Supporting Information

Synthesis and characterization of *N*-heterocyclic carbene-palladium(II) chlorides-1-methylindazole and -1-Methylpyrazole complexes and their catalytic activity toward C-N coupling of aryl chlorides

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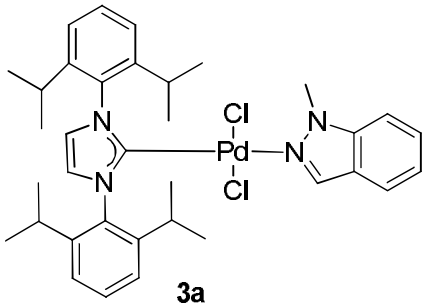
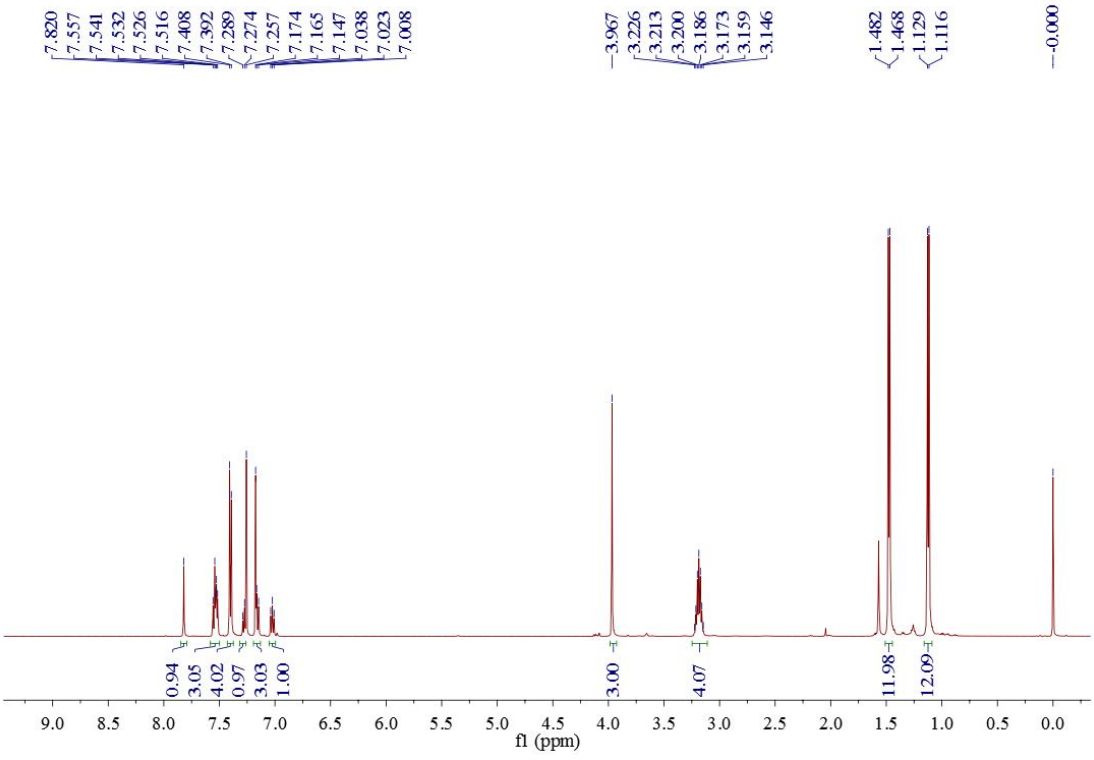
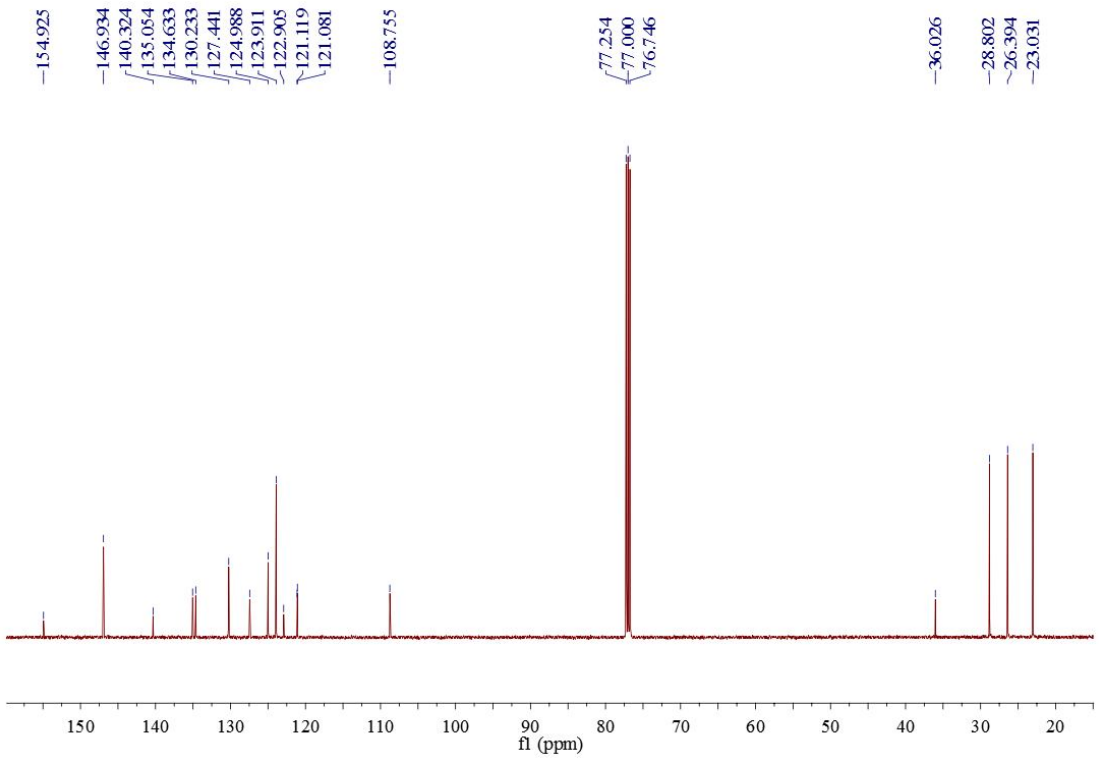


3a

Compound **3a**: yellow solid. m.p. 287 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.82 (s, 1H), 7.56-7.52 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.17-7.15 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.97 (s, 3H), 3.19 (hept, *J* = 6.5 Hz, 4H), 1.48 (d, *J* = 6.5 Hz, 12H), 1.12 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.9, 146.9, 140.3, 135.1, 134.6, 130.2, 127.4, 125.0, 123.9, 122.9, 121.11, 121.08, 108.8, 36.0, 28.8, 26.4, 23.0. MS (ESI): 661 $[M\text{-}Cl]^+$. HRMS (ESI) calcd. for $C_{35}H_{44}ClN_4Pd$ $[M\text{-}Cl]^+$: 661.2294; found: 661.2281. Anal. calcd. for $C_{35}H_{44}Cl_2N_4Pd$: C, 60.22%; H, 6.53%; N, 8.03%; found: C, 60.09%; H, 6.24%; N, 8.04%. IR (neat) ν 2960, 2925, 2860, 1618, 1506, 1464, 1441, 1413, 1379, 1351, 1329, 1211, 1155, 1121, 1056, 1031, 972, 944, 911, 816, 802, 783 cm^{-1}.

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122.905
121.119
121.081
108.755
77.254
77.000
76.746
36.026
28.802
26.394
23.031
150
140
130
120
110
100
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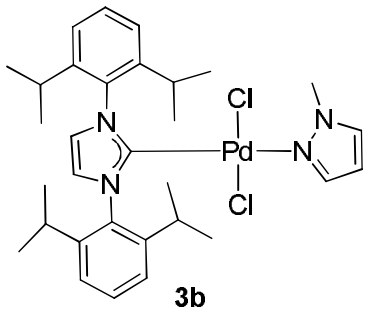
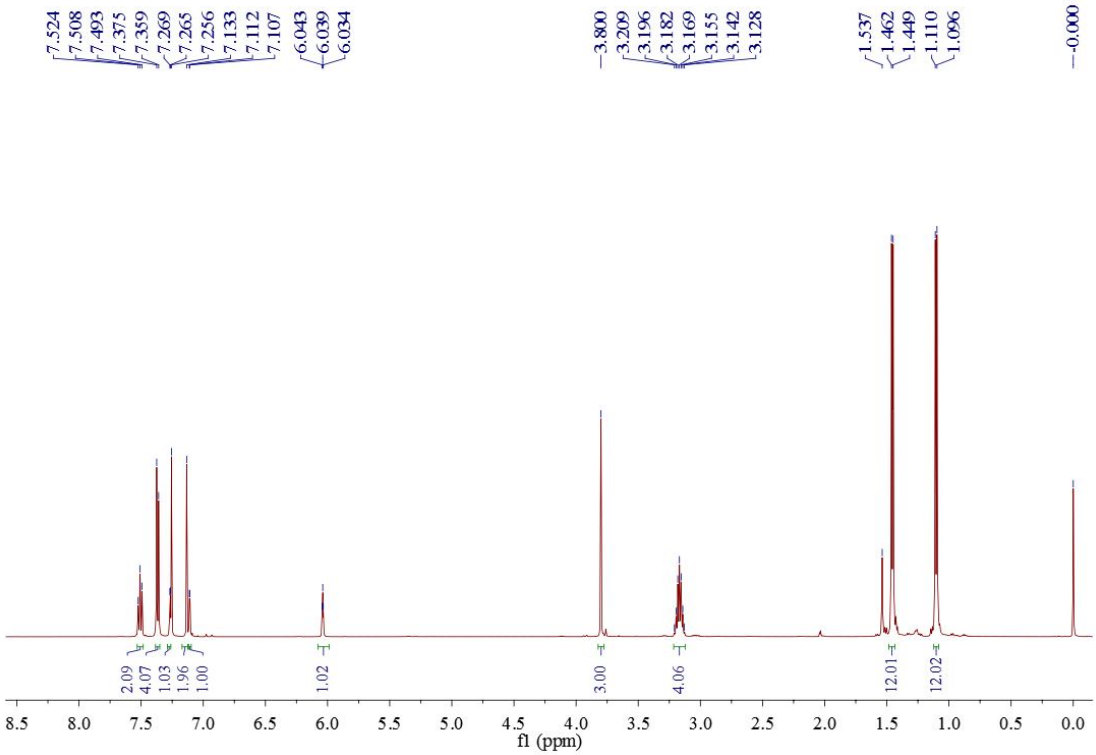
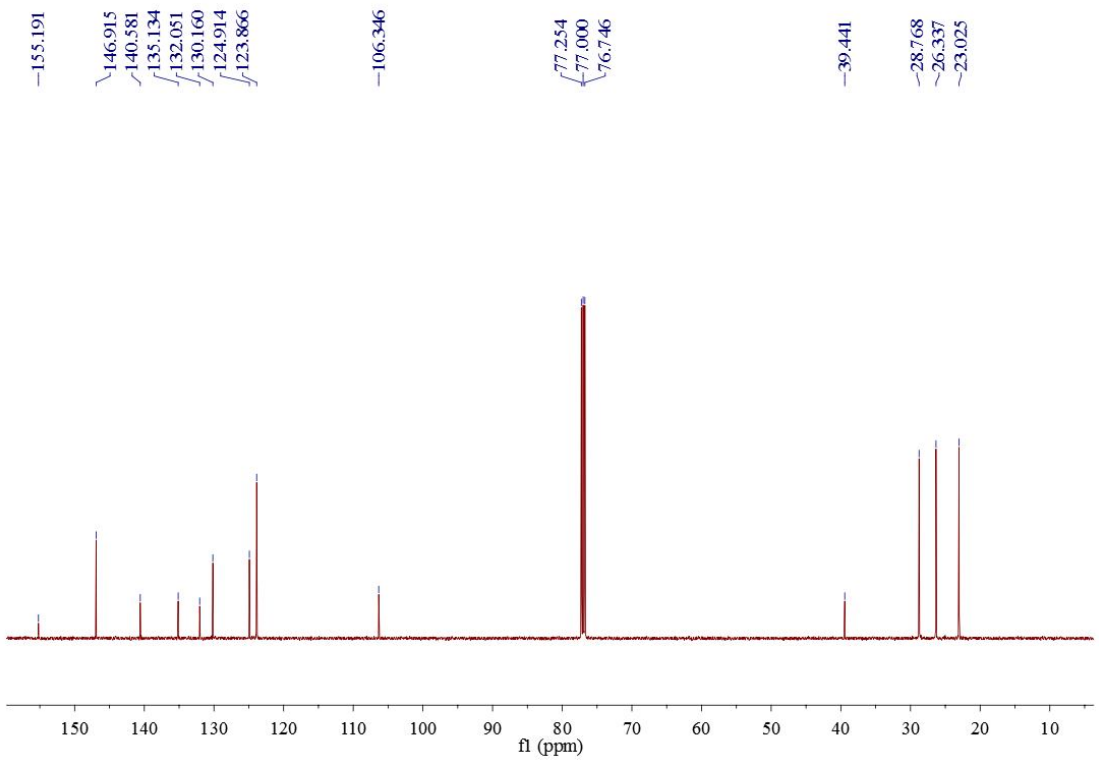
80
70
60
50
40
30
20
f1 (ppm)



3b

Compound **3b**: yellow solid. m.p. 295 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.51 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.13 (s, 2H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.04 (t, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.17 (hept, *J* = 7.0 Hz, 4H), 1.46 (d, *J* = 7.0 Hz, 12H), 1.10 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.2, 146.9, 140.6, 135.1, 132.1, 130.2, 124.9, 123.9, 106.3, 39.4, 28.8, 26.3, 23.0. MS (ESI): 611 $[M\text{-}Cl]^+$. HRMS (ESI): calcd for $C_{31}H_{42}ClN_4Pd$ $[M\text{-}Cl]^+$: 611.2136; found: 611.2154. Anal. Calcd for $C_{31}H_{42}Cl_2N_4Pd$: C, 57.46; H, 6.53; N, 8.65. Found: C, 57.50; H, 6.61; N, 8.71. IR (neat) ν 2960, 2921, 2866, 1522, 1468, 1457, 1411, 1382, 1346, 1330, 1284, 1208, 1120, 1105, 1083, 1060, 937, 889, 801, 764 cm^{-1}.

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135.134
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39.441
28.768
26.337
23.025
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140
130
120
110
100
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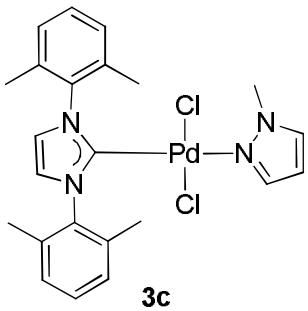
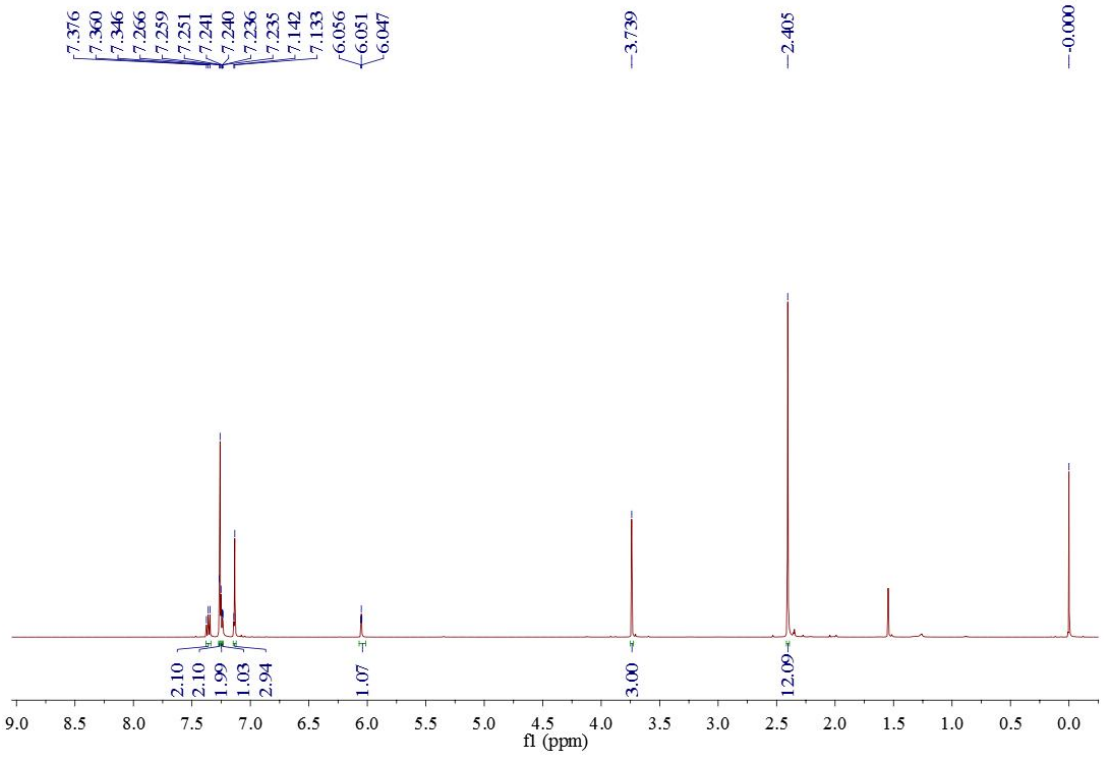
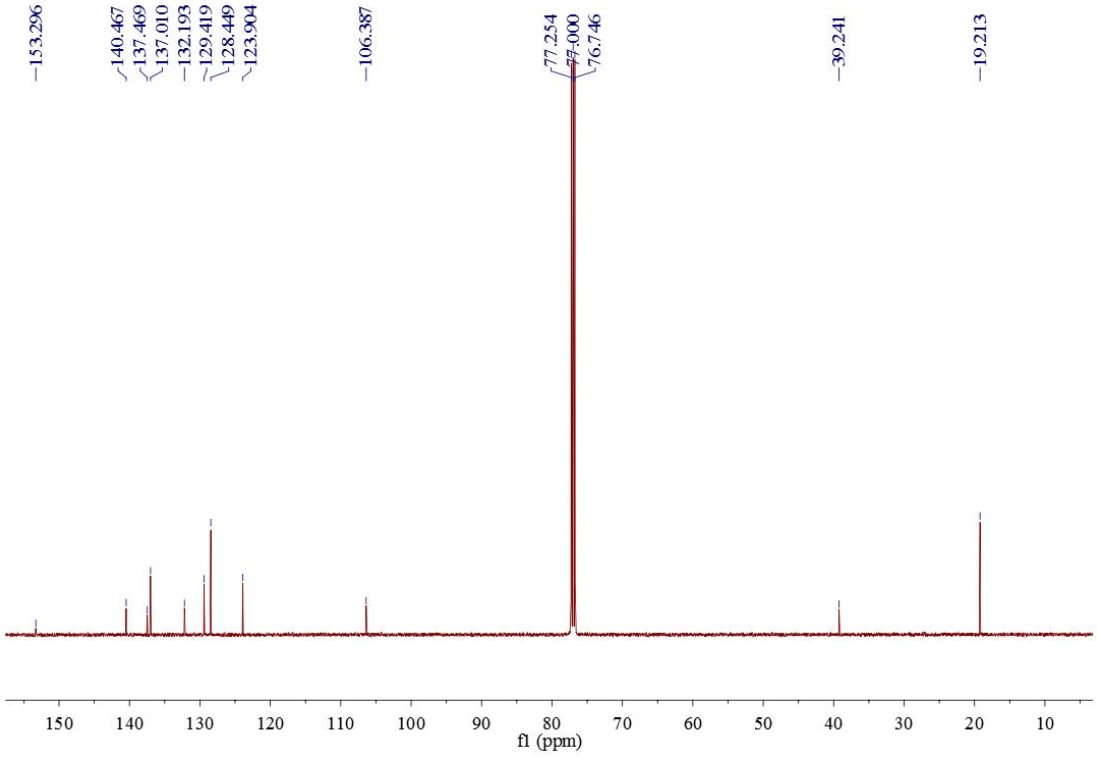
80
70
60
50
40
30
20
10
f1 (ppm)



3c

Compound **3c**: yellow solid. m.p. 287 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.27 (s, 2H), 7.25 (s, 2H), 7.24 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.14-7.13 (m, 3H), 6.05 (t, *J* = 2.5 Hz, 1H), 3.74 (s, 3H), 2.41 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.3, 140.5, 137.5, 137.0, 132.2, 129.4, 128.4, 123.9, 106.4, 39.2, 19.2. HRMS (ESI): calcd for $C_{23}H_{26}ClN_4Pd$ $[M\text{-}Cl]^+$, 499.0811; found, 499.0899. Anal. Calcd for $C_{23}H_{26}Cl_2N_4Pd$: C, 51.56; H, 4.89; N, 10.46. Found: C, 51.60; H, 4.98; N, 10.26. MS (ESI): 499 $[M\text{-}Cl]^+$. HRMS (ESI) calcd. for $C_{23}H_{26}ClN_4Pd$ $[M\text{-}Cl]^+$: 499.0881; found: 499.0899. IR (neat) ν 2963, 1523, 1475, 1406, 1361, 1331, 1285, 1261, 1224, 1159, 1098, 1019, 945, 866, 797, 779, 760 cm^{-1}.

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137.010
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129.419
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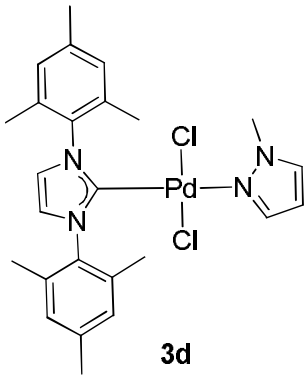
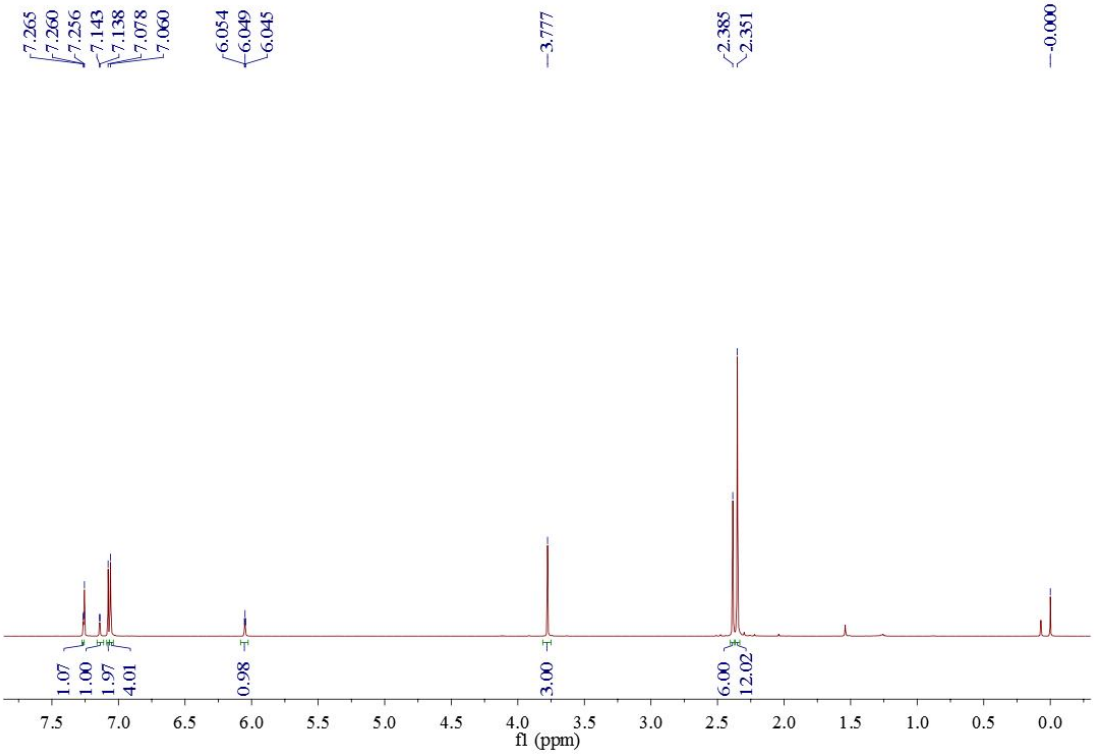
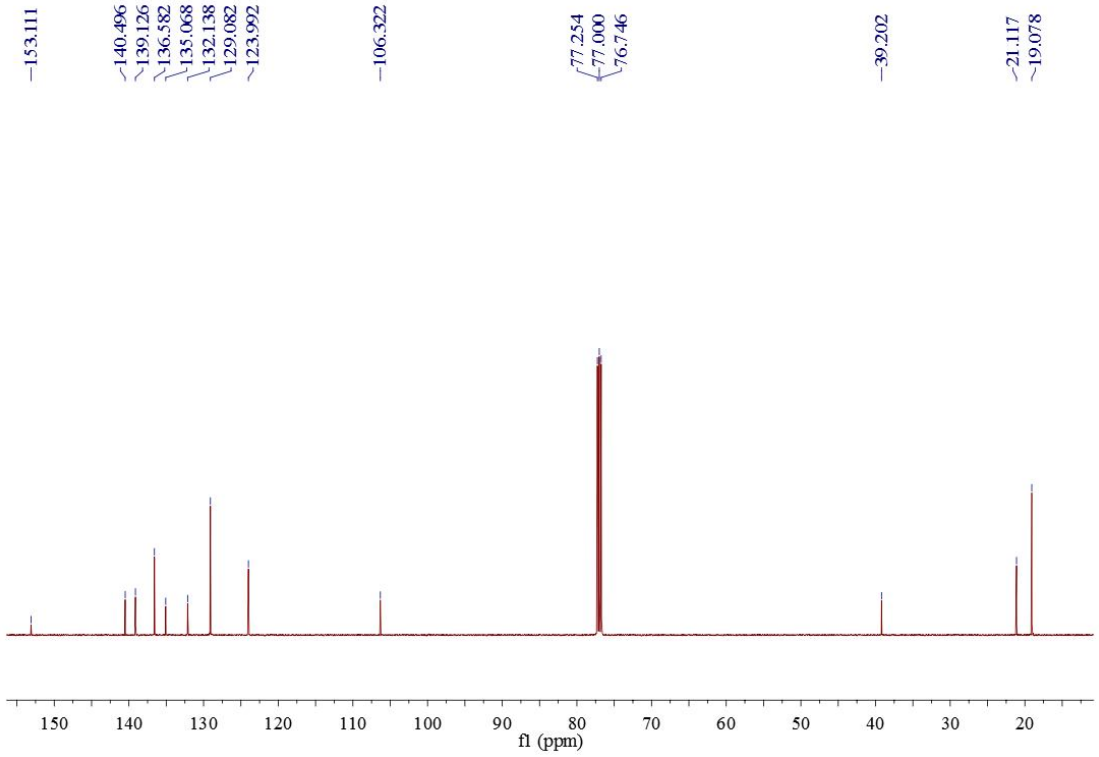
77.000
76.746
39.241
19.213
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



3d

Compound **3d**: yellow solid. m.p. 291 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.26 (d, *J* = 2.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.08 (s, 2H), 7.06 (s, 4H), 6.05 (t, *J* = 2.5 Hz, 1H), 3.78 (s, 3H), 2.39 (s, 6H), 2.35 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.1, 140.5, 139.1, 136.6, 135.1, 132.1, 129.1, 124.0, 106.3, 39.2, 21.1, 19.1. MS (ESI): 527 $[M\text{-}Cl]^+$. HRMS (ESI): calcd for $C_{25}H_{30}ClN_4Pd$ $[M\text{-}Cl]^+$, 527.1214; found, 527.1195. Anal. Calcd for $C_{25}H_{30}Cl_2N_4Pd$: C, 53.25; H, 5.36; N, 9.94. Found: C, 52.99; H, 5.32; N, 9.83. IR (neat) ν 3523, 2968, 2921, 2855, 1609, 1520, 1486, 1438, 1425, 1410, 1374, 1338, 1281, 1261, 1224, 1162, 1101, 1076, 1039, 992, 928, 868, 853, 801, 750 cm^{-1}.

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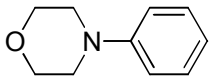
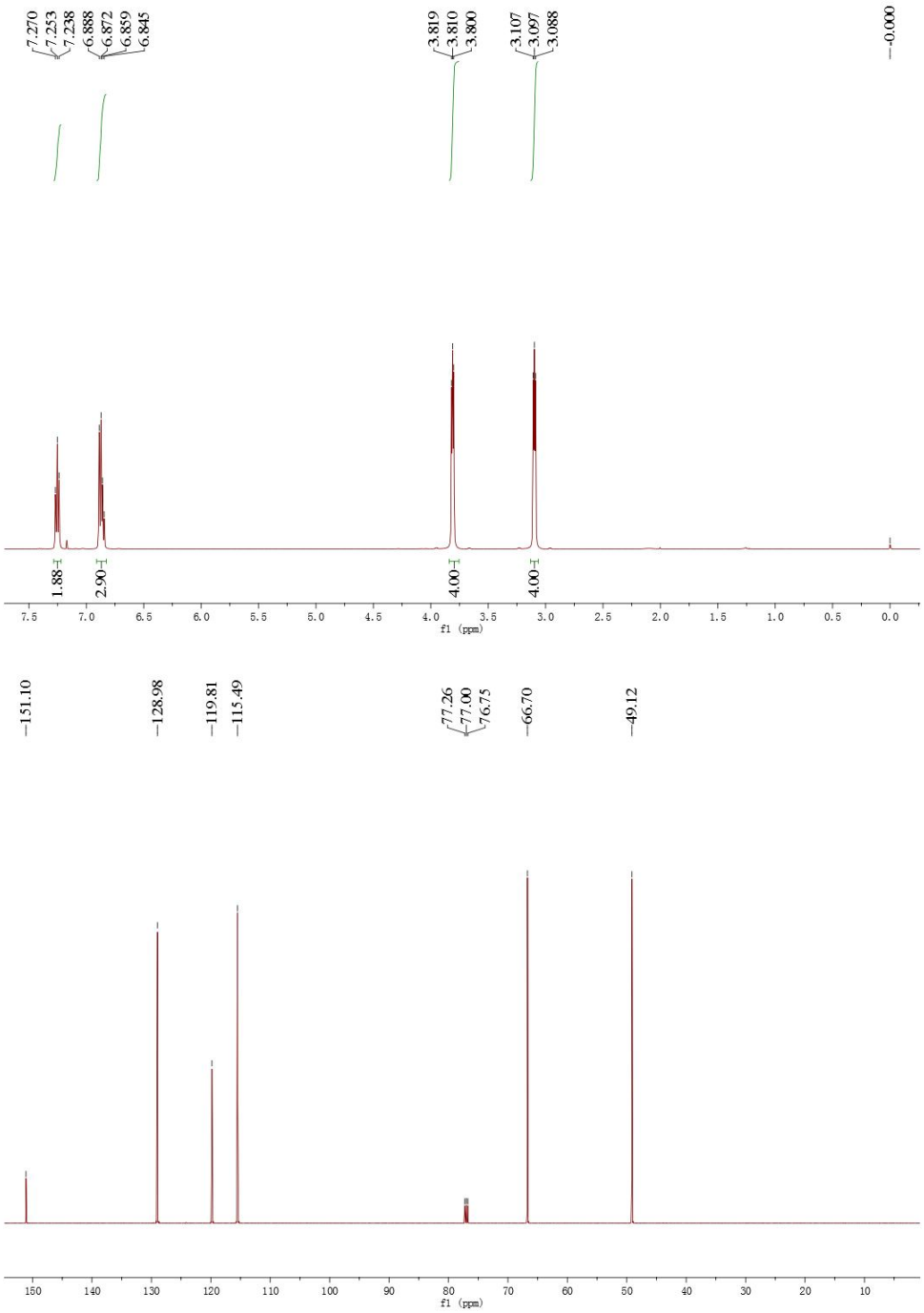
77.000
76.746
39.202
21.117
19.078
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

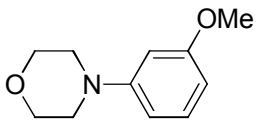


6a

Compound **6a**[1]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.25 (t, *J* = 8.0 Hz, 2H), 6.89-6.85 (m, 3H), 3.81 (t, *J* = 5.0 Hz, 4H), 3.10 (t, *J* = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.1, 129.0, 119.8, 115.5, 66.7, 49.1.

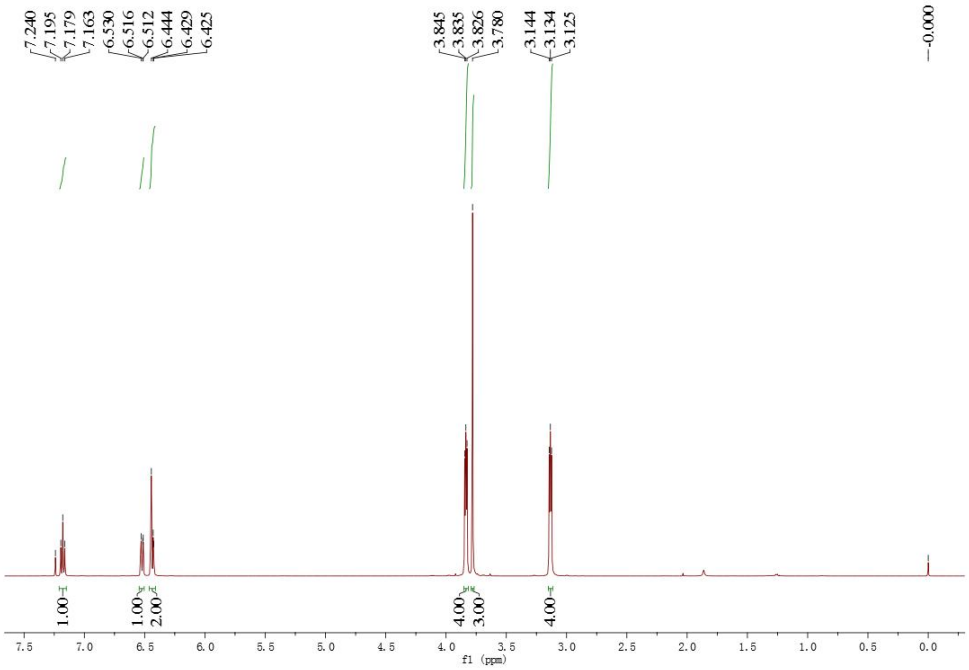


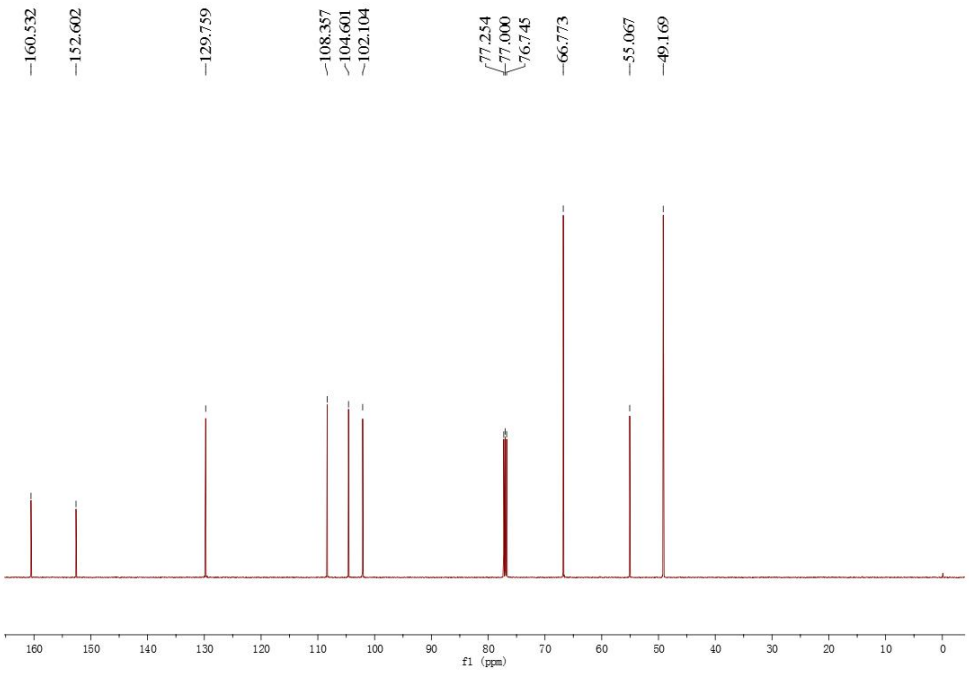
(1) P. Huang, Y.-X. Wang, H.-F. Yu and J.-M. Lu, *Organometallics,* 2014, **33**, 1587.

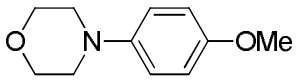


6b

Compound **6b**[1]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.18 (t, J = 8.0 Hz, 1H), 6.53-6.51 (m, 1H), 6.44-6.43 (m, 2H), 3.84 (t, J = 5.0 Hz, 4H), 3.78 (s, 3H), 3.13 (t, J = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.5, 152.6, 129.8, 108.4, 104.6, 102.1, 66.8, 55.1, 49.2.

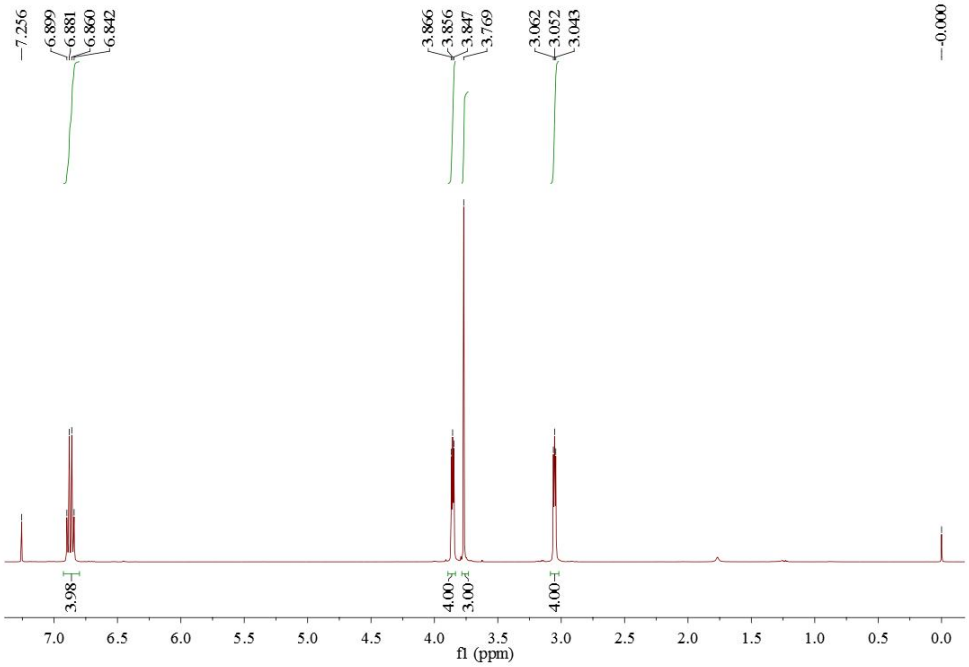


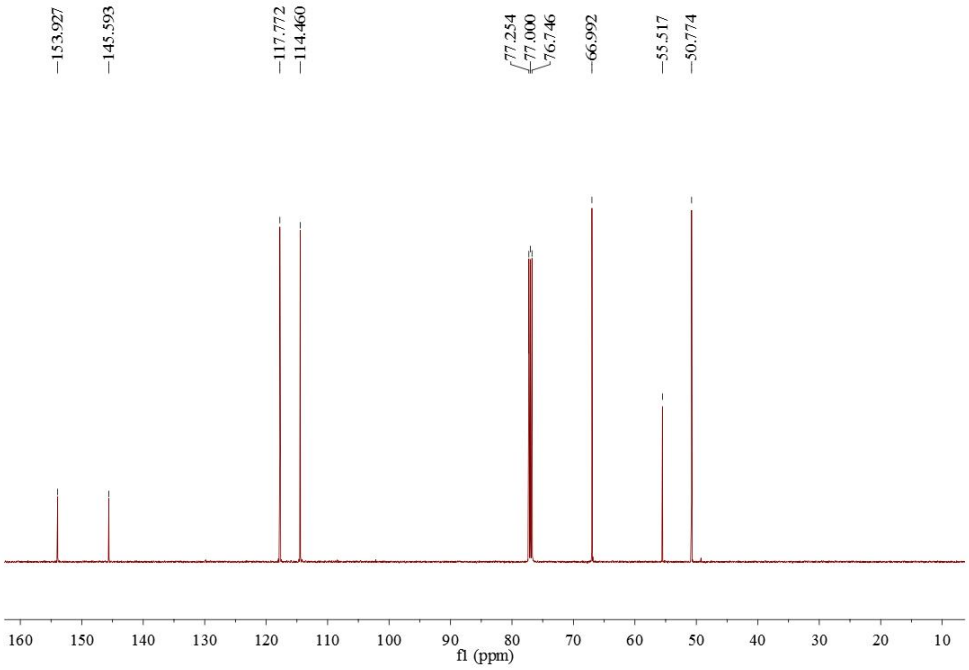


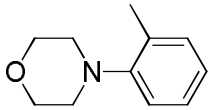


6c

Compound **6c**[1]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 6.89 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 3.86 (t, J = 5.0 Hz, 4H), 3.77 (s, 3H), 3.05 (t, J = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.9, 145.6, 117.8, 114.5, 67.0, 55.5, 50.8.

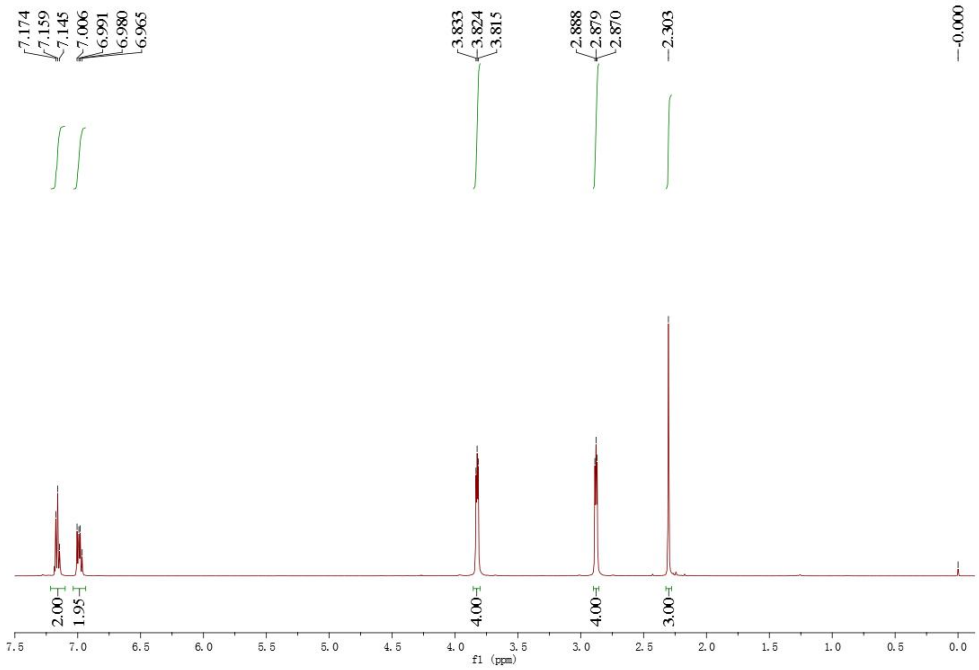


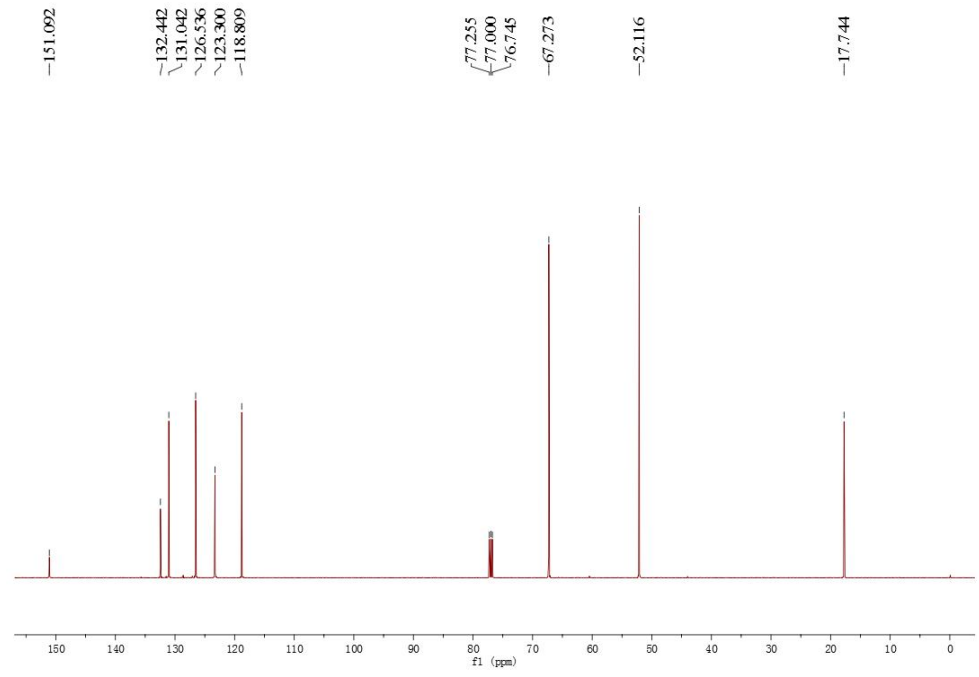


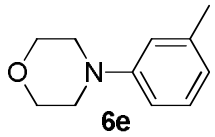


6d

Compound **6d**[1]: colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.16 (t, J = 8.0 Hz, 2H), 7.01-6.97 (m, 2H), 3.82 (t, J = 4.5 Hz, 4H), 2.88 (t, J = 4.5 Hz, 4H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.1, 132.4, 131.0, 126.5, 123.3, 118.8, 67.3, 52.1, 17.7.

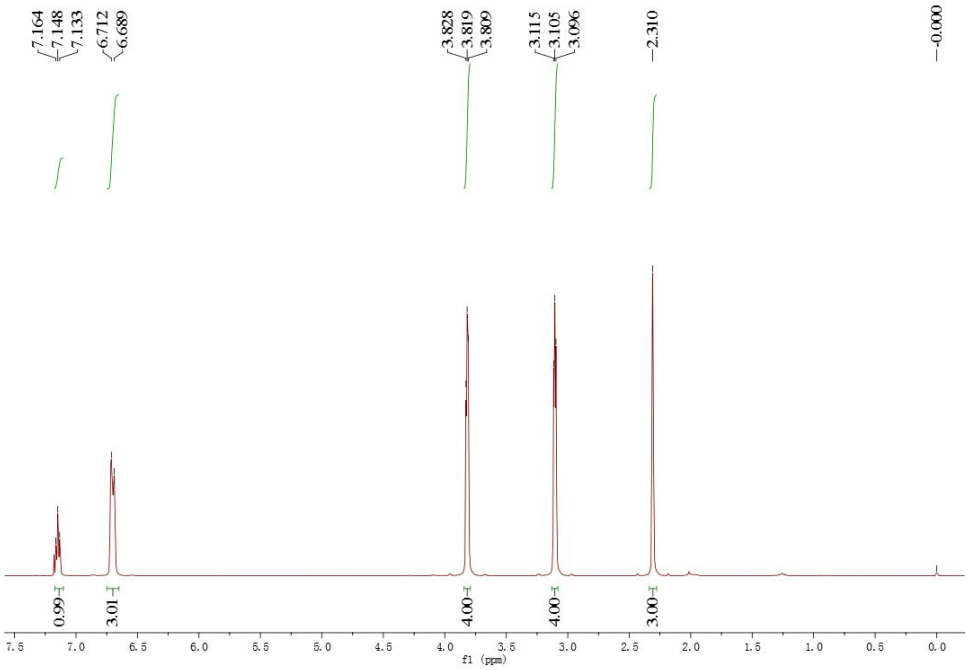


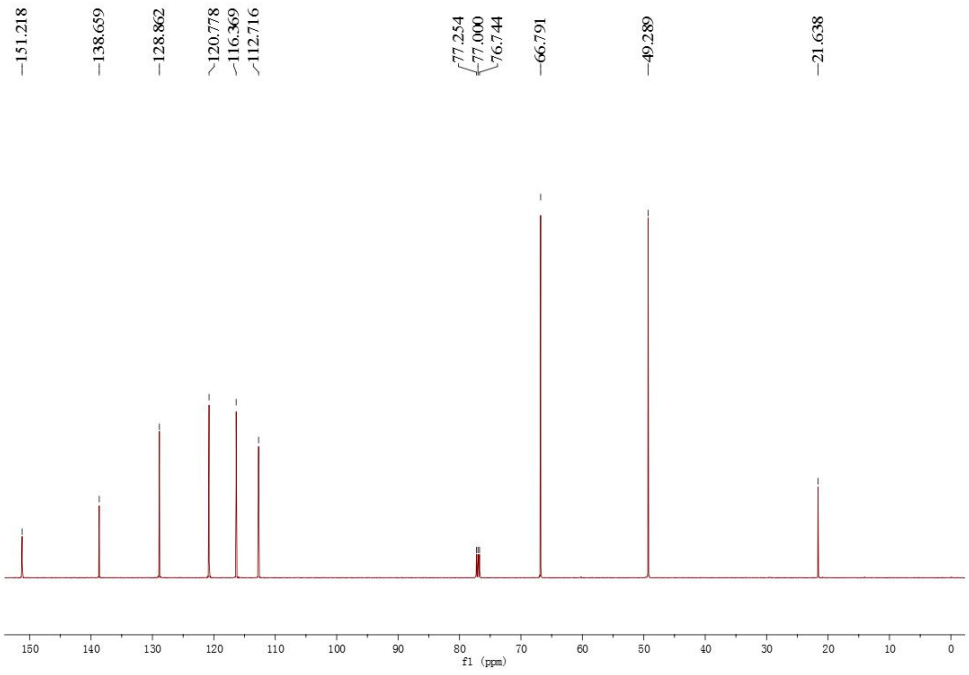


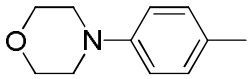


6e

Compound **6e**[1]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.16-7.13 (m, 1H), 6.71-6.69 (m, 3H), 3.82 (t, J = 5.0 Hz, 4H), 3.11 (t, J = 5.0 Hz, 4H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.2, 138.7, 128.9, 120.8, 116.4, 112.7, 66.8, 49.3, 21.6.

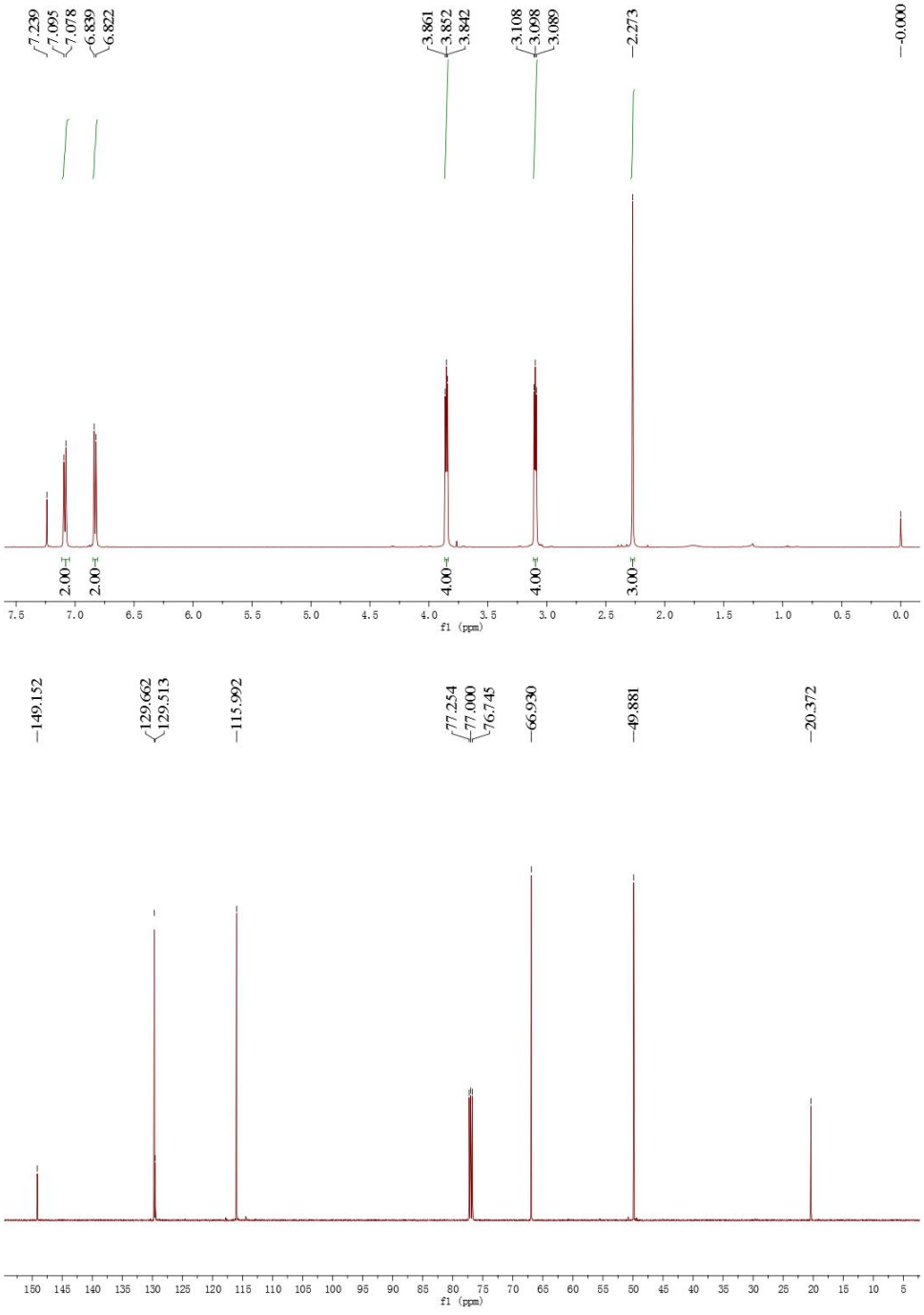


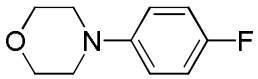




6f

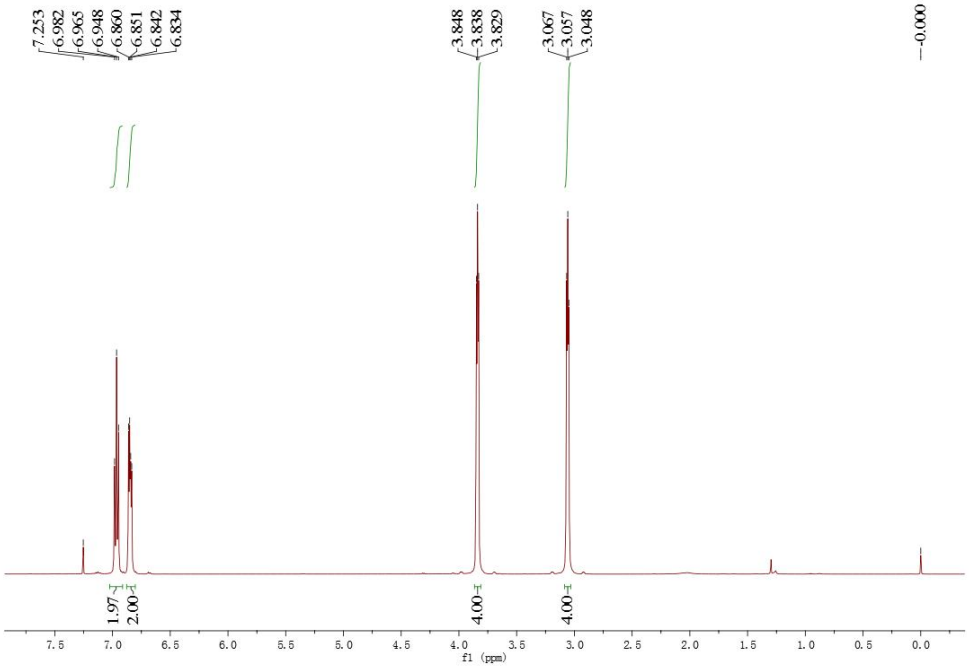
Compound **6f**[l]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.85 (t, *J* = 5.0 Hz, 4H), 3.10 (t, *J* = 5.0 Hz, 4H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.2, 129.7, 129.5, 116.0, 66.9, 49.9, 20.4.

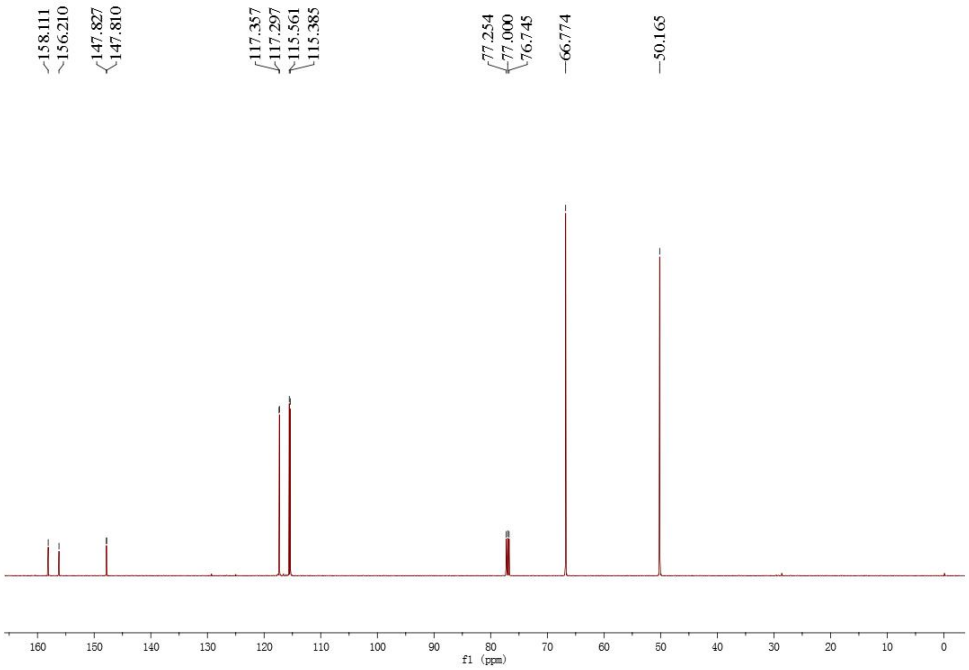


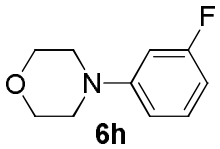


6g

Compound **6g**[1]: colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 6.97 (t, J = 8.5 Hz, 2H), 6.85 (dd, J = 8.5, 4.0 Hz, 2H), 3.84 (t, J = 5.0 Hz, 4H), 3.06 (t, J = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.2 (d, $J_{C\text{-}F}$ = 237.625 Hz), 147.8 (d, $J_{C\text{-}F}$ = 2.125 Hz), 117.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 115.5 (d, $J_{C\text{-}F}$ = 22 Hz), 66.8, 50.2.

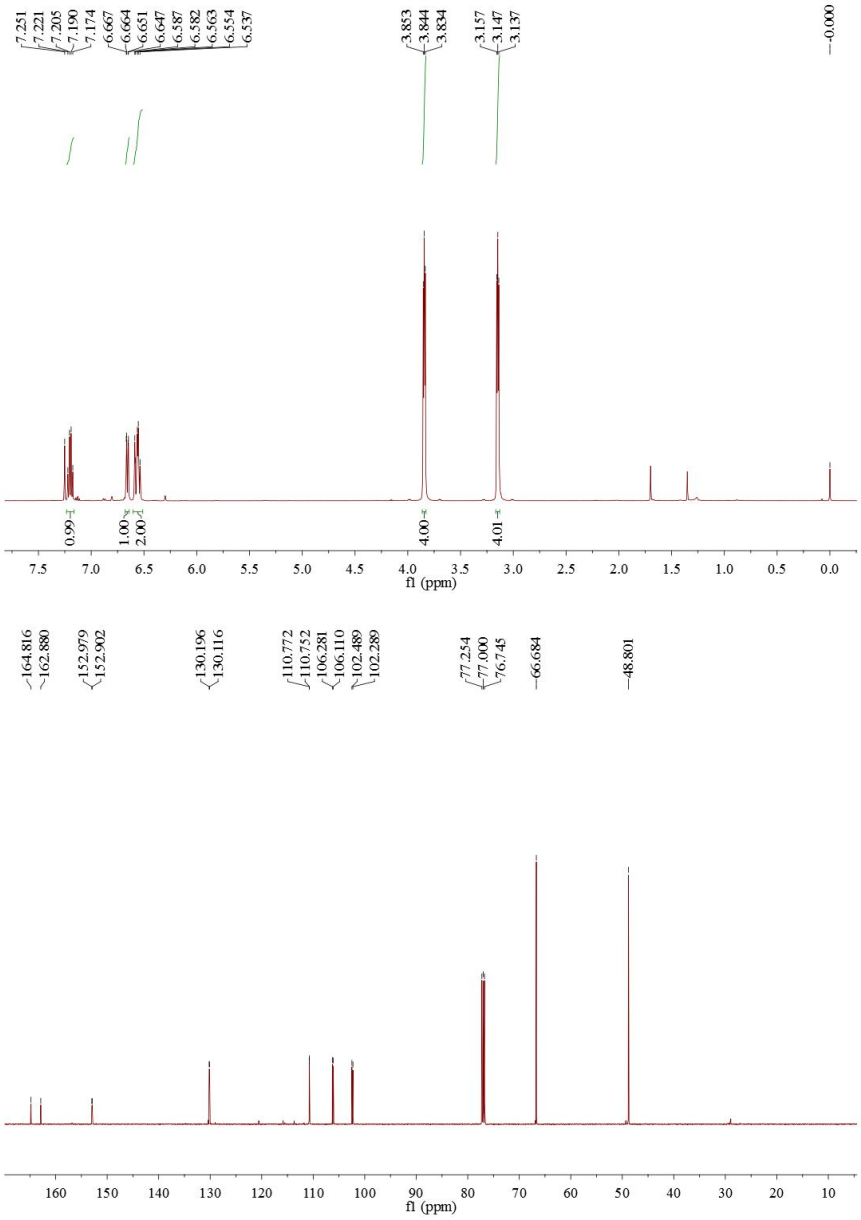




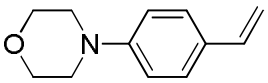


6h

Compound **6h**[2]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.20 (dd, J = 10.5, 8.0 Hz, 1H), 6.66 (dd, J = 8.0, 2.0 Hz, 1H), 6.59-6.54 (m, 2H), 3.84 (t, J = 5.0 Hz, 4H), 3.15 (t, J = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.8 (d, $J_{C\text{-}F}$ = 242.0 Hz), 152.9 (d, $J_{C\text{-}F}$ = 9.625 Hz), 130.2 (d, $J_{C\text{-}F}$ = 10.0 Hz), 110.8 (d, $J_{C\text{-}F}$ = 2.5Hz), 106.2 (d, $J_{C\text{-}F}$ = 21.375 Hz), 102.4 (d, $J_{C\text{-}F}$ = 25.0 Hz), 66.7, 48.8.

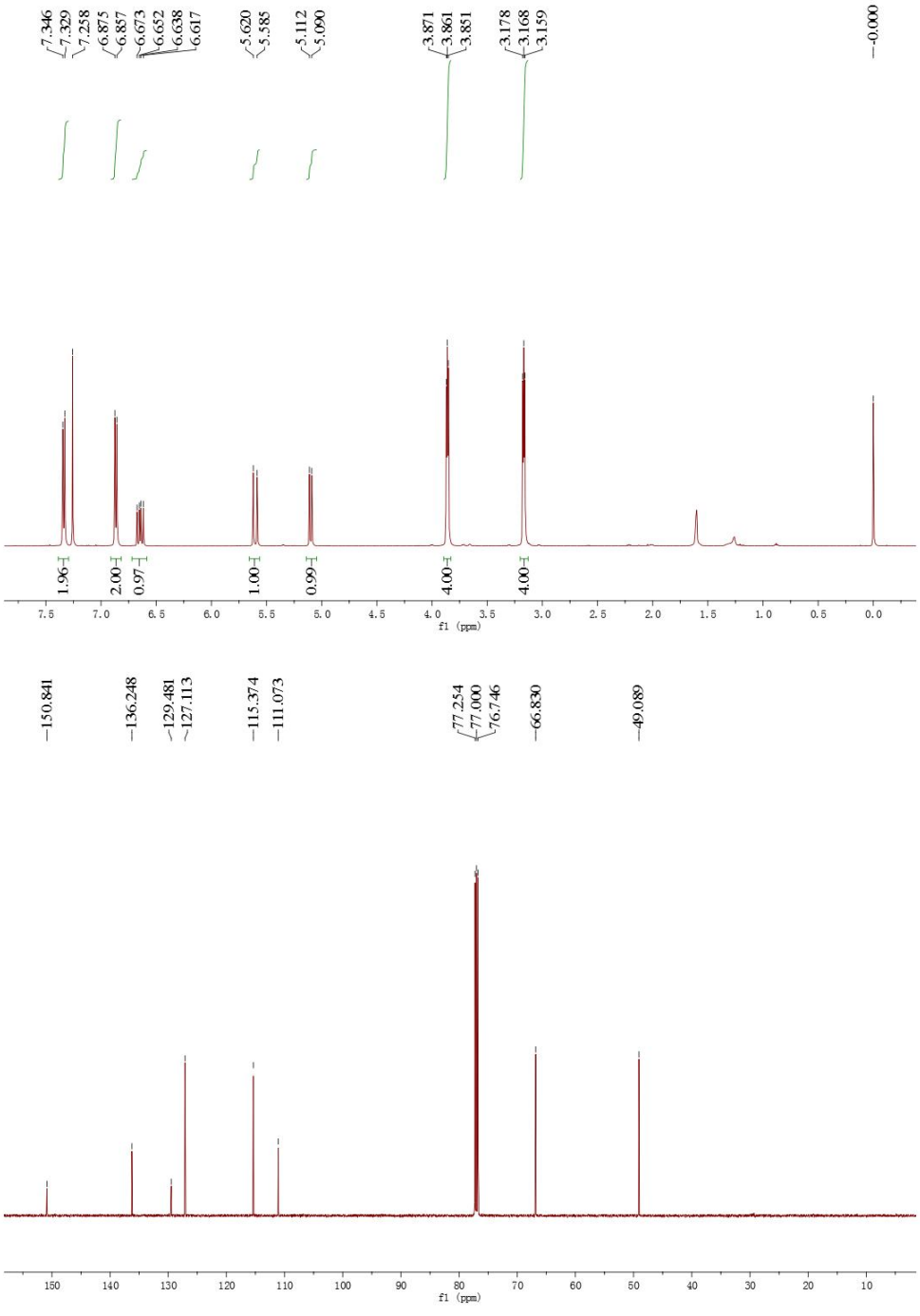


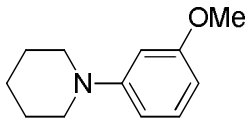
(2) H. G. Lee, P. J. Phillip and S. L. Buchwald, *J. Am. Chem. Soc.*, 2014, **136**, 3792.



6i

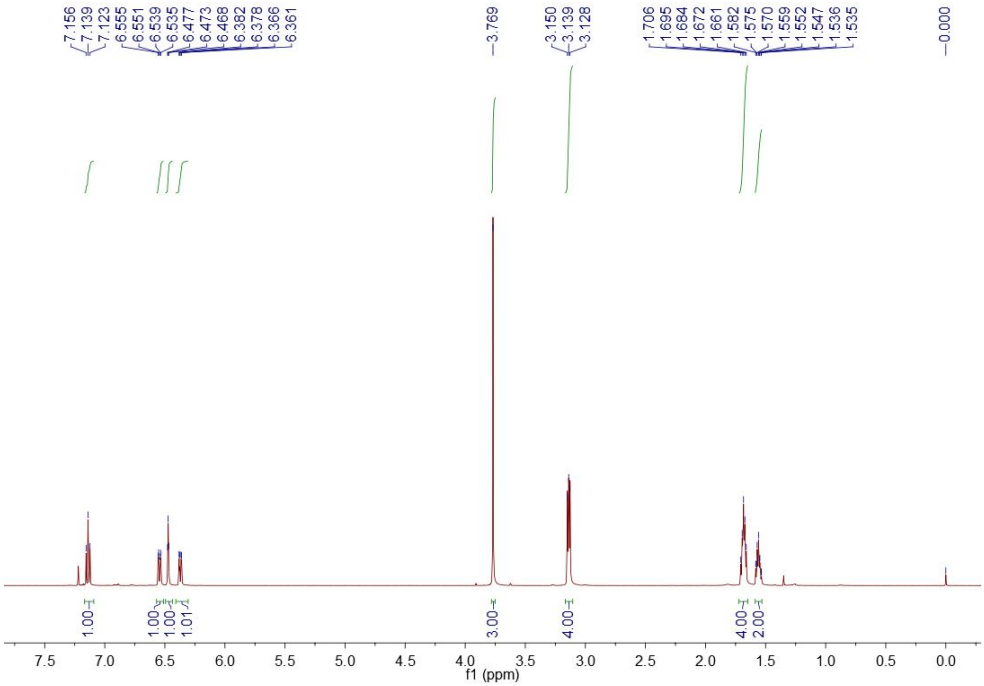
Compound **6i**[1]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.65 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.60 (d, *J* = 17.5 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 3.86 (t, *J* = 5.0 Hz, 4H), 3.17 (t, *J* = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.8, 136.2, 129.5, 127.1, 115.4, 111.1, 66.8, 49.1.

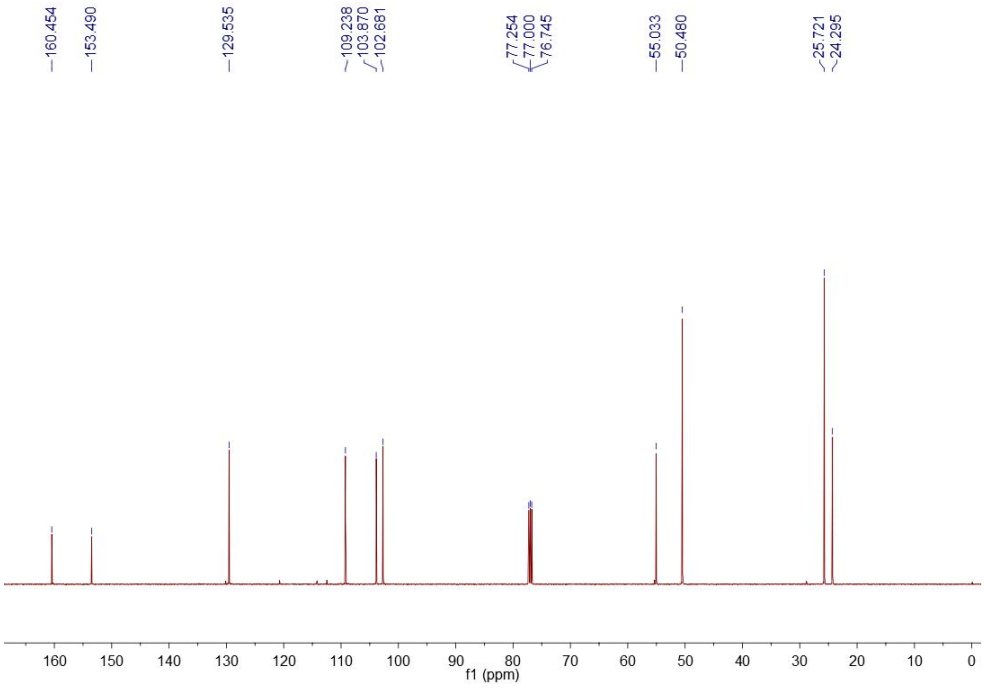


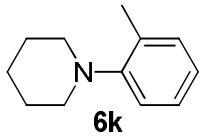


6j

Compound **6j**[1]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.14 (t, J = 8.0 Hz, 1H), 6.55 (dd, J = 8.0, 2.0 Hz, 1H), 6.47 (t, J = 2.0 Hz, 1H), 6.37 (dd, J = 8.0, 2.0 Hz, 1H), 3.77 (s, 3H), 3.14 (t, J = 5.5 Hz, 4H), 1.71-1.66 (m, 4H), 1.58-1.54 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.5, 153.5, 129.5, 109.2, 103.9, 102.7, 55.0, 50.5, 25.7, 24.3.

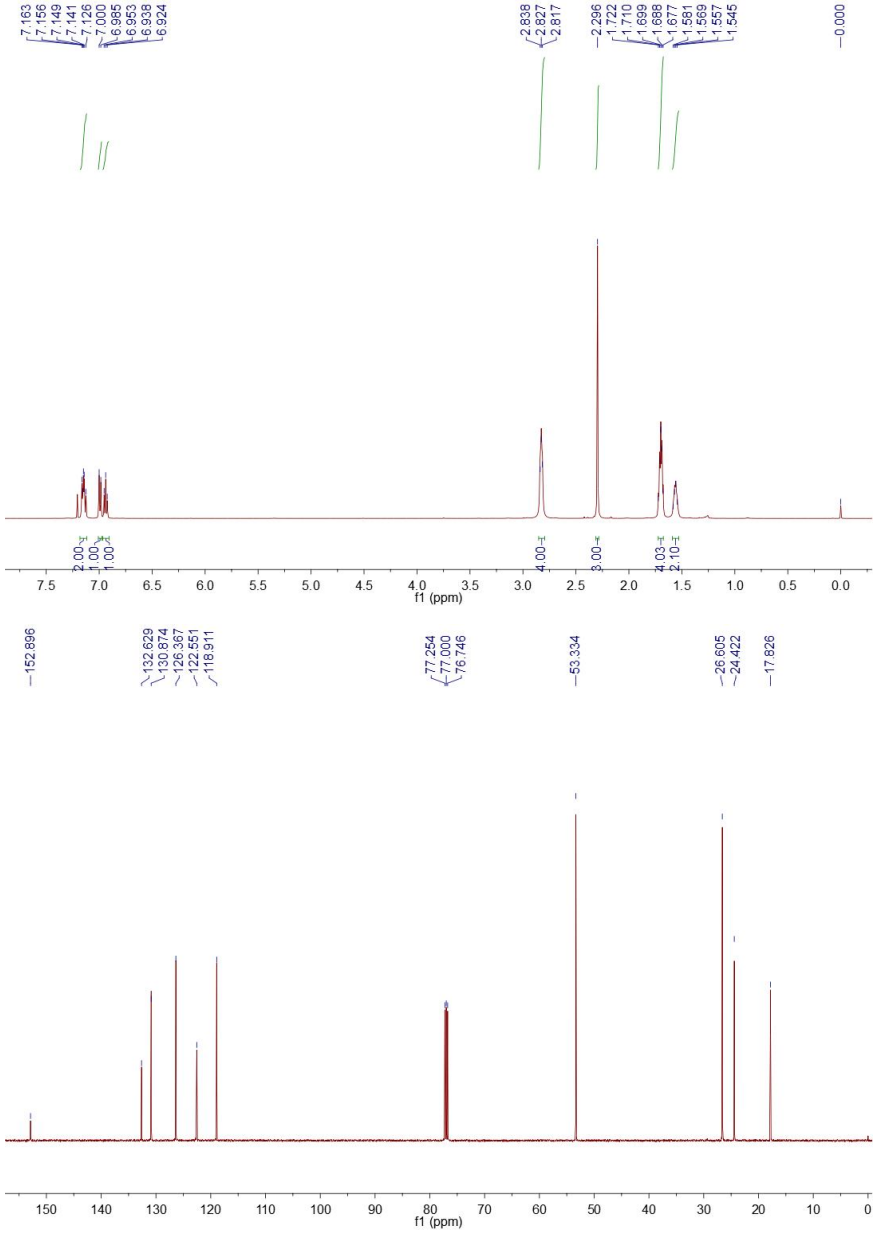




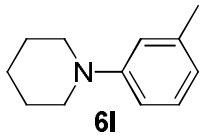


6k

Compound **6k**[3]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.16-7.13 (m, 2H), 6.99 (d, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 2.83 (t, J = 5.5 Hz, 4H), 2.30 (s, 3H), 1.72-1.68 (m, 4H), 1.58-1.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.9, 132.6, 130.9, 126.4, 122.6, 118.9, 53.3, 26.6, 24.4, 17.8.

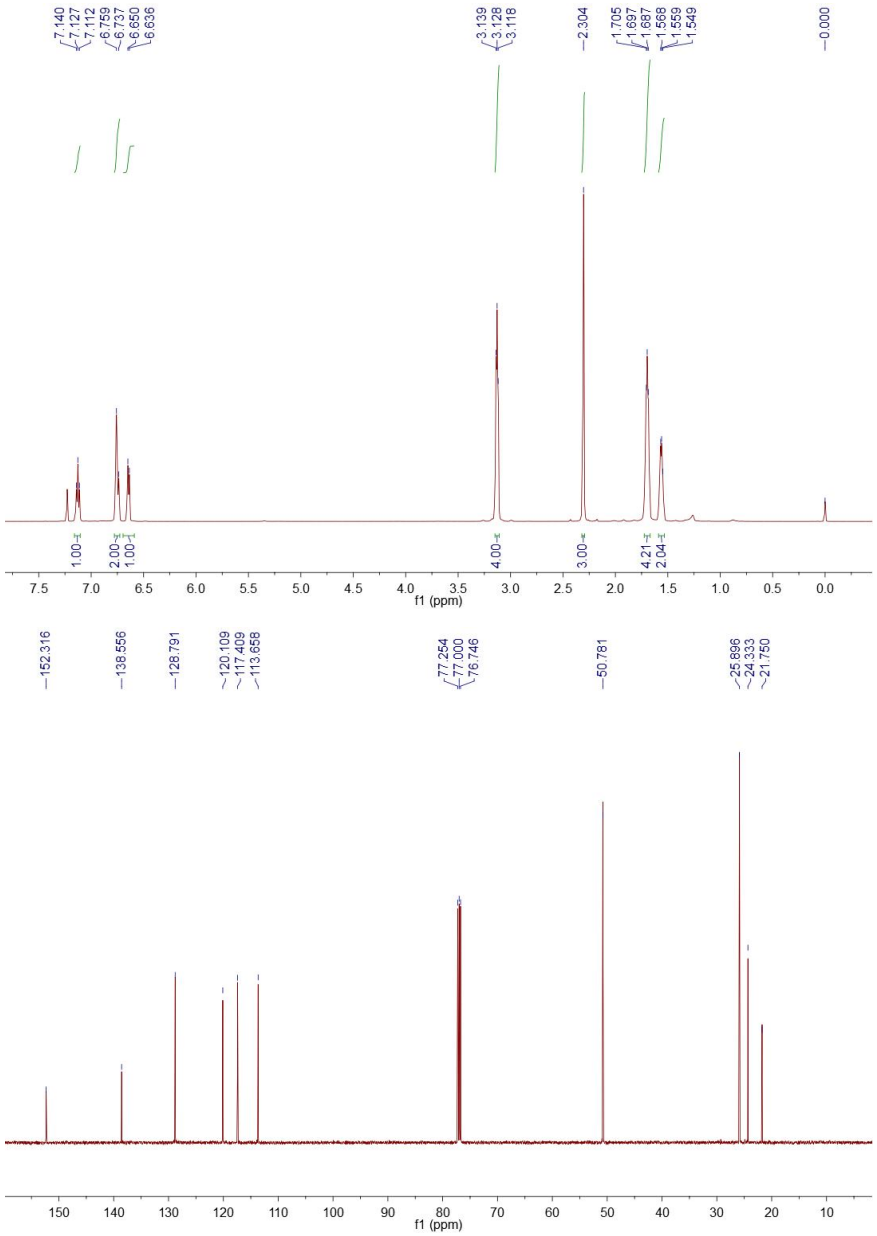


(3) D. Gerristma, T. Brenstrum, J. McNulty and A. Capretta, *Tetrahedron Lett.*, 2004, **45**, 8319.

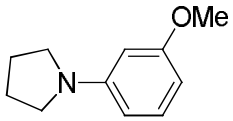


6l

Compound **6l**[4]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.13 (t, J = 7.5 Hz, 1H), 6.76-6.74 (m, 2H), 6.64 (d, J = 7.0 Hz, 1H), 3.13 (t, J = 5.0 Hz, 4H), 2.30 (s, 3H), 1.71-1.69 (m, 4H), 1.57-1.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.3, 138.6, 128.8, 120.1, 117.4, 113.7, 50.8, 25.9, 24.3, 21.8.

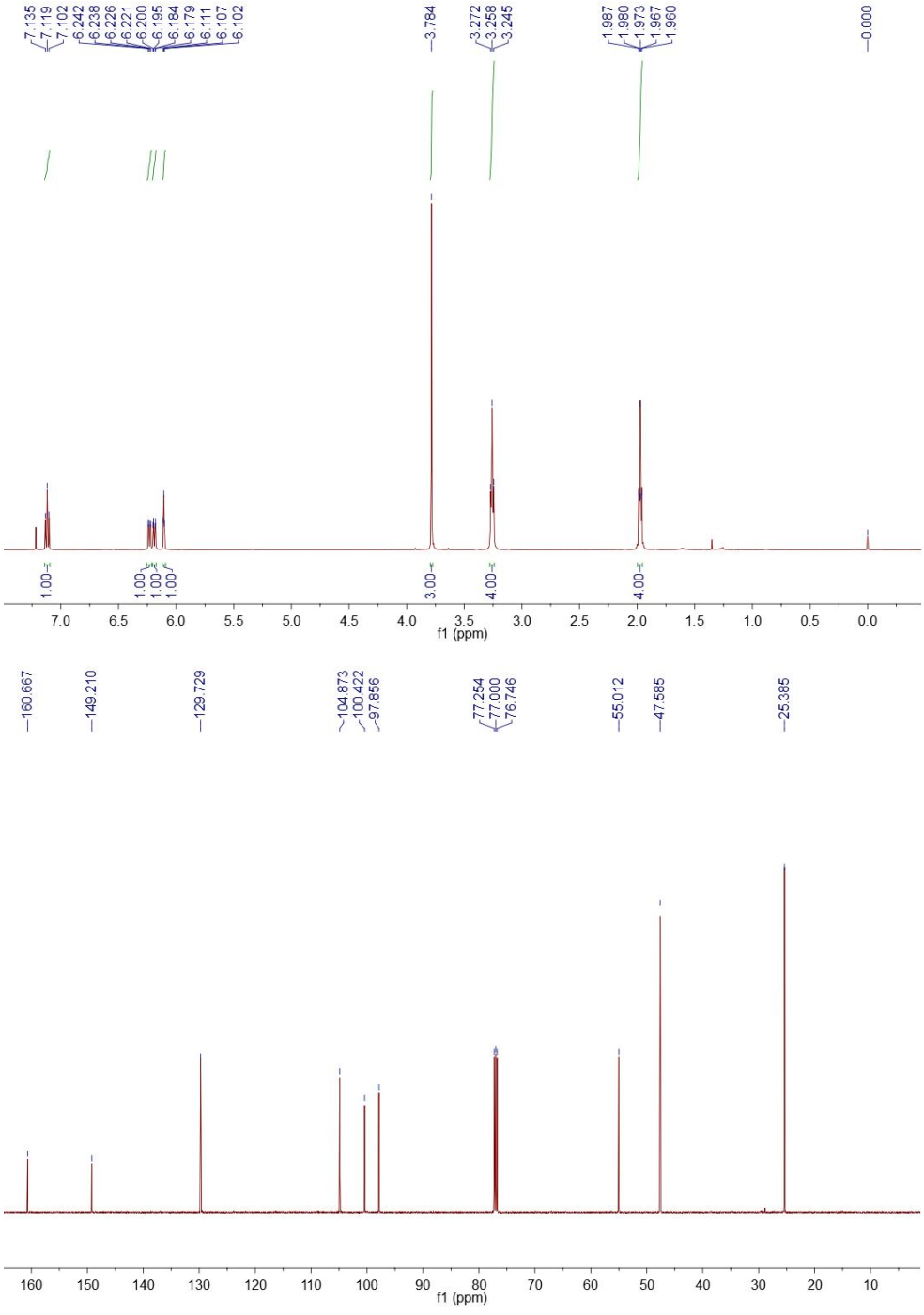


(4) B. Lv, P.-B. Li, C.-L. Fu, L.-Q. Xue, Z.-Y. Lin and S.-M. Ma, *Adv. Synth. Catal.*, 2011, **353**, 100.

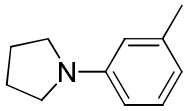


6m

Compound **6m**[5]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.12 (t, J = 8.5 Hz, 1H), 6.23 (dd, J = 8.5, 2.0 Hz, 1H), 6.19 (dd, J = 8.5, 2.0 Hz, 1H), 6.11 (t, J = 2.0 Hz, 1H), 3.78 (s, 3H), 3.26 (t, J = 7.0 Hz, 4H), 1.99-1.96 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.7, 149.2, 129.7, 104.9, 100.4, 97.9, 55.0, 47.6, 25.4.

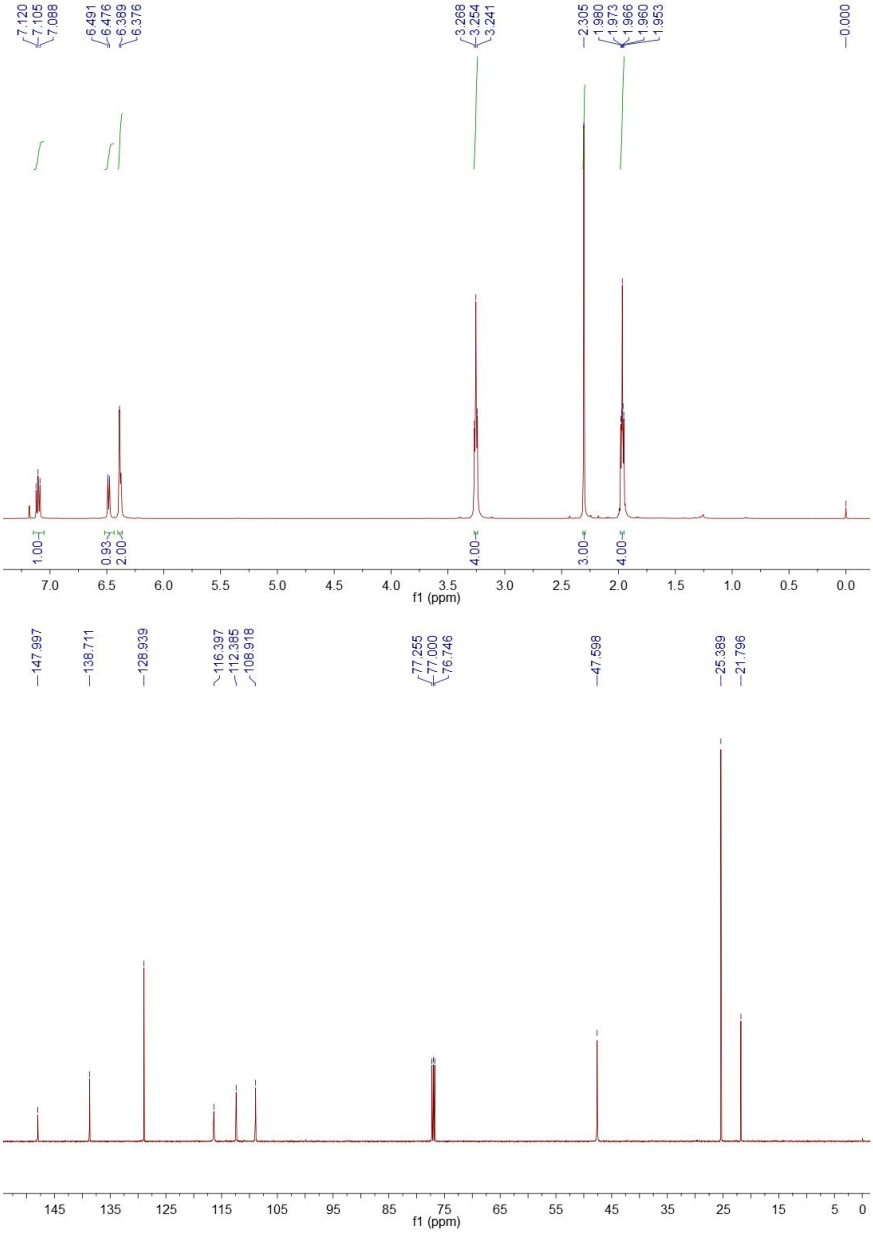


(5) L. Zhu, T.-T. Gao and L.-X. Shao, *Tetrahedron*, 2011, **67**, 5150.

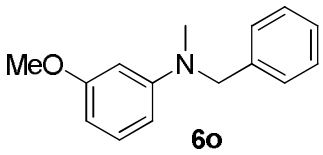


6n

Compound **6n**[6]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.11 (t, J = 7.5 Hz, 1H), 6.48 (d, J = 7.5 Hz, 1H), 6.39-6.38 (m, 2H), 3.25 (t, J = 7.0 Hz, 4H), 2.31 (s, 3H), 1.98-1.95 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.0, 138.7, 128.9, 116.4, 112.4, 108.9, 47.6, 25.4, 21.8.

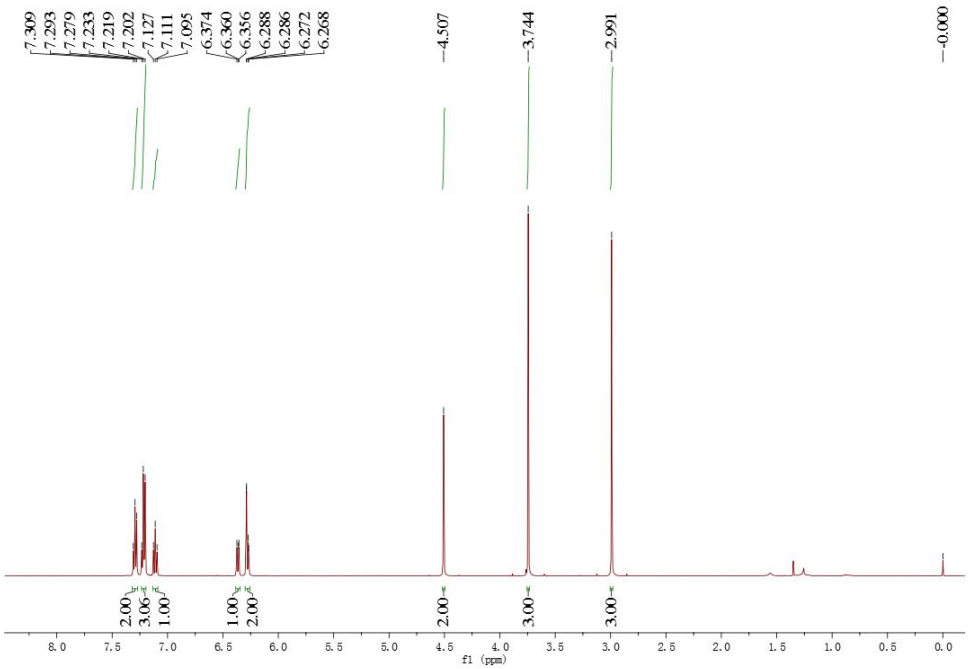


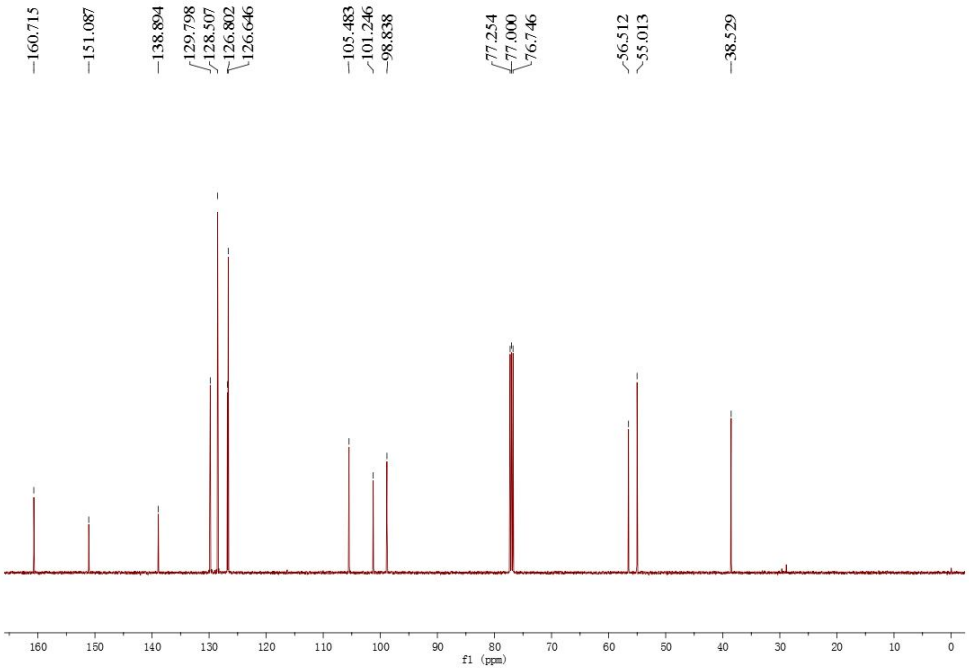
(6) B. Xu, M.-L. Li, X.-D. Zuo, S.-F. Zhu and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 8700.

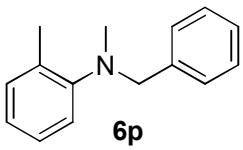


6o

Compound **6o**[5]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23-7.20 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.36 (t, *J* = 7.0 Hz, 1H), 6.29-6.27 (m, 2H), 4.51 (s, 2H), 3.74 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.7, 151.1, 138.9, 129.8, 128.5, 126.8, 126.6, 105.5, 101.2, 98.8, 56.5, 55.0, 38.5.

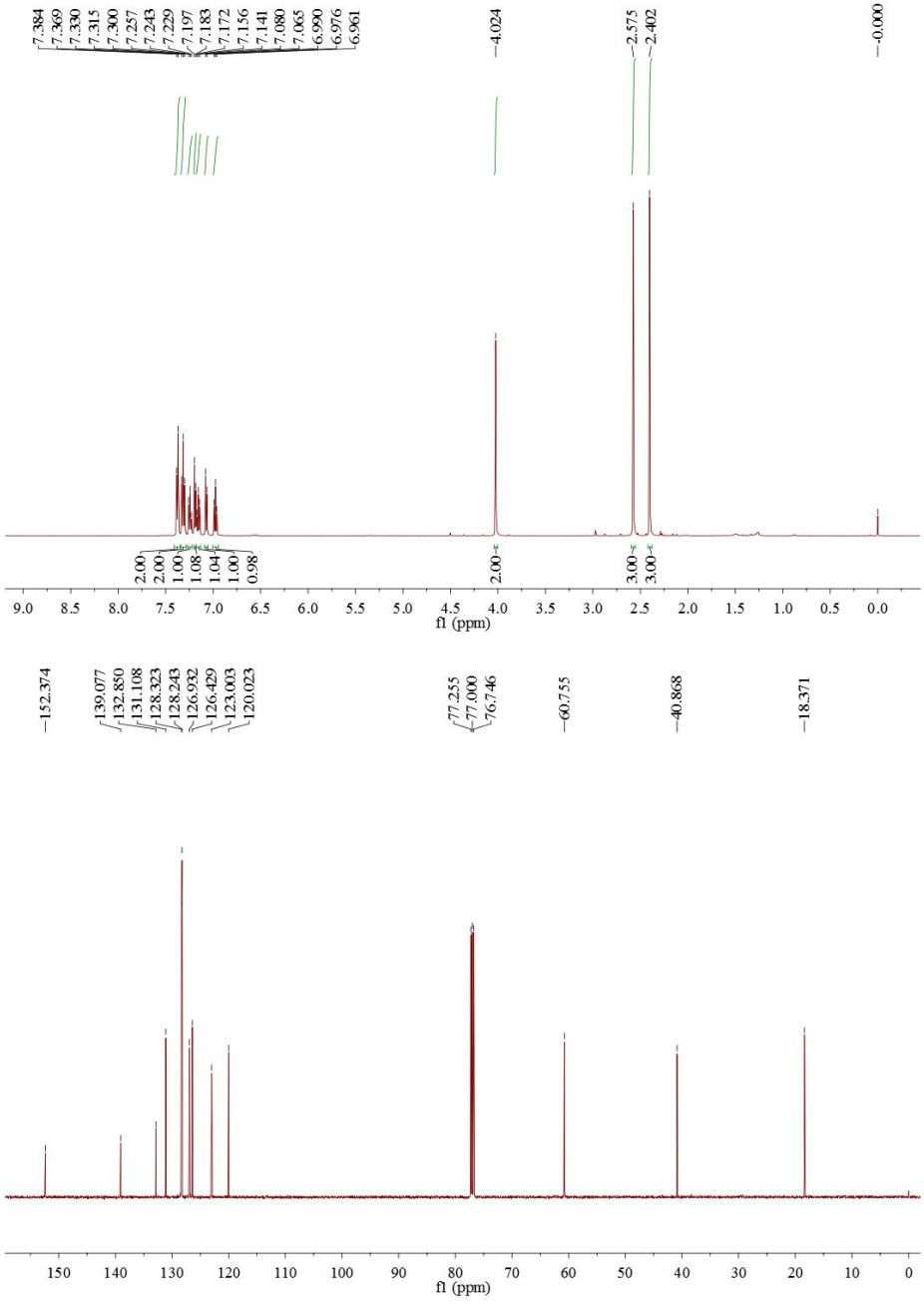




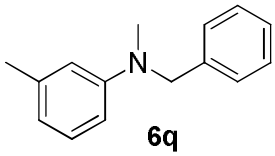


6p

Compound **6p**[7]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.02 (s, 2H), 2.58 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.4, 139.1, 132.9, 131.1, 128.3, 128.2, 126.9, 126.4, 123.0, 120.0, 60.8, 40.9, 18.4.

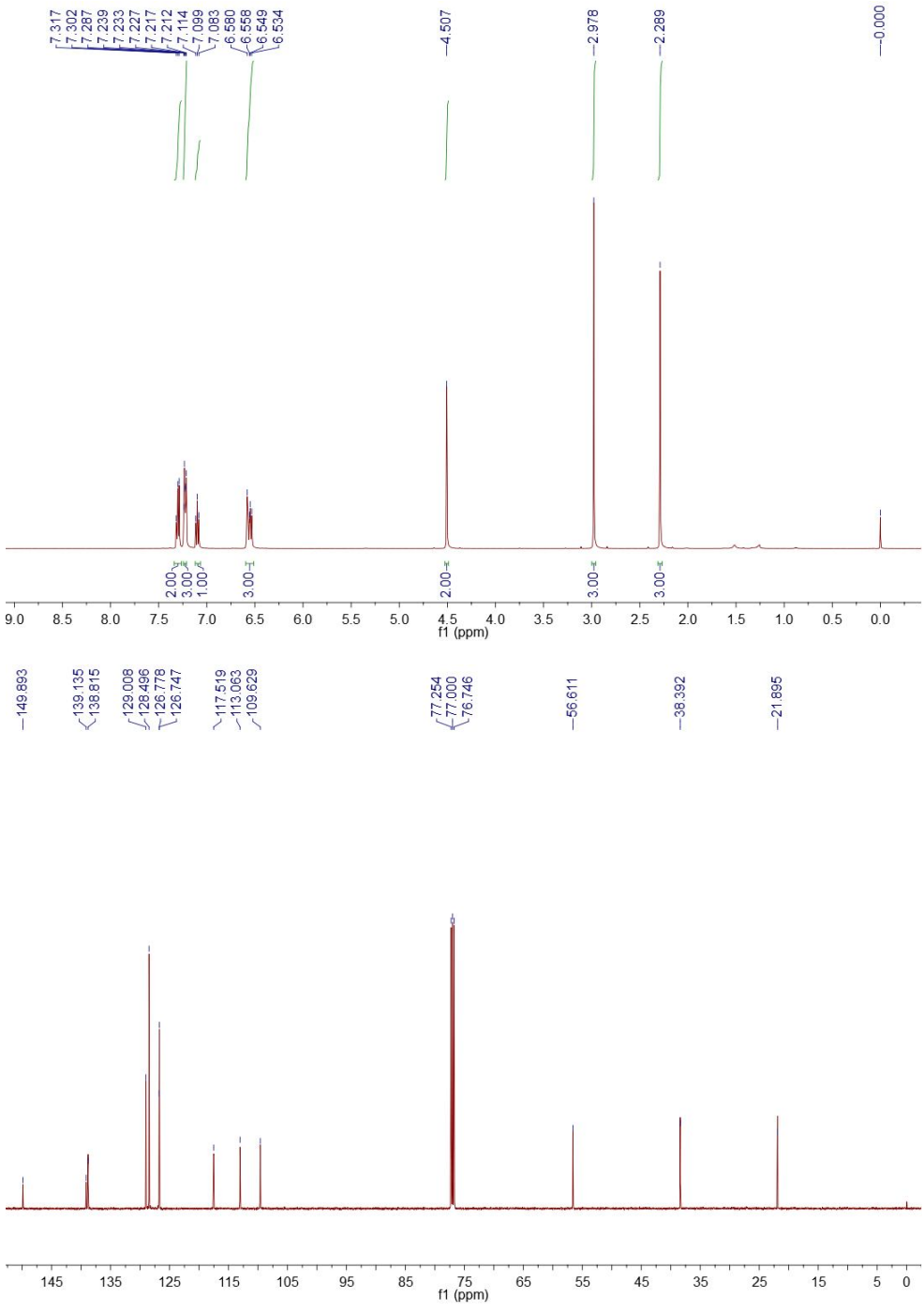


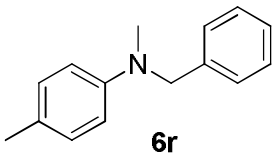
(7) G.-D. Roiban, G. Mehler and M. T. Reetz, *Eur. J. Org. Chem.*, 2014, 2070.



6q

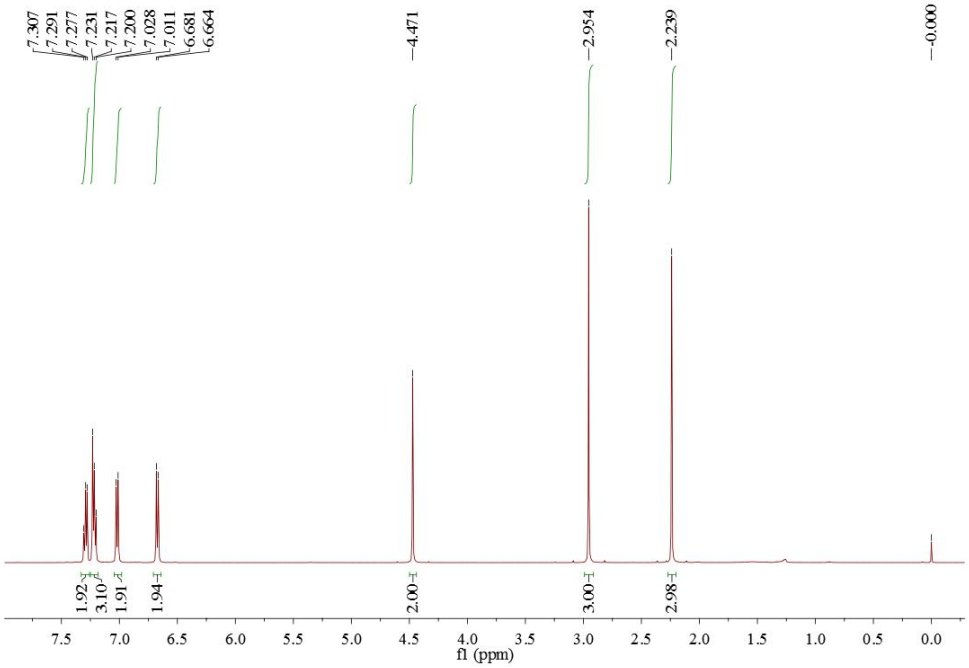
Compound **6q**[1]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.24-7.21 (m, 3H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.58-6.53 (m, 3H), 4.51 (s, 2H), 2.98 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.9, 139.1, 138.8, 129.0, 128.5, 126.8, 126.7, 117.5, 113.1, 109.6, 56.6, 38.4, 21.9.

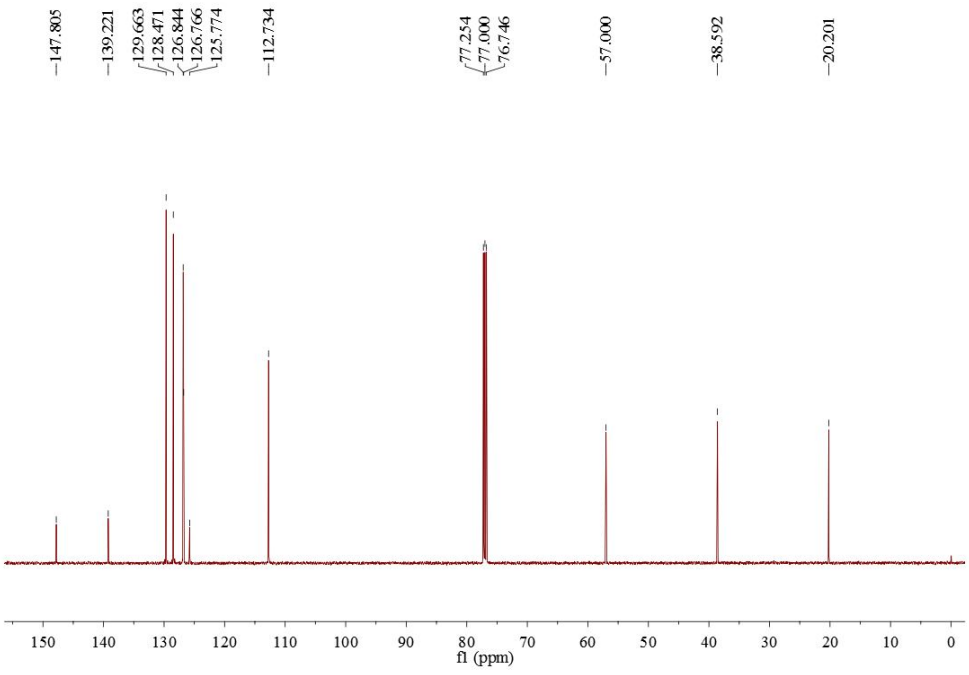


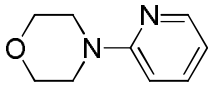


6r

Compound **6r**[1]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.29 (t, *J* = 8.0 Hz, 2H), 7.23-7.20 (m, 3H), 7.02 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 4.47 (s, 2H), 2.95 (s, 3H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.8, 139.2, 129.7, 128.5, 126.84, 126.77, 125.8, 112.7, 57.0, 38.6, 20.2.

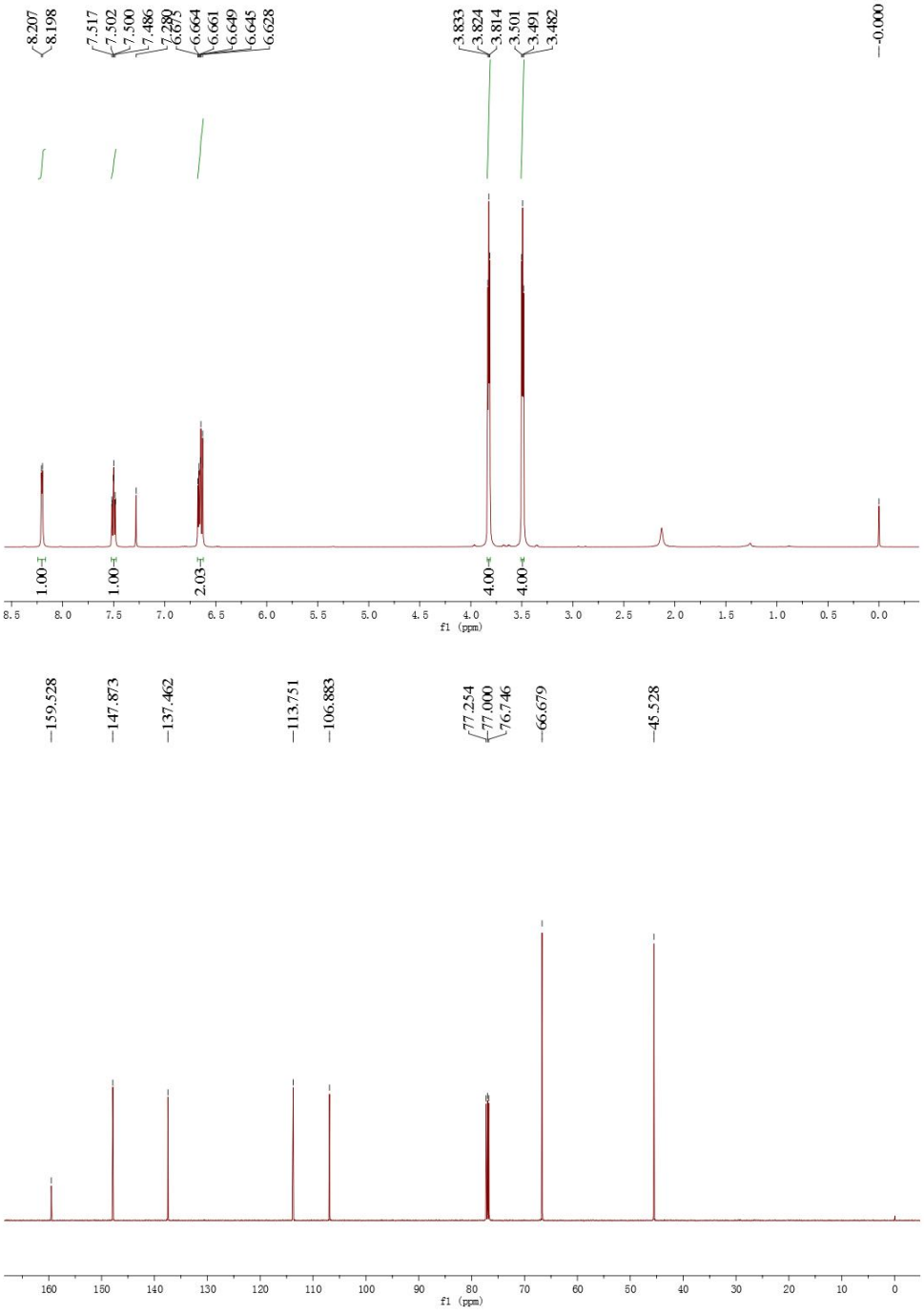


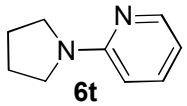




6s

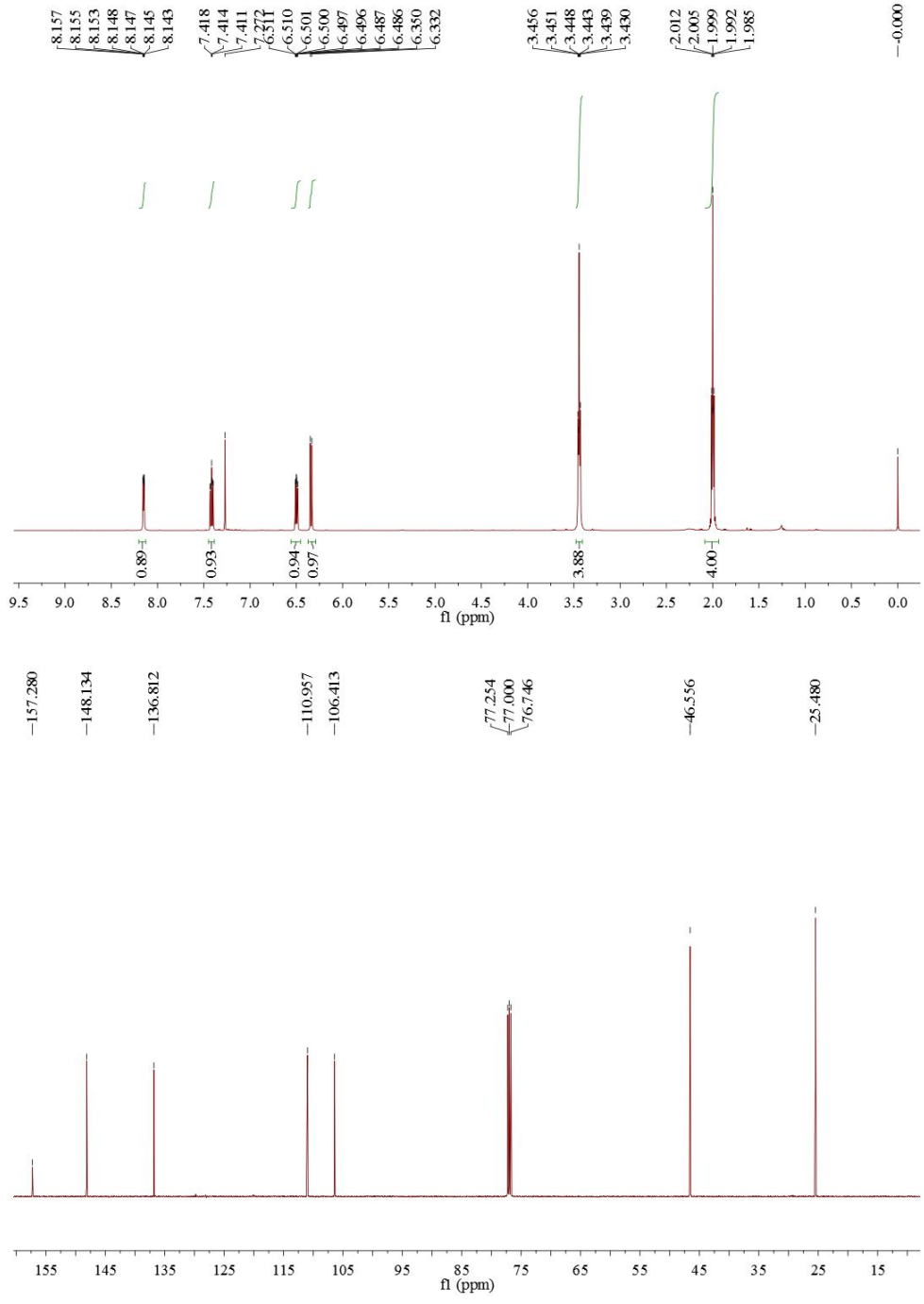
Compound **6s**[1]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 8.20 (d, *J* = 4.5 Hz, 1H), 7.50 (td, *J* = 8.0, 2.0 Hz, 1H), 6.68-6.63 (m, 2H), 3.82 (t, *J* = 5.0 Hz, 4H), 3.49 (t, *J* = 5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.5, 147.9, 137.5, 113.8, 106.9, 66.7, 45.5.



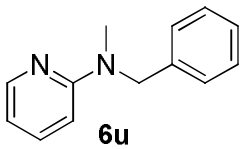


6t

Compound **6t**[8]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 8.16-8.14 (m, 1H), 7.43-7.40 (m, 1H), 6.51-6.49 (m, 1H), 6.34 (d, *J* = 9.0 Hz, 1H), 3.46-3.43 (m, 4H), 2.01-1.99 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.3, 148.1, 136.8, 111.0, 106.4, 46.6, 25.5.

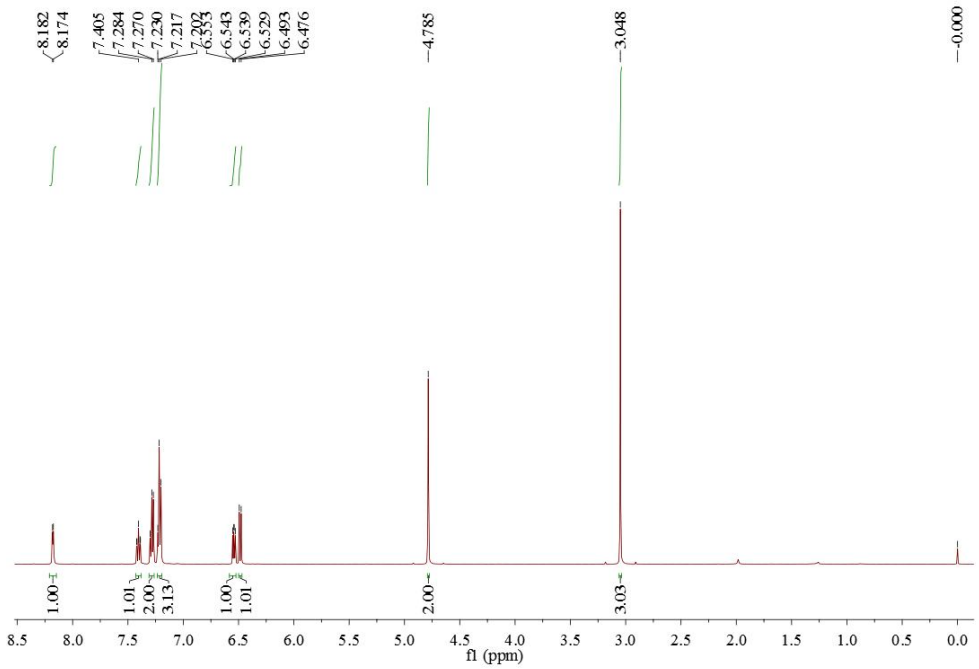


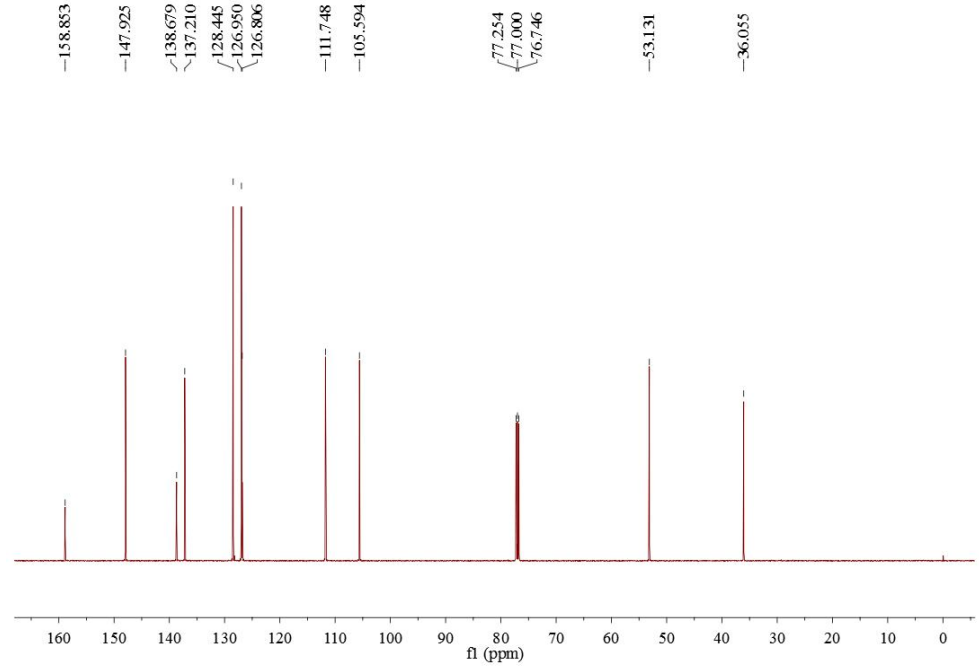
(8) Y. Zhang, X.-Y. Yang, Q.-Z. Yao and D.-W. Ma, *Org. Lett.*, 2012, **14**, 3056.

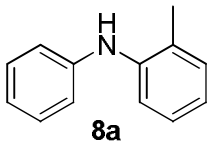


6u

Compound **6u**[1]: yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 8.18 (d, J = 4.0 Hz, 1H), 7.41 (td, J = 9.0, 2.0 Hz, 1H), 7.28 (t, J = 8.0 Hz, 2H), 7.23-7.20 (m, 3H), 6.54 (dd, J = 7.0, 5.0 Hz, 1H), 6.48 (d, J = 8.5 Hz, 1H), 4.79 (s, 2H), 3.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.9, 147.9, 138.7, 137.2, 128.4, 127.0, 126.8, 111.7, 105.6, 53.1, 36.1.

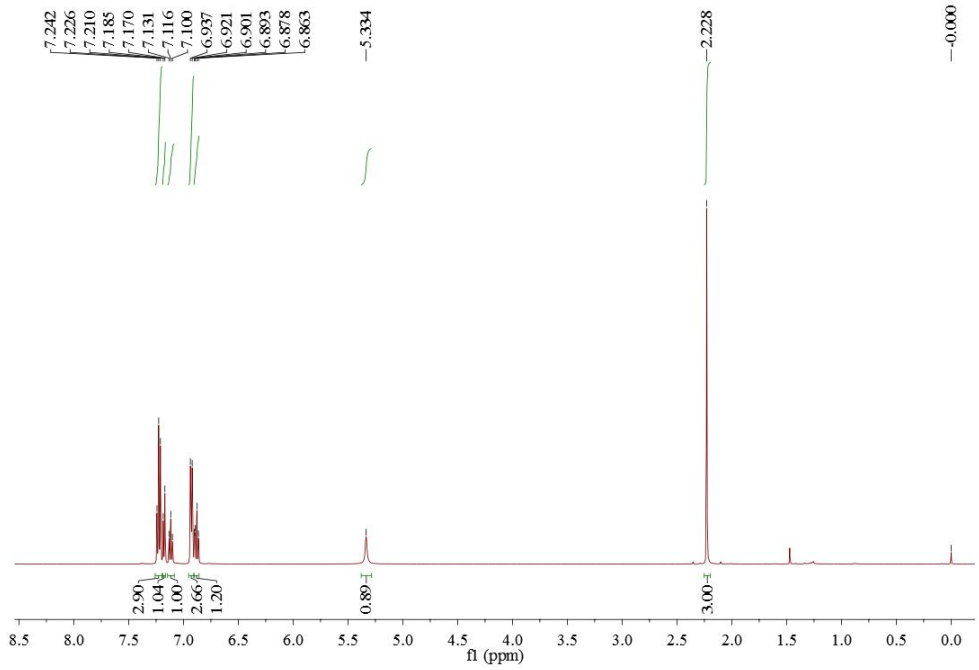


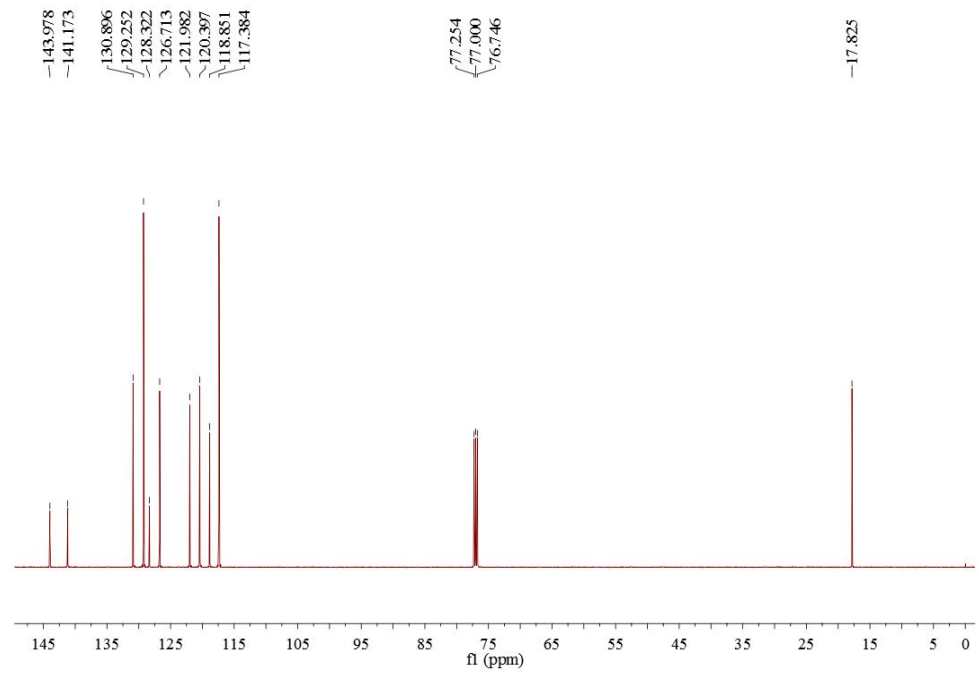


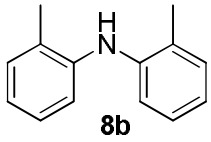


8a

Compound **8a**[1]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.23 (t, *J* = 8.0 Hz, 3H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 3H), 6.90-6.86 (m, 1H), 5.33 (br, 1H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.0, 141.2, 130.9, 129.3, 128.3, 126.7, 122.0, 120.4, 118.9, 117.4, 17.8.

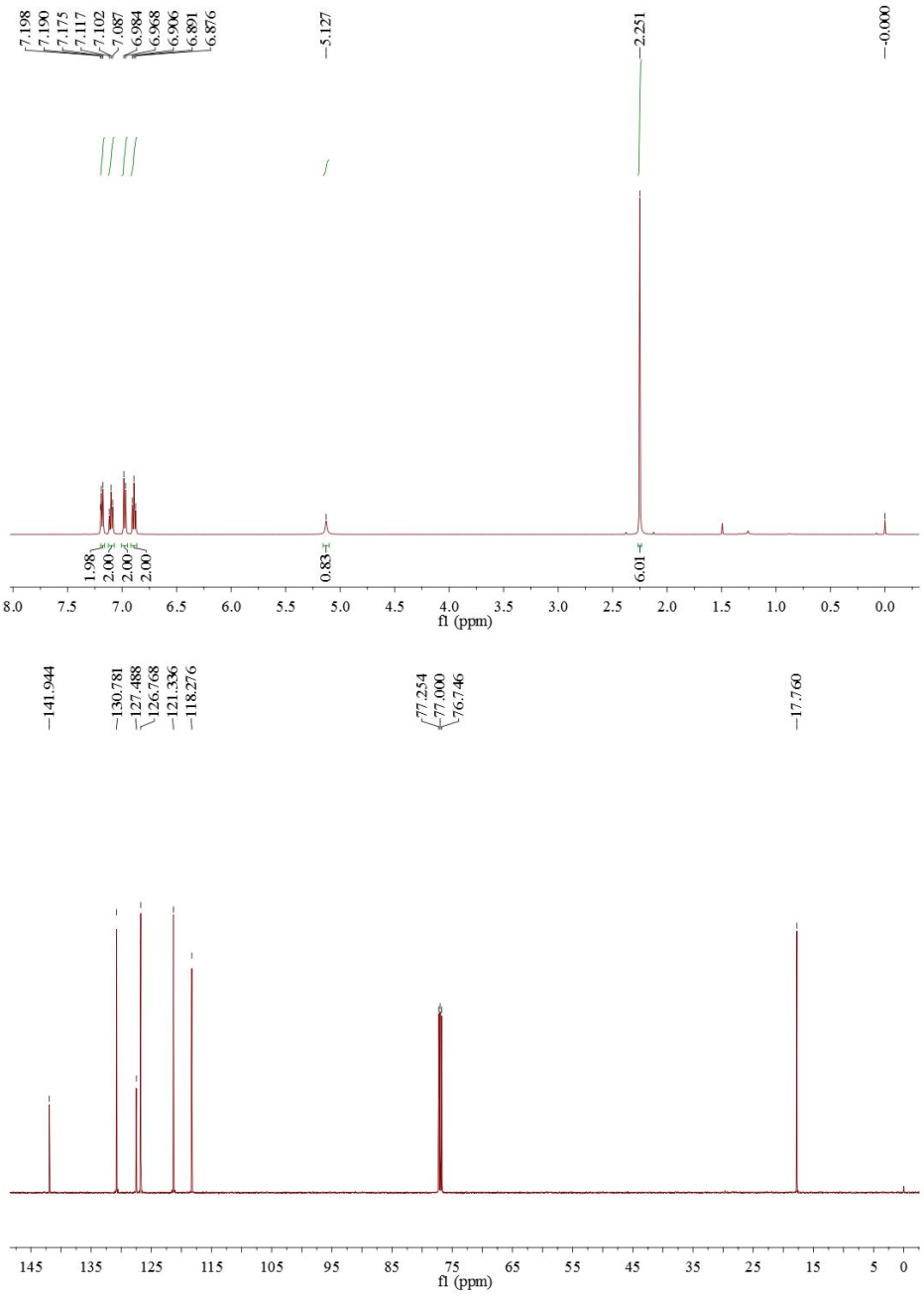




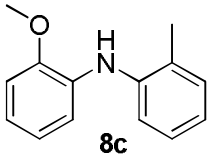


8b

Compound **8b**[9]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.18 (d, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.89 (t, J = 7.5 Hz, 2H), 5.13 (br, 1H), 2.25 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.9, 130.8, 127.5, 126.8, 121.3, 118.3, 17.8.

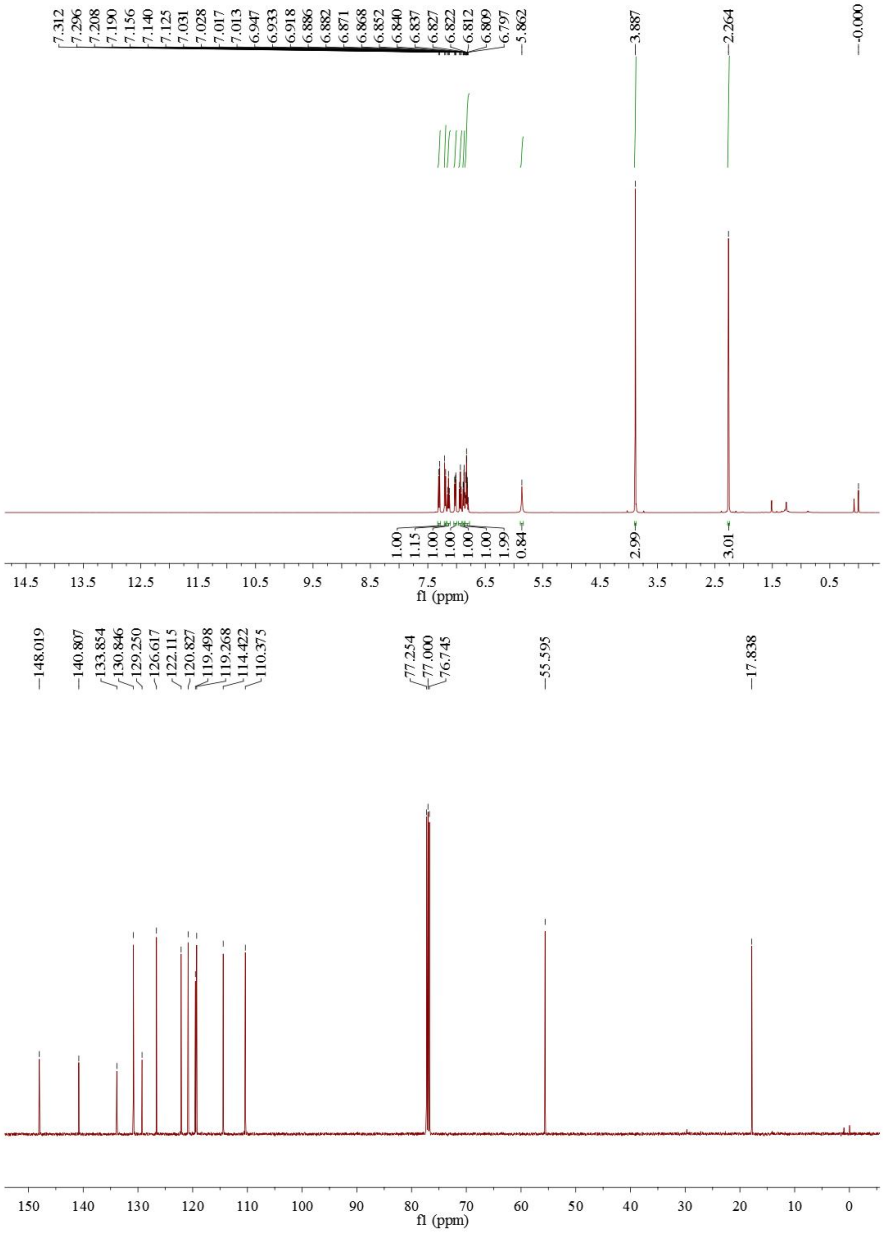


(9) H.-H. Huang and S. L. Buchwald, *Org. Lett.*, 2001, **3**, 3417.

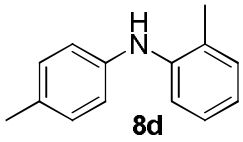


8c

Compound **8c**[10]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.02 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.92-6.87 (m, 1H), 6.85-6.80 (m, 2H), 5.86 (br, 1H), 3.89 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.0, 140.8, 133.9, 130.8, 129.3, 126.6, 122.1, 120.8, 119.5, 119.3, 114.4, 110.4, 55.6, 17.8.

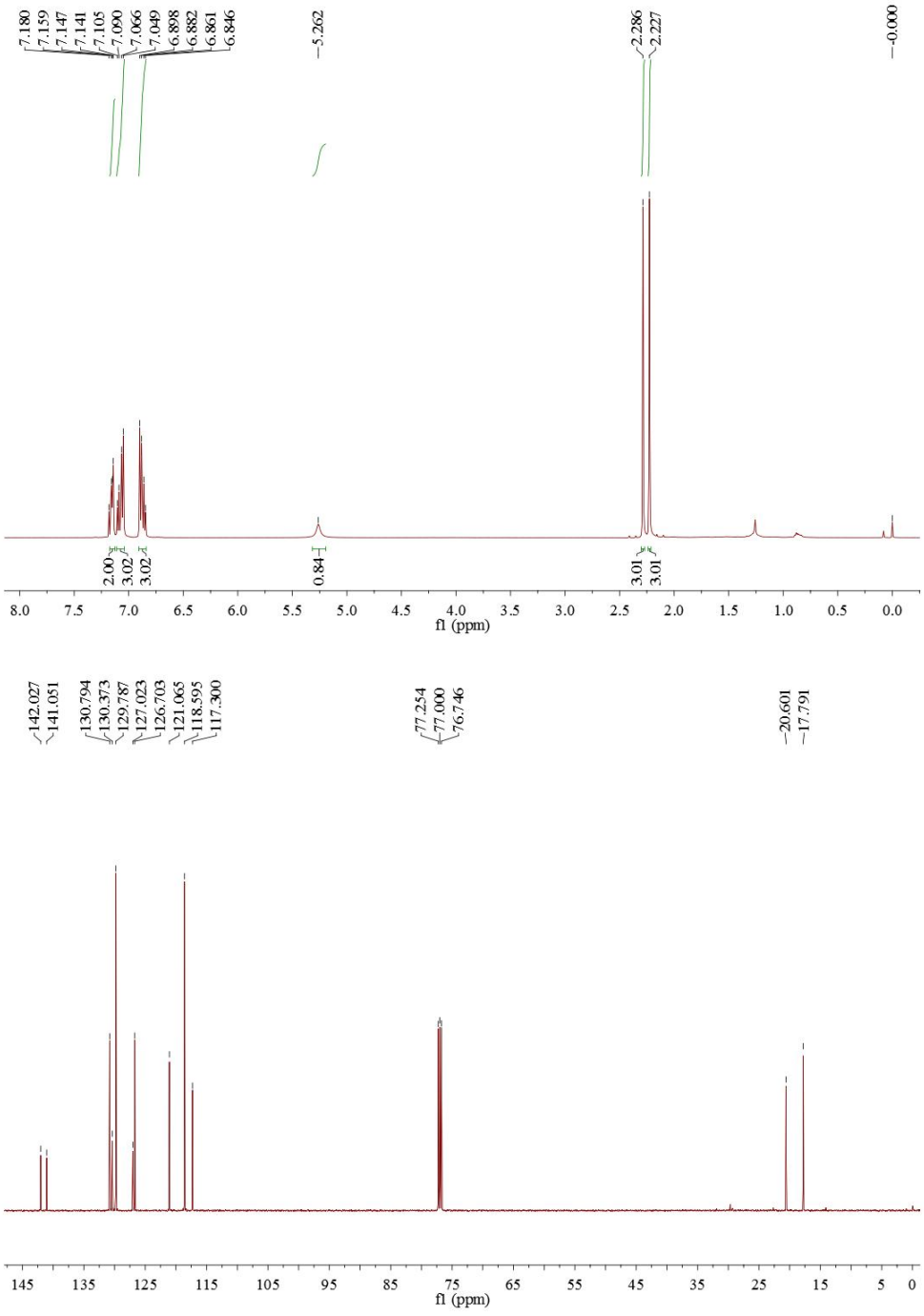


(10) R. E. Tundel, K. W. Anderson and S. L. Buchwald, *J. Org. Chem.*, 2006, **71**, 430.

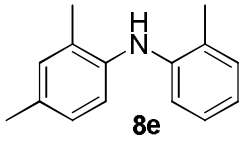


8d

Compound **8d**[11]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.18-7.14 (m, 2H), 7.11-7.05 (m, 3H), 6.99-6.85 (m, 3H), 5.26 (br, 1H), 2.29 (s, 3H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.0, 141.1, 130.8, 130.4, 129.8, 127.0, 126.7, 121.1, 118.6, 117.3, 20.6, 17.8.

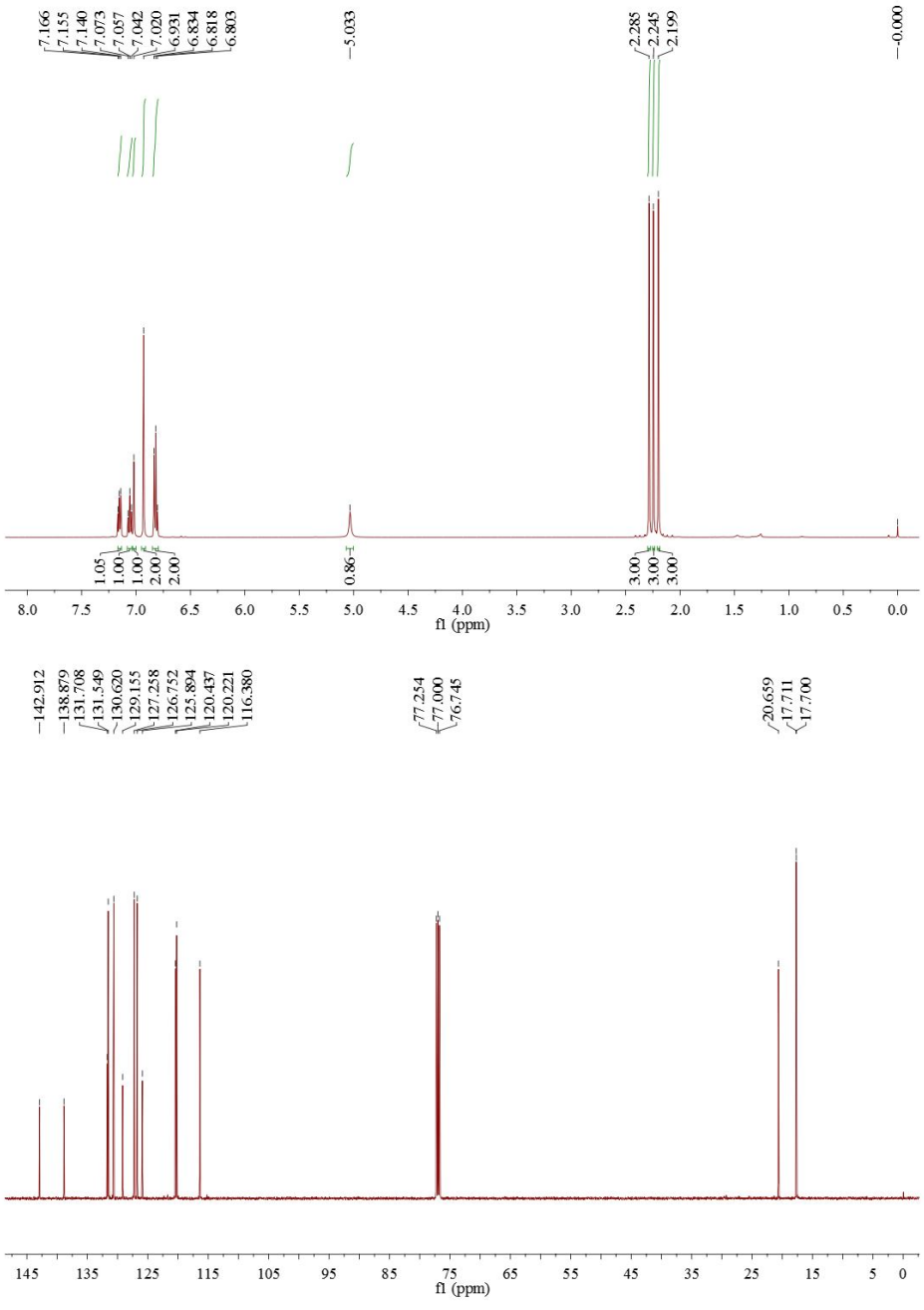


(11) L, Zhang, W.-B. Wang and R.-H. Fan, *Org. Lett.*, 2013, **15**, 2018.

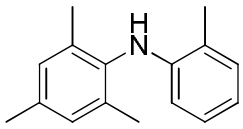


8e

Compound **8e**[12]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.15 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.93 (s, 2H), 6.82 (t, *J* = 7.5 Hz, 2H), 5.03 (br, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.9, 138.9, 131.7, 131.5, 130.6, 129.2, 127.3, 126.8, 125.9, 120.4, 120.2, 116.4, 20.7, 17.71, 17.70.

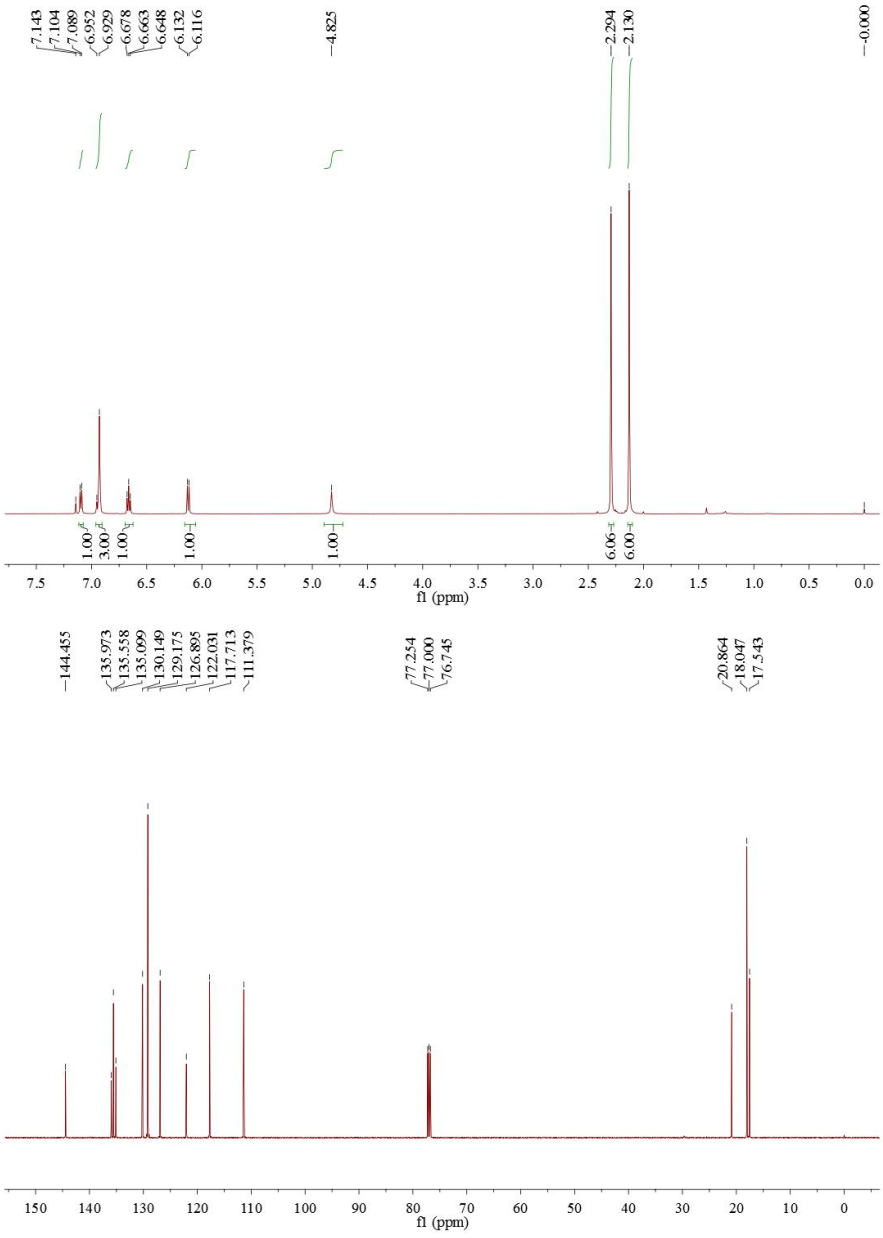


(12) N. H. Park, G. Teverovskiy and S. L. Buchwald, *Org. Lett.*, 2014, **16**, 220.

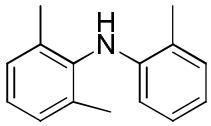


8f

Compound **8f**[13]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.10 (d, *J* = 7.5 Hz, 1H), 6.95-6.93 (m, 3H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.12 (d, *J* = 8.0 Hz, 1H), 4.83 (br, 1H), 2.29 (s, 6H), 2.13 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.5, 136.0, 135.6, 135.1, 130.1, 129.2, 126.9, 122.0, 117.7, 111.4, 20.9, 18.0, 17.5.

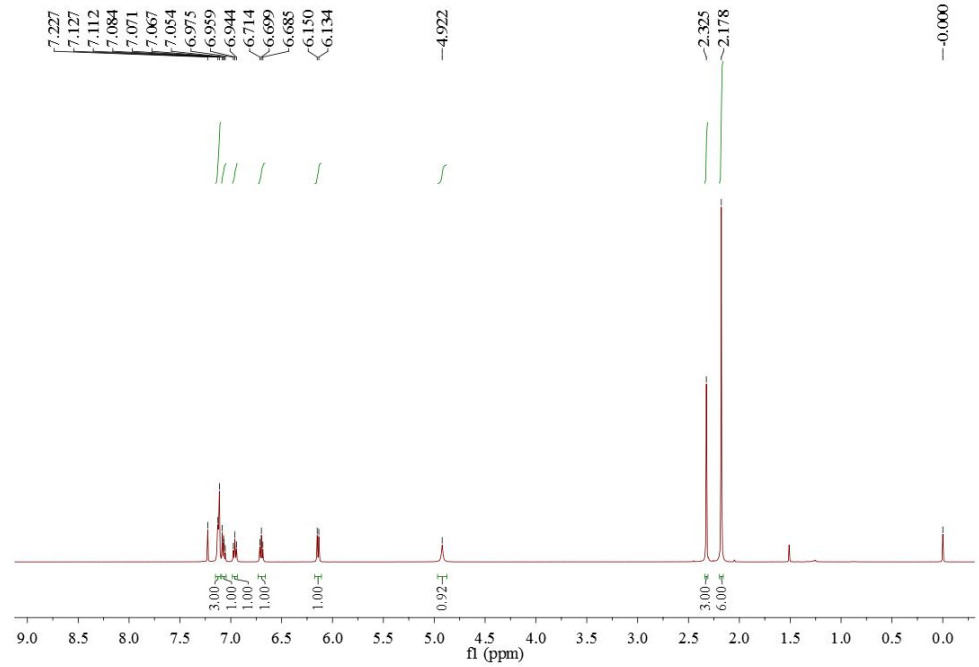


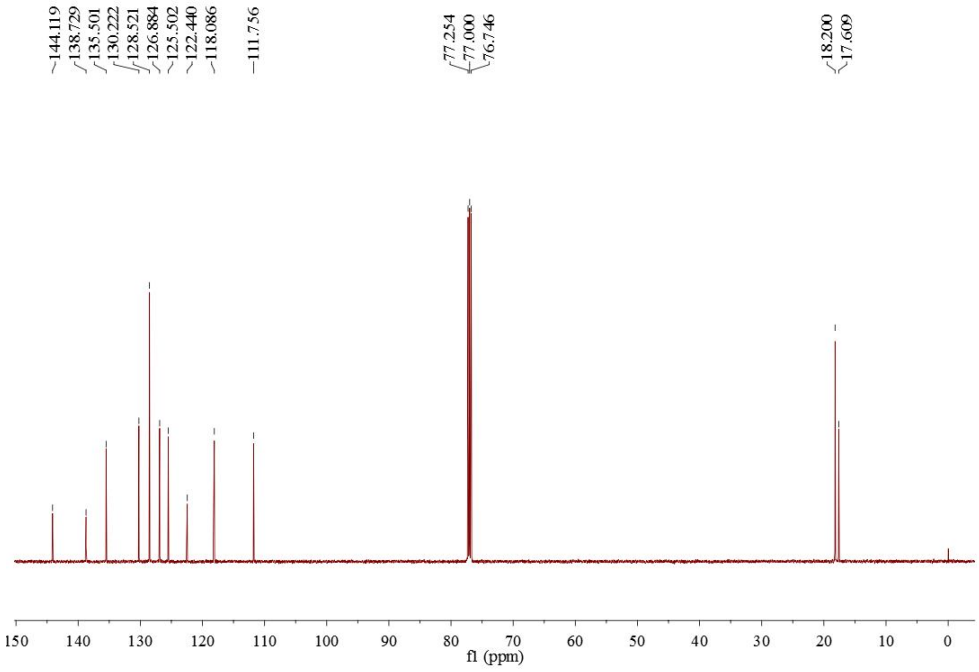
(13) J. L. Krinsky, A. Martínez, C. Godard, S. Castillón and C. Claver, *Adv. Synth. Catal.*, 2014, **356**, 460.

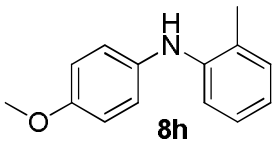


8g

Compound **8g**[5]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.13-7.05 (m, 3H), 6.96 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 4.92 (br, 1H), 2.33 (s, 3H), 2.18 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.1, 138.7, 135.5, 130.2, 128.5, 126.9, 125.5, 122.4, 118.1, 111.8, 18.2, 17.6.

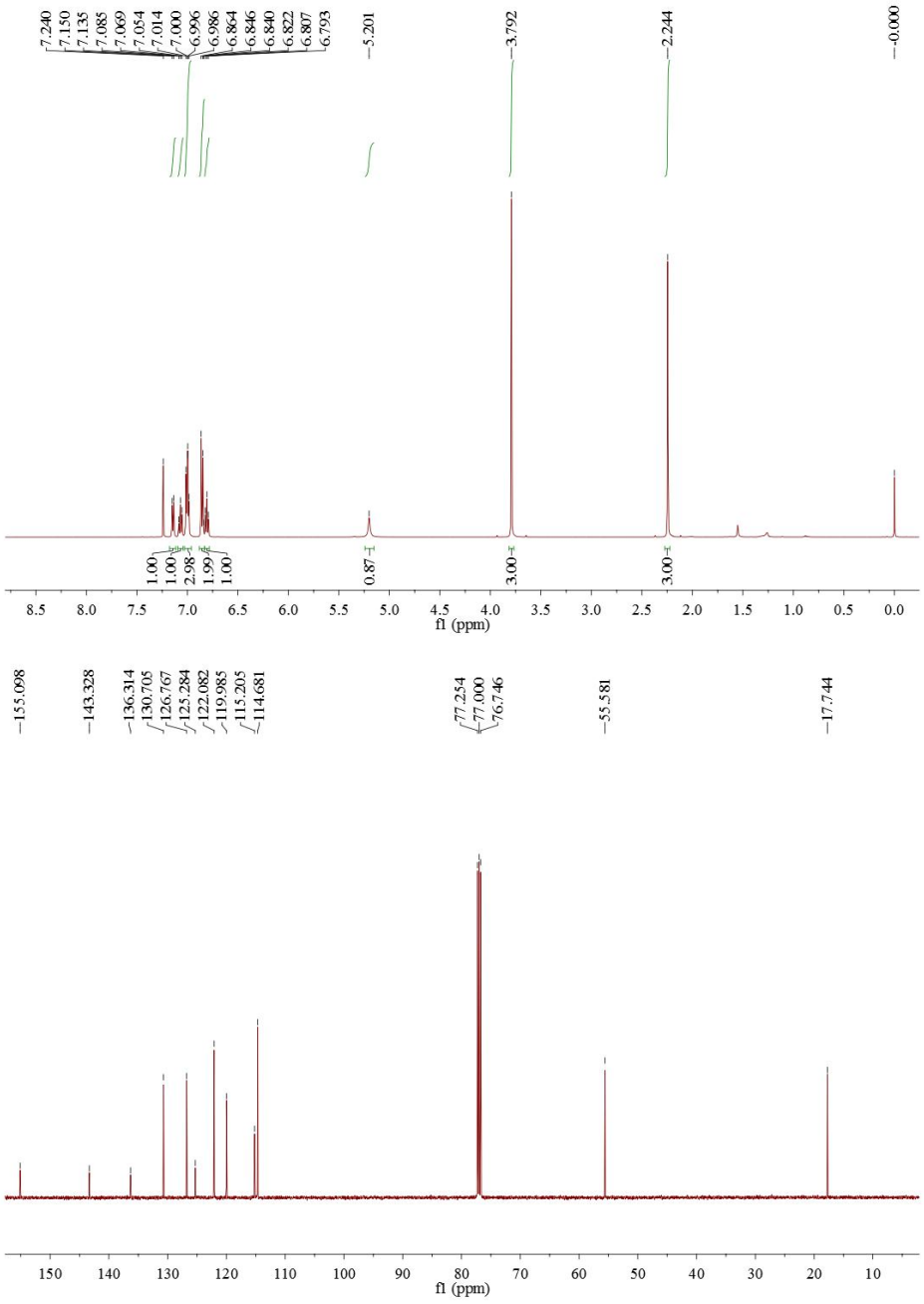




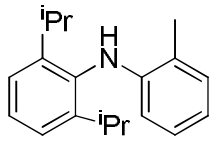


8h

Compound **8h**[14]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.14 (d, J = 7.5 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.01-7.00 (m, 3H), 6.86 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 7.5 Hz, 1H), 5.20 (br, 1H), 3.79 (s, 3H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.1, 143.3, 136.3, 130.7, 126.8, 125.3, 122.1, 120.0, 115.2, 114.7, 55.6, 17.7.

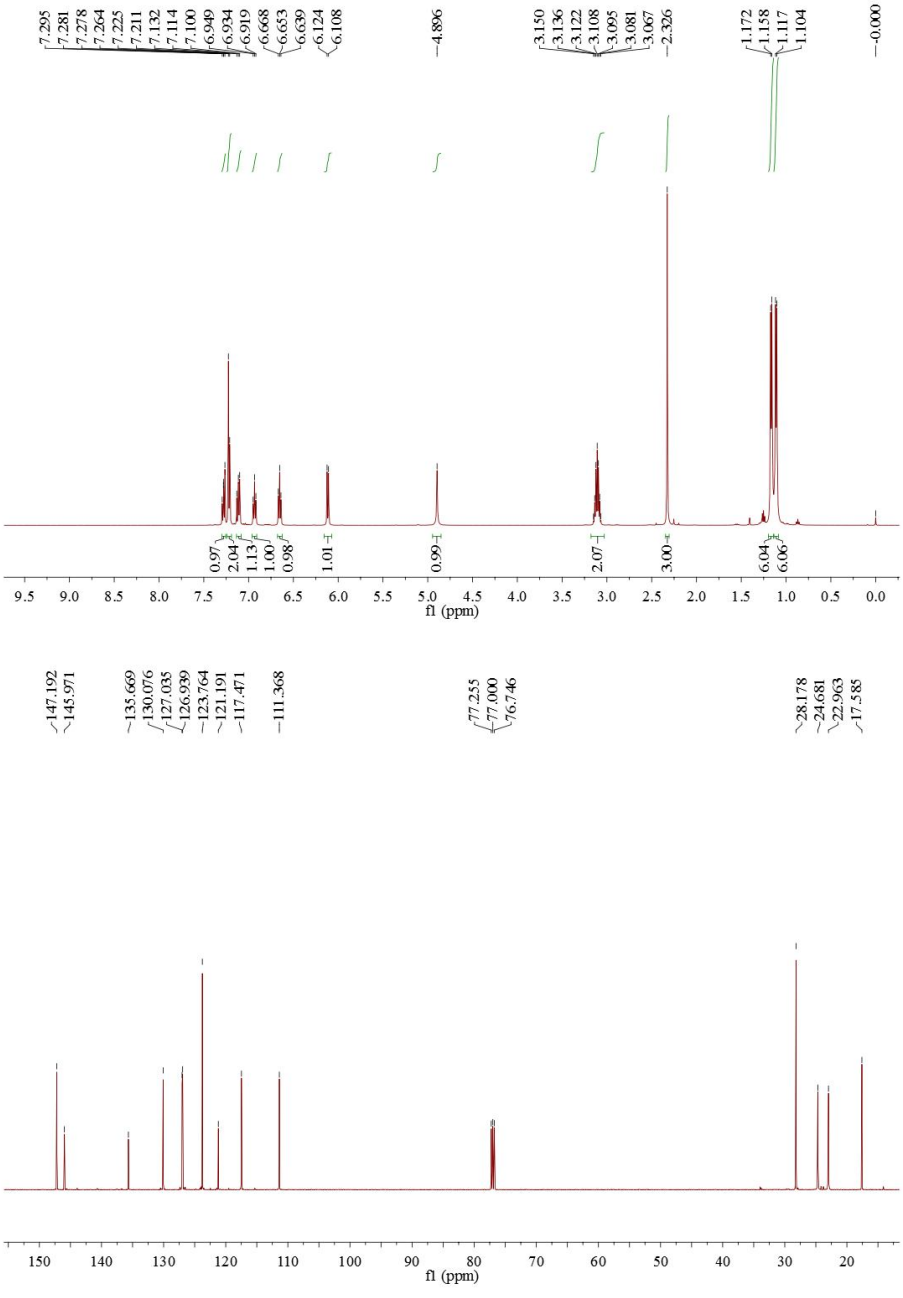


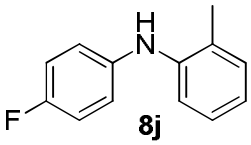
(14) S. H. Kim, M. Kim, J. G. Verkade and Y. Kim, *Eur. J. Org. Chem.*, 2015, 1954.



8i

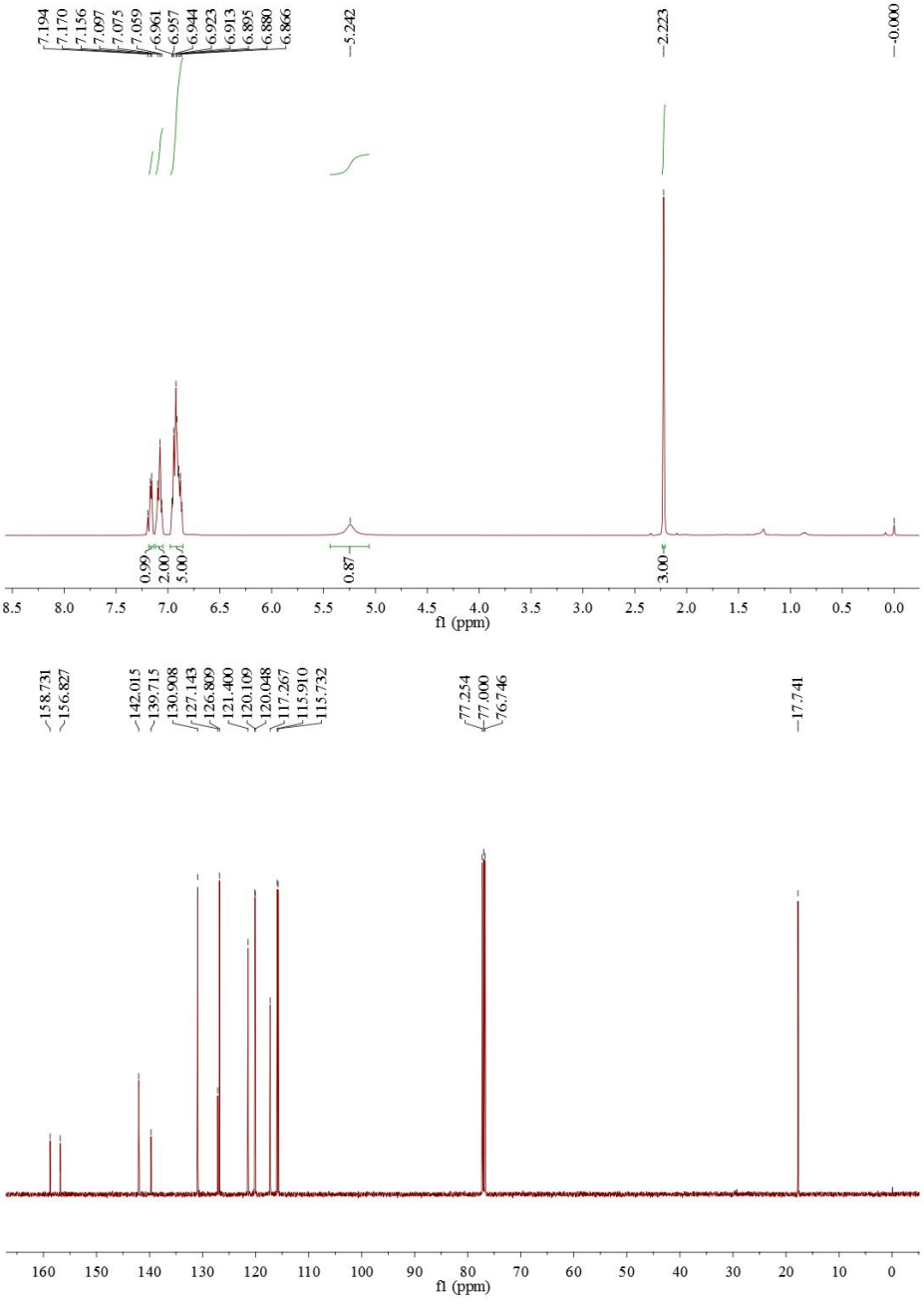
Compound **8i**[14]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.28 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.12 (d, *J* = 8.5 Hz, 1H), 4.90 (s, 1H), 3.11 (hept, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 1.17 (d, *J* = 7.0 Hz, 6H), 1.11 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.2, 146.0, 135.7, 130.1, 127.0, 126.9, 123.8, 121.2, 117.5, 111.4, 28.2, 24.7, 23.0, 17.6.



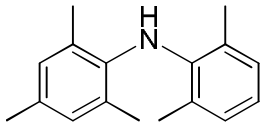


8j

Compound **8j**[15]: pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.16 (d, J = 7.0 Hz, 1H), 7.10-7.06 (m, 2H), 6.96-6.87 (m, 5H), 5.24 (br, 1H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.8 (d, $J_{C\text{-}F}$ = 238.0 Hz), 142.0, 139.7, 130.9, 127.1, 126.8, 121.4, 120.1 (d, $J_{C\text{-}F}$ = 7.625 Hz), 117.3, 115.8 (d, $J_{C\text{-}F}$ = 22.25 Hz), 17.7.

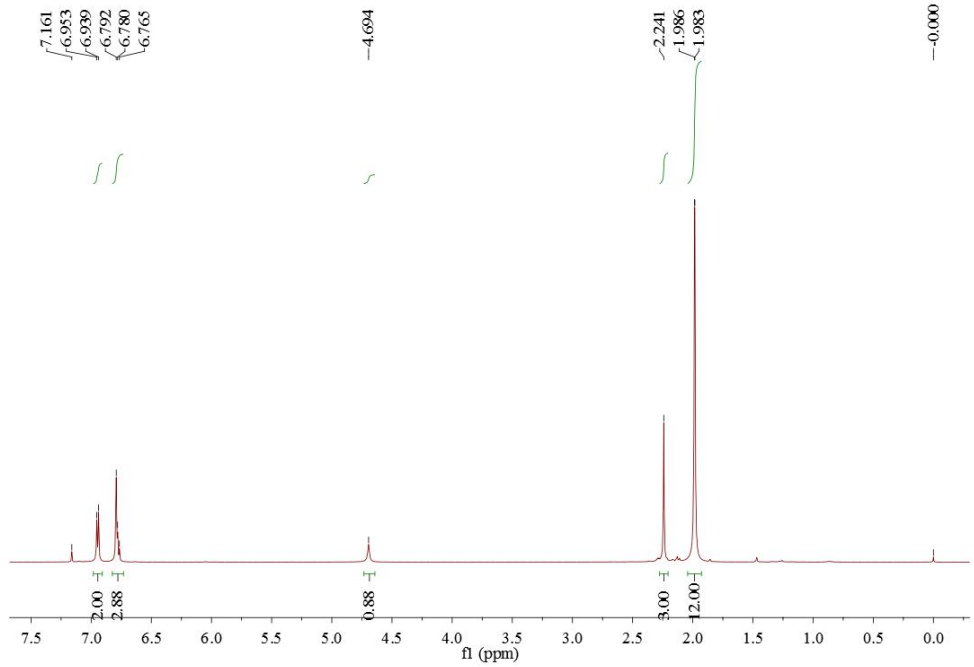


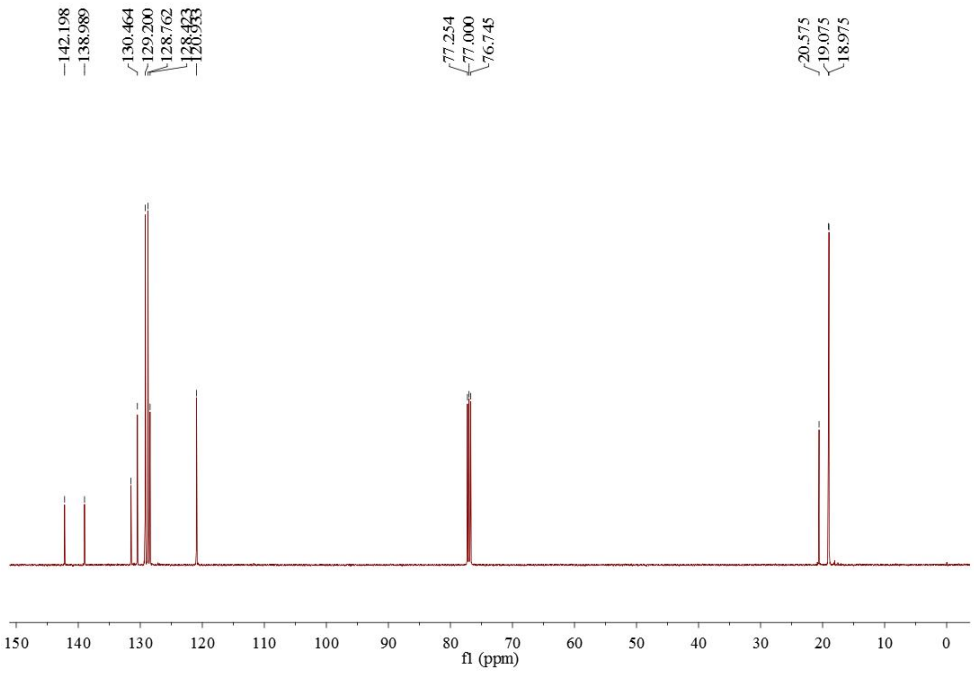
(15) L.-Z. Cai, X.-Y. Qian, W.-J. Song, T.-P. Liu, X.-C. Tao, W.-F. Li and X.-M. Xie, *Tetrahderon*, 2014, **70**, 4754.

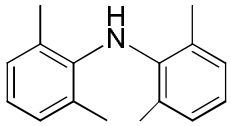


8k

Compound **8k**[3]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 6.95 (d, J = 7.0 Hz, 2H), 6.79-6.77 (m, 3H), 4.69 (br, 1H), 2.24 (s, 3H), 1.986 (s, 6H), 1.983 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.2, 139.0, 130.5, 129.2, 128.8, 128.4, 120.9, 20.6, 19.1, 19.0.

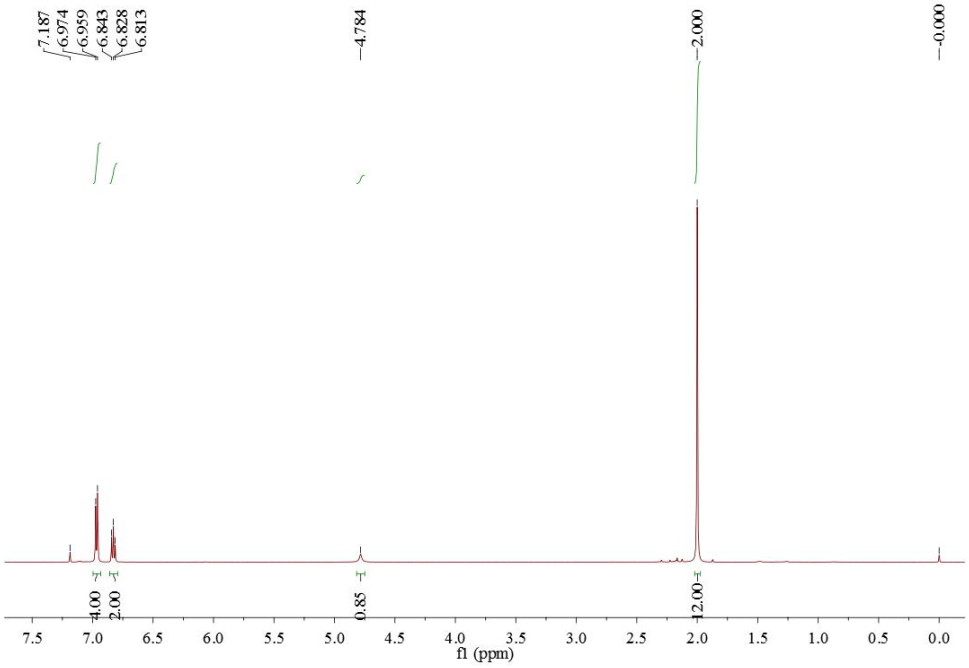


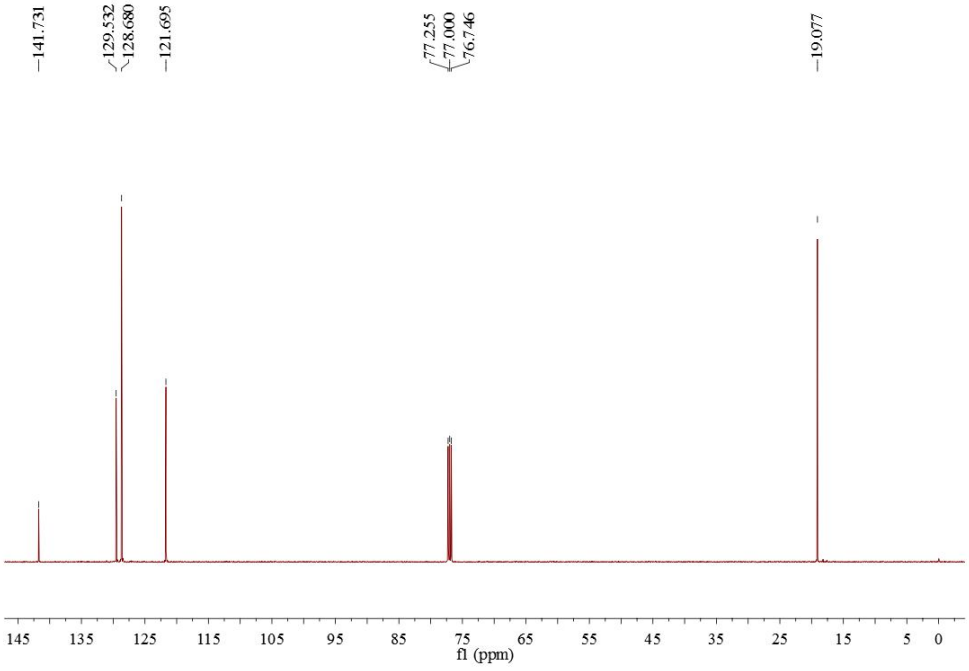


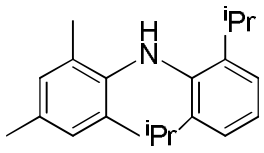


8l

Compound **8l**[3]: white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 6.97 (d, J = 7.5 Hz, 4H), 6.83 (t, J = 7.5 Hz, 2H), 4.78 (br, 1H), 2.00 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.7, 129.5, 128.7, 121.7, 19.1.

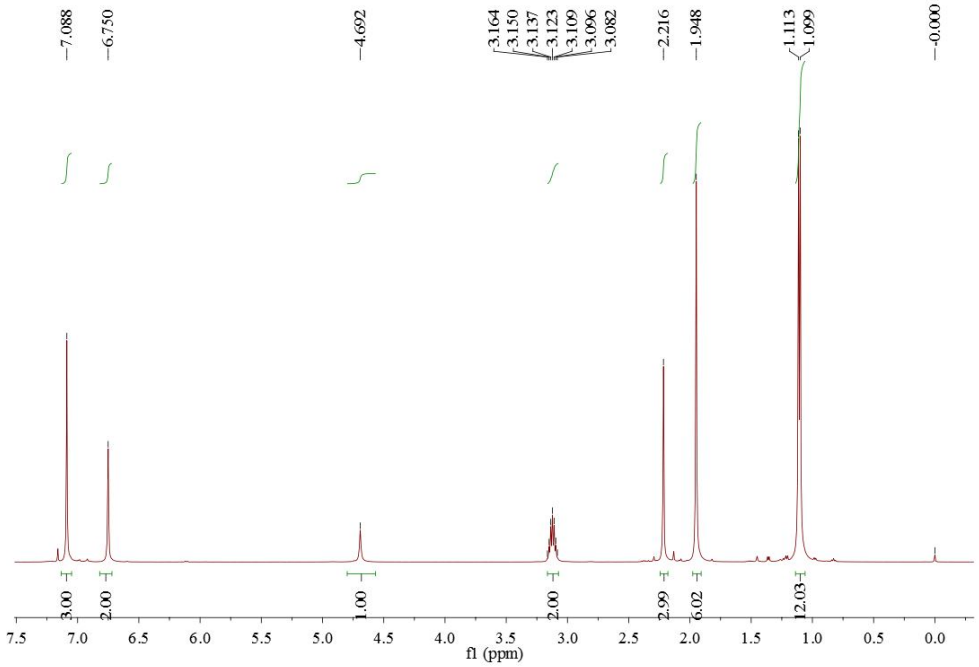


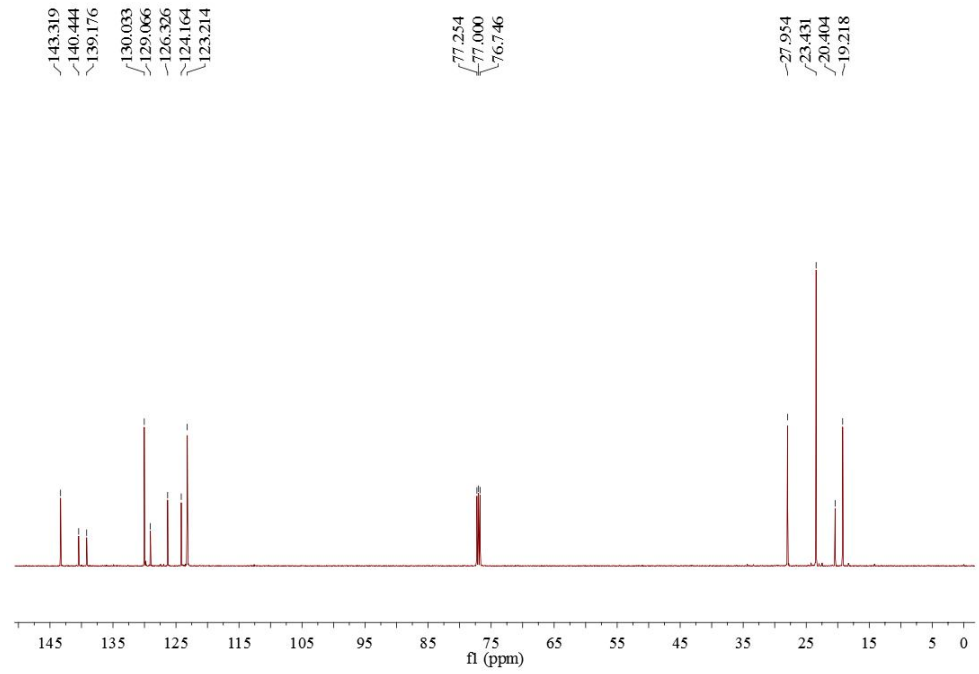


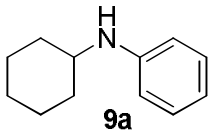


8m

Compound **8m**[3]: colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.09 (s, 3H), 6.75 (2, 3H), 4.69 (br, 1H), 3.12 (hept, J = 7.0 Hz, 2H), 2.22 (s, 3H), 1.95 (s, 6H), 1.11 (d, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.3, 140.4, 139.2, 130.0, 129.1, 126.3, 124.2, 123.2, 28.0, 23.4, 20.4, 19.2.

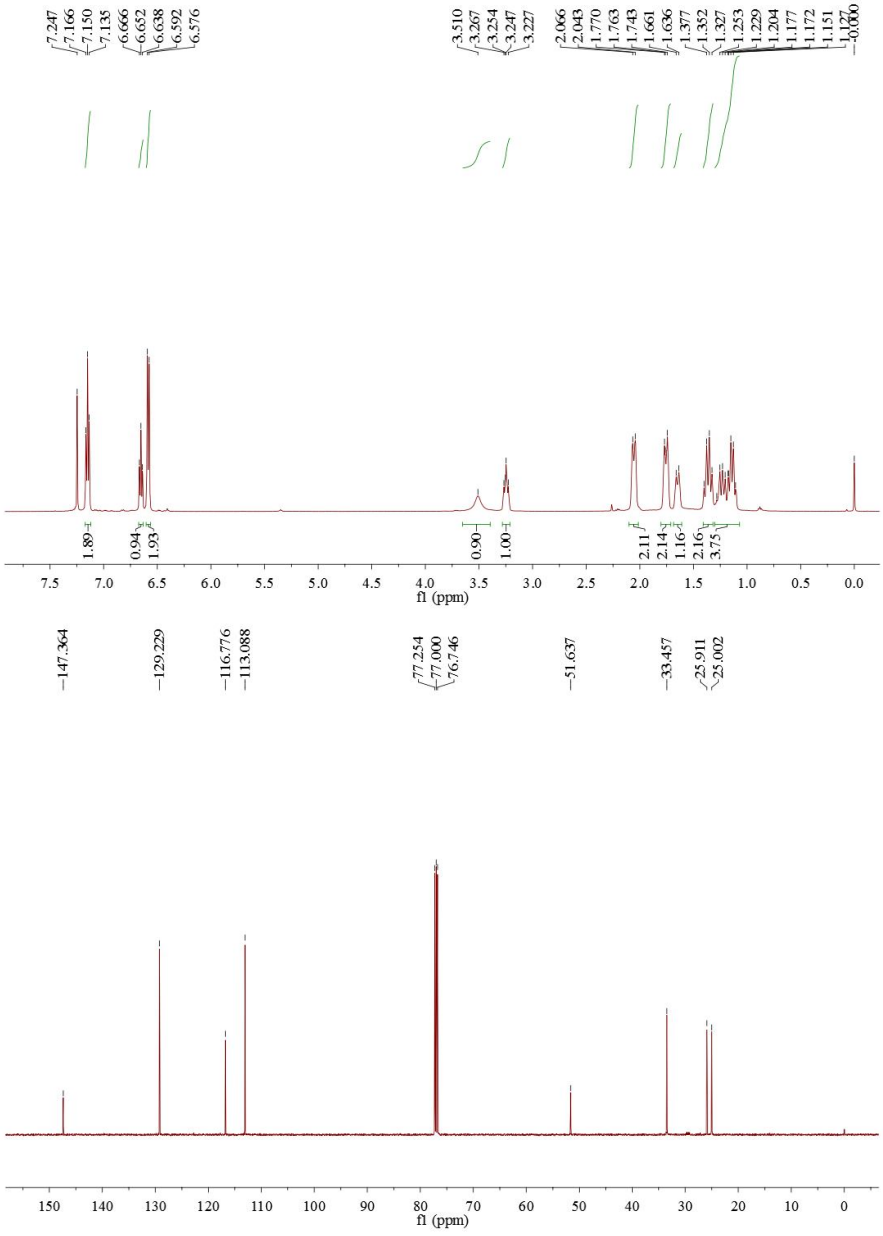




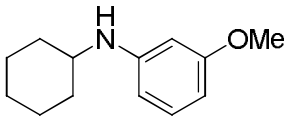


9a

Compound **9a**[16]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.15 (t, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 2H), 3.51 (br, 1H), 3.27-3.23 (m, 1H), 2.07-2.04 (m, 2H), 1.77-1.76 (m, 2H), 1.66-1.64 (m, 1H), 1.40-1.33 (m, 2H), 1.28-1.11 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 129.2, 116.8, 113.1, 51.6, 33.5, 25.9, 25.0.

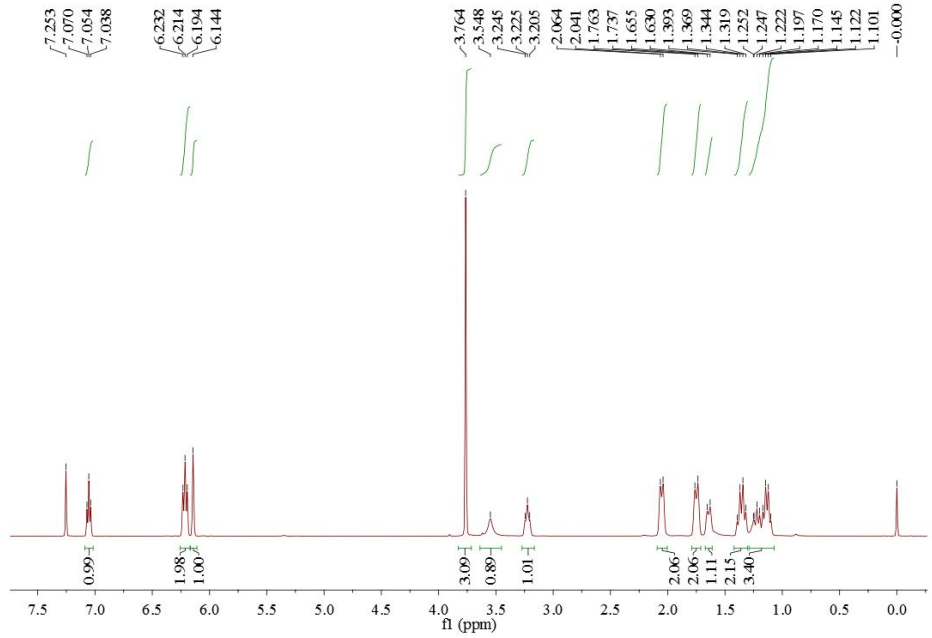


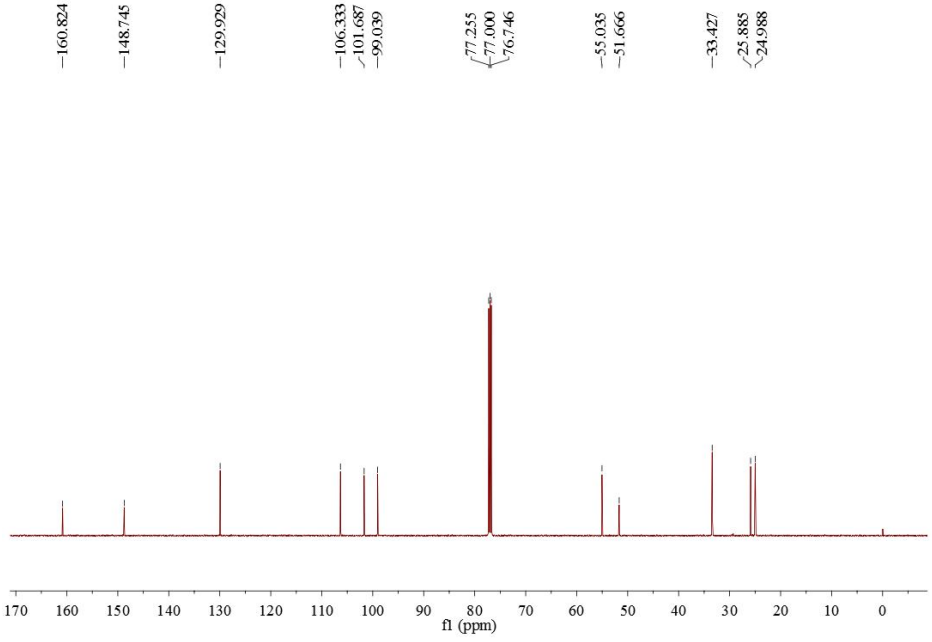
(16) L. Zhu, Y.-M. Ye and L.-X. Shao, *Tetrahedron*, 2012, **68**, 2414.

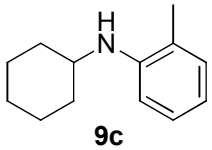


9b

Compound **9b**[16]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.05 (t, *J* = 8.0 Hz, 1H), 6.23-6.19 (m, 2H), 6.14 (s, 1H), 3.76 (s, 3H), 3.55 (br, 1H), 3.25-3.21 (m, 1H), 2.06-2.04 (m, 2H), 1.76-1.74 (m, 2H), 1.66-1.63 (m, 1H), 1.39-1.32 (m, 2H), 1.25-1.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 148.7, 129.9, 106.3, 101.7, 99.0, 55.0, 51.7, 33.4, 25.9, 25.0.

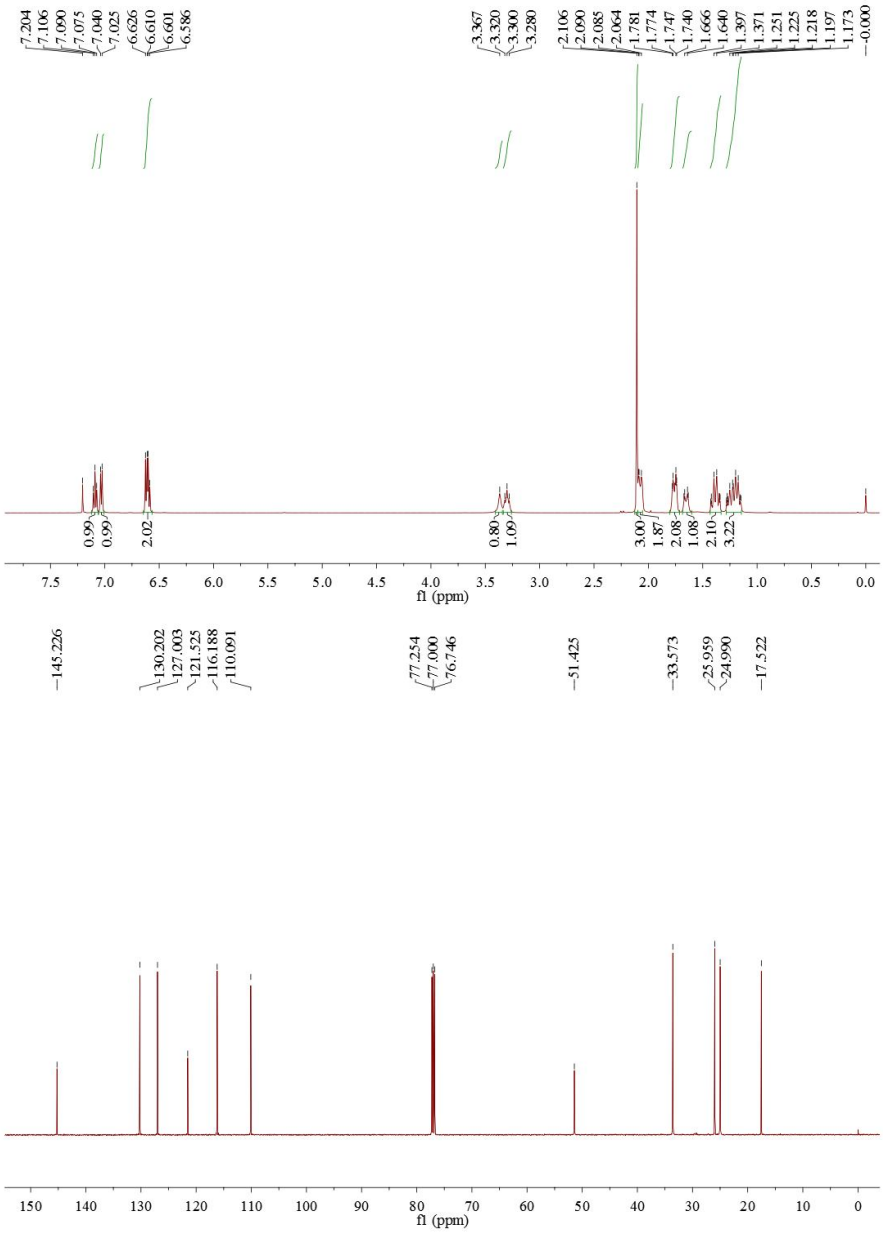






9c

Compound **9c**[17]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.09 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.63-6.59 (m, 2H), 3.37 (br, 1H), 3.32-3.28 (m, 1H), 2.11 (s, 3H), 2.09-2.06 (m, 2H), 1.78-1.74 (m, 2H), 1.67-1.63 (m, 1H), 1.42-1.34 (m, 2H), 1.28-1.15 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 130.2, 127.0, 121.5, 116.2, 110.1, 51.4, 33.6, 26.0, 25.0, 17.5.



(17) Q.-L. Shen, T. Ogata and J. F. Hartwig, *J. Am. Chem. Soc.*, 2008, **130**, 6586.