

Supporting Information

Cobalt–Xantphos Catalyzed, LiCl-Mediated Preparation of Arylzinc

Reagents from Aryl Iodides, Bromides and Chlorides

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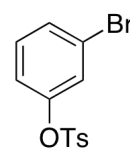
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Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Flash chromatography was performed as described by Still et al.,¹ using 40–63 μm silica gel. ^1H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl_3 (77.0 ppm), respectively. Gas chromatographic (GC) analysis was performed on a GC system equipped with an FID detector and a (5%-phenyl)-methylpolysiloxane capillary column (0.25 mm i.d. x 30 m, 0.25 μm film thickness). The melting points of solid materials were determined by a capillary melting point apparatus and are uncorrected. IR spectra are reported as wavenumber in cm^{-1} . Solid samples were dissolved in CHCl_3 (FTIR: 3019, 1216, 760, 671 cm^{-1}) for measurement, while liquid samples were measured as neat compounds.

Materials. Unless otherwise noted, chemicals were purchased from commercial suppliers and were used as received. THF was distilled over Na/benzophenone before use. Zinc powder (-100 mesh, 99.9%) was preactivated by the treatment with aq. HCl.² $\text{CoCl}_2(\text{Xantphos})$ was prepared according to the literature procedure.³ $\text{Pd}(\text{PPh}_3)_4$ was prepared according to the literature procedure.⁴ $\text{Me}_3\text{SiCH}_2\text{MgCl}$ was prepared from the corresponding halide and magnesium turnings in anhydrous THF and titrated before use. MgCl_2 was prepared from $\text{ClCH}_2\text{CH}_2\text{Cl}$ and magnesium turnings in anhydrous THF. Nona-1,2-diene was prepared according to the literature procedure.⁵

3-Bromophenyl 4-methylbenzenesulfonate: According to the literature procedure,⁶ the title compound was prepared by tosylation of 3-bromophenol (8.65 g, 50 mmol) with tosyl chloride (14.30 g, 75 mmol) and triethylamine



(10.12 g, 100 mmol) in CH_2Cl_2 (200 mL). Silica gel chromatography (eluent: hexane/EtOAc = 50/1, 25/1 and 10/1) of the crude product afforded the title compound as a white solid (15.74 g, 96%).

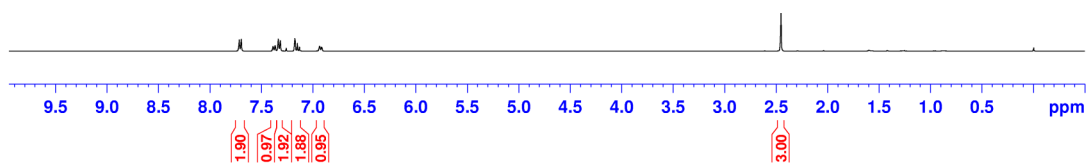
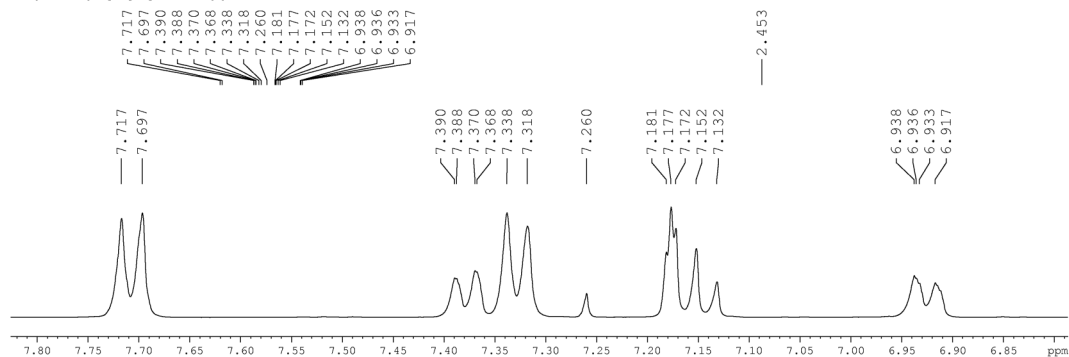
R_f 0.14 (hexane/EtOAc = 25/1); m.p. 51.8-53.6 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.45 (s, 3H), 6.92-6.94 (m, 1H), 7.13-7.18 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.37-7.39 (m, 1H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.7, 121.1, 122.4, 125.8, 128.5, 129.8, 130.3, 130.6, 132.0, 145.7, 149.9; FTIR (NaCl, CHCl_3): 1597, 1582, 1495, 1466, 1377, 1263, 1198, 1180, 1171, 1157, 1094, 1063, 887, 814, 752 (overlapped with CHCl_3 band); HRMS (ESI): Calcd for $\text{C}_{13}\text{H}_{12}^{79}\text{BrO}_3\text{S}$ $[\text{M} + \text{H}]^+$ 326.9691, found 326.9694.

References

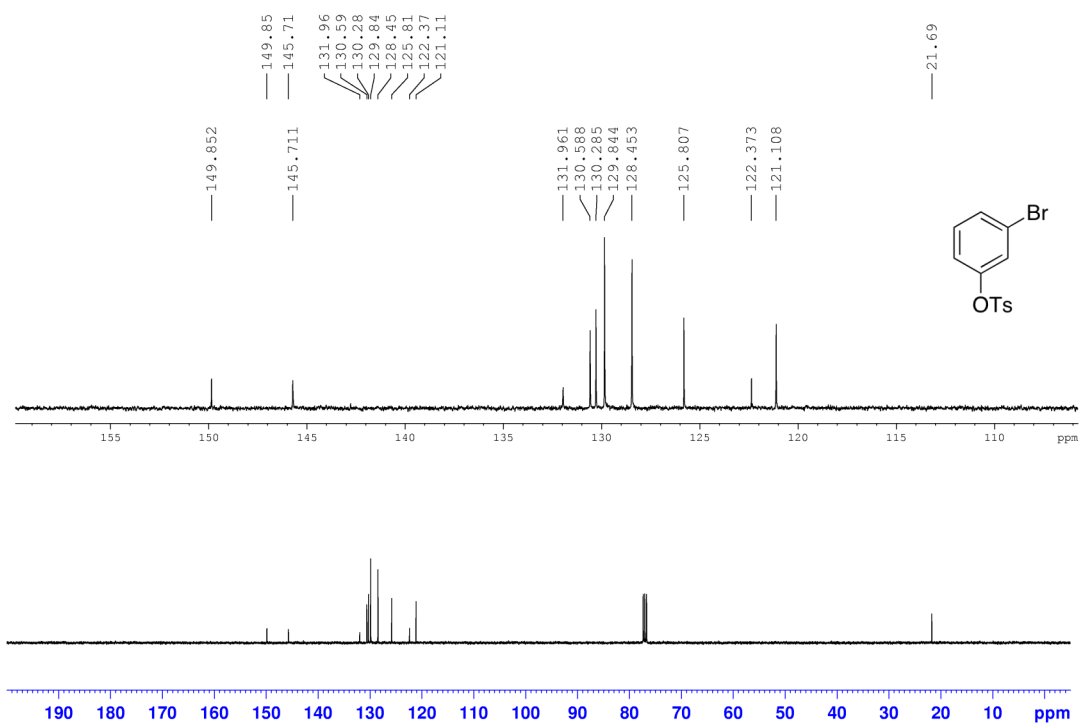
- (1) W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.
- (2) E. Nakamura, In *Organometallics in Synthesis A Manual*, 2nd ed. (Ed.: M. Schlossor), John Wiley & Sons: Chichester, **2002**, 579-664.
- (3) M. M. P. Grutters, C. Müller, D. Vogt, *J. Am. Chem. Soc.* **2006**, *128*, 7414.
- (4) D. R. Coulson, *Inorg. Synth.* **1990**, *28*, 107.
- (5) J. Kuang, S. Ma, *J. Org. Chem.* **2009**, *74*, 1763.
- (6) S. P. Cook, S. J. Danishefsky, *Org. Lett.* **2006**, *8*, 5693.
- (7) The melting point is in good agreement with that reported in literature: S. E. Hazlet, *J. Am. Chem. Soc.* **1937**, *59*, 287.

NMR Spectral Data

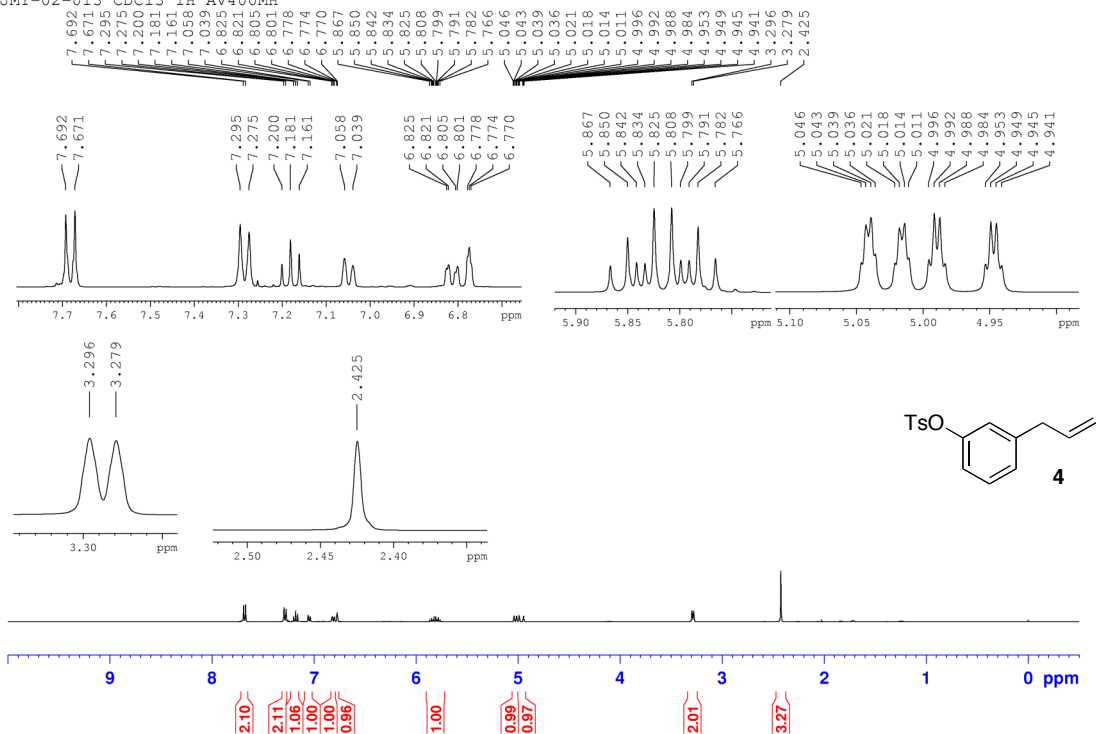
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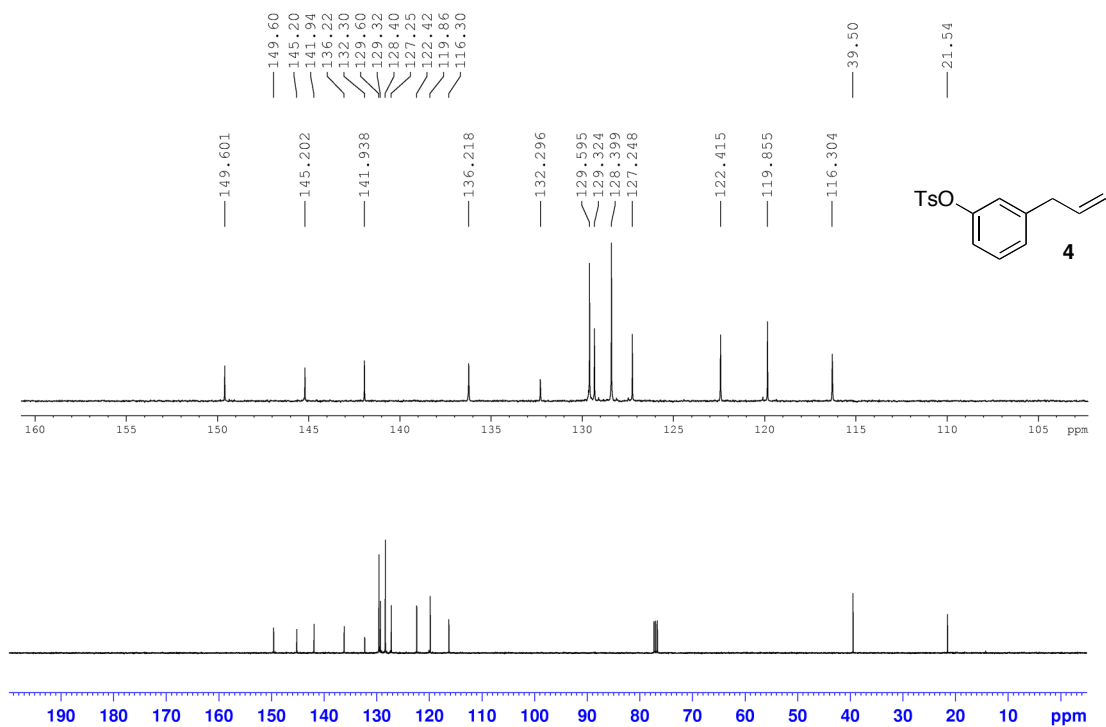
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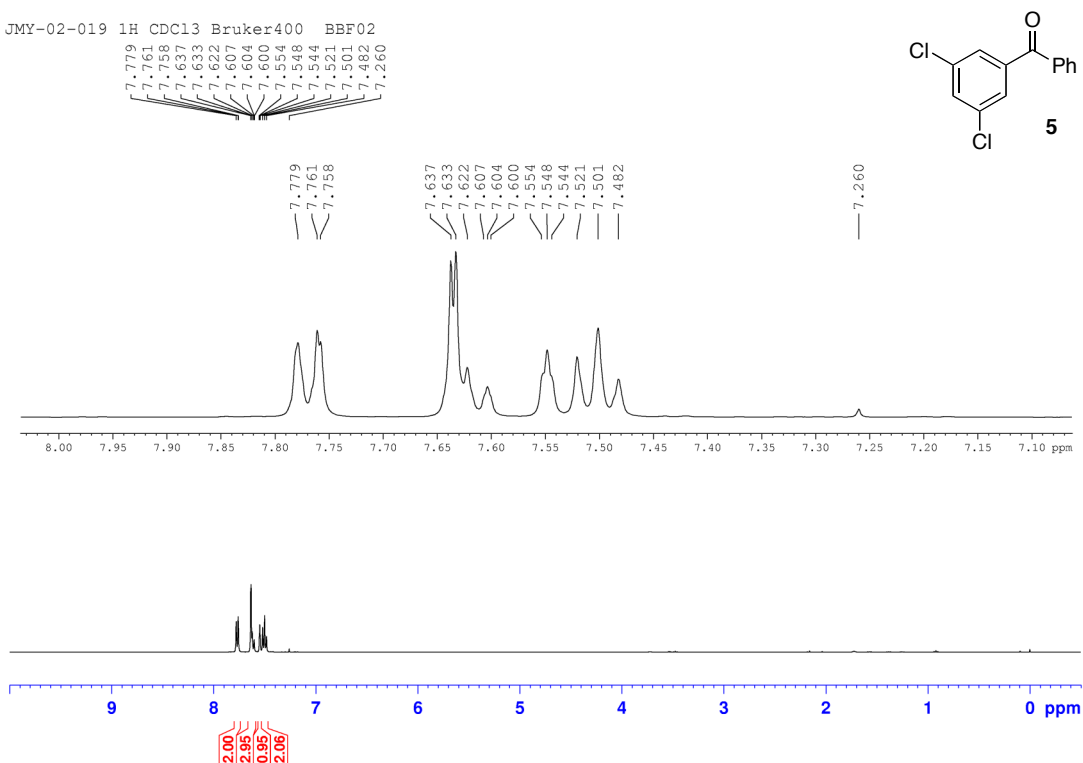
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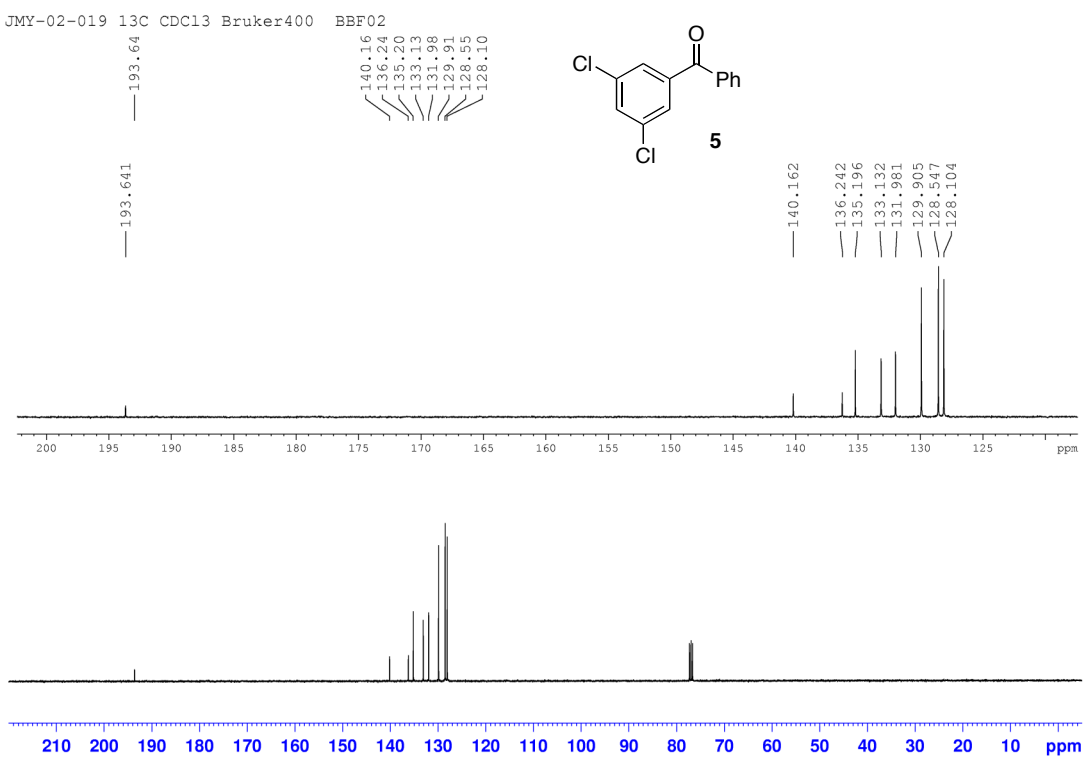
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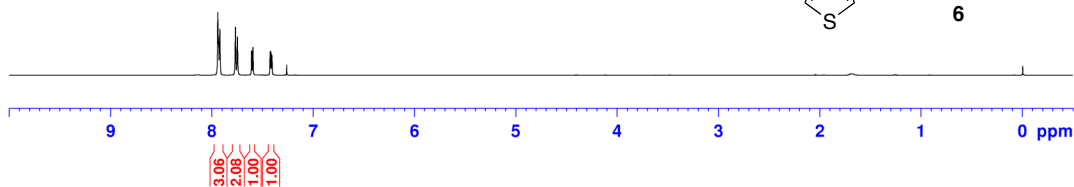
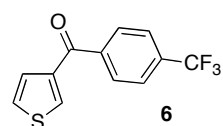
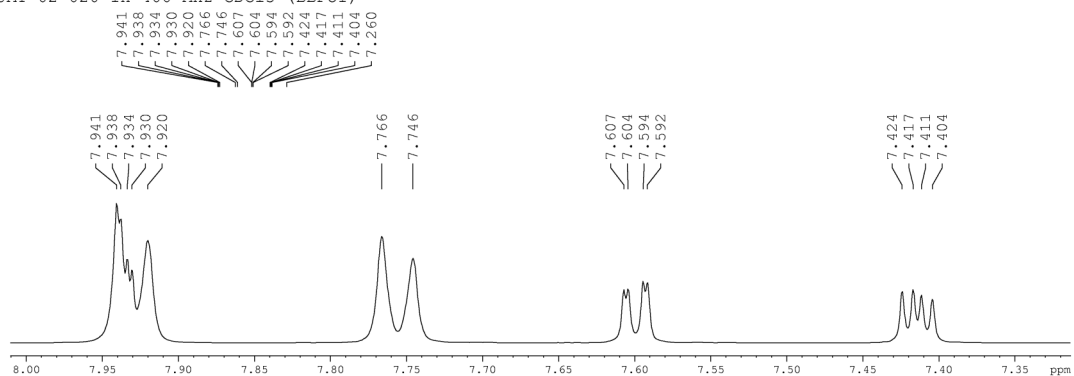
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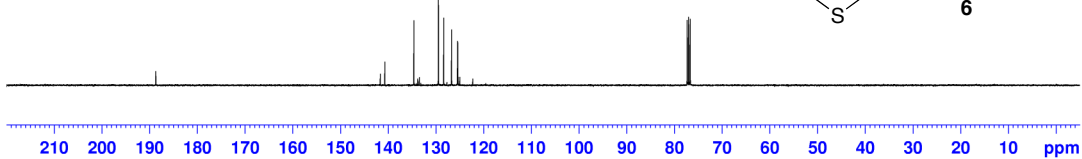
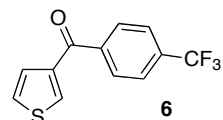
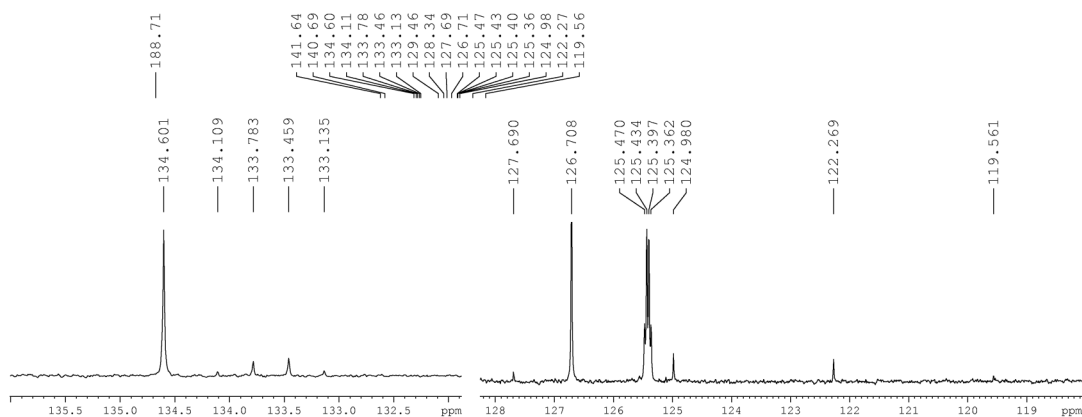
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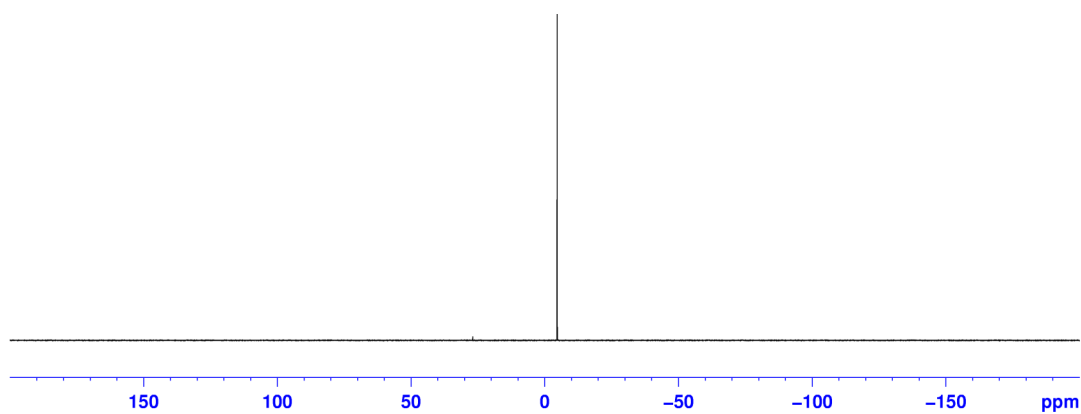
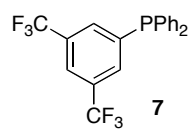
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JMY-02-023 31P{1H} 400 MHz CDCl3 (BBF01)

—26.93

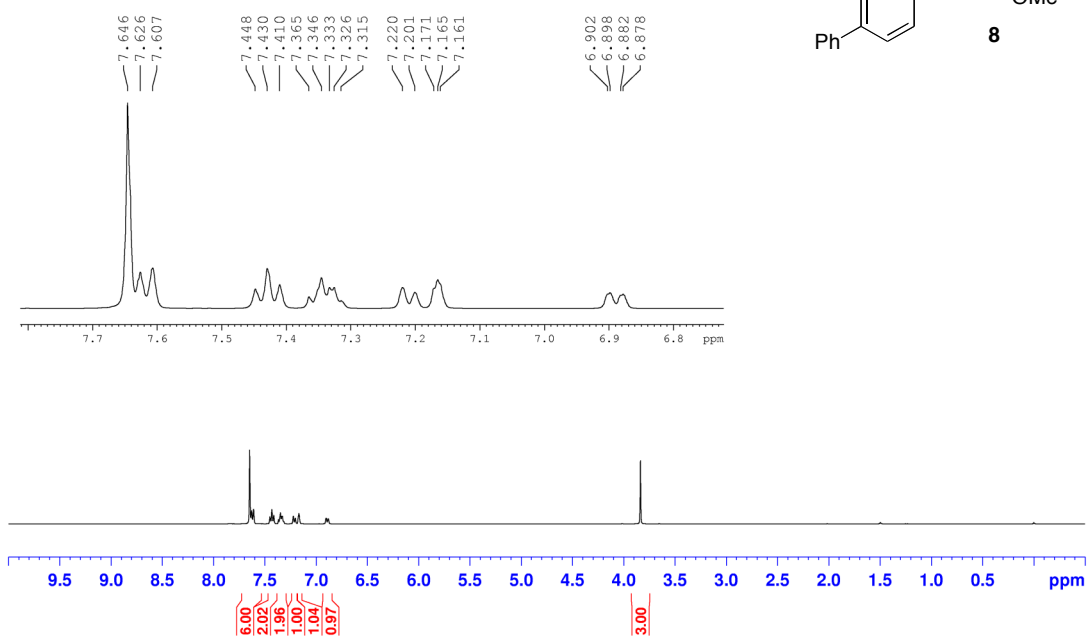
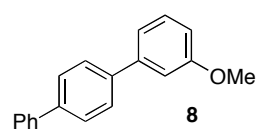
—-4.61



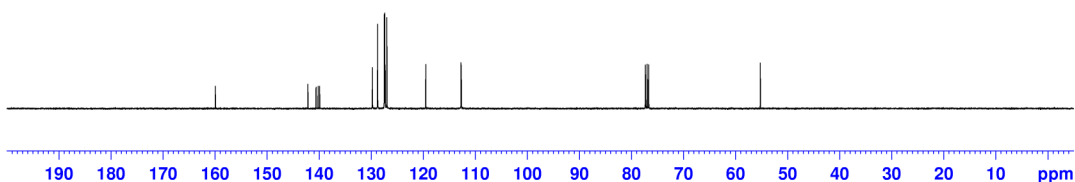
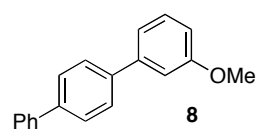
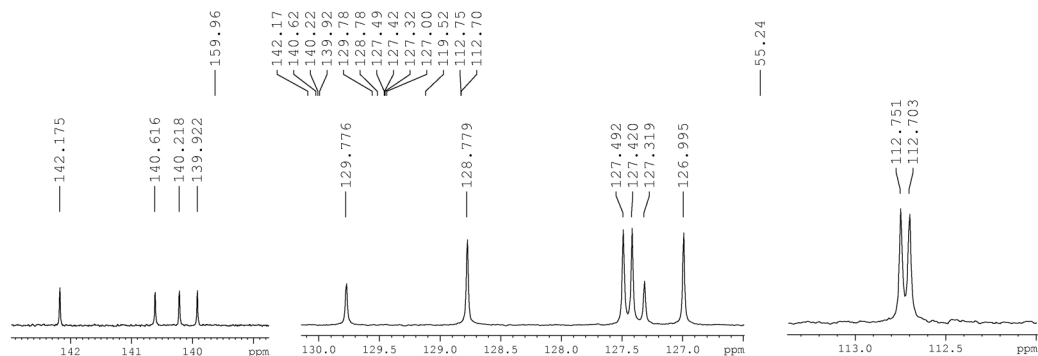
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7.646
7.626
7.607
7.448
7.430
7.410
7.365
7.346
7.333
7.326
7.315
7.220
7.201
7.171
7.165
7.161
6.902
6.898
6.882
6.878

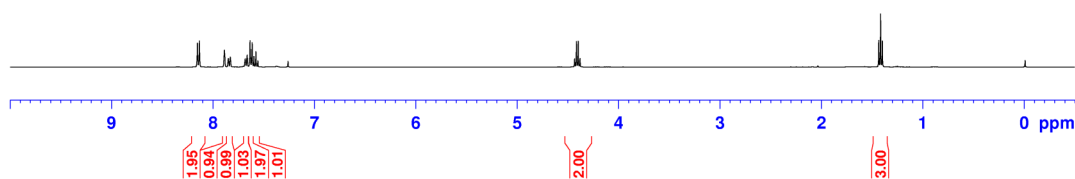
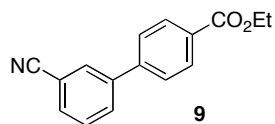
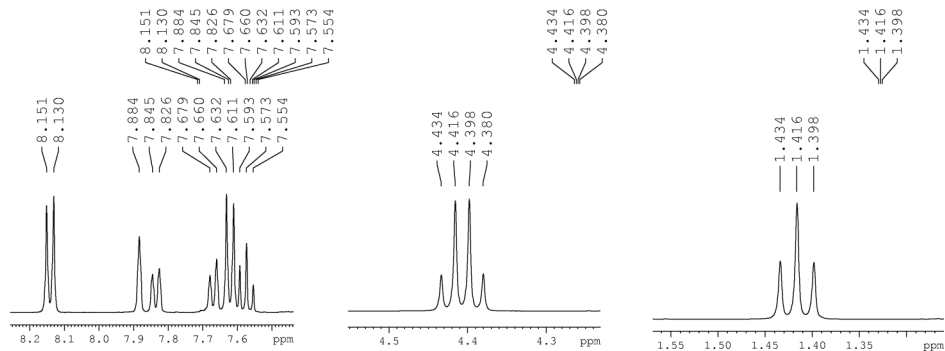
—3.837



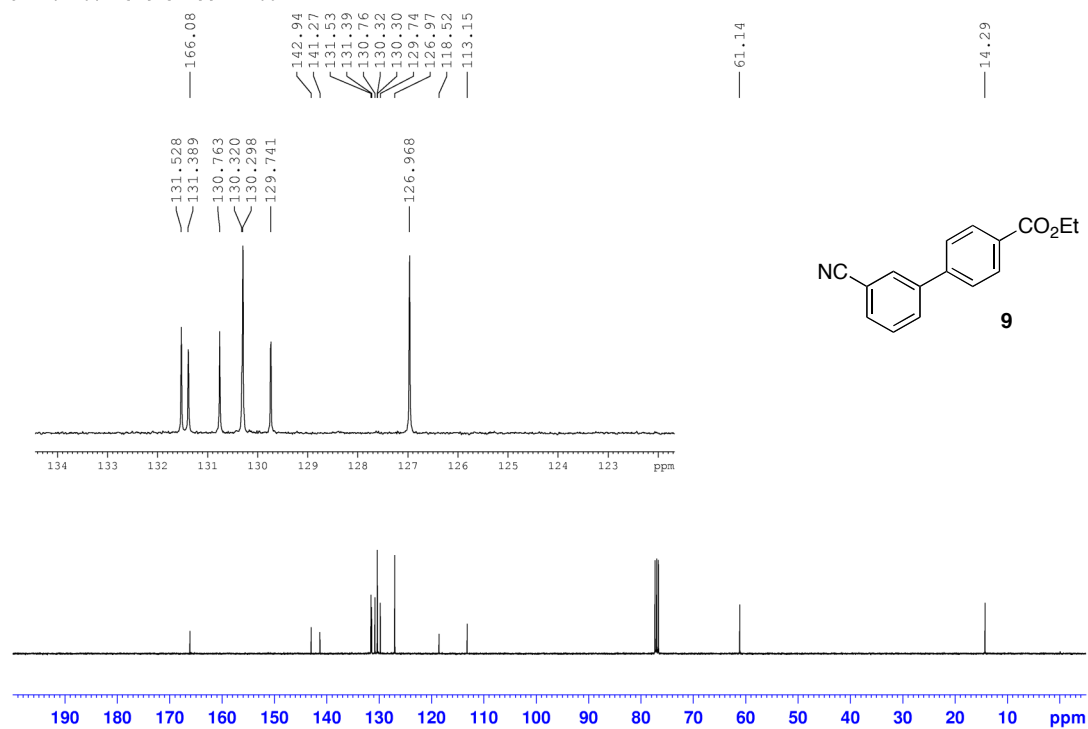
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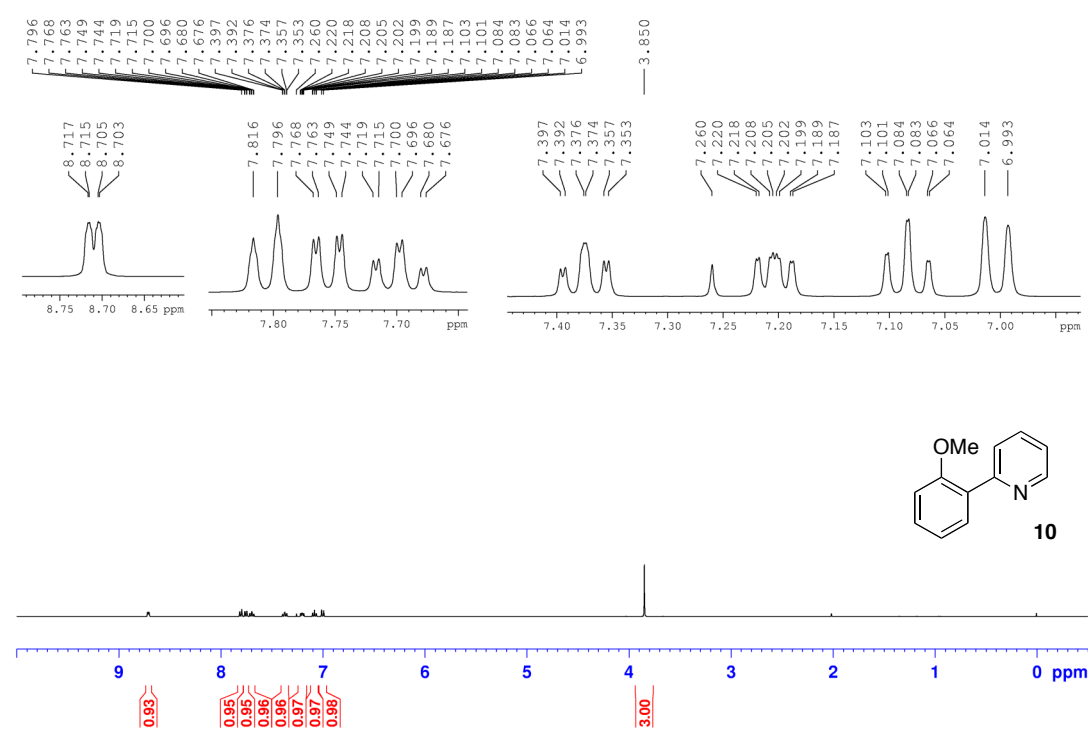
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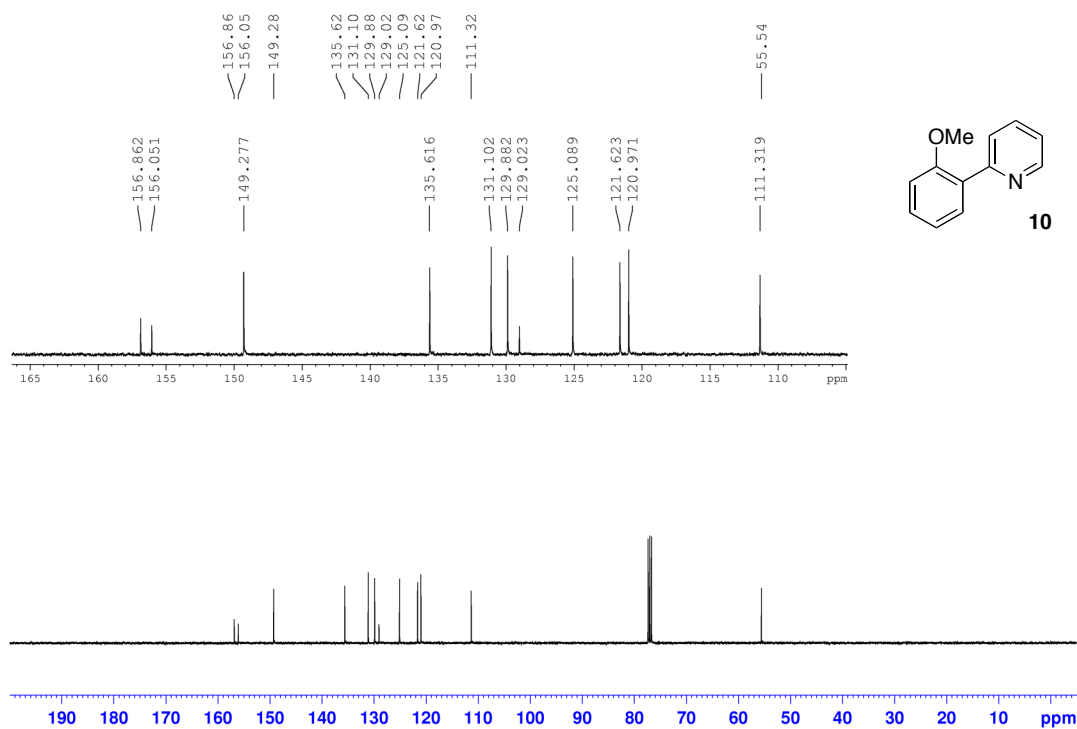
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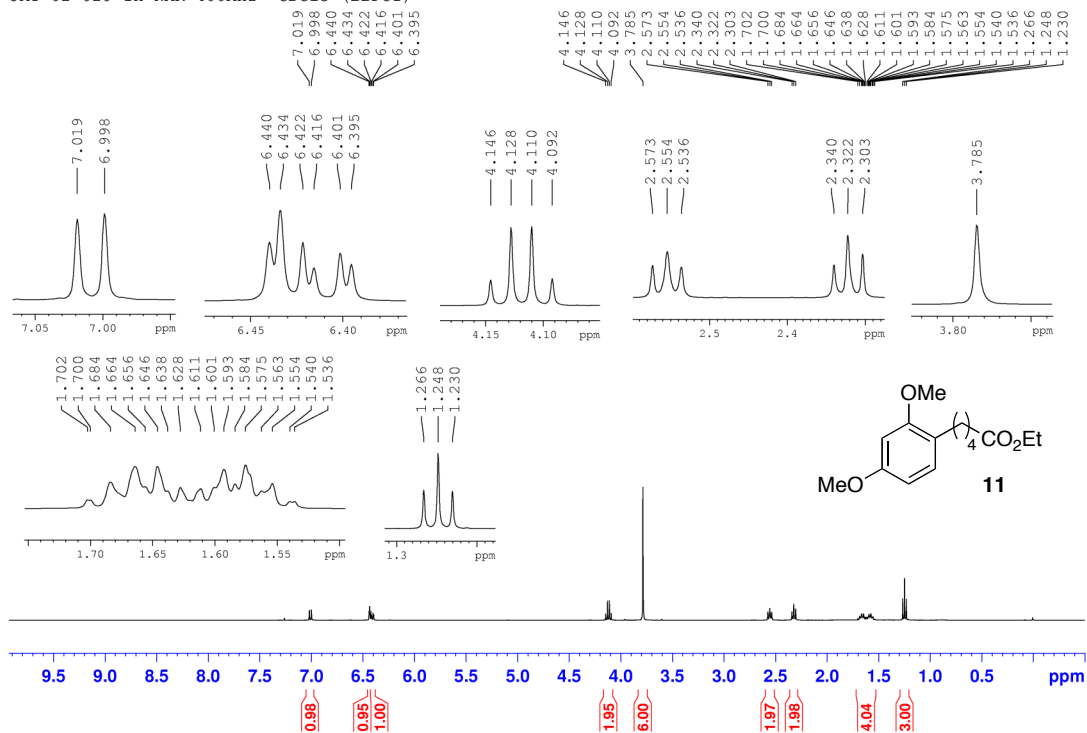
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JMY-02-006 CDCl₃ 13C AV400MH



JMY-02-029 1H NMR 400MHz CDCl₃ (BBFO1)

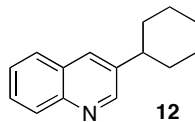


Chemical structure of compound **11** is shown: COc1ccc(cc1OC)CCc2ccc(cc2)C(=O)OCC.

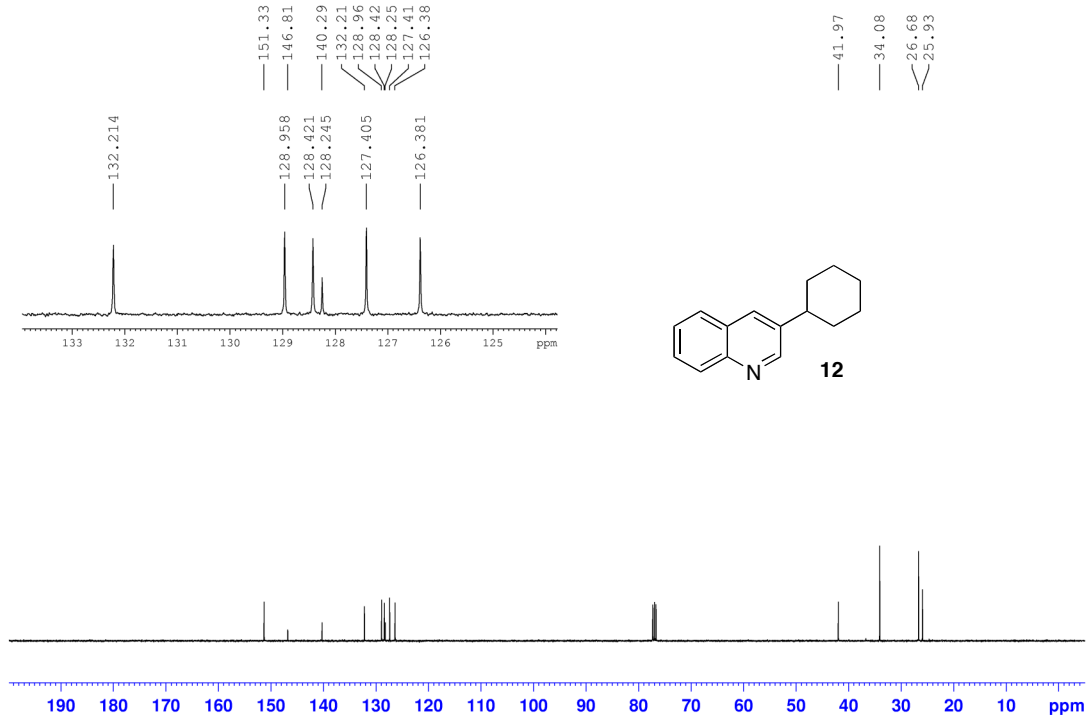
¹³C NMR spectrum (CDCl₃) of compound **11** is shown, with peak assignments (ppm):

- 173.76
- 158.99, 158.17
- 129.81, 122.88
- 103.62, 98.35
- 60.05, 55.22, 55.11
- 34.20
- 29.49, 29.04
- 24.69
- 14.17

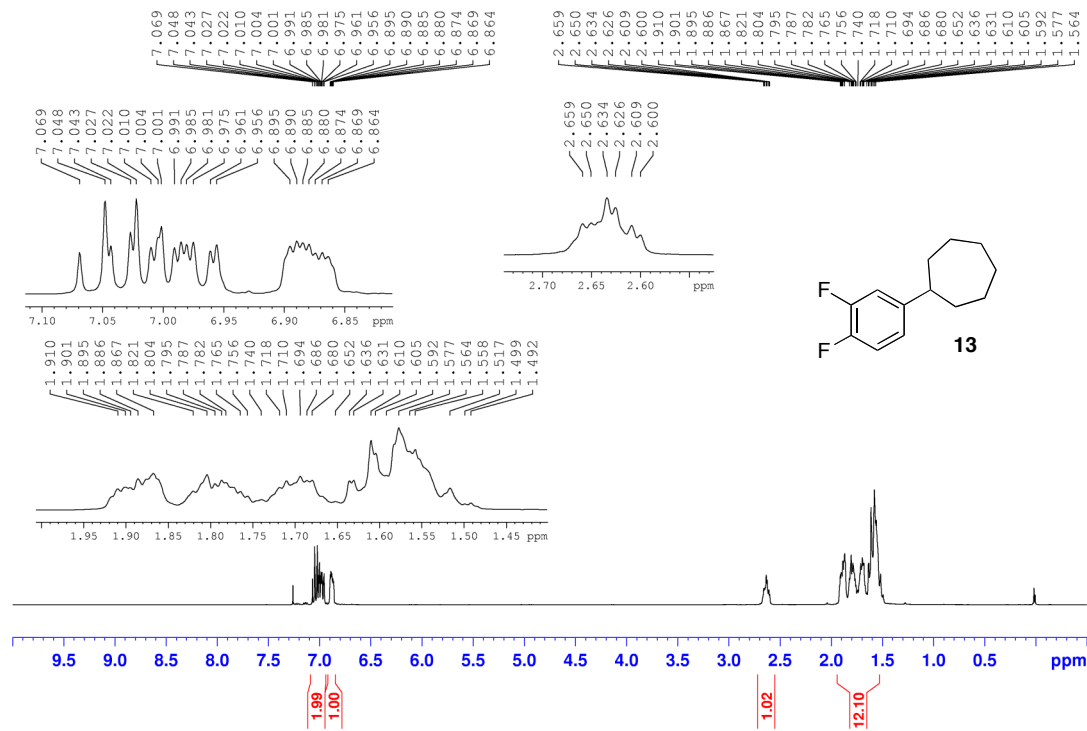
Figure 1 displays the ^1H NMR spectra of compound **1** in CDCl_3 . The spectra are stacked vertically, showing chemical shifts in ppm on the x-axis (ranging from 10 to 0). The top spectrum shows peaks in the aromatic region (7.0–8.9 ppm) with integration values ranging from 0.96 to 2.766. The second spectrum shows peaks in the aliphatic region (1.2–2.8 ppm) with integration values ranging from 1.265 to 2.008. The third spectrum shows peaks in the aliphatic region (1.2–2.8 ppm) with integration values ranging from 1.265 to 2.008. The fourth spectrum shows peaks in the aliphatic region (1.2–2.8 ppm) with integration values ranging from 1.265 to 2.008. The bottom spectrum shows peaks in the aliphatic region (1.2–2.8 ppm) with integration values ranging from 1.265 to 2.008.



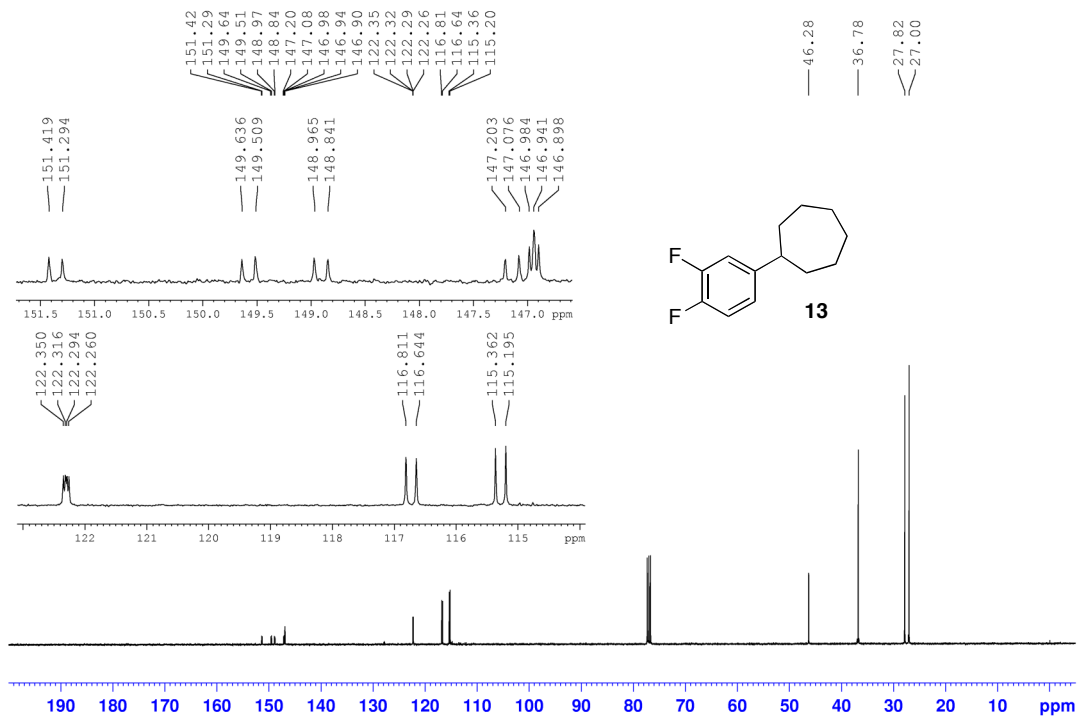
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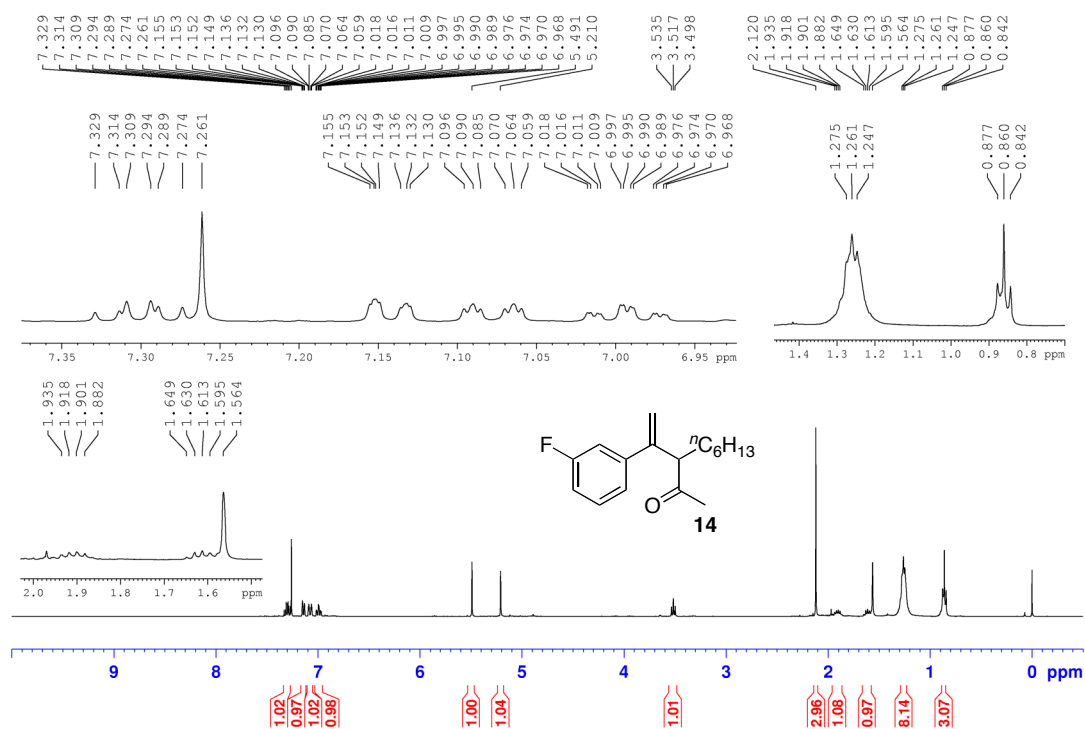
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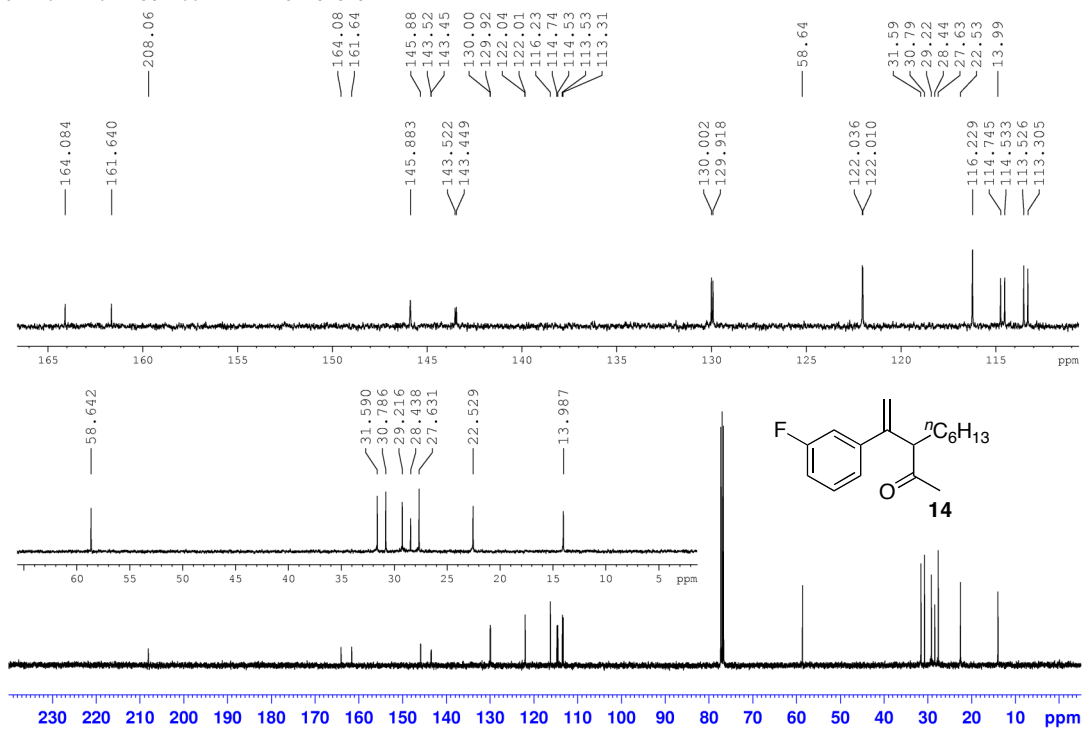
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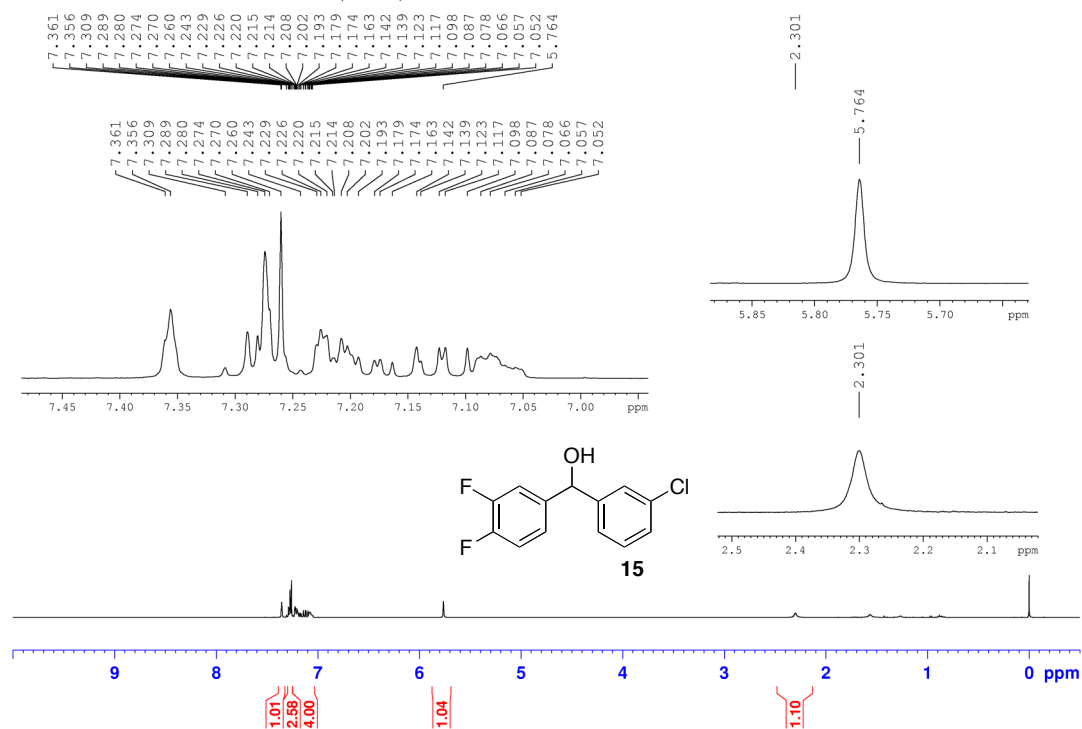
JMY-02-220 ¹H NMR 400 BBFO2 CDCl₃



JMY-02-220 ¹³C 400 NMR BBFO2 CDC13



JMY-02-028 ¹H NMR 400MHz CDC13 (BBFO1)



JMY-02-028 ¹³C NMR 400MHz CDC13 (BBF01)

