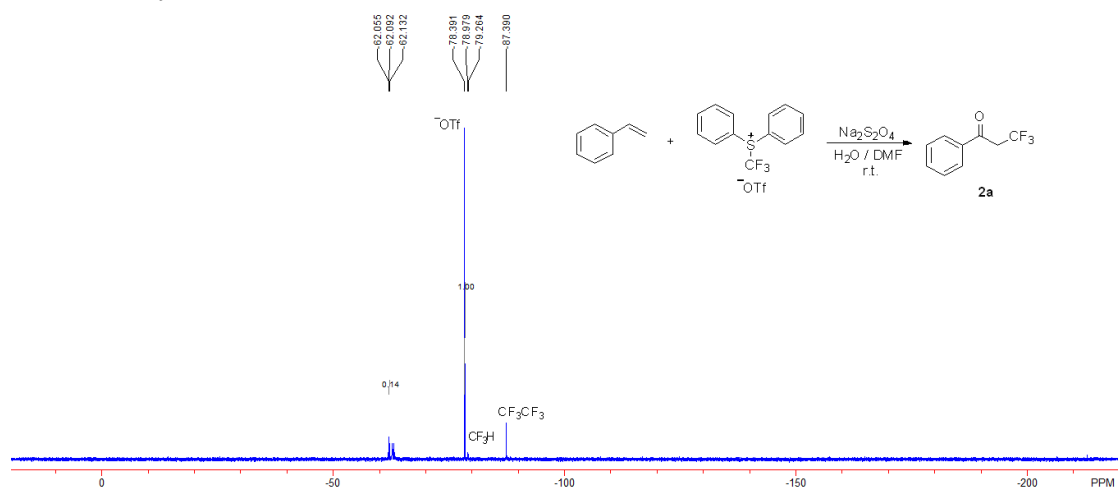


Table 1, entry 6

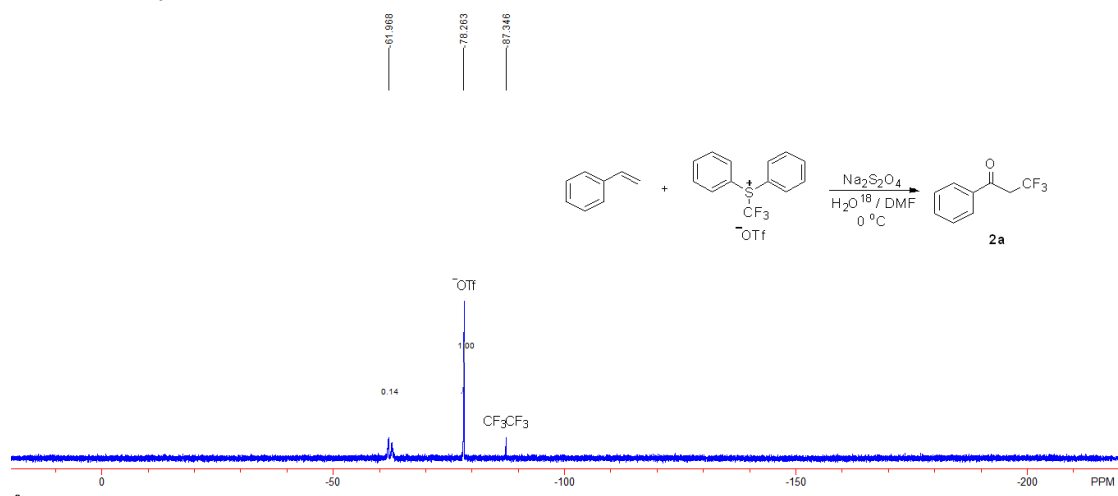


Table 1, entry 7

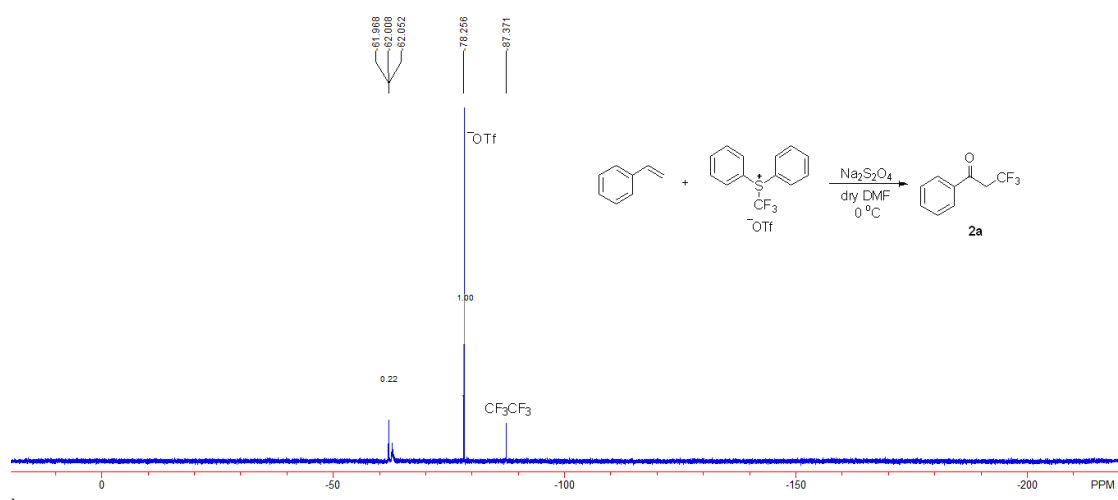


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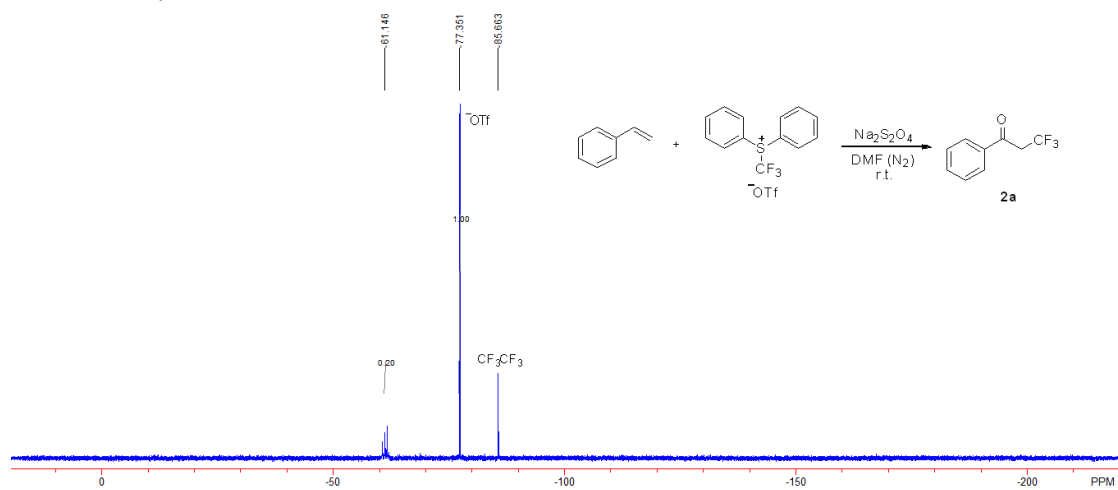


Table 1, entry 13

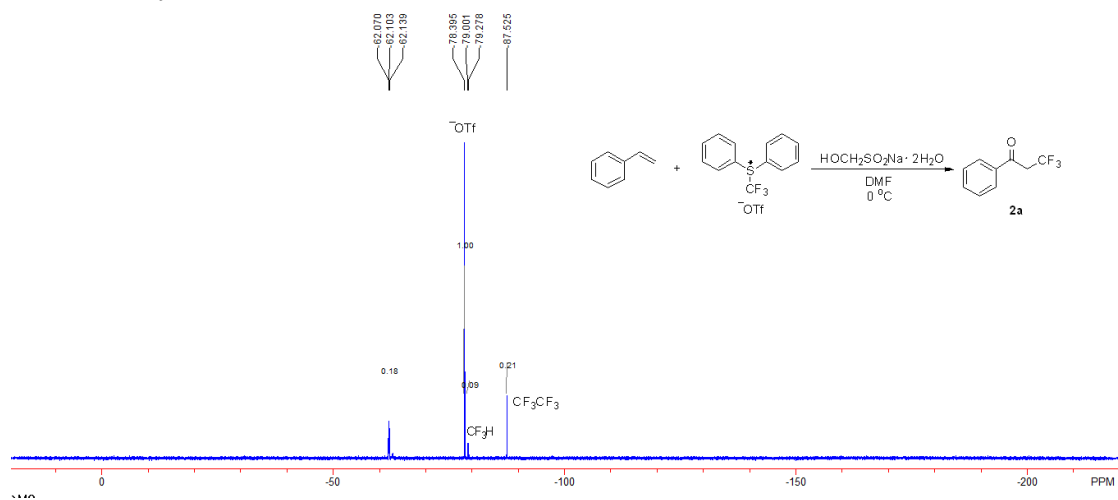


Table 2, entry 1

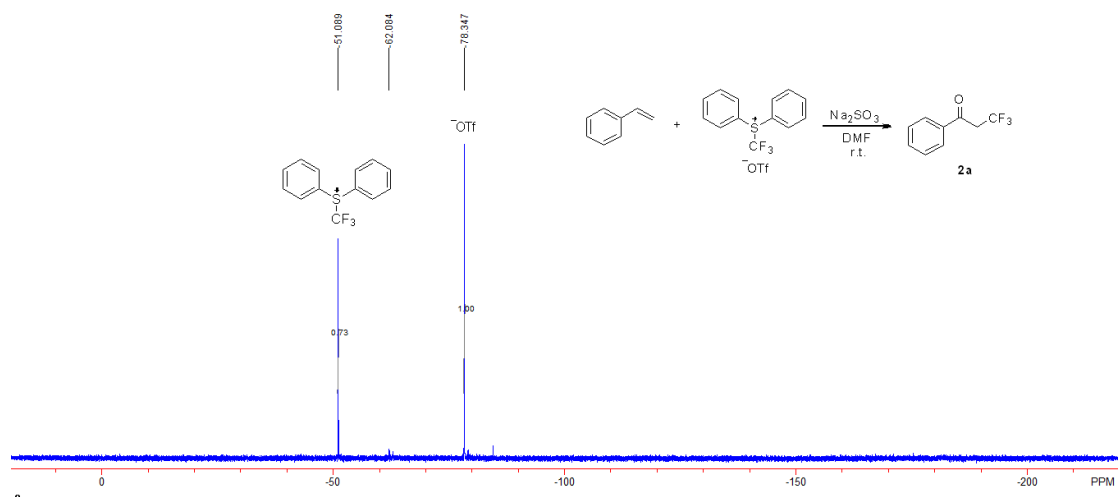


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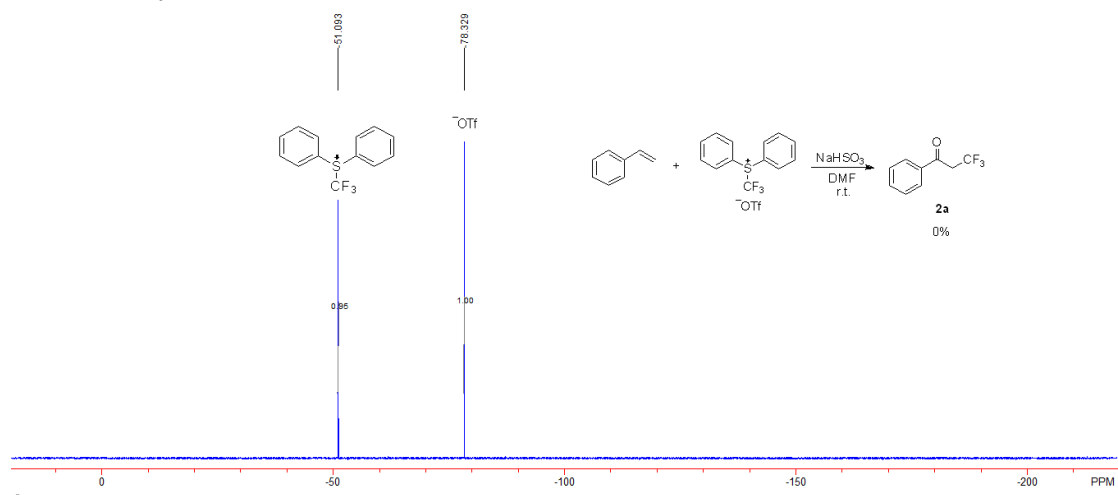


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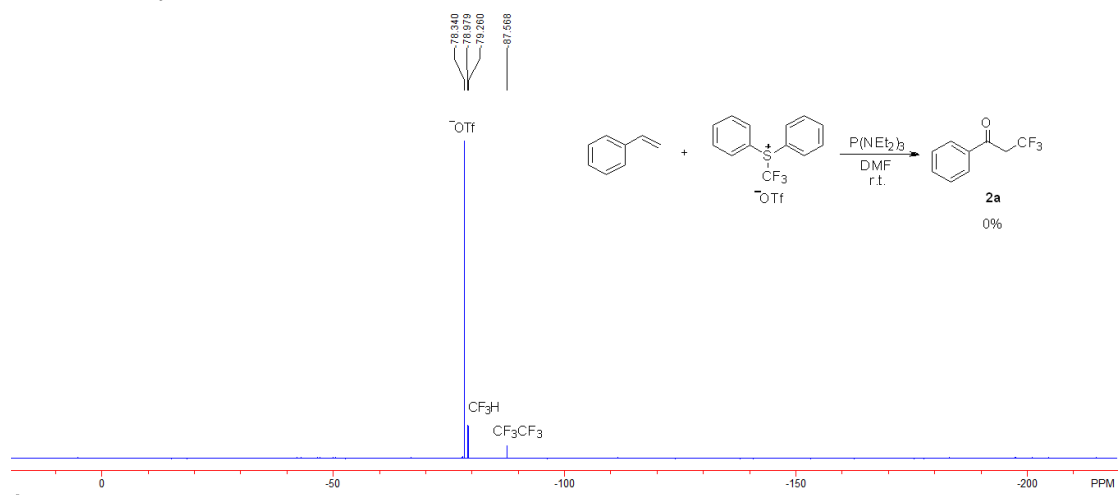


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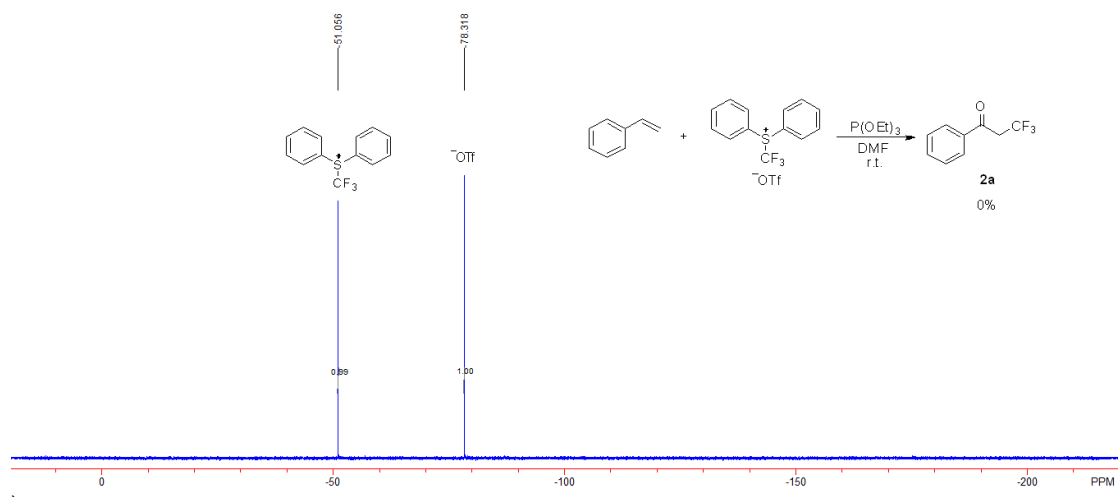


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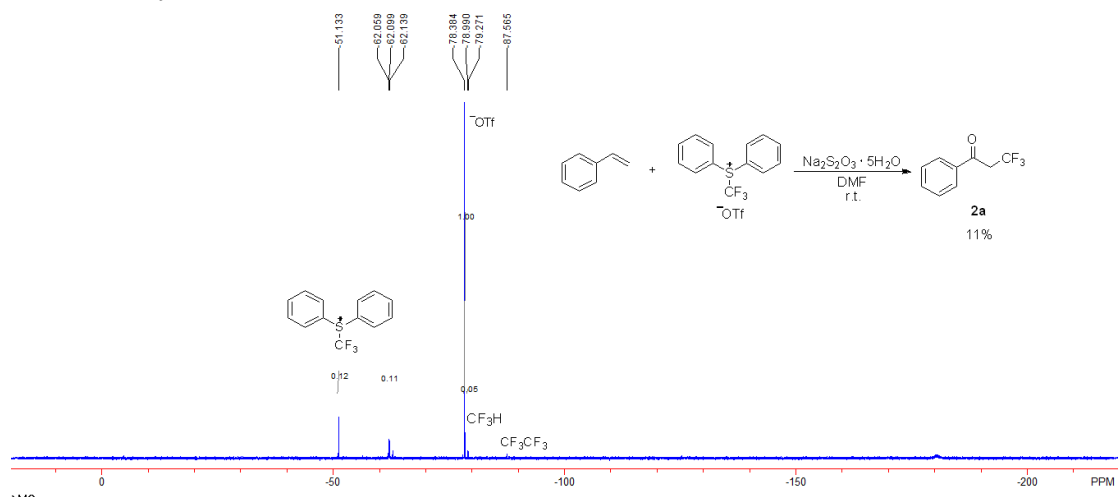


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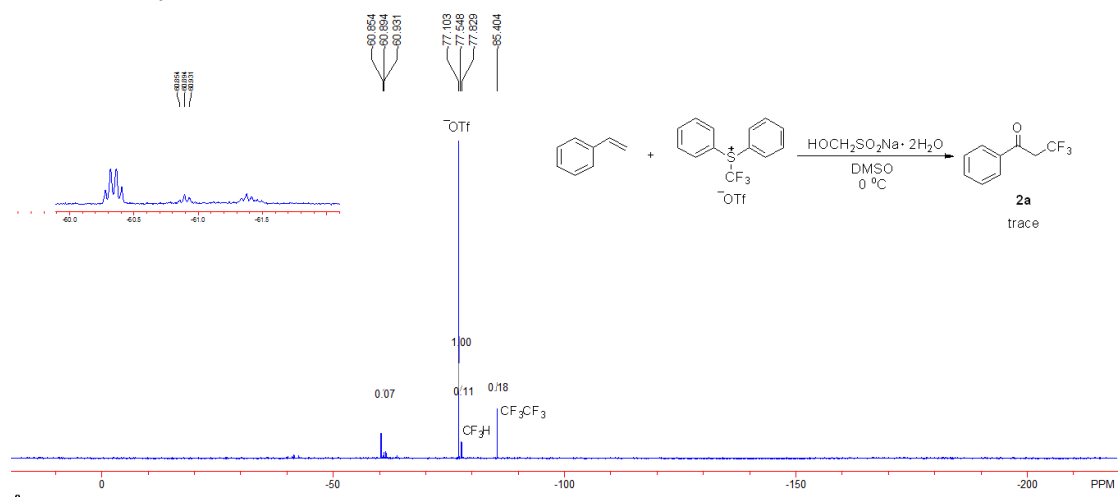


Table 2, entry 7



Table 2, entry 8

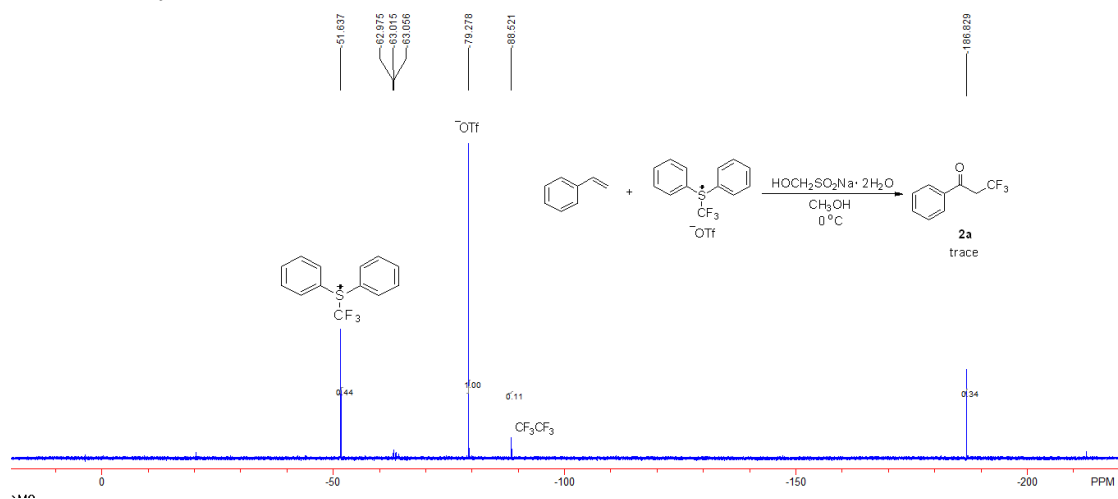


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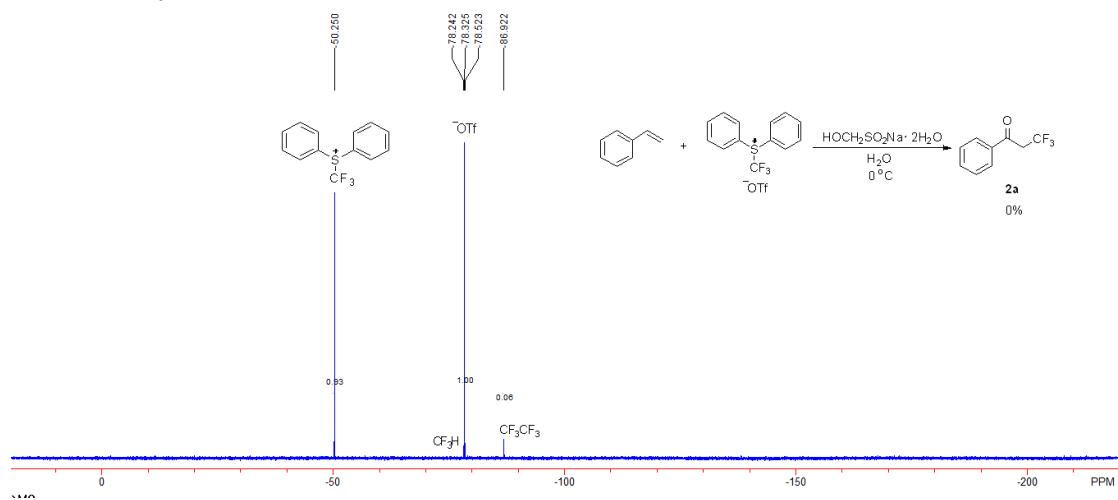


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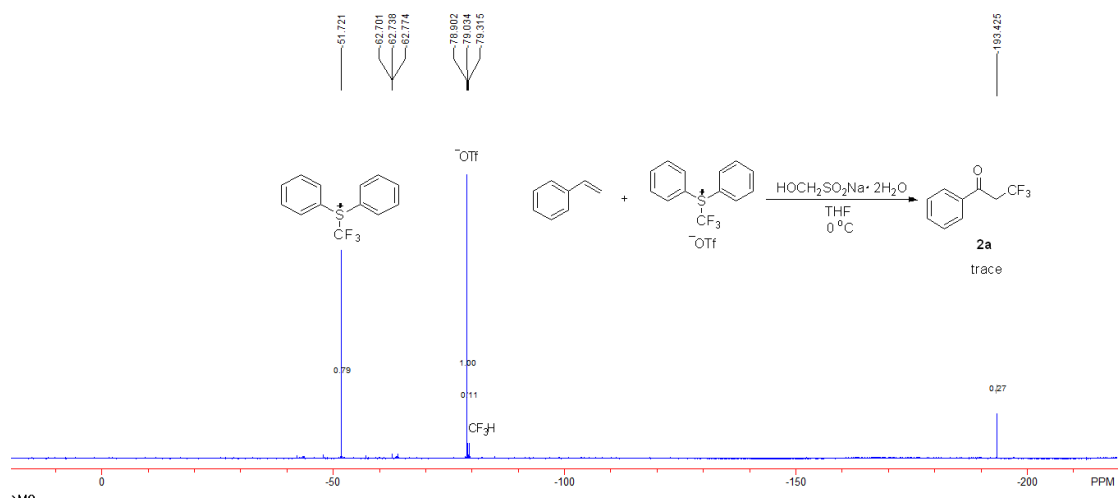


Table 2, entry 11

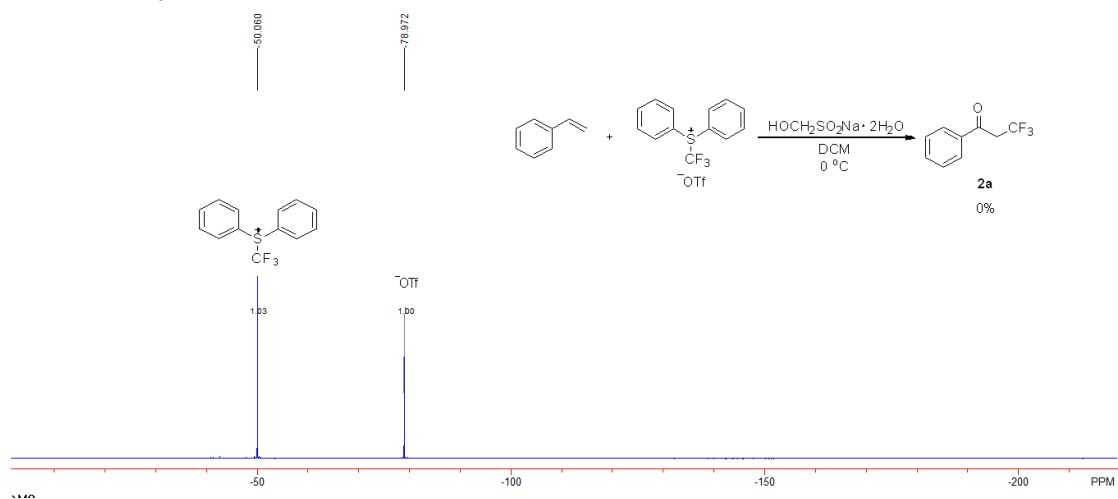
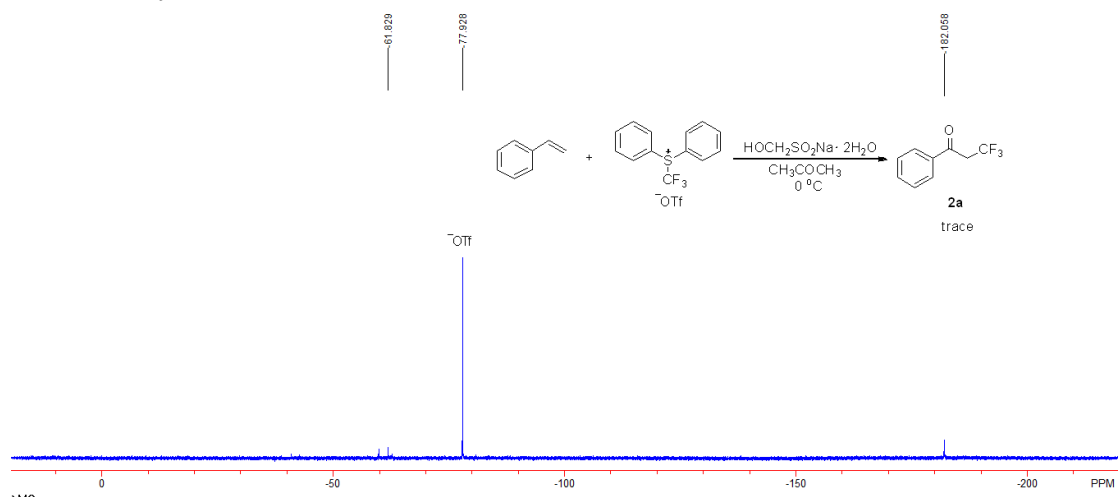
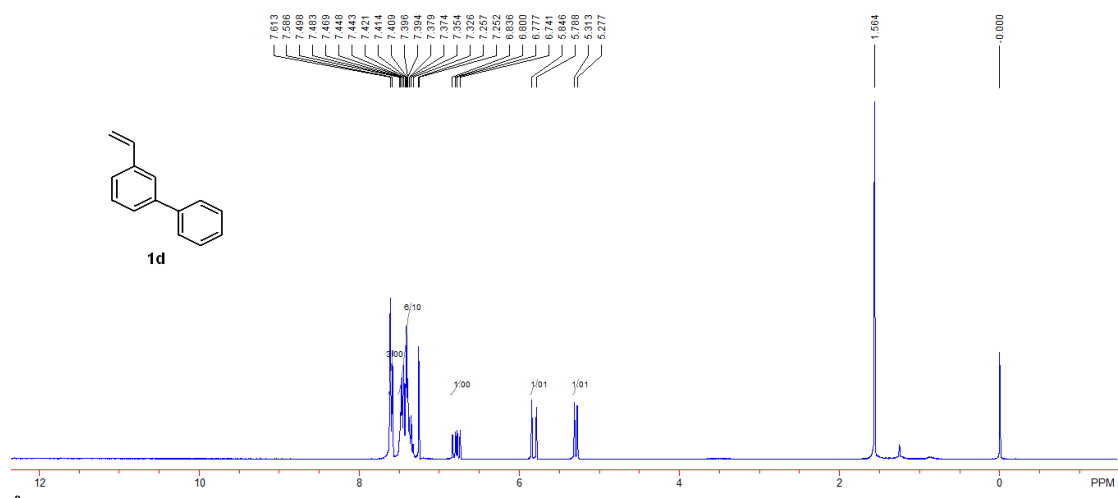
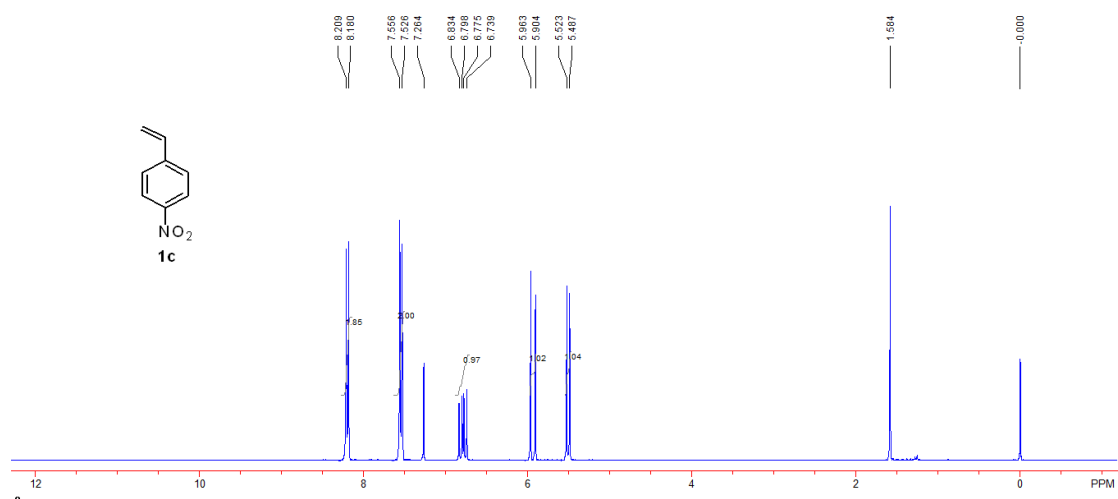
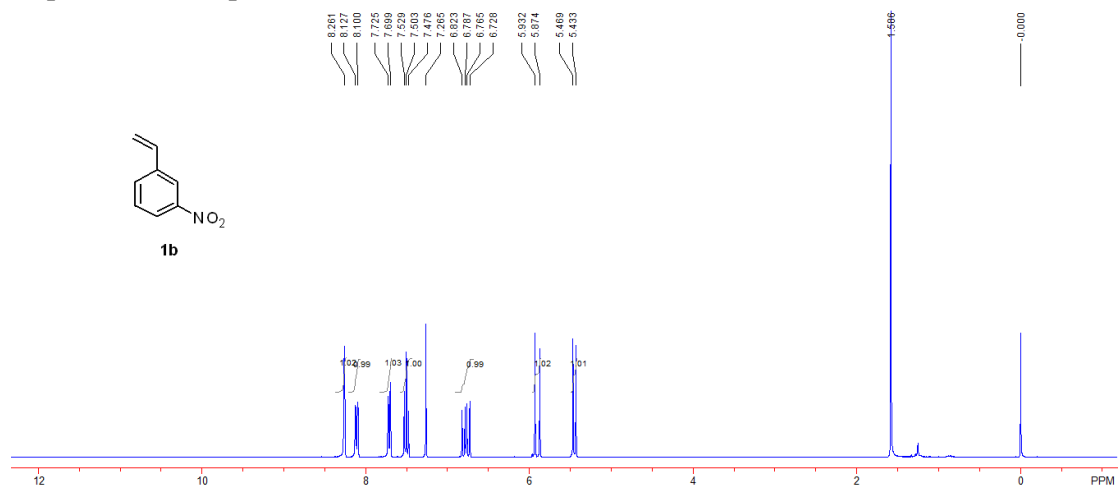
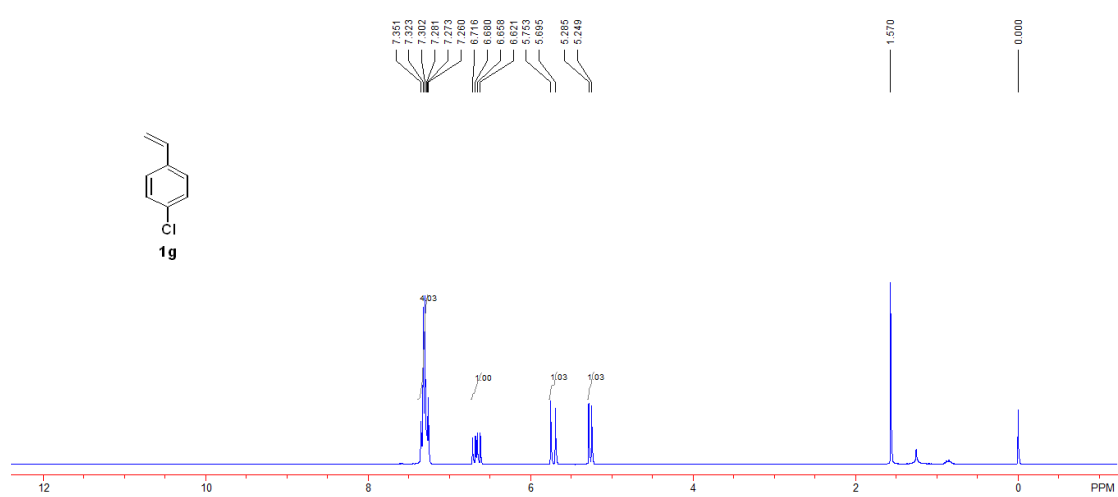
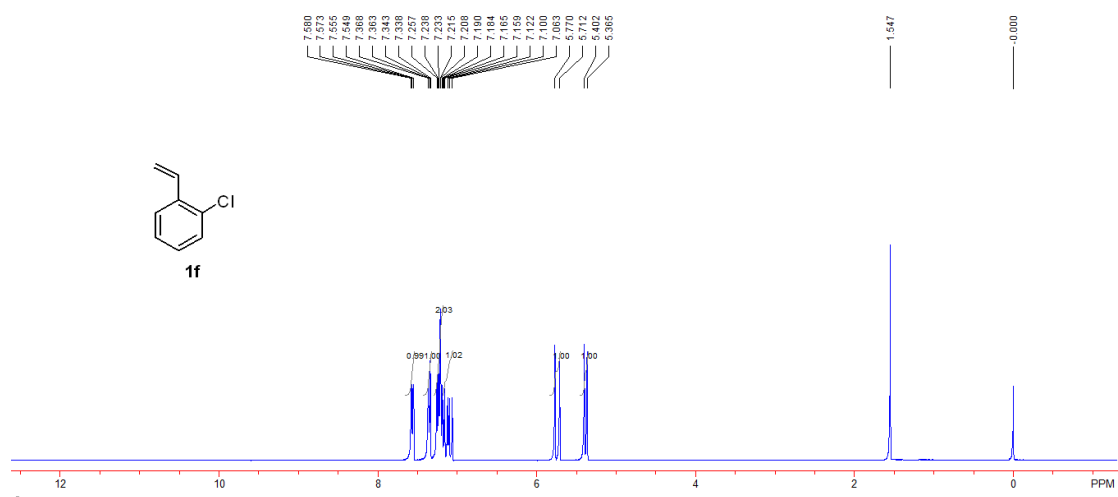
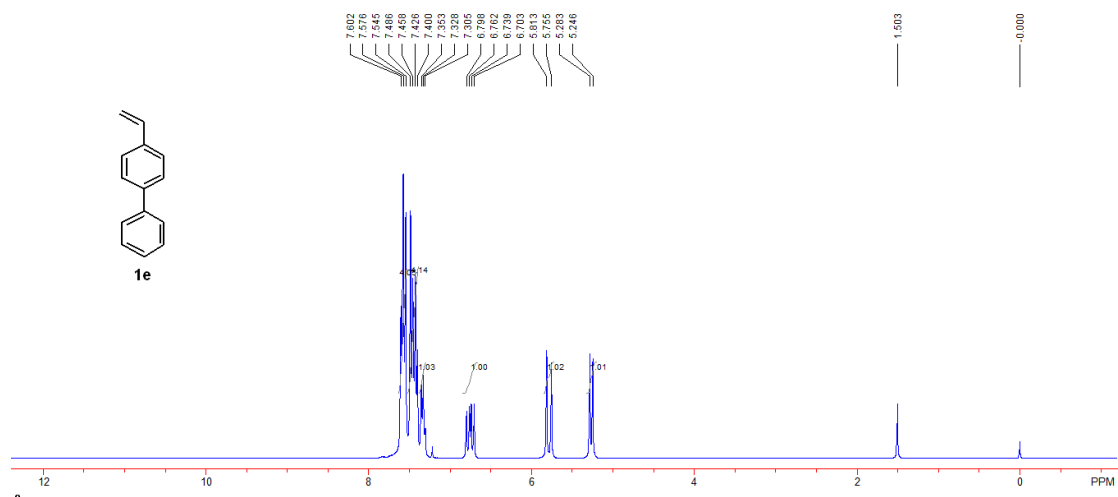


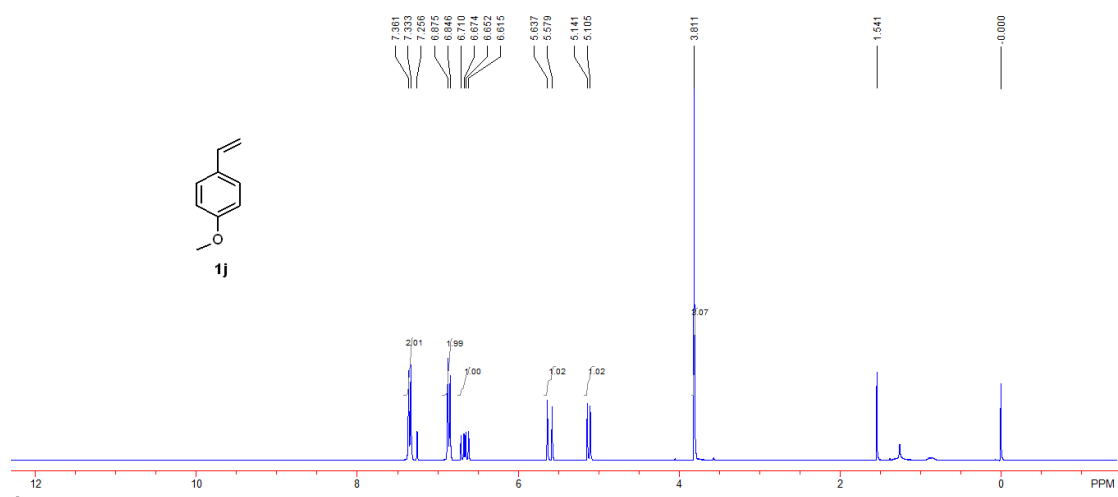
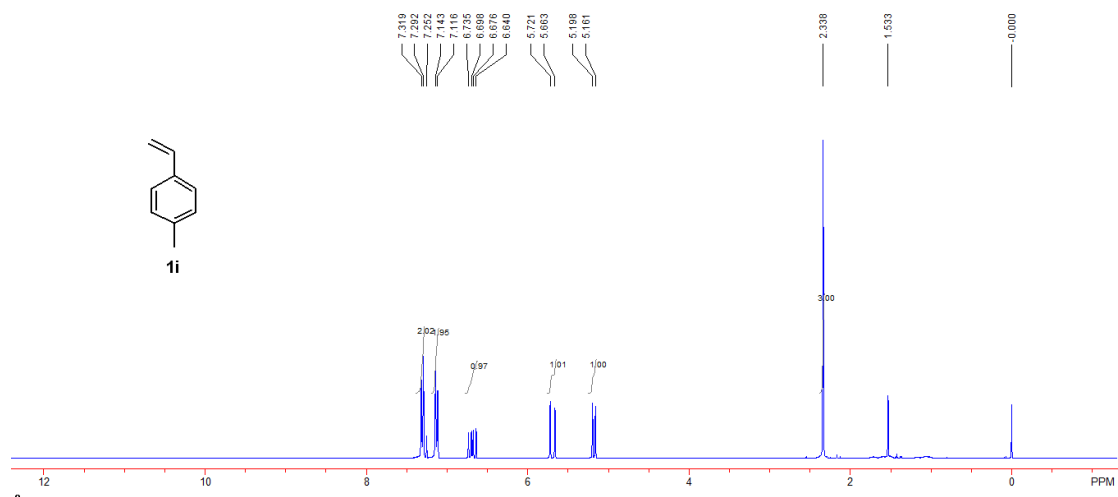
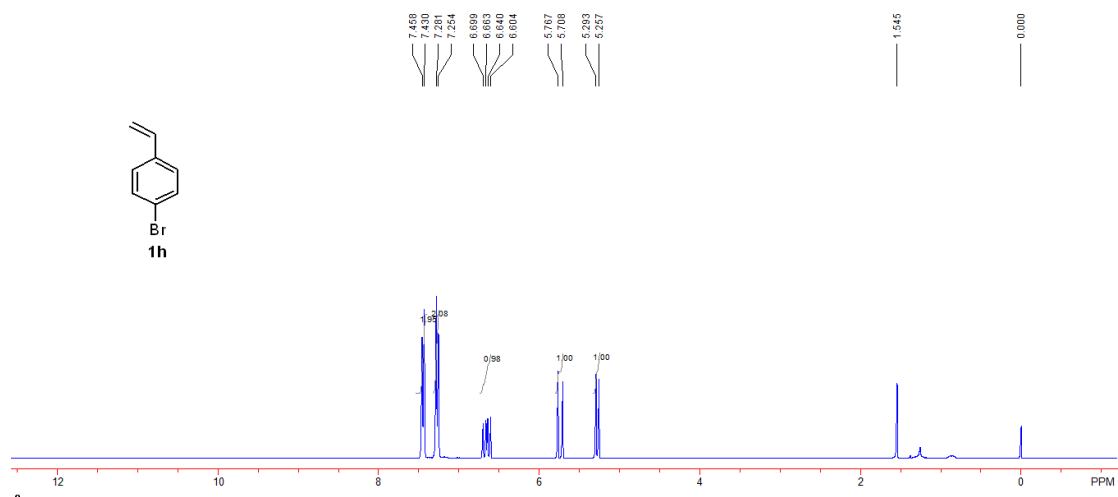
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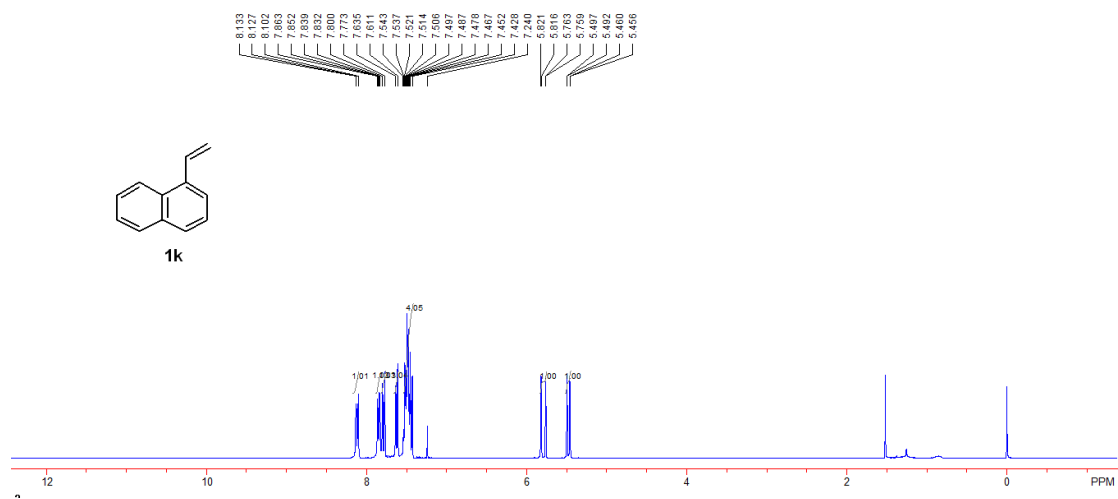


Copies of NMR Spectra for 1b-k









Copies of NMR Spectra for 2a-k

