Supporting Information

Dual functionalized task specific ionic liquid promoted in situ generation of palladium nanoparticles in water: Synergic catalytic system for Suzuki–Miyaura cross coupling

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A) General Information

Phenylboronic acids (Spectrochem, Mumbai) aryl halides (Sigma Aldrich, india) and palladium sources (Sigma Aldrich, India) were used as received. All reactions were carried out in air atmosphere in pre dried glassware. Infrared spectra were measured with an Agilent Cary (IR-

630) spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants are expressed in hertz (Hz). Mass spectra were recorded on a Shimadzu QP2010 GCMS. HR-TEM, FFT were taken on TEM2100F, JEOL.

B) Typical procedure for the preparation of 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro] ionic liquid:

To a vigorously stirred solution of 1-methylpyrrolidine (10 mmol) in toluene (25 mL), 2-chloroethanol (12 mmol) was slowly added at room temperature and quaternisation was carried out at 80 ^{0}C for 24 h, after which it was placed in a freezer at 0 ^{0}C for 4 h. Toluene was decanted and the remaining viscous oil was repeatedly washed with diethyl ether to yield white viscous ionic liquid, which was dried in vacuum furnished 1-(2-hydroxylethyl)-1-methylpyrrolidinium chloride [HEMPy][Cl]. 1-(2-hydroxylethyl)-1-methylpyrrolidinium chloride (10 mmol) was then dissolved in dichloromethane followed by addition of potassium hydroxide (12 mmol) and stirred it for 24 h at room temperature. The suspension was filtered to remove the precipitated potassium chloride salt and the solvent was evaporated under reduced pressure furnished 1-(2-hydroxylethyl)-1-methylpyrrolidine hydroxide [HEMPy] [OH]. Finally, 1-(2-hydroxylethyl)-1-methylpyrrolidine hydroxide (5mmol) was dissolved in water and L-proline (5 mmol) was added slowly at 0-5 ^{0}C after addition it was stirred at room temperature for 12h. The solvent was removed in vacuum to furnish desire ionic liquid *viz* 1-hydroxylethyl-1-methylpyrrolidine prolinate [HEMPy][Pro].

C) General procedure for the Suzuki−Miyaura Coupling

To a mixture of aryl halide (1mmol), arylboronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%), IL (20 mol%) and Na_2CO_3 (1 mmol), water (5 mL) was added and stirred at 80 ^{o}C under aerobic conditions. After completion of reaction monitored by TLC, the reaction mixture was cooled. The product was extracted with ethylacetate (2×10 mL) while the IL-Pd-Nps was remaining in aqueous phase. The aqueous phase containing IL-Pd-NPs washed with ethylacetate. The organic layer was dried with $MgSO_4$ and concentrated on a rotary evaporator to afford the desired biaryl in excellent yield. The crude products were then purified by column chromatography (5 % ethyl

acetate). Synthesized products were confirmed from physical constant, [33] IR, ^{1}H, ^{13}C NMR and Mass analysis.

D) General procedure for the reusability of catalytic system in the Suzuki−Miyaura coupling

A mixture of 4-bromotoluene (1 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (1 mmol), $Pd(OAc)_2$ (2 mol %), and IL (20 mol%) in water (5 mL) was stirred at 80 °C under aerobic condition. After completion of reaction, reaction mixture was cooled to room temperature and extracted by ethylacetate (2×10mL). The combined organic layer was concentrated under reduced pressure, and the residue was isolated by chromatography on a silica gel (300−400 mesh) column using petroleum and ethyl acetate to afford the product. The aqueous phase containing the IL-Pd-Nps was loaded with the fresh reactants and base, for the next run under the same reaction conditions. The aqueous catalytic system was reused for 7 subsequent runs without any loss of catalytic activity.

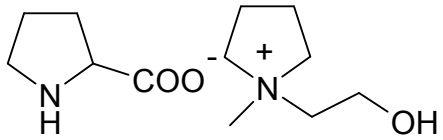
Table 1. Reusability of system for Suzuki-Miyaura reaction[a]

Run	1	2	3	4	5	6	7
Yield(%)[b]	96	96	94	93	92	92	91

[a] 4-bromotoluene (1 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (1 mmol), $Pd(OAc)_2$ (2 mol %) and IL (20 mol%); temp= 80 °C; time= 2 h.

[b] Isolated Yield

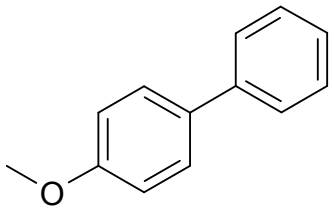
E) Spectral data of synthesized ionic liquid:
1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro] ionic liquid



Yellow viscous liquid, mp 60–62 ^{o}C; IR (ZnSe): 3361, 3260, 2966, 1670, 1584, 1455, 1379, 1085, 997, 936, 772, 630 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ (ppm) 1.53-1.72 (m, 2H), 1.75-1.97 (m, 2H), 2.06 (bs, 2H), 3.04 (s, 2H), 3.42-3.51 (m,4H), 3.83 (s, 1H), 4.05 (bs, 11H); ^{13}C NMR (DMSO-d$_6$, 75 MHz): 18.72, 21.49, 26.73, 43.78, 53.67, 58.95, 62.73, 62.96, 63.00; Ana. Calc. for $C_{12}H_{24}N_2O_3$: C(58.99%), H(9.90%), N(11.47%), O(19.65%); found: C(58.90%), H(9.94%), N(11.47%), O(19.69%).

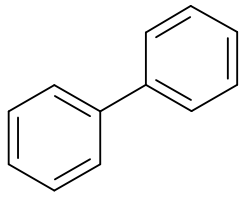
F) Spectral data of synthesized biaryls compounds:

Entry 1, Table 4: 4-methoxybiphenyl



White solid, mp 91–92 ^{o}C (lit.92-93 °C)[33]; IR (KBr): 2960, 2836, 1606, 1522, 1486, 1287, 1250, 1183, 1037, 833, 689cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.88 (s, 3H), 7.00-7.03 (d, 2H, *J*= 9 Hz), 7.31- 7.37 (m, 1H), 7.43-7.48 (t, 2H, *J*= 9 Hz), 7.55-7.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.36, 114.22, 126.69, 126.76, 128.18, 128.75, 133.80, 140.85, 159.17; MS (EI): 184, 181, 154, 152, 127, 113, 99, 88, 76, 63, 51, 32 (m/z).

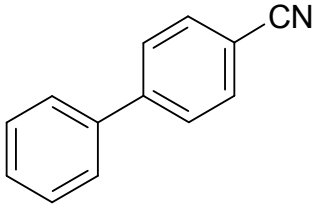
Entry 2, Table 4: biphenyl



White solid, mp 70–72 ^{o}C (lit. 69-70 °C)[33]; IR (KBr): 3034, 1569, 1481, 1428, 728, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.39-7.44 (t, 2H, *J*= 6 Hz), 7.49- 7.54 (m,

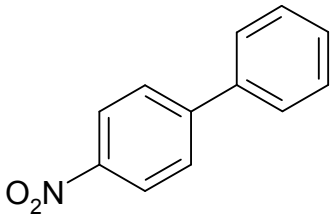
4H), 7.66-7.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 127.22, 127.30, 128.80, 141.32; MS (EI): 154, 153, 128, 115, 102, 89, 76, 63, 51, 39 (m/z).

Entry 3, Table 4: biphenyl-4-carbonitrile



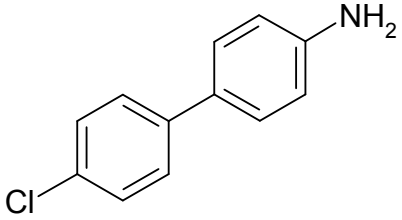
White solid, mp 81-82 °C (lit. 85-86 °C) [33]; IR (KBr): 3060, 2918, 2225, 1682, 1605, 1483, 1397, 1179, 847, 769, 723, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.41-7.52 (m, 3H), 7.58- 7.67 (m, 2H), 7.62-7.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 110.95, 118.90, 127.21, 127.72, 128.65, 129.10, 132.57, 139.18, 145.67.

Entry 4, Table 4: 4-nitrobiphenyl



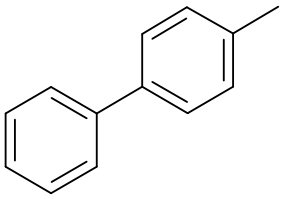
Yellow solid, mp 112-114 °C (lit. 113-114 °C)[33]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.41-7.52 (m, 3H), 7.71- 7.74 (m, 2H), 7.87-7.90 (d, 2H, *J*= 6 Hz), 8.22-8.23 (d, 2H, *J*= 3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 124.45, 127.65, 128.20, 129.45, 129.62, 138.25, 147.04, 147.07; MS (EI): 199, 169, 152, 127, 115, 102, 76, 63, 51 (m/z).

Entry 5, Table 4: 4'-chlorobiphenyl-4-amine



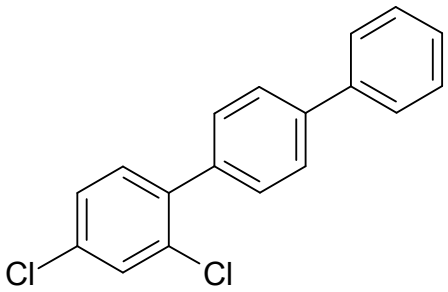
Yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 3.59 (bs, 2H, -NH_2), 6.56-6.59 (d, 4H, *J*=9Hz), 7.24-7.27 (d, 4H, *J*=9Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 110.20, 116.77, 132.02, 145.45.

Entry 6, Table 4: 4-methylbiphenyl



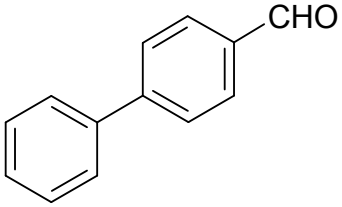
White solid, mp 48°C (lit. 49-50 °C)[33]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.44 (s, 3H), 7.30-7.33 (d, 2H, *J*=9Hz), 7.38-7.41 (m, 1H), 7.46-7.51 (m, 2H), 7.55-7.58 (m, 2H), 7.64-7.68 (m, 2H);^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.21, 126.96, 127.01, 127.05, 128.71, 129.49, 136.78, 138.49, 141.26; MS (EI): 168, 167, 152, 139, 115, 102, 83, 63, 51, 39 (m/z).

Entry 7, Table 4: 2,4-dichloro-1,1':4',1''-terphenyl



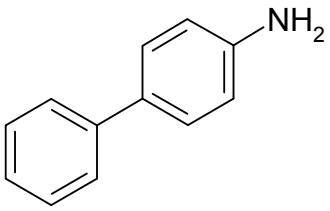
White solid, ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 7.39-7.42 (m, 1H), 7.45-7.47 (m, 3H), 7.49-7.50 (m, 3H), 7.57-7.61 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 121.55, 126.96, 127.66, 128.76, 128.92, 131.87, 140.01, 140.15

Entry 8, Table 4: biphenyl-4-carbaldehyde



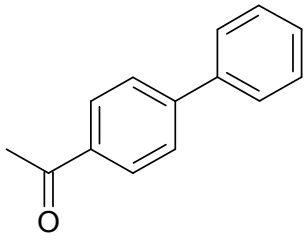
White solid, mp 58-59 °C (lit. 59-60 °C)[33]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.41-7.51 (m, 3H), 7.61-7.64 (m, 2H), 7.73-7.76 (t, 2H, *J*=6 Hz), 7.93-7.96 (dd, 2H, *J*=3 Hz,3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 127.34, 127.63, 128.43, 128.99, 130.21, 135.29, 139.74, 147.11, 191.24.

Entry 10, Table 4: biphenyl-4-amine



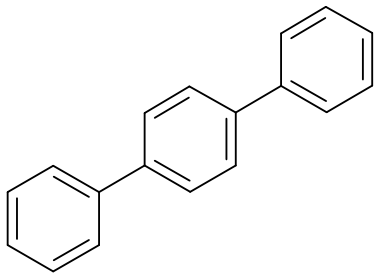
White solid, mp 46°C (lit. 45-47 °C)[33]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.65 (bs, 2H, -NH_2), 6.74-6.80 (t, 2H, *J*=6Hz), 7.28-7.31 (m, 1H), 7.39-7.46 (m, 4H), 7.55-7.58 (t, 2H, *J*= 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 115.40, 126.26, 126.41, 128.02, 128.66, 131.61, 141.20, 145.83; MS (EI): 169, 155, 141, 127, 113, 99, 85, 71, 57, 43, 41 (m/z).

Entry 11, Table 4:1-(biphenyl-4-yl)ethanone



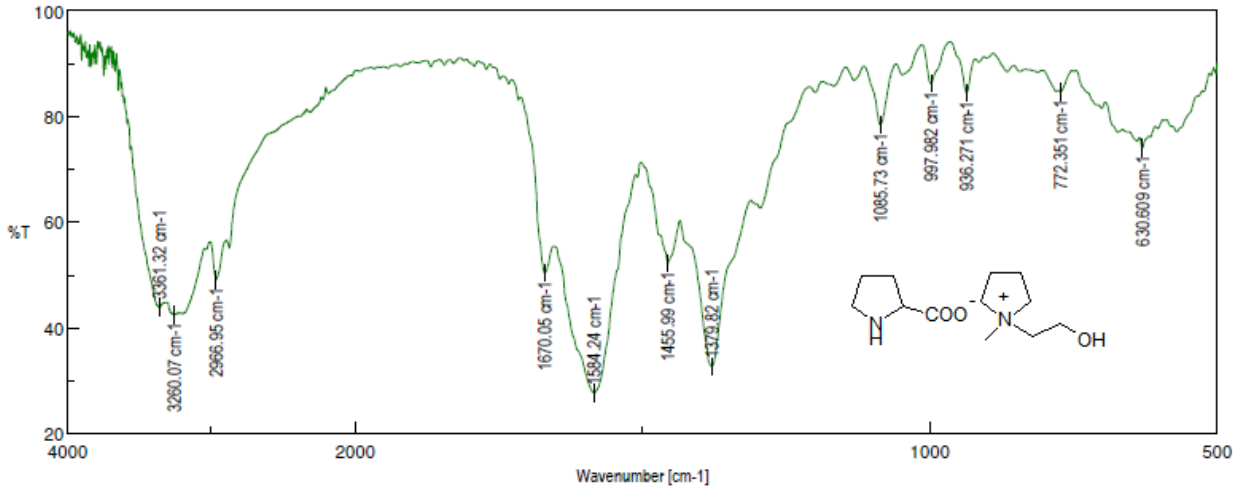
White solid, mp 120^{0}C (lit. 119-120 °C)[33]; IR (KBr): 3073, 2998, 1678, 1602, 1403, 1359, 1283, 1263, 961, 842, 765, 721, 691 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.65 (3H, s, CH_3), 7.42–7.48 (3H, m), 7.62– 7.69 (4H, m), 8.04 (2H, d, *J*=7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 26.61, 127.21, 127.26, 128.21, 128.89, 128.93, 135.89, 139.89, 145.78.

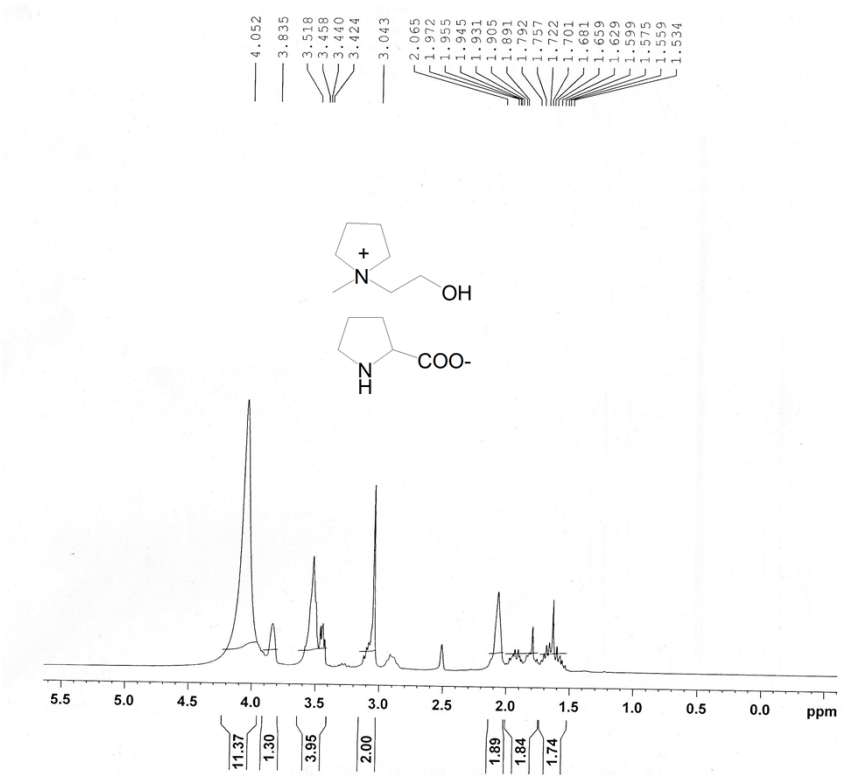
Entry 12, Table 4: 1,1':4',1"-terphenyl



White solid, mp 212-214 °C (lit. 213-214 °C)[33]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.38-7.42 (t, 2H, *J*= 6 Hz), 7.48-7.53 (t, 4H, *J*= 6 Hz), 7.67-7.72 (t, 4H, *J*= 6 Hz), 7.72 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 127.08, 127.37, 127.53, 128.85, 140.14, 140.72.

IR, ^{1}H, ^{13}C and DEPT Spectra of ionic liquid:

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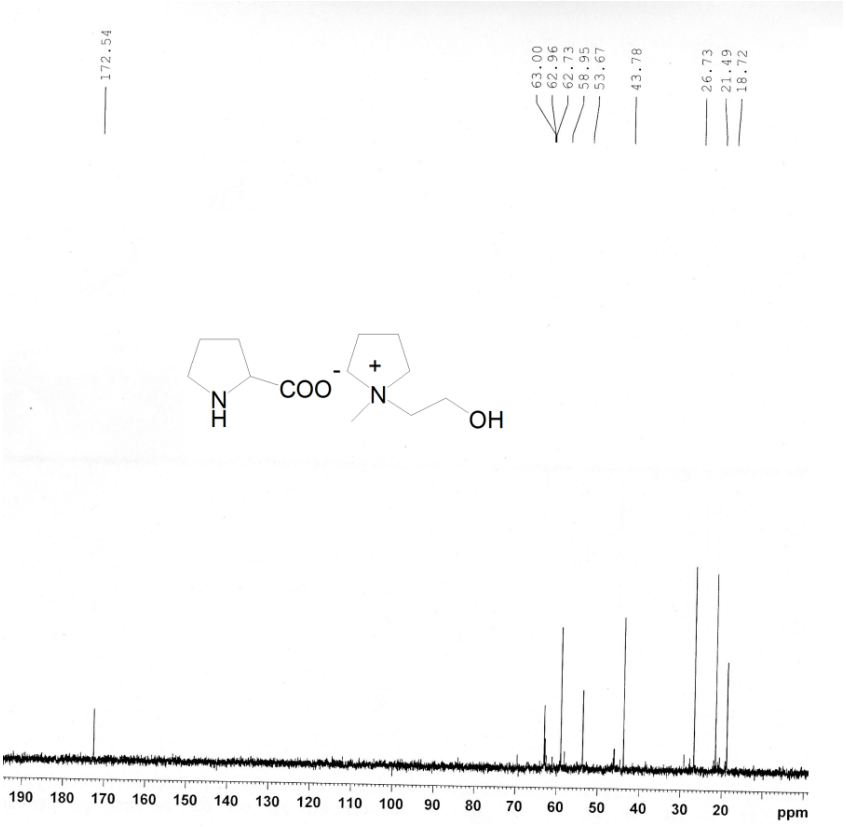
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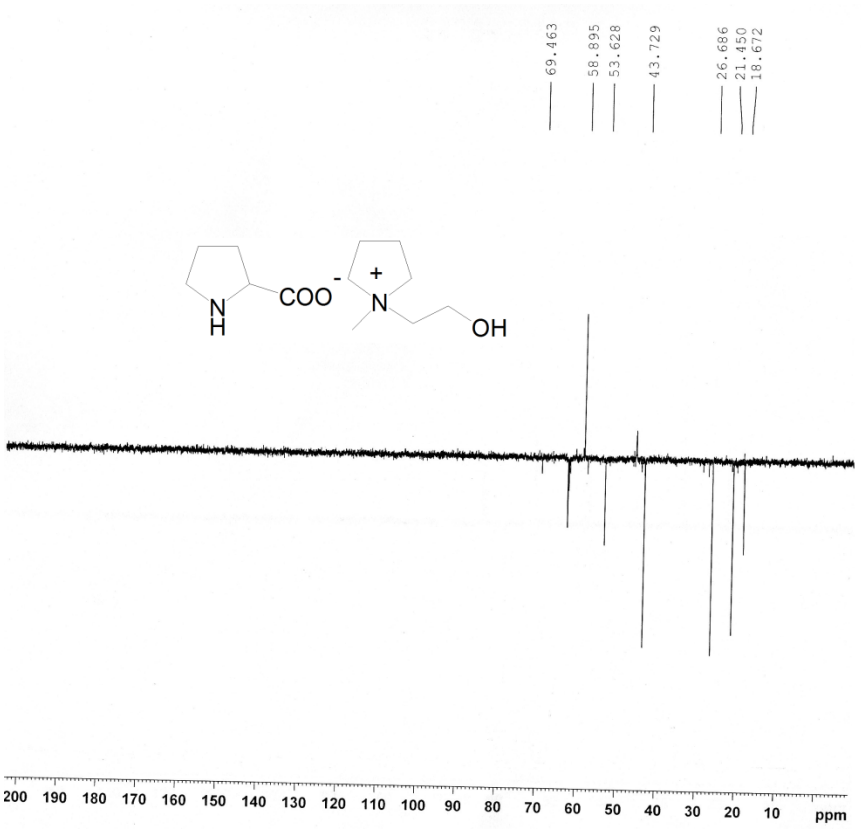

^{1}H, ^{13}C, IR and Mass Spectra of some synthesized biaryls compounds

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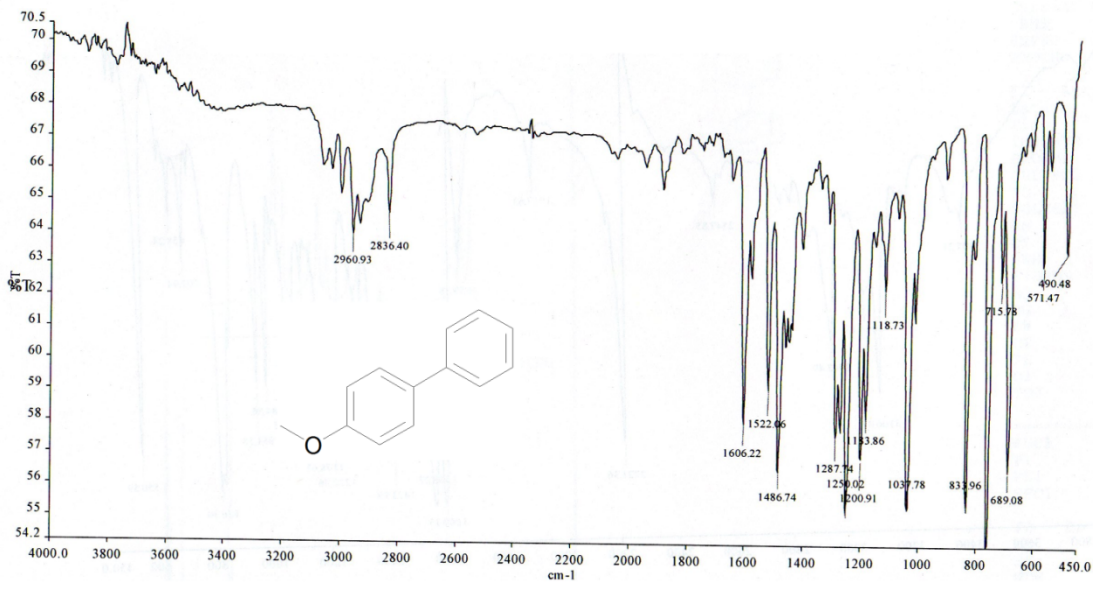

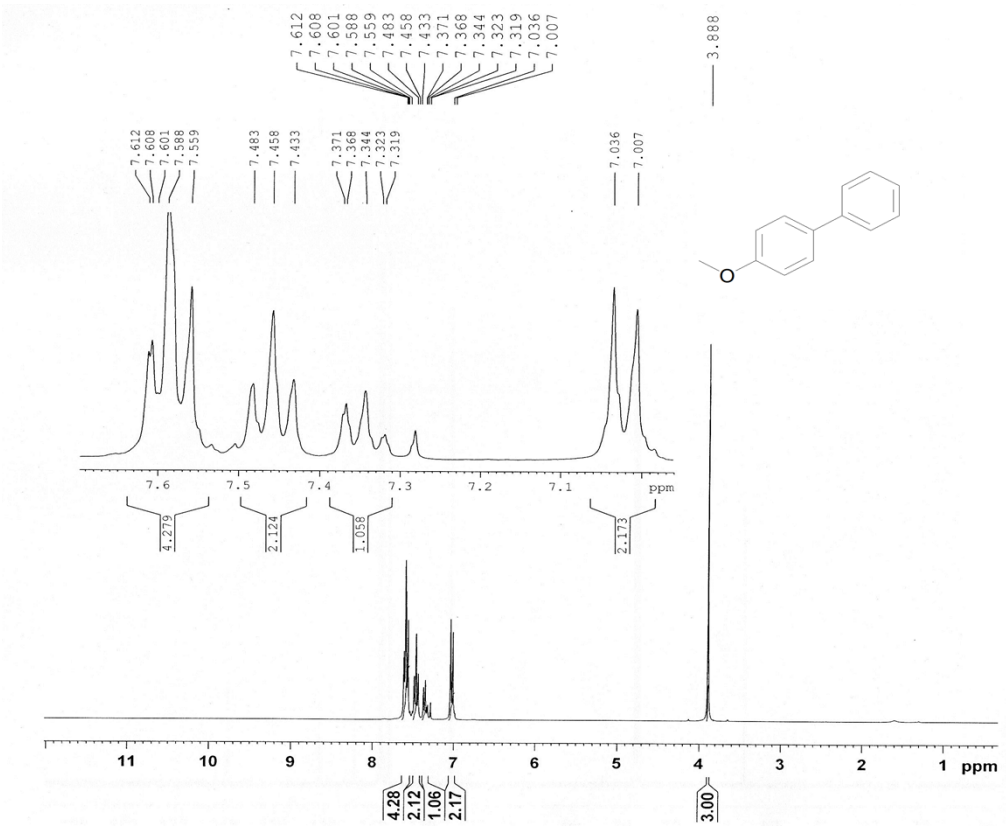
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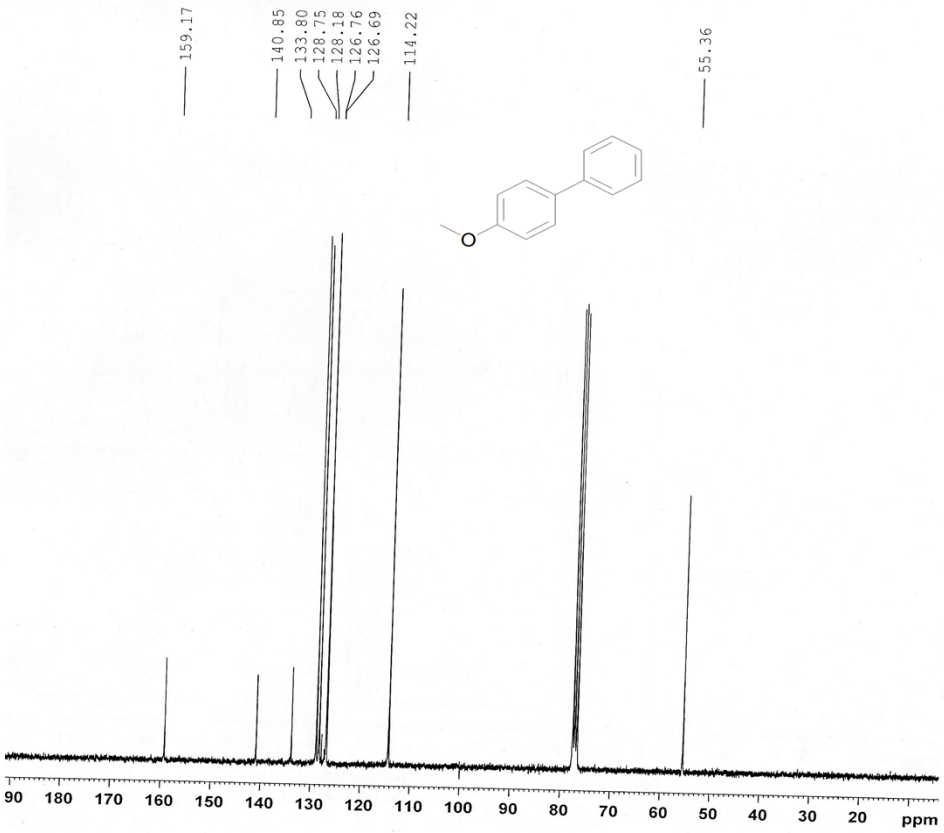
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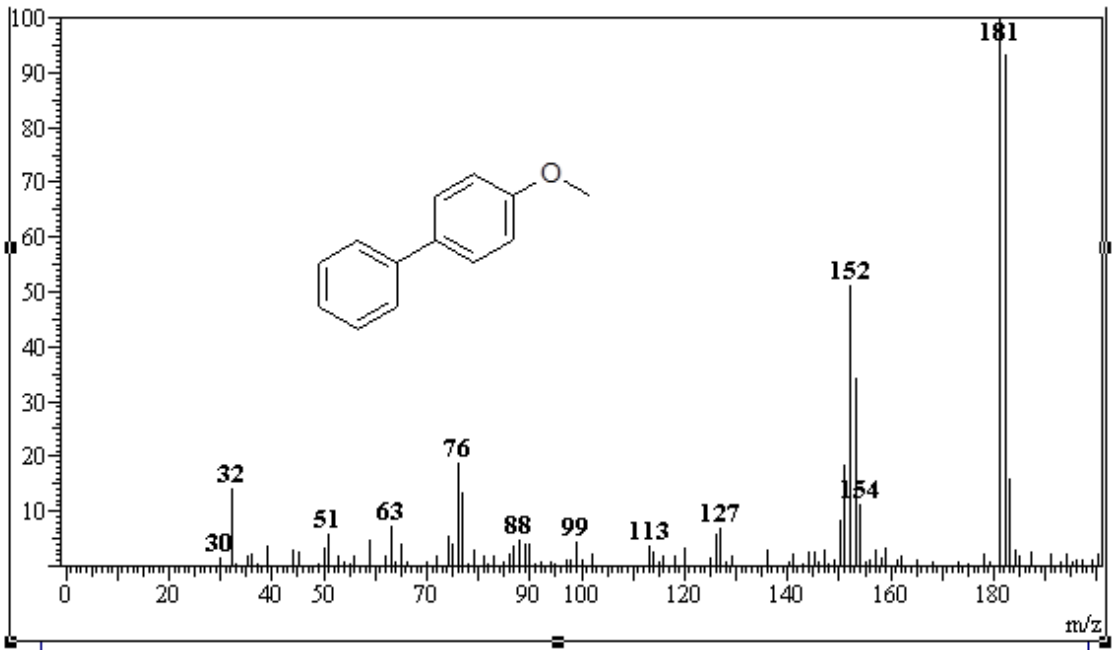

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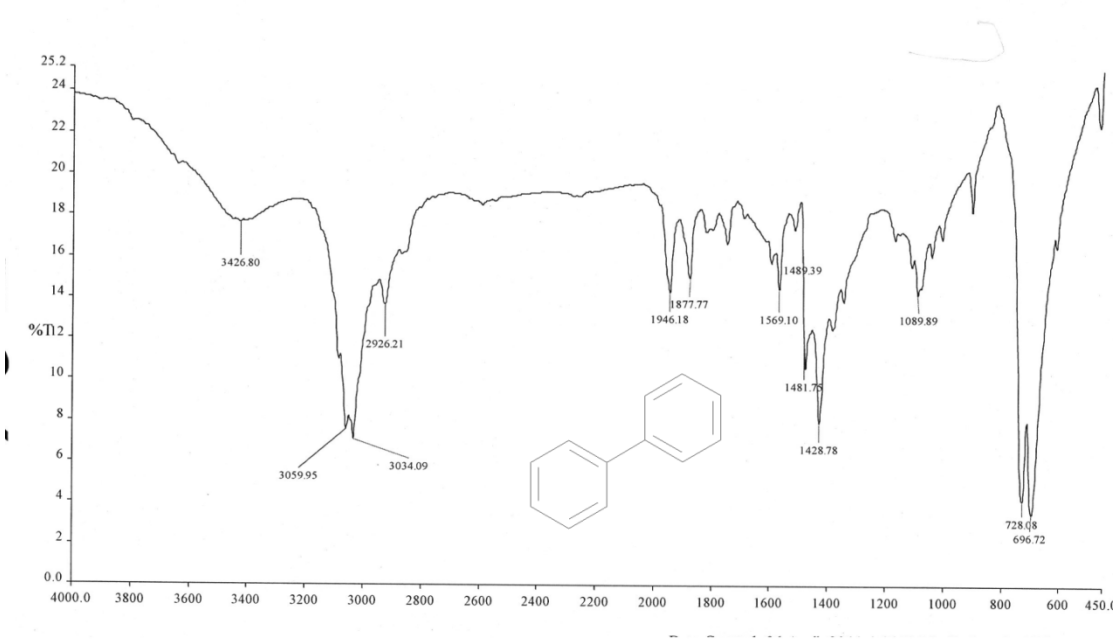

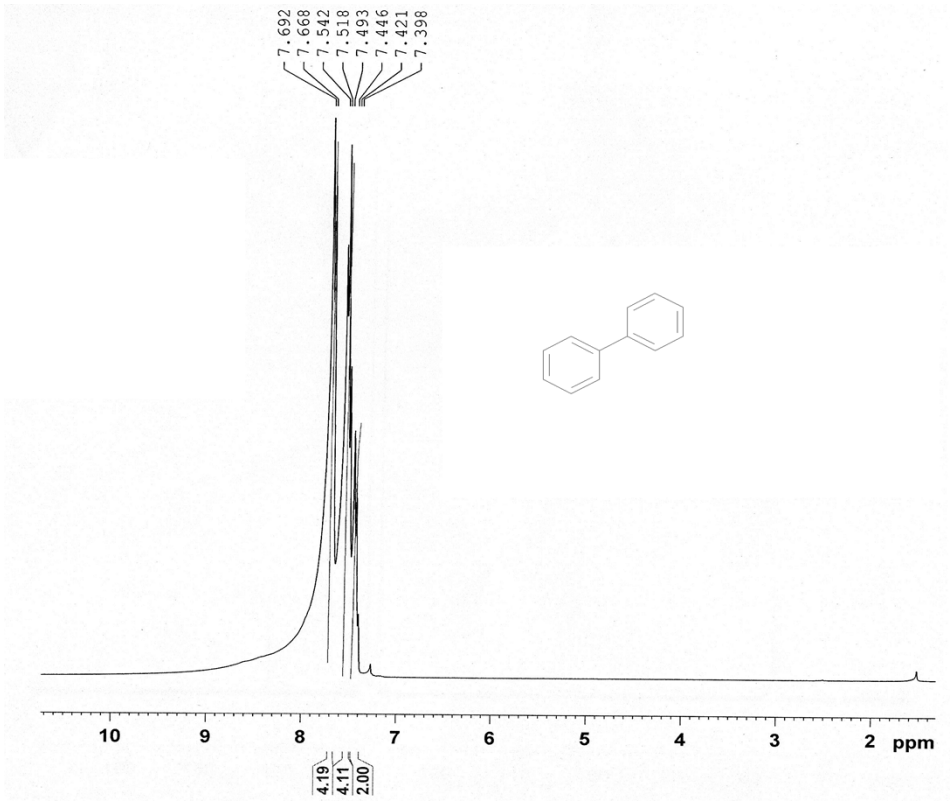
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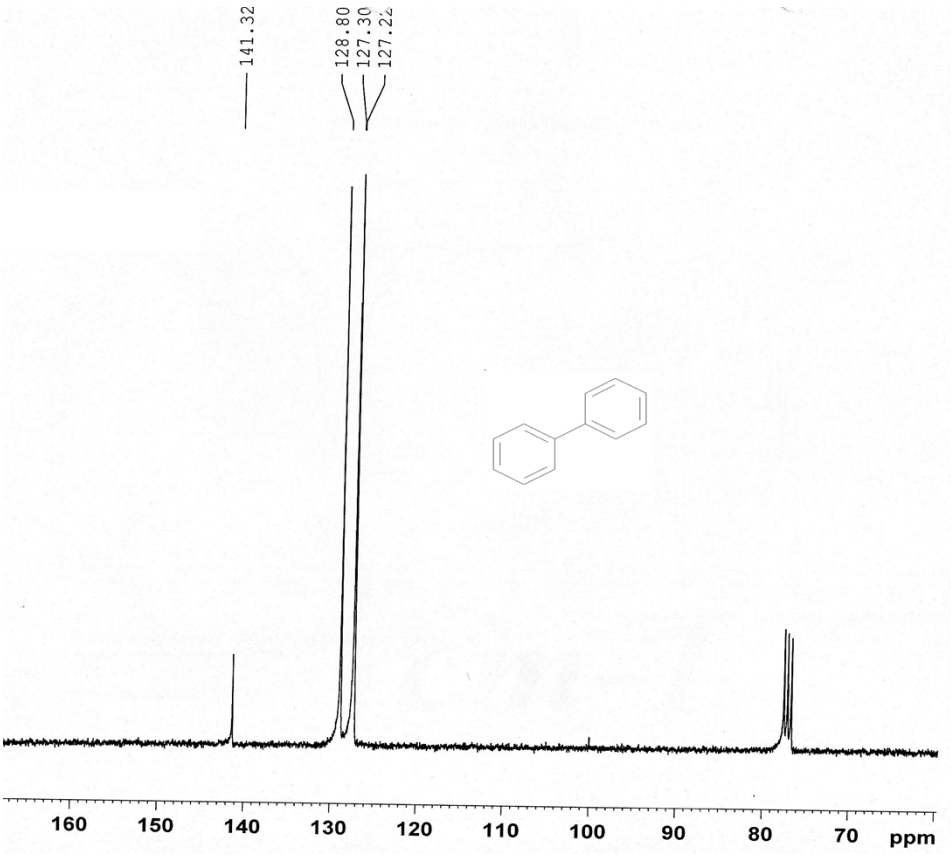
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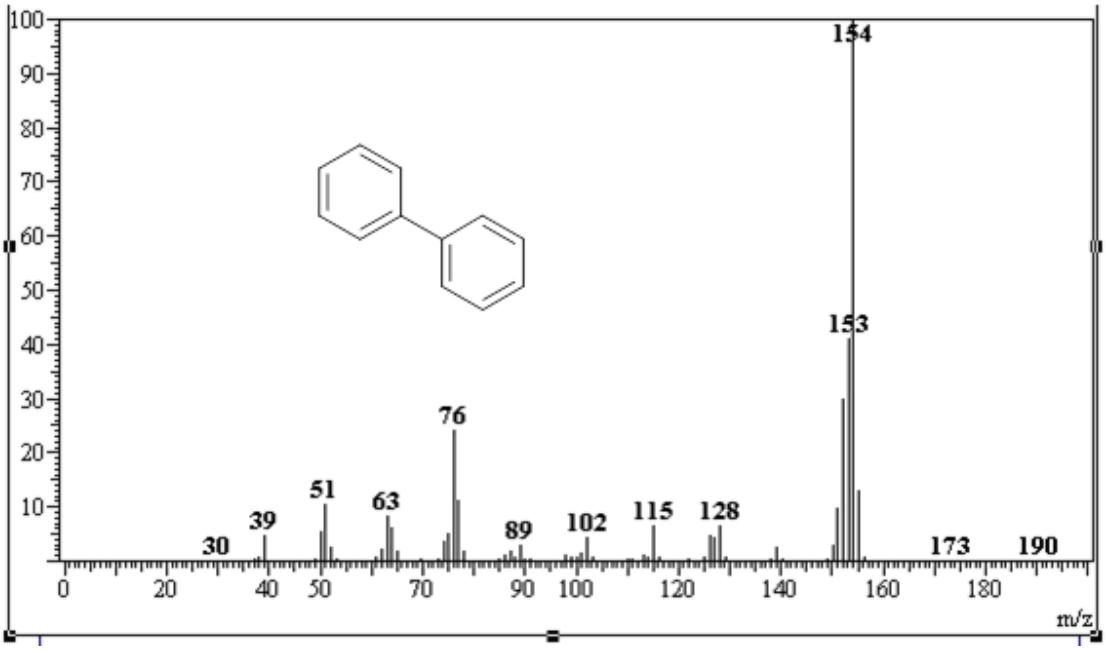

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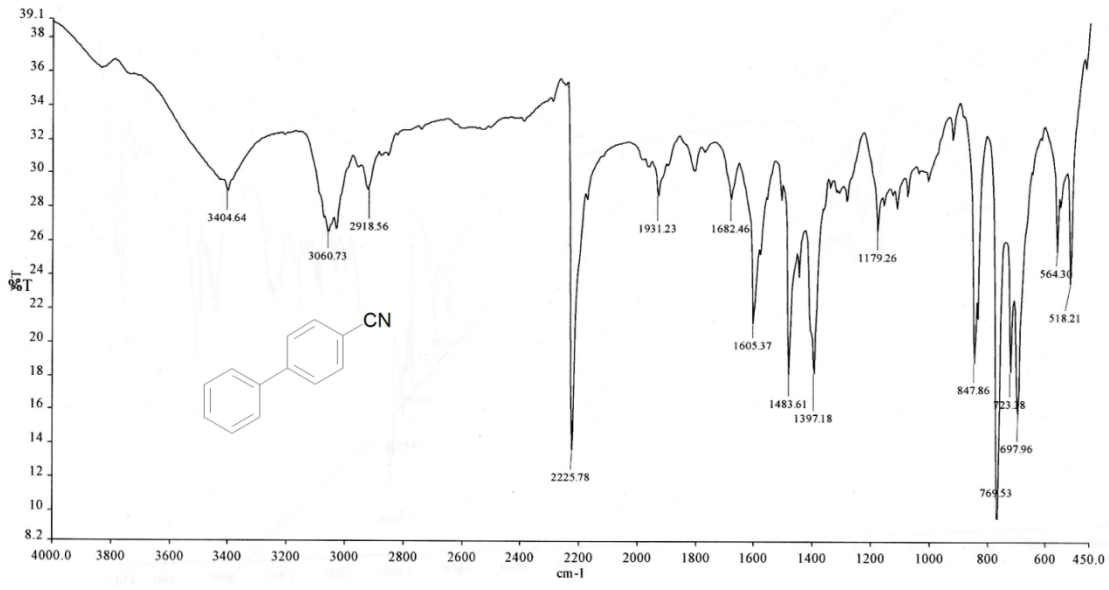

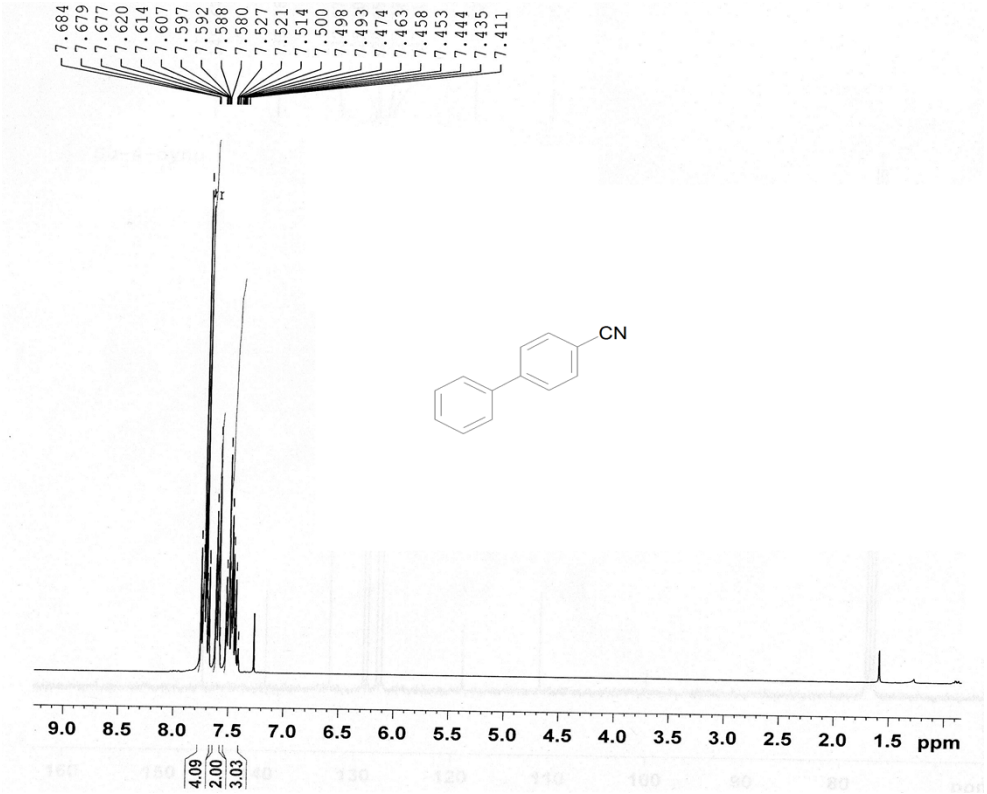
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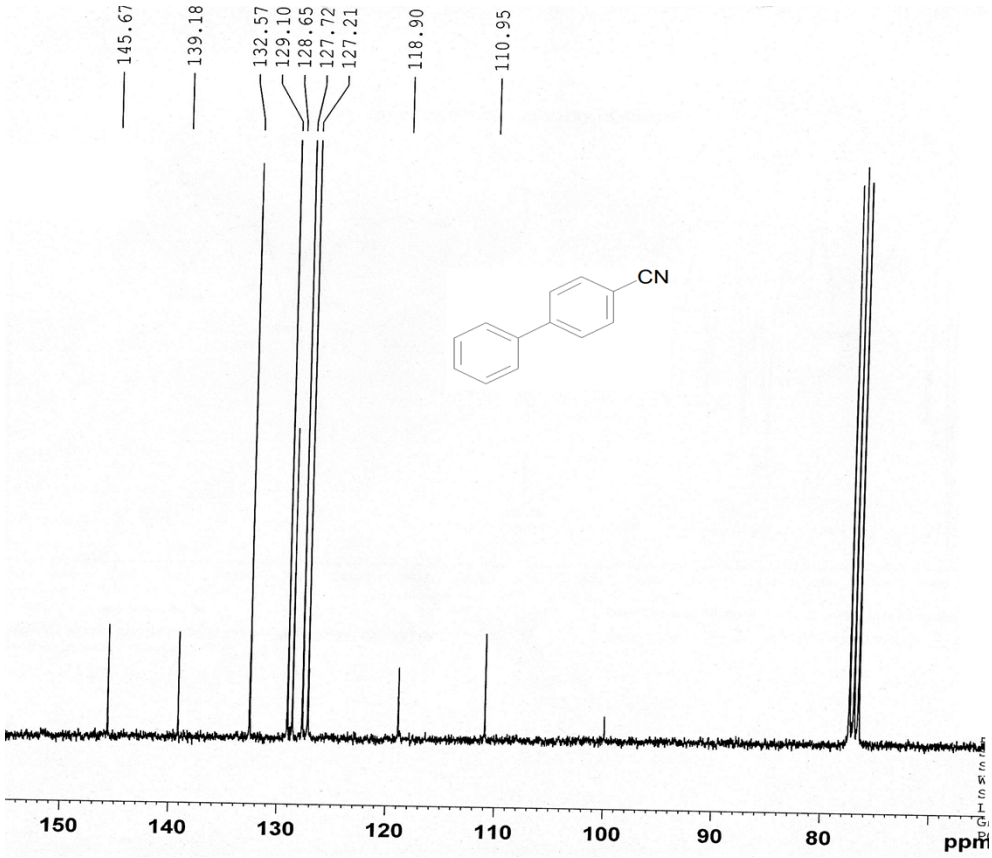
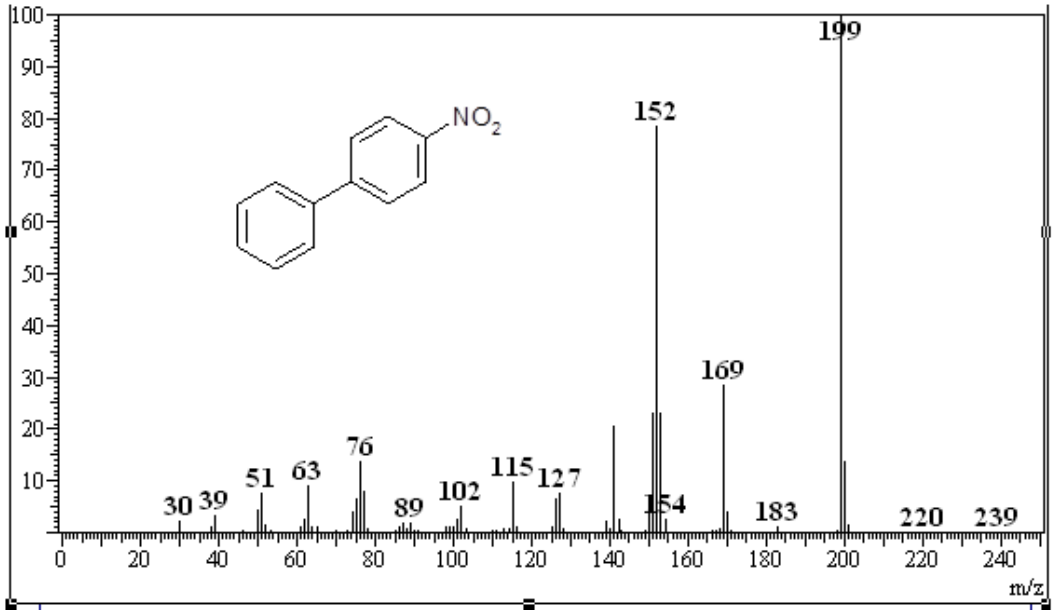
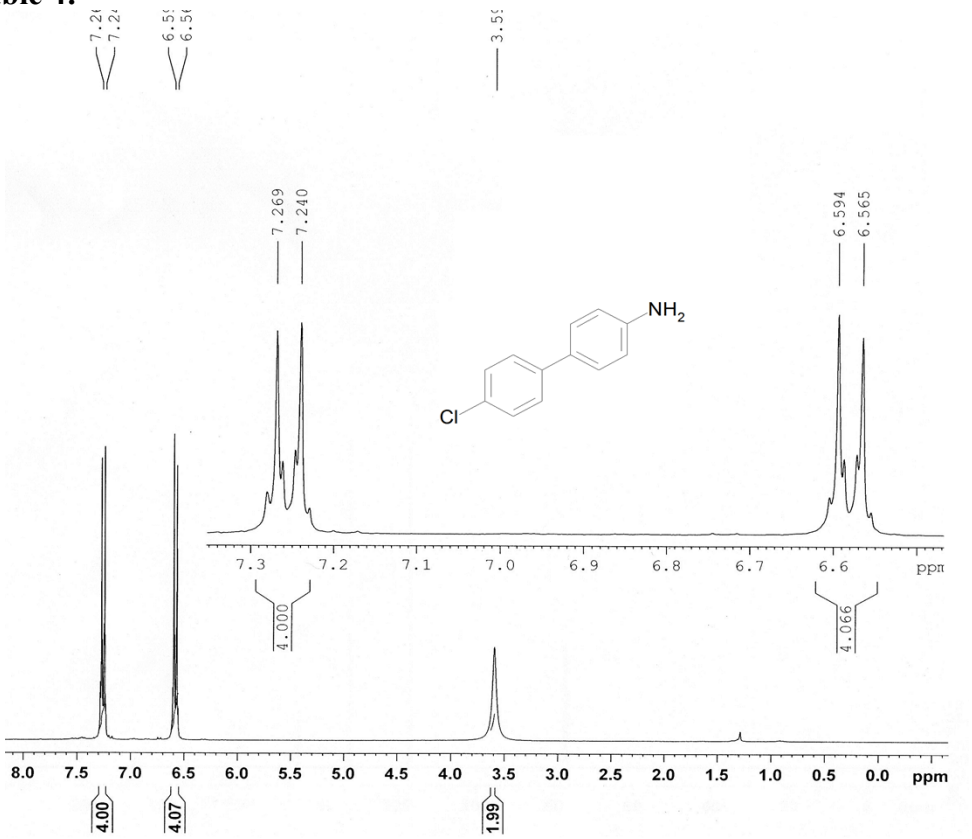
7.411
CN
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
4.09
2.00
3.03

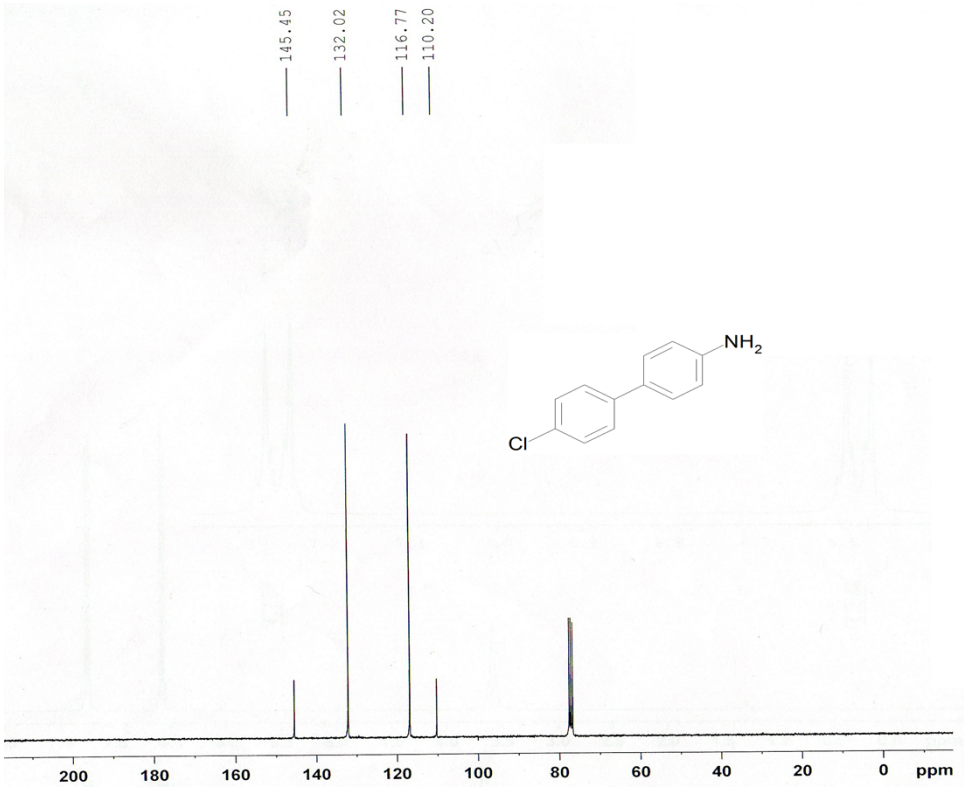

145.67
139.18
132.57
129.10
128.65
127.72
127.21
118.90
110.95
CN
150 140 130 120 110 100 90 80 ppm

Entry 4, table 4:

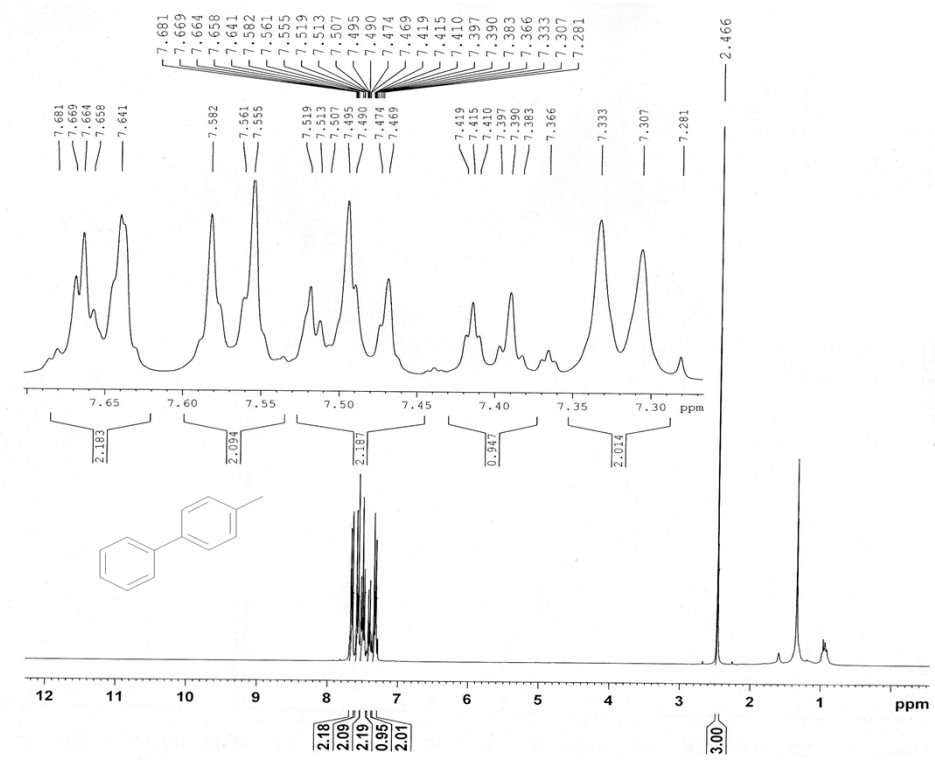


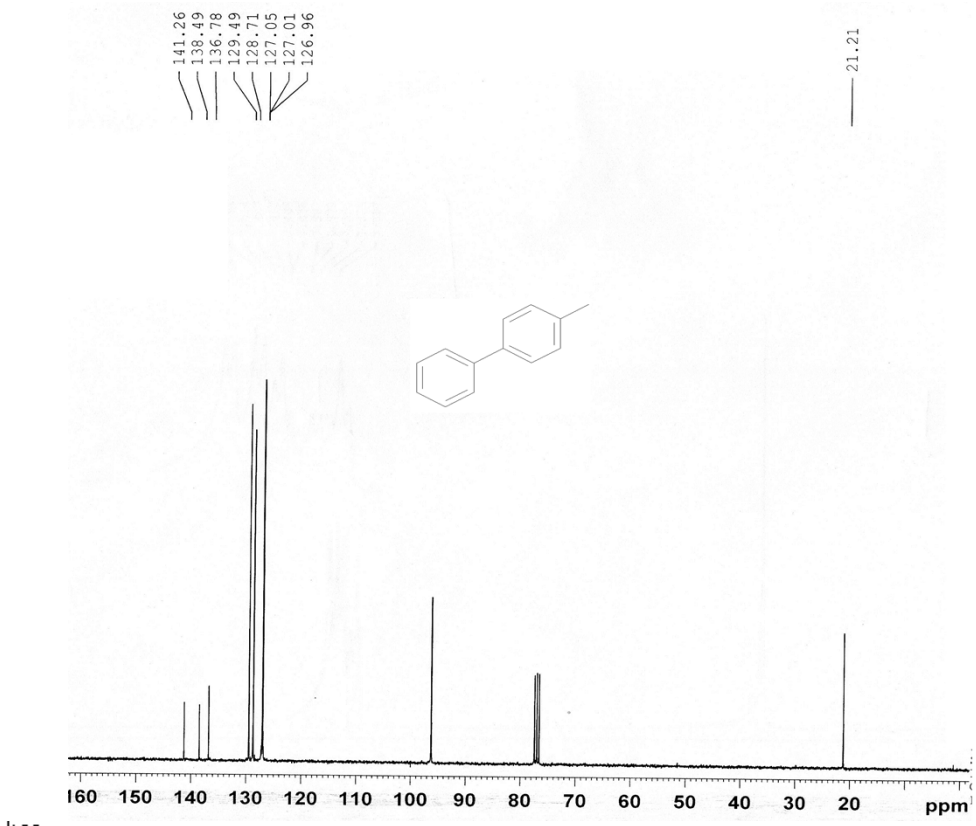
Entry 5 table 4:

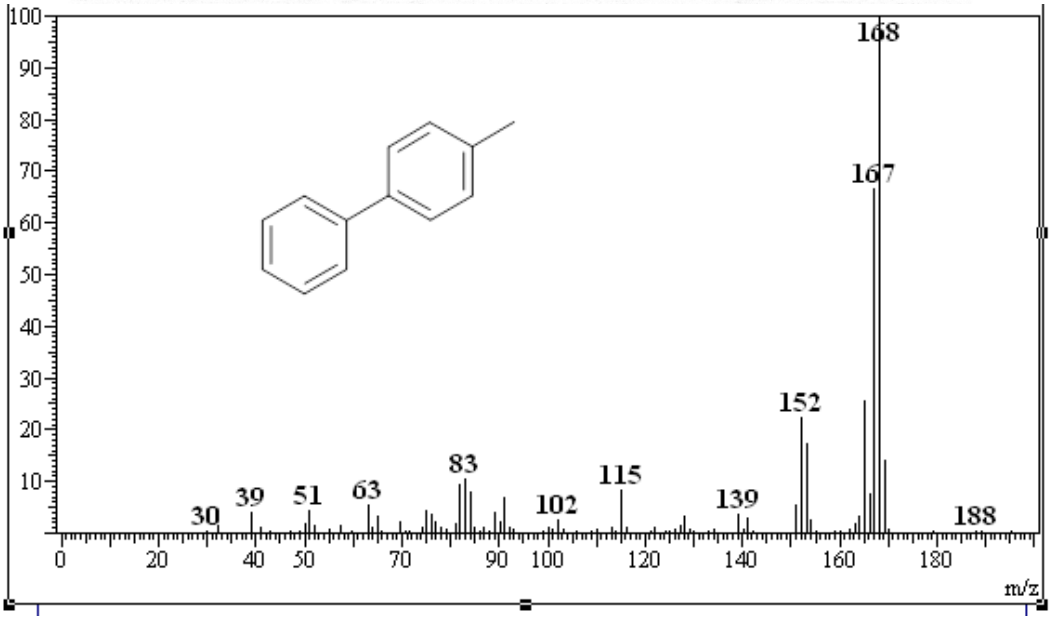




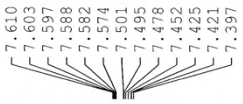
Entry 6 table 4:

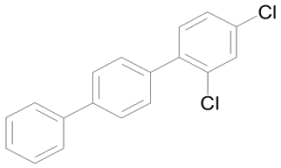


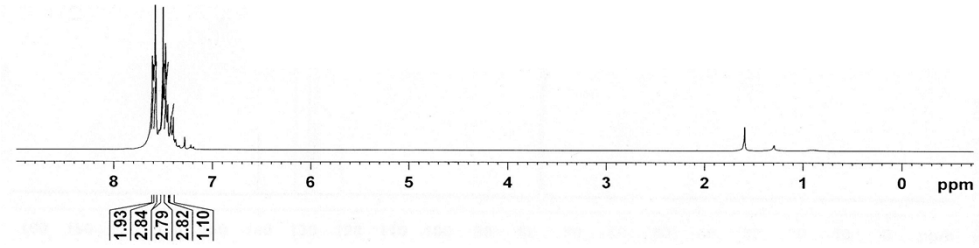

141.26
138.49
136.78
129.49
128.71
127.05
127.01
126.96
21.21
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

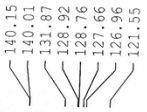

100
90
80
70
60
50
40
30
20
10
168
167
152
83
115
30
39
51
63
102
139
188
0 20 40 50 70 90 100 120 140 160 180
m/z

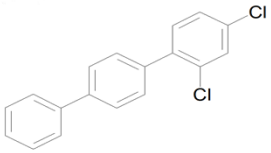
Entry 7, table 4:

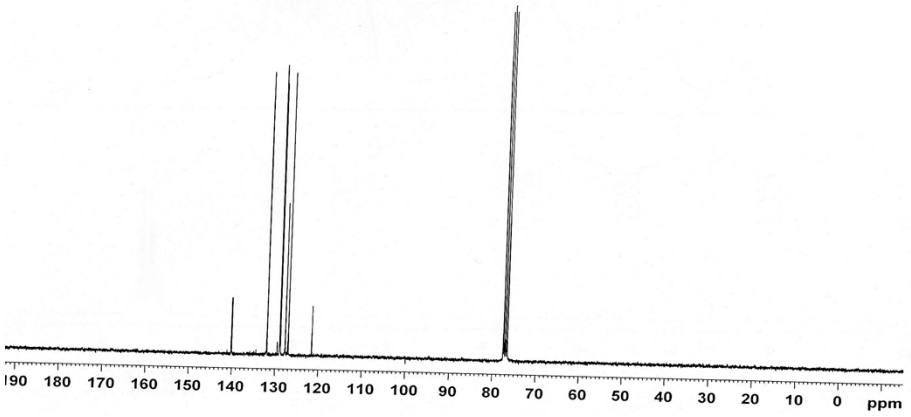




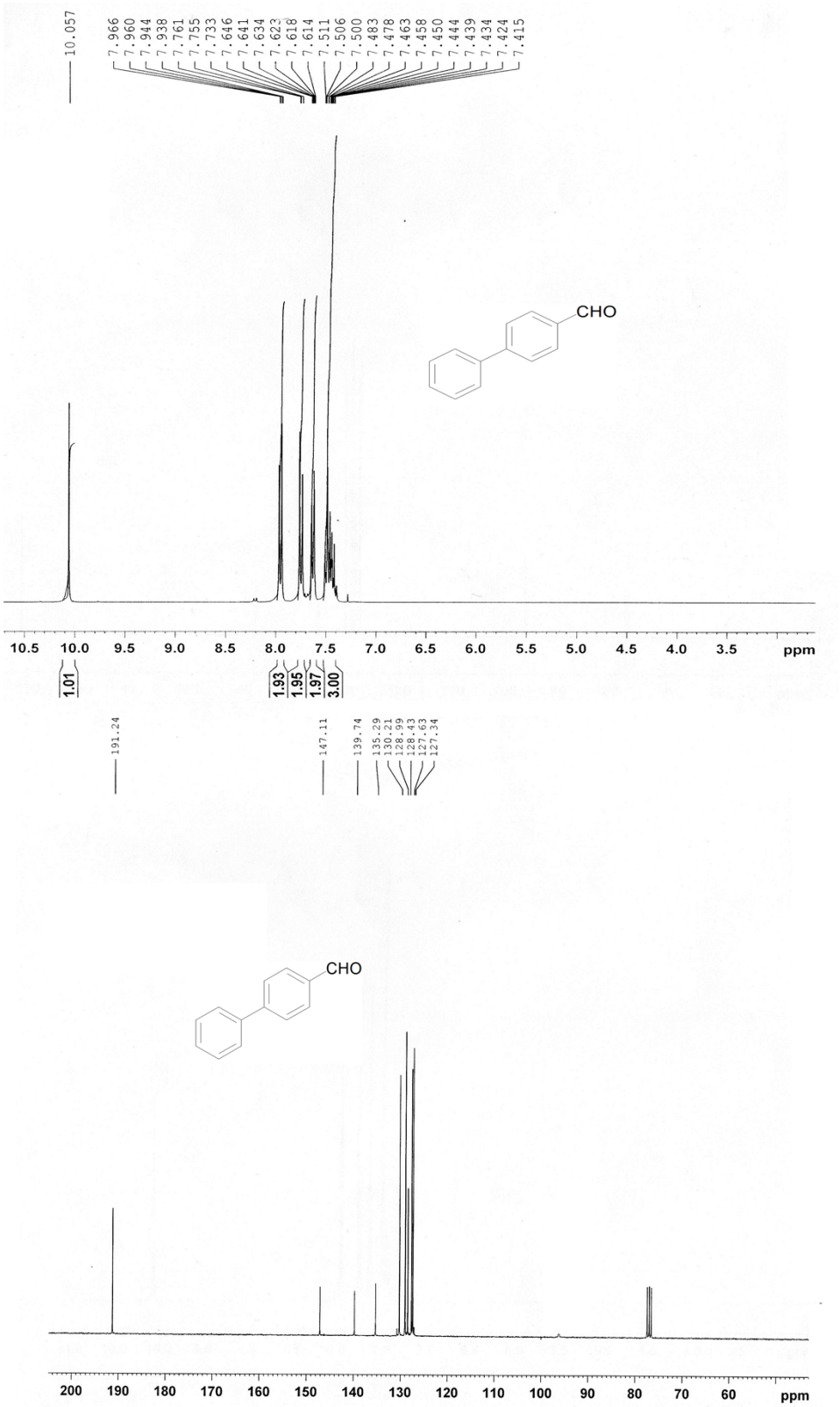




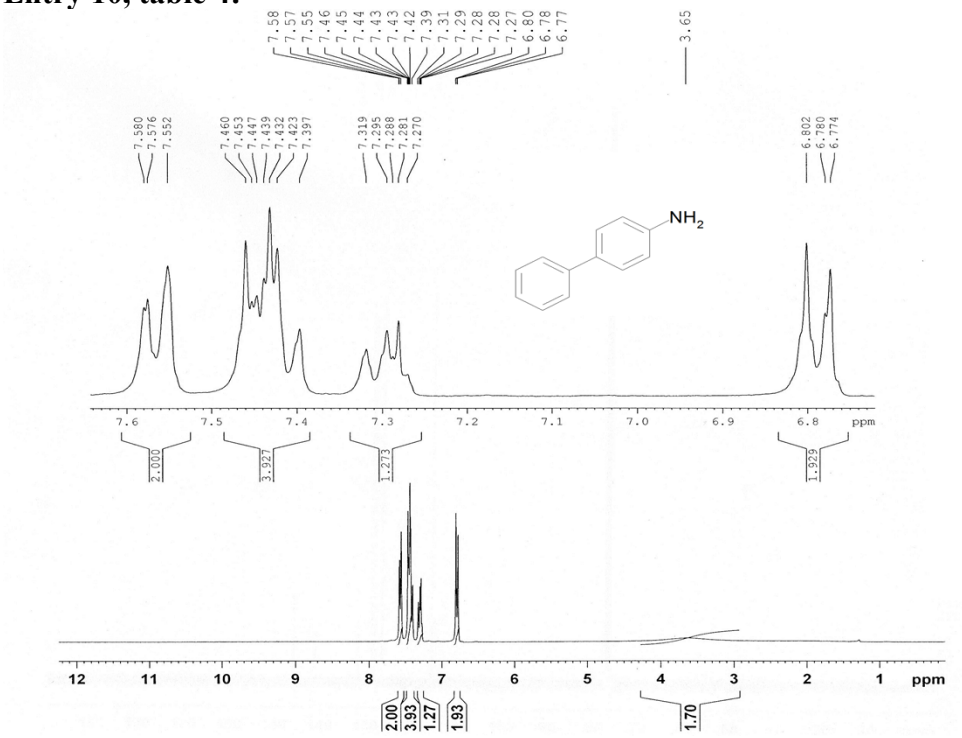


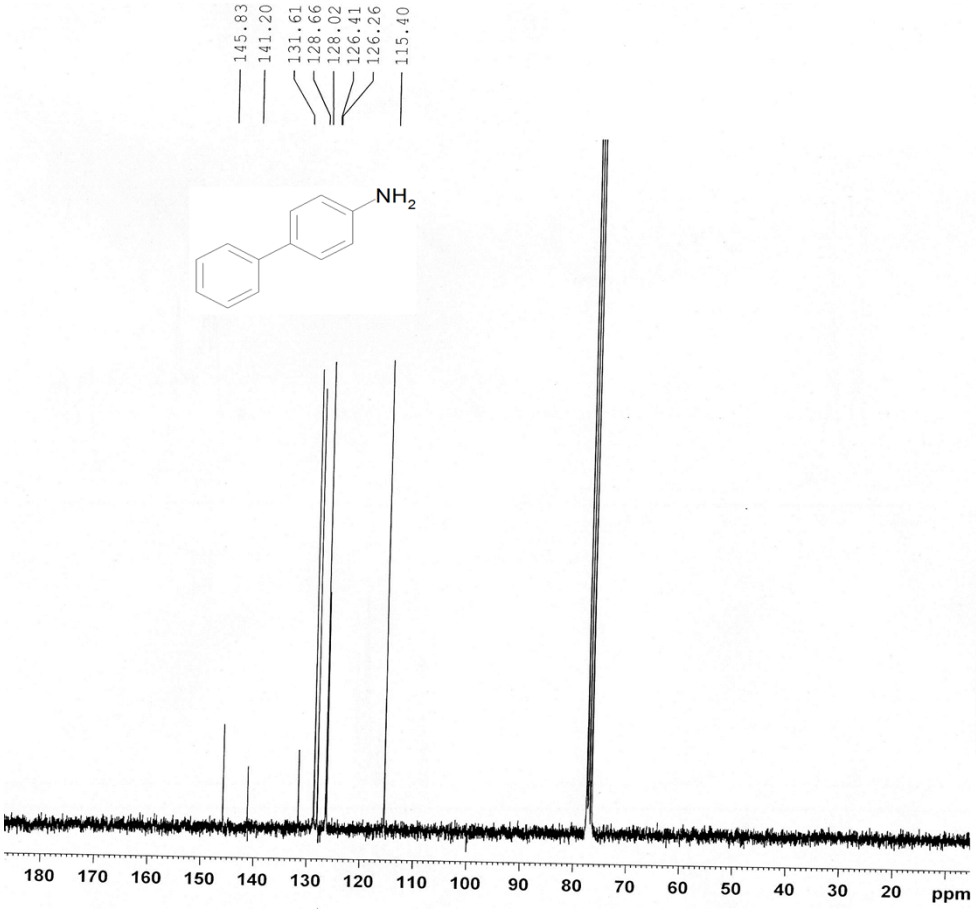


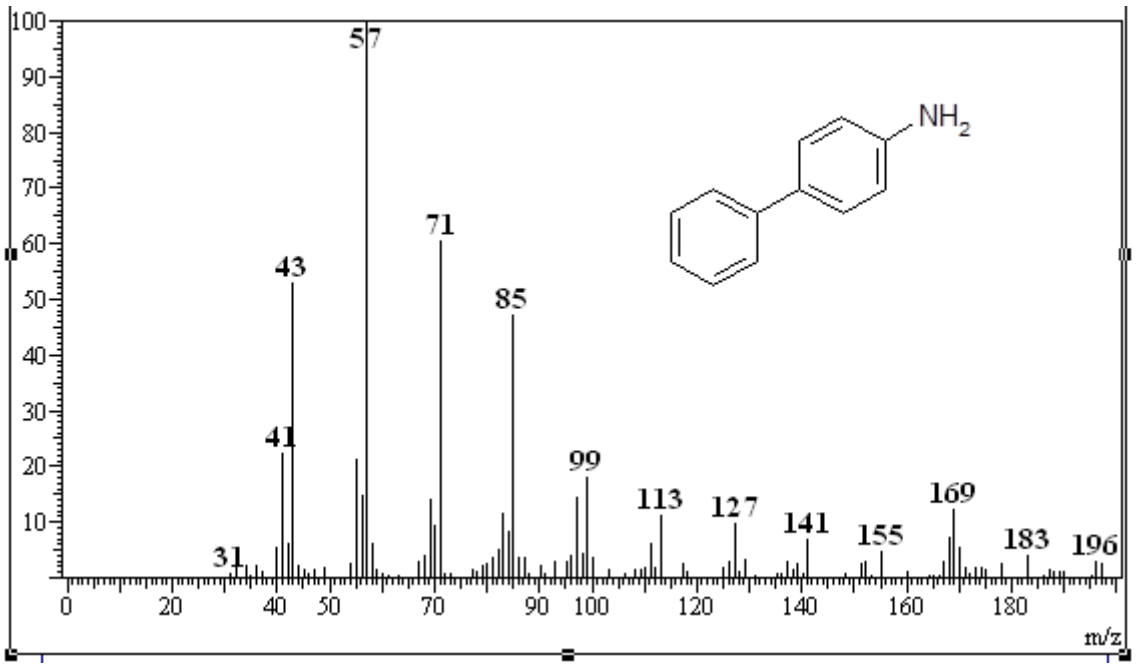
Entry 8, table 4:



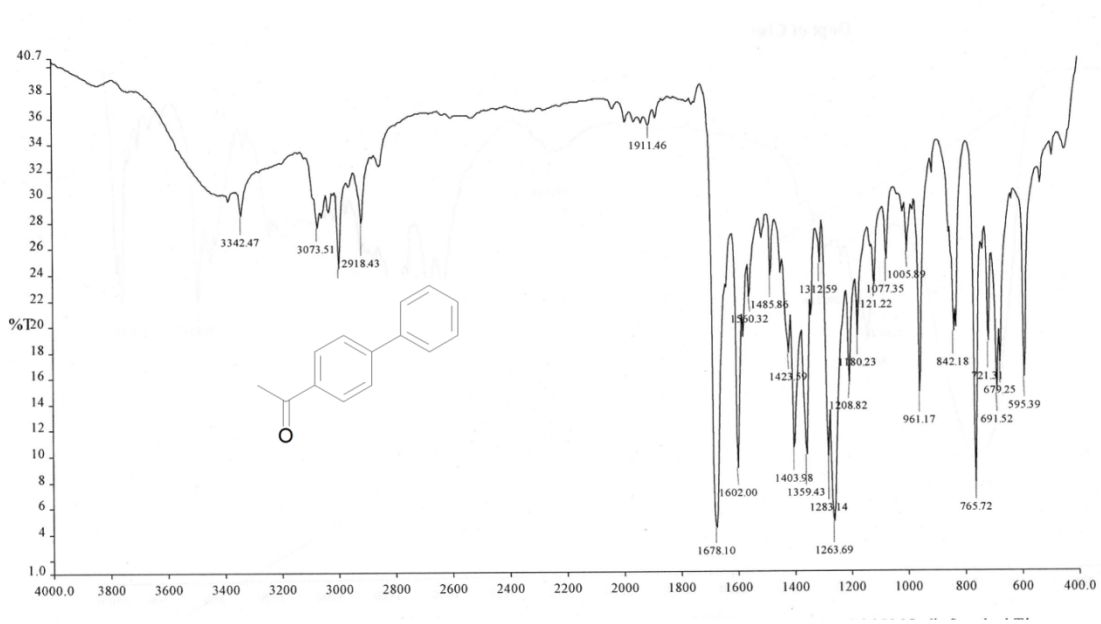
Entry 10, table 4:

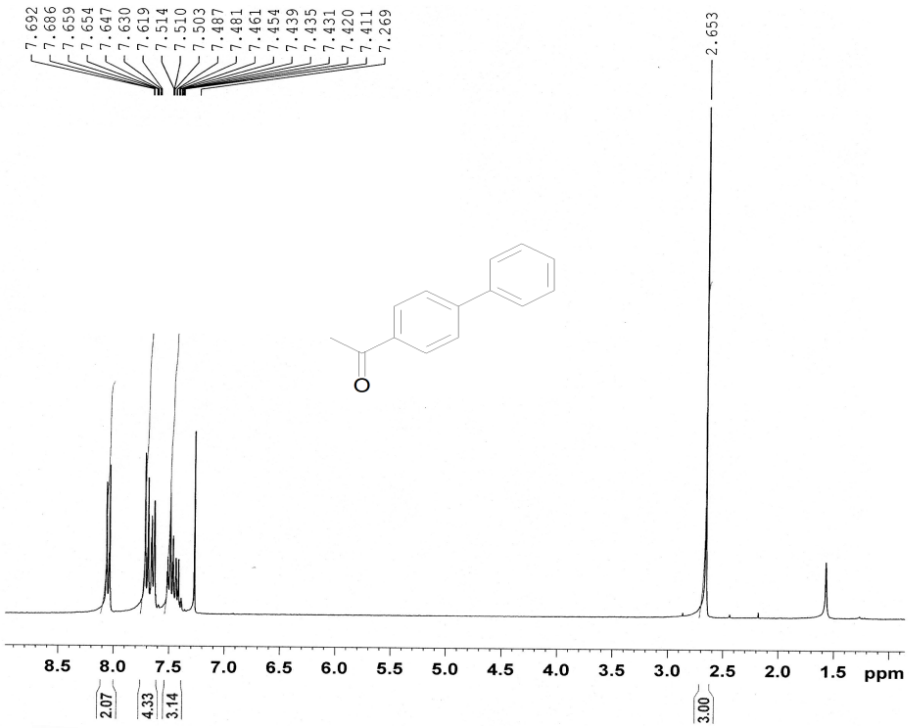


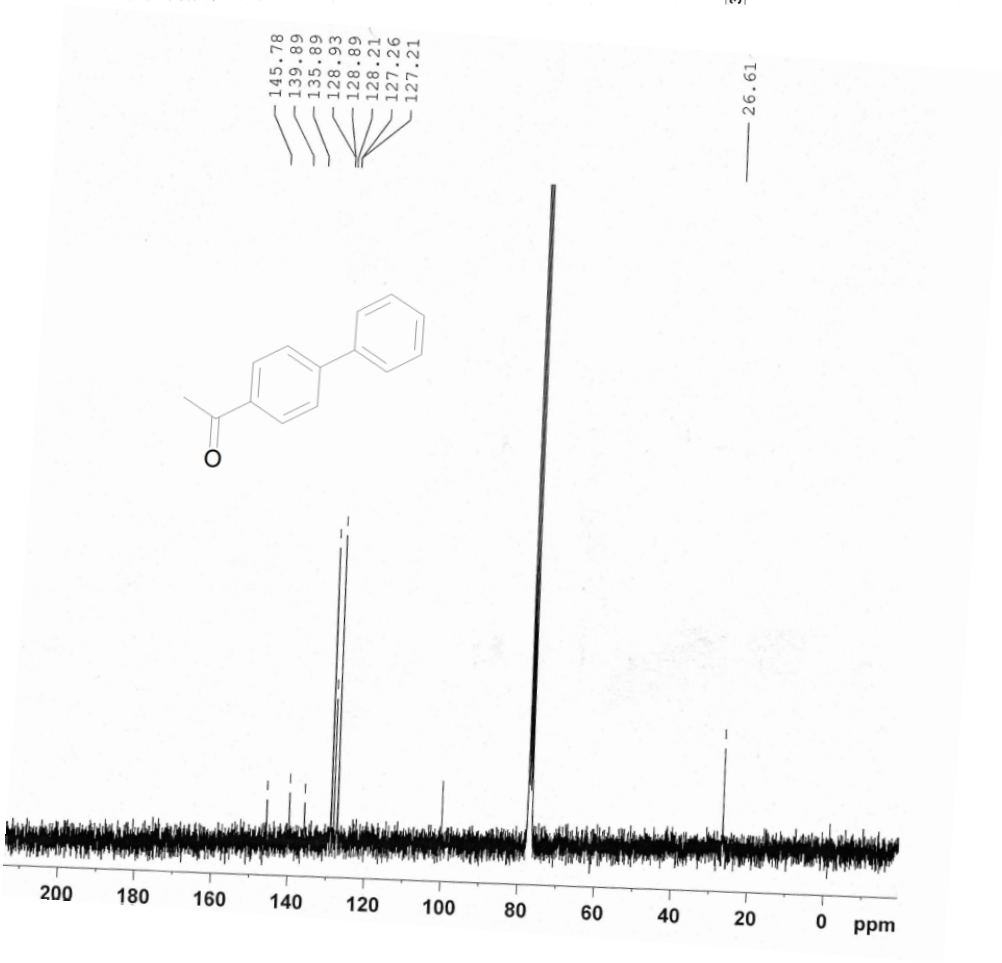




Entry 11, table 4:




7.692
7.686
7.659
7.654
7.647
7.630
7.619
7.514
7.510
7.503
7.487
7.481
7.461
7.454
7.439
7.435
7.431
7.420
7.411
7.269
2.653
O
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 ppm
2.07
4.33
3.14
3.00


145.78
139.89
135.89
128.93
128.89
128.21
127.26
127.21
26.61
O
200 180 160 140 120 100 80 60 40 20 0 ppm

Entry 12, table 4: