

Supporting Information
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Supporting Information

Synthesis of Dibenzyls by nickel-catalyzed homocoupling of benzyl alcohols

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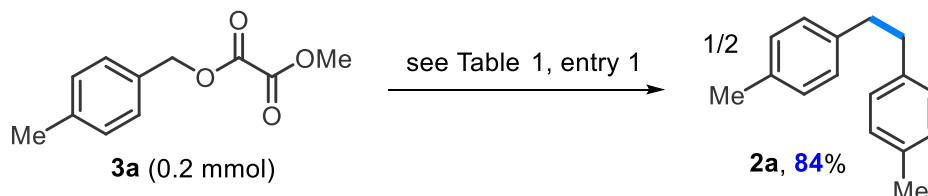
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^b College of Chemical Engineering and Technology, Tianshui Normal University, 60 South Xihe Road, Tianshui, 741001, China.

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1. Mechanistic Investigation

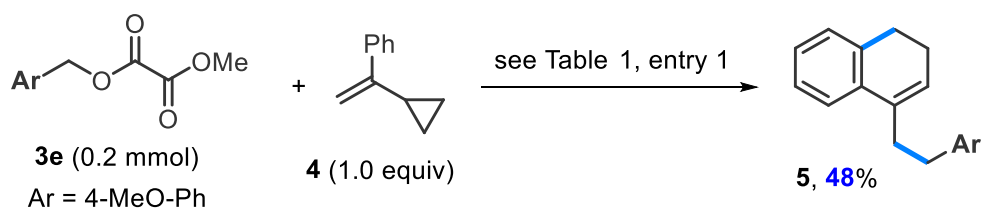
1.1 Reaction of oxalate 3a



General procedure: The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(dppe)Cl₂ (5.3 mg, 0.01 mmol), Mn (27.5 mg, 0.5 mmol), oxalate **3a** (41.6 mg, 0.2 mmol), LiBr (17.5 mg, 0.2 mmol) and DMF (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 110 °C for 16 h. After cooling down to room temperature, it was diluted with ethyl acetate (15 mL), washed with water, brine, and dried over anhydrous Na₂SO₄. A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC. The yield was determined versus the internal standard (dodecane).

1.2 Radical clock experiments

1.2.1 Reaction of 3e in the presence of α -cyclopropylstyrene



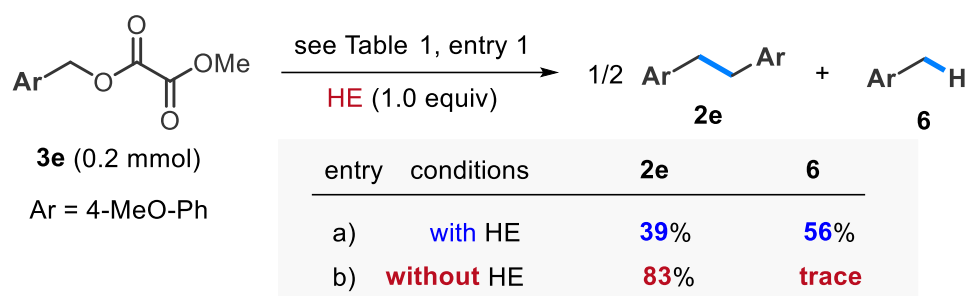
General procedure: The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(dppe)Cl₂ (5.3 mg, 0.01 mmol), Mn (27.5 mg, 0.5 mmol), oxalate **3e** (44.8 mg, 0.2 mmol), α -cyclopropylstyrene **4** (28.8 mg, 0.2 mmol), LiBr (17.5 mg, 0.2 mmol), and DMF (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 110 °C for 16 h. After cooling down to room temperature, it was

diluted with EtOAc (20 mL). The mixture solution was washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford product **5** (25.2 mg, 48% yield) as an oil, known compound.¹

¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 7.6 Hz, 1 H), 7.22-7.11 (m, 5 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 5.83 (t, *J* = 4.4 Hz, 1 H), 3.80 (s, 3 H), 2.81-2.68 (m, 6 H), 2.51-2.20 (m, 2 H).

¹³C NMR (100 MHz, CDCl₃) δ 157.9, 137.0, 136.0, 134.9, 134.5, 129.5, 127.8, 126.7, 126.5, 125.4, 122.7, 113.8, 55.4, 35.2, 34.1, 28.6, 23.2.

1.2.2 The effect of hantzsch ester



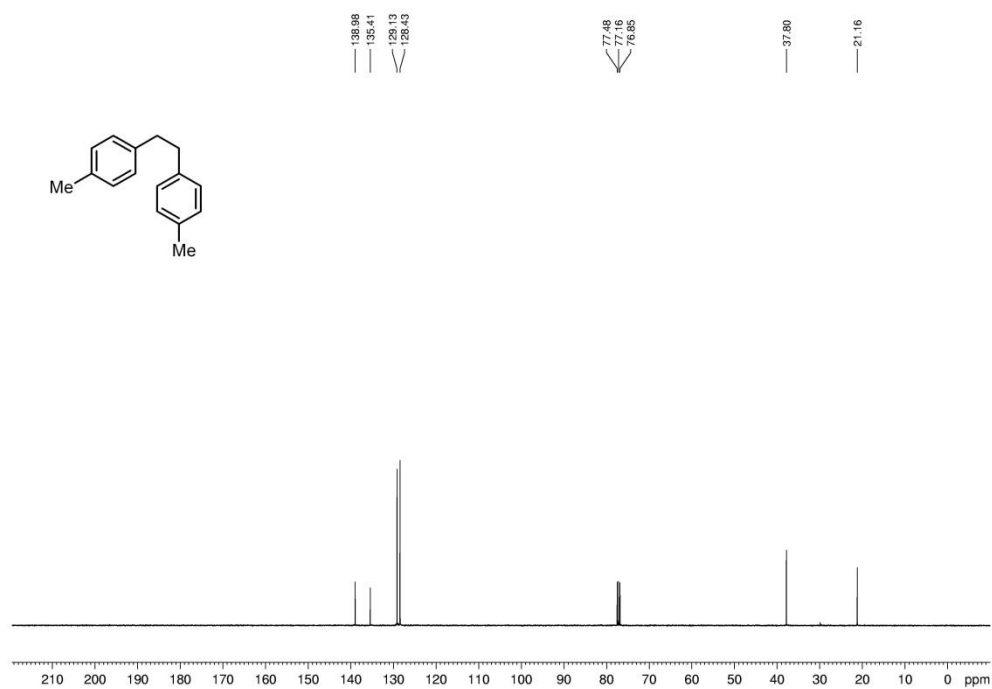
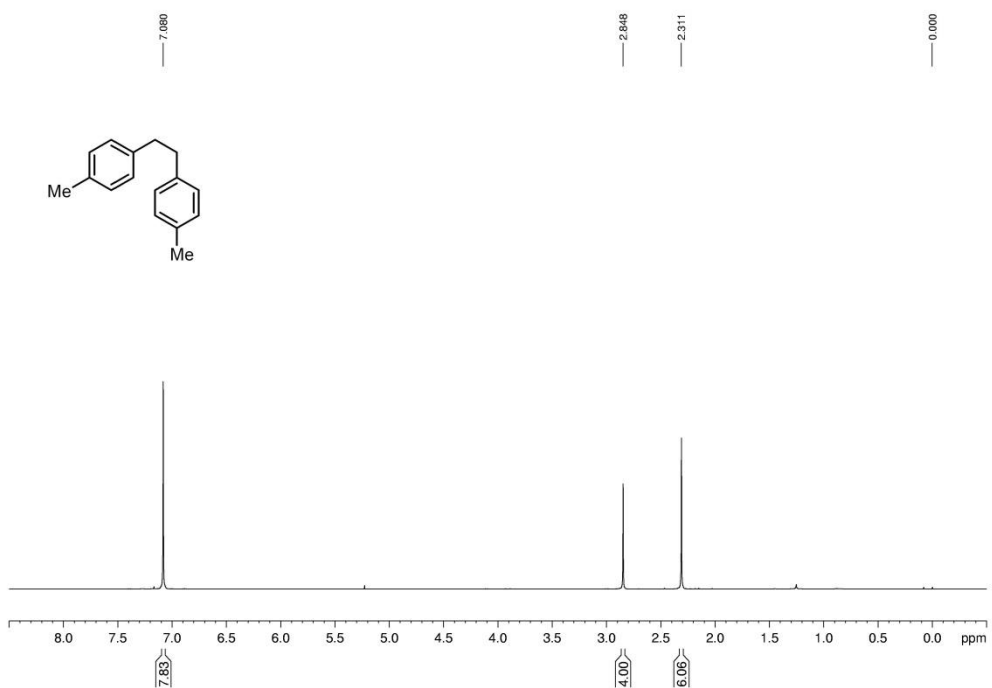
General procedure: The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(dppe)Cl₂ (5.3 mg, 0.01 mmol), Mn (27.5 mg, 0.5 mmol), oxalate **3e** (44.8 mg, 0.2 mmol), LiBr (17.5 mg, 0.2 mmol), [hantzsch ester (50.6 mg, 0.2 mmol) for conditions a], and DMF (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 110 °C for 16 h. After cooling down to room temperature, it was diluted with ethyl acetate (15 mL), washed with water, brine, and dried over anhydrous Na₂SO₄. A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC. The yield was determined versus the internal standard (dodecane).

2. Reference:

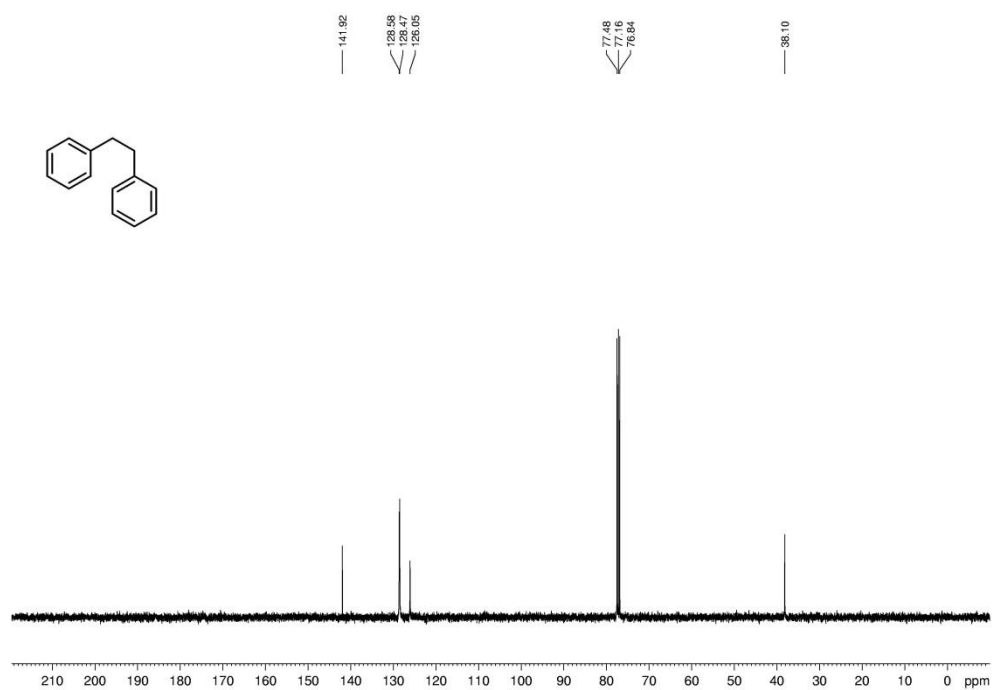
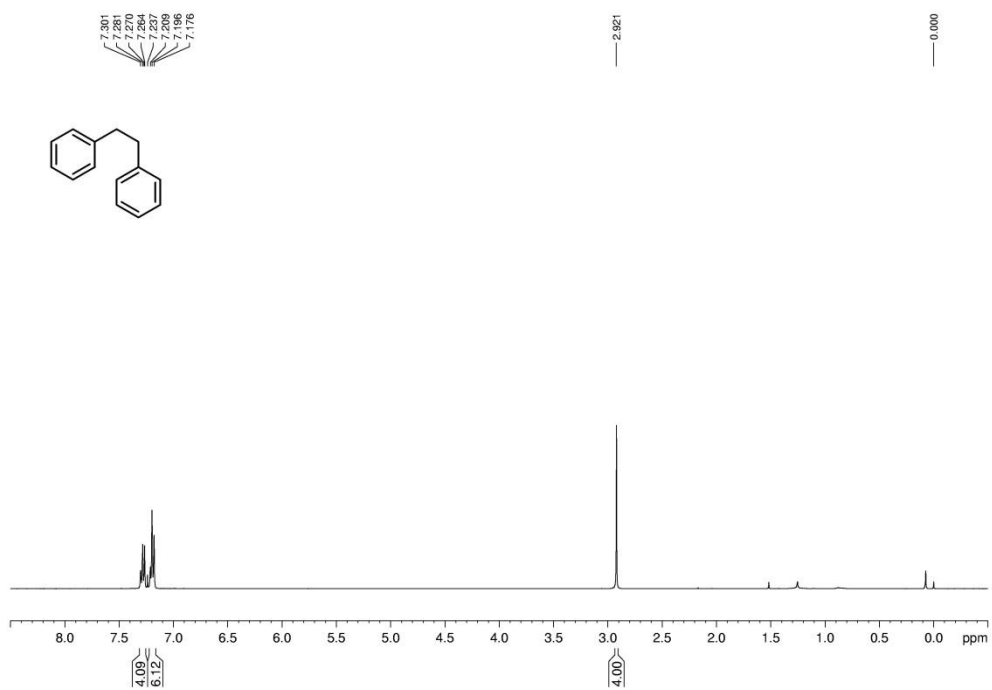
(1) Guo, P.; Wang, K.; Jin, W.-J.; Xie, H.; Qi, L.; Liu, X.-Y.; Shu, X.-Z. *J. Am. Chem. Soc.* **2021**, 143, 513.

3. Copies of NMR Spectra

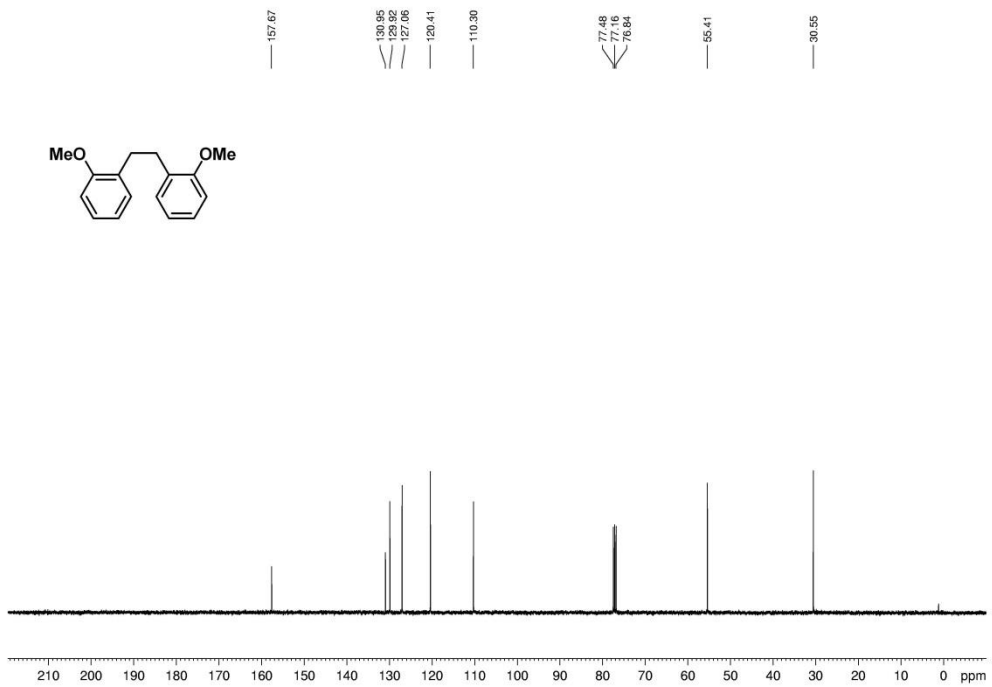
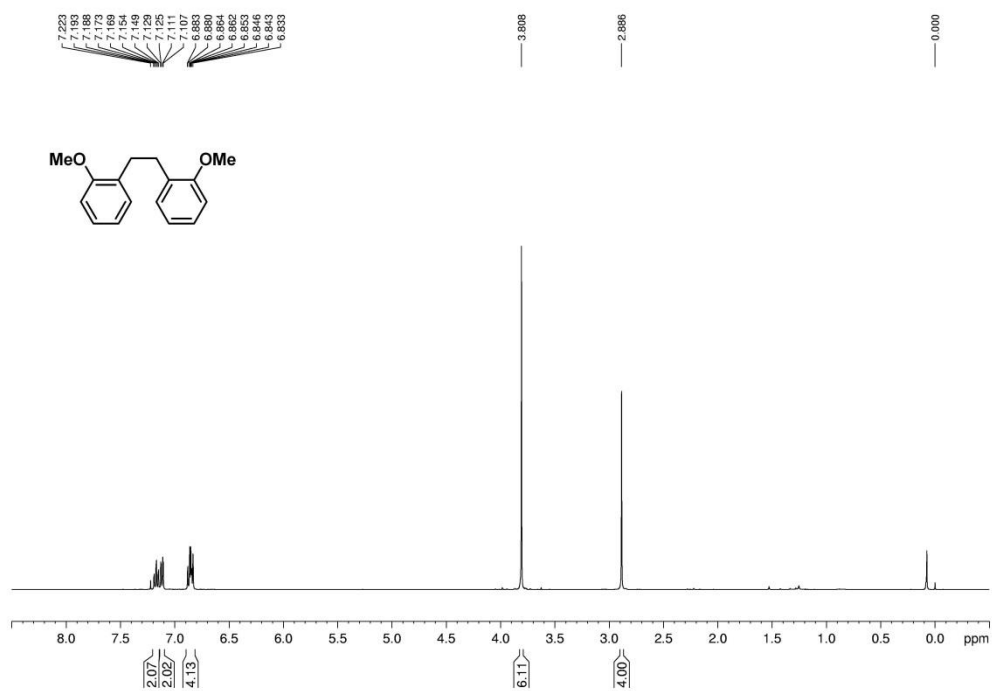
2a; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



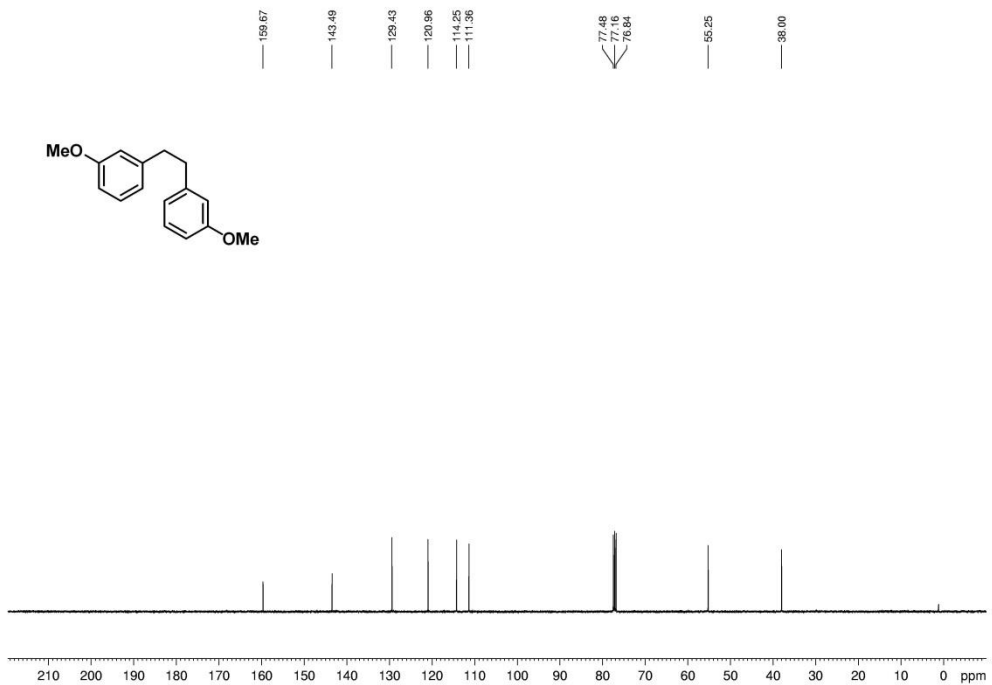
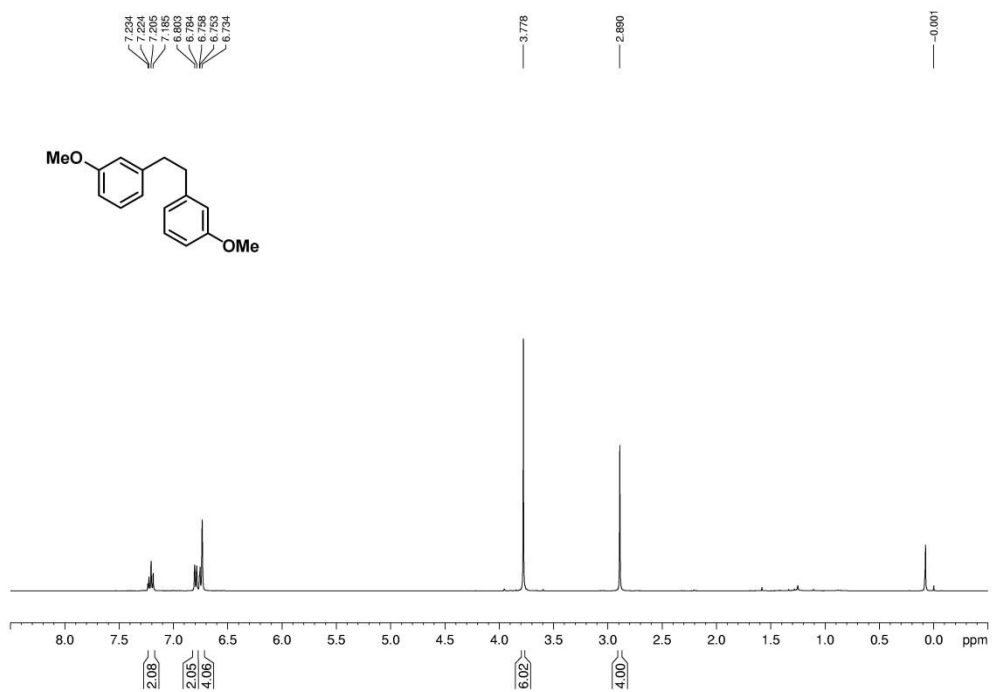
2b; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



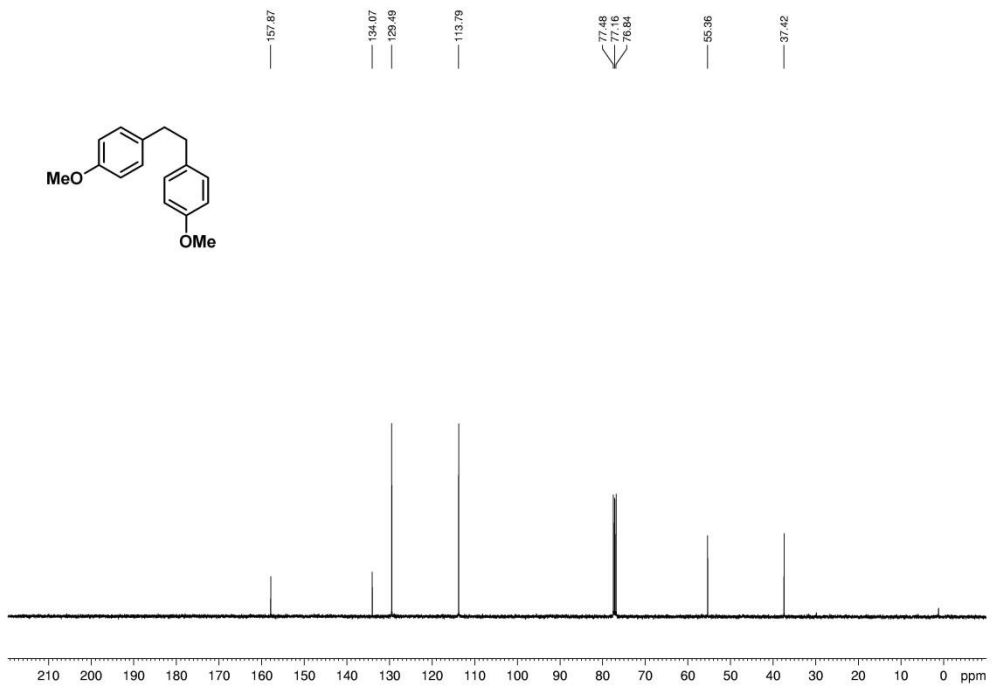
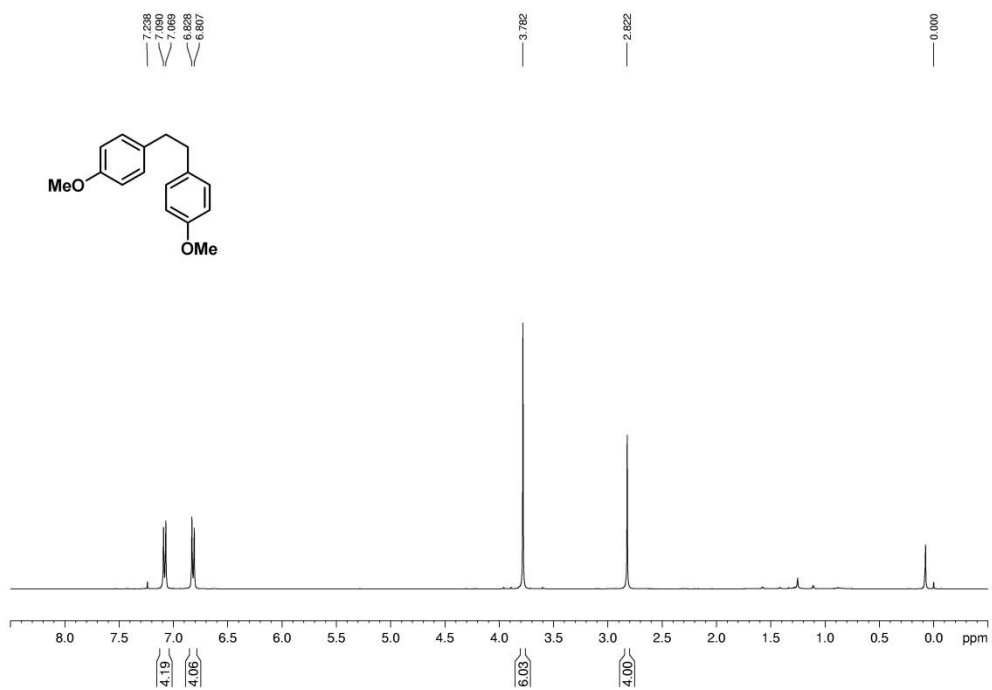
2c; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



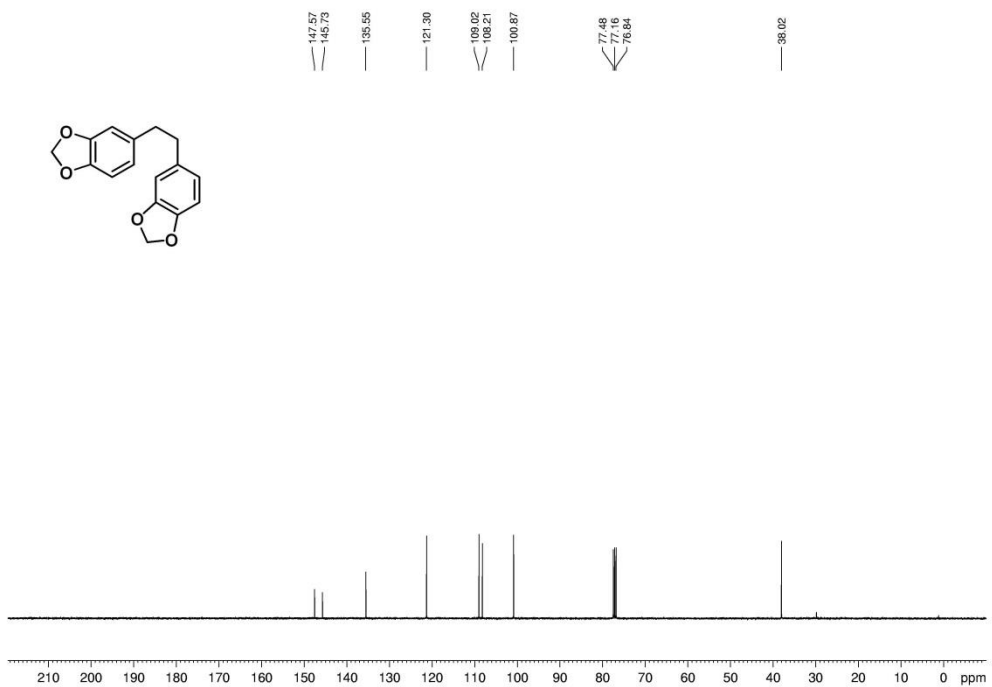
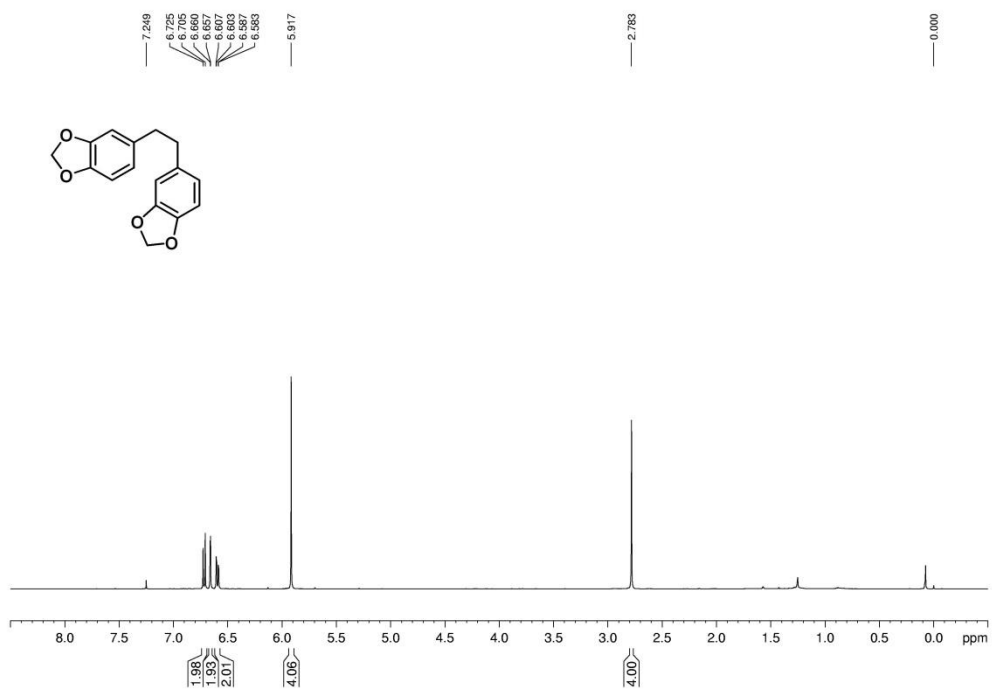
2d; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



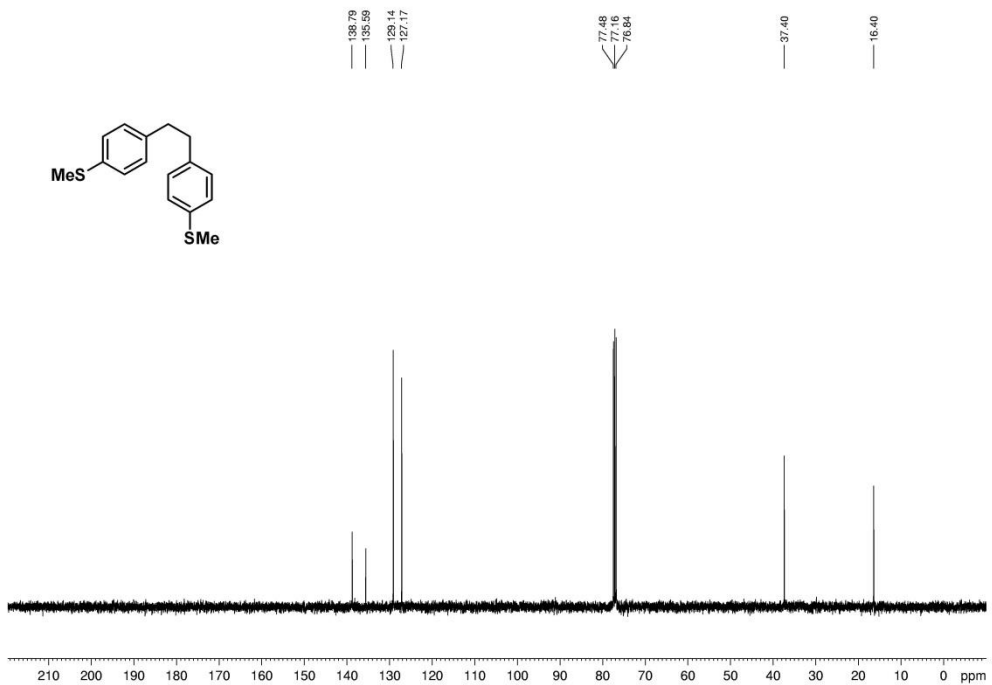
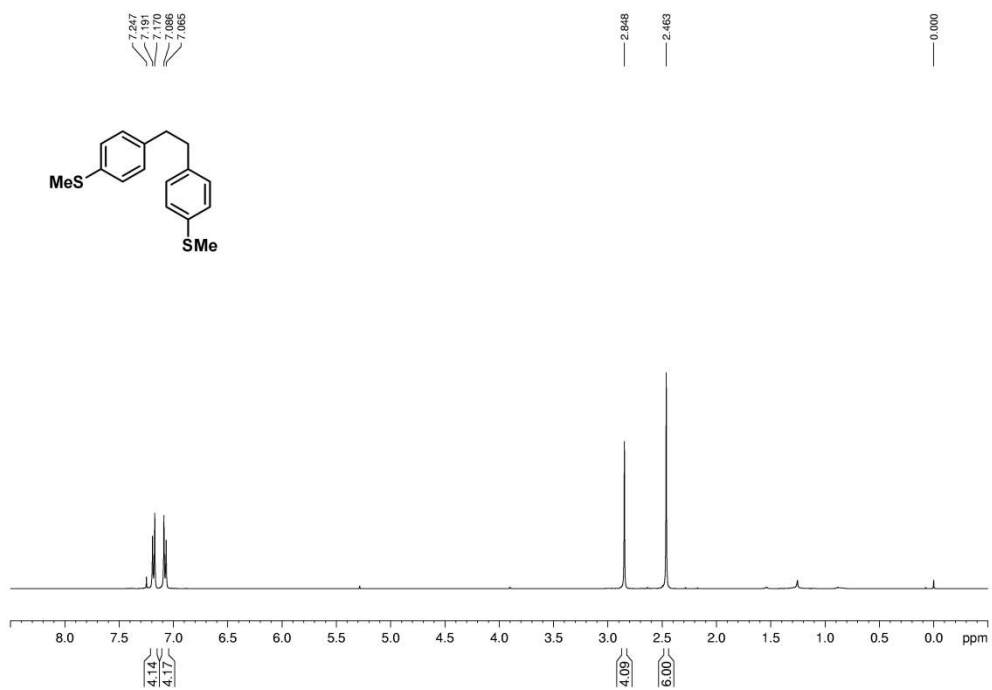
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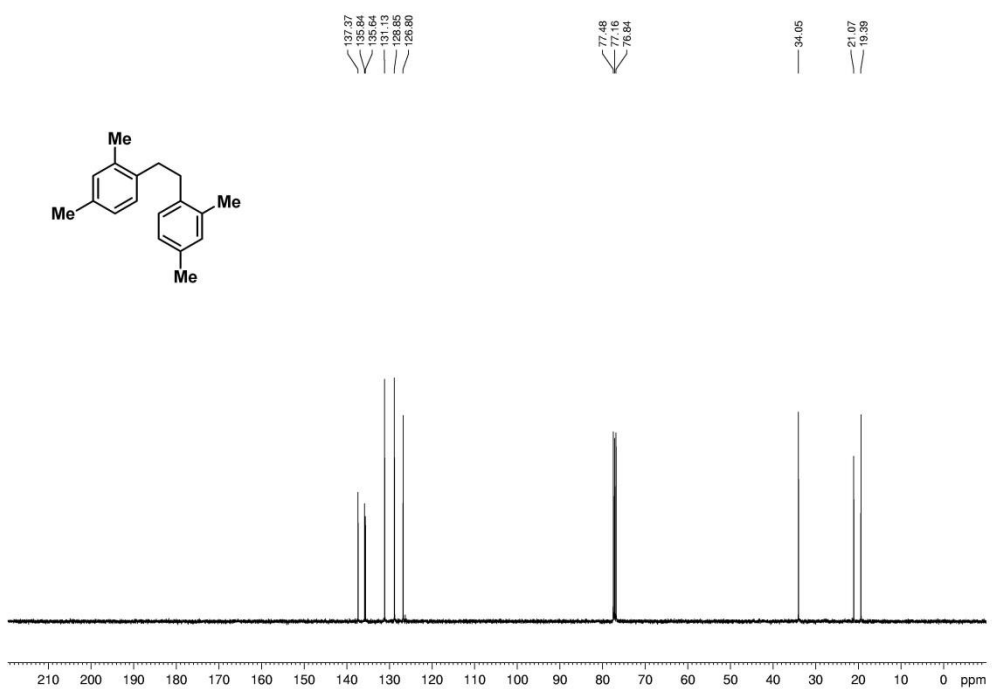
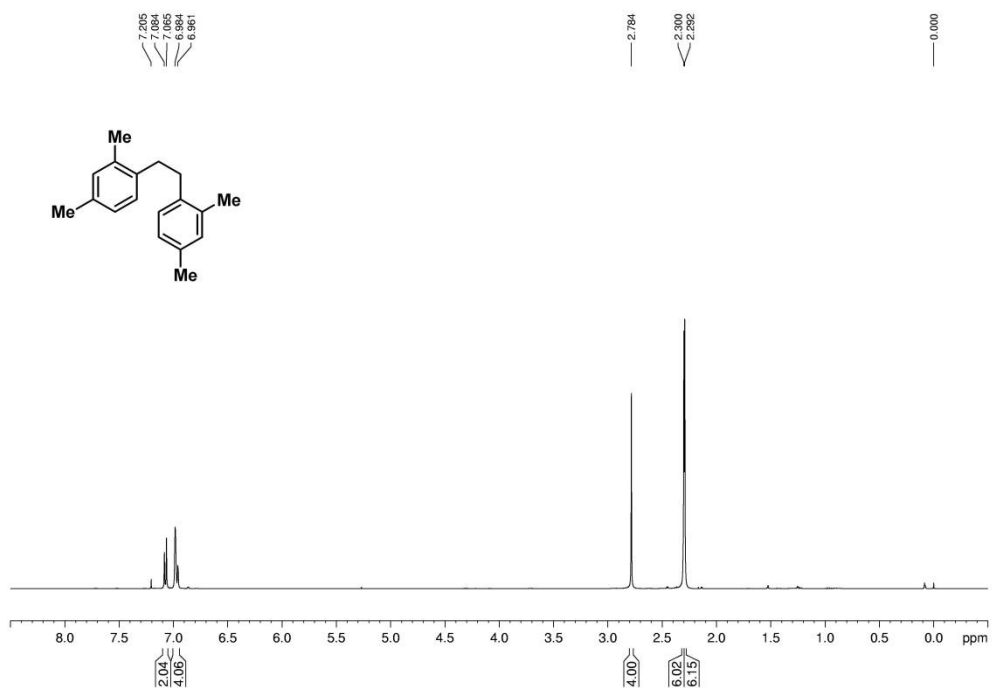
2f; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



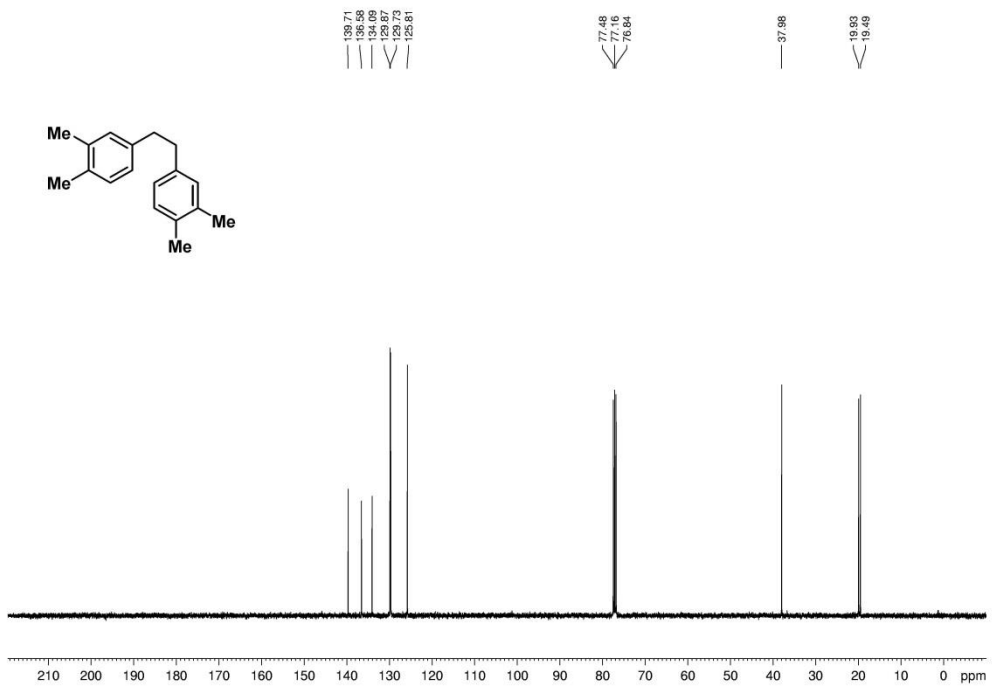
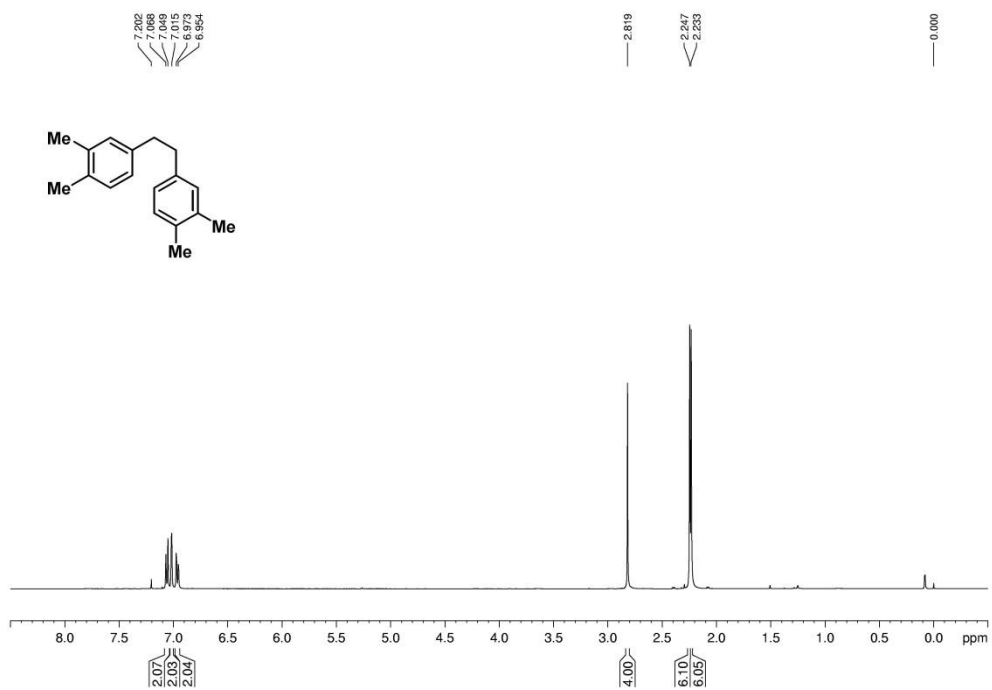
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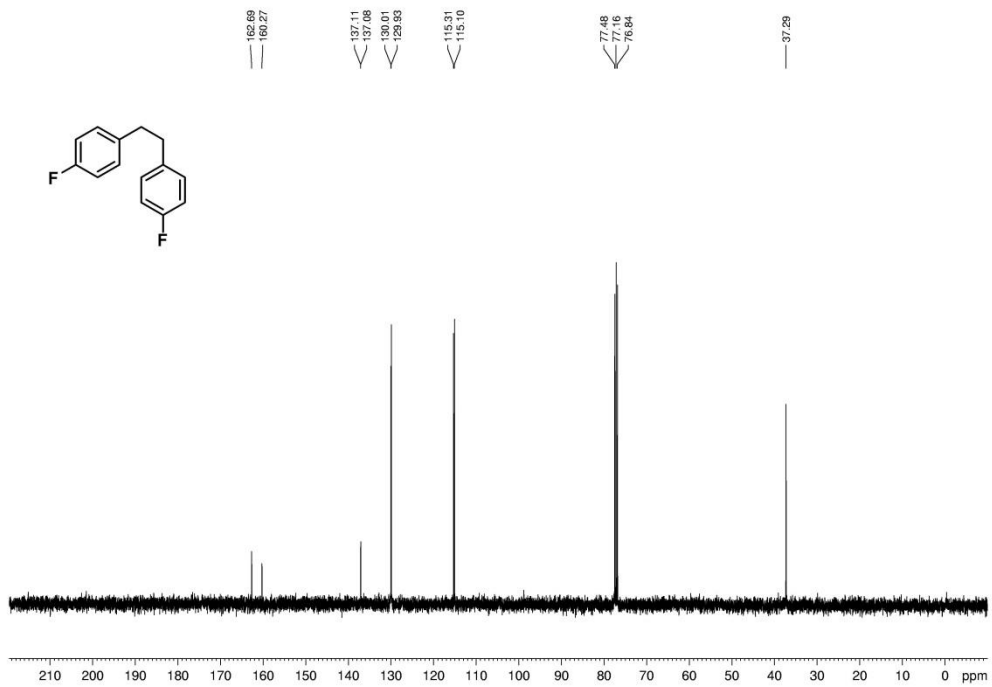
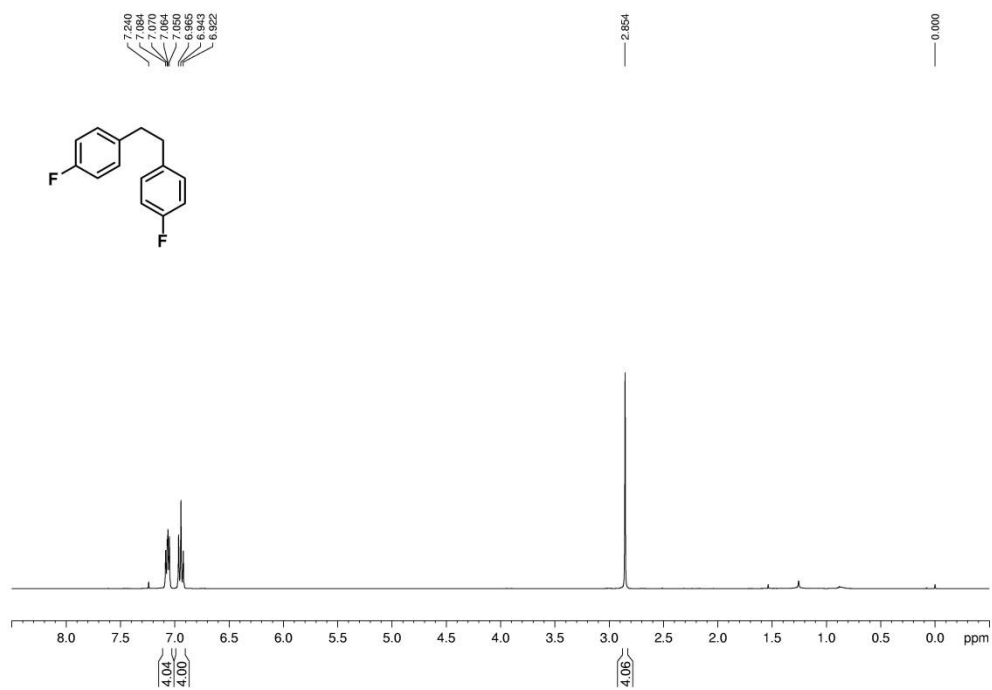
2h; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



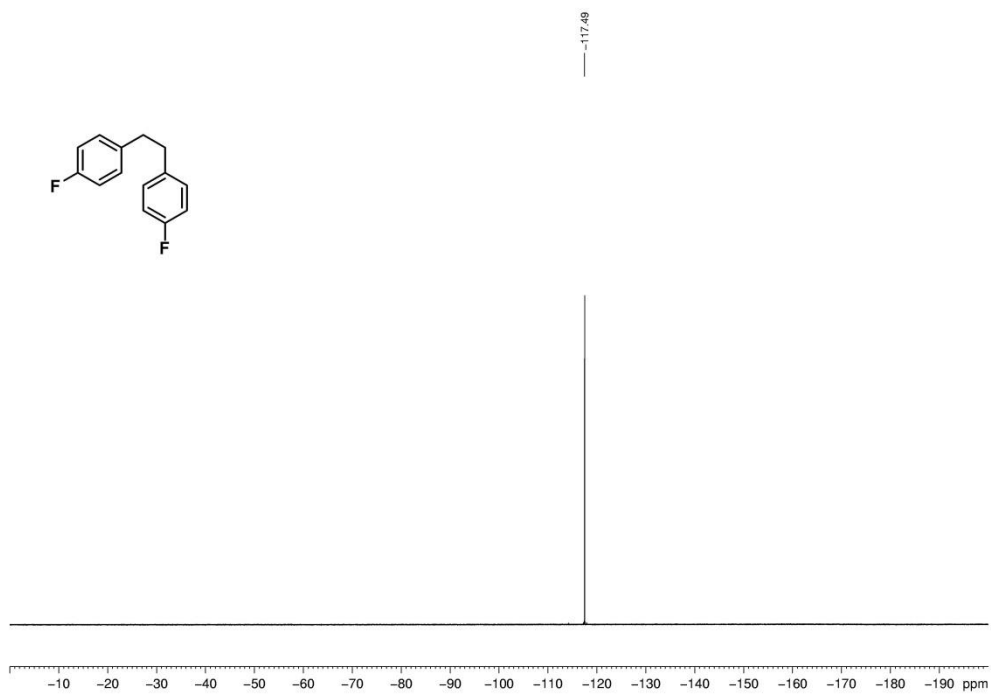
2i; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



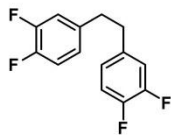
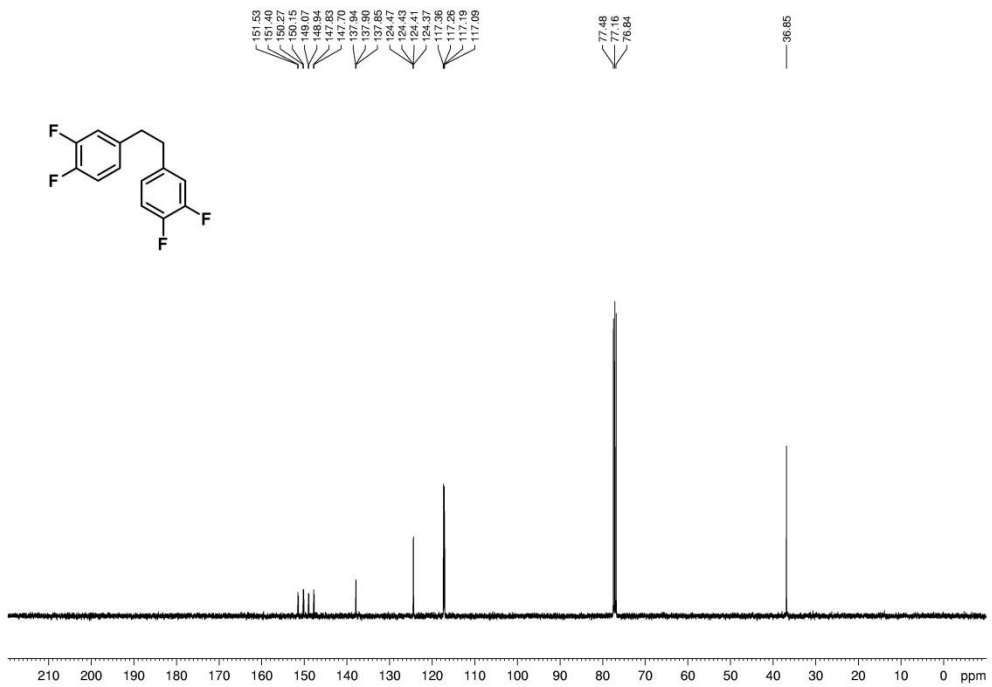
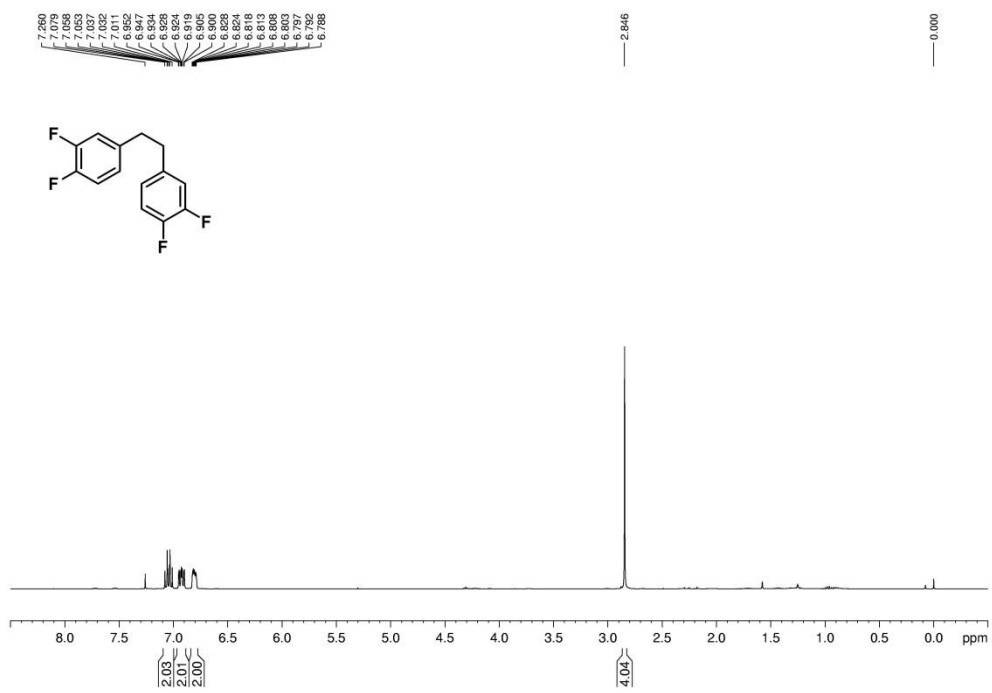
2j; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



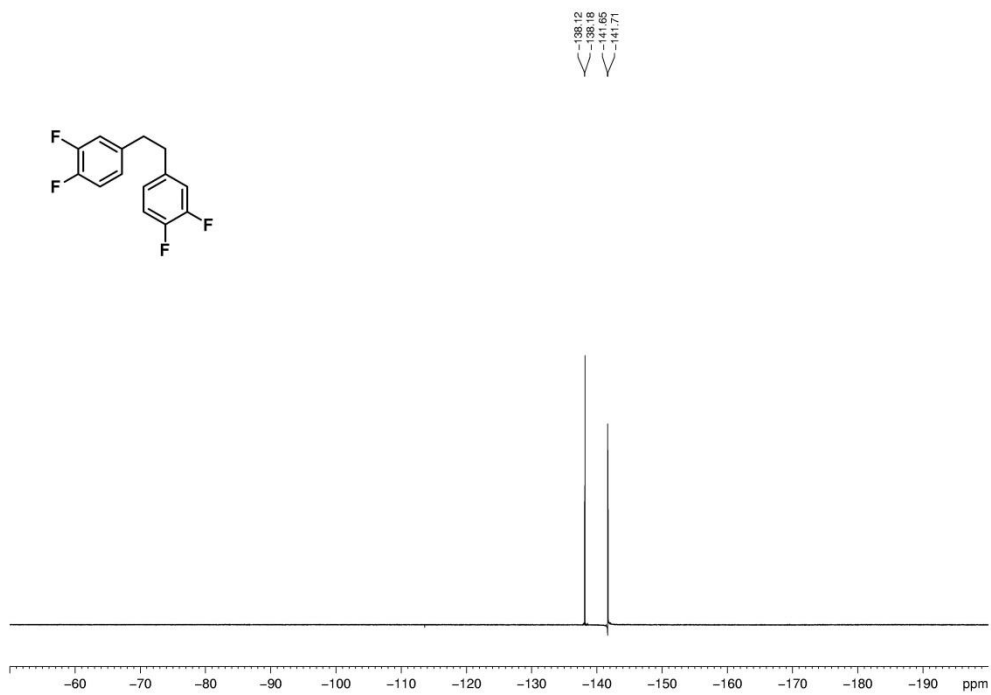
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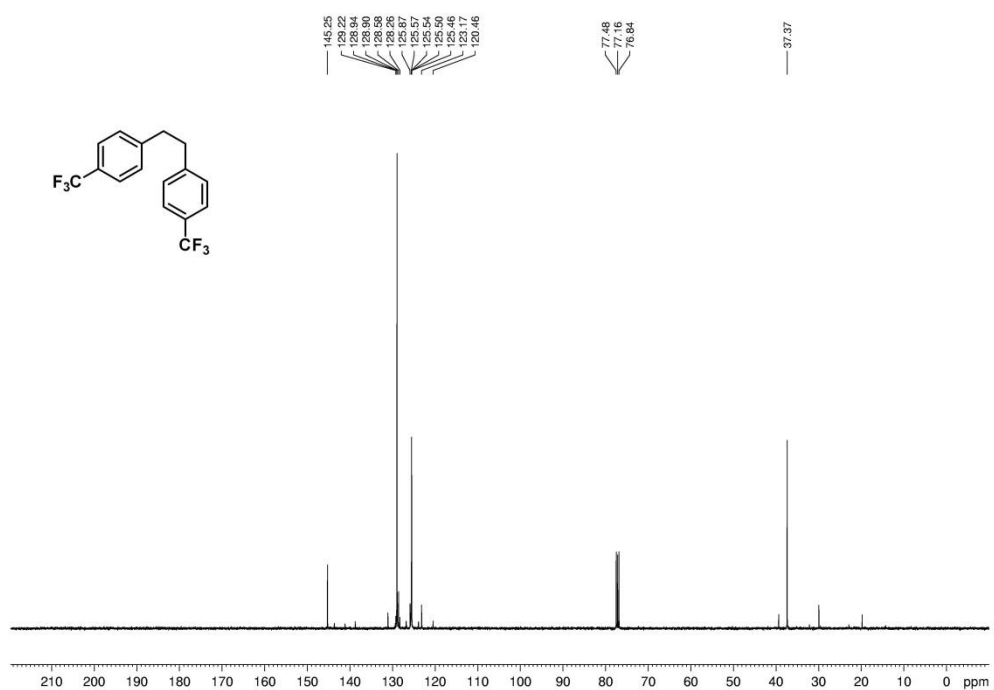
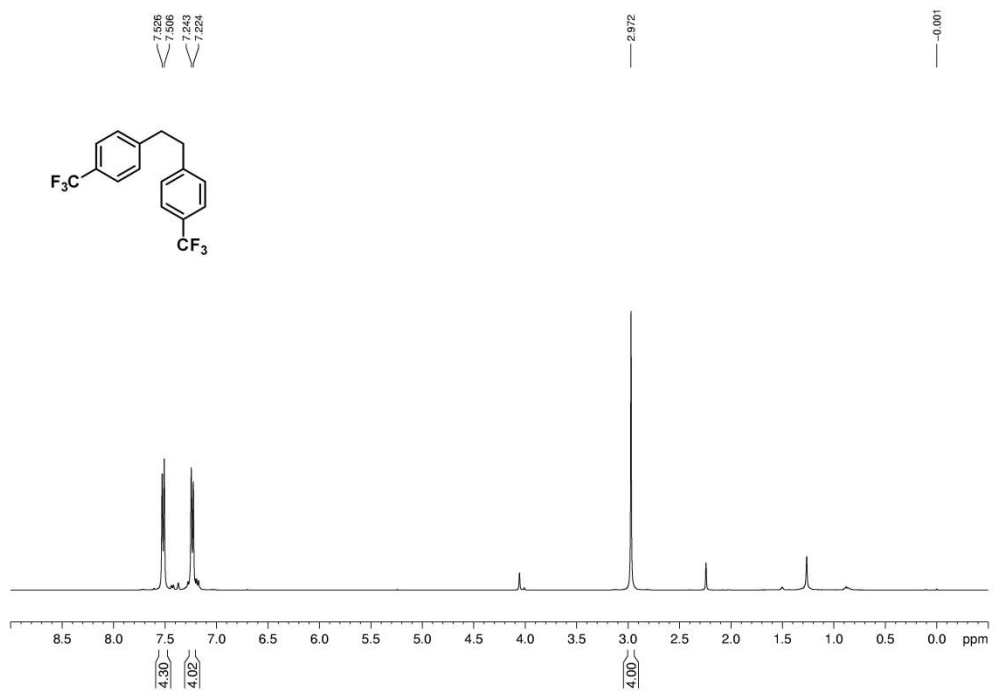
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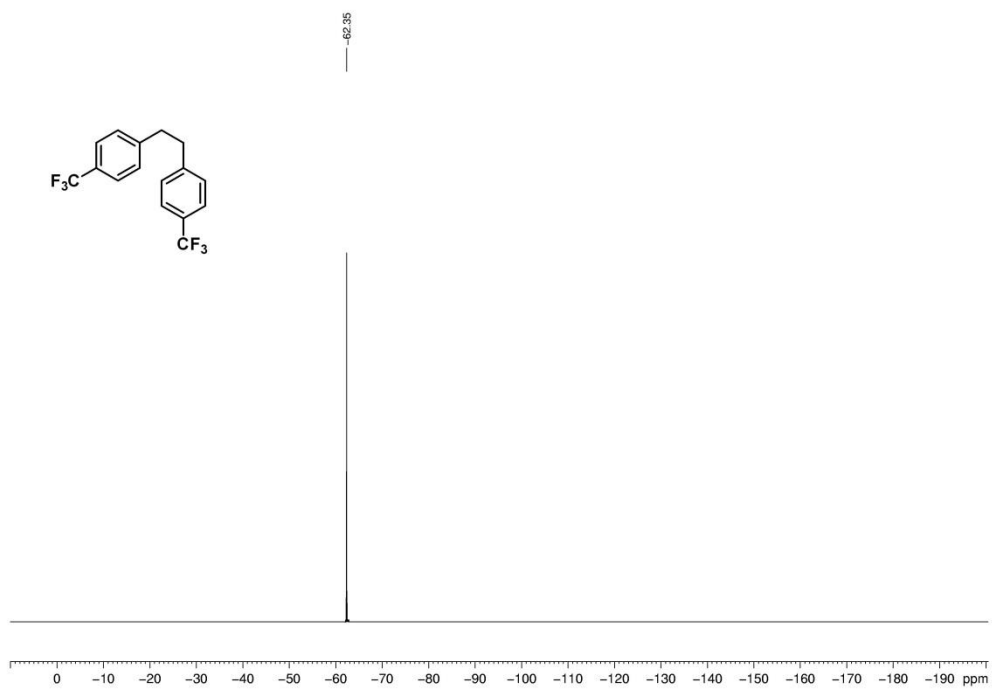
2k; ^{19}F NMR (376 MHz, CDCl_3)



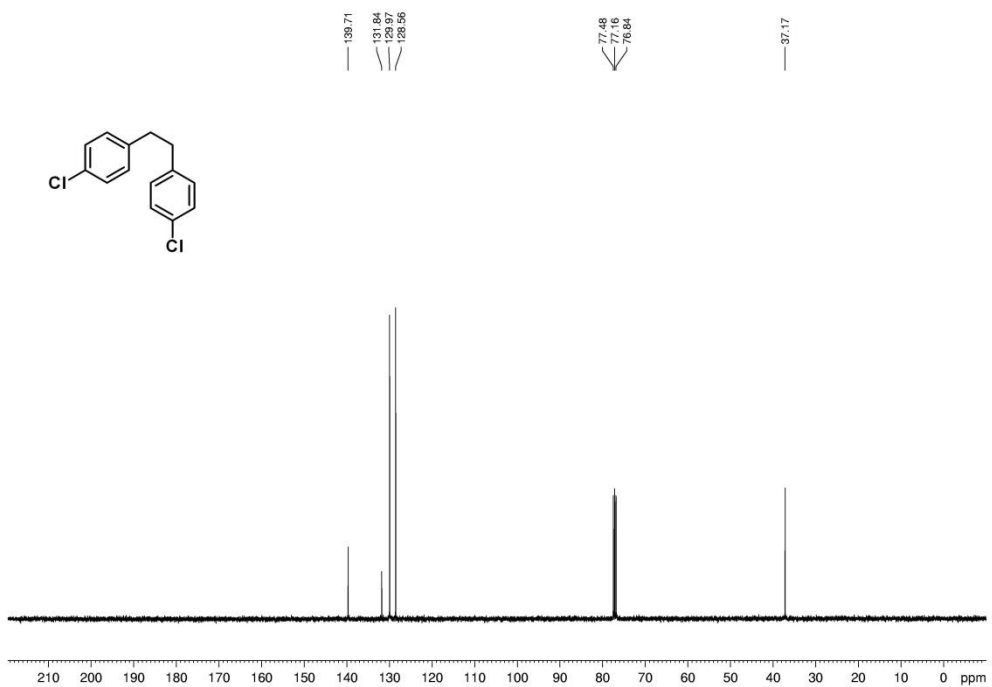
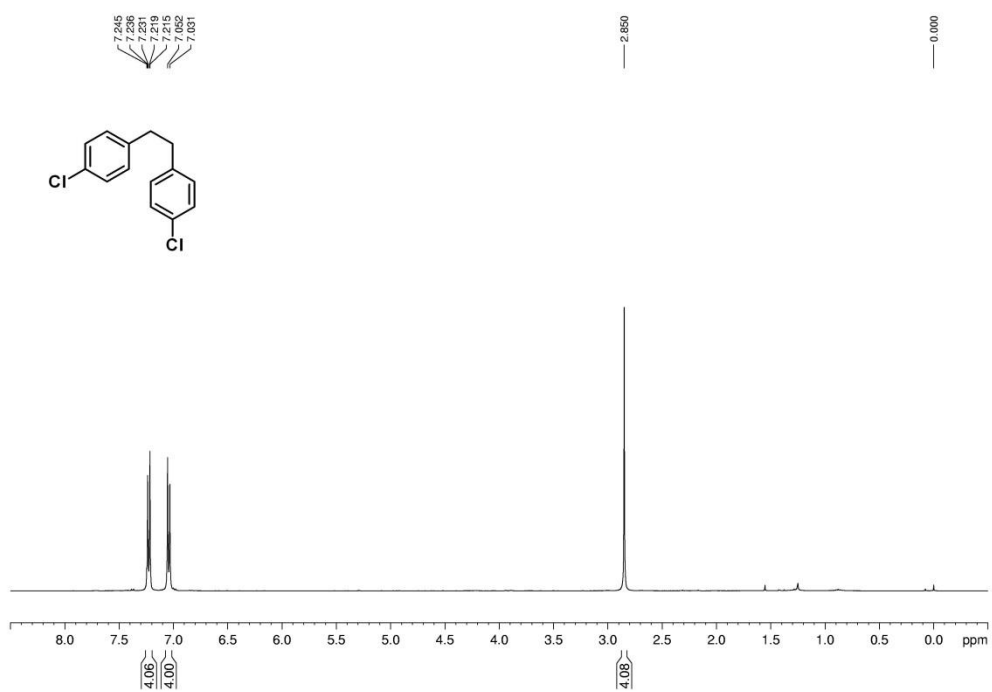
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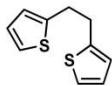
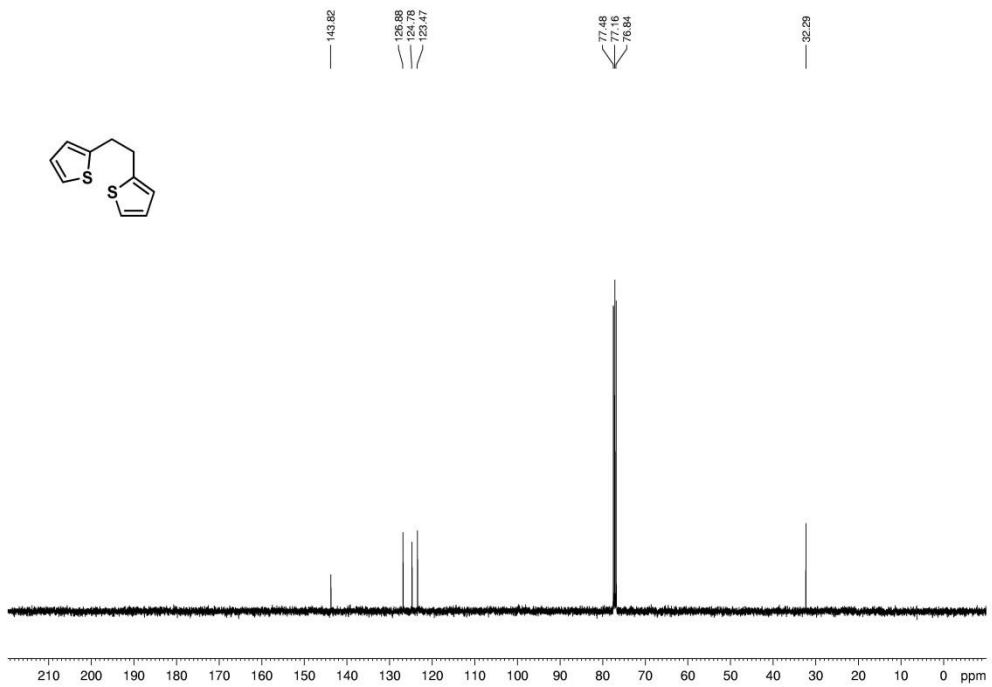
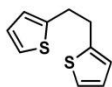
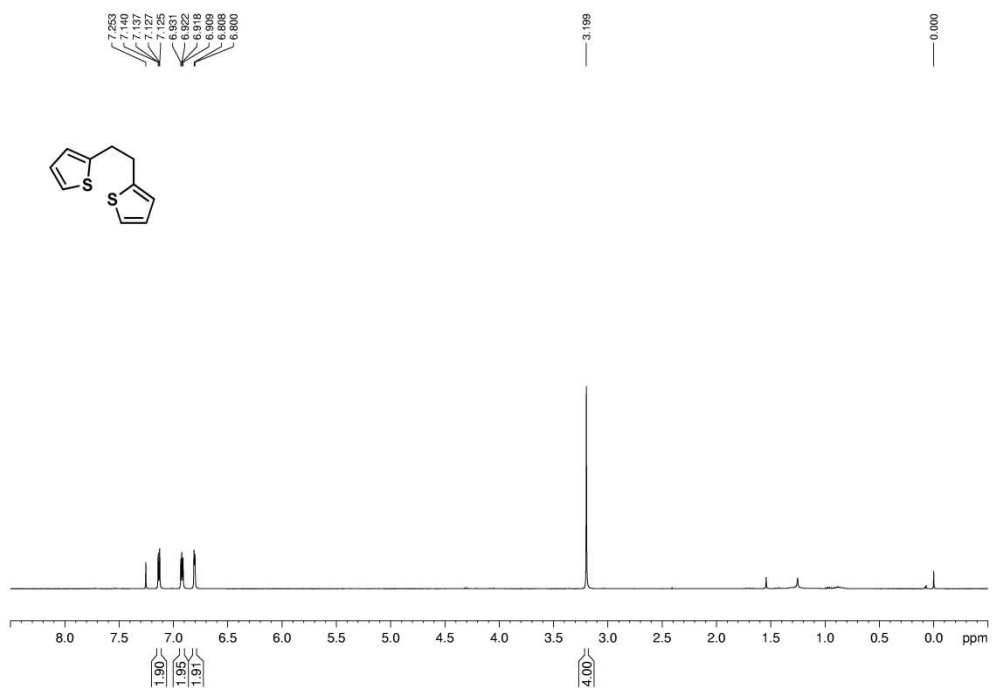
2l; ^{19}F NMR (376 MHz, CDCl_3)



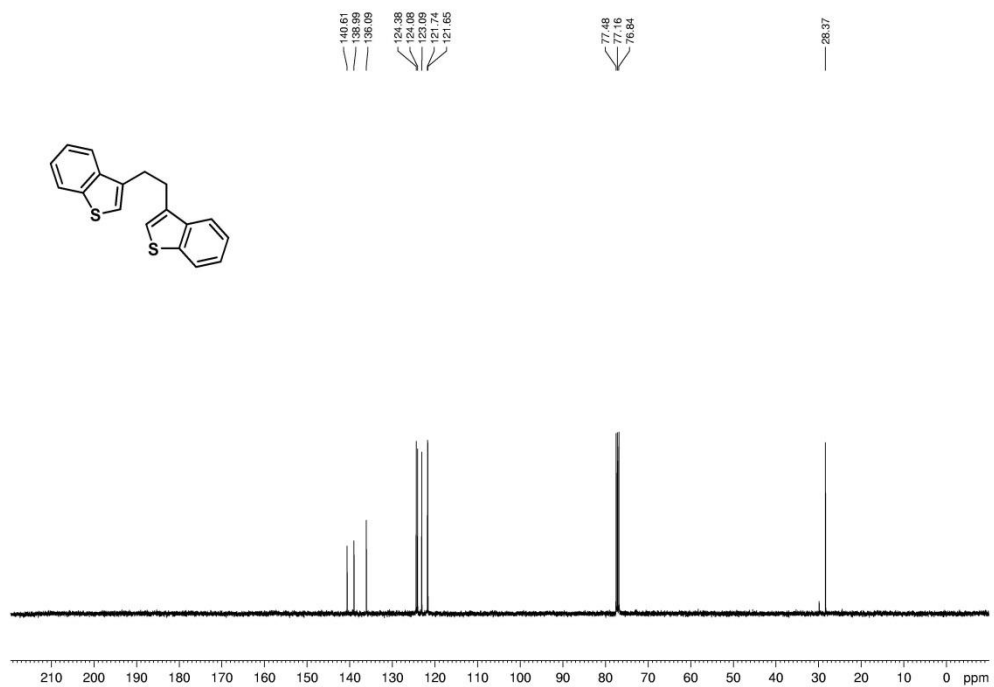
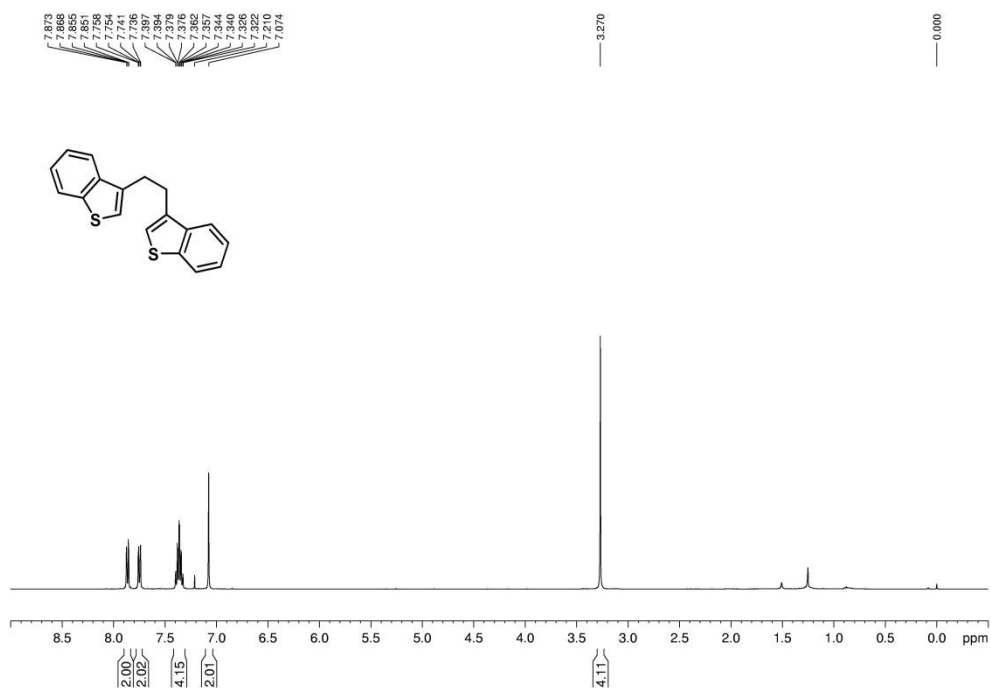
2m; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



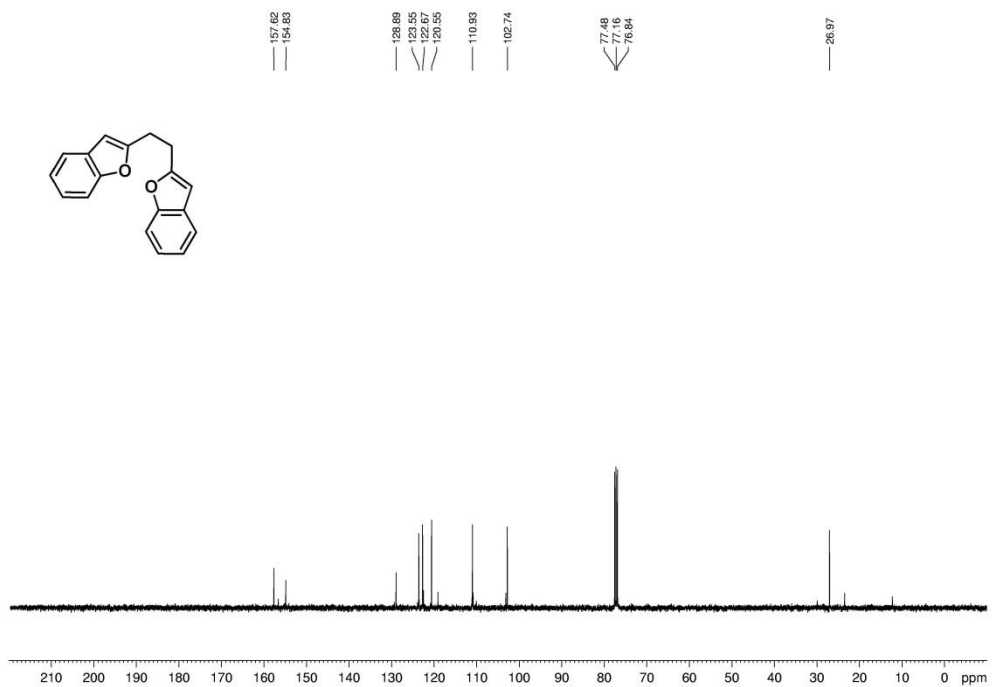
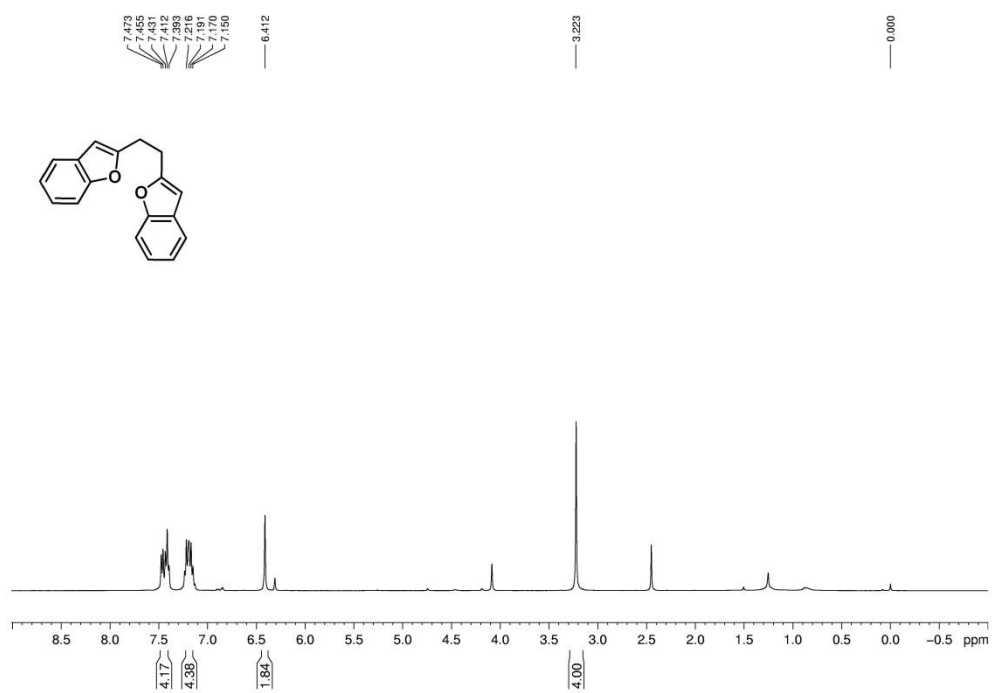
2n; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



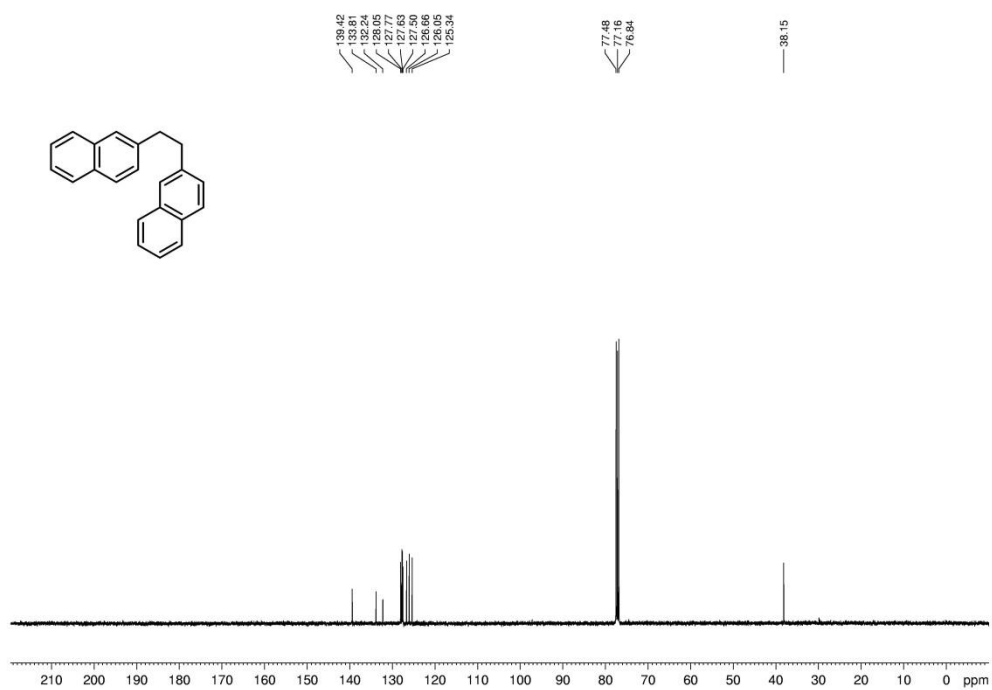
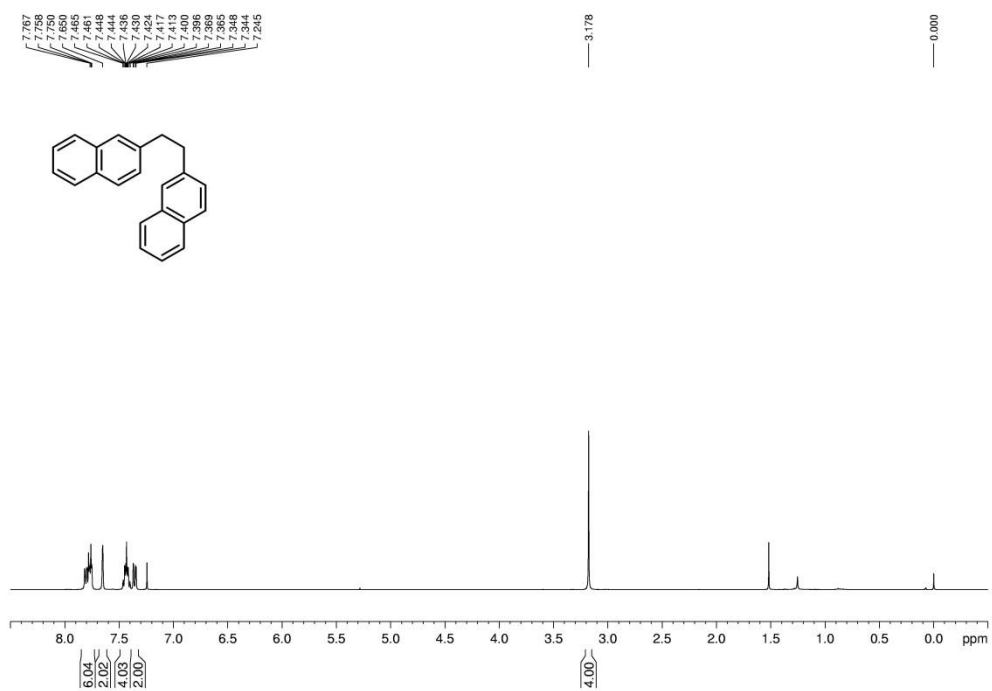
2o; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



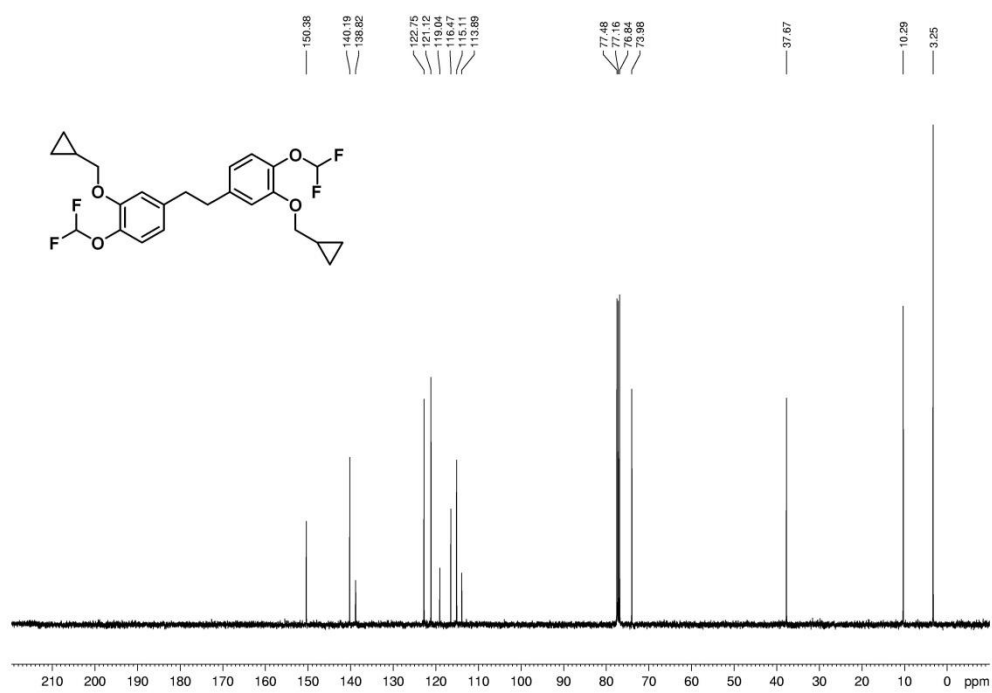
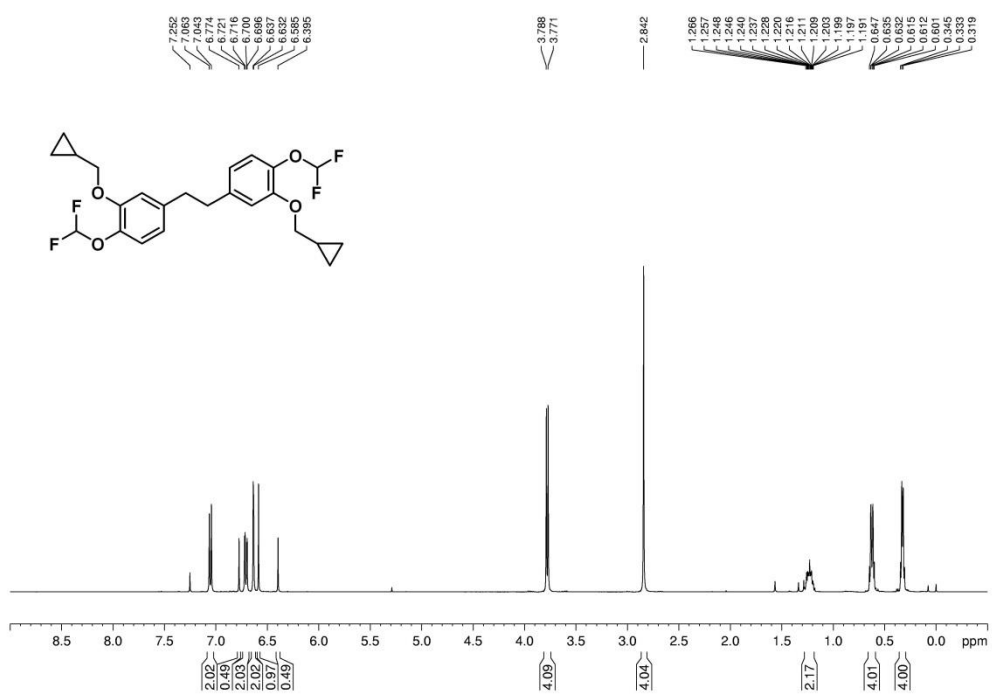
2p; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



2q; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



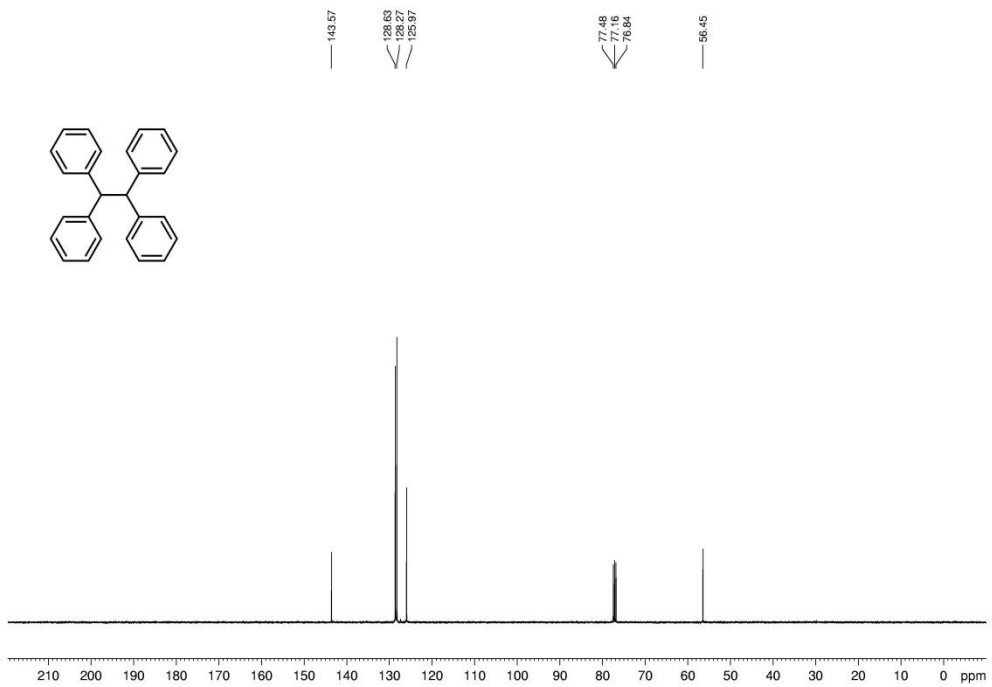
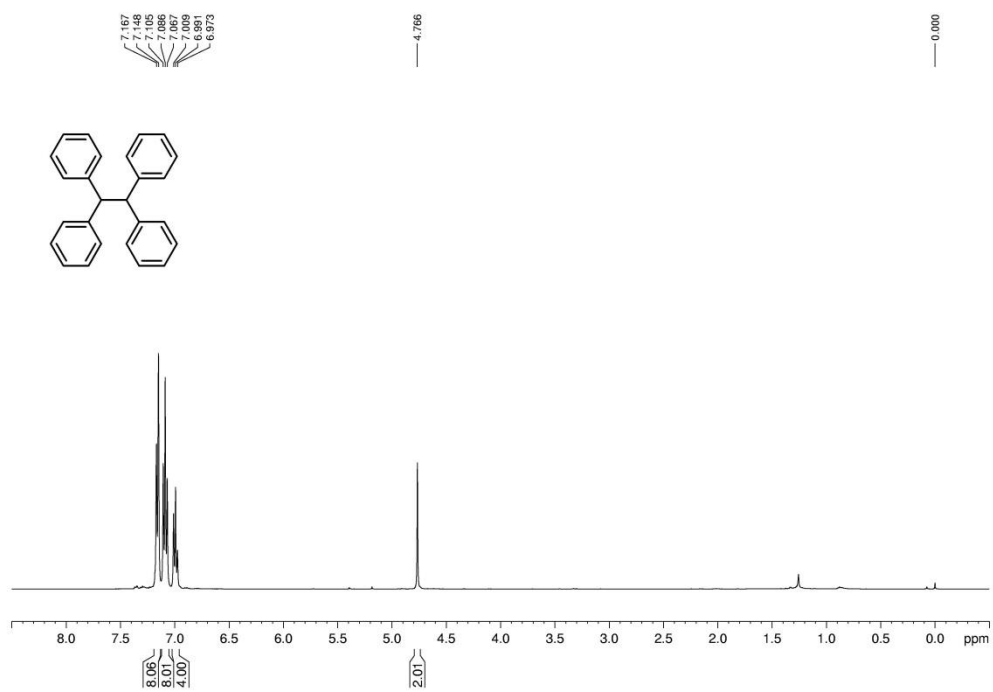
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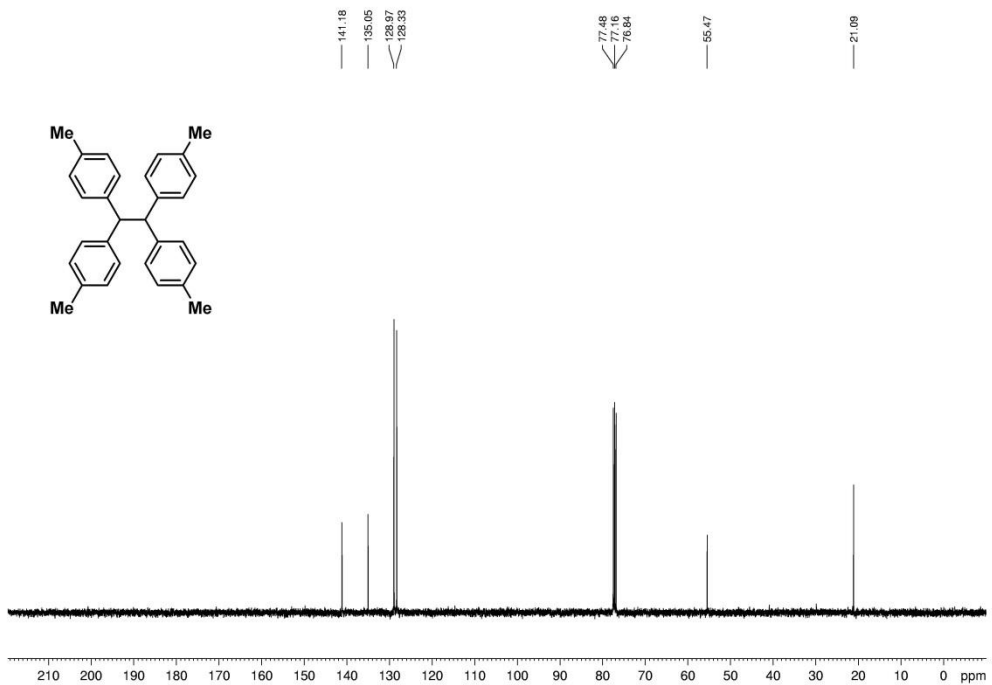
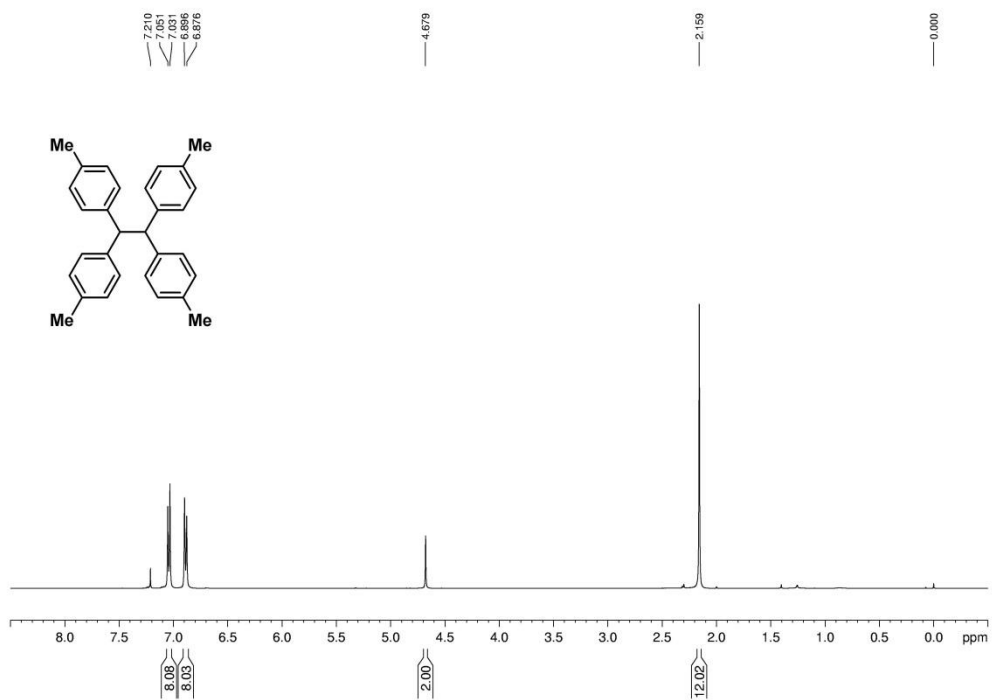
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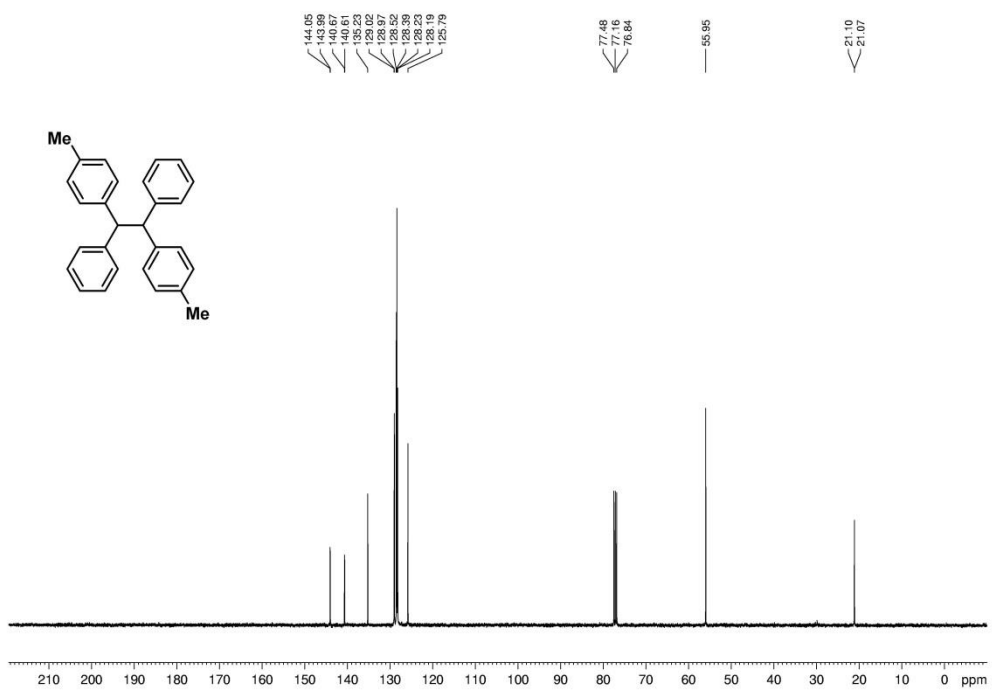
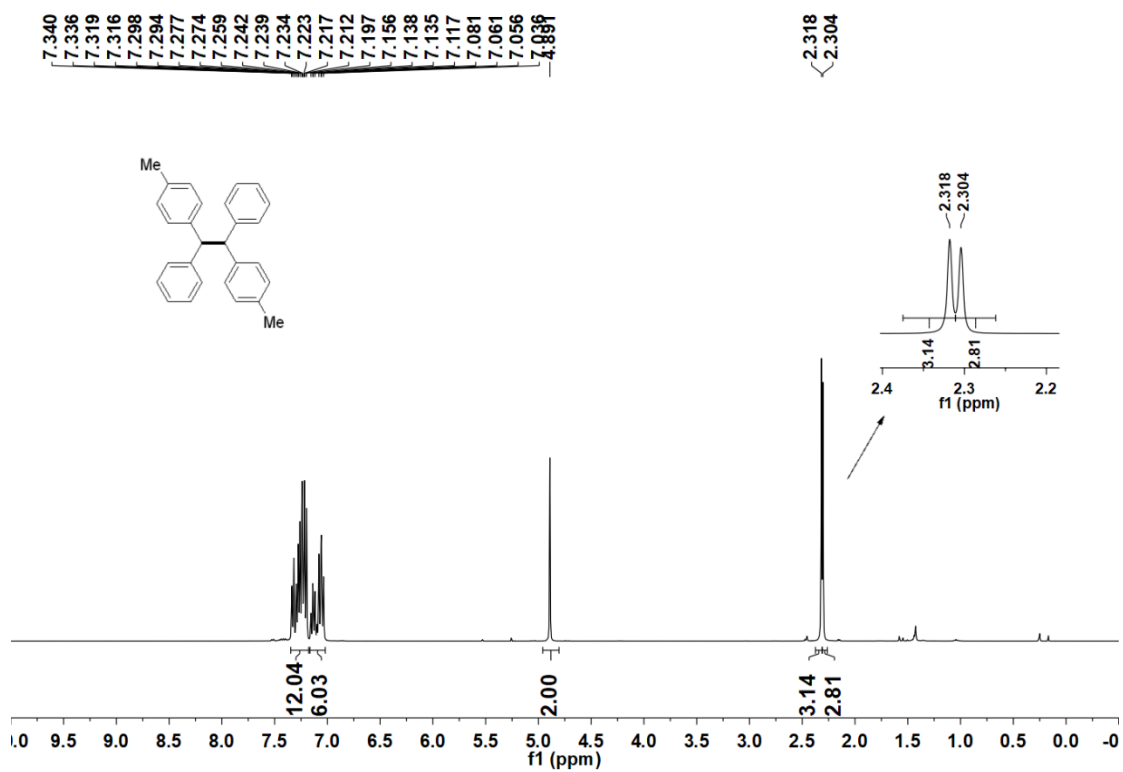
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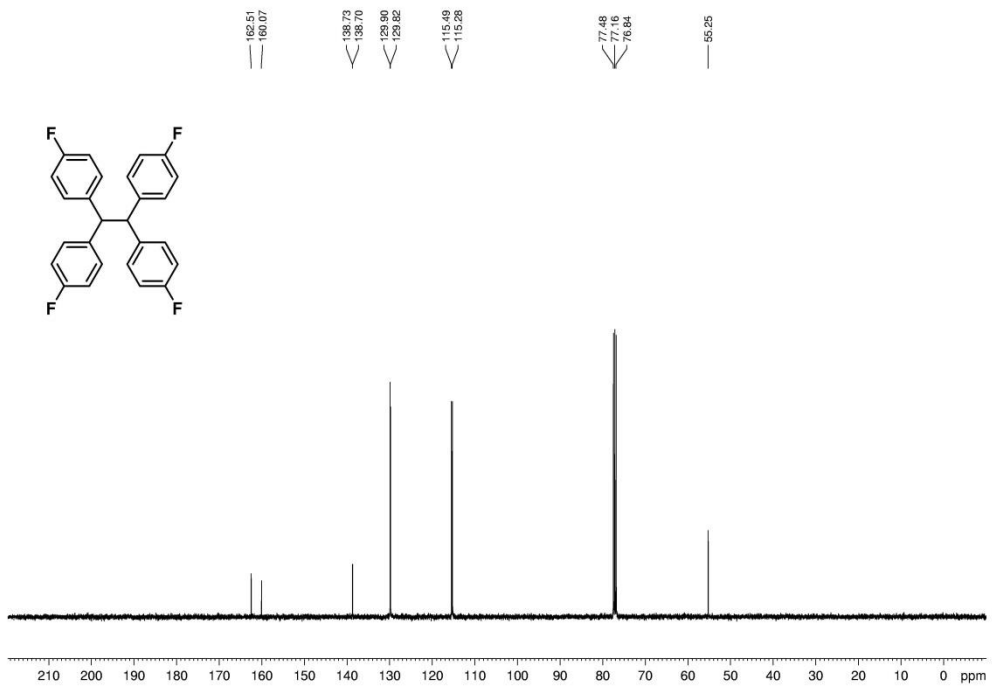
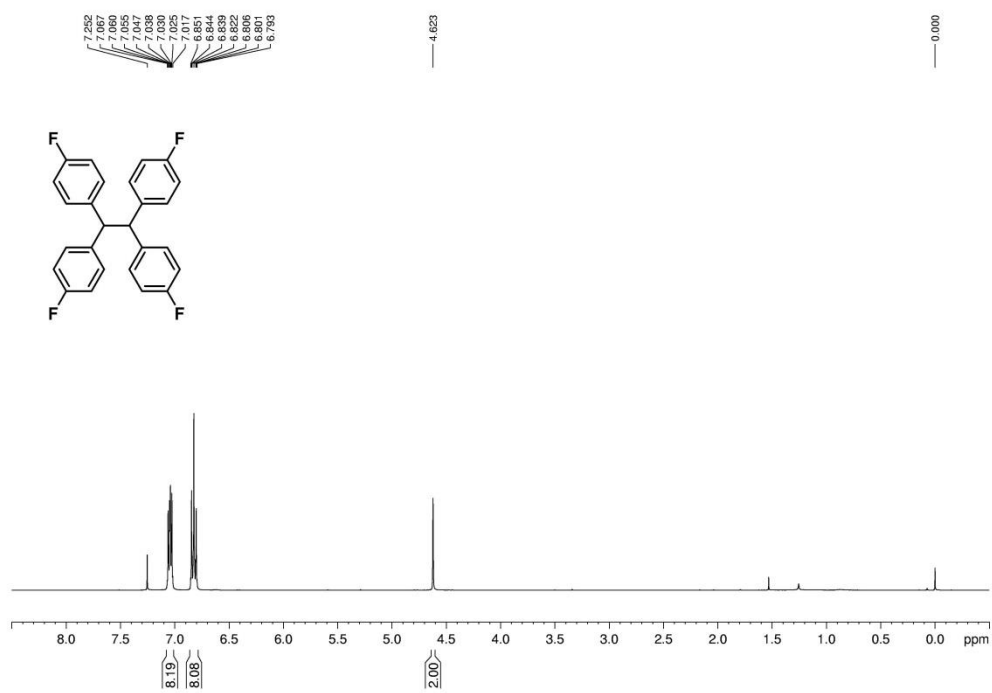
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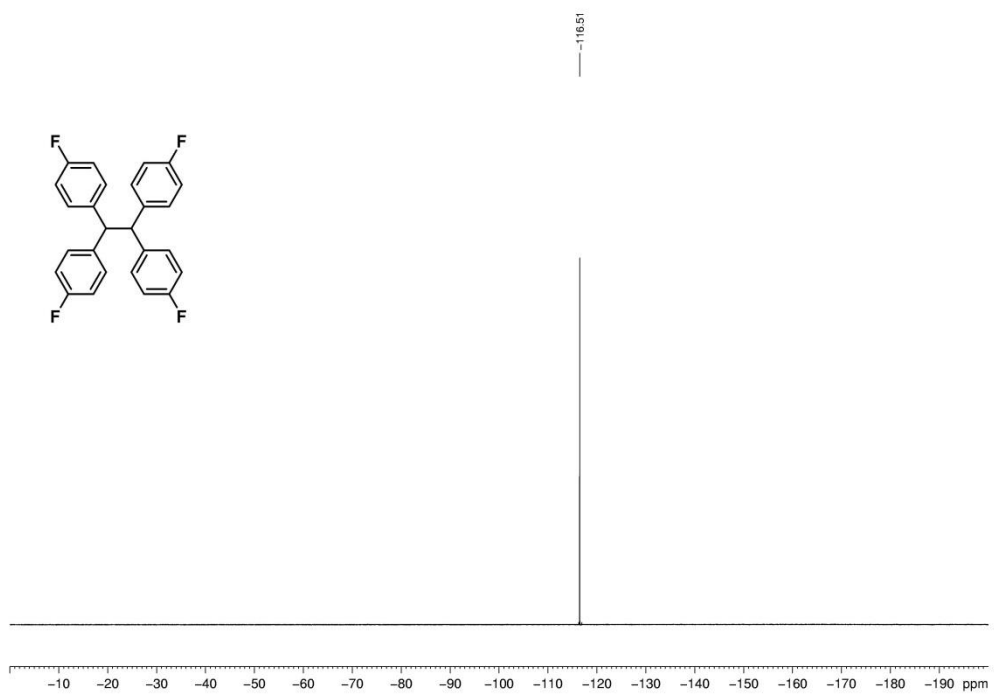
2u; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



2v; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)



2v; ^{19}F NMR (376 MHz, CDCl_3)



5; ^1H NMR (400 MHz, CDCl_3); ^{13}C NMR (100 MHz, CDCl_3)

