

Direct Benzylic Alkylation via Ni-Catalyzed Selective sp^3 C-O Activation

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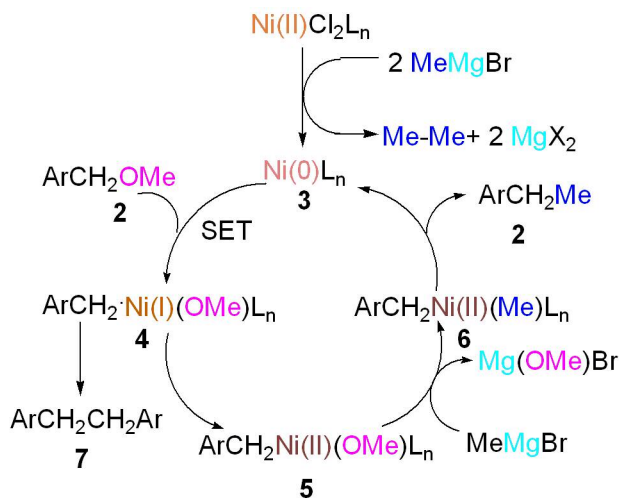
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Scheme 1. Plausible Mechanism on the Direct Alkylation via Ni(0)-Catalyzed Benzylic sp³ C-O Activation.



This alkylation was hypothesized through the pathway as Scheme 1. Ni(II) catalyst was reduced by MeMgBr to generate active species Ni(0) **3**. Benzyl methyl ether **1** could oxidatively add to Ni(0) through the SET process to produce the Ni(II) species **5**, which could undergo transmetalation with MeMgBr to form benzyl alkyl Ni(II) species **6**. After the reductive elimination to produce the desired product **2**, Ni(0) was regenerated to facilitate this catalytic cycle. The byproduct **7** of benzyl group partially supported those SET processes.¹ Further clearly understanding towards the mechanism is underway.

1. Patel, K. M.; Baltisberger, R. J.; Stenberg, V. I.; Woolsey, N. F. *J. Org. Chem.* **1982**, *7*, 4250.

Supporting Information

General: All reactions were carried out under N₂ atmosphere. All the metal reagents were purchased from Alfa Aesar and Acros Chemical and used without further purification. NiCl₂(dppf) was synthesized according to literature methods¹. The solvents were freshly distilled over sodium with the use of diphenyl ketone as an indicator. ¹H NMR (300 MHz) and ¹³C NMR (75.4 MHz) were registered on 300M spectrometers with CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in units (ppm) by assigning TMS resonance in the ¹H spectrum as 0.00 ppm and CDCl₃ resonance in the ¹³C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. GC, HPLC, MS, and HRMS were performed by the Analytical Center in Peking University.

General procedure for the synthesis of methoxymethyl naphthalene.

Methoxymethyl naphthalene were made from the naphthalenylmethanol and iodomethane in dry THF at rt~60 °C using sodium hydride as base. Various of naphthalenylmethanols was made from 2-naphthaldehyde and corresponding Grignard reagents.

2-(Methoxymethyl)naphthalene (1a) ¹H NMR (300 MHz, CDCl₃): δ 3.42 (s, 3H), 4.61 (s, 2H), 7.45-7.48 (m, 3H), 7.78-7.84 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 58.1, 74.7, 125.6, 125.8, 126.0, 126.4, 127.6, 127.8, 128.1, 132.9, 133.2, 135.6. MS (EI) *m/z*: 172 (M⁺).

2-(Methoxy(phenyl)methyl)naphthalene (1h) ¹H NMR (300 MHz, CDCl₃): δ 3.34 (s, 3H), 5.32 (s, 1H), 7.16-7.41 (m, 8H), 7.69-7.82 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 56.8, 85.3, 124.8, 125.6, 125.8, 126.0, 126.9, 127.4, 127.6, 127.9, 128.2, 128.3, 132.8, 133.1, 139.4, 141.9. MS (EI) *m/z*: 248 (M⁺).

2-(1-Methoxyethyl)naphthalene (1i) ¹H NMR (300 MHz, CDCl₃): 1.50 (d, *J*=3.3Hz, s3H), 3.23-3.25 (m, 3H), 4.43 (d, 3.2Hz, 1H), 7.43-7.47 (m 3H), 7.72-7.84 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 23.8, 56.5, 79.7, 124.0, 125.1, 125.7, 126.0, 127.6, 127.8, 128.3, 133.0, 133.2, 140.8. MS (EI) *m/z*: 186 (M⁺).

2-(1-Methoxypropyl)naphthalene (1j) ¹H NMR (300 MHz, CDCl₃): 0.86-0.91 (m, 3H), 1.72-1.96 (m, 2H), 3.23-3.26 (m, 3H) 4.16 (t, *J*=6.6Hz, 1H), 7.41-7.49 (m, 3H), 7.70-7.83 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 10.2, 30.7, 56.6, 85.6, 124.4, 125.6, 125.9, 126.0,

127.6, 127.7, 128.2, 133.0, 133.1, 139.5. MS (EI) m/z: 200 (M⁺)

1-(Methoxymethyl)naphthalene (1k) H NMR (300 MHz, CDCl₃): δ 3.23-3.26 (m, 3H), 4.70 (s, 2H), 7.21-7.36 (m, 4H), 7.60-7.68 (m, 2H), 7.92-7.95 (m, 1H). ¹³C NMR (75.4 MHz, CDCl₃): 57.9, 72.9, 123.8, 125.0, 125.6, 126.0, 126.3, 128.4, 128.44, 131.6, 133.5, 133.6. MS (EI) m/z: 172 (M⁺). 2924, 1098, 792, 774.8,

The procedure for the synthesis of the 2-(ethoxymethyl) naphthalene (1b)

2-(bromomethyl)naphthalene(1.1050g, 5mmol) in THF(5ml) was added to EtONa(1.7g, 25mmol) in EtOH(4ml). Afterwards, the reaction mixture was stirred for 15h at 45°. Water was added to the cooled solution and the residue was extracted 3 times with ethyl acetate. The organic layer was washed with water and dried over MgSO₄. The product was obtained by column chromatography(55%). ¹H NMR (300 MHz, CDCl₃): δ 1.13-1.18 (m, 3H), 3.41-3.48 (m, 2H), 4.52 (s, 2H), 7.31-7.36 (m, 3H), 7.65-7.71 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 15.2, 65.6, 72.7, 125.7, 125.9, 126.2, 127.6, 127.8, 128.0, 132.8, 133.2, 136.0. MS (EI) m/z: 186 (M⁺).

The procedure for the synthesis of the 2-(tert-butoxymethyl)naphthalene (1c)

2-(bromomethyl)naphthalene(1.1050g, 5mmol) in THF(5ml) was added to ^tBuOK(1.68g, 15mmol) and 18-crown-6(0.066g, 0.25mmol) in THF(3ml). Afterwards, the reaction mixture was stirred for 15h at 45°. Water was added to the cooled solution and the residue was extracted 3 times with ethyl acetate. The organic layer was washed with water and dried over MgSO₄. The product was obtained by column chromatography(40%). ¹H NMR (300 MHz, CDCl₃): δ 1.26 (s, 9H), 1.98 (s, 2H), 4.82-4.88 (m, 3H), 5.18-5.23 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 27.6, 64.1, 73.4, 125.3, 125.6, 125.64, 125.7, 127.5, 127.7, 127.8, 133.3, 137.2. MS (EI) m/z: 214 (M⁺).

2-(Phenoxymethyl)naphthalene (1d)

2-(phenoxymethyl)naphthalene were made from the phenol and 2-(bromomethyl)naphthalene in DMF at 70° using potassium carbonate as base(65%). ¹H NMR (300 MHz, CDCl₃): δ 5.18 (s, 2H), 6.96-7.85 (12H). ¹³C NMR (75.4 MHz, CDCl₃): 70.0, 114.8, 120.9, 125.2, 126.0, 126.2, 126.25, 127.7, 127.9, 128.3, 129.5, 133.0, 133.2, 134.5. MS (EI) m/z: 234 (M⁺).

Trimethyl(naphthalen-2-ylmethoxy)silane (1e)

Trimethyl(naphthalen-2-ylmethoxy)silane was made from 2-(bromomethyl)naphthalene and TMSCl in CH₂Cl₂ at room temperature using Et₃N as base(69%). ¹H NMR (300 MHz, CDCl₃): δ 0.19-0.21 (m, 9H), 4.85 (s, 2H), 7.42-7.45 (m, 3H), 7.78-7.82 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): -0.37, 64.7, 124.8, 124.9, 125.5, 125.9, 127.6, 127.8, 127.9, 132.7, 133.3, 138.4. MS (EI) m/z: 230 (M⁺).

Naphthalen-2-ylmethyl acetate (1f)

Naphthalen-2-ylmethyl acetate was made from naphthalen-2-ylmethanol and acetyl chloride in CH_2Cl_2 at room temperature using Et_3N as base(77%). ^1H NMR (300 MHz, CDCl_3): δ 2.12 (s, 3H), 5.26 (s, 2H), 7.47-7.50 (m, 3H), 7.81-7.85 (m, 4H). ^{13}C NMR (75.4 MHz, CDCl_3): 21.0, 66.4, 125.8, 126.2, 126.23, 127.3, 127.6, 127.9, 128.3, 133.0, 133.1, 133.3. MS (EI) m/z: 200 (M^+).

Naphthalen-2-ylmethanol (1g)

Naphthalen-2-ylmethanol was prepared according to literature methods⁴ from 2-naphthaldehyde. ^1H NMR (300 MHz, CDCl_3): δ 2.02 (s, 1H), 4.82 (s, 2H), 7.25-7.51 (m, 3H), 7.78-7.84 (m, 4H). ^{13}C NMR (75.4 MHz, CDCl_3): 65.4, 125.1, 125.4, 125.9, 126.1, 127.7, 127.8, 128.3, 132.9, 133.3, 138.3. MS (EI) m/z: 158 (M^+).

(Methoxymethyl)benzene (1s)

(Methoxymethyl)benzene was prepared according to literature methods⁵. ^1H NMR (300 MHz, CDCl_3): δ 3.38 (s, 3H), 4.45 (s, 2H), 7.33-7.35 (m, 5H). ^{13}C NMR (75.4 MHz, CDCl_3): 58.0, 74.6, 127.56, 127.6, 128.3, 138.1. MS (EI) m/z: 122 (M^+).

General procedure for the synthesis of methoxymethylbiphenyl

A mixture of Na_2CO_3 (20mmol), $\text{Pd}(\text{OAc})_2$ (0.05mmol), aryl halide(10mmol), arylboronic acid(15mmol), distilled water(21ml) and acetone(18ml) was stirred for 12h, afterward, the reaction solution was extracted four times with ethyl acetate. The combined organic phase was dried with MgSO_4 . After removing the solvent, the residue was purified by column chromatography on a silica gel column.

4-(Methoxymethyl)biphenyl (1l)

4-(Methoxymethyl)biphenyl was made from 1-bromo-4-(methoxymethyl)benzene and phenylboronic acid according to the general procedure. 1-bromo-4-(methoxymethyl)benzene was prepared from 1-bromo-4-(bromomethyl)benzene and MeONa according to the literature methods⁵. ^1H NMR (300 MHz, CDCl_3): δ 3.26 (s, 3H), 4.34 (s, 3H), 7.19-7.31 (m, 5H), 7.43-7.47 (m, 4H). ^{13}C NMR (75.4 MHz, CDCl_3): 58.0, 74.2, 126.9, 127.0, 127.1, 128.0, 128.6, 137.1, 140.4, 140.7. MS (EI) m/z: 198(M^+).

3-(Methoxymethyl)biphenyl (1m)

3-(Methoxymethyl)biphenyl was made from 1-bromo-3-(methoxymethyl)benzene and phenylboronic acid according to the general procedure. 1-bromo-3-(methoxymethyl)benzene was prepared from 1-bromo-3-(bromomethyl)benzene and MeONa according to the literature methods⁵. ^1H NMR (300 MHz, CDCl_3): δ 3.21 (s, 3H), 4.31 (s, 2H), 7.14-7.44 (m, 9H). ^{13}C NMR (75.4 MHz, CDCl_3): 57.9, 74.4, 126.2, 126.4, 127.0, 127.1,

128.5, 128.6, 138.6, 140.8. MS (EI) m/z: 198(M⁺).

2-(Methoxymethyl)biphenyl (1n)

2-(Methoxymethyl)biphenyl was made from 1-bromo-2-(methoxymethyl)benzene and phenylboronic acid according to the general procedure. 1-bromo-2-(methoxymethyl)benzene was prepared from 1-bromo-2-(bromomethyl)benzene and MeONa according to the literature methods⁵. ¹H NMR (300 MHz, CDCl₃): δ 3.27-3.29 (m, 3H), 4.32 (s, 2H), 7.26-7.54 (m, 9H). ¹³C NMR (75.4 MHz, CDCl₃): 58.0, 72.3, 127.0, 127.3, 127.5, 127.9, 129.0, 129.1, 129.8, 135.3, 140.7, 141.7. MS (EI) m/z: 198(M⁺).

4-Fluoro-4'-(methoxymethyl)biphenyl (1o)

4-Fluoro-4'-(methoxymethyl)biphenyl was made from 1-bromo-4-fluorobenzene and 4-(methoxymethyl)phenylboronic acid according to the general procedure. 4-(methoxymethyl)-phenylboronic acid was prepared from 1-bromo-2-(methoxymethyl)benzene Mg and trimethyl borate according to the literature methods⁶. ¹H NMR (300 MHz, CDCl₃): δ 3.41 (s, 3H), 4.49 (s, 2H), 7.07-7.14 (m, 2H), 7.38-7.55 (m, 6H). ¹³C NMR (75.4 MHz, CDCl₃): 58.1, 74.3, 115.4, 115.7, 126.9, 128.1, 128.5, 128.6, 137.2, 139.5, 160.7, 164.0. MS (EI) m/z: 216 (M⁺).

4-Methoxy-4'-(methoxymethyl)biphenyl (1p)

4-Methoxy-4'-(methoxymethyl)biphenyl was made from 1-bromo-4-(methoxymethyl)benzene and 4-methoxyphenylboronic acid according to the general procedure. ¹H NMR (300 MHz, CDCl₃): δ 3.41 (s, 3H), 3.84 (s, 3H), 4.49 (s, 2H), 6.96-6.99 (m, 2H), 7.37-7.40 (m, 2H), 7.52-7.56 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 55.3, 58.1, 74.4, 144.1, 126.7, 128.0, 128.2, 133.4, 136.5, 140.1, 159.1. MS (EI) m/z: 228 (M⁺).

4-(Methoxymethyl)-4'-methylbiphenyl (1q)

4-(Methoxymethyl)-4'-methylbiphenyl was made from 1-bromo-4-(methoxymethyl)benzene and p-tolylboronic acid according to the general procedure. ¹H NMR (300 MHz, CDCl₃): δ 2.34 (s, 3H), 3.36 (s, 3H), 4.44 (s, 2H), 7.18-7.55 (m, 8H). ¹³C NMR (75.4 MHz, CDCl₃): 20.9, 57.9, 74.3, 126.76, 126.77, 128.0, 129.4, 136.80, 136.82, 137.8, 140.3. MS (EI) m/z: 212 (M⁺).

4'-(Methoxymethyl)biphenyl-4-ol (1r)

4'-(Methoxymethyl)biphenyl-4-ol was made from 4-bromophenol and 4-(methoxymethyl)phenylboronic acid according to the general procedure. ¹H NMR (300 MHz, DMSO-d₆): δ 3.30 (s, 3H), 4.42 (s, 2H), 6.90 (d, J=4.2Hz, 2H), 7.35 (d, J=4.05Hz, 2H), 7.49-7.58 (m, 4H), 9.62 (s, 1H). ¹³C NMR (75.4 MHz, DMSO-d₆): 57.6, 73.6, 115.9, 126.0, 127.9, 128.3, 130.8, 136.5, 139.6, 157.3.

The procedure for the synthesis of the 2-methoxy-6-(methoxymethyl)naphthalene (3)

2-Methoxy-6-(methoxymethyl)naphthalene were made from the (6-methoxynaphthalen-2-yl)methanol and iodomethane in dry THF at 60 °C using sodium hydride as base. The (6-methoxynaphthalen-2-yl)methanol was prepared according to the literature method⁷.

¹H NMR (300 MHz, CDCl₃): δ 3.38 (s, 3H), 3.84 (s, 3H), 4.54 (s, 2H), 7.09-7.15 (m, 2H), 7.39-7.42 (m, 1H), 7.67-7.71 (m, 3H). ¹³C NMR (75.4 MHz, CDCl₃): 55.1, 57.9, 74.7, 105.5, 118.8, 126.3, 126.4, 126.9, 128.6, 129.2, 133.2, 134.0, 157.5. MS (EI) m/z: 202 (M⁺).

Typical procedures for the benzylic alkylation

NiCl₂(dppf) (6.8 mg, 0.01 mmol), dppf(5.5mg, 0.01mmol), 2-(Methoxymethyl)naphthalene (86.0 mg, 0.5 mmol), and 4 mL of freshly distilled toluene (ether) were added into a dry Schlenk tube under a nitrogen atmosphere, and the methylmagnesium bromide (0.25mL, 3M in ether) was added at room temperature later. The reaction mixture was heated to appointed temperature and stirred for 15 h. The solution was cooled to room temperature and quenched with 1M aqueous HCl. The residue was extracted with ethyl acetate. The organic layer was washed with water, and dried over MgSO₄. The solvent was removed and the product was obtained by column chromatography.

2-Ethynaphthalene (2a). ¹H NMR (300 MHz, CDCl₃): δ 1.29-1.34 (m, 3H), 2.76-2.84 (m, 2H), 7.31-7.45 (m, 3H), 7.61 (s, 1H), 7.74-7.80 (m, 3H). ¹³C NMR (75.4 MHz, CDCl₃): 1.55, 29.0, 125.0, 125.5, 125.8, 127.1, 127.4, 127.6, 127.8, 131.9, 133.7, 141.7. MS (EI) m/z: 156 (M⁺). IR (KBr, cm⁻¹): ν 3051, 2964, 2929, 1509, 1453, 888, 853, 816, 743.

2-(1-Phenylethyl)naphthalene (2b). ¹H NMR (300 MHz, CDCl₃): δ 1.72 (d, J=3.6Hz, 3H), 4.30 (d, J=3.6Hz, 1H), 7.18-7.45 (m, 8H), 7.70-7.80 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃): 21.7, 44.8, 125.3, 125.33, 125.9, 126.1, 126.8, 127.5, 127.69, 127.7, 127.9, 128.4, 132.0, 133.5, 143.7, 146.2. MS (EI) m/z: 232 (M⁺). IR (KBr, cm⁻¹): ν 3054, 2966, 2929, 1600, 1493, 1451, 856, 819, 745, 700.

2-Propylnaphthalene (2e). ¹H NMR (300 MHz, CDCl₃): δ 0.94-0.99 (m, 3H), 1.69-1.76 (m, 2H), 2.71-2.77 (m, 2H), 7.31-7.81 (m, 7H). ¹³C NMR (75.4 MHz, CDCl₃): 13.9, 24.5, 38.2, 125.0, 125.8, 126.4, 127.4, 127.44, 127.6, 127.7, 131.7, 133.5, 140.3. MS (EI) m/z: 170 (M⁺). IR (KBr, cm⁻¹): ν 2957, 2929, 2870, 1508, 1464, 848, 814, 743.

1-Ethynaphthalene (2g). ¹H NMR (300 MHz, CDCl₃): δ 1.37 (t, J=7.8Hz, 3H), 3.09-3.12 (m, 2H), 7.21-7.51 (m, 4H), 7.69-8.07 (m, 3H). ¹³C NMR (75.4 MHz, CDCl₃): 15.0, 25.9, 123.7, 124.8, 125.4, 125.6, 126.4, 128.7, 131.7, 133.8, 140.2. MS (EI) m/z: 156 (M⁺). IR (KBr, cm⁻¹): ν 2966, 1454, 797, 776.

4-Ethylbiphenyl (2h). ¹H NMR (300 MHz, CDCl₃): δ 1.23-1.29 (m, 3H), 2.63-2.71 (m, 2H), 7.25-7.59 (m, 9H). ¹³C NMR (75.4 MHz, CDCl₃): 15.6, 28.5, 126.9, 127.0, 127.03, 128.3, 128.7, 138.6, 141.1, 143.3. MS (EI) m/z: 182 (M⁺). IR (KBr, cm⁻¹): ν 3027, 2964,

2929, 1487, 1451, 835, 759, 731, 695.

3-Ethylbiphenyl (2i). ^1H NMR (300 MHz, CDCl_3): δ 1.24-1.30 (m, 3H), 2.66-2.74 (m, 2H), 7.16-7.60 (m, 9H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.7, 29.0, 124.5, 126.8, 127.1, 127.2, 128.66, 128.7, 141.3, 144.7. MS (EI) m/z : 182 (M^+). IR (KBr, cm^{-1}): ν 3030, 2965, 2930, 1599, 1479, 890, 800, 754, 698.

2-Ethylbiphenyl (2j). ^1H NMR (300 MHz, CDCl_3): δ 1.07-1.12 (m, 3H), 2.56-2.63 (m, 2H), 7.19-7.43 (m, 9H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.6, 26.1, 125.5, 126.7, 127.4, 128.0, 128.5, 129.2, 129.9, 141.6. MS (EI) m/z : 182 (M^+). IR (KBr, cm^{-1}): ν 3059, 1479, 749, 701.

4-Ethyl-4'-methylbiphenyl (2k). ^1H NMR (300 MHz, CDCl_3): δ 1.25 (t, $J=7.5\text{Hz}$, 3H), 2.36 (s, 3H), 2.62-2.70 (m, 2H), 7.20-7.25 (m, 4H), 7.46-7.51 (m, 4H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.6, 21.0, 28.5, 126.8, 126.84, 128.2, 129.4, 136.6, 138.3, 138.5, 143.0. MS (EI) m/z : 196 (M^+). IR (KBr, cm^{-1}): ν 2965, 1498, 908, 810, 732.

4-Ethyl-4'-methoxybiphenyl (2l). ^1H NMR (300 MHz, CDCl_3): δ 1.25 (t, $J=7.8\text{Hz}$, 3H), 2.65 (d, $J=3.75\text{Hz}$, 2H), 3.78 (s, 3H), 6.92-6.95 (m, 2H), 7.21-7.24 (m, 2H), 7.45-7.51 (m, 4H). C NMR (75.4 MHz, CDCl_3): 15.6, 28.4, 55.2, 114.1, 126.6, 127.9, 128.2, 133.6, 138.1, 142.6, 158.8. MS (EI) m/z : 212 (M^+). IR (KBr, cm^{-1}): ν 2965, 1498, 1247, 907, 822, 735-704.

4'-Ethylbiphenyl-4-ol (2m). ^1H NMR (300 MHz, CDCl_3): δ 1.24-1.29 (m, 3H), 2.64-2.72 (m, 2H), 4.85 (s, 1H), 6.88-6.91 (m, 2H), 7.24-7.27 (m, 2H), 7.45-7.49 (m, 4H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.6, 28.5, 115.6, 126.6, 128.2, 128.23, 134.0, 138.2, 142.8, 154.7. IR (KBr, cm^{-1}): ν 3419, 2963, 2928, 1610, 1498, 1263, 818.

2-Ethyl-6-methoxynaphthalene (4). ^1H NMR (300 MHz, CDCl_3): δ 1.30 (t, $J=7.8\text{Hz}$, 3H), 2.76-2.81 (m, 2H), 3.90 (s, 3H), 7.11-7.14 (m, 2H), 7.30-7.33 (m, 1H), 7.55-7.69 (m, 3H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.6, 28.8, 55.2, 105.6, 118.6, 125.4, 126.6, 127.5, 128.9, 129.1, 132.8, 139.4, 157.0. MS (EI) m/z : 186 (M^+). IR (KBr, cm^{-1}): ν 2961, 2927, 1605, 1487, 1462, 1267, 1224, 1172, 1162, 1030, 854, 817.

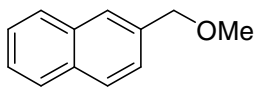
2-Ethyl-6-methylnaphthalene (5a) Path A: 2-Ethyl-6-methylnaphthalene was prepared from 2-Ethyl-6-methoxynaphthalene with literature method.⁸ Path B: Ni(acac)₂ (9.0 mg, 0.035 mmol), dppf (5.5 mg, 0.01 mmol), PCy₃ (14.0 mg, 0.05 mmol), 2-methoxy-6-(methoxymethyl)naphthalene (49.6 mg, 0.5 mmol), and 4 mL of freshly distilled toluene were added into a dry Schlenck tube under a nitrogen atmosphere, and the methylmagnesium bromide (0.25mL, 3M in ether) was added at room temperature later. The reaction mixture was heated to 70 °C and stirred for 12 h. The solution was cooled to room temperature and quenched with 1M aqueous HCl. The residue was extracted with ethyl acetate. The organic layer was washed with water, and dried over MgSO₄. The solvent was removed and the product was obtained by column chromatography (39.0mg, 93%). ^1H NMR (300 MHz, CDCl_3): δ 1.27-1.33 (m, 3H), 2.48 (s, 3H), 2.74-2.82 (m, 2H),

7.25-7.32 (m, 2H), 7.56 (s, 1H), 7.65-7.68 (m, 2H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.5, 21.6, 28.9, 125.2, 126.5, 127.05, 127.11, 127.2, 128.1, 131.9, 132.1, 134.5, 140.8. MS (EI) m/z : 170 (M^+). IR (KBr, cm^{-1}): ν 3050, 2962, 2929, 2854, 1606, 1502, 1461, 887, 821.

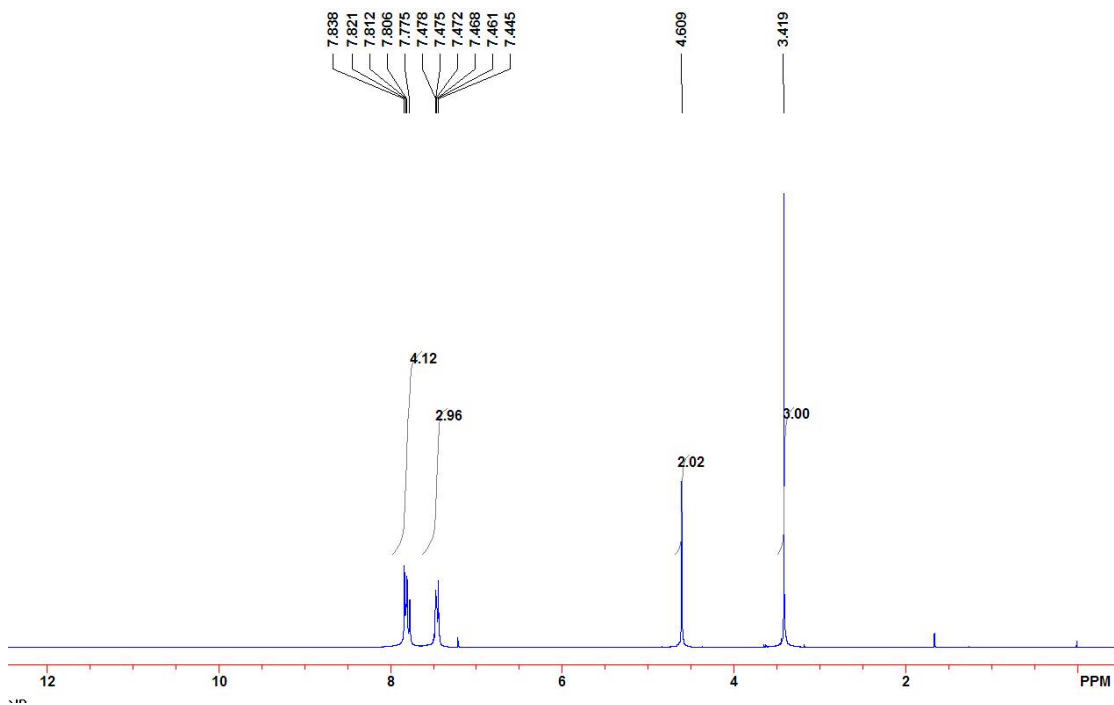
2-Ethyl-6-phenylnaphthalene (5b) 2-ethyl-6-phenylnaphthalene was prepared from 2-Ethyl-6-methoxynaphthalene with literature method⁸. ^1H NMR (300 MHz, CDCl_3): δ 1.33 (t, 7.8Hz, 3H), 2.77-2.83 (m, 2H), 7.35-8.00 (m, 11H). ^{13}C NMR (75.4 MHz, CDCl_3): 15.6, 29.1, 125.3, 125.5, 125.54, 127.2, 127.3, 127.34, 127.5, 127.9, 128.1, 128.8, 132.6, 137.7, 141.2, 141.9. MS (EI) m/z : 232 (M^+). IR (KBr, cm^{-1}): ν 2964, 906, 731, 696.

Reference:

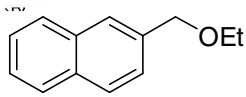
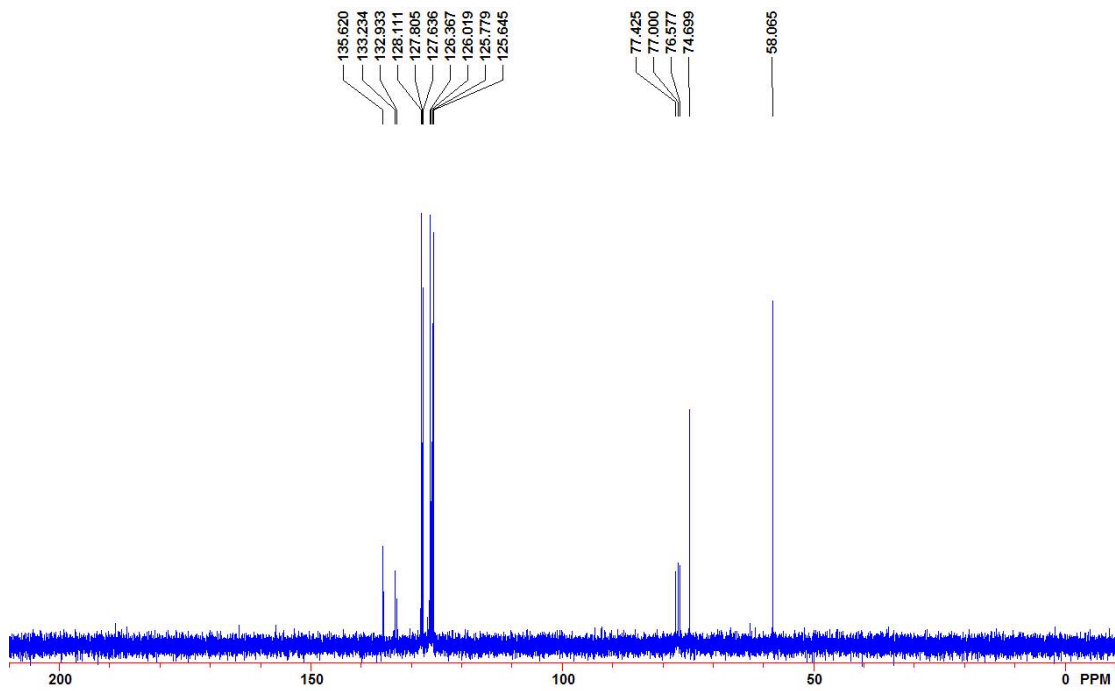
- 1 Dalew, A. R.; Lichtenberg, D.; Katcher, M.; Davison, A. *Inorganic chemistry* **1978**, *17*, 2859
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- 8 Guan, B.; Xiang, S.; Wu, T.; Wang, B. Zhao, K.; Shi, Z. **2008**, *Chem. Comm.* in press..



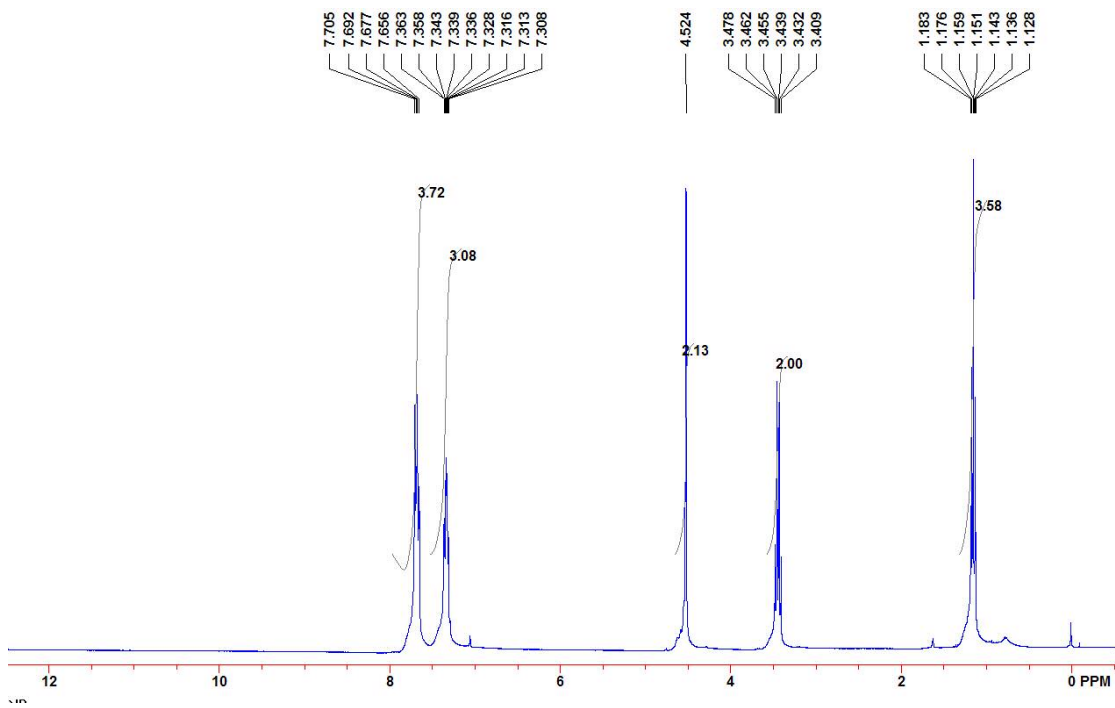
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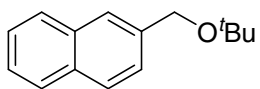
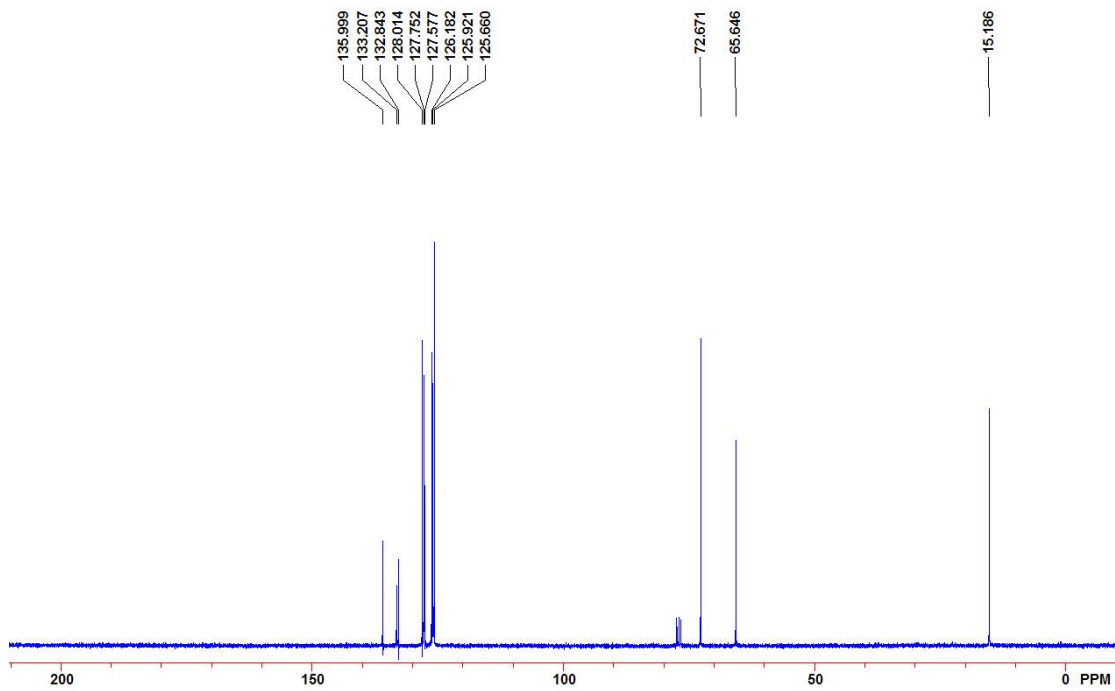
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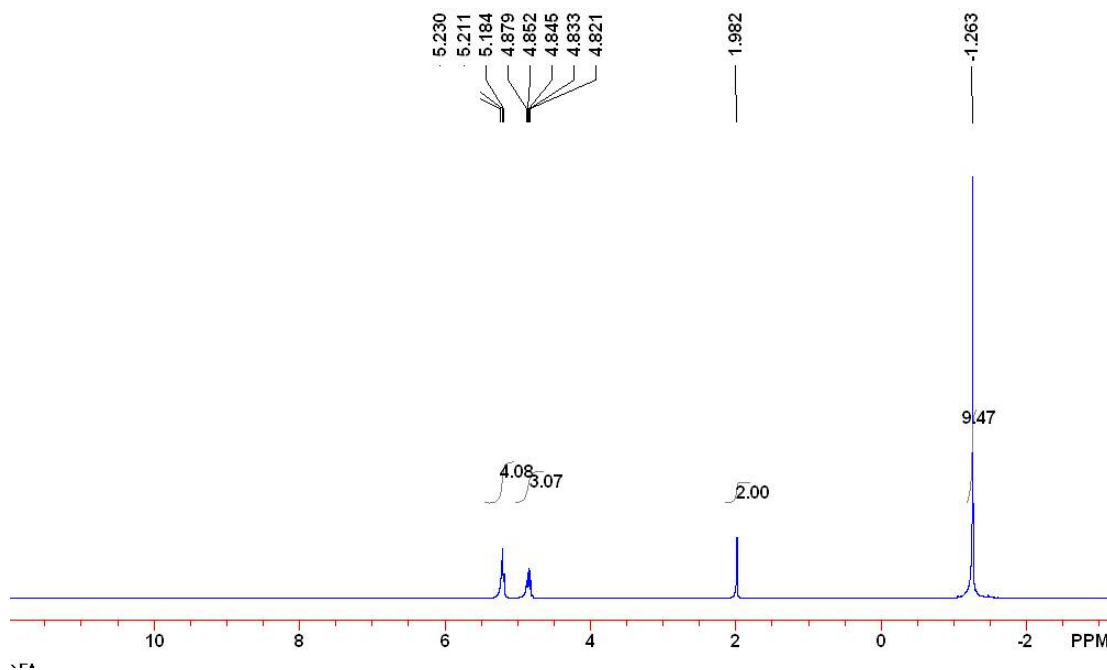
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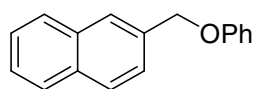
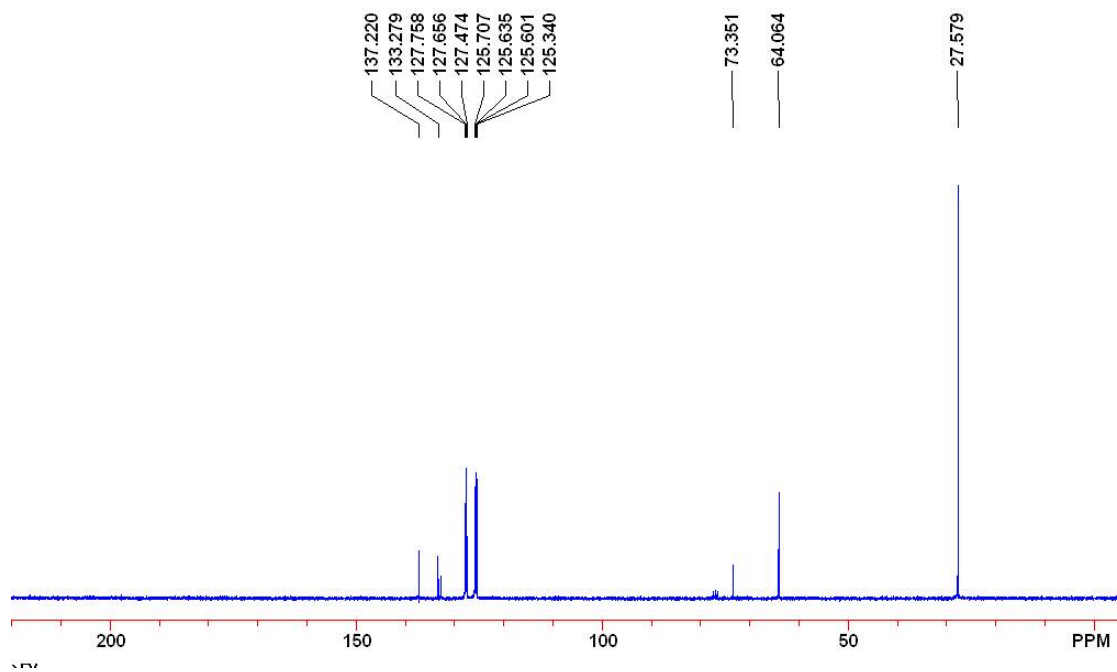
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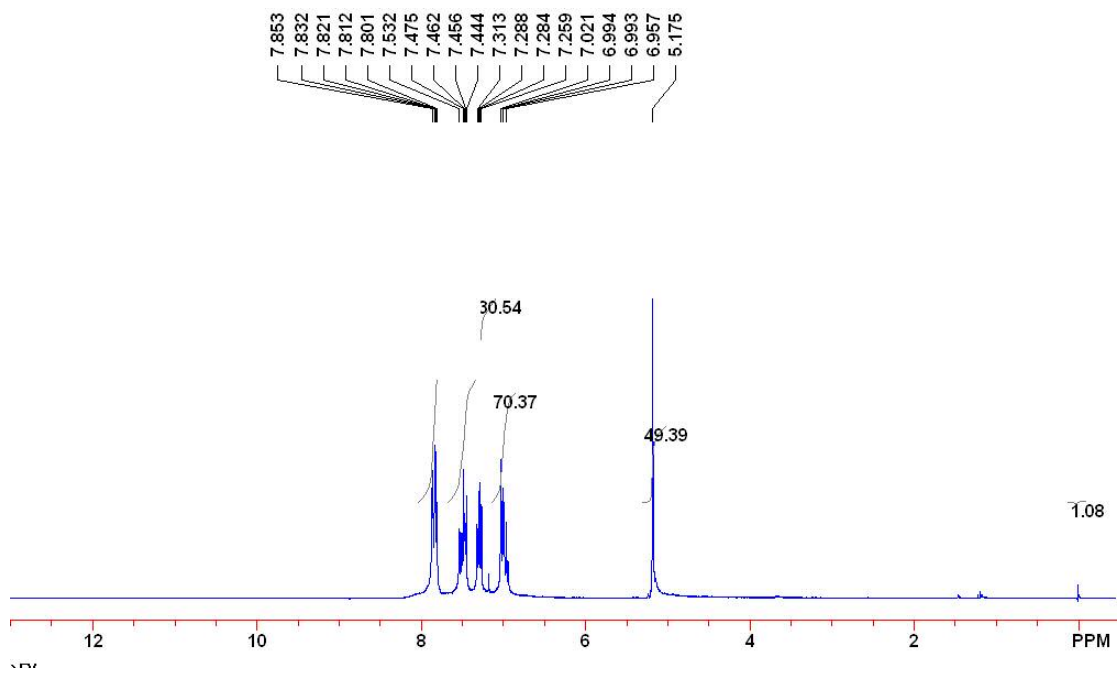
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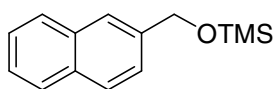
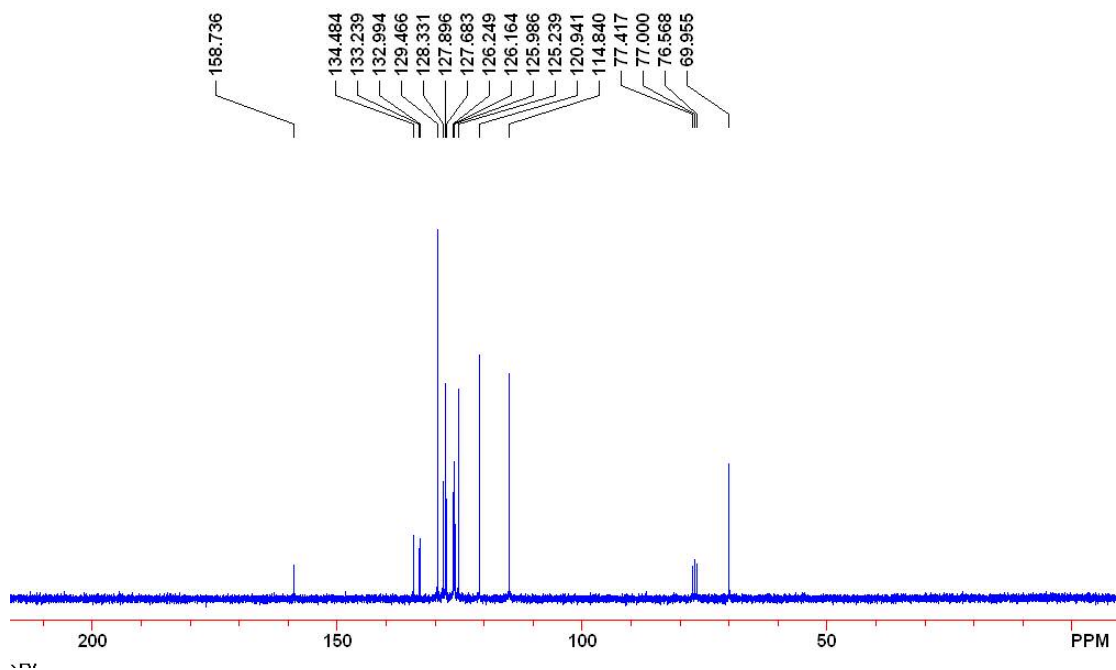
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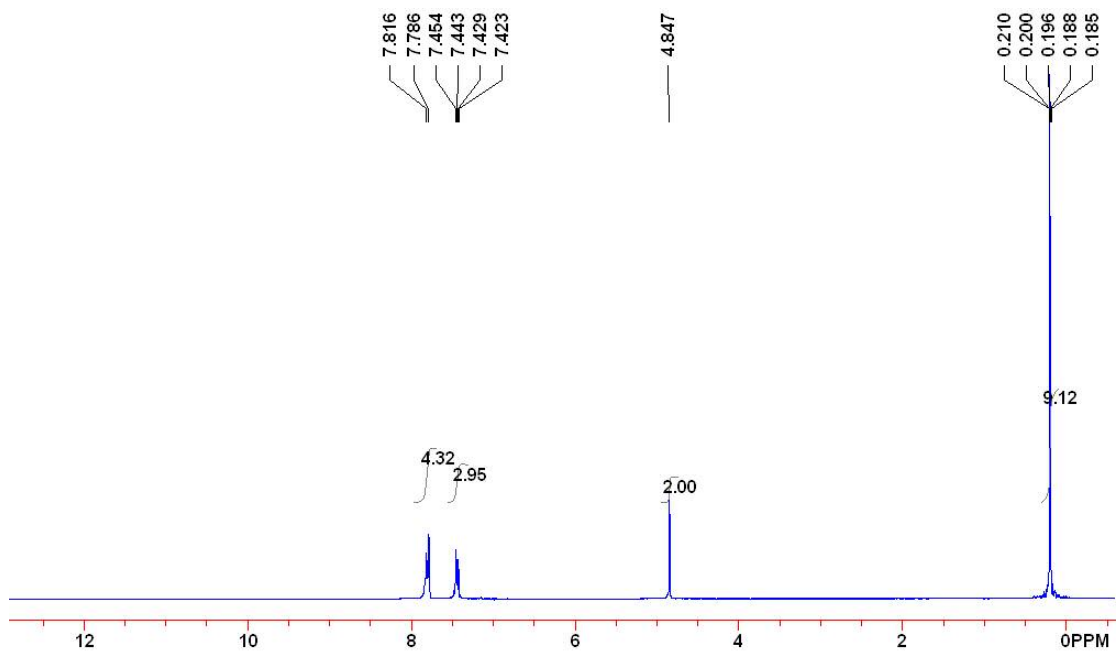
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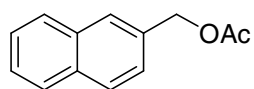
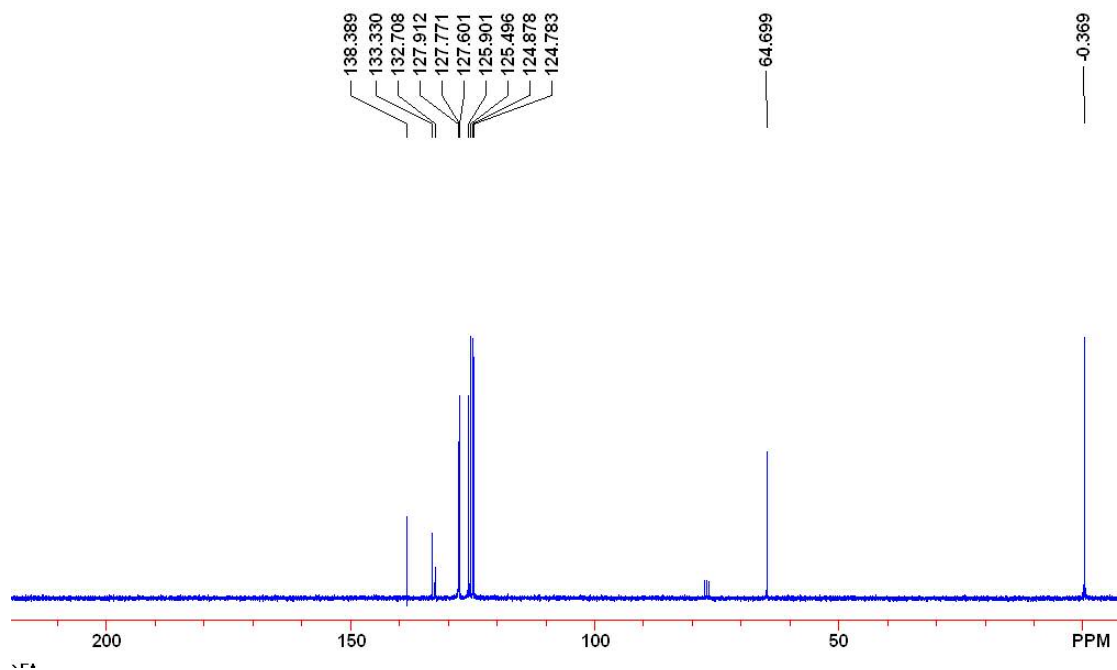
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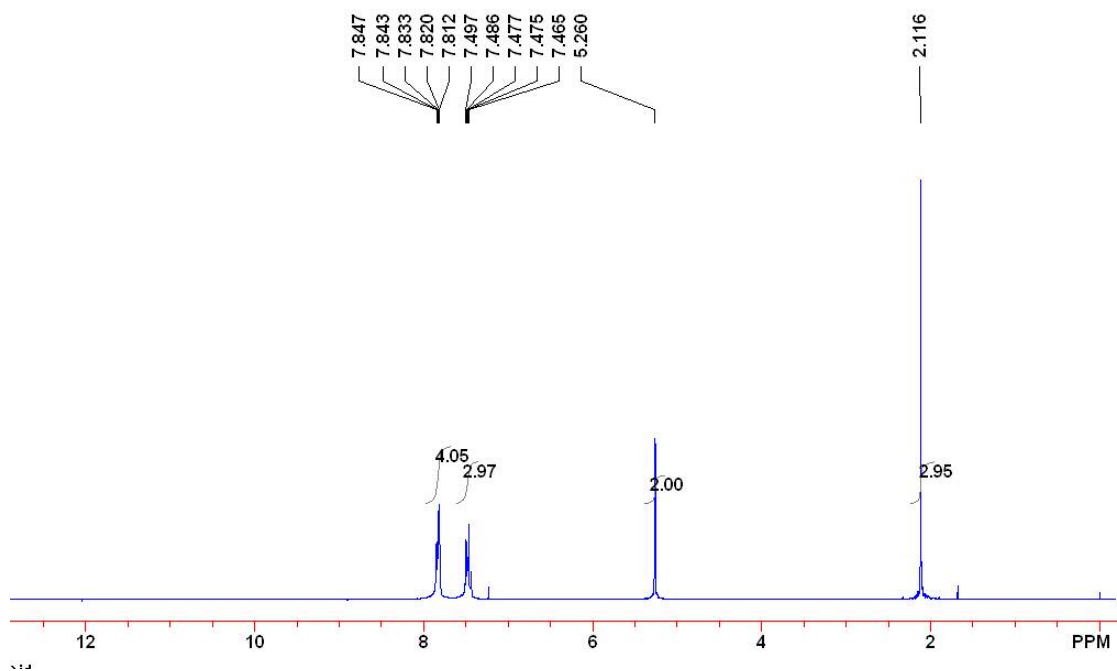
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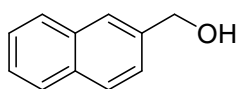
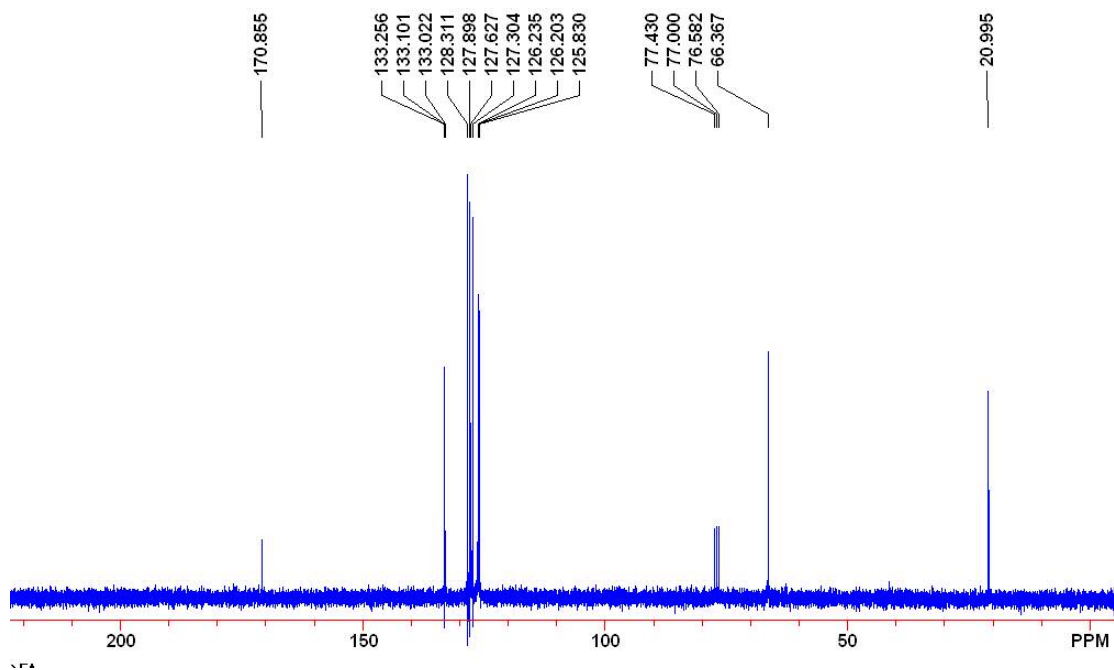
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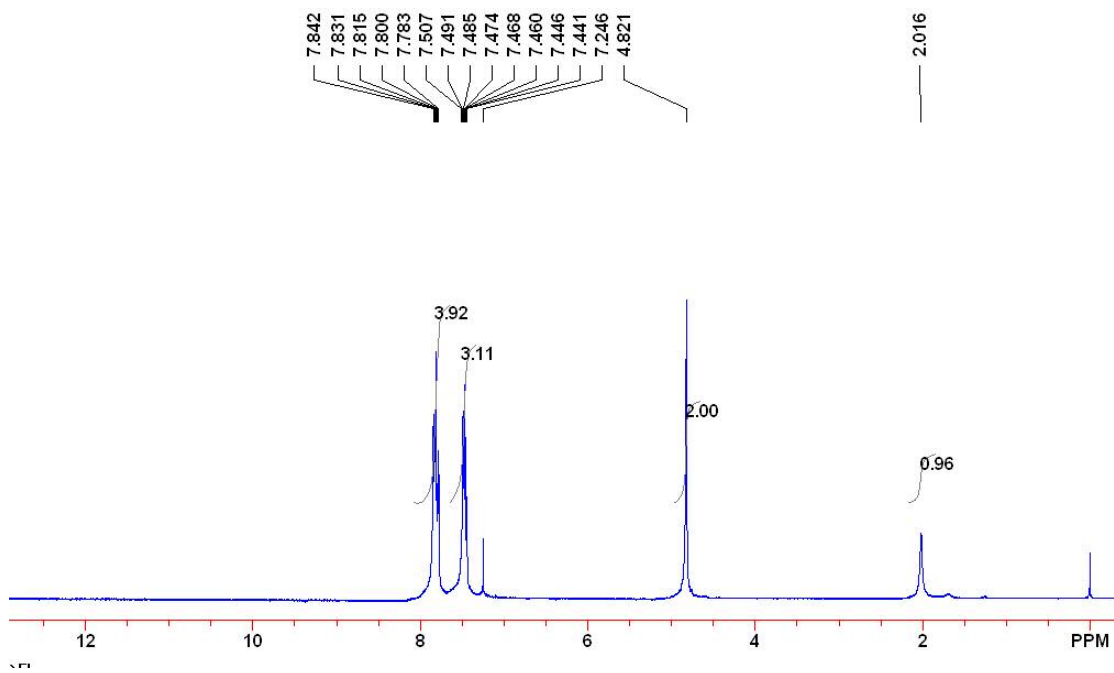
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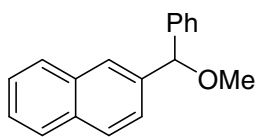
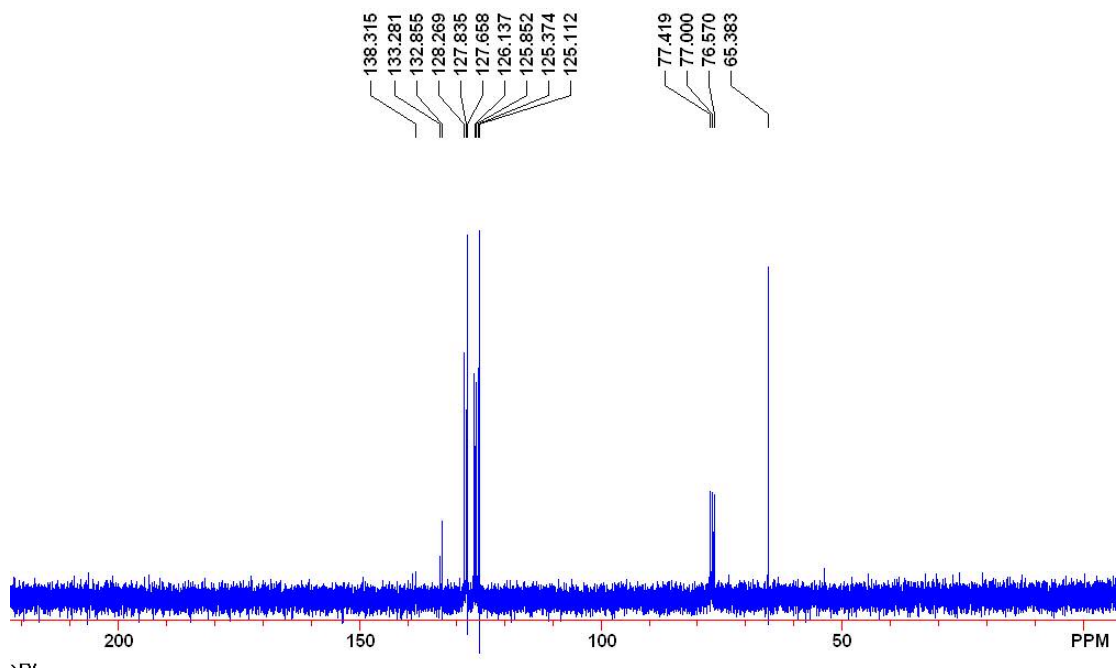
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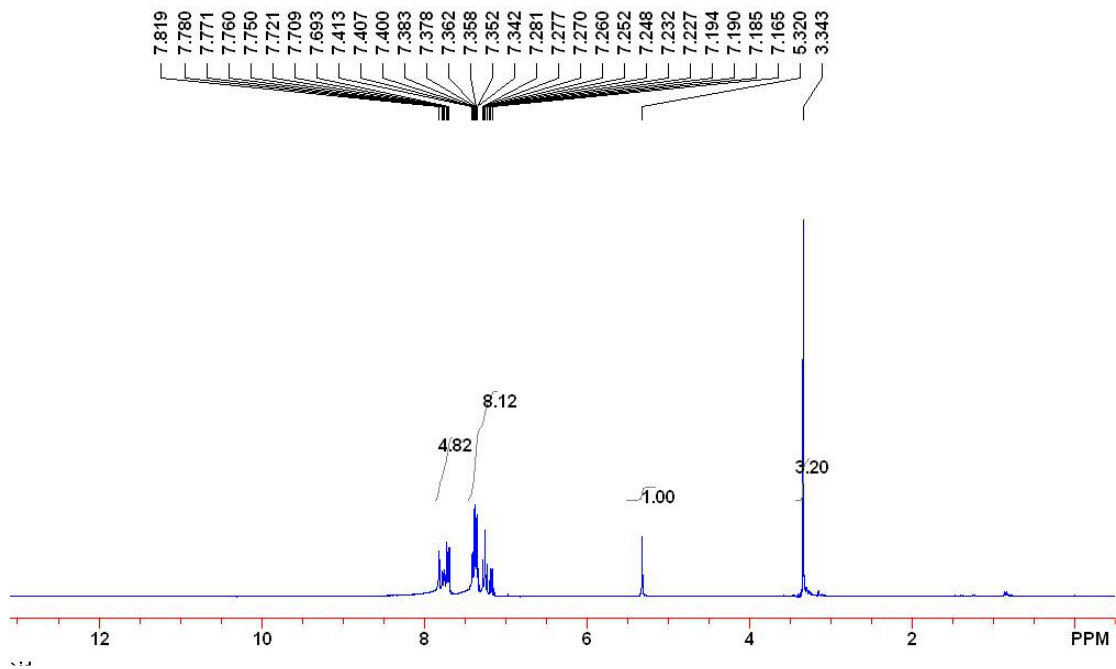
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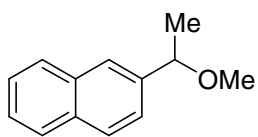
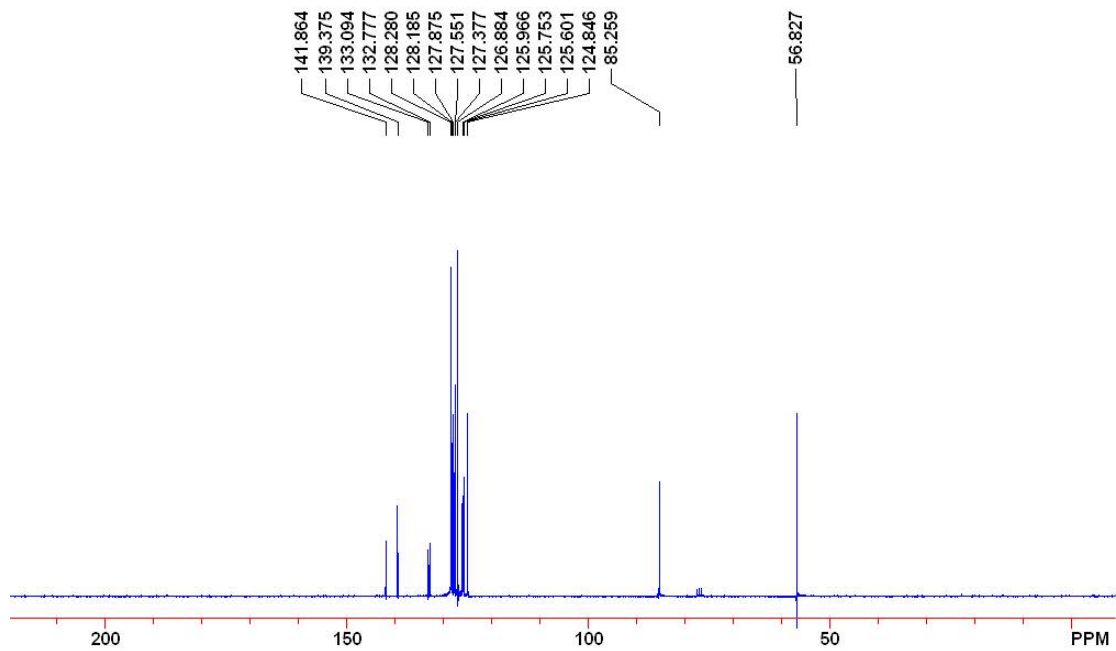
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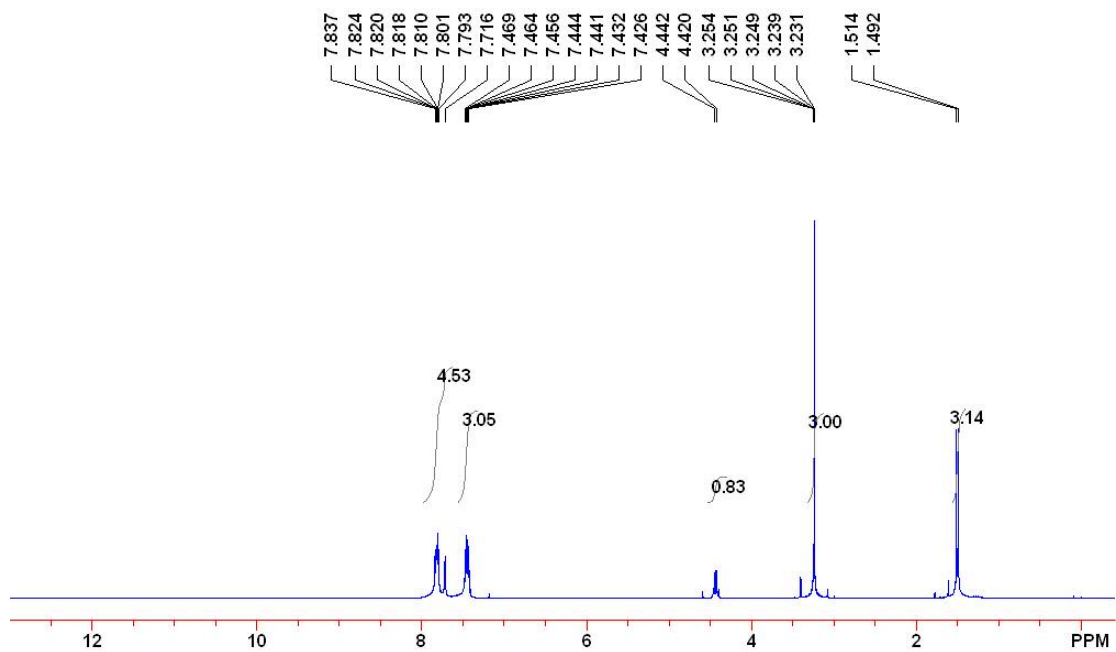
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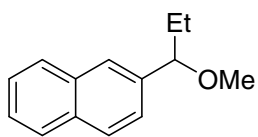
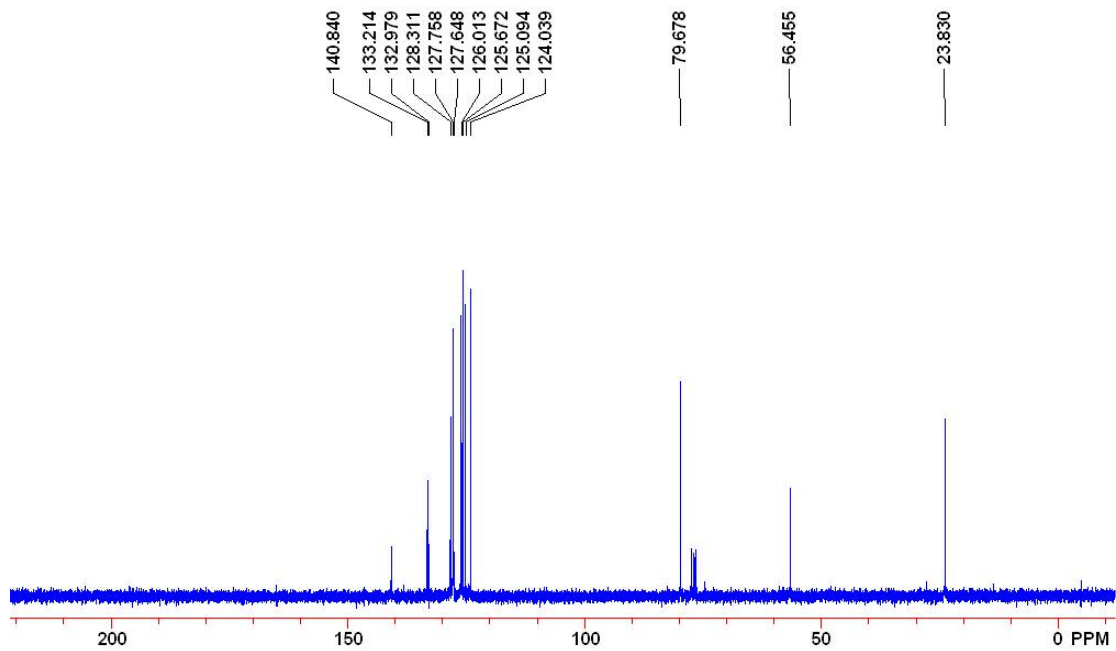
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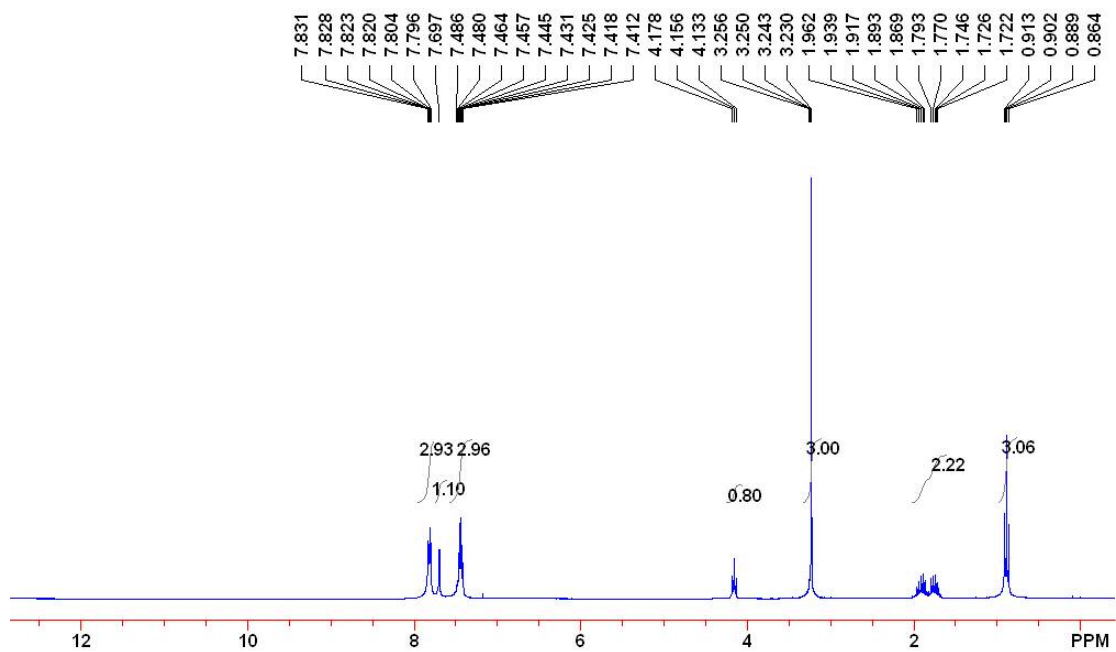
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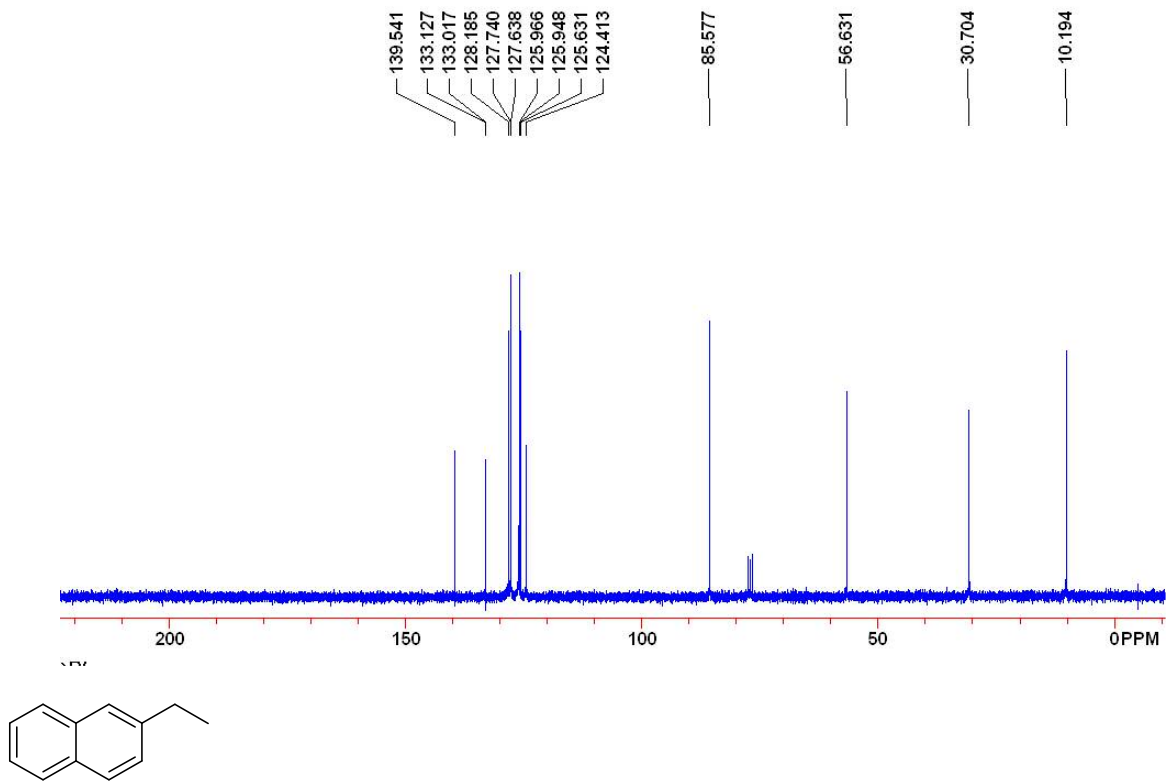
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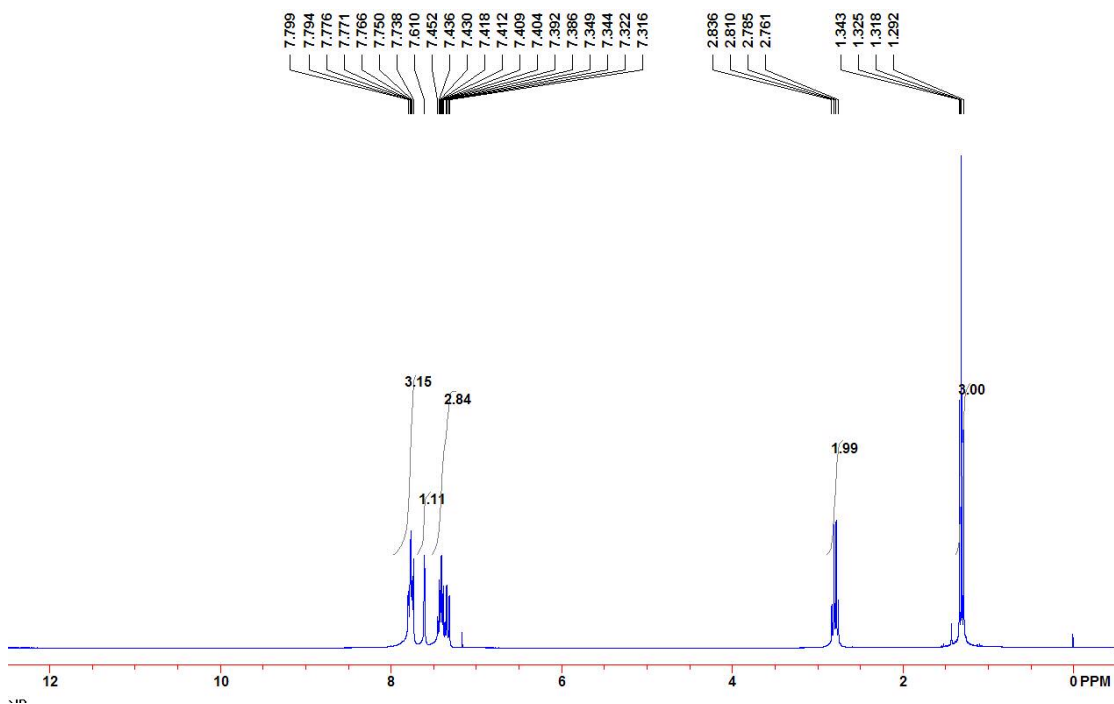
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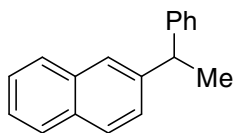
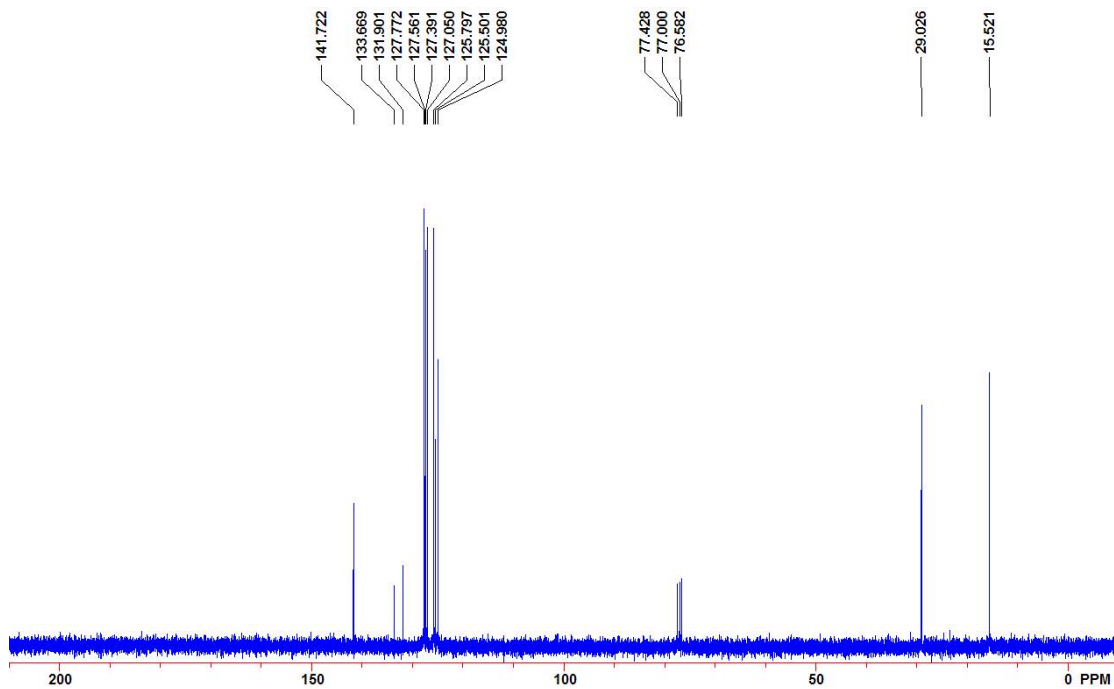
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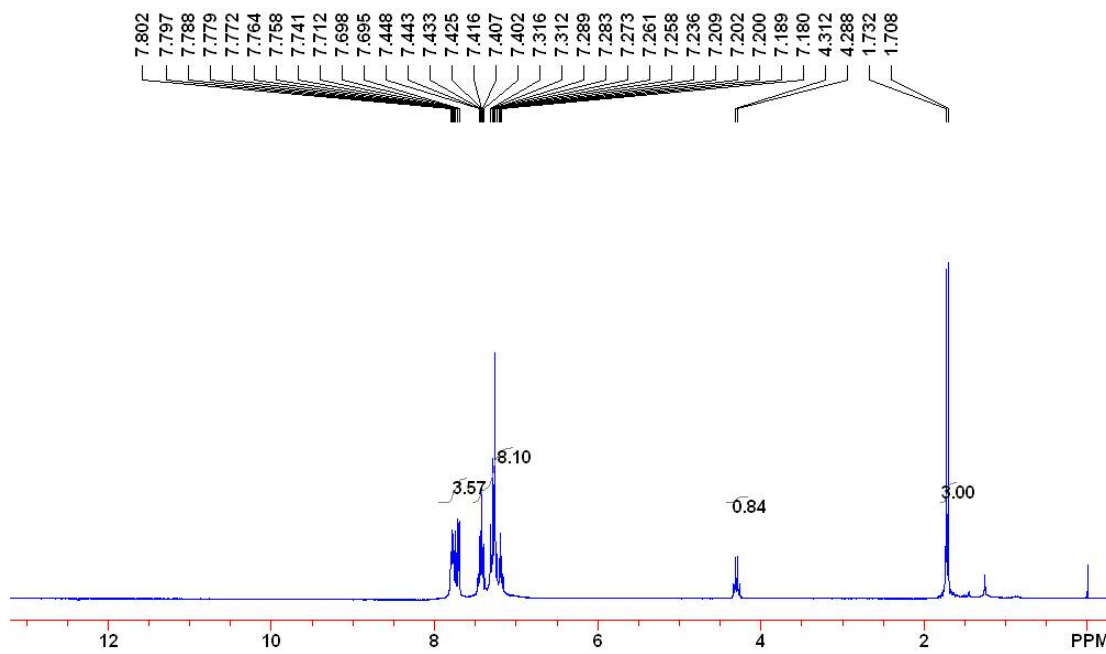
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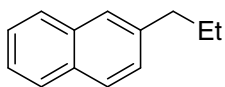
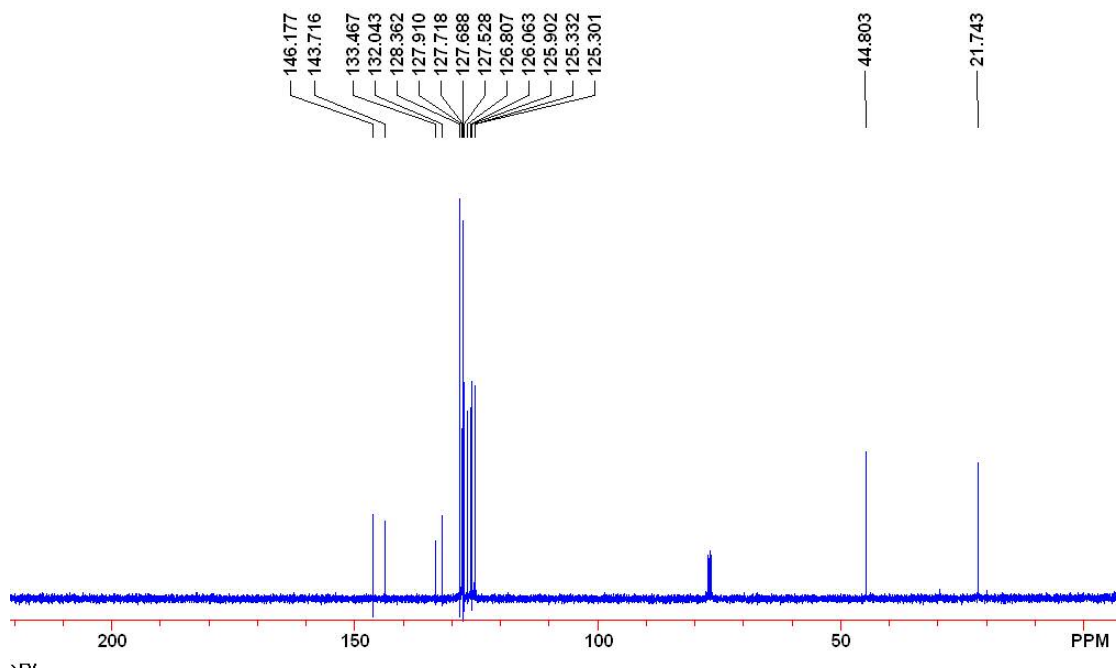
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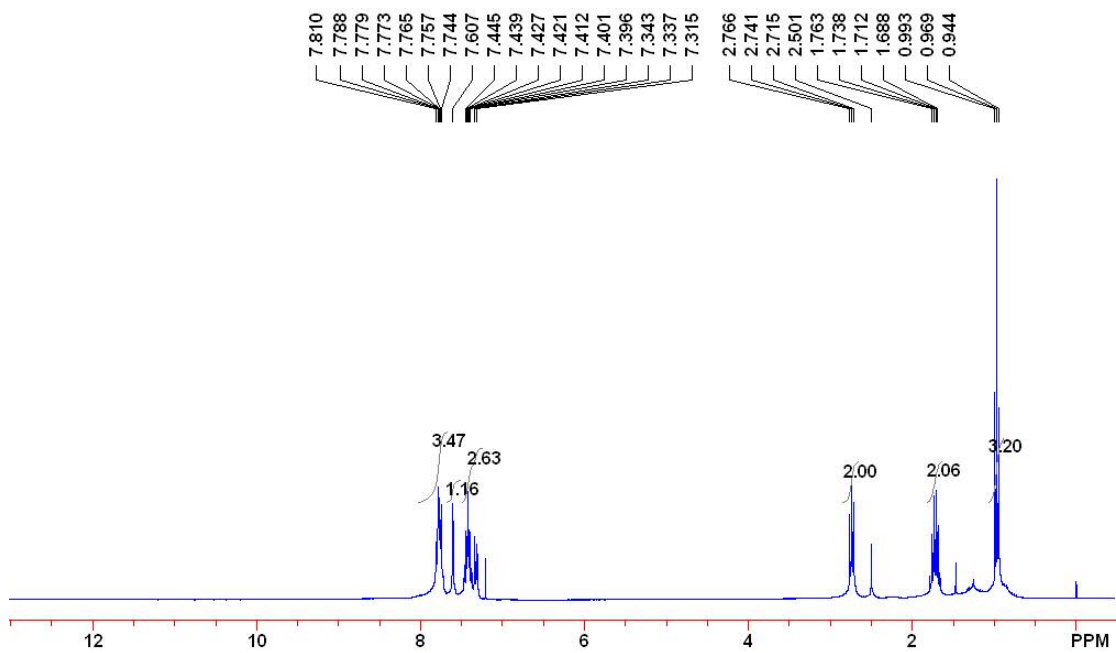
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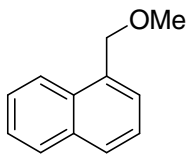
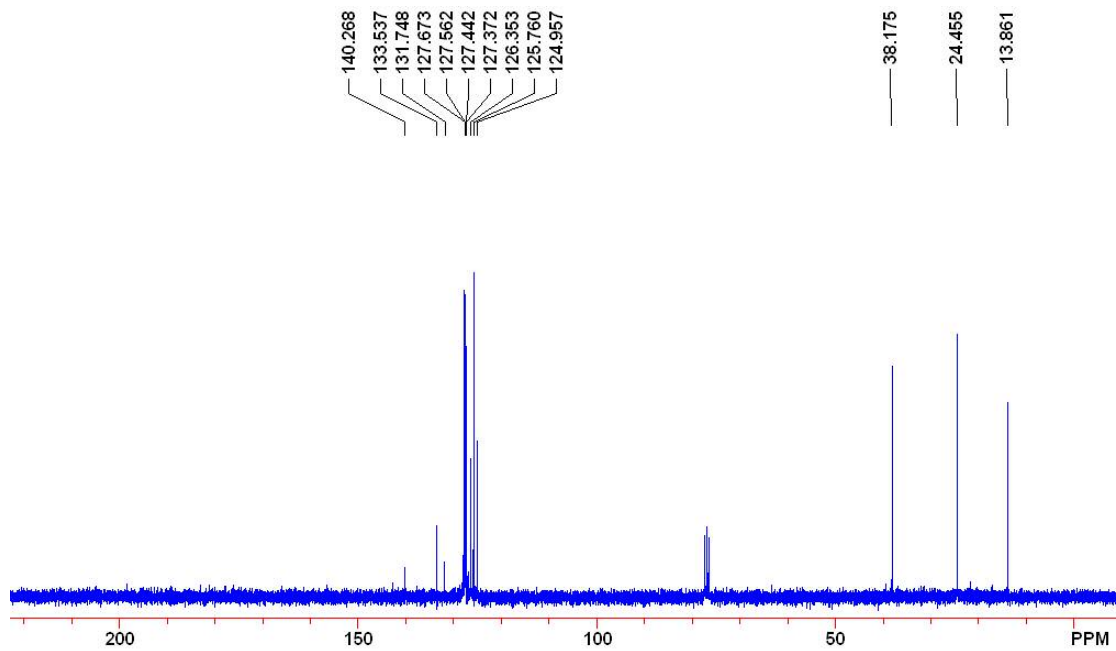
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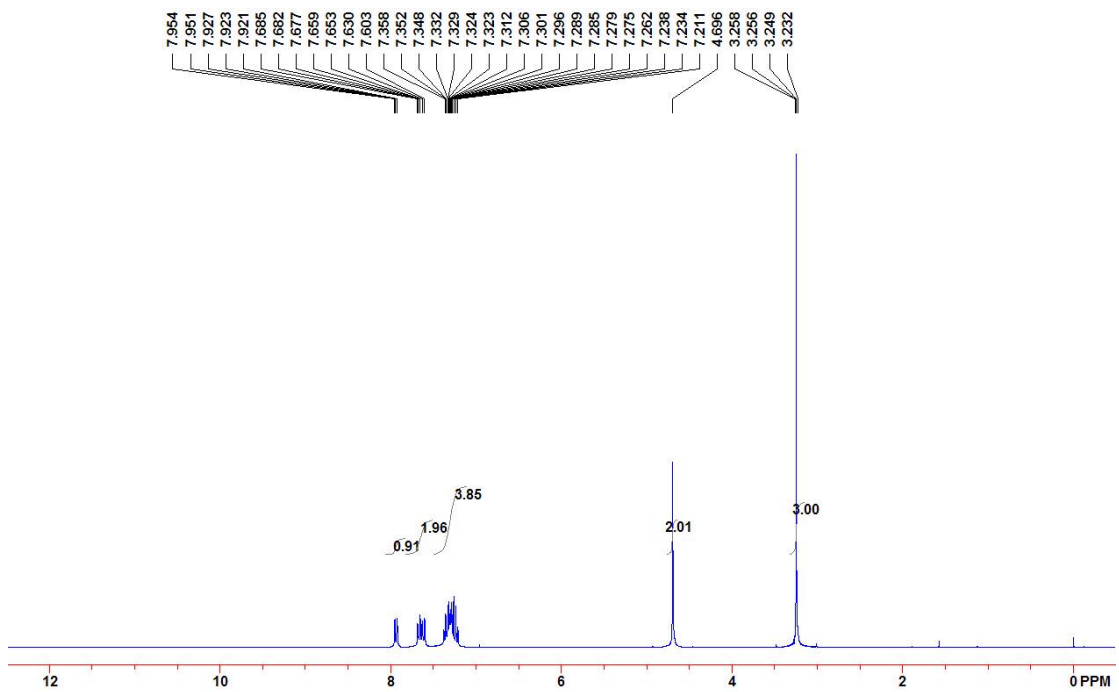
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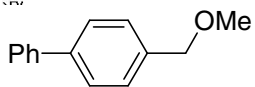
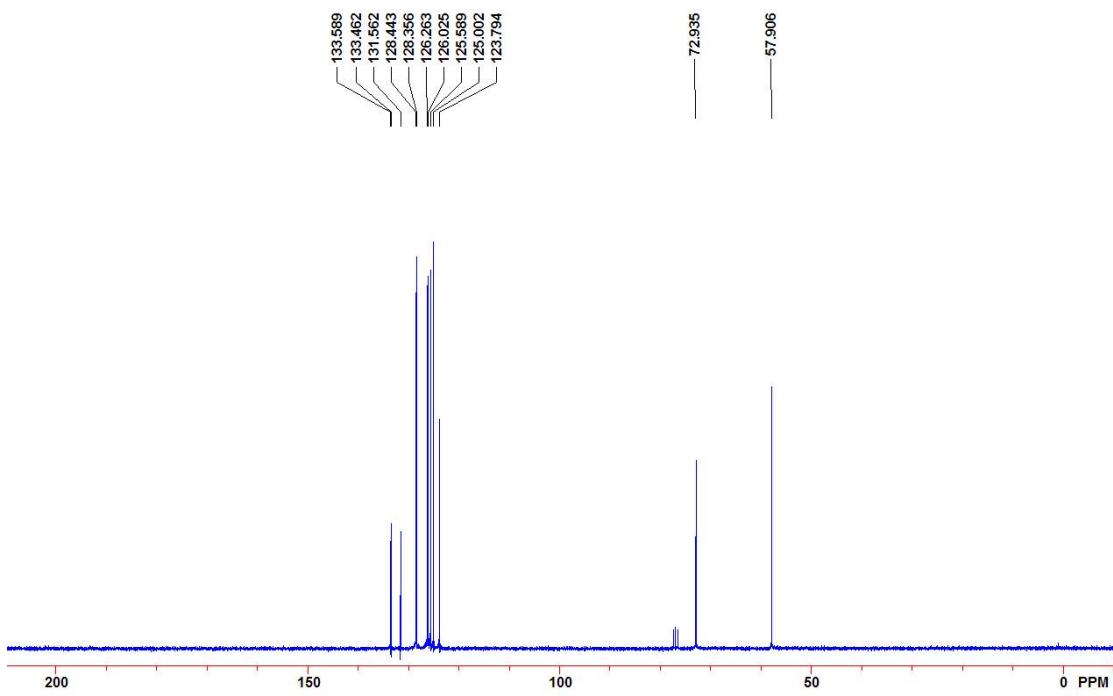
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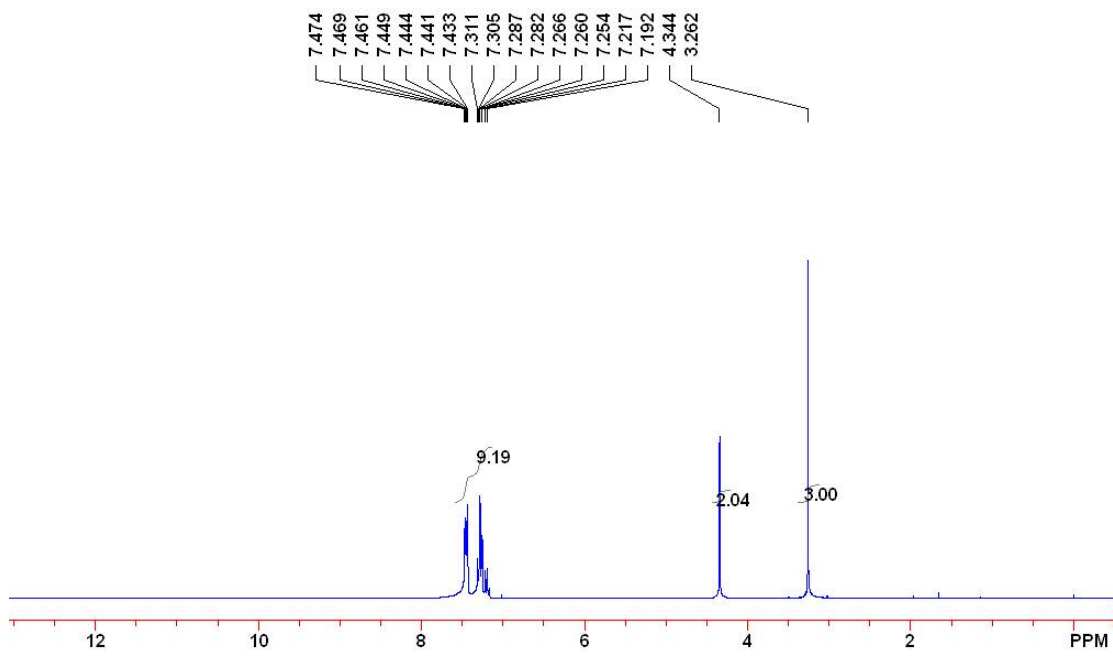
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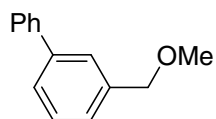
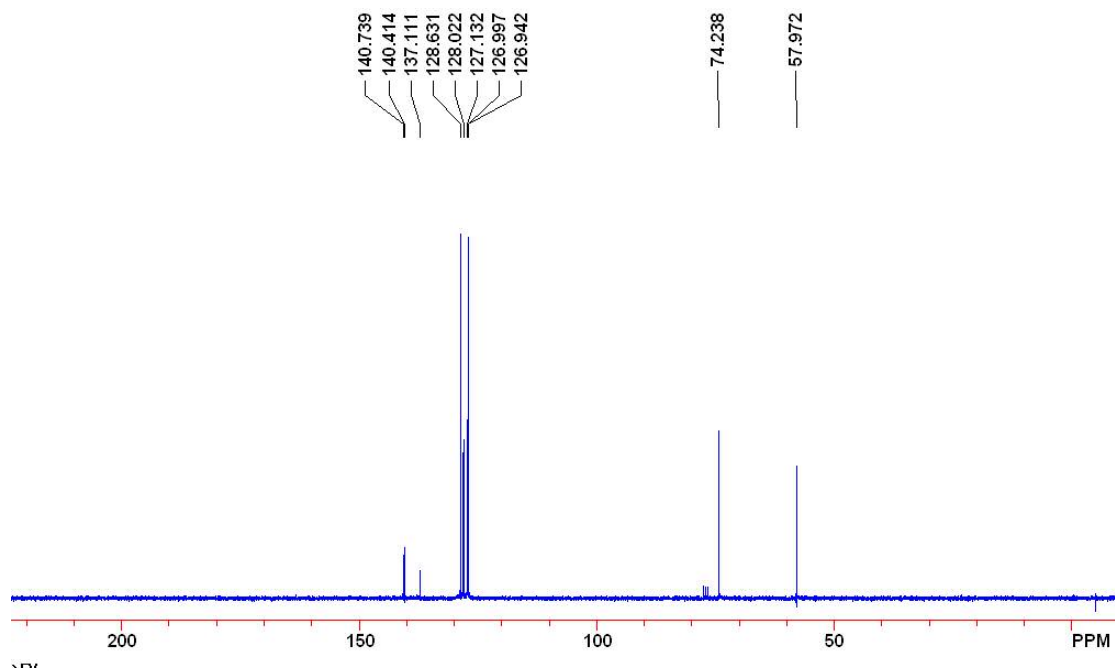
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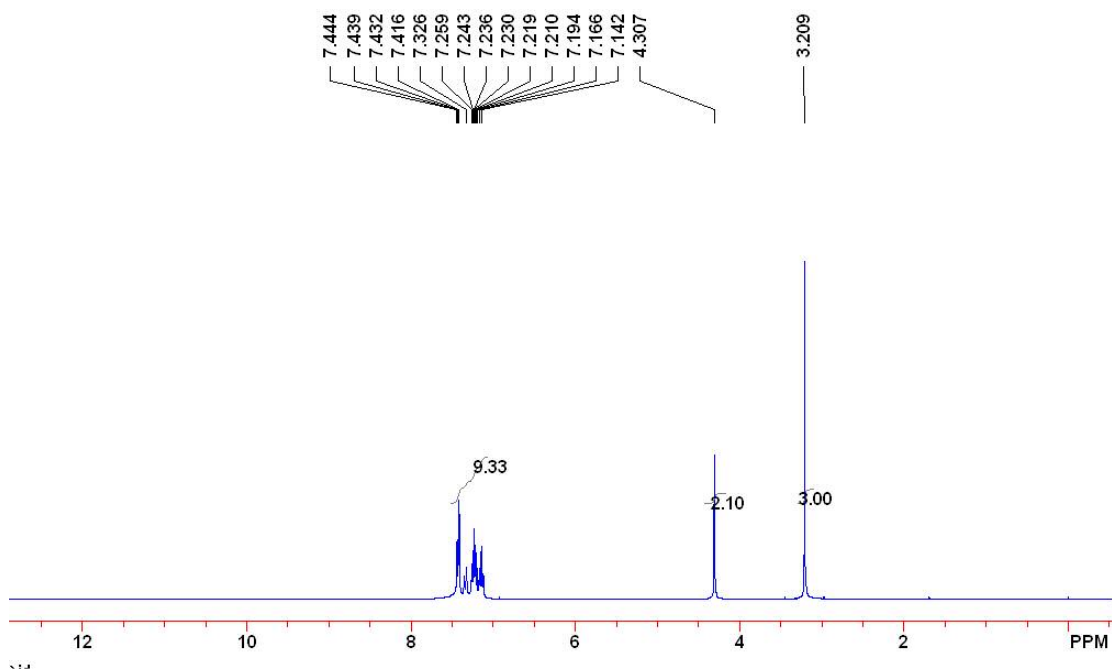
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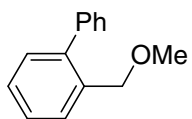
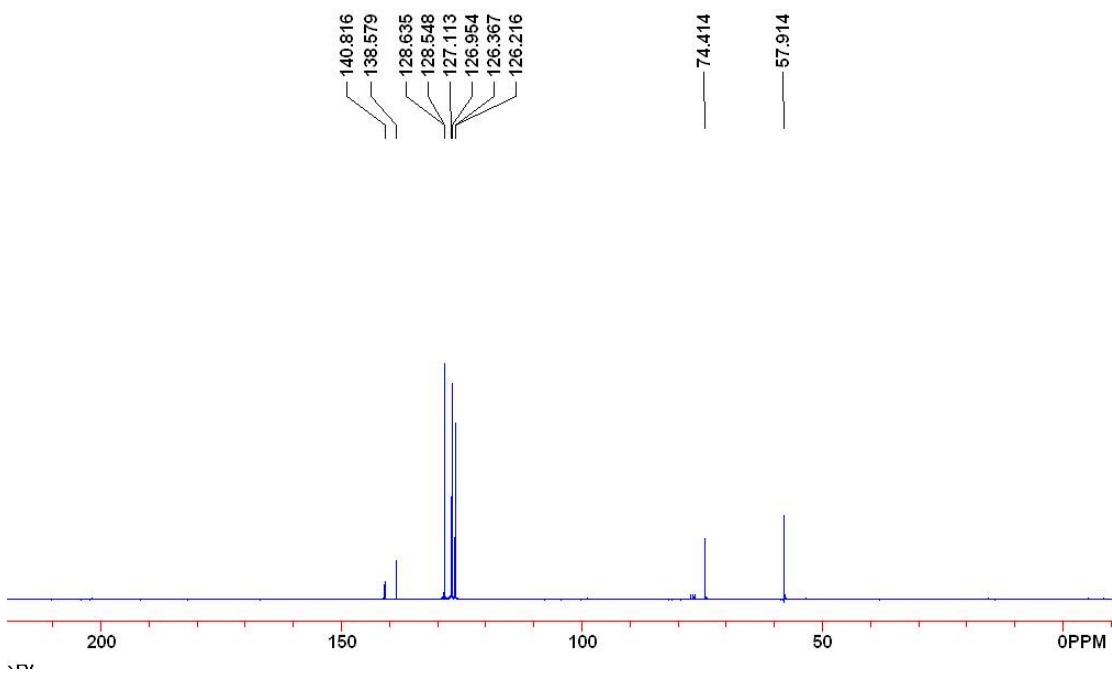
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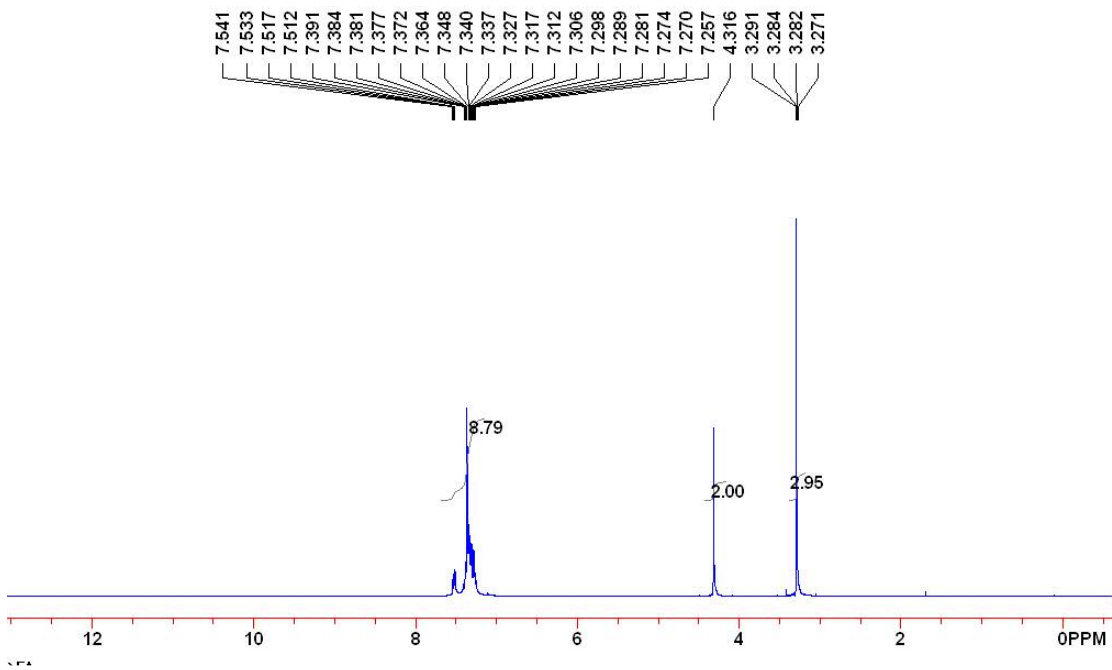
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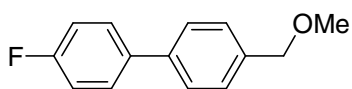
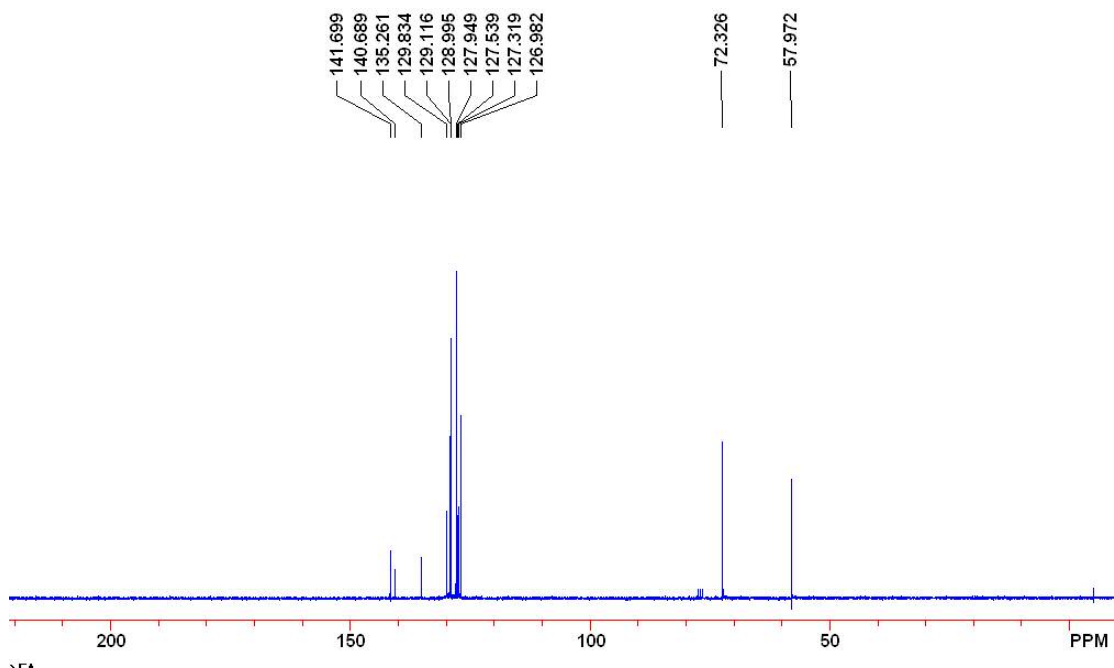
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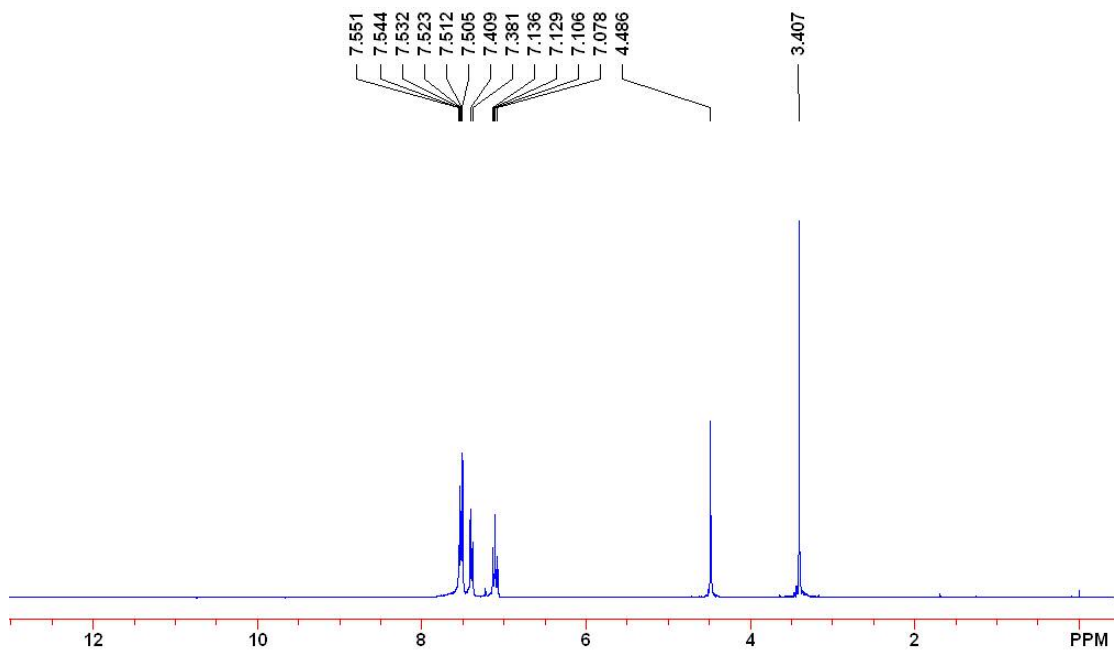
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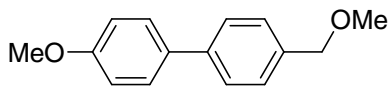
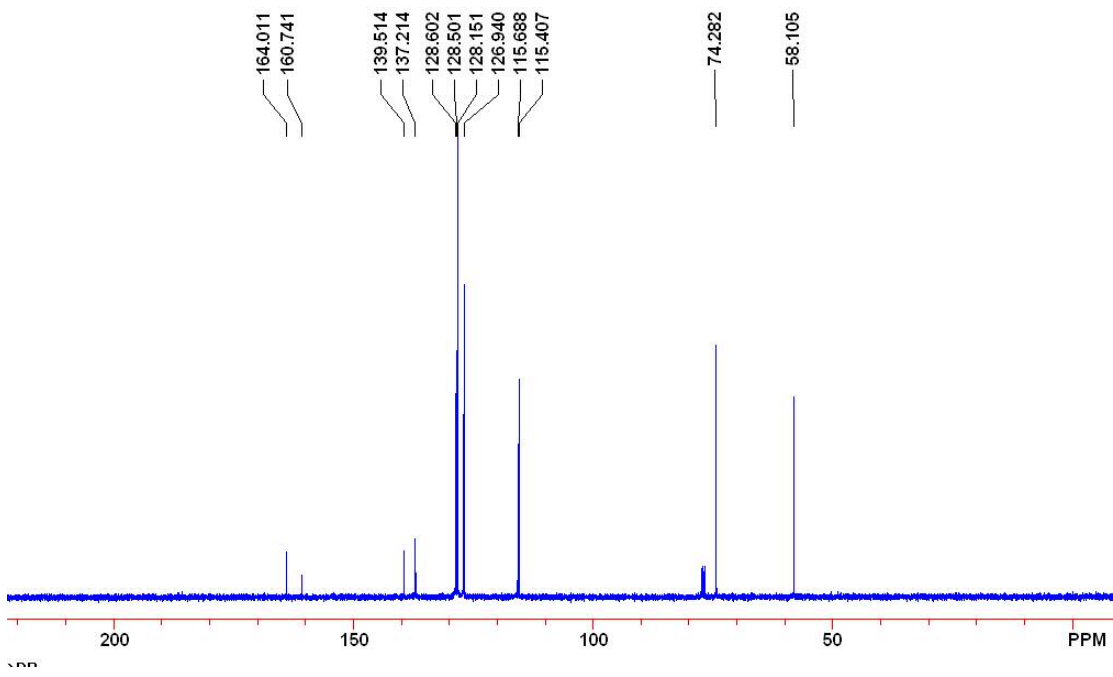
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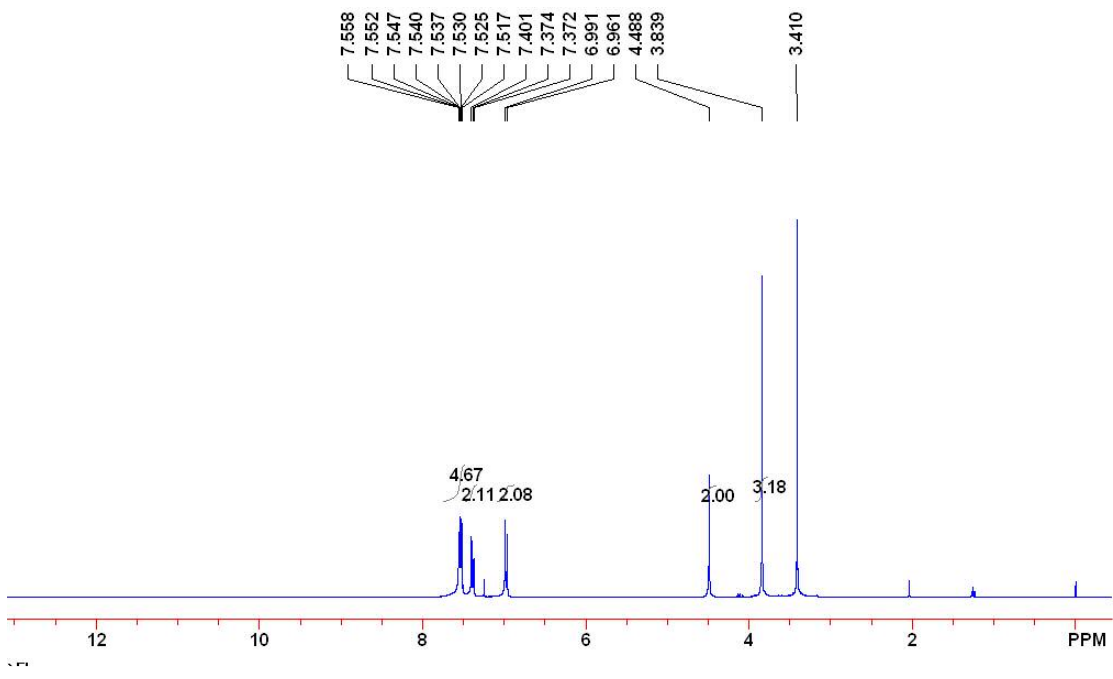
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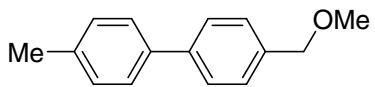
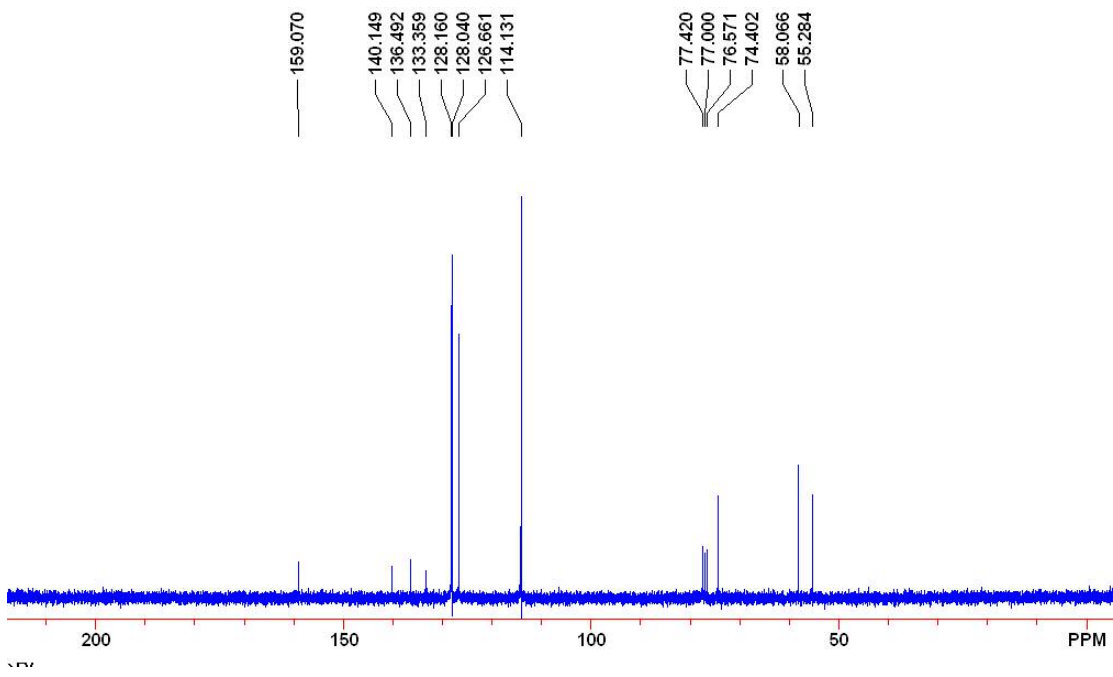
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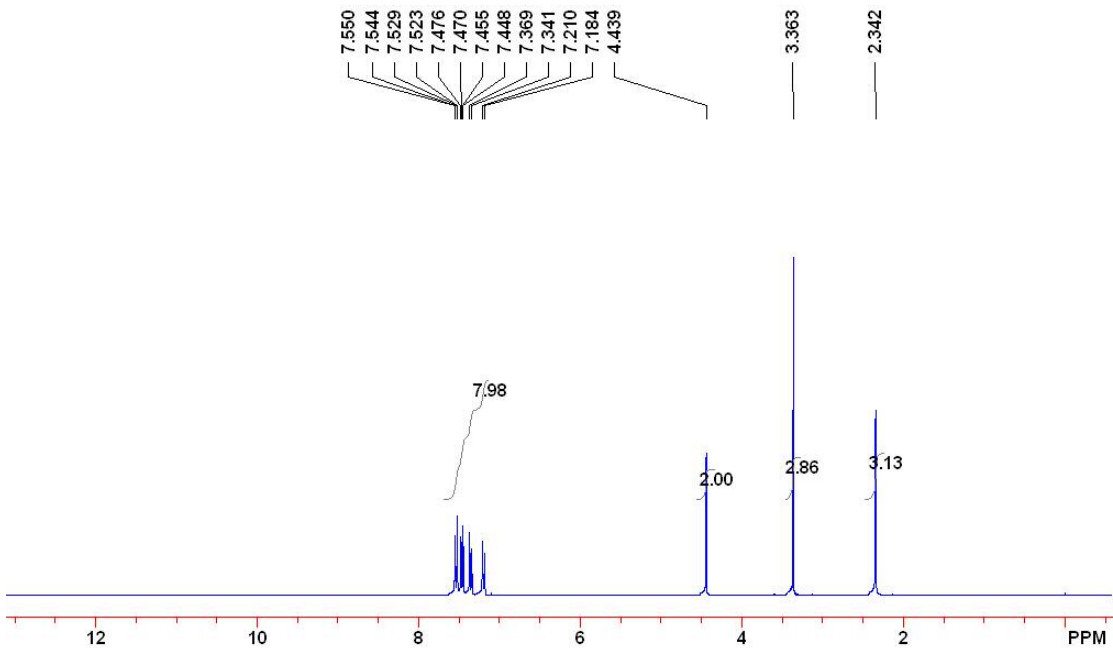
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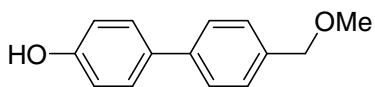
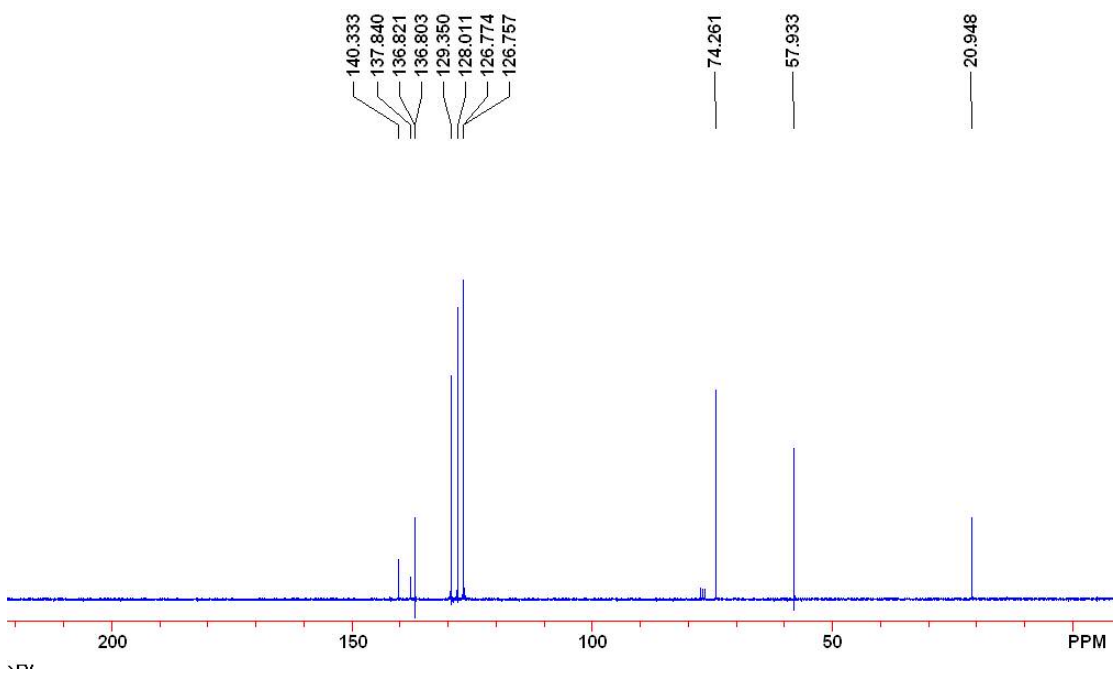
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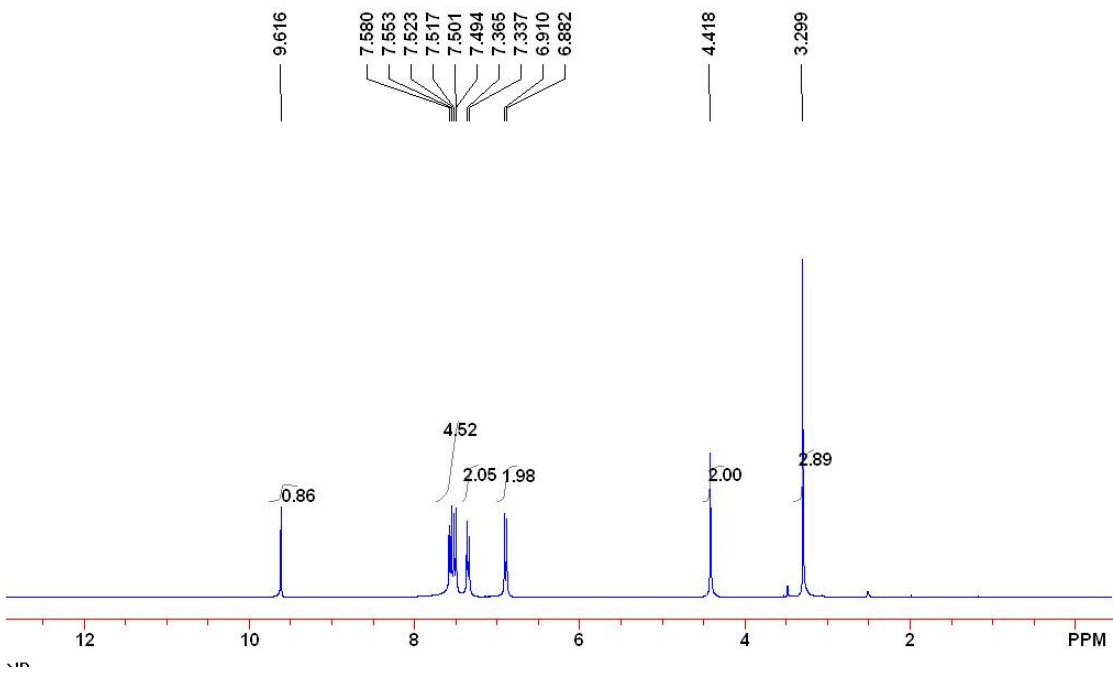
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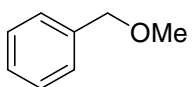
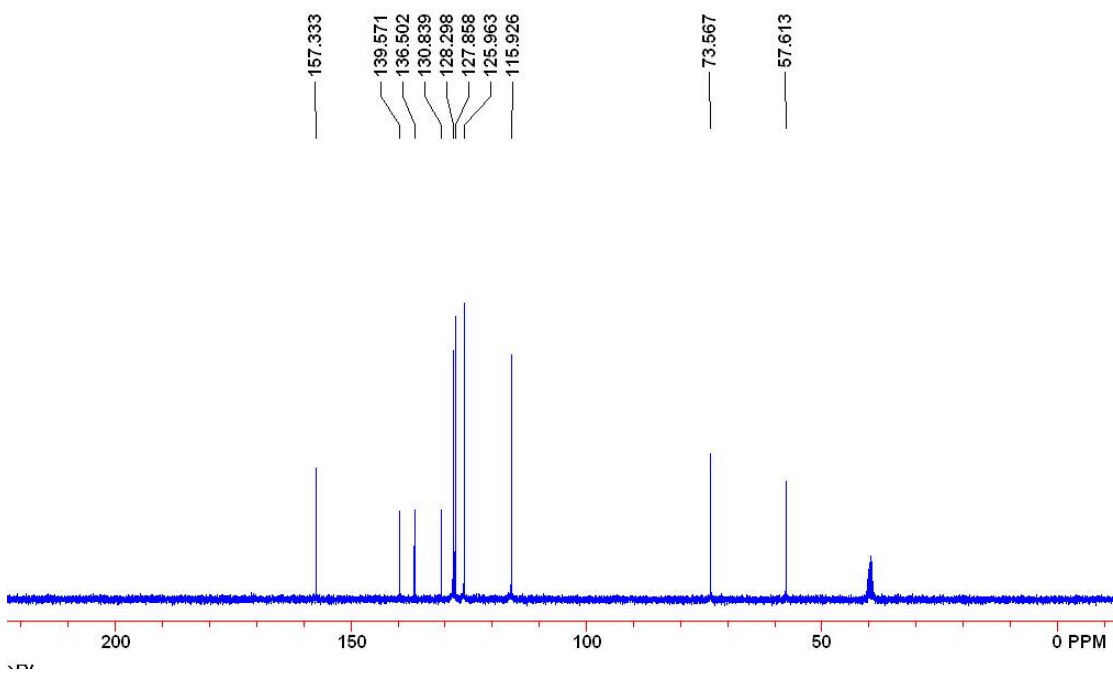
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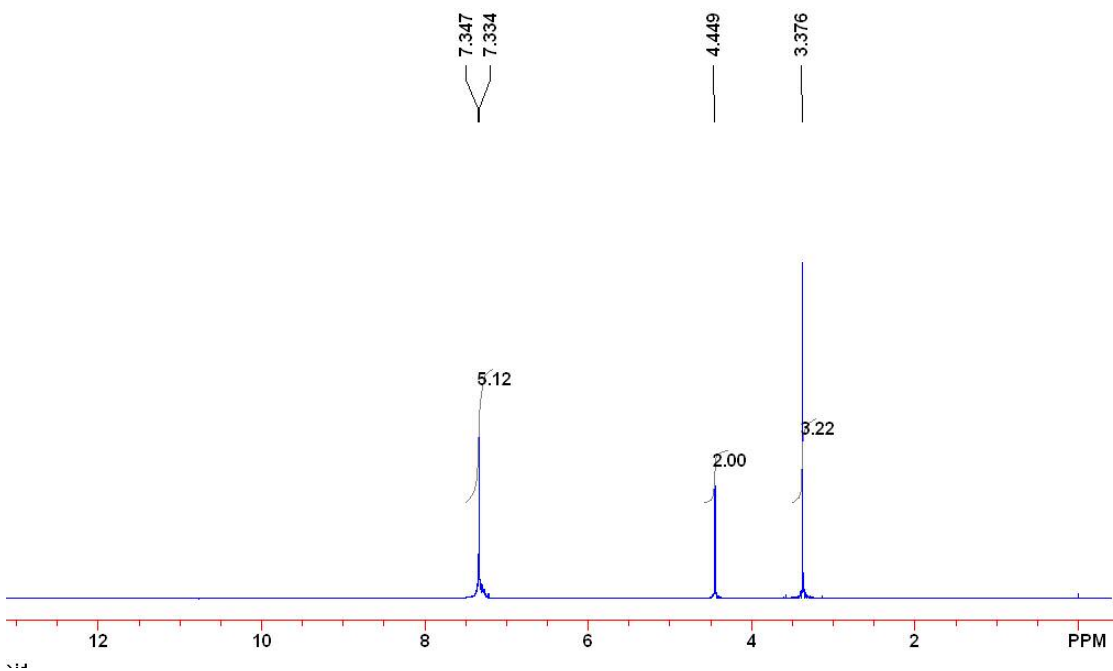
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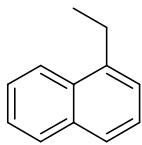
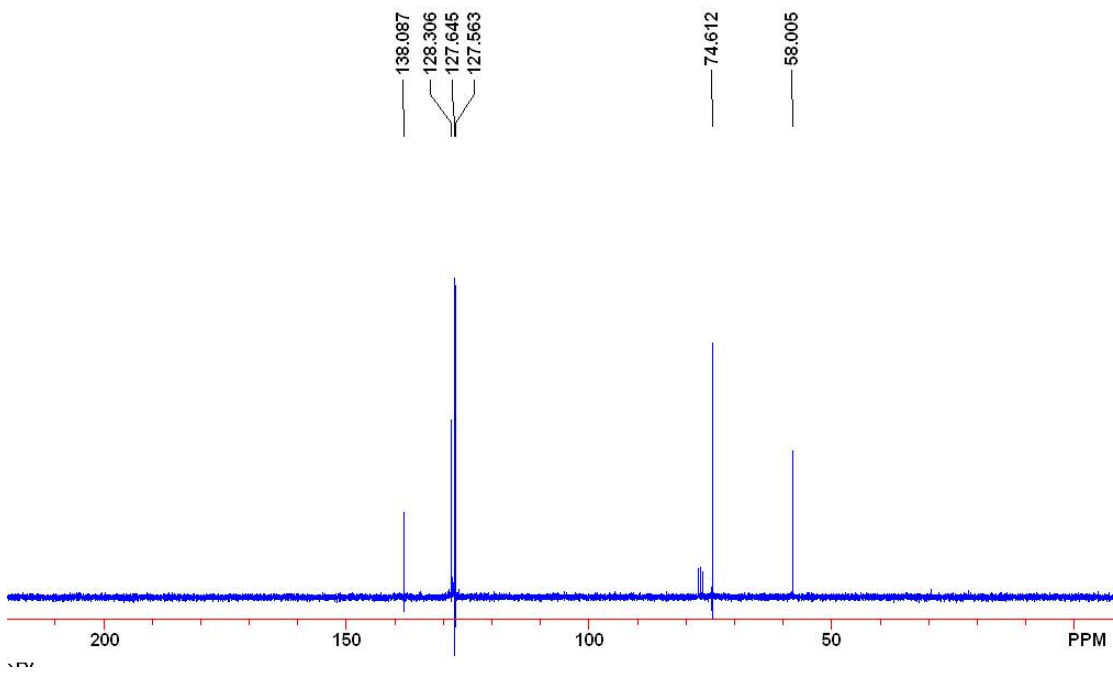
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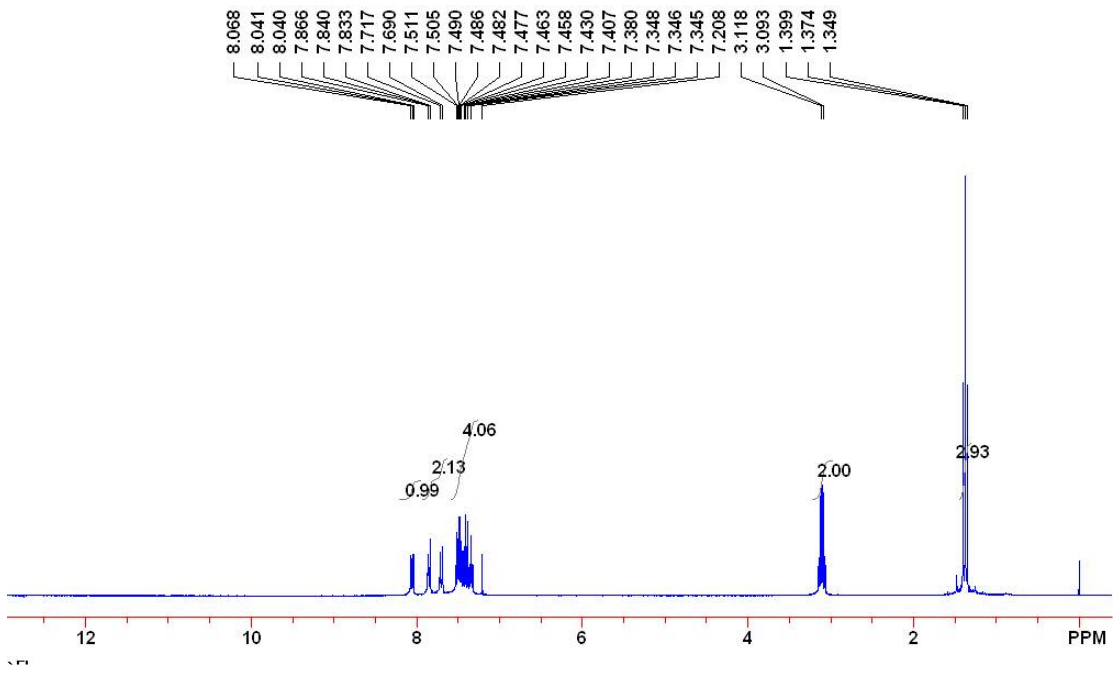
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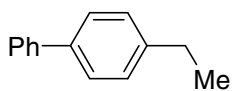
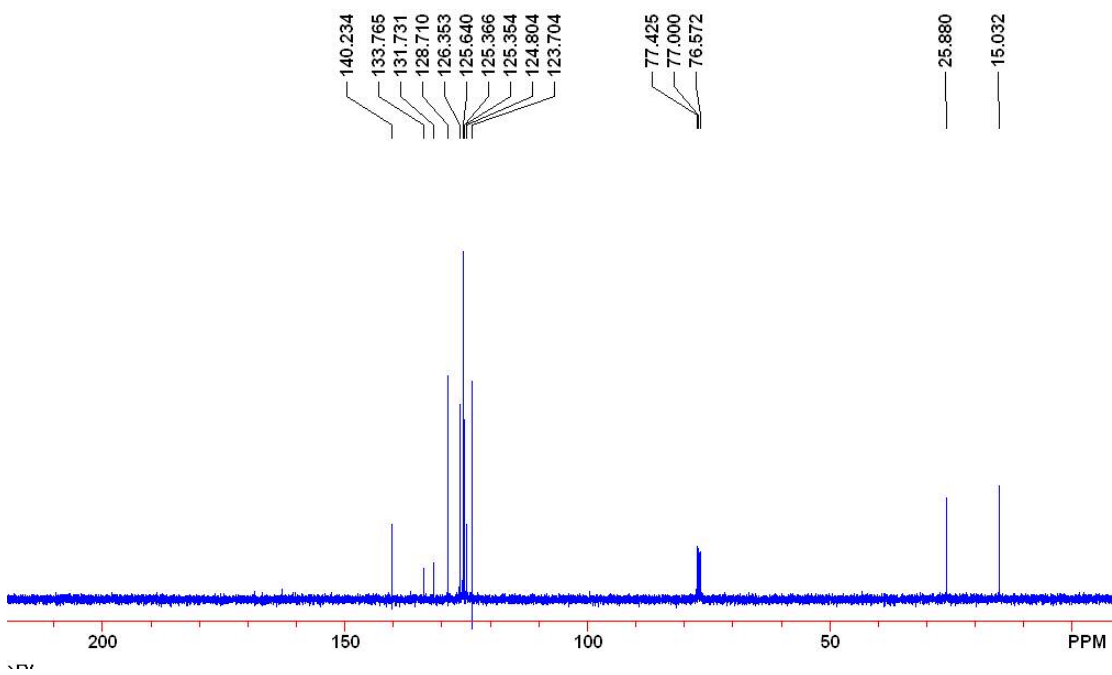
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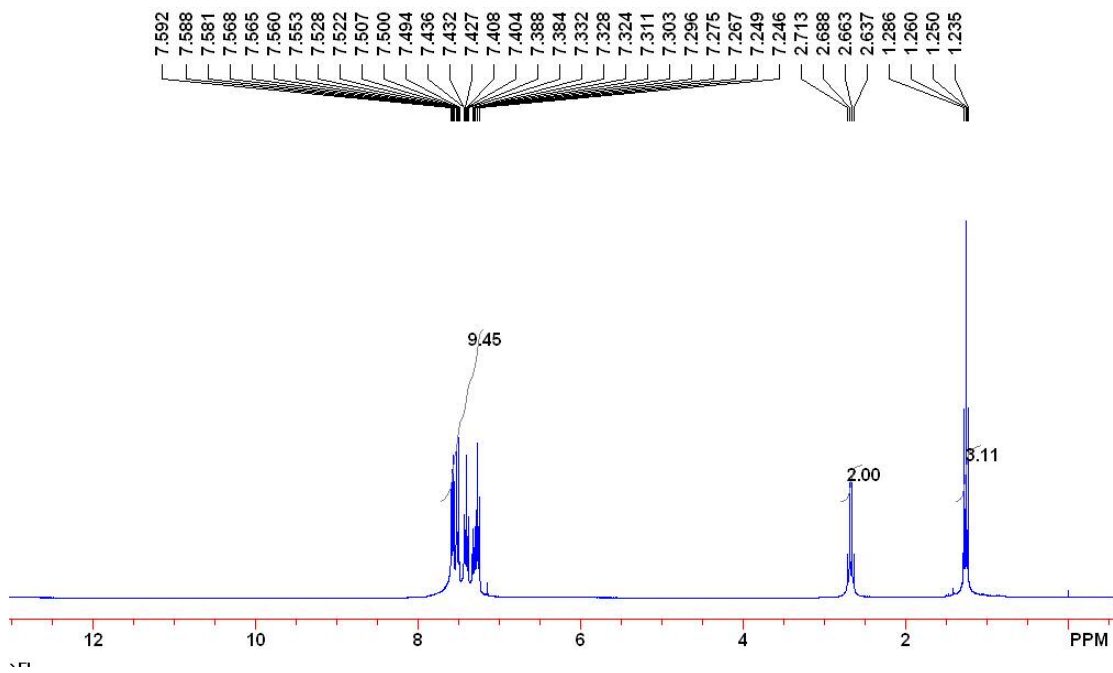
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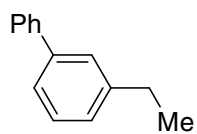
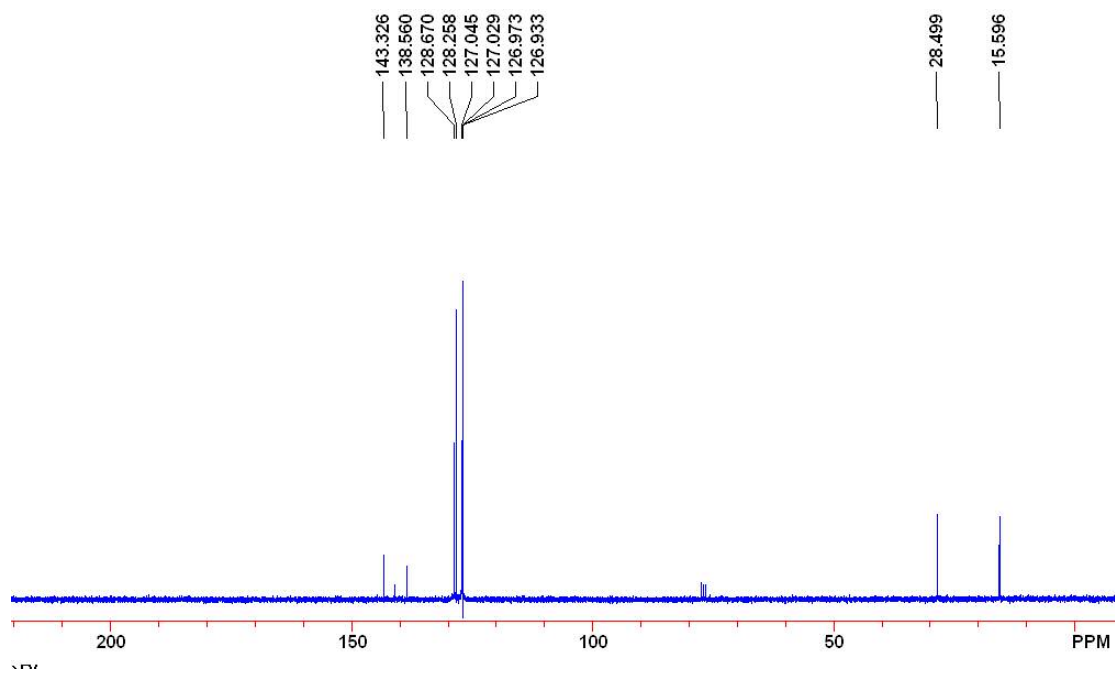
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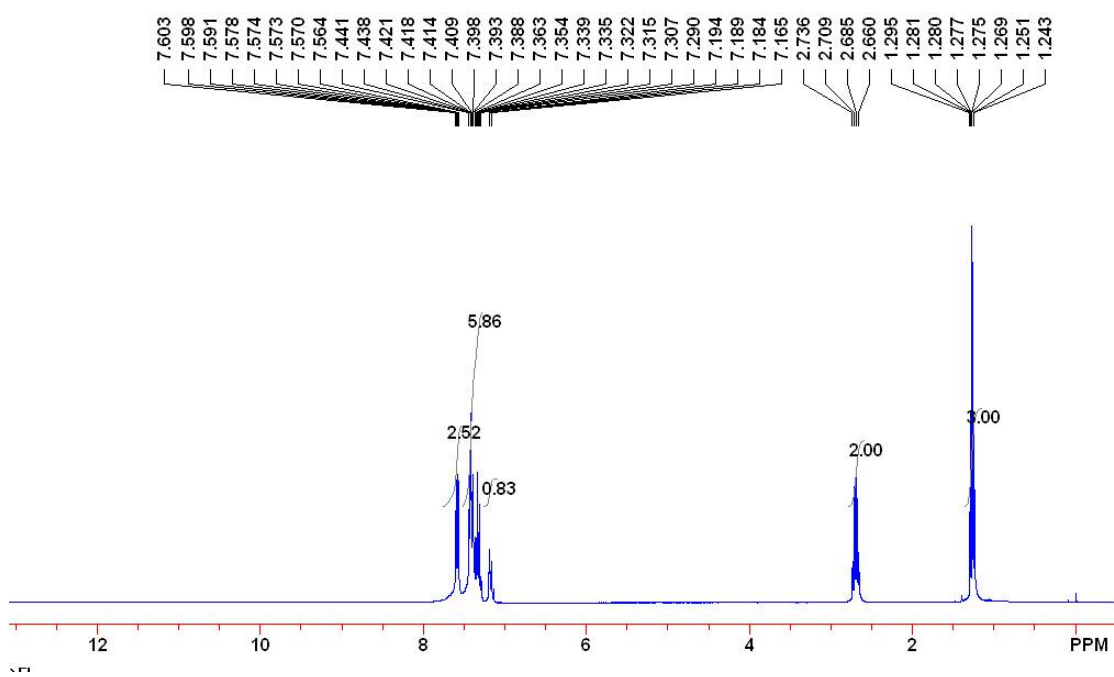
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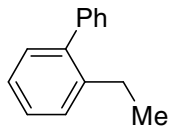
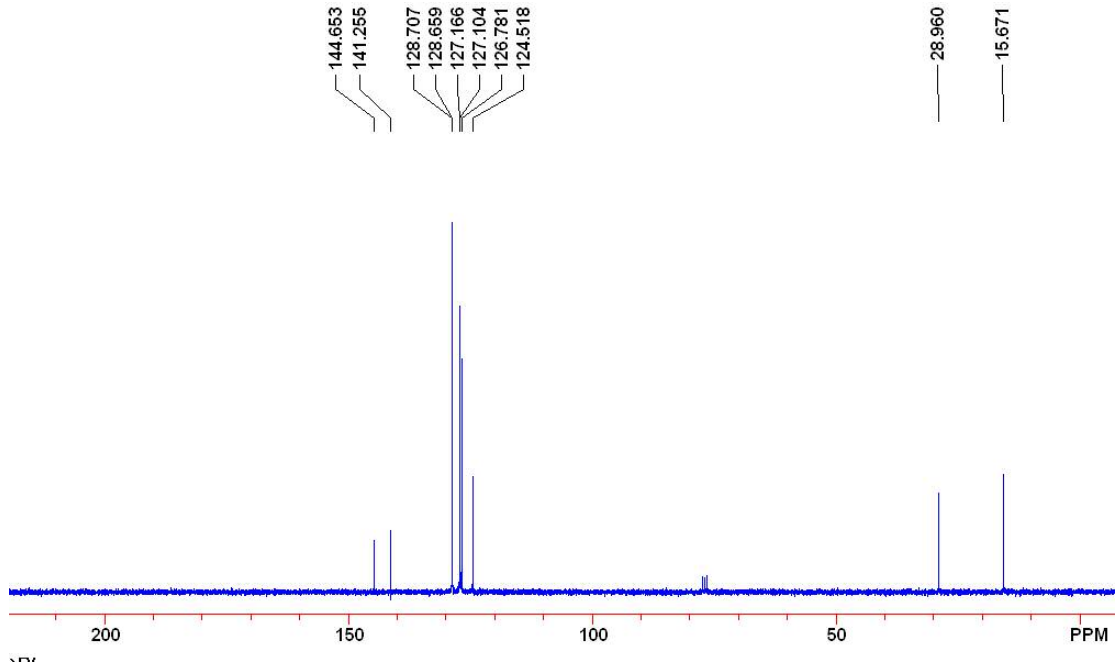
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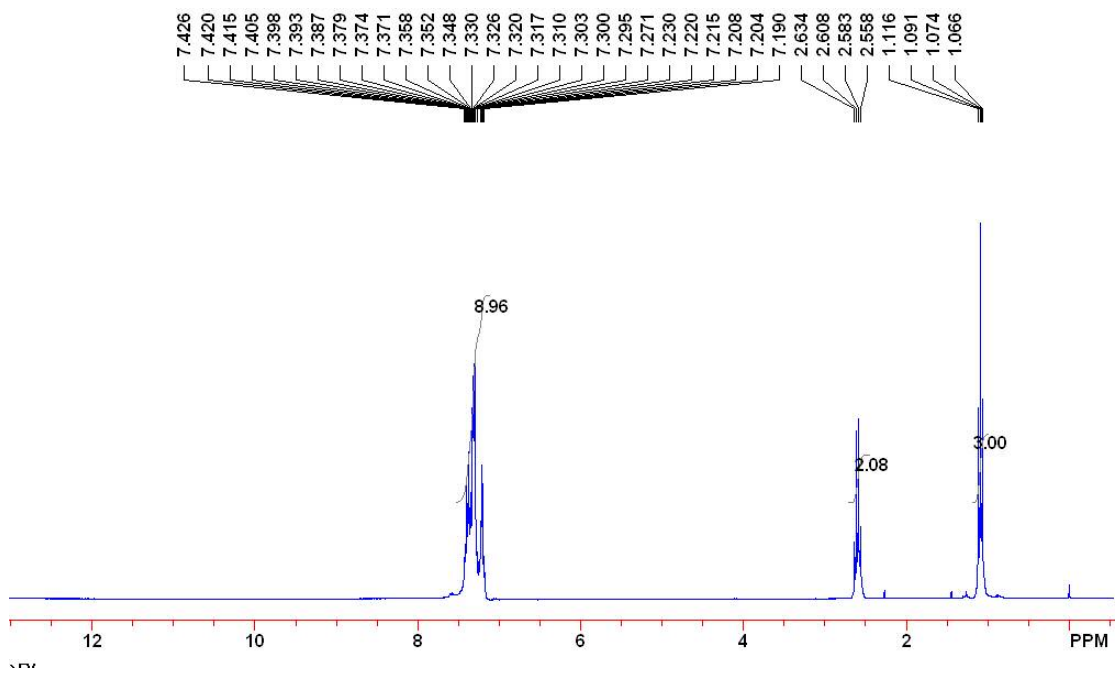
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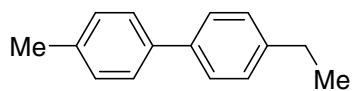
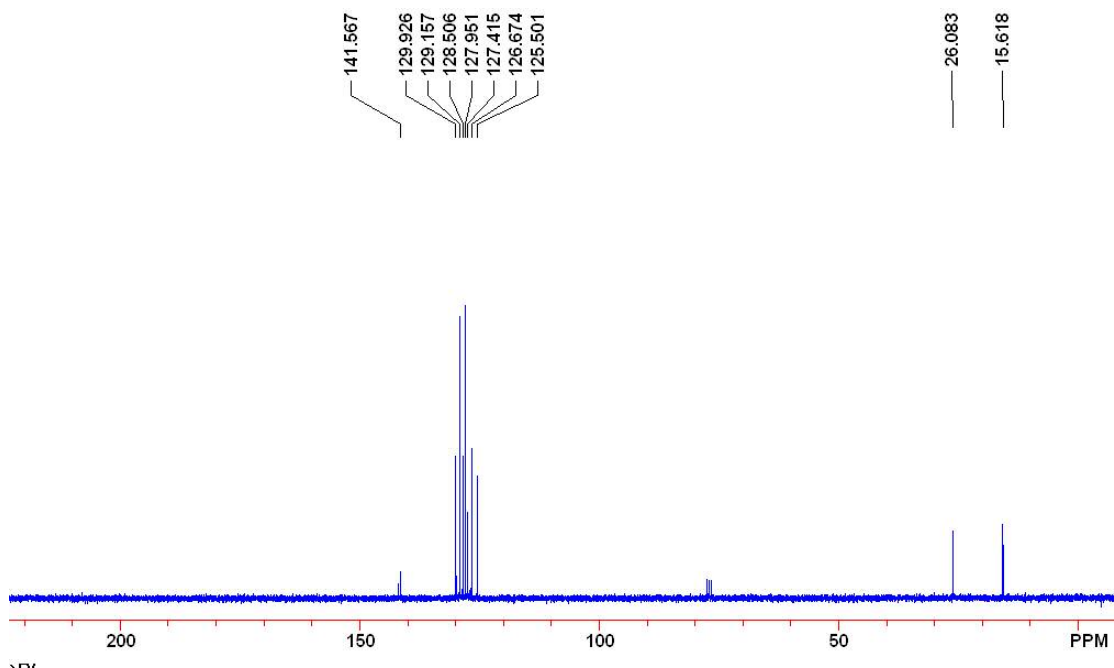
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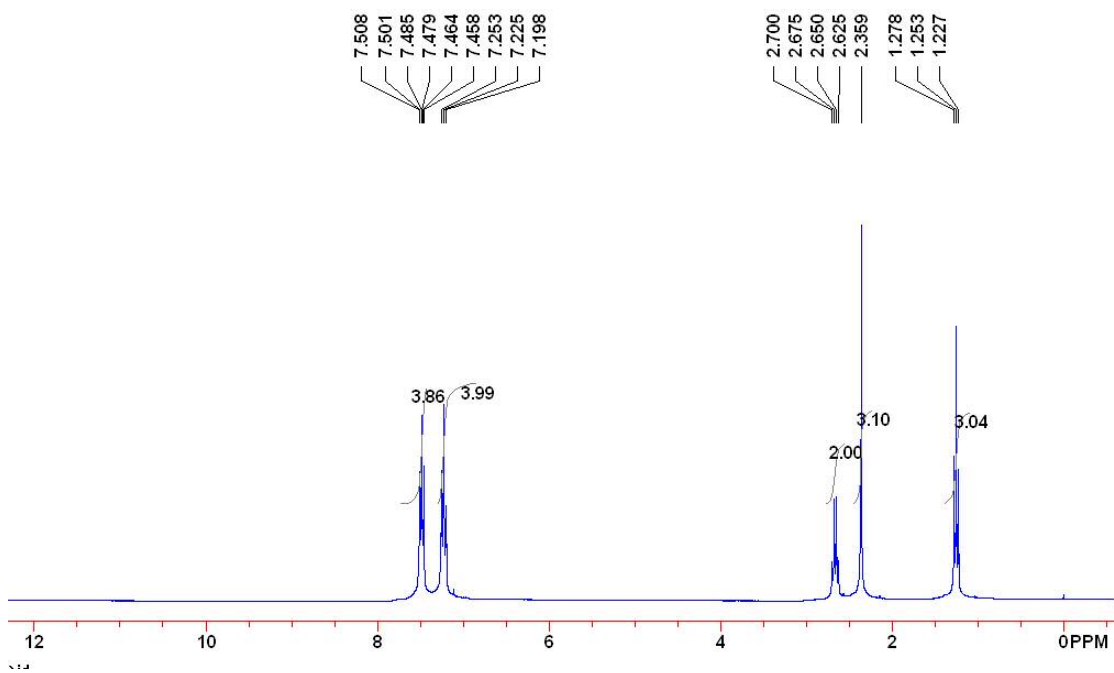
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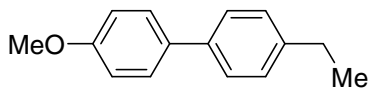
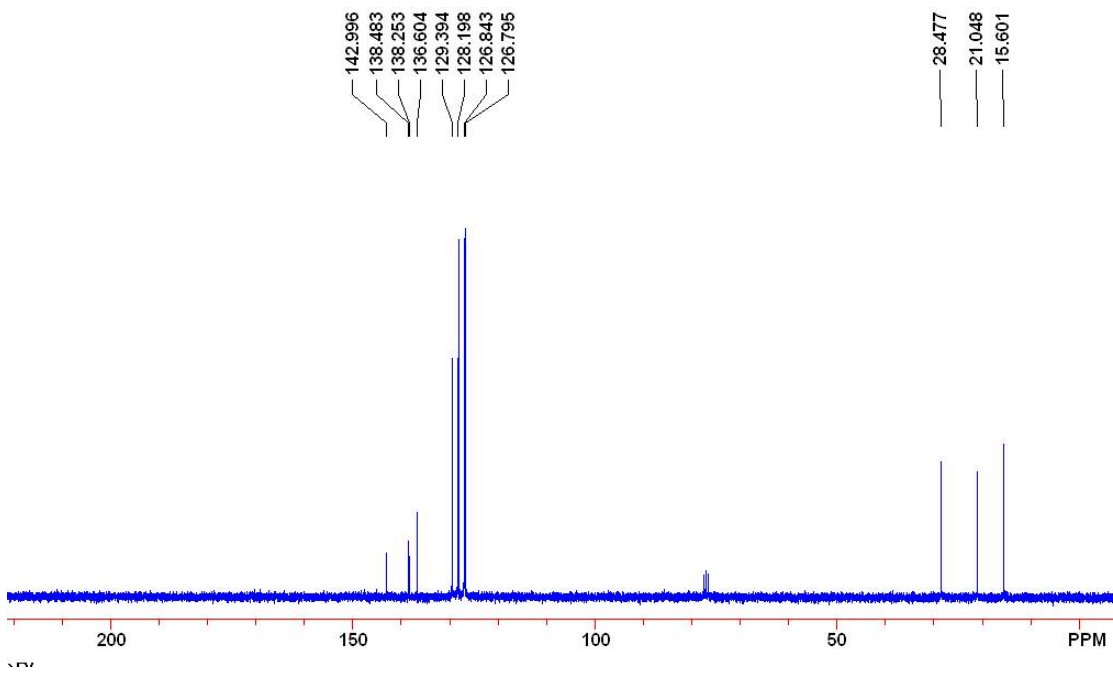
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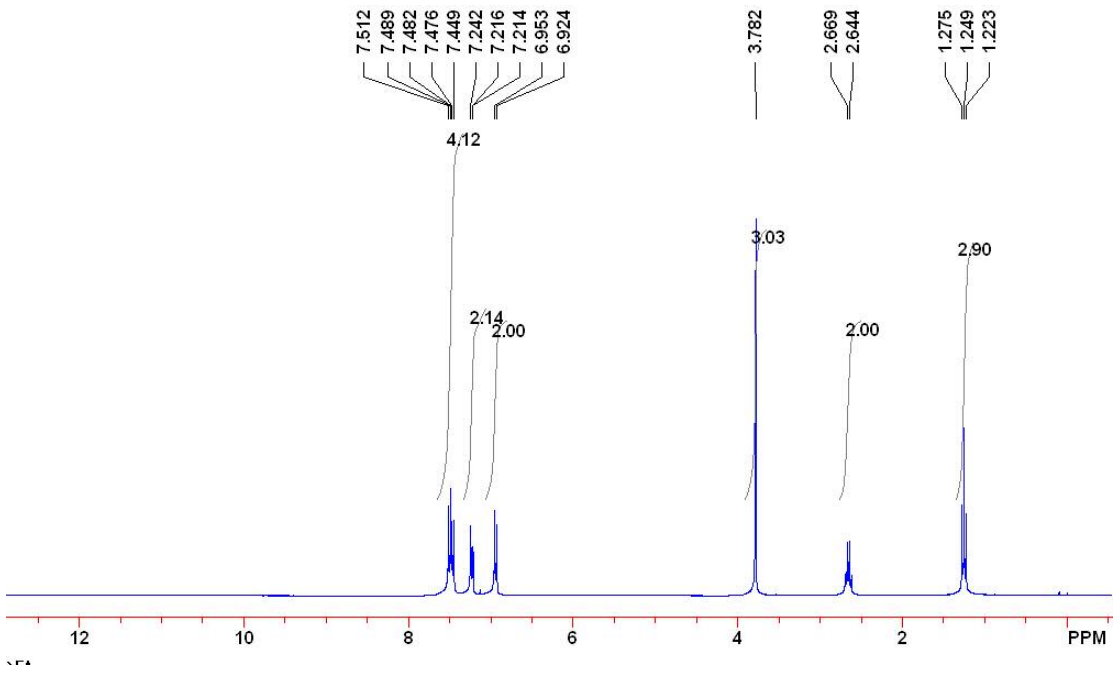
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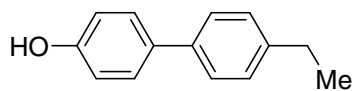
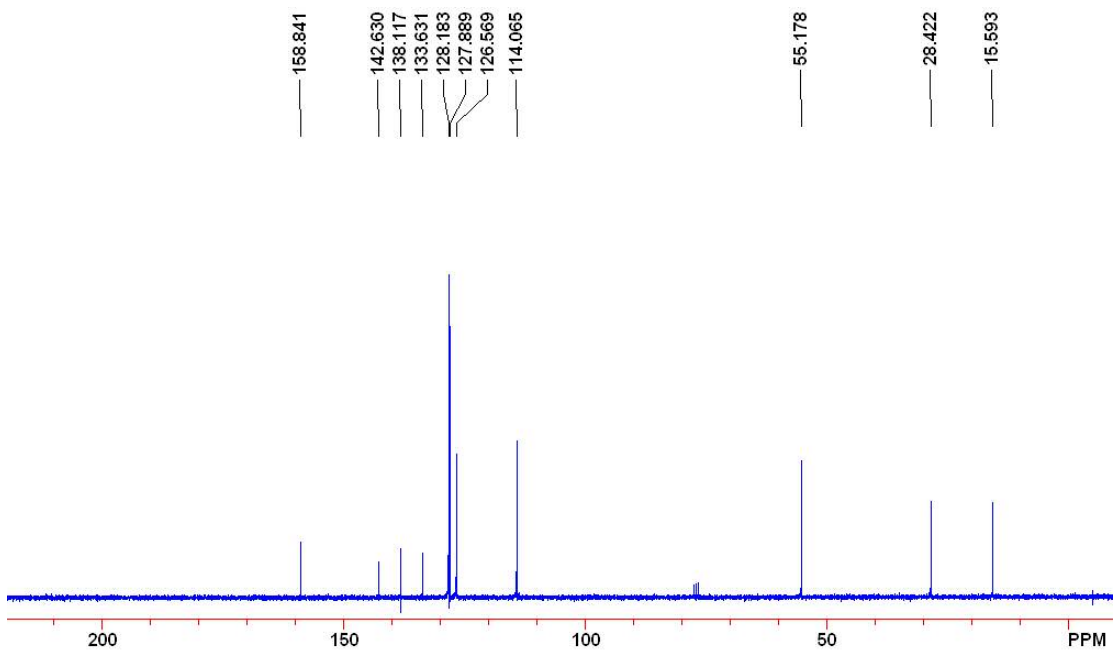
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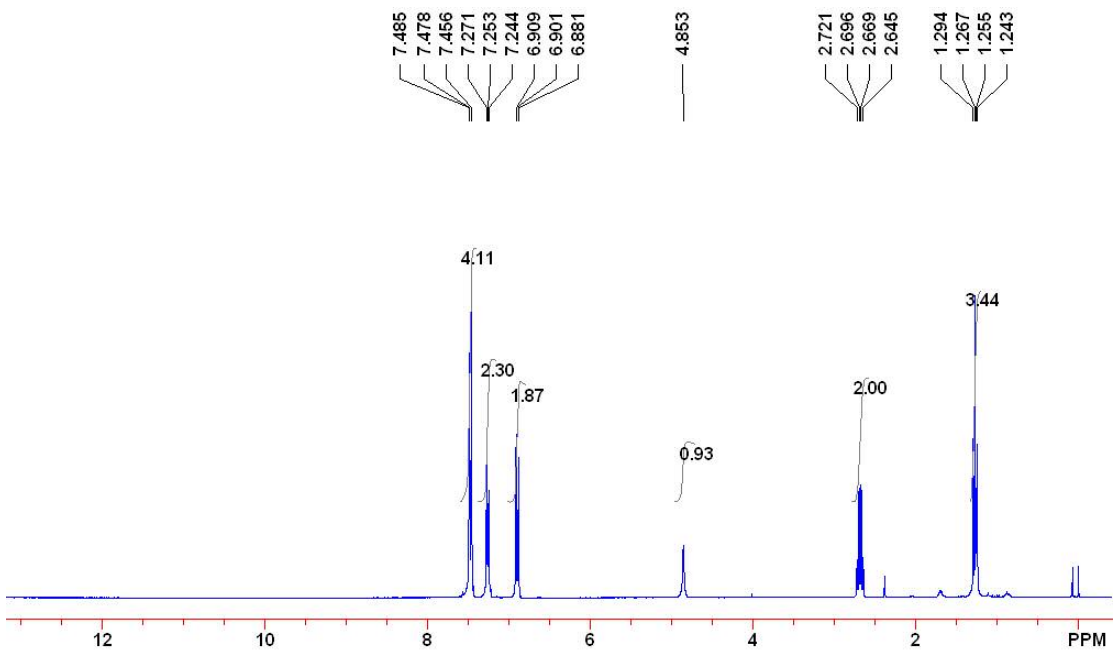
21 ¹H NMR



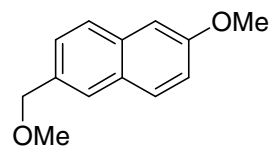
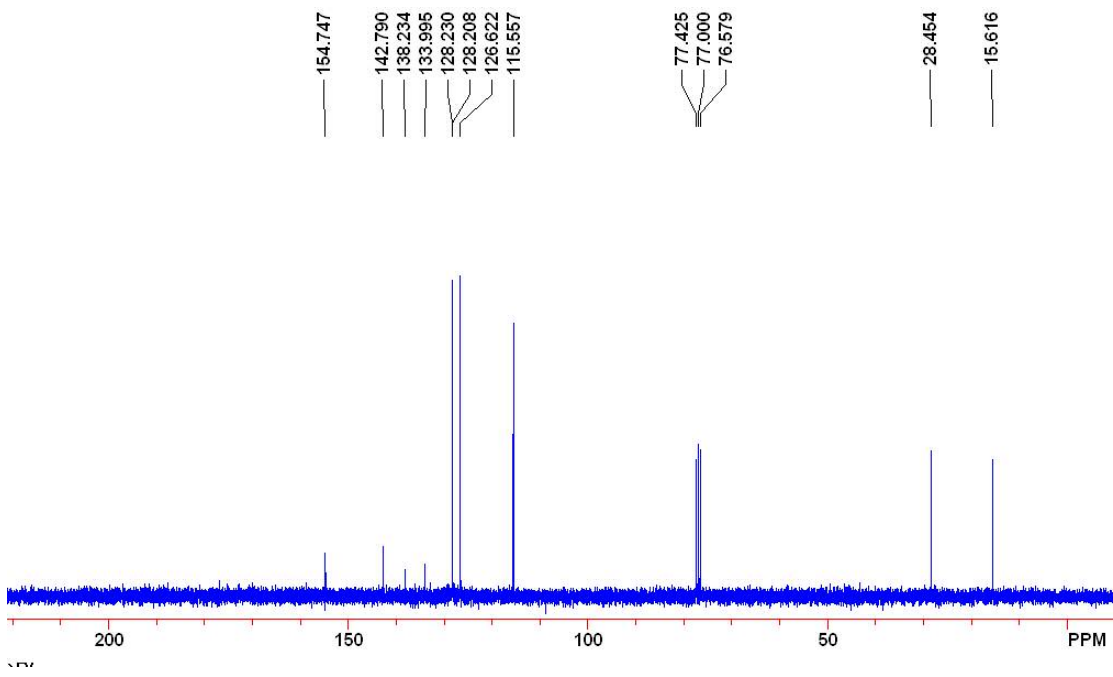
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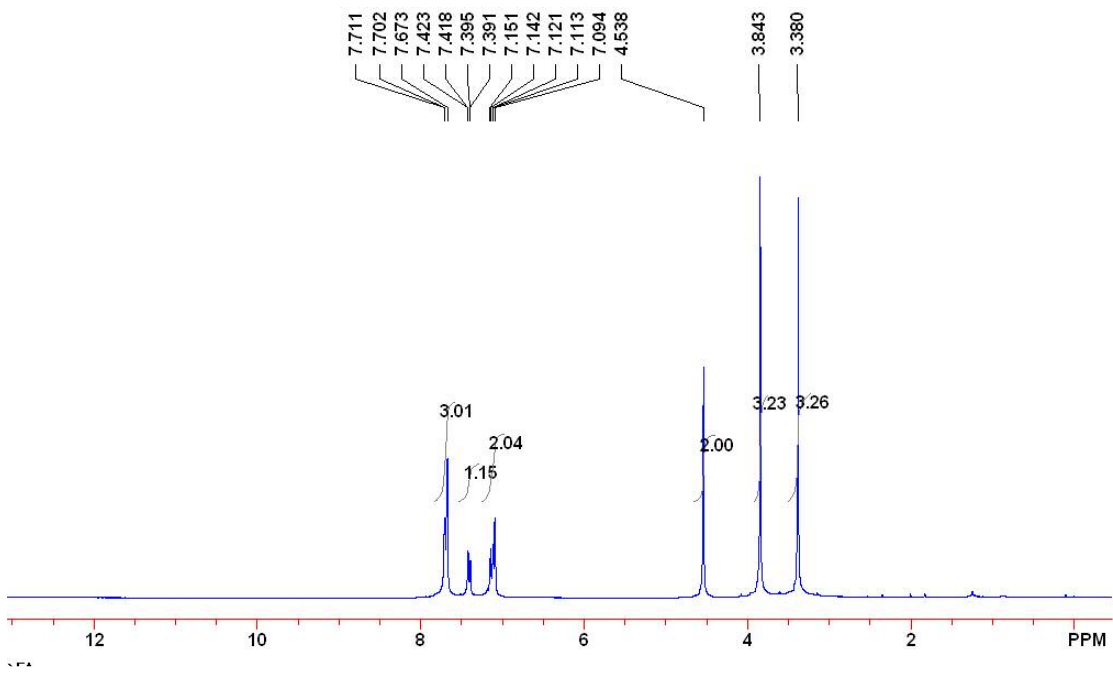
$2\text{m } ^1\text{H NMR}$



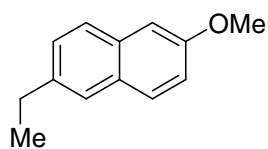
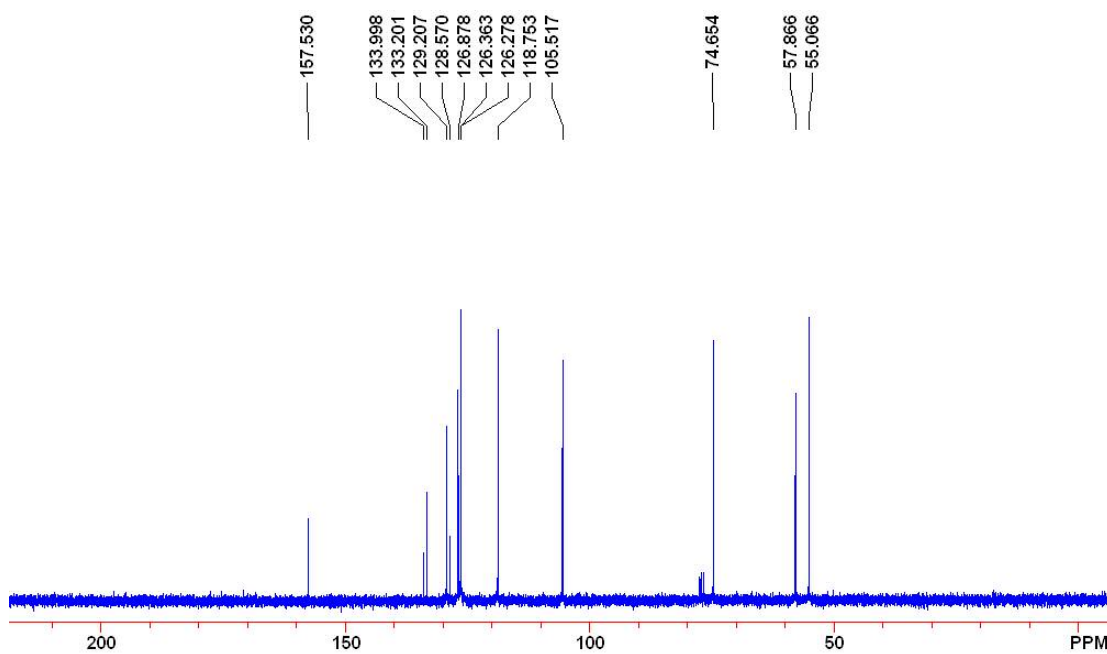
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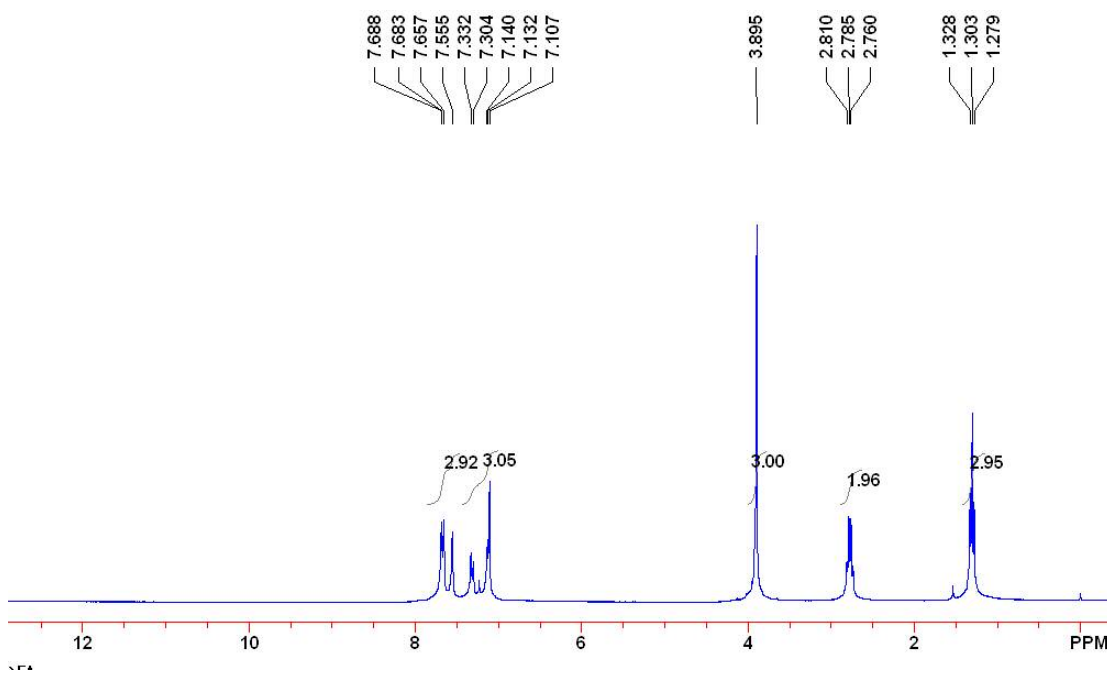
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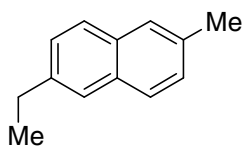
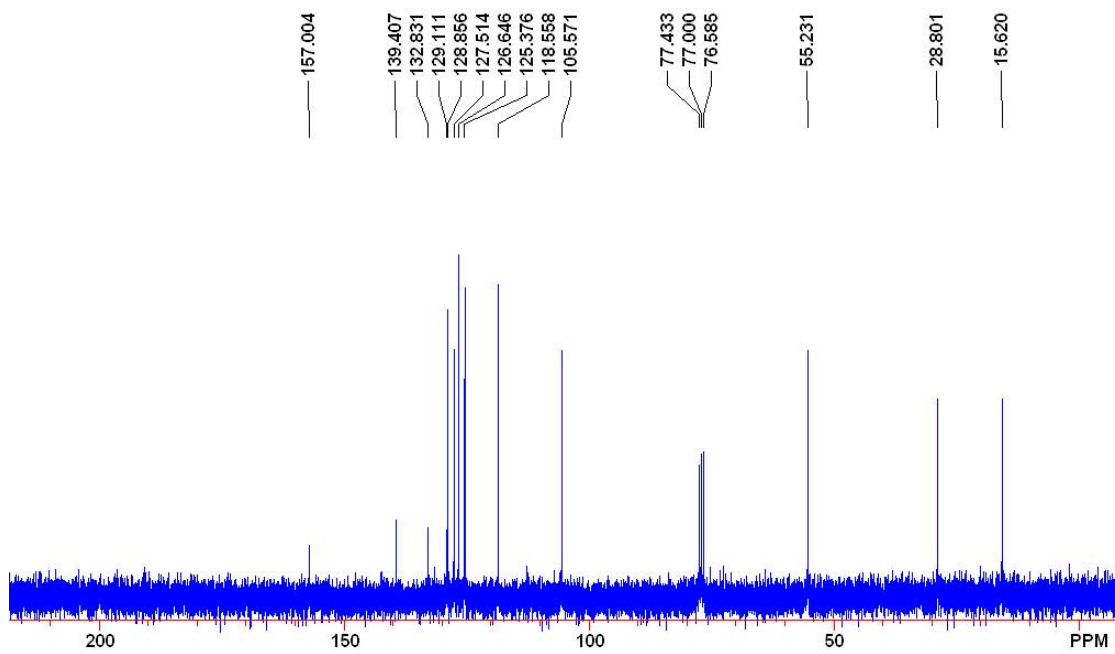
3 ^{13}C NMR



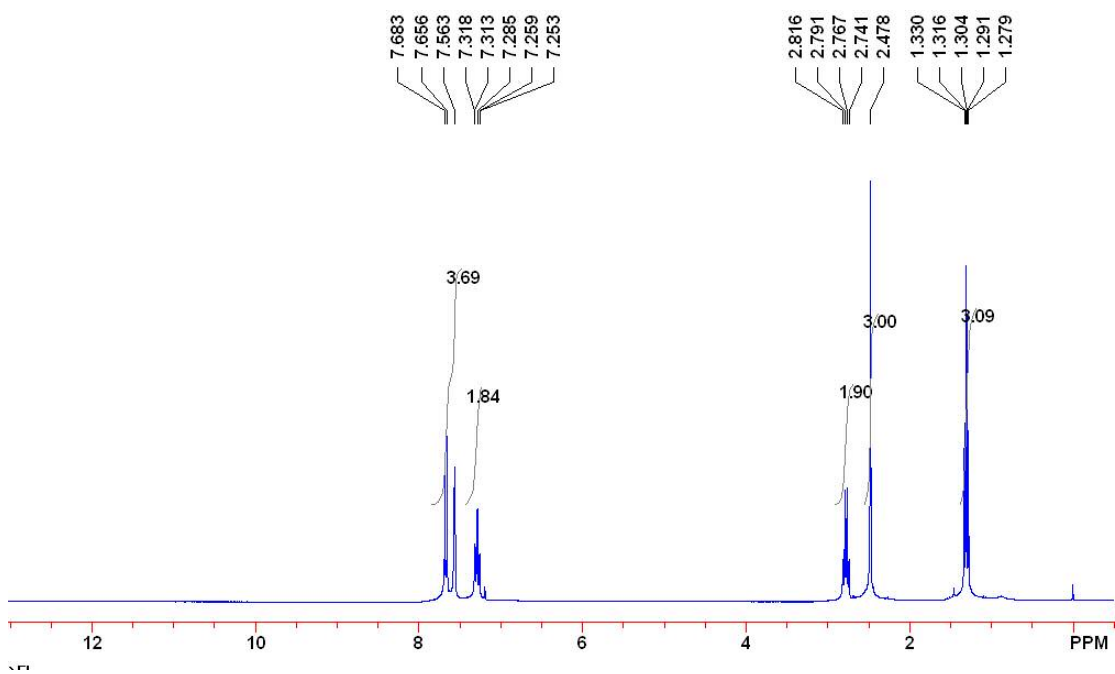
4 ^1H NMR



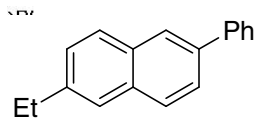
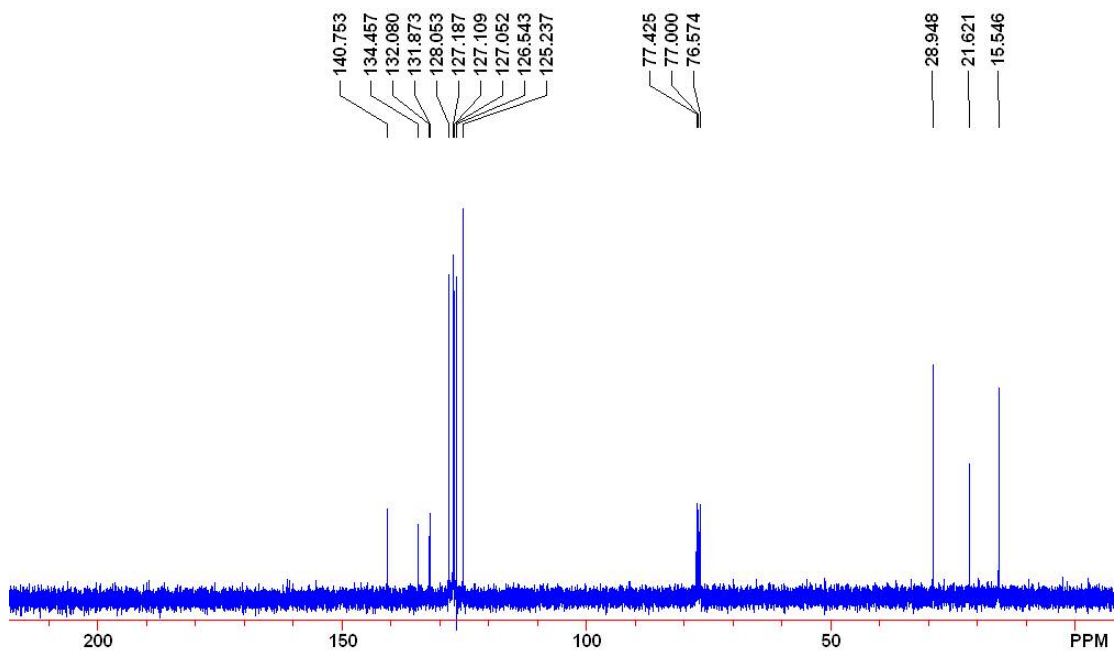
4 ^{13}C NMR



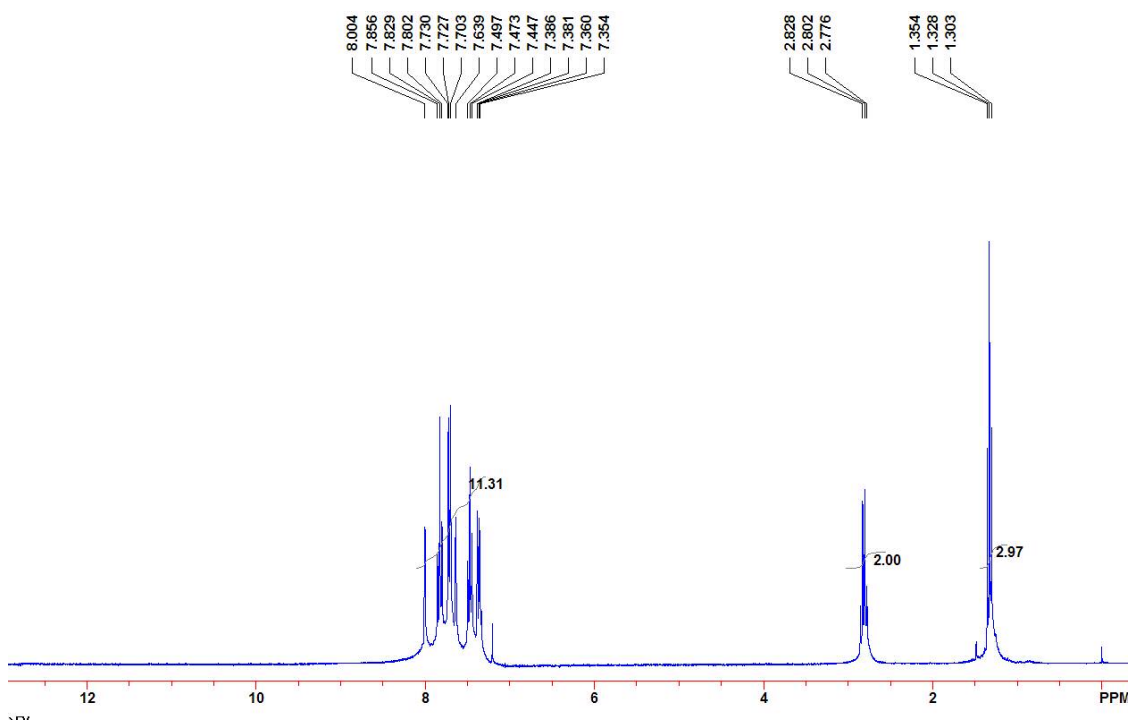
5a ^1H NMR



5b ¹³CNMR



5b ¹HNMR



5b ¹³CNMR

