# Supporting Information

# Palladium-Catalyzed Carbonylation of Iminoquinones and Aryl Iodides to Access Aryl *p*-Amino Benzoates

Siqi Wang,[+,a] Lingyun Yao,[+,a] Jun Ying,*[a] and Xiao-Feng Wu*[b]

[a] Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, China.

[b] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, Liaoning, China; Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straβe 29a, 18059 Rostock, Germany.

*E-mail: yingjun@zstu.edu.cn

*E-mail: xiao-feng.wu@catalysis.de

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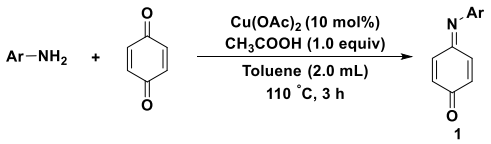
## 1. General experimental information

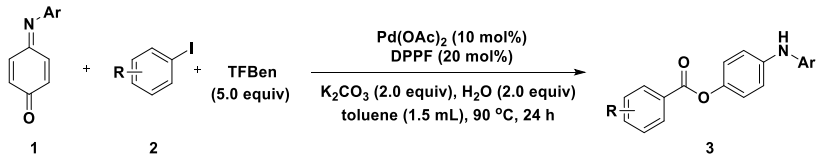
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). $^{1}$H NMR (400 MHz) chemical shifts were reported in ppm ($\delta$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. $^{13}$C NMR (100 MHz) chemical shifts were reported in ppm ($\delta$) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

## 2. General procedure for the synthesis of iminoquinone derivatives (1a-1g)[1]



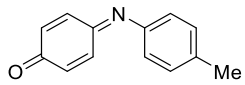

In an oven-dried tube (15 mL) equipped with a stirring bar was charged with $Cu(OAc)_2$ (18.2 mg, 0.1mmol, 10 mol%), *p*-benzoquinone (1.7 mmol, 1.7 equiv) and an aryl amine (1.0 mmol, 1.0 equiv) in the presence of air atmosphere. Then toluene (10.0 mL) and glacial acetic acid (60.1 mg, 1.0 mmol, 1.0 equiv) were added via a syringe and the resulting mixture was heated for 3 h at 110 $^{o}$C with stirring. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 10:1) to afford iminoquinone **1**.

## 3. General procedure for the carbonylative synthesis of aryl *p*-amino benzoates (3aa-3ap, 3ba-3ga)

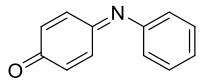



In an oven-dried *In-Ex* tube (15 mL), an iminoquinone **1** (0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPPF (22.2 mg, 0.04 mmol, 20 mol%), $K_2CO_3$ (55.3 mg, 0.4 mmol, 2.0 equiv) were added to the *Ex* tube and TFBen (210.1 mg, 1.0 mmol, 5.0 equiv) was added to the *In* tube. Then the tube was placed under vacuum and refilled with nitrogen three times. An aryl iodide **2** (0.2 mmol, 1.0 equiv), $H_2O$ (7.2 mg, 0.4 mmol, 2.0 equiv) and toluene (1.5 mL) were added into the *Ex* tube via syringe. The tube was sealed and stirred at 90 °C for 24 h. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 10:1) to obtain product **3**.

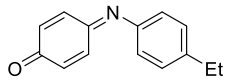
## 4. Characterization data of iminoquinone derivatives (1a-1g)



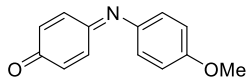
**4-(*p*-tolylimino)cyclohexa-2,5-dien-1-one (1a)[1].** Red solid in 53% yield, mp 63.8 – 65.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.29 (dd, $J$ = 10.0, 2.6 Hz, 1H), 7.22 – 7.20 (m, 2H), 7.13 (dd, $J$ = 10.3, 2.6 Hz, 1H), 6.81 (d, $J$ = 8.2 Hz, 2H), 6.67 (dd, $J$ = 10.0, 2.2 Hz, 1H), 6.52 (dd, $J$ = 10.3, 2.2 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.9, 157.3, 147.1, 142.1, 136.7, 133.4, 132.7, 129.8, 128.4, 121.3, 21.2.



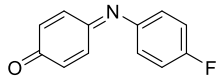
**4-(phenylimino)cyclohexa-2,5-dien-1-one (1b)[1].** Red solid in 52% yield, mp 71.7 – 73.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 (t, $J$ = 7.2 Hz, 2H), 7.32 – 7.19 (m, 2H), 7.07 (d, $J$ = 10.3 Hz, 1H), 6.88 (d, $J$ = 7.9 Hz, 2H), 6.68 (d, $J$ = 10.0 Hz, 1H), 6.53 (d, $J$ = 10.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.7, 157.5, 149.5, 141.9, 136.6, 133.6, 132.9, 129.1, 128.3, 126.3, 120.7.



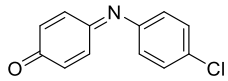
**4-((4-ethylphenyl)imino)cyclohexa-2,5-dien-1-one (1c).** Red oil in 59% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.29 (dd, $J$ = 10.0, 2.6 Hz, 1H), 7.23 (d, $J$ = 8.2 Hz, 2H), 7.13 (dd, $J$ = 10.3, 2.6 Hz, 1H), 6.83 (d, $J$ = 8.2 Hz, 2H), 6.66 (dd, $J$ = 10.0, 2.1 Hz, 1H), 6.51 (dd, $J$ = 10.3, 2.2 Hz, 1H), 2.67 (q, $J$ = 7.6 Hz, 2H), 1.25 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.8, 157.2, 147.3, 143.0, 142.1, 133.3, 132.6, 128.6, 128.4, 121.3, 28.5, 15.6.



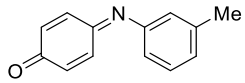
**4-((4-methoxyphenyl)imino)cyclohexa-2,5-dien-1-one (1d)[1].** Red solid in 50% yield, mp 69.9 – 71.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.30 (dd, $J$ = 10.0, 2.7 Hz, 1H), 7.21 (dd, $J$ = 10.3, 2.7 Hz, 1H), 6.98 – 6.91 (m, 4H), 6.68 (dd, $J$ = 10.0, 2.2 Hz, 1H), 6.55 (dd, $J$ = 10.3, 2.2 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.9, 159.1, 156.7, 143.0, 142.3, 133.2, 132.4, 128.4, 123.8, 114.7, 55.7.




**4-((4-fluorophenyl)imino)cyclohexa-2,5-dien-1-one (1e) [1].** Red solid in 46% yield, mp 84.1–87.4 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.29 (dd, $J$ = 10.0, 2.6 Hz, 1H), 7.12 – 7.10 (m, 3H), 6.91 – 6.89 (m, 2H), 6.70 (dd, $J$ = 10.1, 2.2 Hz, 1H), 6.56 (dd, $J$ = 10.3, 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.6, 161.4 (d, $J$ = 246.9 Hz, 1C), 157.8, 145.6 (d, $J$ = 2.9 Hz, 1C), 141.9, 133.8, 133.0, 128.0, 122.7 (d, $J$ = 8.2 Hz, 1C), 116.2 (d, $J$ = 22.8 Hz, 1C).

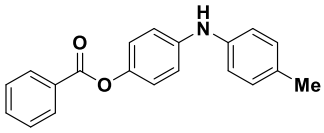



**4-((4-chlorophenyl)imino)cyclohexa-2,5-dien-1-one (1f)[2].** Red solid in 49% yield, mp 76.9 – 78.7 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39 – 7.37 (m, 2H), 7.28 (dd, $J$ = 10.1, 2.6 Hz, 1H), 7.05 (dd, $J$ = 10.3, 2.6 Hz, 1H), 6.85 – 6.83 (m, 2H), 6.69 (dd, $J$ = 10.1, 2.2 Hz, 1H), 6.55 (dd, $J$ = 10.3, 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.3, 157.7, 147.8, 141.6, 133.7, 133.0, 131.8, 129.2, 127.8, 122.0.

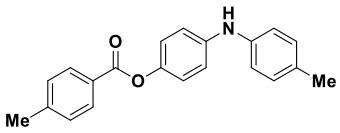



**4-(*m*-tolylimino)cyclohexa-2,5-dien-1-one (1g).** Red oil in 53% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.32 – 7.25 (m, 1H), 7.12 – 7.03 (m, 1H), 6.72 – 6.65 (m, 1H), 6.53 (dd, $J$ = 10.3, 2.2 Hz, 1H), 2.38 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.8, 157.4, 149.6, 142.0, 139.2, 133.5, 132.9, 129.0, 128.5, 127.1, 121.4, 117.8, 21.5.

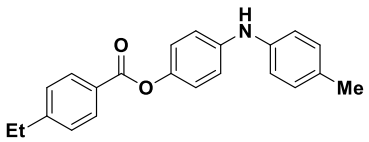
## 5. Characterization data of products (3aa-3ap, 3ba-3ga) and compound 4



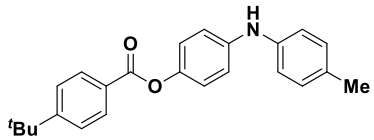
**4-(*p*-tolylamino)phenyl benzoate (3aa).** Yellow solid, 57.6 mg, 95% yield, mp 117.0 – 118.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.23 – 8.19 (m, 2H), 7.66 – 7.61 (m, 1H), 7.51 (t, $J$ = 7.7 Hz, 2H), 7.12 – 7.08 (m, 4H), 7.07 – 7.04 (m, 2H), 7.02 – 6.98 (m, 2H), 5.66 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 144.5, 142.0, 140.6, 133.6, 131.1, 130.3, 130.0, 129.9, 128.7, 122.5, 118.9, 118.0, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{18}NO_2^+$ 304.1332; found: 304.1335.



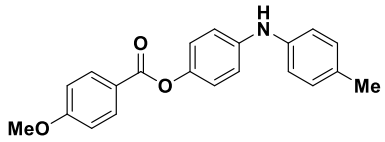
**4-(*p*-tolylamino)phenyl 4-methylbenzoate (3ab).** Yellow solid, 59.6 mg, 94% yield, mp 137.0 – 138.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09 (d, $J$ = 8.1 Hz, 2H), 7.31 (d, $J$ = 8.1 Hz, 2H), 7.11 – 7.03 (m, 6H), 7.00 (d, $J$ = 8.3 Hz, 2H), 5.62 (s, 1H), 2.45 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.8, 144.6, 144.4, 141.8, 140.6, 131.1, 130.3, 130.0, 129.4, 127.1, 122.5, 118.8, 118.0, 21.9, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NO_2^+$ 318.1489; found: 318.1495.



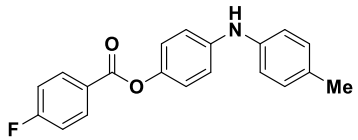
**4-(*p*-tolylamino)phenyl 4-ethylbenzoate (3ac).** Red solid, 62.3 mg, 94% yield, mp 121.6 – 123.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.12 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.2 Hz, 2H), 7.11 – 7.03 (m, 6H), 7.00 (d, $J$ = 8.3 Hz, 2H), 5.63 (s, 1H), 2.75 (q, $J$ = 7.6 Hz, 2H), 2.32 (s, 3H), 1.29 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.8, 150.6, 144.6, 141.8, 140.6, 131.0, 130.4, 130.0, 128.2, 127.3, 122.5, 118.8, 118.0, 29.2, 20.8, 15.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{22}NO_2^+$ 332.1645; found: 332.1653.



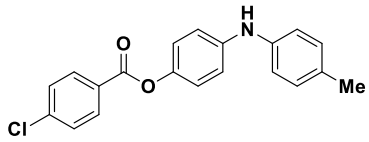

**4-(*p*-tolylamino)phenyl 4-(tert-butyl)benzoate (3ad).** Red oil, 53.9 mg, 75% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.15 – 8.11 (m, 2H), 7.53 (d, $J$ = 8.6 Hz, 2H), 7.11 – 7.03 (m, 6H), 7.02 – 6.98 (m, 2H), 5.62 (s, 1H), 2.31 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 157.4, 144.6, 141.8, 140.7, 131.1, 130.2, 130.0, 127.1, 125.7, 122.5, 118.8, 118.1, 35.3, 31.3, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{26}NO_2^+$ 360.1958; found: 360.1964.



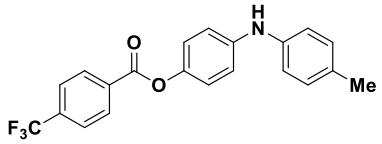

**4-(*p*-tolylamino)phenyl 4-methoxybenzoate (3ae).** Yellow solid, 62.6 mg, 94% yield, mp 131.5 – 133.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.15 (d, $J$ = 8.9 Hz, 2H), 7.11 – 7.02 (m, 6H), 7.01 – 6.96 (m, 4H), 5.61 (s, 1H), 3.90 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) $\delta$ 165.5, 164.0, 144.6, 141.8, 140.7, 132.4, 131.1, 130.0, 122.6, 122.2, 118.8, 118.1, 113.9, 55.7, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NO_3^+$ 334.1438; found: 334.1441.



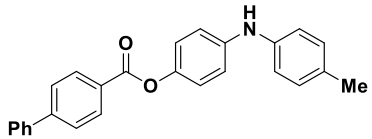

**4-(*p*-tolylamino)phenyl 4-fluorobenzoate (3af).** Yellow solid, 48.8 mg, 76% yield, mp 124.3 – 126.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, $J$ = 8.7, 5.5 Hz, 2H), 7.18 (t, $J$ = 8.6 Hz, 2H), 7.12 – 7.03 (m, 6H), 7.00 (d, $J$ = 8.3 Hz, 2H), 5.63 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 166.2 (d, $J$ = 254.8 Hz, 1C), 164.8, 144.3, 142.1, 140.5, 132.9 (d, $J$ = 9.4 Hz, 1C), 131.2, 130.1, 126.1 (d, $J$ = 2.8 Hz, 1C), 122.4, 119.0, 117.9, 115.9 (d, $J$ = 22.0 Hz, 1C), 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}FNO_2^+$ 322.1238; found: 322.1244.



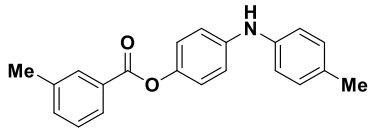
**4-(*p*-tolylamino)phenyl 4-chlorobenzoate (3ag).** Red solid, 43.8 mg, 76% yield, mp 135.0 – 136.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.13 (d, $J$ = 8.5 Hz, 2H), 7.48 (d, $J$ = 8.5 Hz, 2H), 7.12 – 7.03 (m, 6H), 7.00 (d, $J$ = 8.3 Hz, 2H), 5.63 (s, 1H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.9, 144.2, 142.1, 140.4, 140.1, 131.6, 131.3, 130.1, 129.0, 128.3, 122.4, 119.0, 117.8, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}ClNO_2^+$ 338.0942; found: 338.0947.



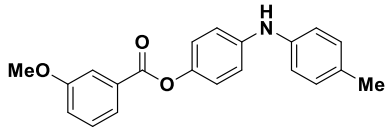
**4-(*p*-tolylamino)phenyl 4-(trifluoromethyl)benzoate (3ah).** Yellow solid, 58.6 mg, 79% yield, mp 136.6 – 139.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.32 (d, $J$ = 8.2 Hz, 2H), 7.78 (d, $J$ = 8.3 Hz, 2H), 7.13 – 7.08 (m, 4H), 7.08 – 7.03 (m, 2H), 7.03 – 6.99 (m, 2H), 5.66 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 164.6, 144.1, 142.3, 140.3, 135.1 (q, $J$ = 32.5 Hz, 1C), 133.2, 131.4, 130.7, 130.1, 125.7 (q, $J$ = 3.7 Hz, 1C), 122.3, 119.2, 117.8, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{17}F_3NO_2^+$ 372.1206; found: 372.1208.



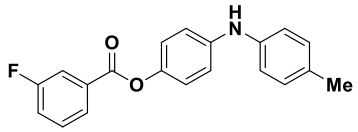
**4-(*p*-tolylamino)phenyl [1,1'-biphenyl]-4-carboxylate (3ai).** Red solid, 63.7 mg, 76% yield, mp 162.6 – 164.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.27 (d, $J$ = 8.3 Hz, 2H), 7.74 (d, $J$ = 8.3 Hz, 2H), 7.67 (d, $J$ = 7.3 Hz, 2H), 7.50 (t, $J$ = 7.5 Hz, 2H), 7.43 (t, $J$ = 7.3 Hz, 1H), 7.14 – 7.09 (m, 4H), 7.06 (d, $J$ = 8.9 Hz, 2H), 7.01 (d, $J$ = 8.3 Hz, 2H), 5.64 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.6, 146.3, 144.5, 142.0, 140.6, 140.1, 131.1, 130.8, 130.1, 129.1, 128.6, 128.4, 127.5, 127.3, 122.5, 118.9, 118.0, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{22}NO_2^+$ 380.1645; found: 380.1643.



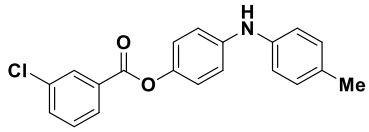

**4-(*p*-tolylamino)phenyl 3-methylbenzoate (3aj).** Yellow solid, 58.3 mg, 92% yield, mp 86.9 – 88.5 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 8.6 Hz, 2H), 7.46 – 7.36 (m, 2H), 7.12 – 7.03 (m, 6H), 7.00 (d, $J$ = 8.3 Hz, 2H), 5.62 (s, 1H), 2.45 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.9, 144.5, 141.9, 140.6, 138.5, 134.4, 131.1, 130.8, 130.1, 129.8, 128.6, 127.4, 122.5, 118.9, 118.0, 21.4, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NO_2^+$ 318.1489; found: 318.1491.



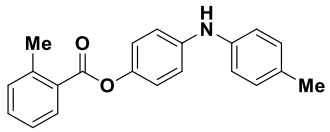

**4-(*p*-tolylamino)phenyl 3-methoxybenzoate (3ak).** Yellow solid, 59.3 mg, 89% yield, mp 94.5 – 96.3 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 7.7 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.42 (t, $J$ = 8.0 Hz, 1H), 7.18 (dd, $J$ = 8.2, 2.0 Hz, 1H), 7.12 – 7.03 (m, 6H), 7.01 (d, $J$ = 8.4 Hz, 2H), 5.65 (s, 1H), 3.89 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.6, 159.8, 144.4, 142.0, 140.5, 131.1, 130.0, 129.7, 122.7, 122.5, 120.2 118.9, 117.9, 114.6, 55.6, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NO_3^+$ 334.1438; found: 334.1442.



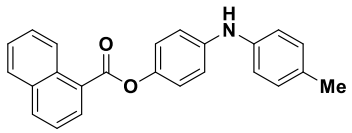

**4-(*p*-tolylamino)phenyl 3-fluorobenzoate (3al).** Yellow solid, 53.9 mg, 84% yield, mp 103.2 – 106.3 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 7.8 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.49 (td, $J$ = 8.0, 5.6 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.13 – 6.99 (m, 8H), 5.65 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.6 (d, $J$ = 2.9 Hz, 1C), 162.7 (d, $J$ = 247.4 Hz, 1C), 144.2, 142.2, 140.4, 132.0 (d, $J$ = 7.5 Hz, 1C), 131.3, 130.3 (d, $J$ = 7.8 Hz, 1C), 130.1, 126.0 (d, $J$ = 2.9 Hz, 1C), 122.3, 120.7 (d, $J$ = 21.3 Hz, 1C), 119.0, 117.8, 117.1 (d, $J$ = 23.2 Hz, 1C), 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}FNO_2^+$ 322.1238; found: 322.1241.



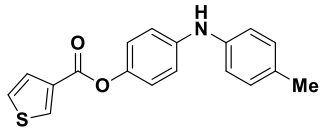

**4-(*p*-tolylamino)phenyl 3-chlorobenzoate (3am).** Yellow solid, 58.1 mg, 86% yield, mp 108.4 – 110.5 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 (s, 1H), 8.09 (d, $J$ = 7.8 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.46 (t, $J$ = 7.9 Hz, 1H), 7.13 – 6.99 (m, 8H), 5.65 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 144.1, 142.2, 140.4, 134.8, 133.6, 131.6, 131.3, 130.3, 130.1, 130.0, 123.0, 128.4, 122.3, 119.0, 117.8, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}ClNO_2^+$ 338.0942; found: 338.0944.



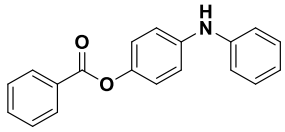

**4-(*p*-tolylamino)phenyl 2-methylbenzoate (3an).** Red oil, 60.3 mg, 95% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (d, $J$ = 7.3 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.33 (t, $J$ = 7.4 Hz, 2H), 7.12 – 7.04 (m, 6H), 7.01 (d, $J$ = 8.4 Hz, 2H), 5.64 (s, 1H), 2.69 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.5, 144.4, 141.9, 141.3, 140.6, 132.7, 132.0, 131.2 131.0, 130.0, 128.9, 126.0, 122.6, 118.8, 118.1, 22.1, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NO_2^+$ 318.1489; found: 304.1492.



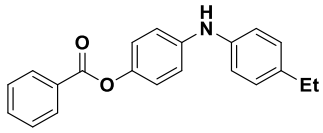

**4-(*p*-tolylamino)phenyl 1-naphthoate (3ao).** Red solid, 50.1 mg, 71% yield, mp 105.7 – 107.6 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.05 (d, $J$ = 8.6 Hz, 1H), 8.46 (d, $J$ = 6.7 Hz, 1H), 8.11 (d, $J$ = 8.2 Hz, 1H), 7.93 (d, $J$ = 8.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.58 (t, $J$ = 7.8 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.12 – 7.08 (m, 4H), 7.03 (d, $J$ = 8.3 Hz, 2H), 5.66 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.4, 144.5, 142.0, 140.6, 134.3, 134.1, 131.8, 131.23, 131.16, 130.1, 128.8, 128.2, 126.5, 126.3, 126.0, 124.7, 122.7, 118.9, 118.1, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{20}NO_2^+$ 354.1489; found: 354.1490.



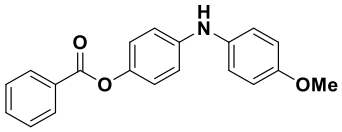

**4-(*p*-tolylamino)phenyl thiophene-3-carboxylate (3ap).** Yellow solid, 50.7 mg, 82% yield, mp 104.1 – 106.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.05 (d, $J$ = 8.6 Hz, 1H), 8.46 (d, $J$ = 6.7 Hz, 1H), 8.11 (d, $J$ = 8.2 Hz, 1H), 7.93 (d, $J$ = 8.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.58 (t, $J$ = 7.8 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.12 – 7.08 (m, 4H), 7.03 (d, $J$ = 8.3 Hz, 2H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.4, 144.5, 142.0, 140.6, 134.3, 134.1, 131.8, 131.23, 131.16, 130.1, 128.8, 128.2, 126.5, 126.3, 126.0, 124.7, 122.7, 118.9, 118.1, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO_2S^+$ 310.0896; found: 310.0896.



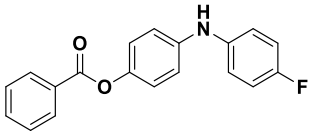

**4-(phenylamino)phenyl benzoate (3ba)[3].** Yellow solid, 46.8 mg, 81% yield, mp 96.1 – 98.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 – 8.19 (m, 2H), 7.65 – 7.61 (m, 1H), 7.53 – 7.48 (m, 2H), 7.29 – 7.25 (m, 2H), 7.11 (s, 4H), 7.06 (dd, $J$ = 8.5, 1.0 Hz, 2H), 6.93 (t, $J$ = 7.3 Hz, 1H), 5.72 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 145.0, 143.4, 141.1, 133.6, 130.3, 129.8, 129.5, 128.7, 122.6, 121.2, 119.0, 117.8.



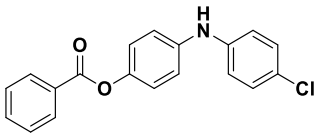

**4-((4-ethylphenyl)amino)phenyl benzoate (3ca).** Red solid, 57.1 mg, 90% yield, mp 129.7 – 131.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.23 – 8.21 (m, 2H), 7.66 – 7.62 (m, 1H), 7.52 (t, $J$ = 7.7 Hz, 2H), 7.14 – 7.01 (m, 8H), 5.66 (s, 1H), 2.62 (q, $J$ = 7.6 Hz, 2H), 1.25 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 144.5, 141.9, 140.8, 137.6, 133.6, 130.3, 129.9, 128.8, 128.7, 122.5, 118.8, 118.0, 28.3, 15.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NO_2^+$ 318.1489; found: 318.1491.



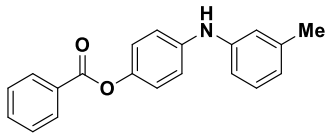

**4-((4-methoxyphenyl)amino)phenyl benzoate (3da).** Yellow solid, 54.3 mg, 85% yield, mp 141.8 – 142.5 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 – 8.19 (m, 2H), 7.63 (t, $J$ = 7.4 Hz, 1H), 7.51 (t, $J$ = 7.7 Hz, 2H), 7.10 – 7.04 (m, 4H), 6.96 – 6.92 (m, 2H), 6.89 – 6.85 (m, 2H), 5.51 (s, 1H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.8, 155.5, 143.9, 143.2, 136.0, 133.6, 130.3, 129.9, 128.7, 122.5, 122.2, 116.6, 114.9, 55.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{18}NO_3^+$ 320.1281; found: 320.1283.



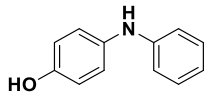

**4-((4-fluorophenyl)amino)phenyl benzoate (3ea).** White solid, 47.3 mg, 77% yield, mp 102.7 – 104.6 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.22 – 8.20 (m, 2H), 7.64 (t, $J$ = 7.4 Hz, 1H), 7.52 (t, $J$ = 7.7 Hz, 2H), 7.12 – 7.08 (m, 2H), 7.06 – 6.96 (m, 6H), 5.66 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.8, 158.2 (d, $J$ = 240.1 Hz, 1C), 144.6, 141.9, 139.2 (d, $J$ = 2.2 Hz, 1C), 133.6, 130.3, 129.8, 128.7, 122.6, 120.5 (d, $J$ = 7.8 Hz, 1C), 117.9, 116.1 (d, $J$ = 22.5 Hz, 1C). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{15}FNO_2^+$ 308.1081; found: 308.1084.




**4-((4-chlorophenyl)amino)phenyl benzoate (3fa)[4].** White solid, 49.1 mg, 76% yield, mp 106.8 – 108.1 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 – 8.18 (m, 2H), 7.65 (t, $J$ = 7.4 Hz, 1H), 7.52 (t, $J$ = 7.7 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.05 (m, 4H), 7.00 – 6.95 (m, 2H), 5.74 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 145.3, 142.1, 140.6, 133.7, 130.3, 129.7, 129.4, 128.7, 125.7, 122.7, 119.3, 118.8.




**4-(*m*-tolylamino)phenyl benzoate (3ga).** Red solid, 55.7 mg, 92% yield, mp 74.5 – 76.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.23 – 8.21 (m, 2H), 7.67 – 7.63 (m, 1H), 7.52 (t, $J$ = 7.7 Hz, 2H), 7.17 (t, $J$ = 7.6 Hz, 1H), 7.12 (s, 4H), 6.89 (d, $J$ = 7.9 Hz, 2H), 6.77 (d, $J$ = 7.4 Hz, 1H), 5.70 (s, 1H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 165.7, 144.9, 143.3, 141.2, 139.4, 133.6, 130.3, 129.8, 129.4, 128.7, 122.5, 122.1, 119.0, 118.4, 114.9, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{18}NO_2^+$ 304.1332; found: 304.1338.




**4-(phenylamino)phenol (4).[5]** Yellow soild, 55.7 mg, 56% yield, mp 64.2 – 66.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.03 (d, $J$ = 8.7 Hz, 2H), 6.91 (d, $J$ = 7.8 Hz, 2H), 6.85 (t, $J$ = 7.3 Hz, 1H), 6.82 – 6.77 (m, 2H), 4.93 (s, 1H),; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 151.2, 145.3, 136.0, 129.5, 122.6, 119.8, 116.3, 115.9.

## 6. References

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(4) Bradfield, A. E.; Cooper, L. H. N.; Orton, K. J. P. Halogenation of *p*-hydroxydiphenylamine. *J. Chem. Soc.* **1927**, 2854-2864.

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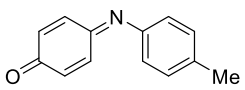
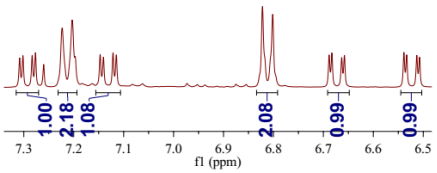
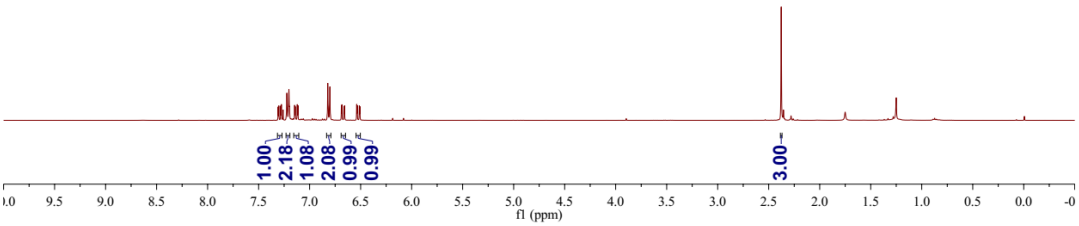
## 7. $^{1}H$, $^{13}C$ NMR spectra of iminoquinone derivatives (1a-1g)

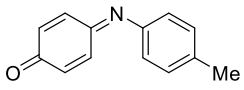

**1a**

**400 MHz in $CDCl_3$**



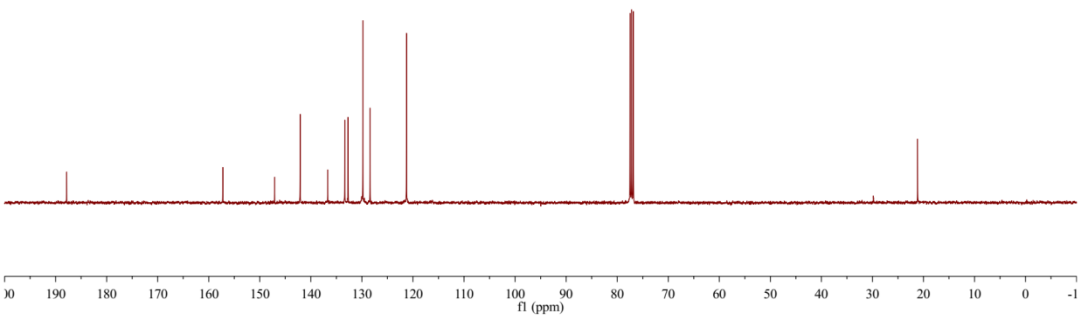



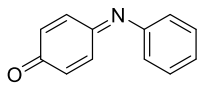




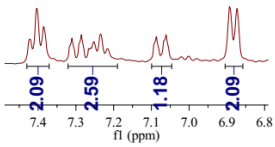

**1a**

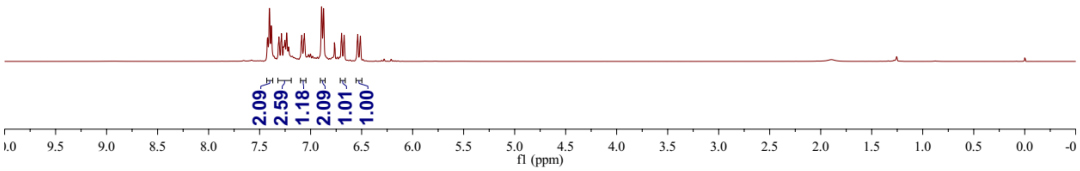
**100 MHz in $CDCl_3$**



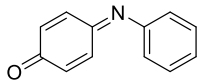




**1b**
**400 MHz in $CDCl_3$**

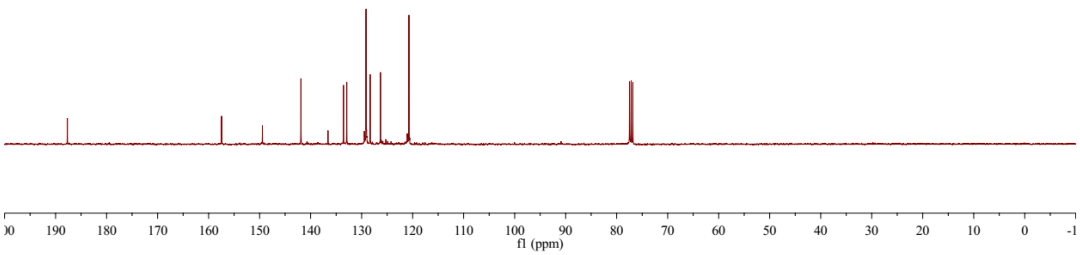


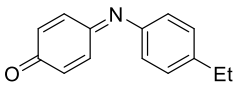







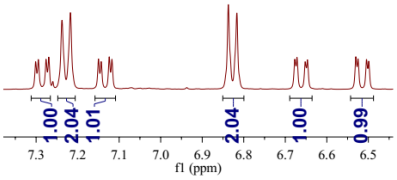

**1b**
**100 MHz in $CDCl_3$**

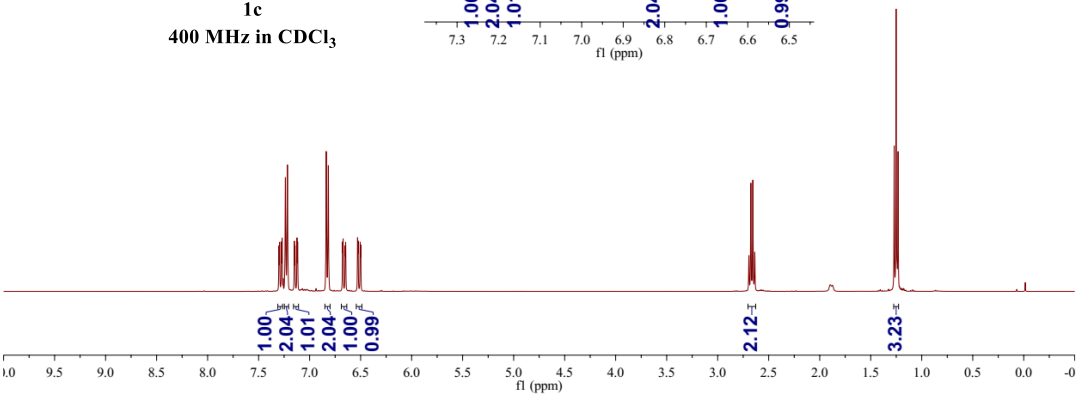


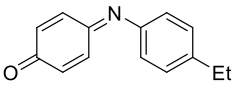

**1c**

**400 MHz in $CDCl_3$**



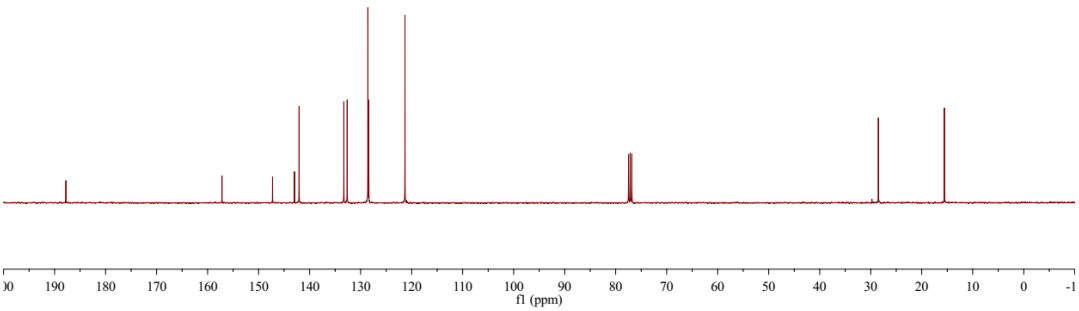



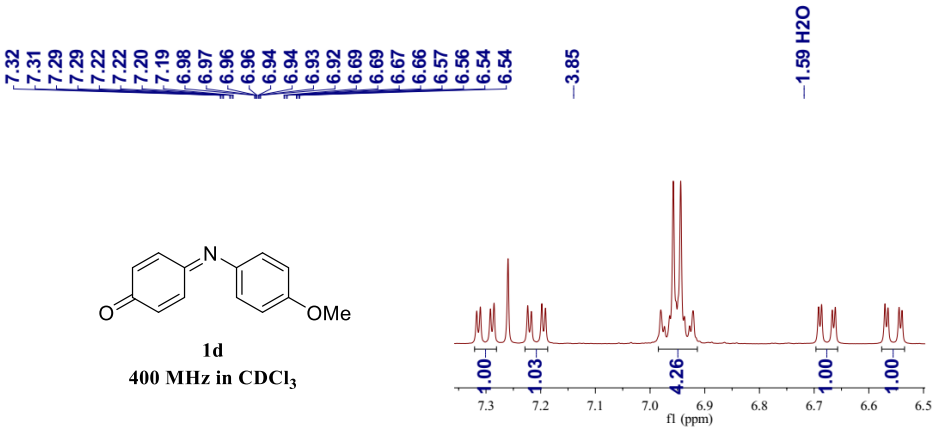


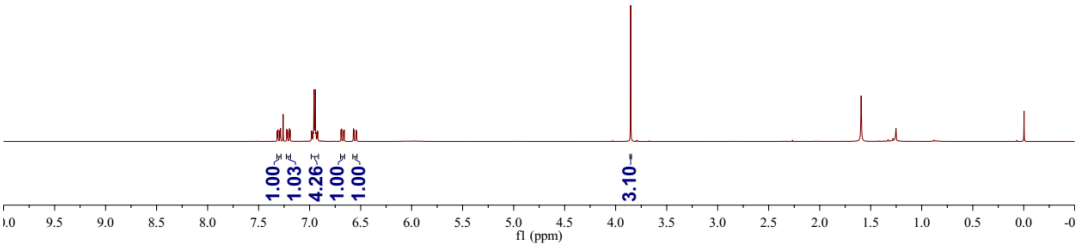


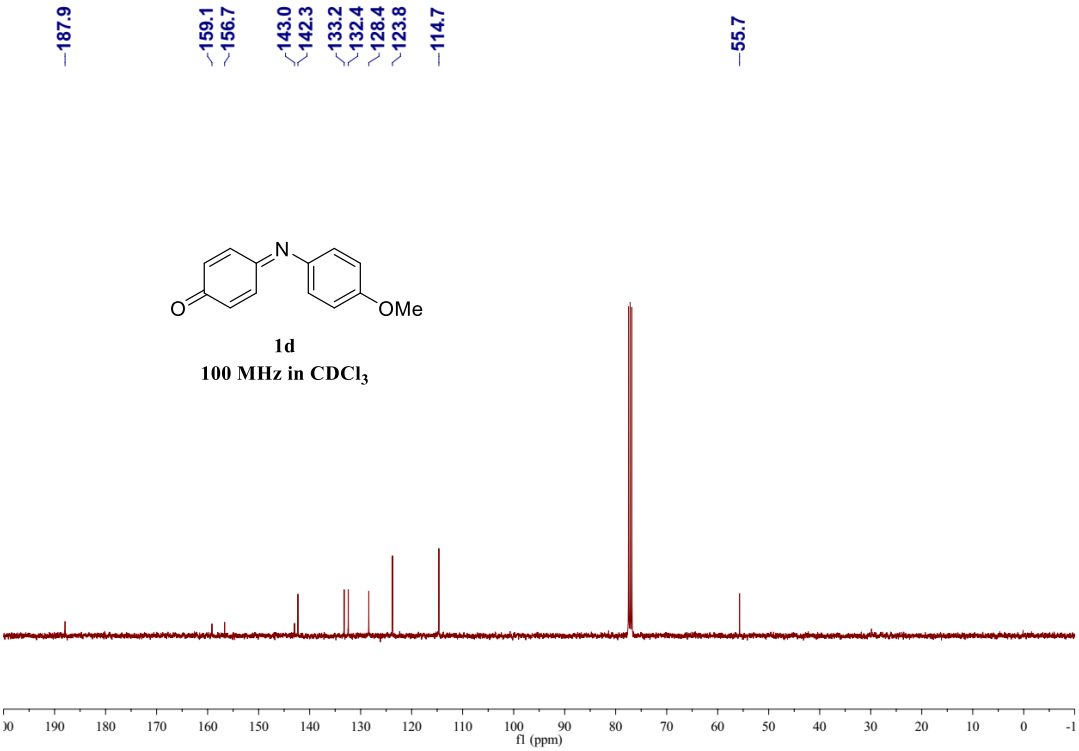

**1c**

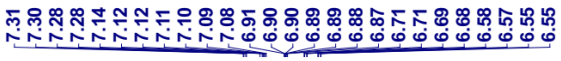
**100 MHz in $CDCl_3$**

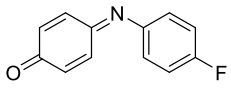



7.32
7.31
7.29
7.29
7.22
7.22
7.20
7.19
6.98
6.97
6.96
6.96
6.94
6.94
6.93
6.92
6.69
6.69
6.67
6.66
6.57
6.56
6.54
6.54
3.85
1.59 H2O
N
O
OMe
1d
400 MHz in CDCl3
1.00
1.03
4.26
1.00
1.00
f1 (ppm)


1.00
1.03
4.26
1.00
1.00
3.10
f1 (ppm)

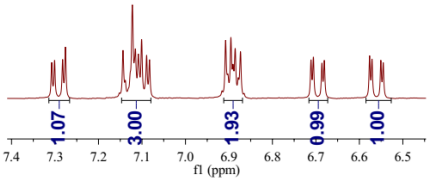

187.9
159.1
156.7
143.0
142.3
133.2
132.4
128.4
123.8
114.7
55.7
N
O
OMe
1d
100 MHz in CDCl3
f1 (ppm)

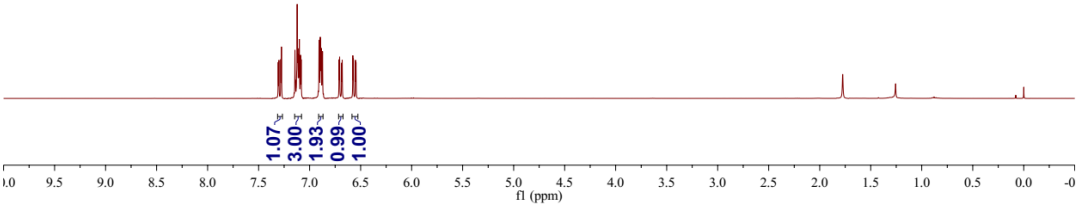


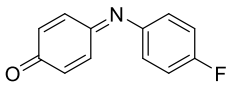

**1e**

**400 MHz in $CDCl_3$**



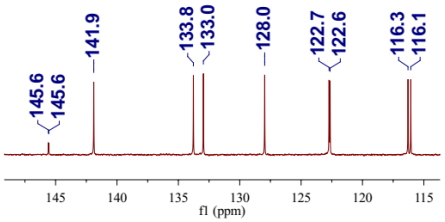



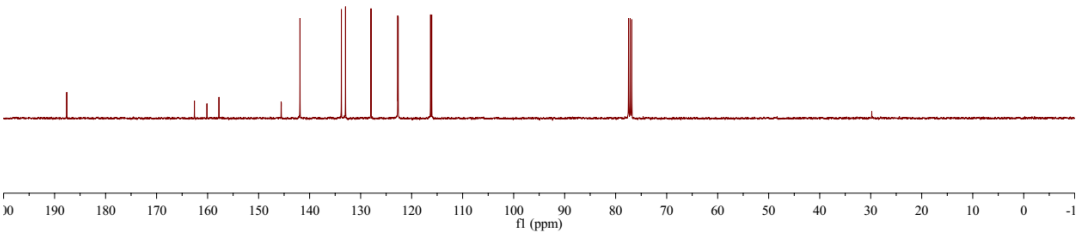


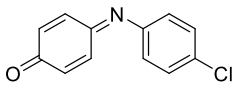



**1e**

**100 MHz in $CDCl_3$**

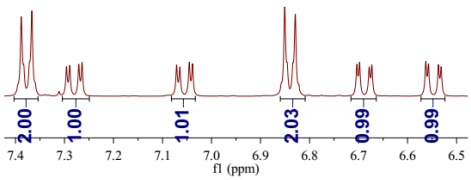


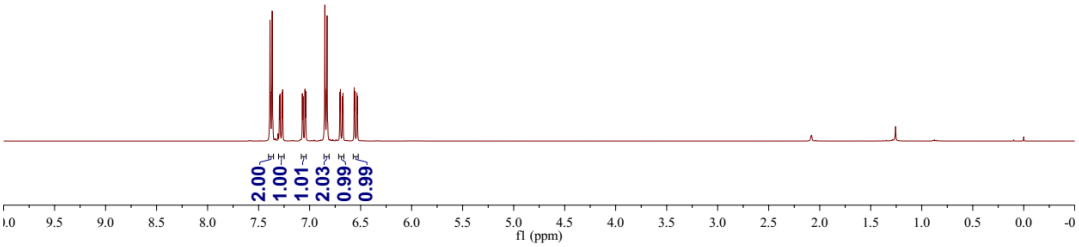



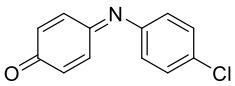

**1f**

**400 MHz in $CDCl_3$**



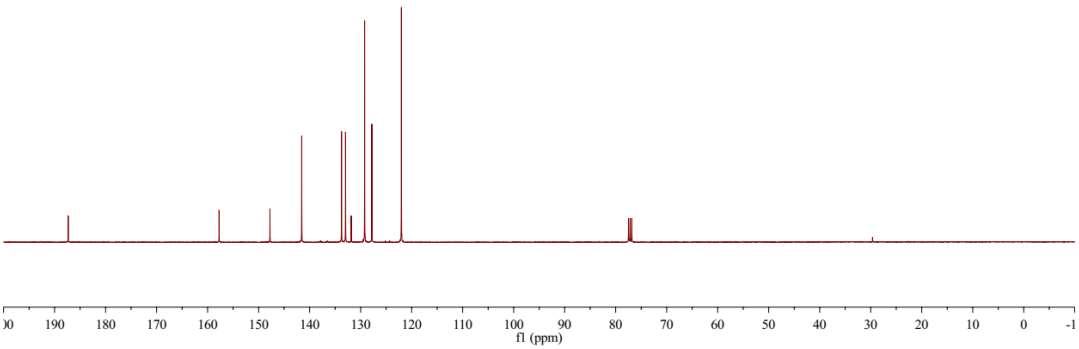



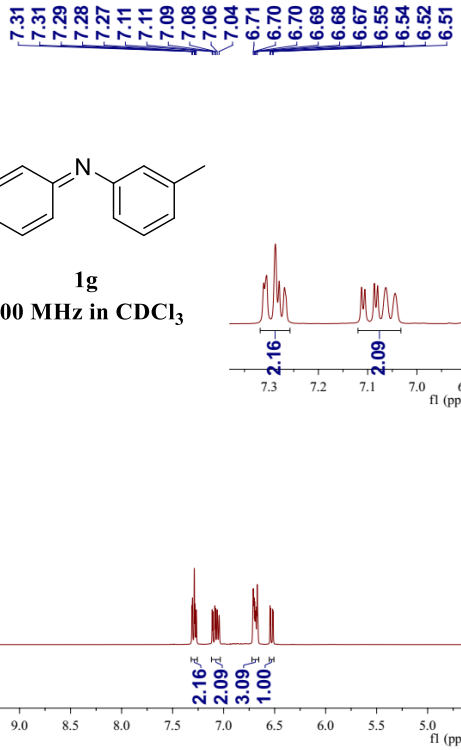





**1f**

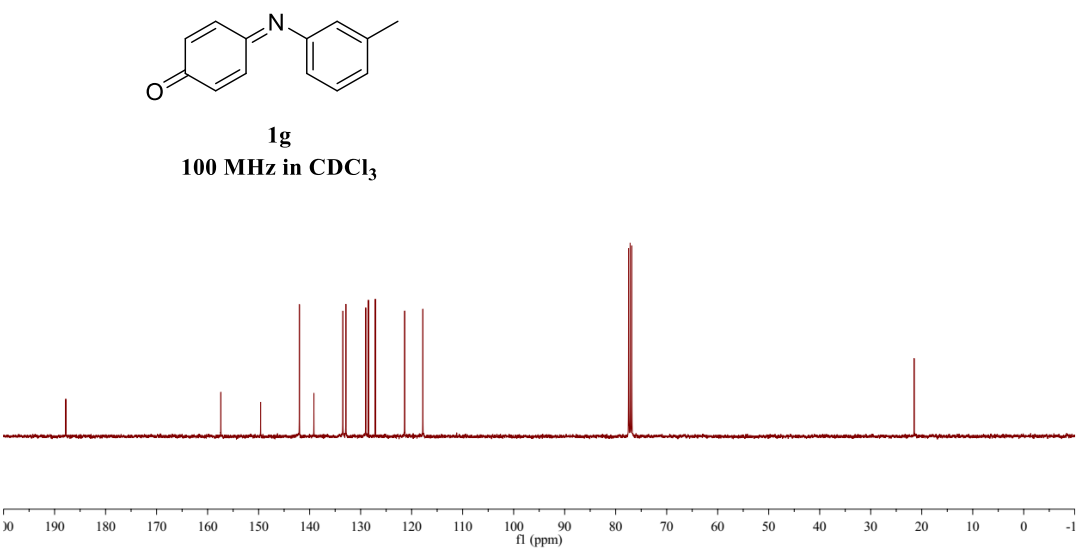
**100 MHz in $CDCl_3$**






**1g**

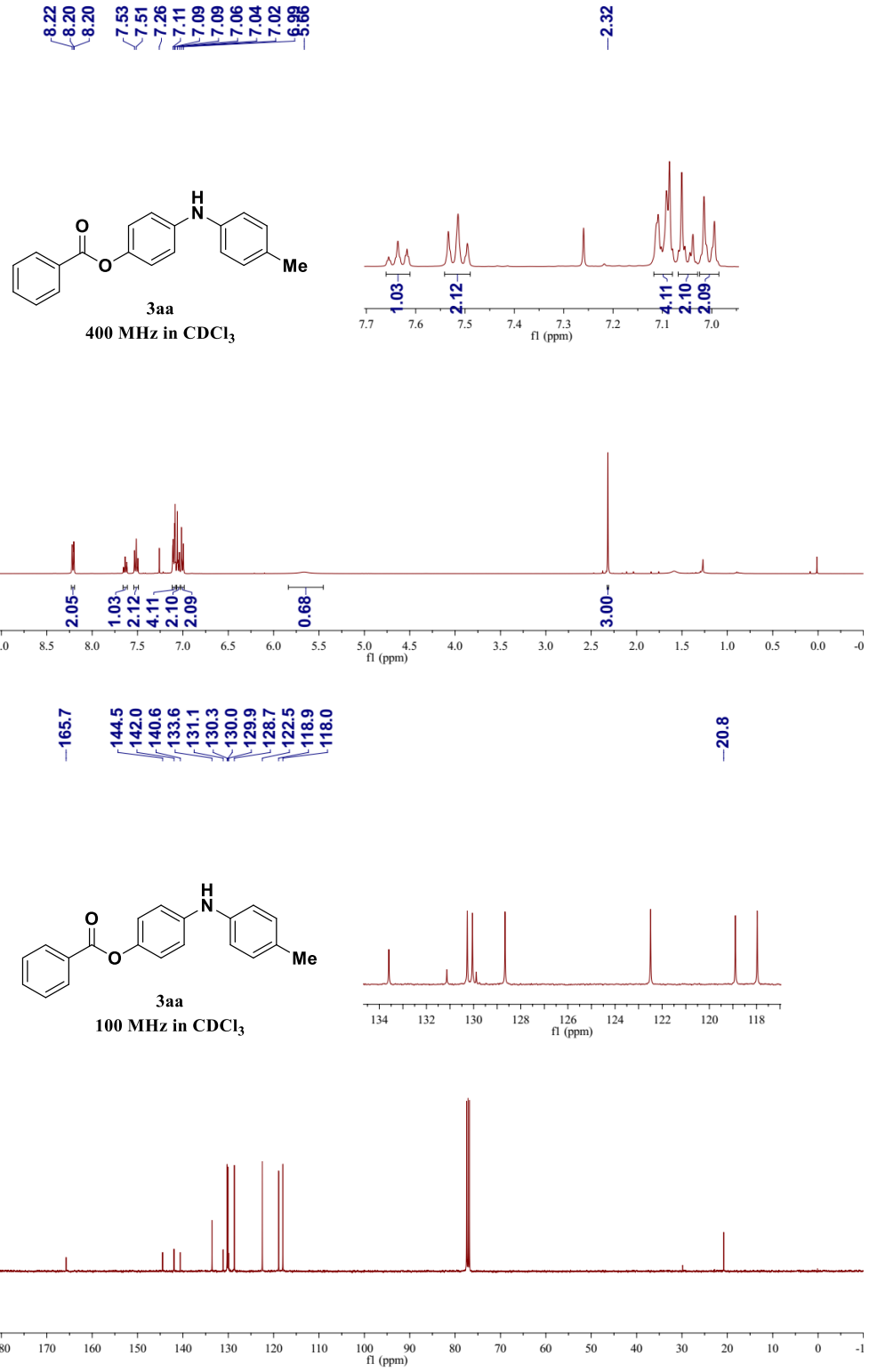
**400 MHz in $CDCl_3$**

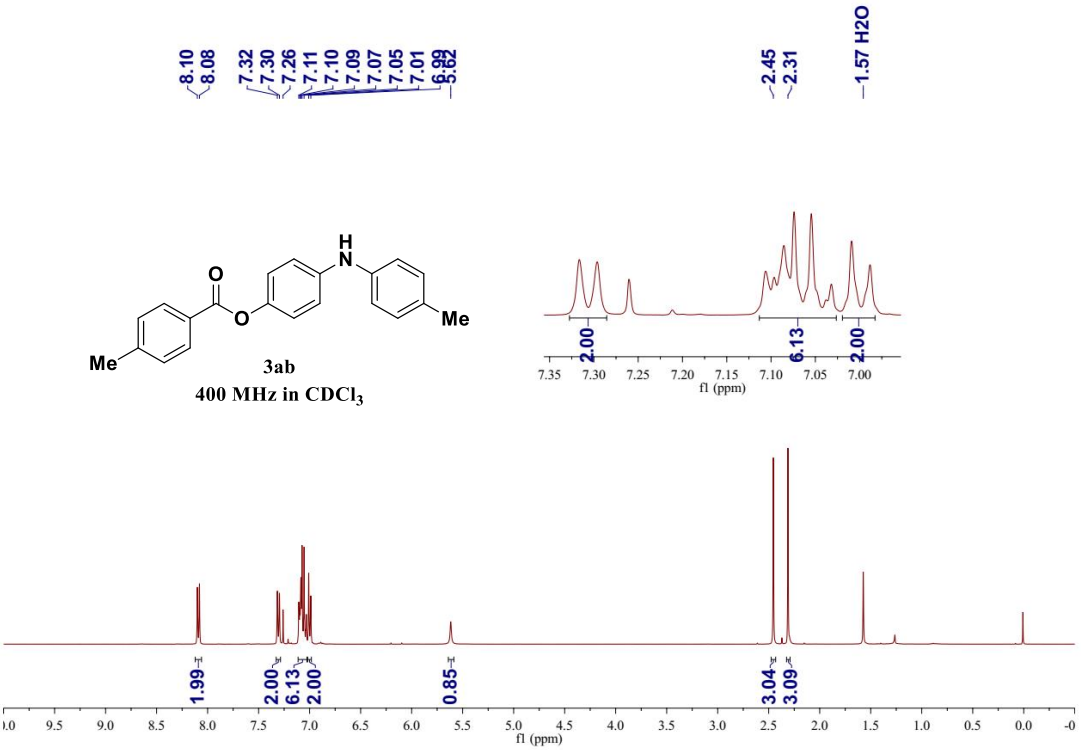


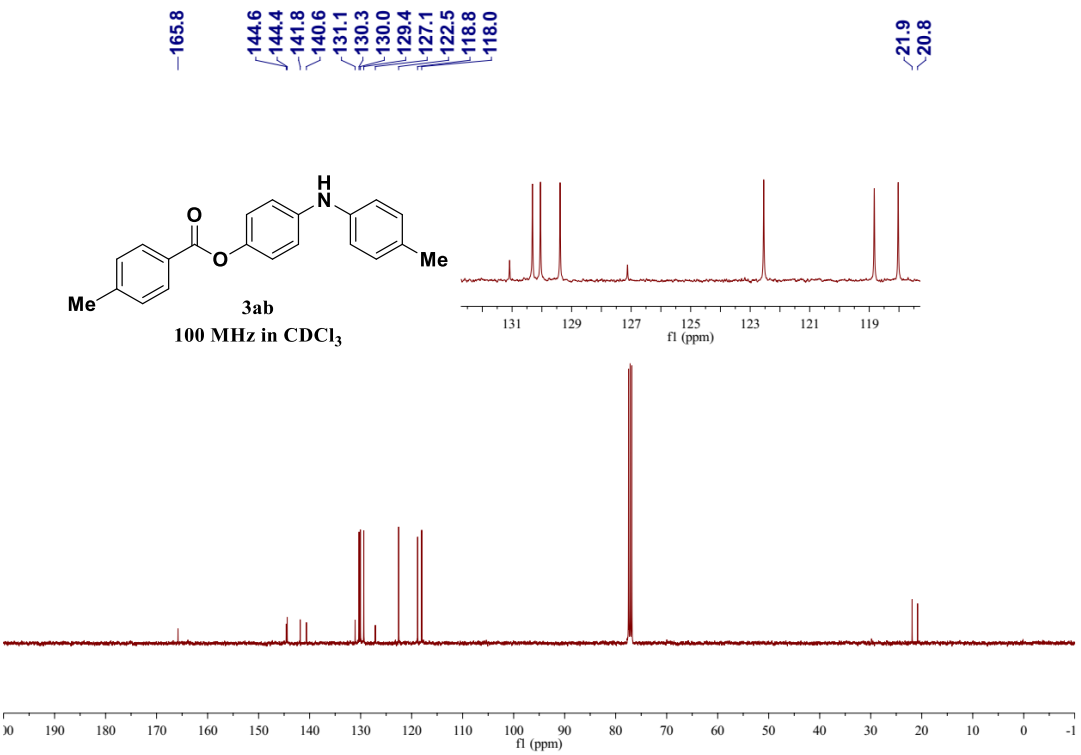

**1g**

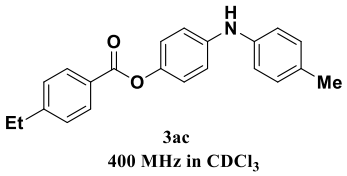
**100 MHz in $CDCl_3$**

## 8. $^{1}H$, $^{13}C$ NMR products (3aa-3ap, 3ba-3ga) and compound 4

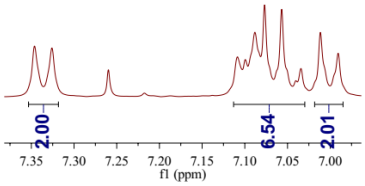


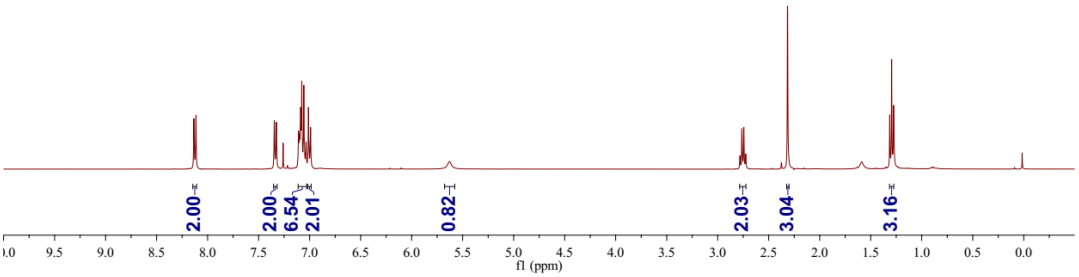

8.10
8.08
7.32
7.30
7.26
7.11
7.10
7.09
7.07
7.05
7.01
6.99
6.82
2.45
2.31
1.57 H2O
H
N
O
O
Me
Me
3ab
400 MHz in CDCl3
2.00
6.13
2.00
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
1.99
2.00
6.13
2.00
0.85
3.04
3.09
f1 (ppm)

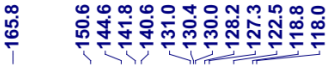

165.8
144.6
144.4
141.8
140.6
131.1
130.3
130.0
129.4
127.1
122.5
118.8
118.0
21.9
20.8
H
N
O
O
Me
Me
3ab
100 MHz in CDCl3
131 129 127 125 123 121 119
f1 (ppm)
f1 (ppm)

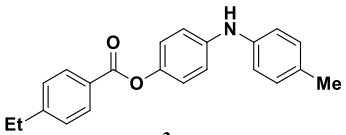




3ac
400 MHz in $CDCl_3$

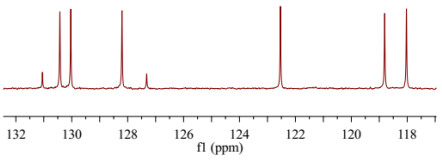


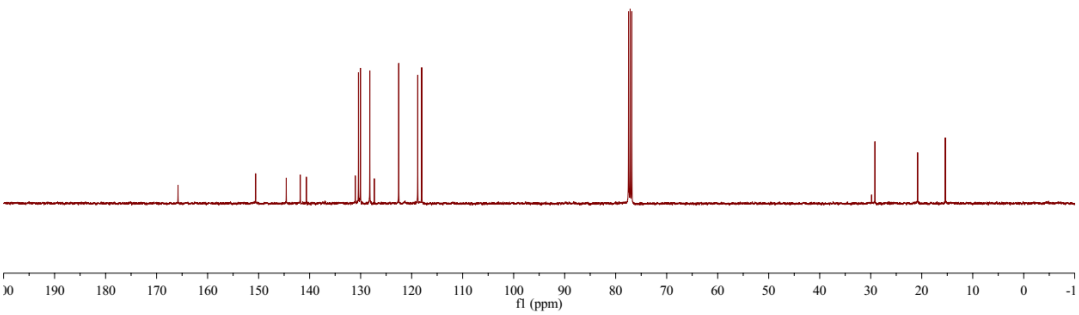



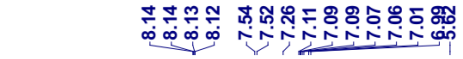



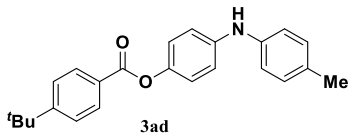




3ac
100 MHz in $CDCl_3$



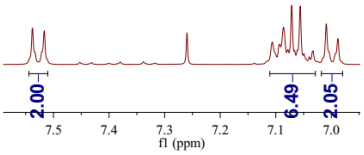



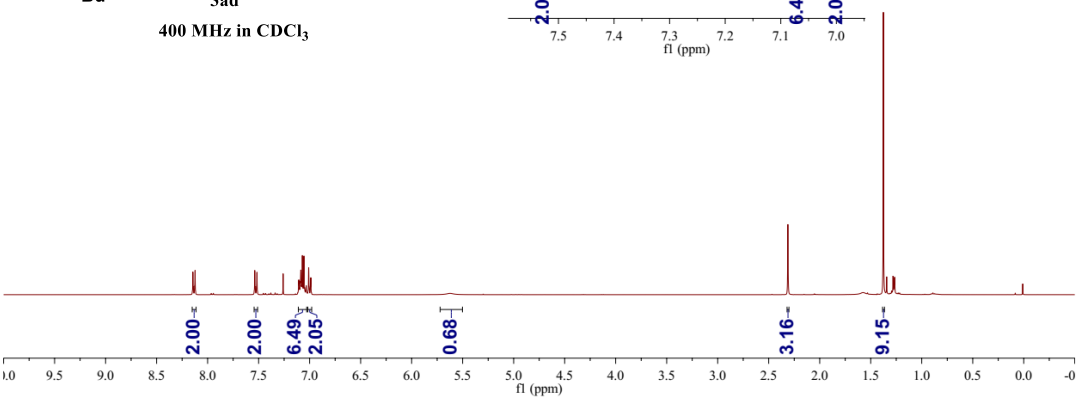


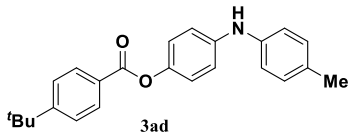

3ad

400 MHz in $CDCl_3$



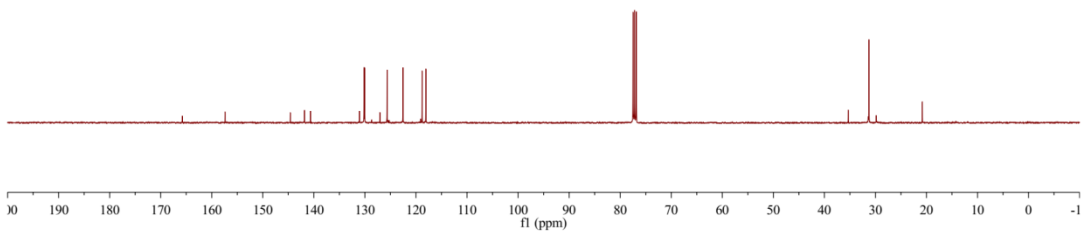



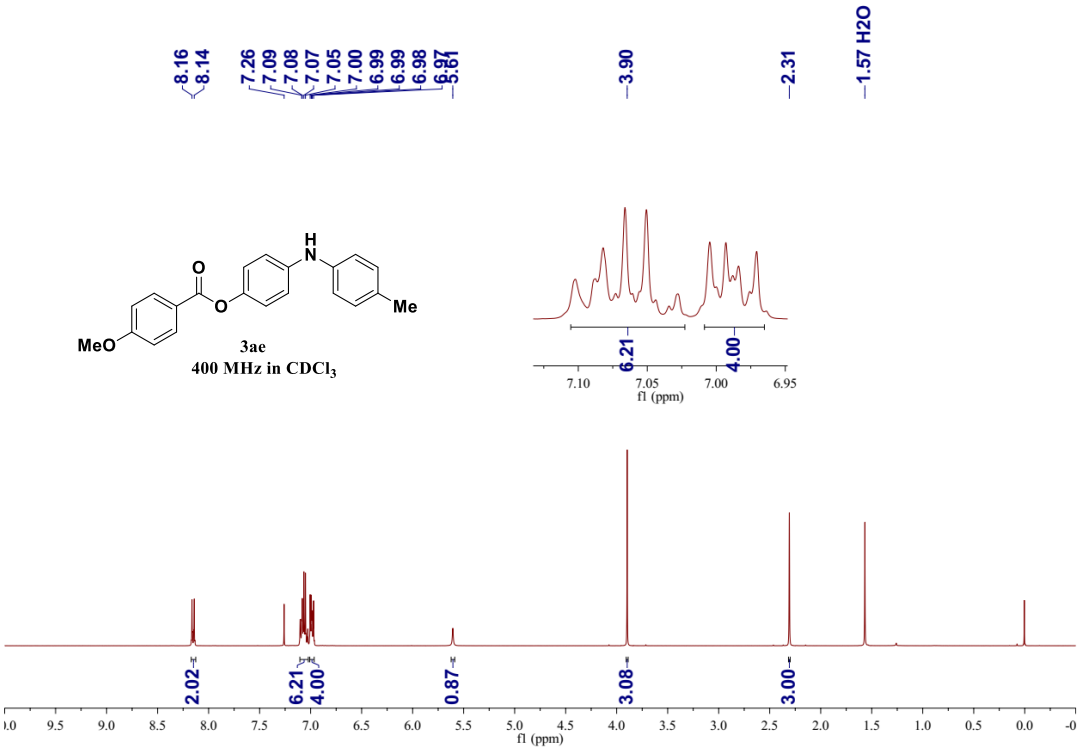


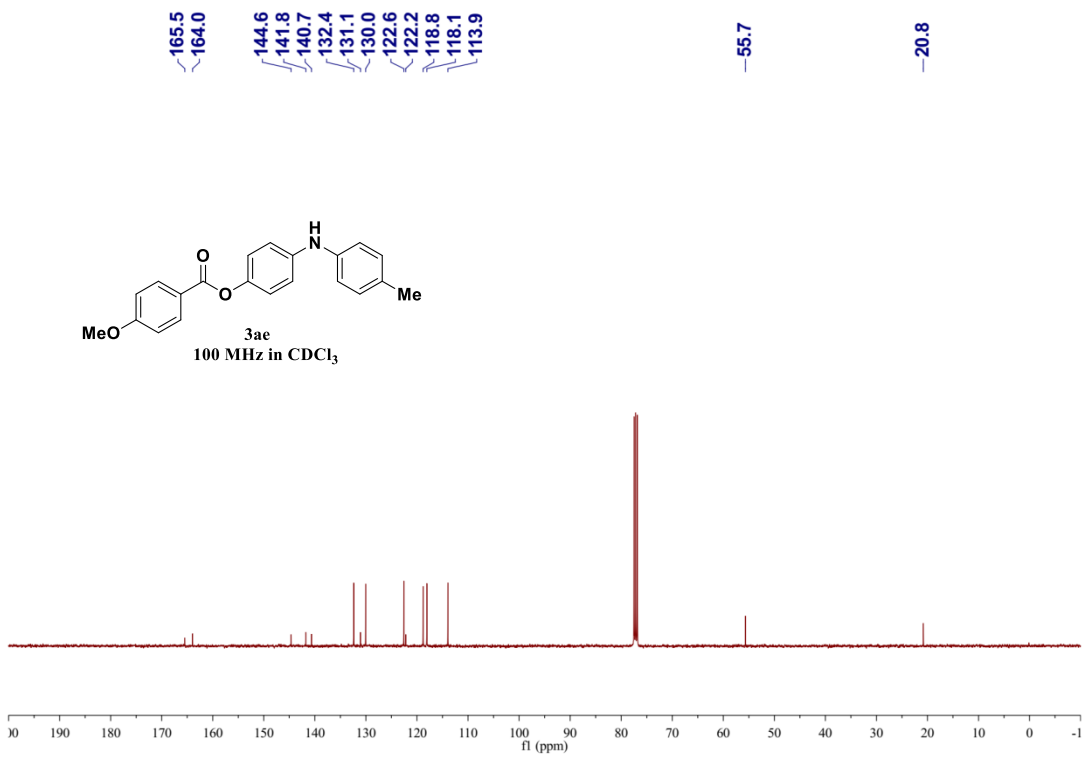


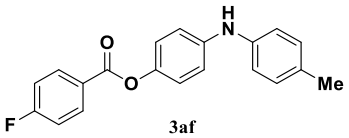

3ad

100 MHz in $CDCl_3$



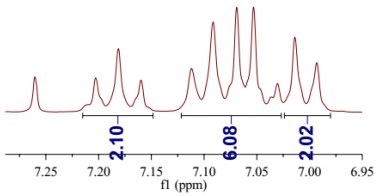

8.16
8.14
7.26
7.09
7.08
7.07
7.05
7.00
6.99
6.99
6.98
6.97
6.91
3.90
2.31
1.57 H2O
MeO
Me
3ae
400 MHz in CDCl3
6.21
4.00
7.10
7.05
7.00
6.95
f1 (ppm)
2.02
6.21
4.00
0.87
3.08
3.00
f1 (ppm)

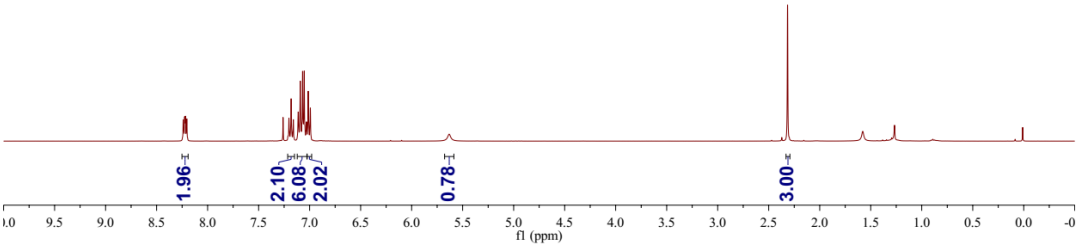

165.5
164.0
144.6
141.8
140.7
132.4
131.1
130.0
122.6
122.2
118.8
118.1
113.9
55.7
20.8
MeO
Me
3ae
100 MHz in CDCl3
f1 (ppm)

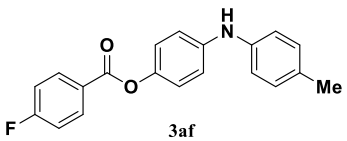

3af

400 MHz in $CDCl_3$



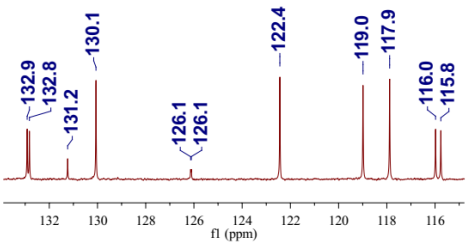



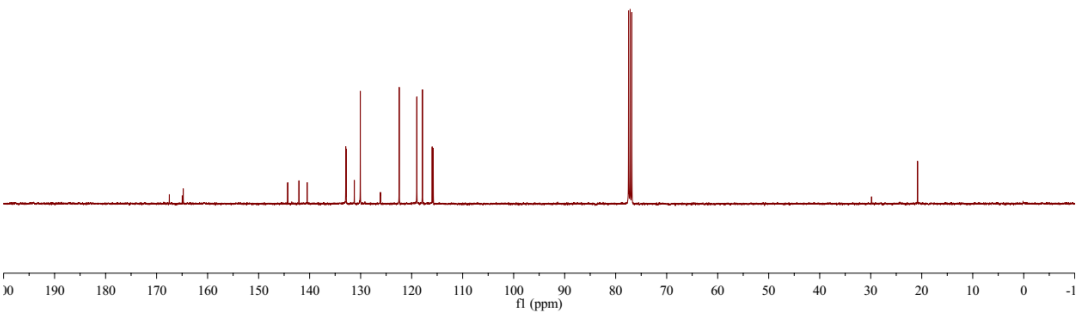


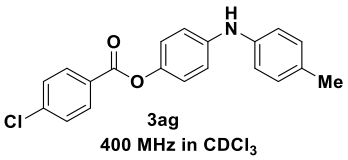




3af

100 MHz in $CDCl_3$

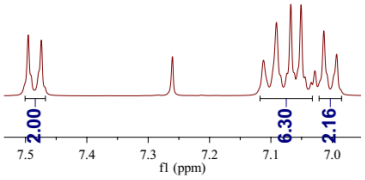


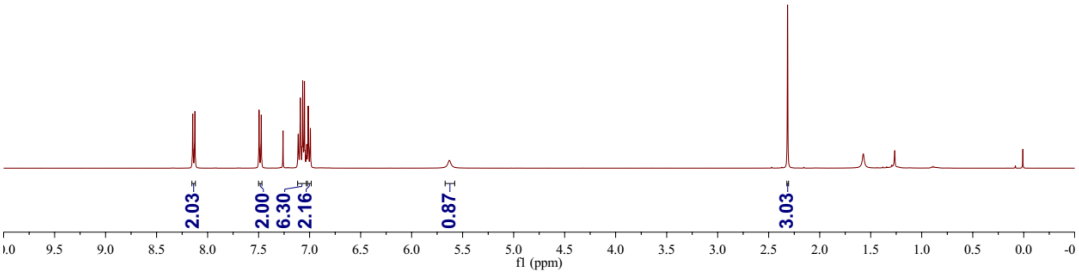



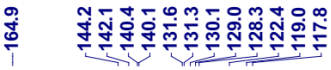



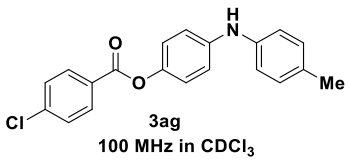

3ag

400 MHz in $CDCl_3$



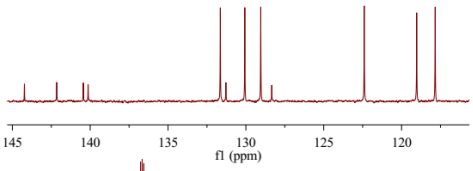



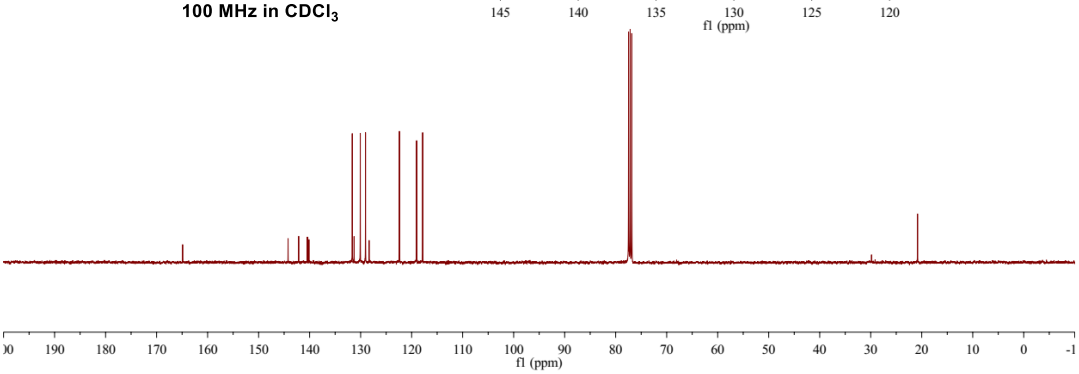



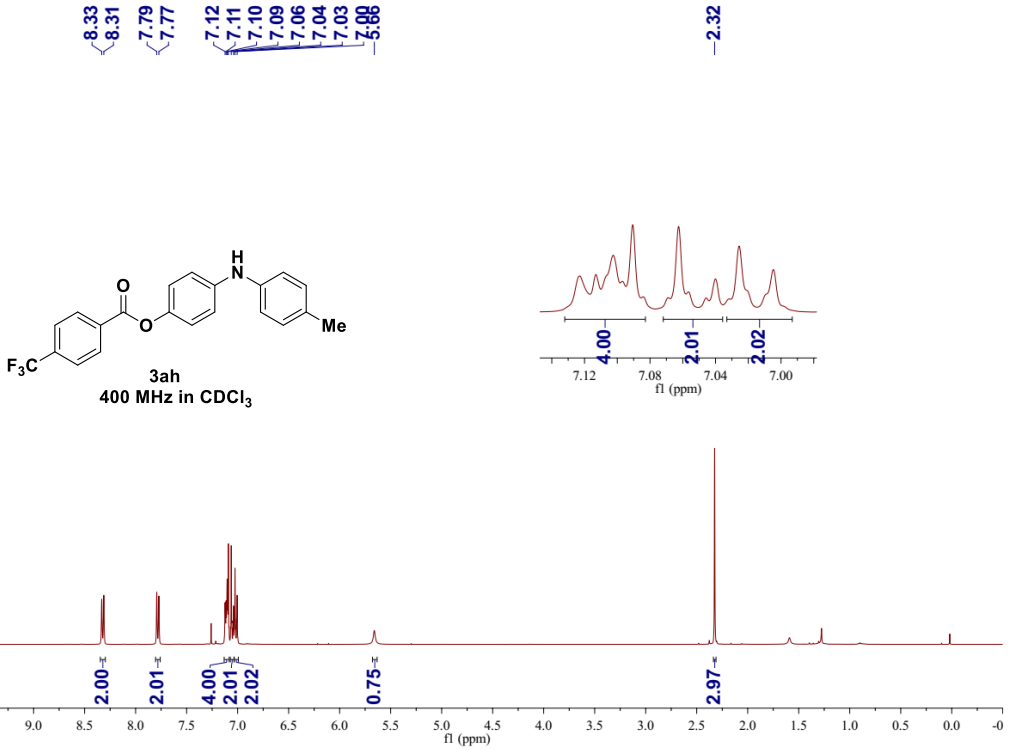



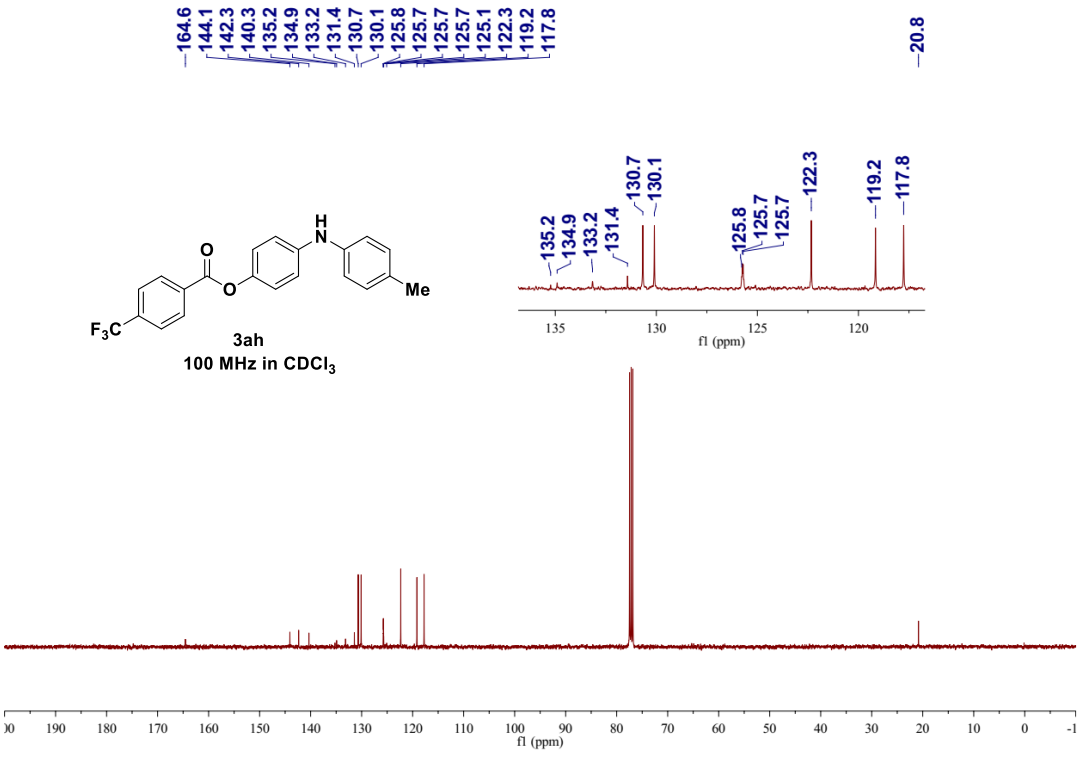

3ag

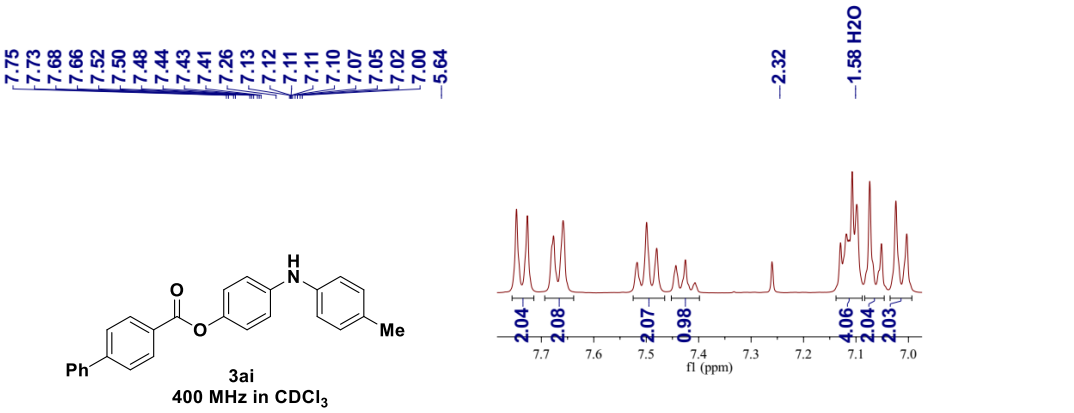
100 MHz in $CDCl_3$




8.33
8.31
7.79
7.77
7.12
7.11
7.10
7.09
7.06
7.04
7.03
2.32
3ah
400 MHz in CDCl3
4.00
2.01
2.02
7.12
7.08
7.04
7.00
f1 (ppm)
2.00
2.01
4.00
2.01
2.02
0.75
2.97
f1 (ppm)

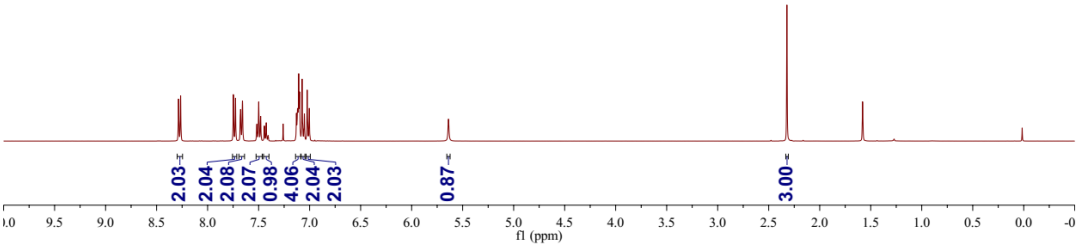

164.6
144.1
142.3
140.3
135.2
134.9
133.2
131.4
130.7
130.1
125.8
125.7
125.7
125.7
125.1
122.3
119.2
117.8
20.8
3ah
100 MHz in CDCl3
135.2
134.9
133.2
131.4
130.7
130.1
125.8
125.7
125.7
122.3
119.2
117.8
135
130
125
120
f1 (ppm)
f1 (ppm)



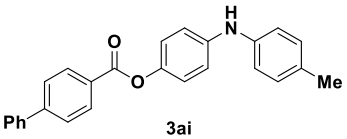




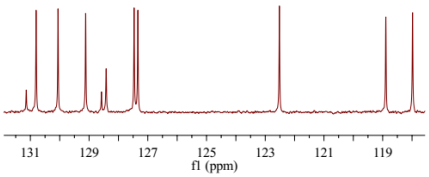
3ai
400 MHz in $CDCl_3$

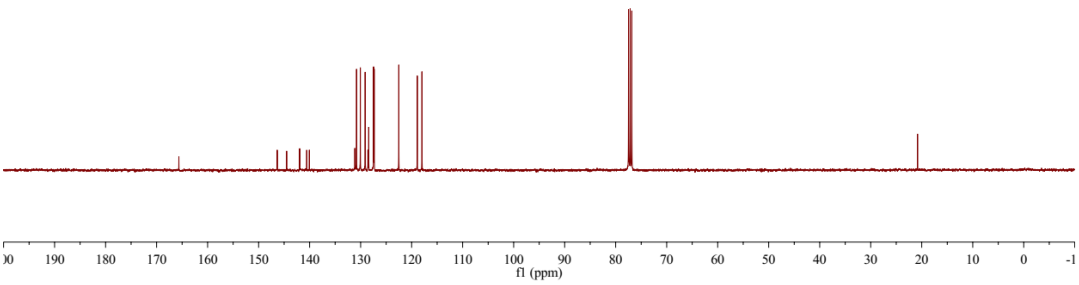


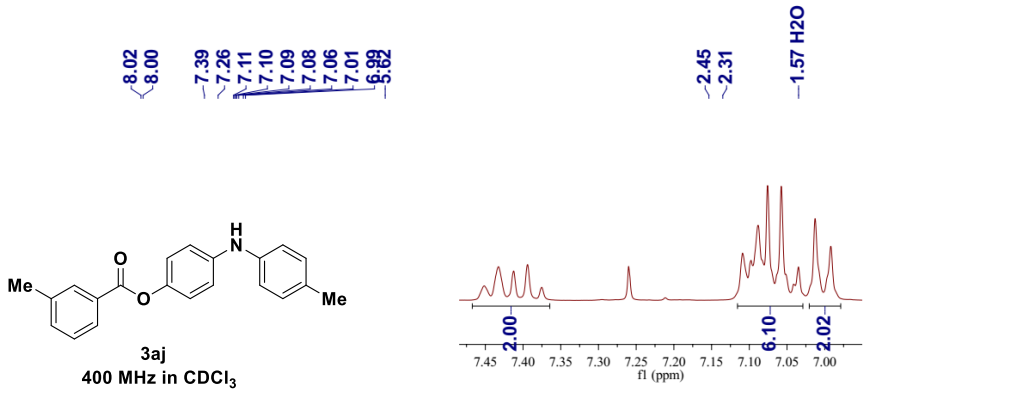


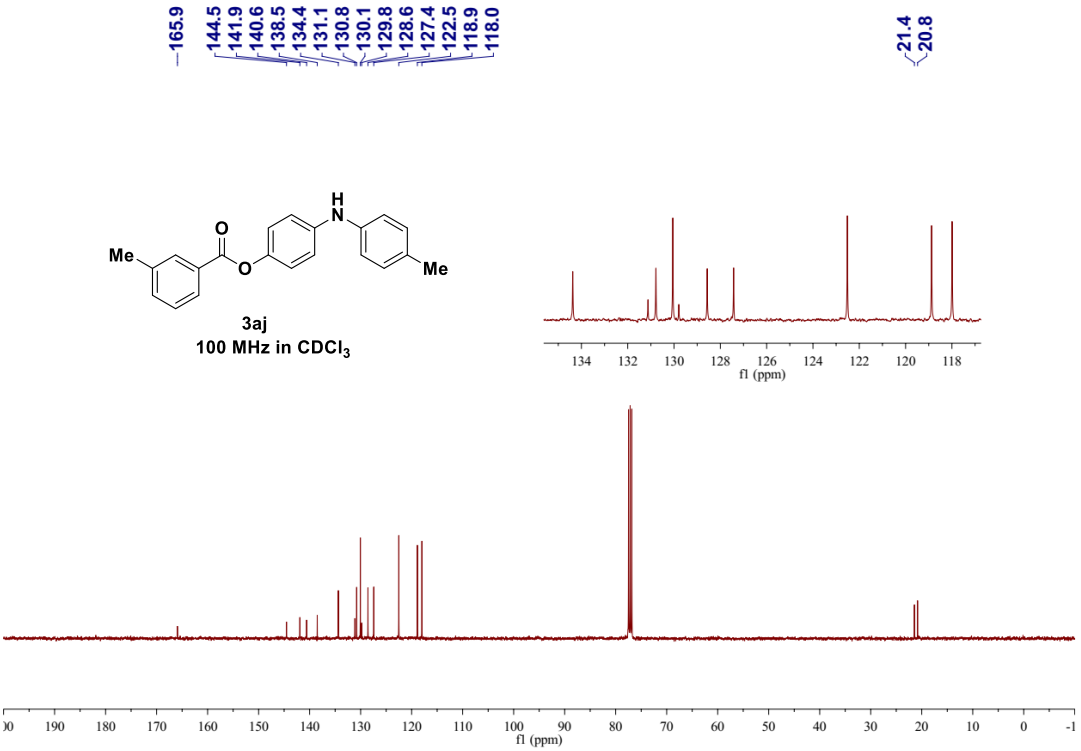


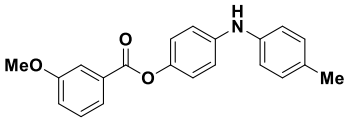

3ai
100 MHz in $CDCl_3$



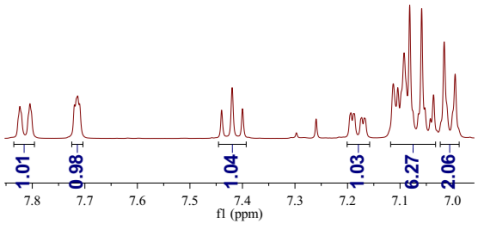



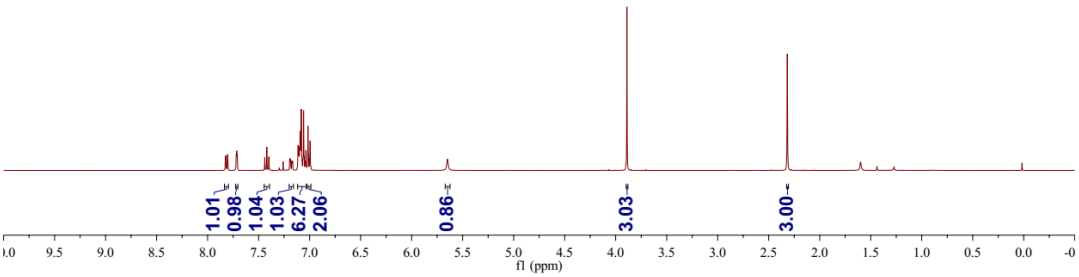

8.02
8.00
7.39
7.26
7.11
7.10
7.09
7.08
7.06
7.01
6.99
5.62
2.45
2.31
1.57 H2O
Me
O
O
H
N
Me
3aj
400 MHz in CDCl3
2.00
6.10
2.02
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
1.96
2.00
6.10
2.02
0.89
3.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

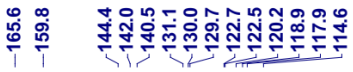

165.9
144.5
141.9
140.6
138.5
134.4
131.1
130.8
130.1
129.8
128.6
127.4
122.5
118.9
118.0
21.4
20.8
Me
O
O
H
N
Me
3aj
100 MHz in CDCl3
134 132 130 128 126 124 122 120 118
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

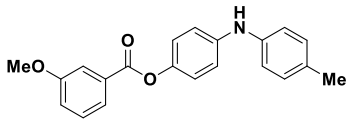




3ak
400 MHz in $CDCl_3$

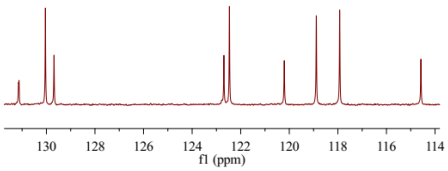


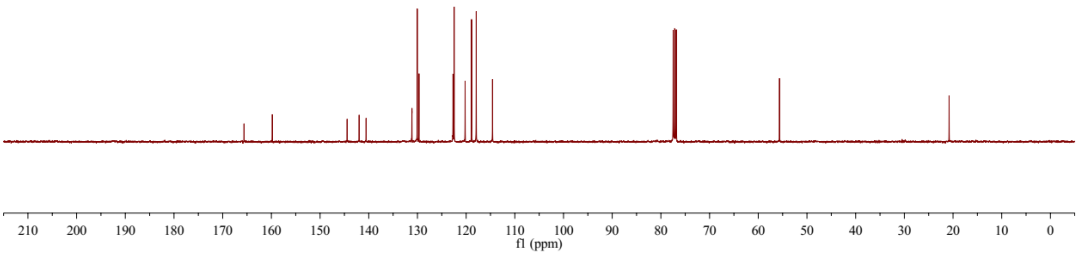



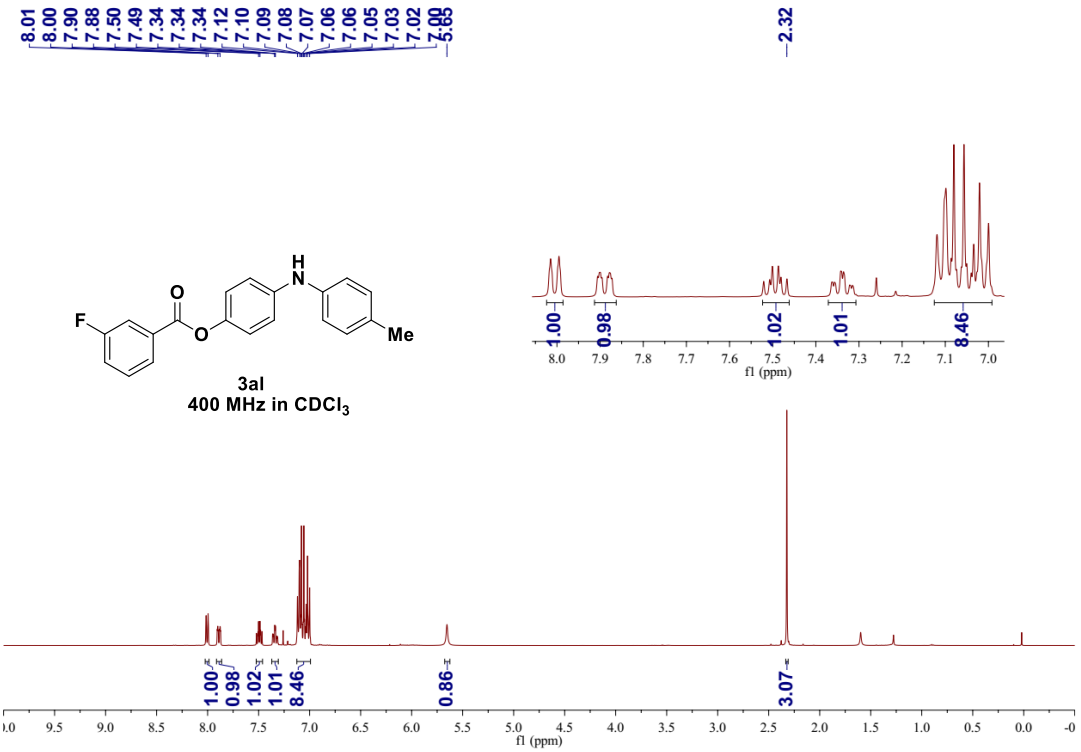



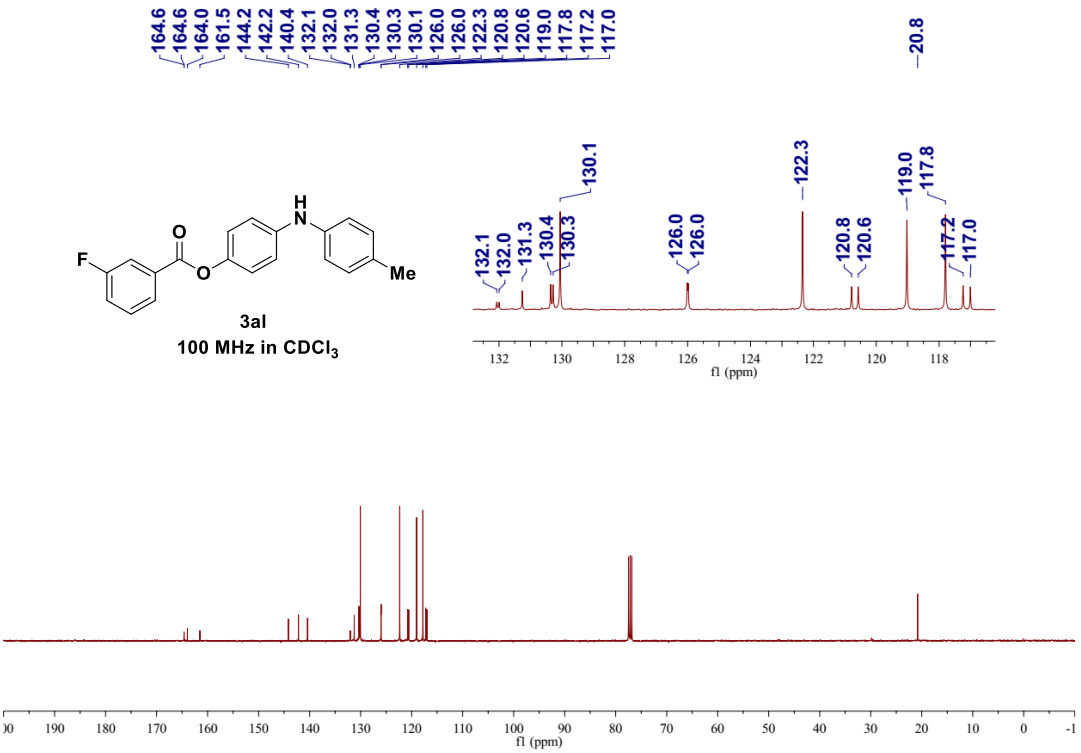



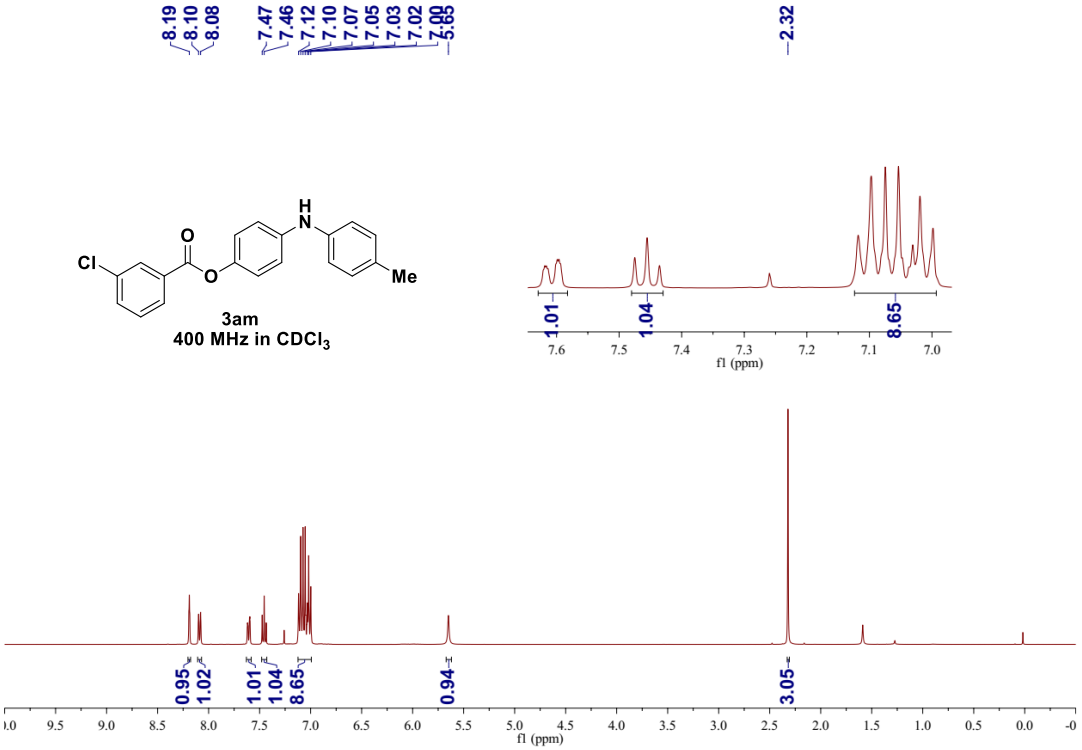

3ak
100 MHz in $CDCl_3$

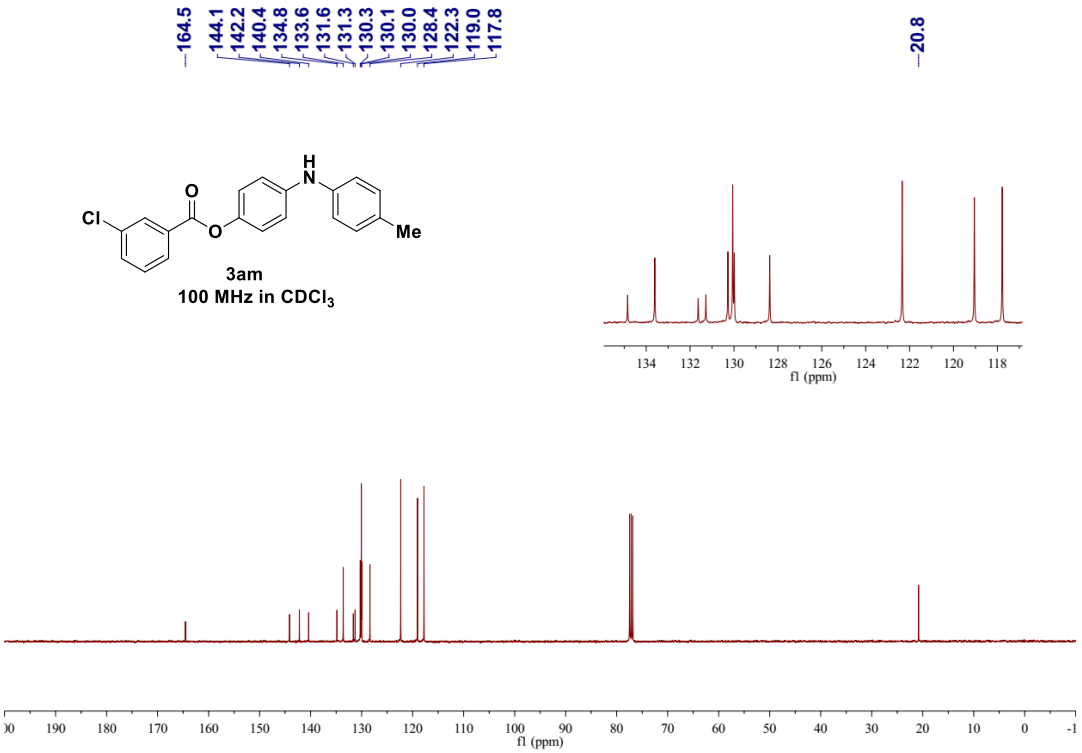


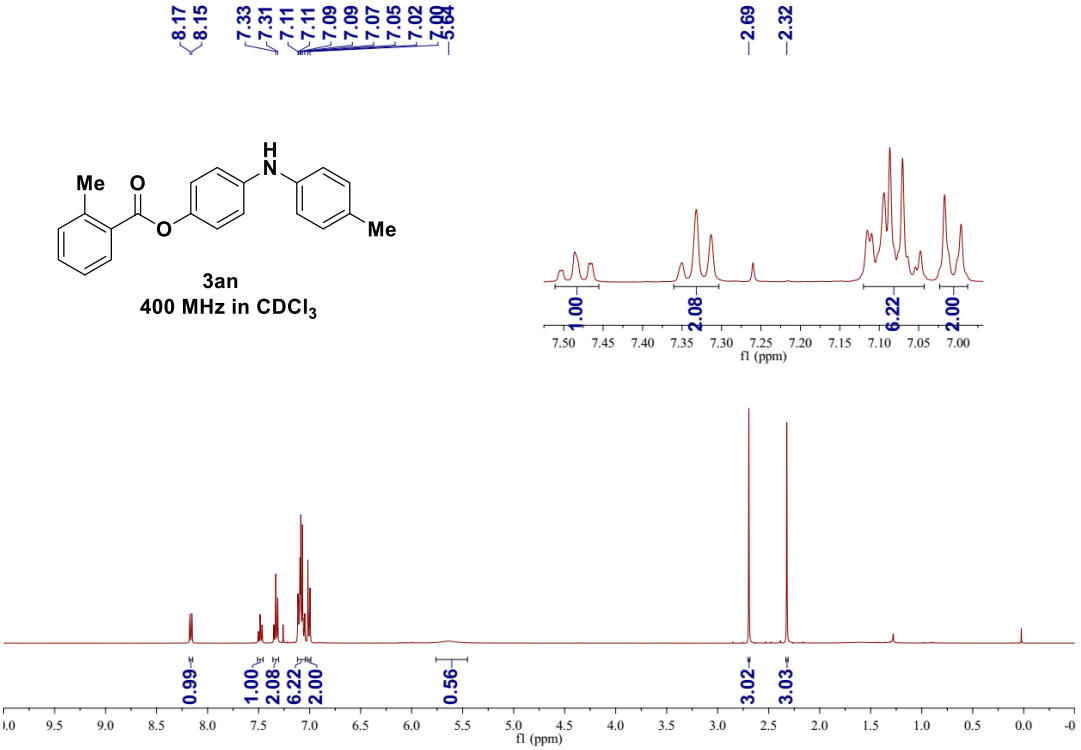



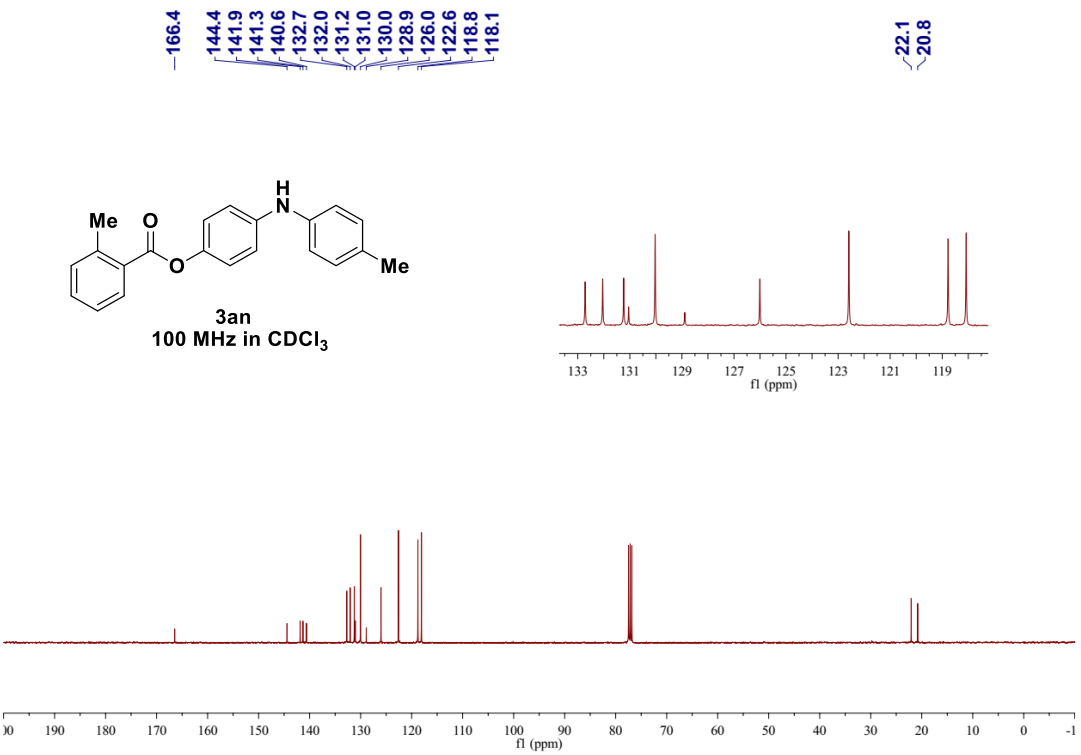

8.01
8.00
7.90
7.88
7.50
7.49
7.34
7.34
7.34
7.12
7.10
7.09
7.08
7.07
7.06
7.06
7.05
7.03
7.02
7.00
5.85
2.32
F
O
O
H
N
Me
3al
400 MHz in CDCl3
1.00
0.98
1.02
1.01
8.46
f1 (ppm)
1.00
0.98
1.02
1.01
8.46
0.86
3.07
f1 (ppm)

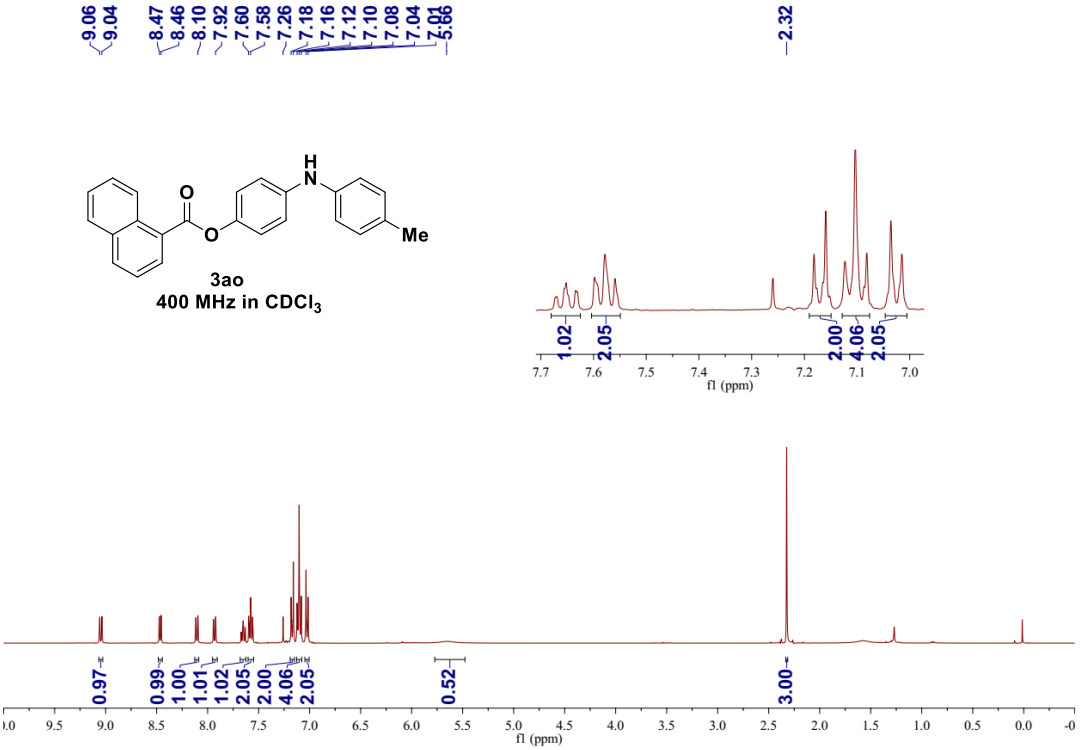

164.6
164.6
164.0
161.5
144.2
142.2
140.4
132.1
132.0
131.3
130.4
130.3
130.1
126.0
126.0
122.3
120.8
120.6
119.0
117.8
117.2
117.0
20.8
F
O
O
H
N
Me
3al
100 MHz in CDCl3
132.1
132.0
131.3
130.4
130.3
130.1
126.0
126.0
122.3
120.8
120.6
119.0
117.8
117.2
117.0
f1 (ppm)
f1 (ppm)

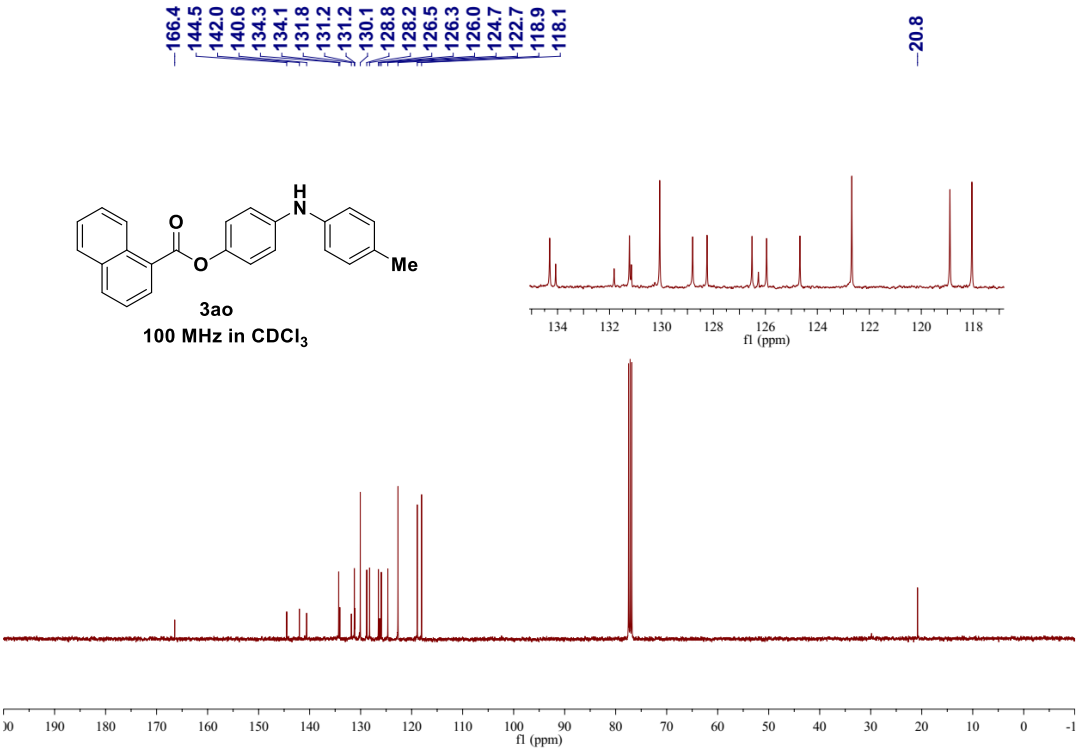

8.19
8.10
8.08
7.47
7.46
7.12
7.10
7.07
7.05
7.03
7.02
7.00
5.85
2.32
Cl
O
O
H
N
Me
3am
400 MHz in CDCl3
1.01
1.04
8.65
fl (ppm)
0.95
1.02
1.01
1.04
8.65
0.94
3.05
fl (ppm)

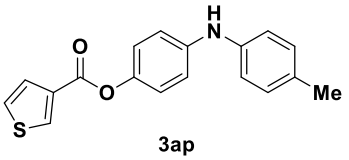

164.5
144.1
142.2
140.4
134.8
133.6
131.6
131.3
130.3
130.1
130.0
128.4
122.3
119.0
117.8
20.8
Cl
O
O
H
N
Me
3am
100 MHz in CDCl3
fl (ppm)
fl (ppm)


8.17
8.15
7.33
7.31
7.11
7.11
7.09
7.09
7.07
7.05
7.02
5.84
2.69
2.32
Me
O
O
H
N
Me
3an
400 MHz in CDCl3
1.00
2.08
6.22
2.00
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
0.99
1.00
2.08
6.22
2.00
0.56
3.02
3.03
f1 (ppm)


166.4
144.4
141.9
141.3
140.6
132.7
132.0
131.2
131.0
130.0
128.9
126.0
122.6
118.8
118.1
22.1
20.8
Me
O
O
H
N
Me
3an
100 MHz in CDCl3
133 131 129 127 125 123 121 119
f1 (ppm)
f1 (ppm)

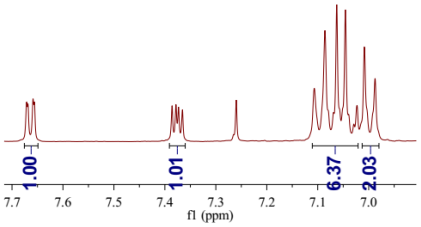

9.06
9.04
8.47
8.46
8.10
7.92
7.60
7.58
7.26
7.18
7.16
7.12
7.10
7.08
7.04
7.01
5.86
2.32
H
N
O
O
Me
3ao
400 MHz in CDCl3
1.02
2.05
2.00
4.06
2.05
fl (ppm)
0.97
0.99
1.00
1.01
1.02
2.05
2.00
4.06
2.05
0.52
3.00
fl (ppm)

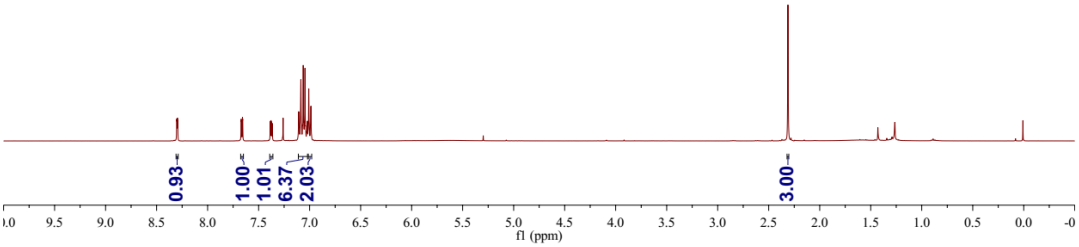

166.4
144.5
142.0
140.6
134.3
134.1
131.8
131.2
131.2
130.1
128.8
128.2
126.5
126.3
126.0
124.7
122.7
118.9
118.1
20.8
H
N
O
O
Me
3ao
100 MHz in CDCl3
fl (ppm)
fl (ppm)

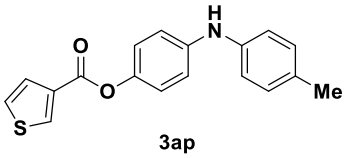

3ap

400 MHz in $CDCl_3$



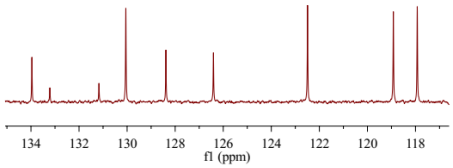



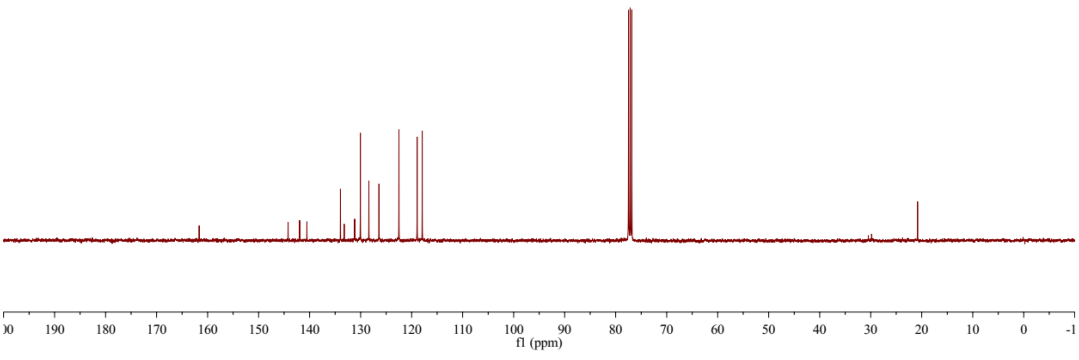


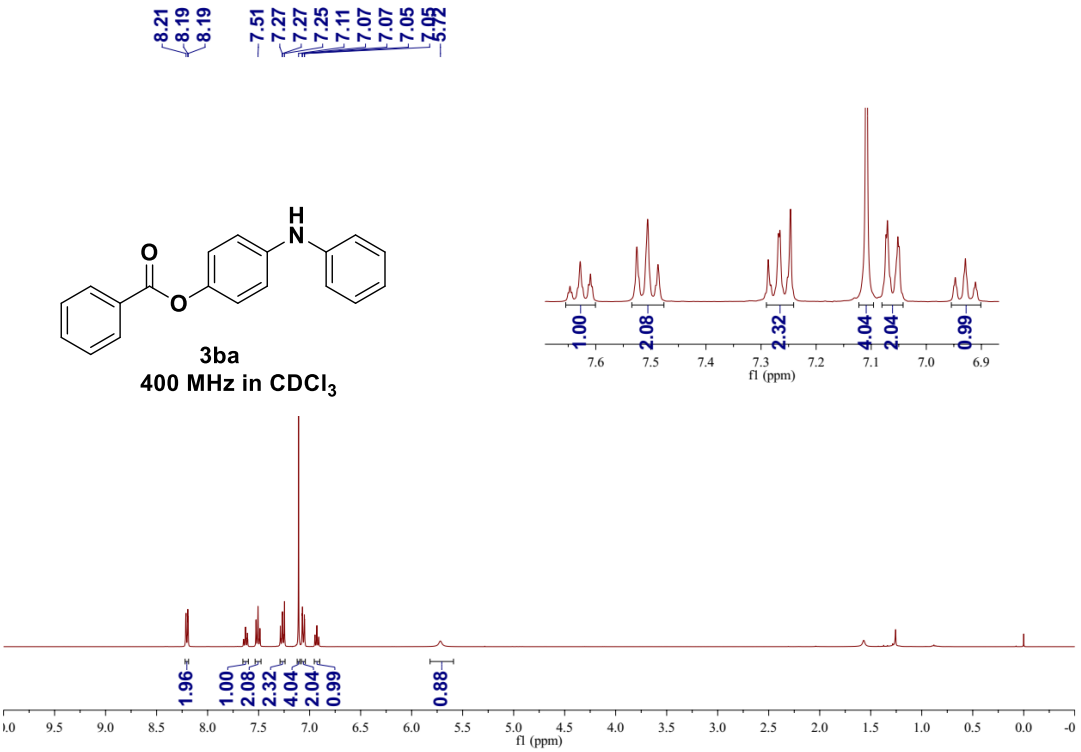



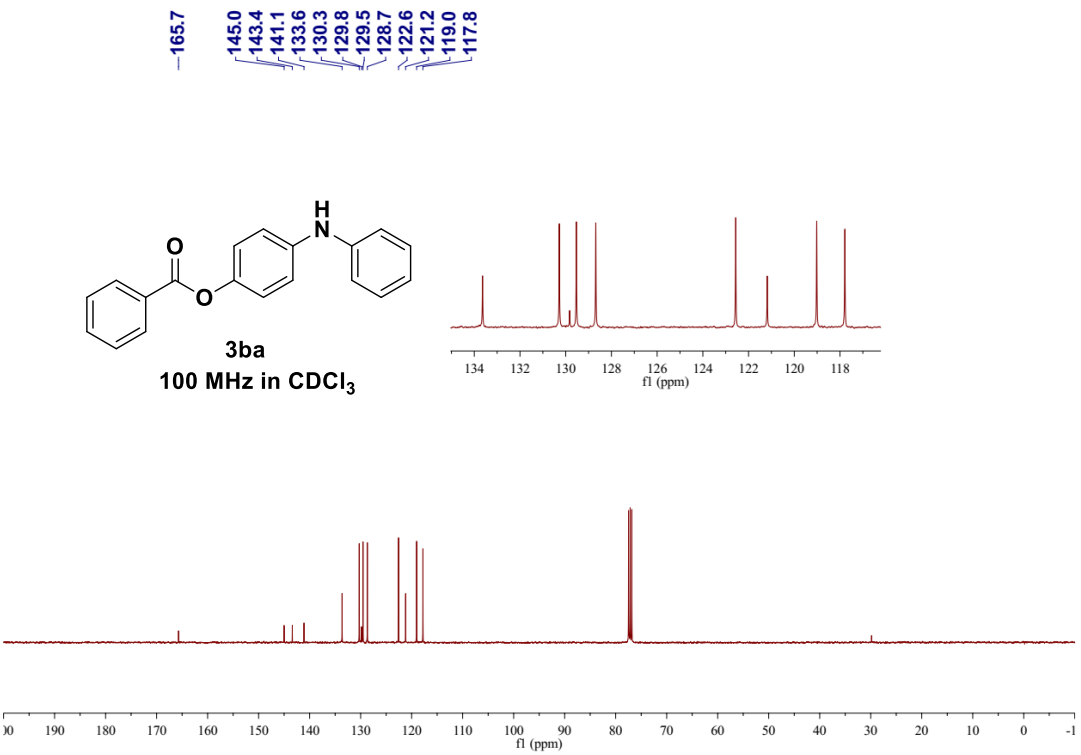

3ap

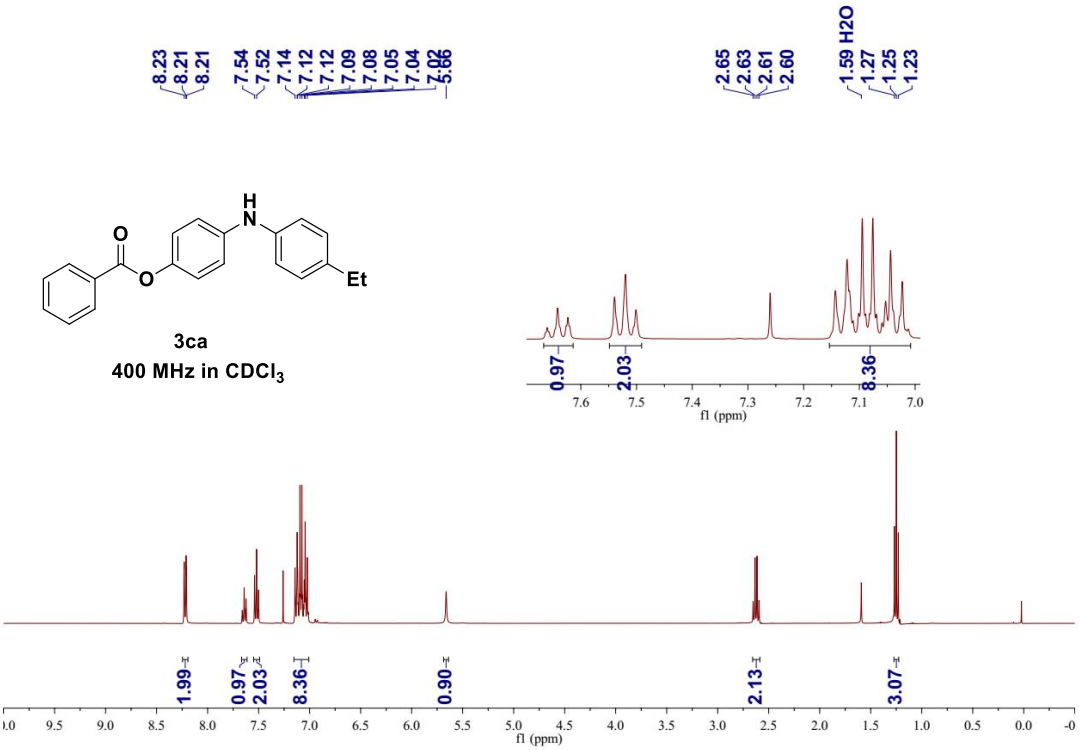
100 MHz in $CDCl_3$

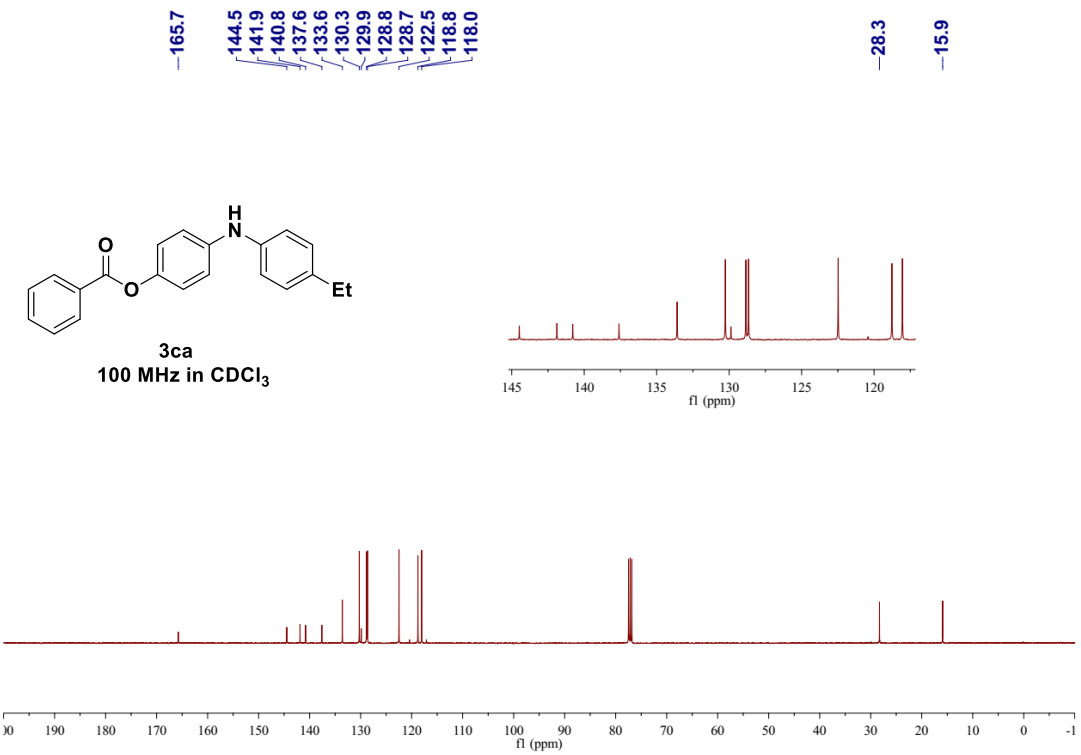


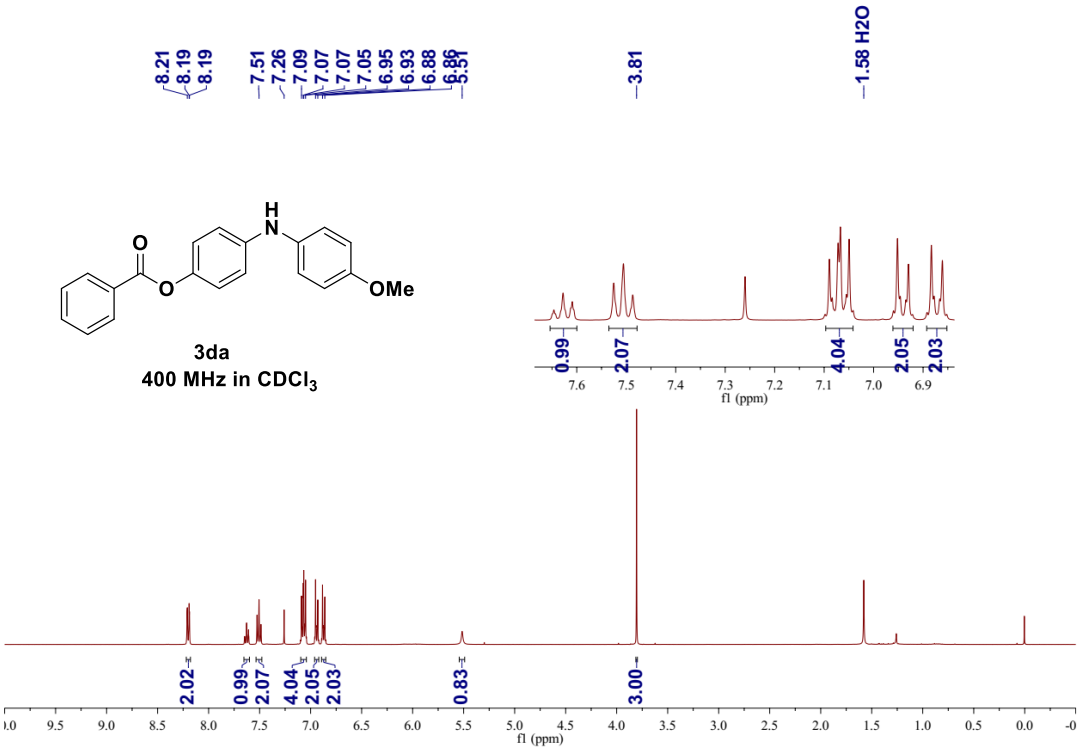



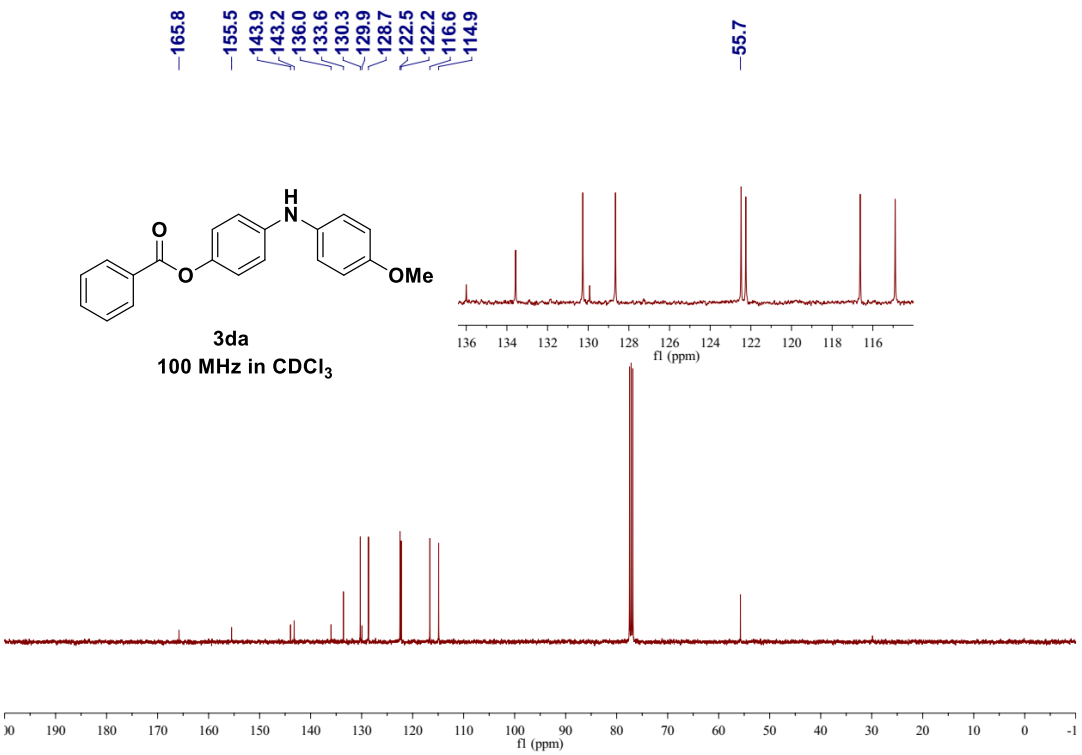

8.21
8.19
8.19
7.51
7.27
7.27
7.25
7.11
7.07
7.07
7.05
7.05
5.12
O
O
H
N
3ba
400 MHz in CDCl3
1.00
2.08
2.32
4.04
2.04
0.99
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
1.96
1.00
2.08
2.32
4.04
2.04
0.99
0.88
f1 (ppm)

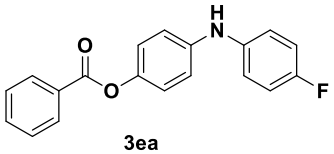

165.7
145.0
143.4
141.1
133.6
130.3
129.8
129.5
128.7
122.6
121.2
119.0
117.8
O
O
H
N
3ba
100 MHz in CDCl3
134
132
130
128
126
124
122
120
118
f1 (ppm)
f1 (ppm)


8.23
8.21
8.21
7.54
7.52
7.14
7.12
7.12
7.09
7.08
7.05
7.04
2.65
2.63
2.61
2.60
1.59 H2O
1.27
1.25
1.23
O
O
H
N
Et
3ca
400 MHz in CDCl3
0.97
2.03
8.36
f1 (ppm)
1.99
0.97
2.03
8.36
0.90
2.13
3.07
f1 (ppm)

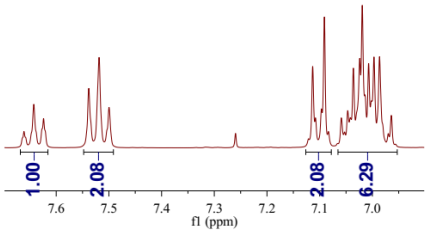

165.7
144.5
141.9
140.8
137.6
133.6
130.3
129.9
128.8
128.7
122.5
118.8
118.0
28.3
15.9
O
O
H
N
Et
3ca
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

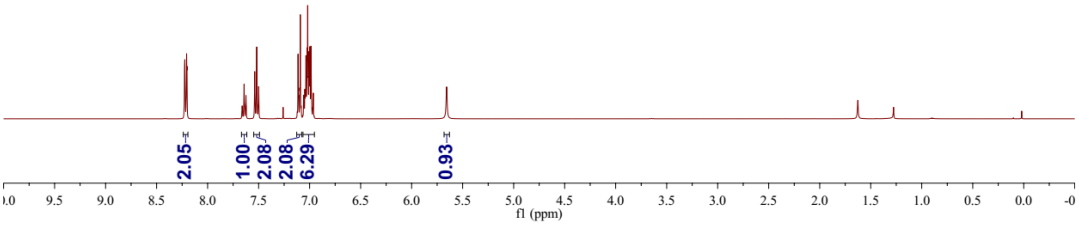

8.21
8.19
8.19
7.51
7.26
7.09
7.07
7.07
7.05
6.95
6.93
6.88
6.86
5.51
3.81
1.58 H2O
O
O
H
N
OMe
3da
400 MHz in CDCl3
0.99
2.07
4.04
2.05
2.03
fl (ppm)
2.02
0.99
2.07
4.04
2.05
2.03
0.83
3.00
fl (ppm)

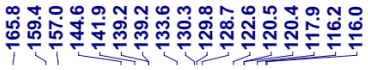

165.8
155.5
143.9
143.2
136.0
133.6
130.3
129.9
128.7
122.5
122.2
116.6
114.9
55.7
O
O
H
N
OMe
3da
100 MHz in CDCl3
fl (ppm)
fl (ppm)

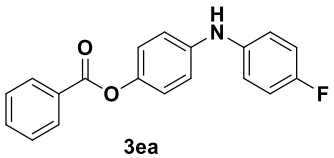




3ea
400 MHz in $CDCl_3$

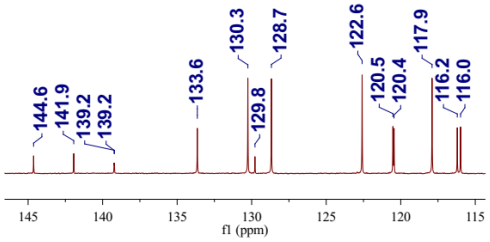


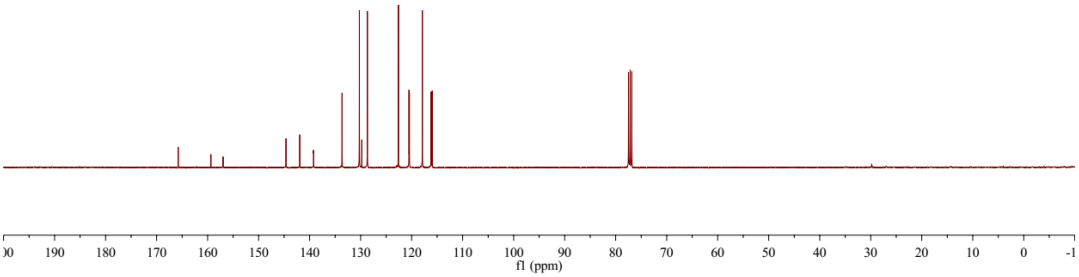



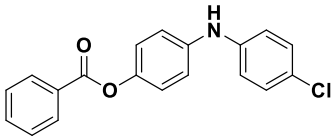




3ea
100 MHz in $CDCl_3$

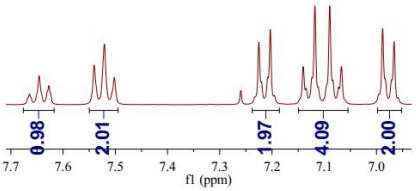


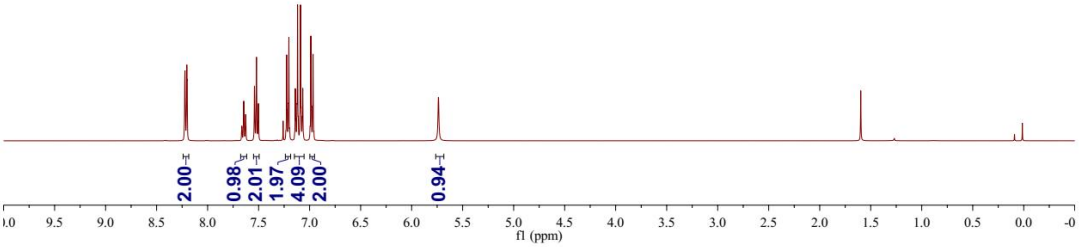



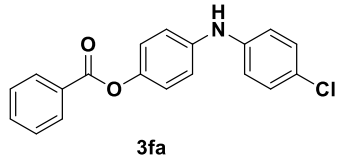

3fa

400 MHz in $CDCl_3$



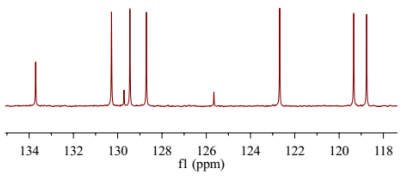



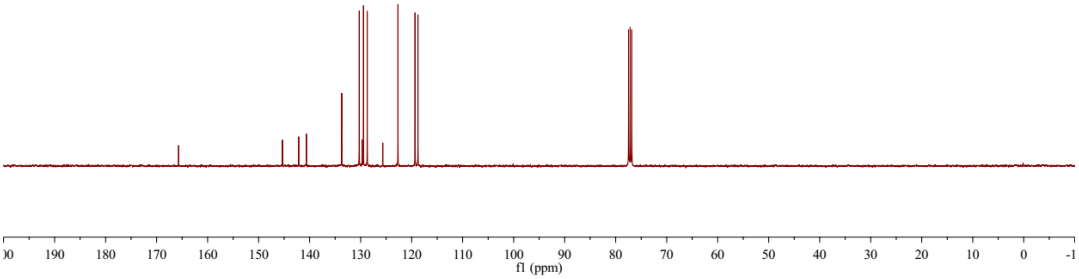


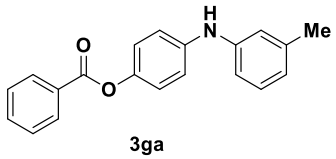



3fa

100 MHz in $CDCl_3$

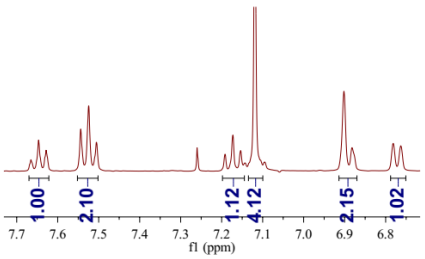


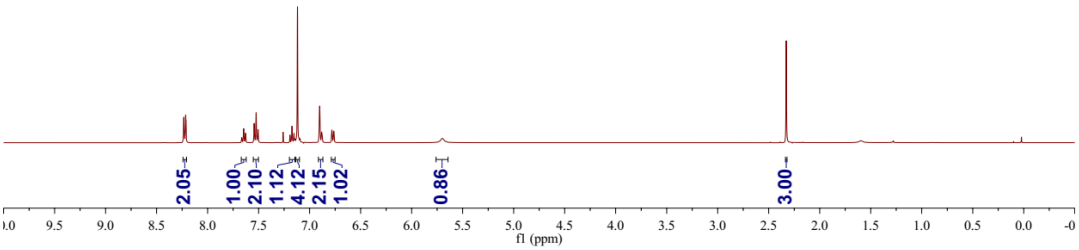



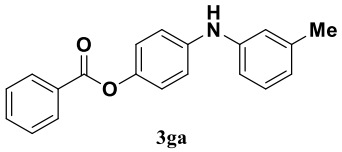

3ga

100 MHz in $CDCl_3$



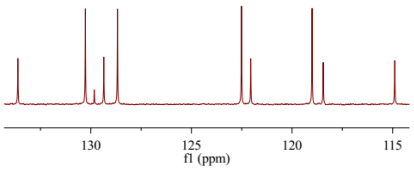



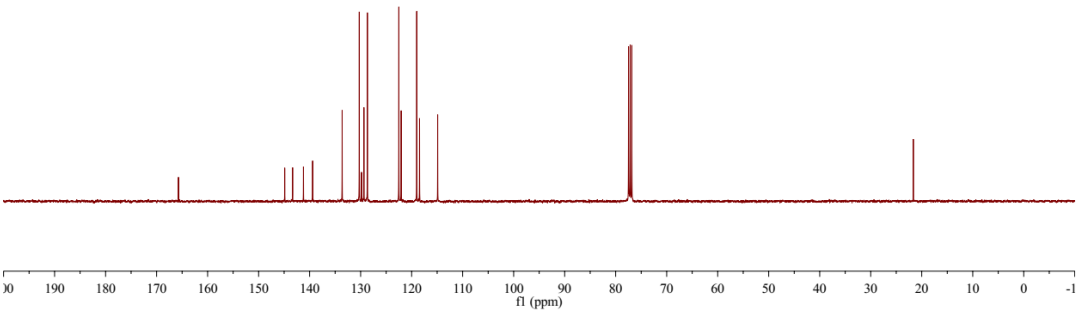


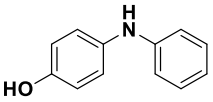



3ga

100 MHz in $CDCl_3$

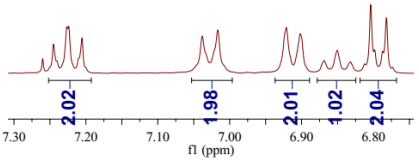


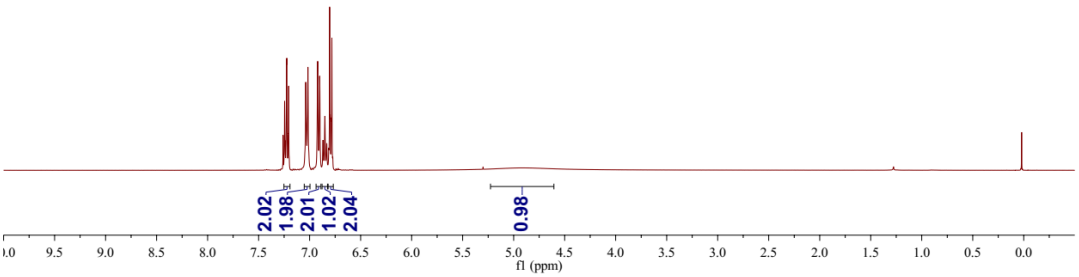



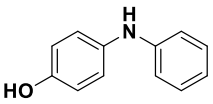

4

400 MHz in $CDCl_3$








4

100 MHz in $CDCl_3$