Supporting information

Copper-catalyzed alkylarylation of activated alkenes using isocyanides as the alkyl source: An efficient radical access to 3,3-dialkylated oxindoles

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General experimental procedure

NMR spectra were recorded on a 300 MHz or 400 MHz instrument using $CDCl_3$ as solvent unless and otherwise stated (s = singlet, d = doublet, t = triplet, m = multiplet). The ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. For the Mass spectrometry, ion source temperature was 150-250 °C, as required. High-resolution EI-mass spectra were performed with a resolution of 10,000. For chromatography, analytical TLC plates and 70-230 mesh silica gel were used. All the solvents and chemicals were purchased and used as available.

Synthesis of starting material

All of acrylamides **1** were synthesized according to the literature[1] and the NMR spectroscopy were in full accordance with the data in the literature.[1]

Typical experimental procedure

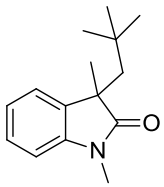
N-methyl-*N*-phenylmethacrylamide (1 equiv., 0.2 mmol), Cu_2O (15 mol%, 0.03 mmol), dicumyl peroxide (3 equiv, 0.60 mmol), isocyanide (5 equiv., 1.0 mmol), EtOAc (1 mL) were consecutively loaded to an oven dried 10 mL screw cap vial equipped with a magnetic stirring bar and then stirred at 120 °C for 24 h. The resulting reaction mixture was cooled to the ambient temperature and subjected to the column chromatography to afford desired 2-oxindole. The products were further identified by ^{1}H NMR, ^{13}C NMR and HRMS.

References:

[1] a) T. Wu, X. Mu, G. Liu, *Angew. Chem.* **2011**, *123*, 12786; *Angew. Chem. Int. Ed.* **2011**, *50*, 12578; b) X. Mu, T. Wu, H.-Y. Wang, Y.-L. Guo, G. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 878; c) D. C. Fabry, M. Stodulski, S. Hoerner, T. Gulder, *Chem. Eur. J.* **2012**, *18*, 10834.

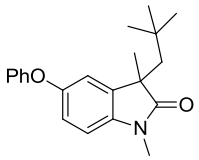
Characterization of products

1,3-Dimethyl-3-neopentylindolin-2-one (**3a**)



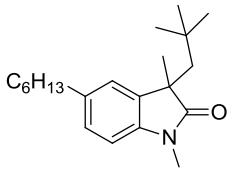
Pale yellow solid, m.p. 77-79°C, Yield 77%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–7.16 (m, 2H), 7.04 (dt, J = 8.3, 4.2 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.22 (s, 3H), 2.16 (d, J = 14.4 Hz, 1H), 1.86 (d, J = 14.4 Hz, 1H), 1.30 (s, 3H), 0.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 142.8, 134.2, 127.5, 123.9, 121.9, 108.0, 50.8, 47.4, 31.8, 30.8, 28.3, 26.2. HRMS (ESI) for $C_{15}H_{22}NO$ $[M+H]^+$ calculated 232.1696, found 232.1700.

1,3-Dimethyl-3-neopentyl-5-phenoxyindolin-2-one (**3b**)



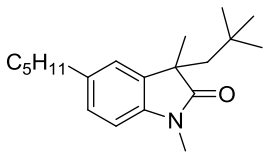
Pale yellow solid, m.p. 81-83°C, Yield 82%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.23 (m, 2H), 7.12-7.02 (m, 1H), 6.95 (ddd, J = 9.0, 7.9, 1.7 Hz, 4H), 6.81 (d, J = 8.2 Hz, 1H), 3.23 (s, 3H), 2.15 (d, J = 14.4 Hz, 1H), 1.79 (d, J = 14.4 Hz, 1H), 1.28 (s, 3H), 0.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.8, 158.5, 152.0, 138.9, 136.0, 129.7, 122.6, 119.0, 117.5, 116.6, 108.6, 50.8, 47.8, 31.8, 30.9, 28.2, 26.4. HRMS (ESI) for $C_{21}H_{26}NO_2$ $[M+H]^+$ calculated 324.1958, found 324.1967.

5-Hexyl-1,3-dimethyl-3-neopentylindolin-2-one (**3c**)



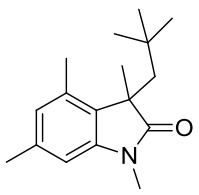
Pale yellow oil, Yield 75%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (dd, J = 11.2, 3.3 Hz, 2H), 6.75 (d, J = 7.8 Hz, 1H), 3.20 (s, 3H), 2.58 (t, J = 7.6 Hz, 2H), 2.15 (d, J = 14.3 Hz, 1H), 1.84 (d, J = 14.4 Hz, 1H), 1.58 (dd, J = 7.9, 4.9 Hz, 2H), 1.29 (s, 9H), 0.87 (t, J = 6.4 Hz, 3H), 0.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 140.6, 136.7, 134.1, 127.3, 124.1, 107.7, 50.8, 47.5, 35.7, 31.9, 31.8, 31.7, 30.8, 28.8, 28.2, 26.2, 22.6, 14.1. HRMS (ESI) for $C_{21}H_{34}NO$ $[M+H]^+$ calculated 316.2635, found 316.2634.

1,3-Dimethyl-3-neopentyl-5-pentylindolin-2-one (**3d**)



Pale yellow oil, Yield 77%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10-6.99 (m, 2H), 6.75 (d, J = 7.8 Hz, 1H), 3.20 (s, 3H), 2.64-2.52 (m, 2H), 2.15 (d, J = 14.3 Hz, 1H), 1.84 (d, J = 14.3 Hz, 1H), 1.70-1.49 (m, 2H), 1.39-1.19 (m, 7H), 0.88 (t, J = 6.8 Hz, 3H), 0.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 140.6, 136.7, 134.1, 127.2, 124.1, 107.7, 50.8, 47.5, 35.6, 31.8, 31.6, 31.3, 30.8, 28.3, 26.3, 22.5, 14.1. HRMS (ESI) for $C_{20}H_{32}NO$ $[M+H]^+$ calculated 302.2478, found 302.2478.

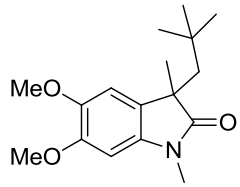
1,3,4,6-Tetramethyl-3-neopentylindolin-2-one (**3e**)



Pale yellow solid, m.p. 73-75°C, Yield 87%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.62 (s, 1H), 6.53 (s, 1H), 3.18 (s, 3H), 2.35 (s, 6H), 2.06 (d, J = 3.0 Hz, 2H), 1.34 (s, 3H), 0.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 143.2, 137.4, 134.6, 128.3, 125.5, 106.8, 49.1, 48.0, 31.7, 30.0, 26.3, 25.5, 21.6, 18.7. HRMS (ESI) for $C_{17}H_{26}NO$ $[M+H]^+$ calculated 260.2009, found

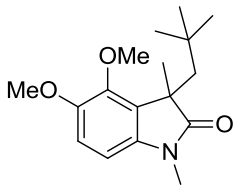
260.2014.

5,6-Dimethoxy-1,3-dimethyl-3-neopentylindolin-2-one (**3f**)



Pale yellow oil, Yield 66%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.81 (s, 1H), 6.50 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.22 (s, 3H), 2.14 (d, J = 14.4 Hz, 1H), 1.80 (d, J = 14.4 Hz, 1H), 1.27 (s, 3H), 0.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.3, 149.2, 144.8, 136.5, 124.8, 109.3, 94.1, 57.0, 56.3, 50.7, 47.6, 31.7, 30.8, 28.4, 26.3. HRMS (ESI) for $C_{17}H_{26}NO_3$ $[M+H]^+$ calculated 292.1907, found 292.1906.

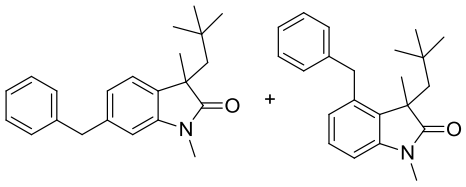
4,5-Dimethoxy-1,3-dimethyl-3-neopentylindolin-2-one (3f')



Pale yellow oil, Yield 17%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83 (d, J = 8.3 Hz, 1H), 6.50 (d, J = 8.3 Hz, 1H), 3.96 (s, 3H), 3.83 (s, 3H), 3.17 (s, 3H), 2.19 (d, J = 14.0 Hz, 1H), 2.00 (d, J = 14.0 Hz, 1H), 1.39 (s, 3H), 0.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8, 148.8, 147.0, 137.3, 126.3, 112.1, 102.4, 60.6, 56.5, 49.4, 48.1, 31.6, 30.3, 26.4, 26.2. HRMS (ESI) for $C_{17}H_{26}NO_3$ $[M+H]^+$ calculated 292.1907, found 292.1906.

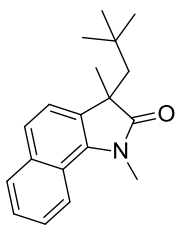
6-Benzyl-1,3-dimethyl-3-neopentylindolin-2-one +

4-Benzyl-1,3-dimethyl-3-neopentylin-dolin-2-one (**3g**)



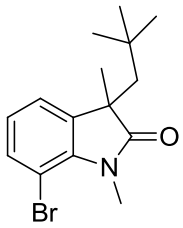
Pale yellow oil, Yield 86%, (*dr* = 3:1) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.45 (m, 1.44H), 7.39-7.24 (m, 3.37H), 7.24-7.17 (m, 3.03H), 7.12 (dd, J = 13.3, 7.7 Hz, 1.60H), 6.87 (d, J = 7.5 Hz, 0.70H), 6.78-6.67 (m, 0.52H), 6.65 (s, 0.70H), 4.27-4.04 (m, 0.55H), 4.00 (s, 1.43H), 3.21 (s, 0.70H), 3.15 (s, 2.11H), 2.14 (dd, J = 9.0, 5.3 Hz, 1.07H), 1.83 (d, J = 14.4 Hz, 1.00H), 1.35 (s, 0.74H), 1.26 (s, 2.32H), 0.68 (s, 2.25H), 0.61 (s, 6.45H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 181.0, 149.2, 143.2, 143.1, 140.9, 140.8, 140.1, 137.8, 132.0, 131.4, 129.2, 128.9, 128.6, 128.2, 127.7, 126.7, 126.3, 126.2, 124.6, 124.4, 123.8, 122.7, 108.8, 106.6, 72.5, 50.8, 50.0, 48.4, 47.2, 42.2, 37.8, 31.9, 31.8, 30.9, 30.2, 29.7, 28.3, 26.4, 26.3. HRMS (ESI) for $C_{22}H_{28}NO$ $[M+H]^+$ calculated 322.2165, found 322.2165.

1,3-Dimethyl-3-neopentyl-1H-benzo[g]indol-2(3H)-one (**3h**)



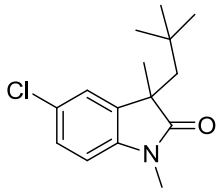
Pale yellow oil, Yield 63%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 7.7 Hz, 1H), 7.52-7.45 (m, 2H), 7.41 (dd, J = 9.6, 7.1 Hz, 2H), 6.92 (d, J = 7.4 Hz, 1H), 3.50 (s, 3H), 2.62 (d, J = 14.1 Hz, 1H), 1.95 (d, J = 14.1 Hz, 1H), 1.72 (s, 3H), 0.52 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 138.3, 136.8, 133.3, 126.5, 126.3, 125.7, 124.2, 122.4, 119.6, 108.1, 57.7, 45.8, 35.4, 31.9, 30.8, 29.5. HRMS (ESI) for $C_{19}H_{24}NO$ $[M+H]^+$ calculated 282.1852, found 282.1855.

4-Bromo-1,3-dimethyl-3-neopentylindolin-2-one (**3i**)



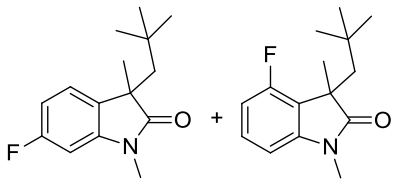
Pale yellow oil, Yield 67%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.1, 1.1 Hz, 1H), 7.11 (dd, J = 7.3, 1.1 Hz, 1H), 6.87 (dd, J = 8.1, 7.4 Hz, 1H), 3.61 (s, 3H), 2.16 (d, J = 14.4 Hz, 1H), 1.83 (d, J = 14.4 Hz, 1H), 1.29 (s, 3H), 0.62 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 140.2, 137.4, 133.2, 123.2, 122.9, 102.4, 51.1, 47.2, 31.8, 30.8, 29.8, 28.6. HRMS (ESI) for $C_{15}H_{21}BrNO$ $[M+H]^+$ calculated 310.0801, found 310.0802.

5-Chloro-1,3-dimethyl-3-neopentylindolin-2-one (**3j**)



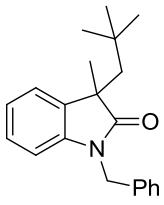
Pale yellow solid, m.p. 133-135^{o}C, Yield 79%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (dd, J = 8.2, 2.1 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 3.21 (s, 3H), 2.16 (d, J = 14.4 Hz, 1H), 1.83 (d, J = 14.4 Hz, 1H), 1.29 (s, 3H), 0.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.5, 141.4, 136.1, 127.5, 127.5, 124.3, 109.0, 50.8, 47.7, 31.8, 30.9, 28.2, 26.4. HRMS (ESI) for $C_{15}H_{21}ClNO$ $[M+H]^+$ calculated 266.1306, found 266.1309.

6-Fluoro-1,3-dimethyl-3-neopentylindolin-2-one + **4-Fluoro-1,3-dimethyl-3-neopentylin-dolin-2-one** (**3l**)



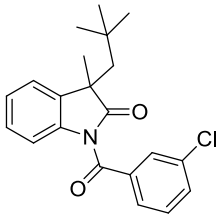
Pale yellow oil, Yield 62%, (*dr* = 3:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (ddd, J = 8.4, 6.7, 4.6 Hz, 1.3H), 7.11 (dd, J = 8.1, 5.4 Hz, 0.41H), 6.87-6.65 (m, 2H), 6.62-6.53 (m, 0.49H), 3.22 (s, 3H), 3.20 (s, 1H), 2.22-1.95 (m, 3H), 1.92-1.70 (m, 1H), 1.46-1.32 (m, 3.2H), 1.27 (d, J = 7.0 Hz, 1.2H), 0.66 (s, 9.3H), 0.61 (s, 3.2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.3, 180.5, 160.9, 157.7, 144.8, 144.6, 144.1, 129.4, 129.3, 124.7, 124.6, 119.9, 119.6, 110.0, 109.8, 108.2, 107.9, 104.3, 104.2, 97.0, 96.6, 50.8, 49.5, 47.1, 47.1, 47.0, 31.8, 31.6, 30.8, 30.1, 28.3, 26.7, 26.4, 26.2. HRMS (ESI) for $C_{15}H_{21}FNO$ $[M+H]^+$ calculated 250.1602, found 250.1600.

1-Benzyl-3-methyl-3-neopentylindolin-2-one (**3m**)



Pale yellow solid, m.p. 95-97^{o}C, Yield 65%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.09 (m, 8H), 7.00 (dd, J = 10.8, 4.2 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.06 (d, J = 15.5 Hz, 1H), 4.78 (d, J = 15.5 Hz, 1H), 2.21 (d, J = 14.4 Hz, 1H), 1.90 (d, J = 14.4 Hz, 1H), 1.35 (s, 3H), 0.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 142.0, 136.1, 134.2, 128.7, 127.6, 127.5, 127.4, 124.0, 122.0, 109.1, 50.5, 47.5, 43.92, 31.9, 31.0, 29.1. HRMS (ESI) for $C_{21}H_{26}NO$ $[M+H]^+$ calculated 308.2009, found 308.2010.

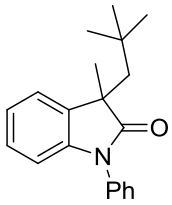
1-(3-Chlorobenzoyl)-3-methyl-3-neopentylindolin-2-one (**3n**)



Pale yellow solid, m.p. 182-184^{o}C, Yield 54%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, J = 2.3 Hz, 1H), 7.61 (dd, J = 8.5, 2.3 Hz, 1H), 7.56-7.49 (m, 2H), 7.49-7.40 (m, 2H), 7.22-7.10 (m, 2H), 2.59 (d, J = 14.5 Hz, 1H), 2.07 (d, J = 14.5 Hz, 1H), 1.67 (s, 3H), 0.69 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 163.3, 142.5, 135.3, 133.8, 133.7, 129.4, 128.9, 128.7, 128.1, 125.9, 54.6, 46.6, 34.2, 32.1, 31.1. HRMS (ESI) for $C_{21}H_{23}ClNO_2$

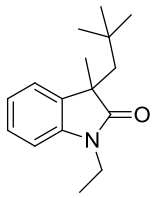
$[M+H]^+$ calculated 356.1412, found 356.1409.

3-Methyl-3-neopentyl-1-phenylindolin-2-one (**3o**)



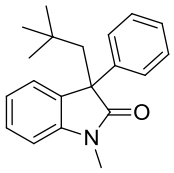
Pale yellow solid, m.p. 80-82°C, Yield 67%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.46 (m, 2H), 7.44-7.32 (m, 3H), 7.27 (dd, J = 7.4, 0.6 Hz, 1H), 7.18 (td, J = 7.7, 1.2 Hz, 1H), 7.07 (dd, J = 10.8, 4.1 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 2.26 (d, J = 14.4 Hz, 1H), 1.95 (d, J = 14.4 Hz, 1H), 1.42 (s, 3H), 0.73 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.3, 142.7, 134.8, 134.0, 129.6, 127.8, 127.4, 126.3, 124.3, 122.5, 109.5, 51.0, 47.6, 32.0, 31.0, 28.9. HRMS (ESI) for $C_{20}H_{24}NO$ $[M+H]^+$ calculated 294.1852, found 294.1855.

1-Ethyl-3-methyl-3-neopentylindolin-2-one (**3p**)



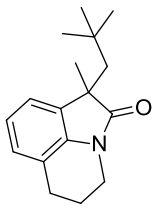
Pale yellow solid, m.p. 57-59°C, Yield 76%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.15 (m, 2H), 7.02 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.88 (dq, J = 14.4, 7.2 Hz, 1H), 3.69 (dq, J = 14.2, 7.1 Hz, 1H), 2.17 (d, J = 14.4 Hz, 1H), 1.86 (d, J = 14.4 Hz, 1H), 1.27 (dd, J = 9.3, 4.9 Hz, 6H), 0.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.6, 141.9, 134.4, 127.4, 124.1, 121.7, 108.2, 50.6, 47.4, 34.5, 31.9, 30.9, 28.6, 12.3. HRMS (ESI) for $C_{16}H_{24}NO$ $[M+H]^+$ calculated 246.1852, found 246.1859.

1-Methyl-3-neopentyl-3-phenylindolin-2-one (**3s**)



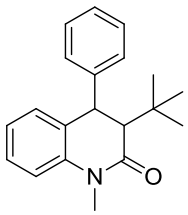
Pale yellow oil, Yield 48%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.38 (m, 2H), 7.37-7.29 (m, 2H), 7.29-7.23 (m, 2H), 7.23-7.17 (m, 1H), 7.10 (td, J = 7.5, 1.1 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H), 3.21 (s, 3H), 2.69 (d, J = 14.3 Hz, 1H), 2.22 (d, J = 14.3 Hz, 1H), 0.70 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.8, 143.8, 142.3, 131.8, 128.4, 128.2, 127.0, 126.8, 126.6, 121.8, 108.3, 55.5, 50.9, 32.1, 31.2, 26.5. HRMS (ESI) for $C_{20}H_{24}NO$ $[M+H]^+$ calculated 294.1852, found 294.1856.

1-Methyl-1-neopentyl-5,6-dihydro-1*H*-pyrrolo[3,2,1-ij]quinolin-2(4*H*)-one (**5a**)



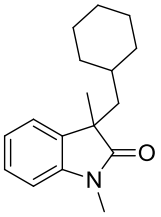
Pale yellow oil, Yield 57%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (t, J = 7.5 Hz, 2H), 6.96-6.84 (m, 1H), 3.72 (td, J = 5.4, 3.2 Hz, 2H), 2.80 (dd, J = 6.1, 3.6 Hz, 2H), 2.15 (d, J = 14.4 Hz, 1H), 2.01 (dt, J = 11.6, 6.0 Hz, 2H), 1.84 (d, J = 14.4 Hz, 1H), 1.30 (s, 3H), 0.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.0, 138.6, 132.7, 126.2, 121.8, 121.4, 120.1, 50.6, 48.8, 38.9, 31.8, 30.8, 28.1, 24.7, 21.2. HRMS (ESI) for $C_{17}H_{24}NO$ $[M+H]^+$ calculated 258.1852, found 258.1853.

3-(*tert*-butyl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (5b)



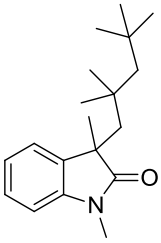
Yellow liquid, Yield 25%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 1H), 7.21 (dd, J = 8.1, 6.6 Hz, 2H), 7.18-7.12 (m, 2H), 7.03 (t, J = 7.5 Hz, 2H), 6.96 (dd, J = 7.3, 1.6 Hz, 2H), 4.31 (s, 1H), 3.41 (s, 3H), 2.68 (d, J = 1.1 Hz, 1H), 0.94 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5, 143.7, 140.7, 129.1, 128.8, 127.9, 127.5, 126.9, 126.6, 123.4, 114.6, 59.3, 43.9, 34.6, 29.6, 28.9. HRMS (ESI) for $C_{20}H_{24}NO$ $[M+H]^+$ calculated 294.1852, found 294.1857.

3-(Cyclohexylmethyl)-1,3-dimethylindolin-2-one (**3t**)



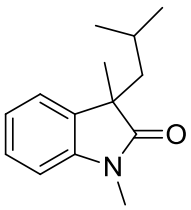
Pale yellow oil, Yield 54%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (td, J = 7.9, 1.3 Hz, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.06 (td, J = 7.5, 0.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.22 (s, 3H), 1.93 (dd, J = 14.0, 6.7 Hz, 1H), 1.73 (dd, J = 14.0, 5.0 Hz, 1H), 1.49 (dd, J = 15.2, 6.5 Hz, 3H), 1.36 (dd, J = 3.8, 2.1 Hz, 1H), 1.31 (s, 3H), 1.27 – 1.16 (m, 2H), 0.96 (dd, J = 16.2, 6.3 Hz, 3H), 0.87 – 0.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.2, 143.1, 134.4, 127.5, 122.7, 122.3, 107.9, 47.9, 45.4, 34.7, 34.5, 33.5, 26.2, 26.2, 26.1, 26.0. HRMS (ESI) for $C_{17}H_{24}NO$ $[M+H]^+$ calculated 258.1852, found 258.1852.

1,3-Dimethyl-3-(2,2,4,4-tetramethylpentyl)indolin-2-one (**3u**)



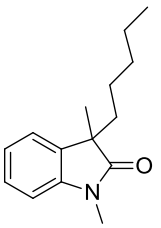
Pale yellow oil, Yield 74%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.14 (m, 2H), 7.03 (td, J = 7.5, 0.9 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.22 (s, 3H), 2.25 (d, J = 14.4 Hz, 1H), 1.93 (d, J = 14.4 Hz, 1H), 1.64-1.34 (m, 1H), 1.28 (s, 3H), 1.18-1.07 (m, 2H), 0.98 (d, J = 14.4 Hz, 2H), 0.88 (s, 9H), 0.70 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.2, 142.8, 134.3, 127.5, 124.2, 121.9, 108.0, 56.7, 52.1, 47.4, 36.7, 32.2, 32.1, 29.7, 29.0, 28.7, 26.2. HRMS (ESI) for $C_{19}H_{30}NO$ $[M+H]^+$ calculated 288.2322, found 288.2315.

3-Isobutyl-1,3-dimethylindolin-2-one (**3v**)



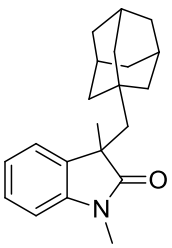
Pale yellow oil, Yield 51%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J = 16.1 Hz, 1H), 7.17 (d, J = 6.8 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 3.22 (s, 3H), 1.94 (dd, J = 13.9, 7.7 Hz, 1H), 1.76 (dd, J = 13.9, 5.4 Hz, 1H), 1.33 (s, 3H), 1.24 (dd, J = 17.3, 8.1 Hz, 2H), 0.63 (dd, J = 13.1, 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 143.2, 134.2, 127.6, 122.8, 122.3, 107.9, 48.1, 46.7, 26.2, 26.2, 25.6, 24.1, 22.8. HRMS (ESI) for $C_{14}H_{20}NO$ $[M+H]^+$ calculated 218.1539, found 218.1537.

1,3-Dimethyl-3-pentylindolin-2-one (**3w**)



Pale yellow oil, Yield 38%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.23 (m, 1H), 7.19-7.14 (m, 1H), 7.06 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (dt, J = 7.7, 0.7 Hz, 1H), 3.21 (s, 3H), 1.88 (ddd, J = 13.2, 12.1, 4.7 Hz, 1H), 1.71 (ddd, J = 13.3, 11.9, 4.5 Hz, 1H), 1.35 (s, 3H), 1.21-1.09 (m, 4H), 1.04-0.91 (m, 1H), 0.90-0.81 (m, 1H), 0.80-0.73 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.9, 143.3, 134.3, 127.5, 122.5, 122.4, 107.8, 48.5, 38.5, 31.9, 26.1, 24.1, 23.8, 22.3, 13.9. HRMS (ESI) for $C_{15}H_{22}NO$ $[M+H]^+$ calculated 232.1696, found 232.1703.

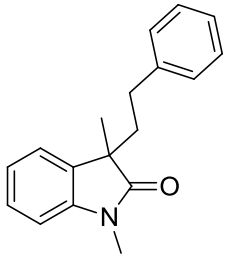
1,3-Dimethyl-3-neopentyl-5-phenoxyindolin-2-one (**3x**)



Pale yellow solid, m.p. 107-109^{o}C, Yield 52%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 3.24 (s, 3H), 2.14-1.87 (m, 3H), 1.71 (dd, J = 15.8, 12.6 Hz, 5H), 1.51 (d, J = 12.2 Hz, 2H), 1.38 (d, J = 12.3 Hz, 2H), 1.27 (s,

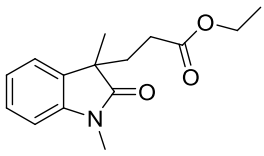
3H), 1.24 (d, J = 8.0 Hz, 1H), 1.17 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.2, 142.6, 134.7, 127.5, 123.6, 122.0, 108.0, 52.0, 46.7, 43.3, 36.7, 33.9, 28.6, 28.5, 26.3. HRMS (ESI) for $C_{21}H_{28}NO$ $[M+H]^+$ calculated 310.2165, found 310.2166.

1,3-Dimethyl-3-phenethylindolin-2-one (3y)



Pale yellow oil, Yield 30%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 1H), 7.24-7.18 (m, 3H), 7.11 (qd, J = 7.2, 1.2 Hz, 2H), 7.05-7.00 (m, 2H), 6.86 (dt, J = 7.7, 0.8 Hz, 1H), 3.21 (s, 3H), 2.36-2.21 (m, 2H), 2.17-2.08 (m, 1H), 2.06-1.97 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.3, 143.4, 141.4, 133.8, 128.3, 128.2, 127.8, 125.8, 122.6, 122.5, 108.0, 48.4, 40.3, 30.9, 26.1, 23.9. HRMS (ESI) for $C_{18}H_{19}NO$ $[M+H]^+$ calculated 266.1466, found 266.1701.

Ethyl 3-(1,3-dimethyl-2-oxoindolin-3-yl)propanoate (**3z**)

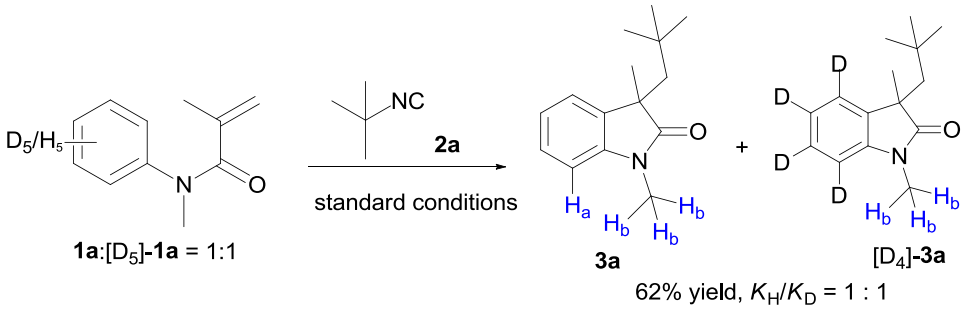


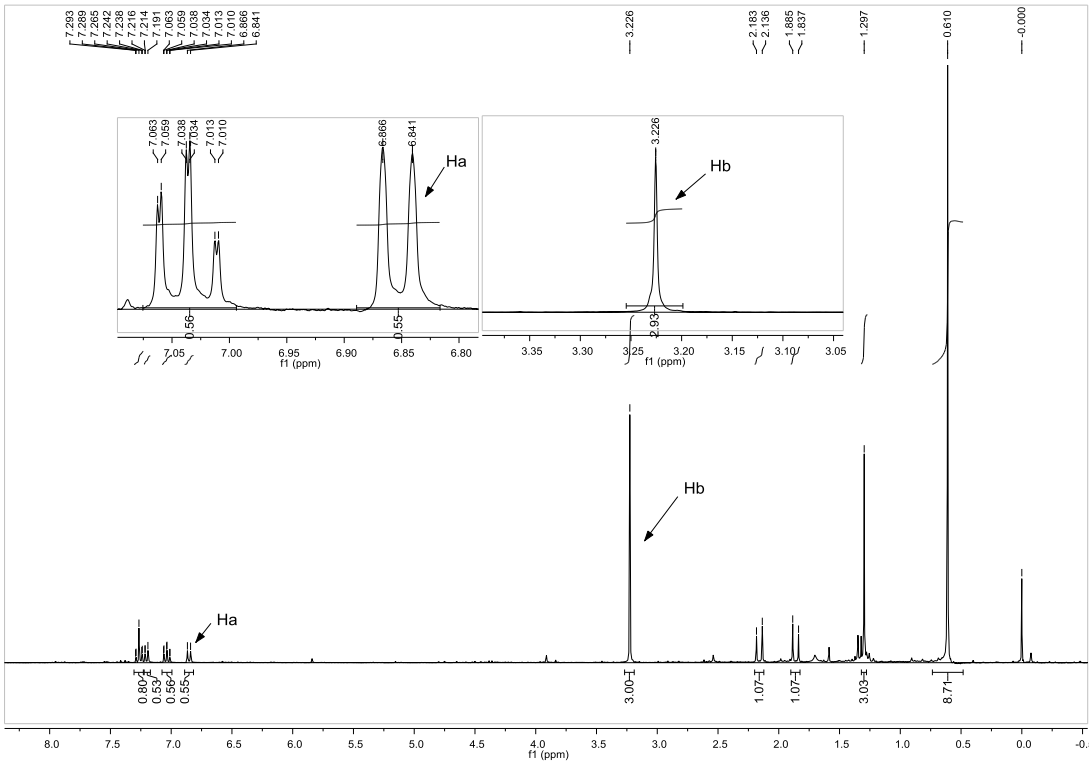
Pale yellow oil, Yield 48%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (td, J = 7.7, 1.3 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.07 (td, J = 7.5, 0.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.10-3.88 (m, 2H), 3.22 (s, 3H), 2.39-2.08 (m, 2H), 2.07-1.76 (m, 2H), 1.39 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.9, 172.8, 143.2, 132.9, 128.1, 122.7, 122.7, 108.1, 60.4, 47.6, 32.9, 29.6, 26.2, 23.6, 14.1. HRMS (ESI) for $C_{15}H_{20}NO_3$ $[M+H]^+$ calculated 262.1438, found 262.1437.

Kinetic Isotopic Effect (KIE) Studies:

a) Intermolecular KIE experiment:

[D_5]-**1a** was synthesized according the literature.[2] **1a** (0.5 equiv, 0.1 mmol), [D_5]-**1a** (0.5 equiv, 0.1 mmol), Cu_2O (15 mol%, 0.03 mmol), dicumyl peroxide (3 equiv, 0.60 mmol), *t*-butyl-isocyanide (5 equiv, 1.0 mmol), EtOAc (1 mL) were consecutively loaded to an oven dried 10 mL screw cap vial equipped with a magnetic stirring bar and then stirred at 120 °C for 24 h. The resulting reaction mixture was cooled to the ambient temperature and subjected to the column chromatography to afford a mixture of products 3**a** and [D_4]-**3a**. The value of KIE was following determined by ^{1}H NMR of the mixture of 3**a** and [D_4]-**3a** and the result is described as follows.

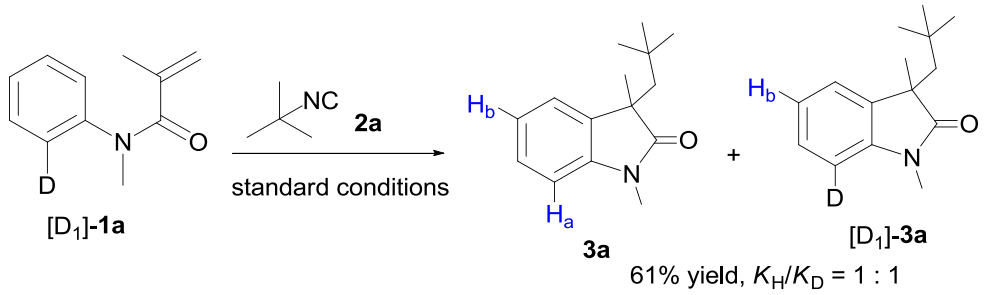


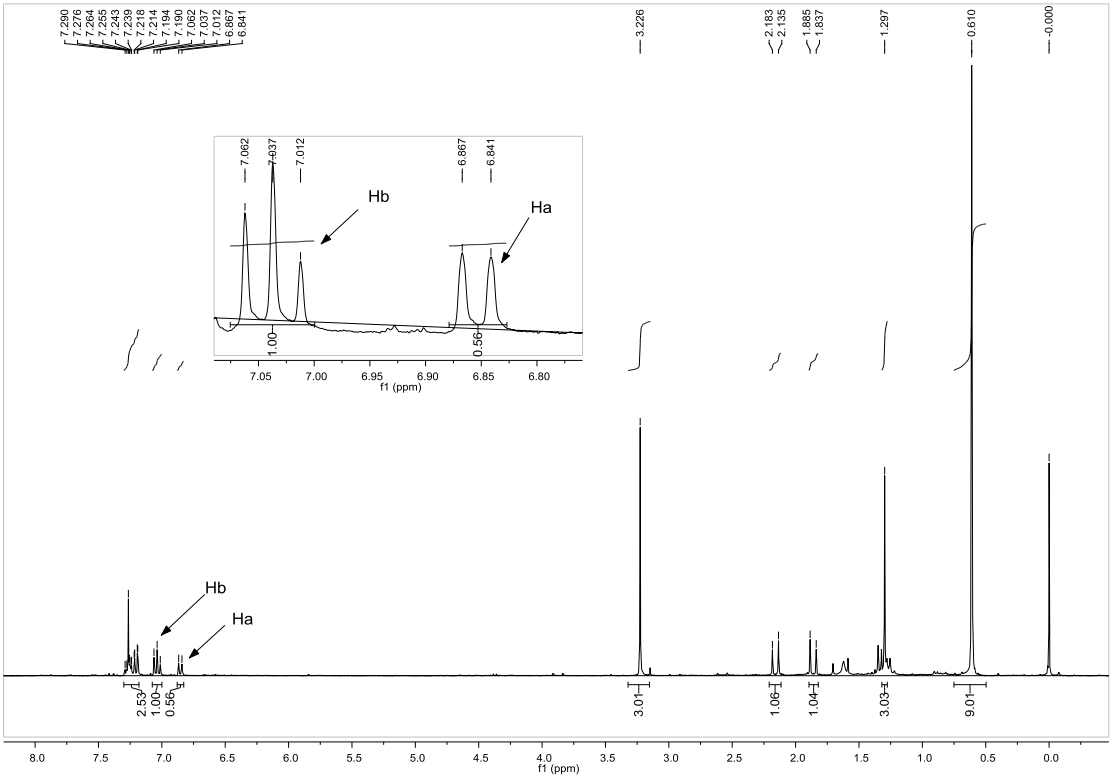


b) Intramolecular KIE experiment:

[D_1]-**1a** was synthesized according the literature.[2] [D_1]-**1a** (1.0 equiv, 0.2 mmol), Cu_2O (15 mol%, 0.03 mmol), dicumyl peroxide (3 equiv, 0.60 mmol), *t*-butyl-isocyanide (5 equiv, 1.0

mmol), EtOAc (1 mL) were consecutively loaded to an oven dried 10 mL screw cap vial equipped with a magnetic stirring bar and then stirred at 120 °C for 24 h. The resulting reaction mixture was cooled to the ambient temperature and subjected to the column chromatography to afford a mixture of products 3**a** and [D_1]-**3a**. The value of KIE was following determined by ^{1}H NMR of the mixture of 3**a** and [D_1]-**3a** and the result is described as follows.

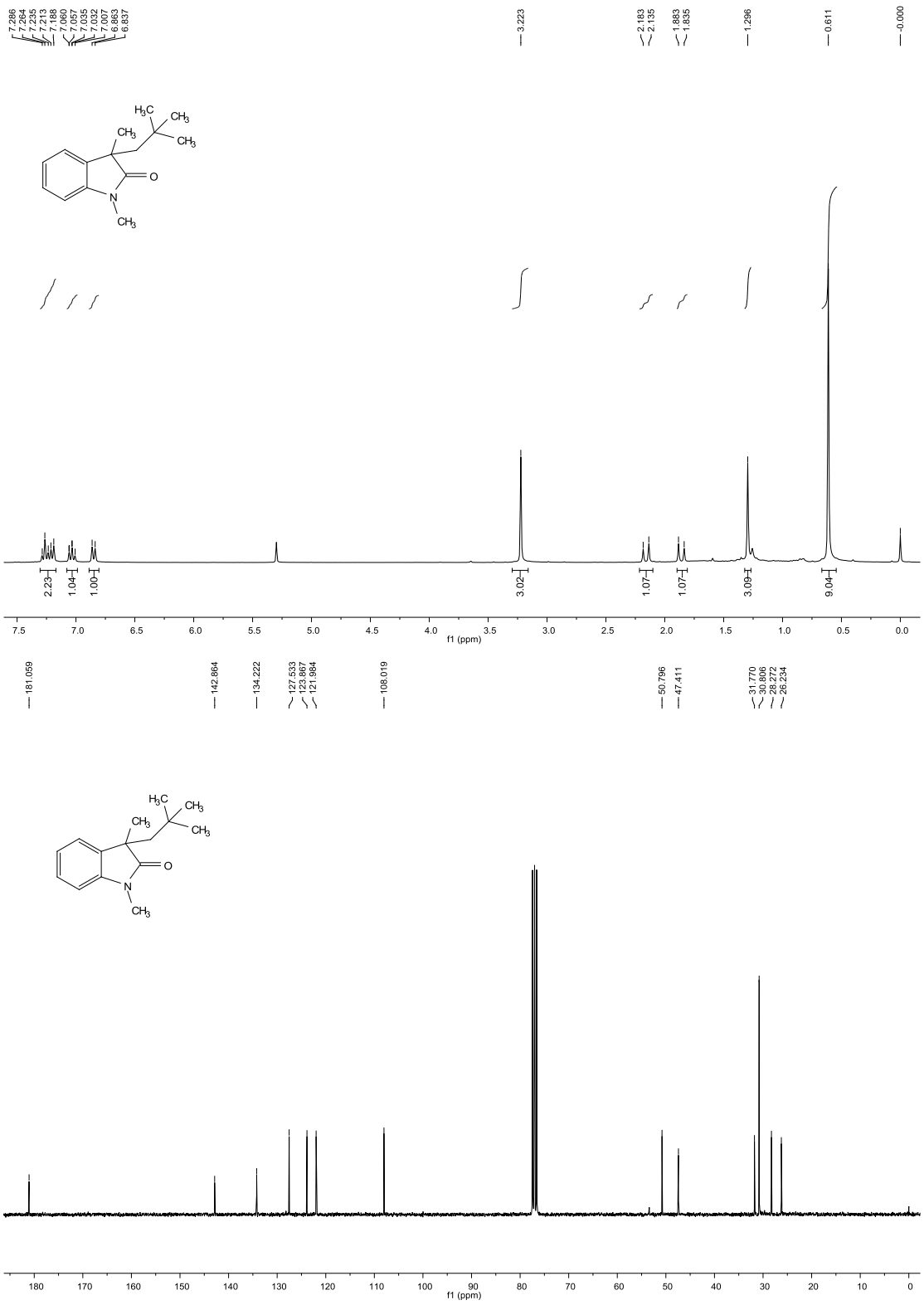




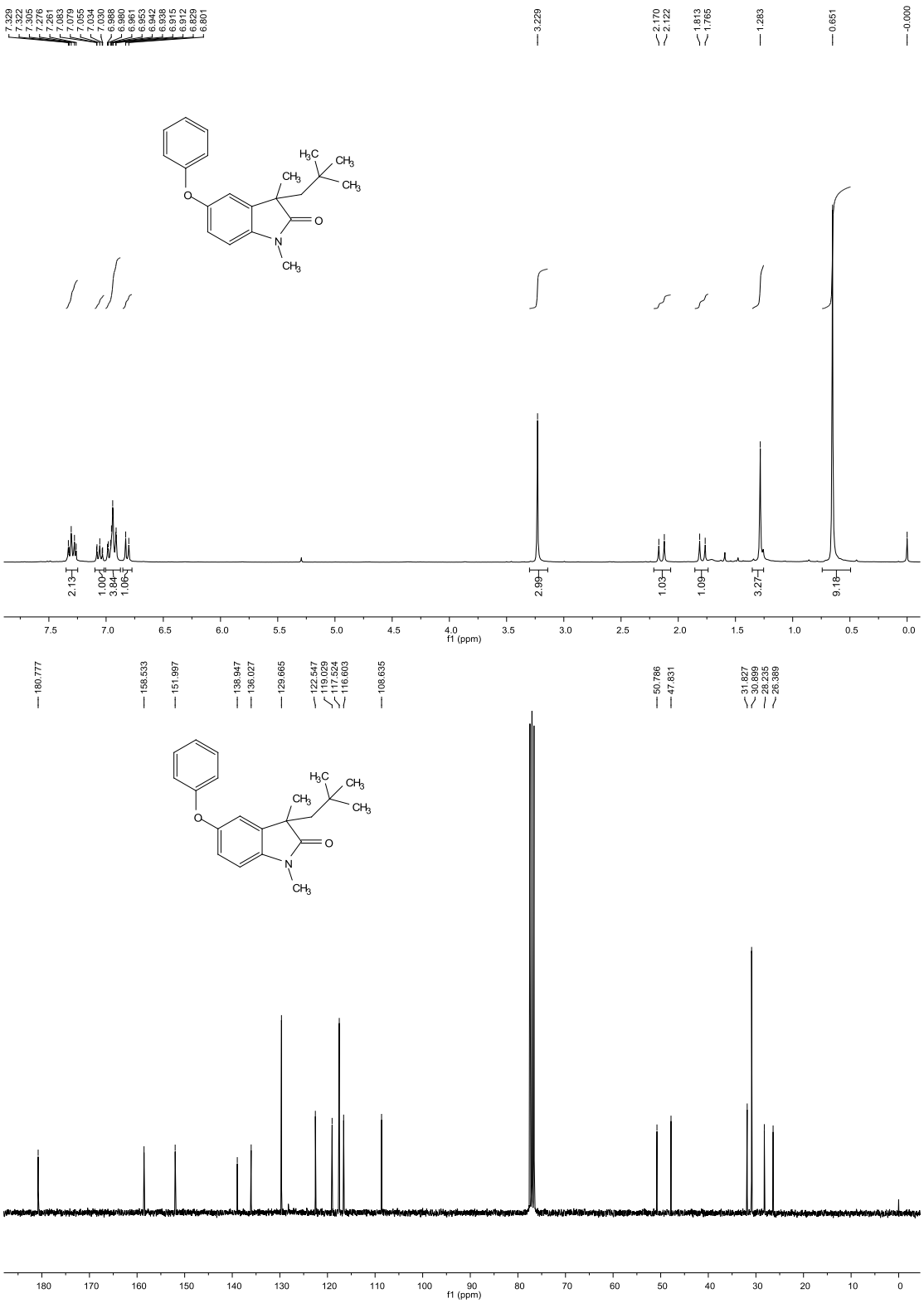
References:

[2] a) A. Pinto, L. Neuville, P. Retailleau, J. Zhu, *Org. Lett.*, **2006**, *8*, 4927-4930; b) I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, G. P. Mcglacken, F. Weissburger, A. H. M. de Vries, L. S. van de Vondervoort, *Chem. Eur. J.*, **2006**, *12*, 8750-8761.

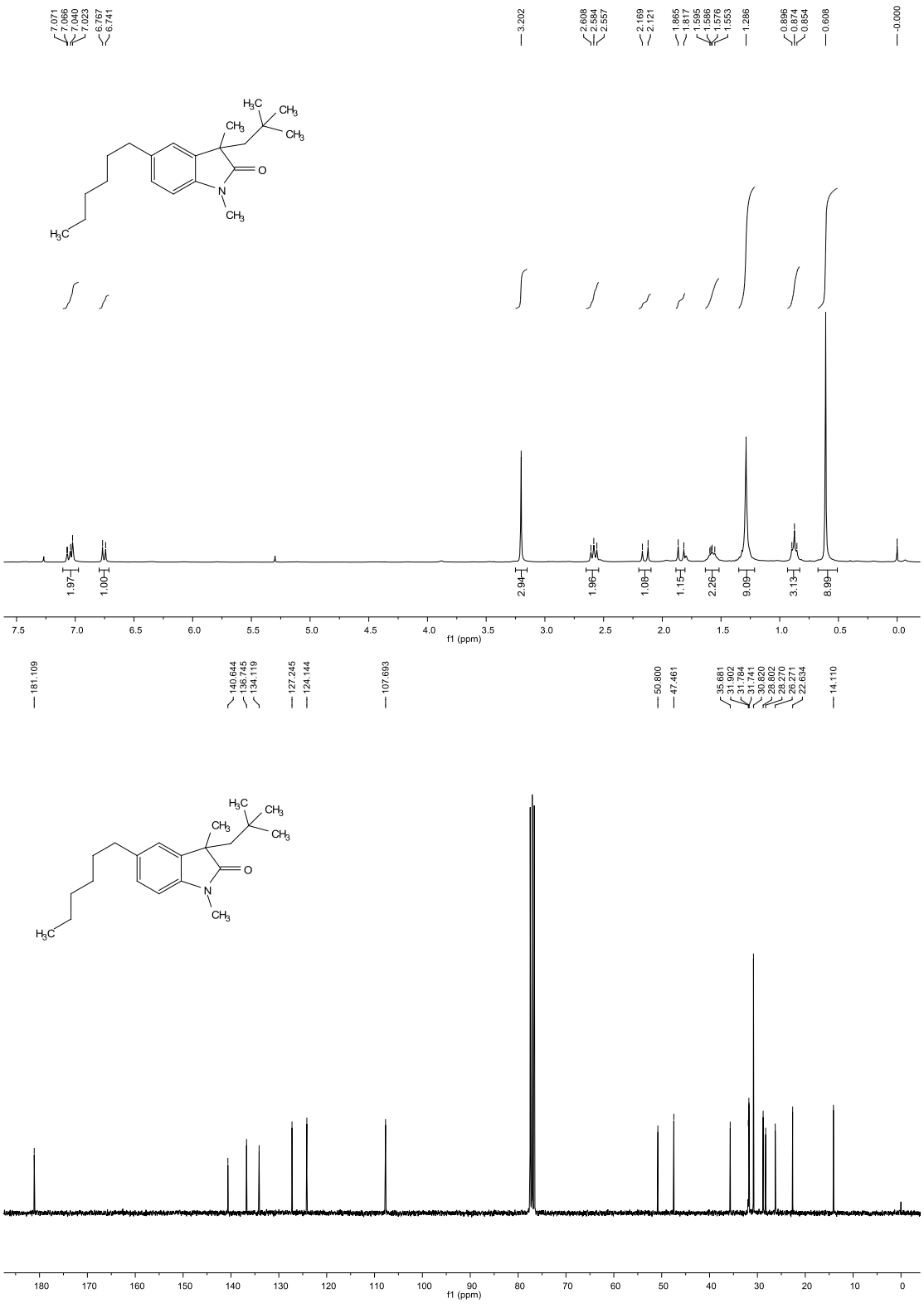
^{1}H and ^{13}C-NMR Spectra of the Products



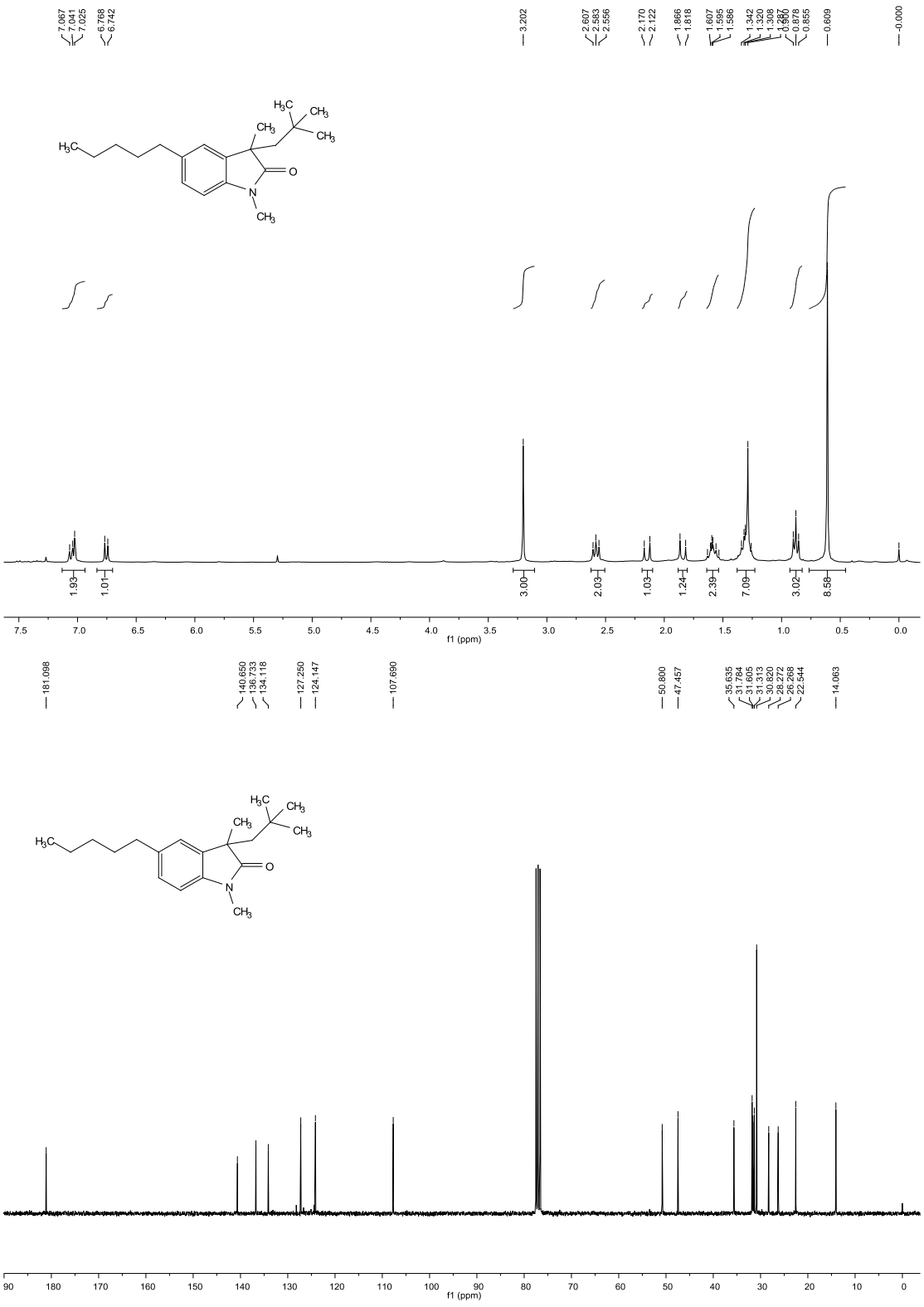
^{1}H and ^{13}C-NMR of 3a



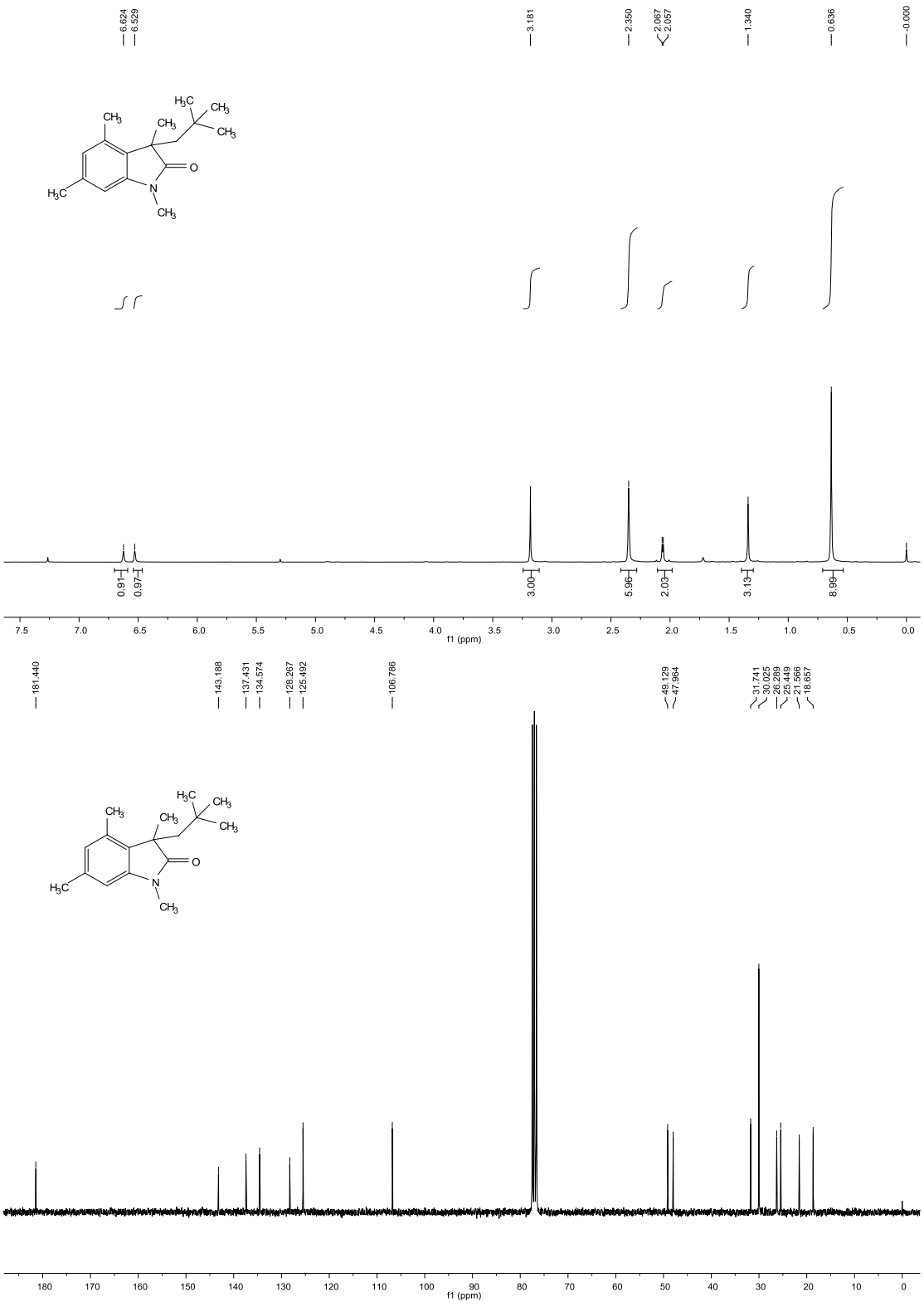
^{1}H and ^{13}C-NMR of 3b



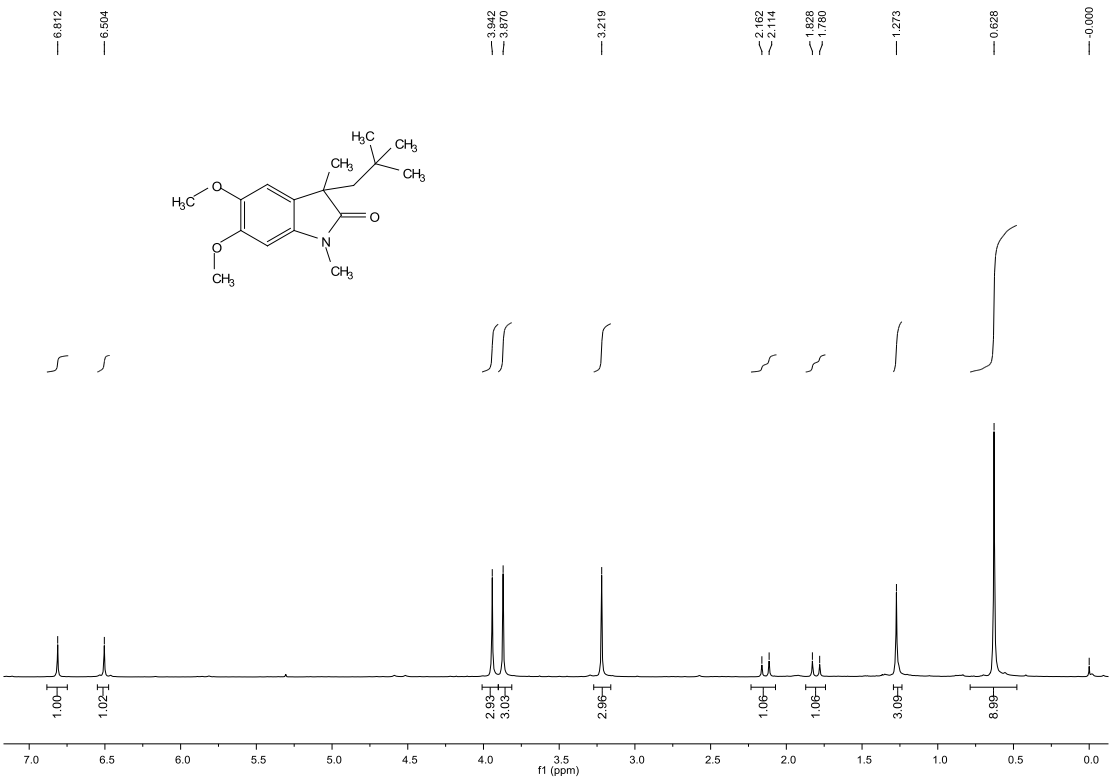
^{1}H and ^{13}C-NMR of 3c

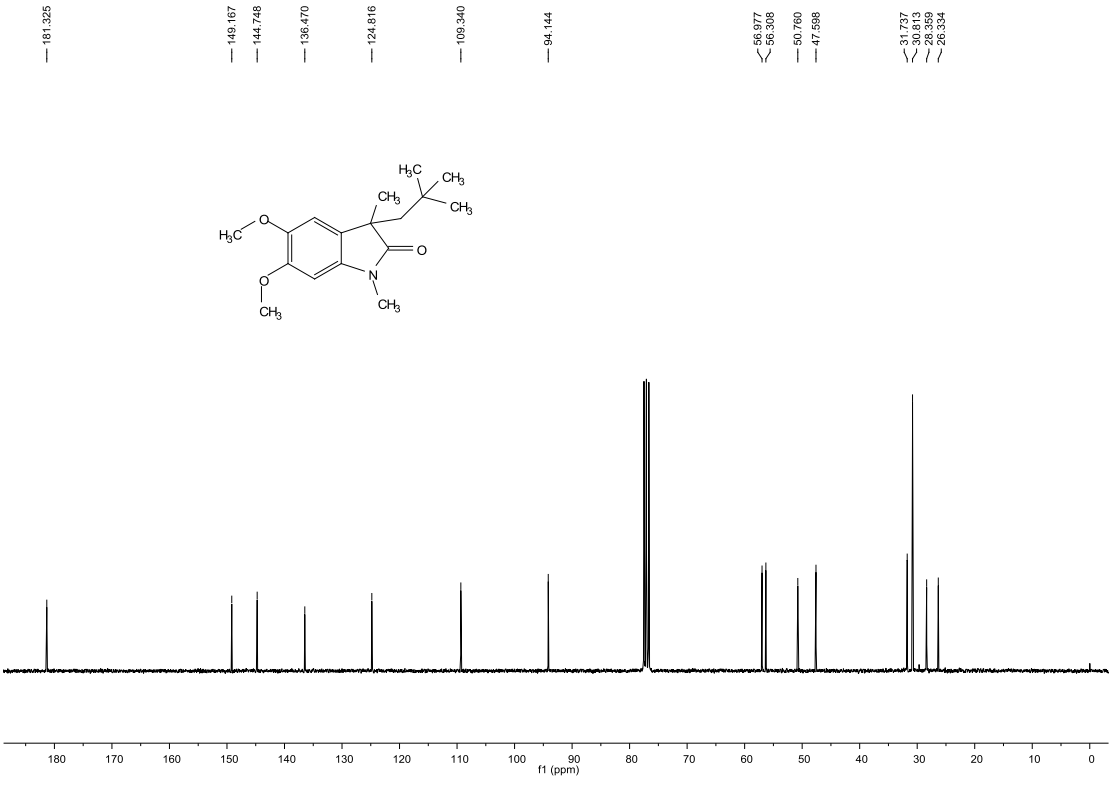


^{1}H and ^{13}C-NMR of 3d

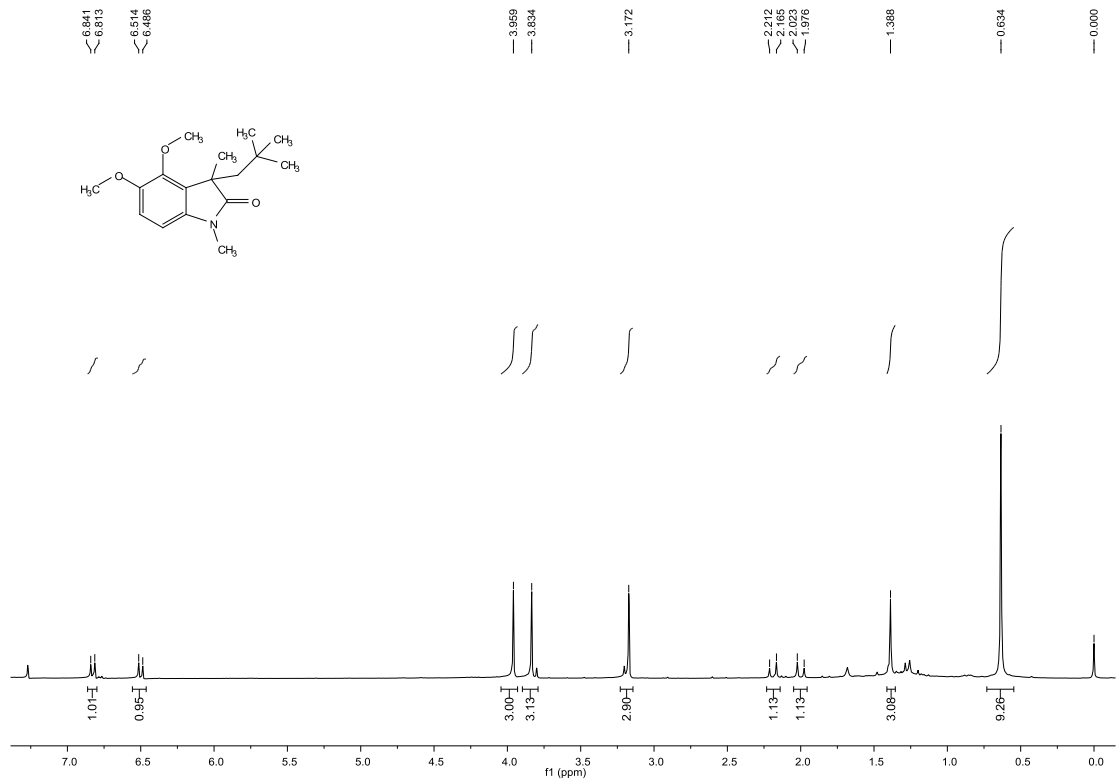


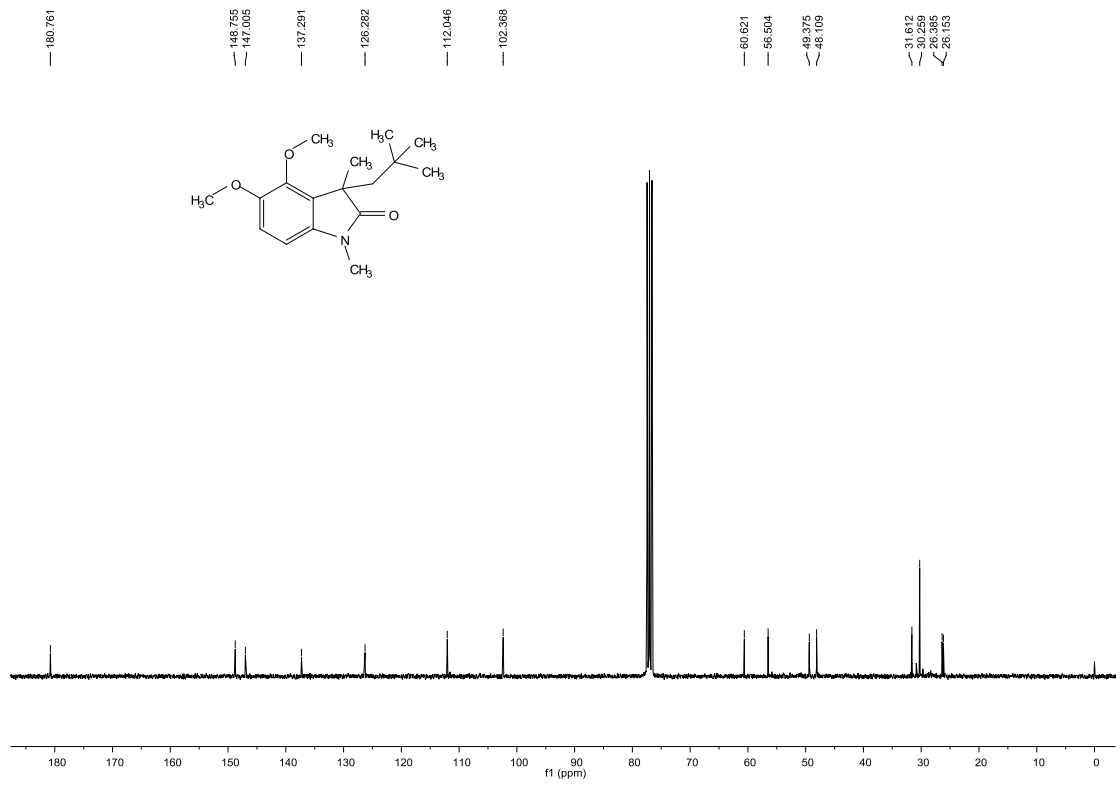
^{1}H and ^{13}C-NMR of 3e





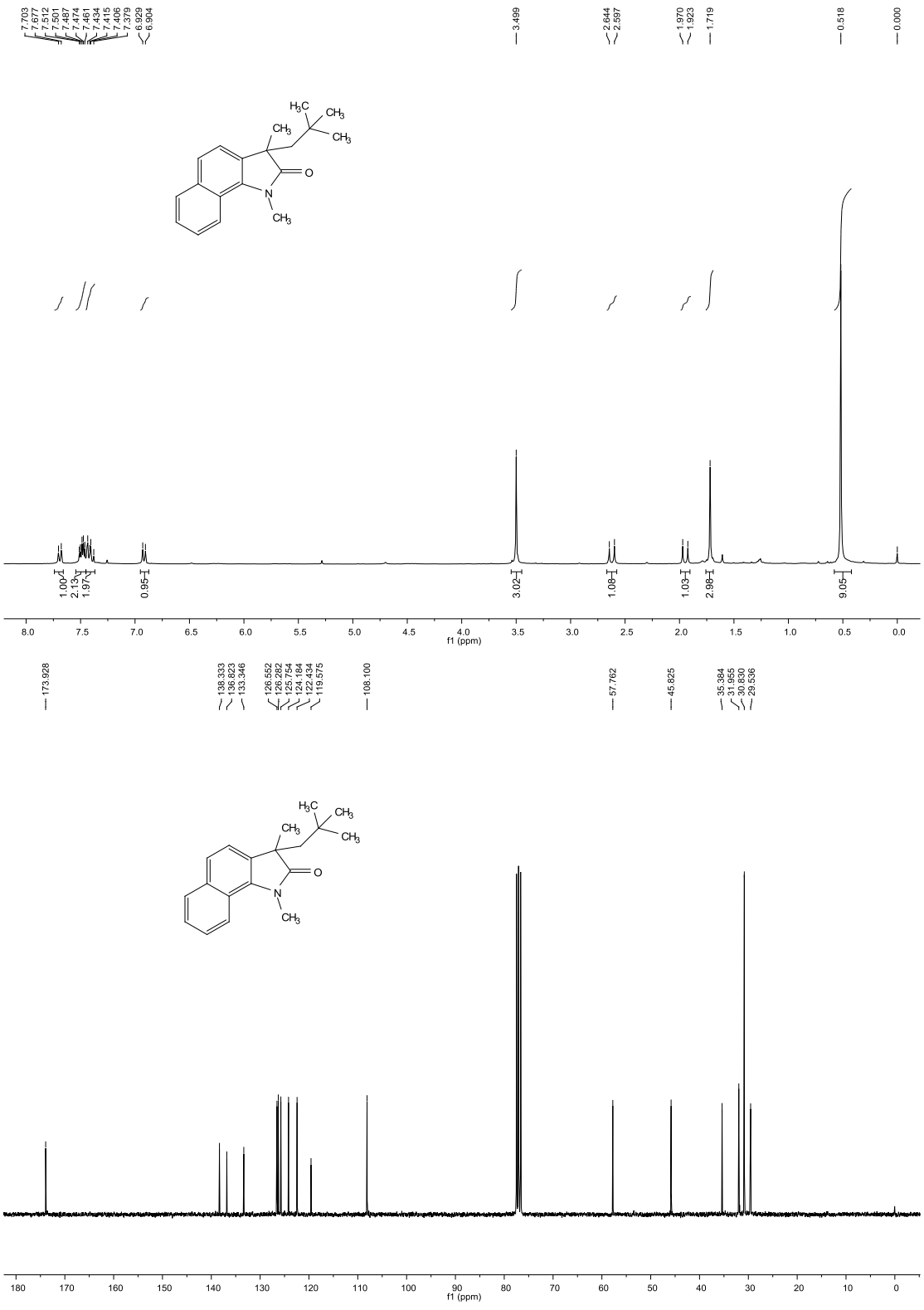
^{1}H and ^{13}C-NMR of 3f



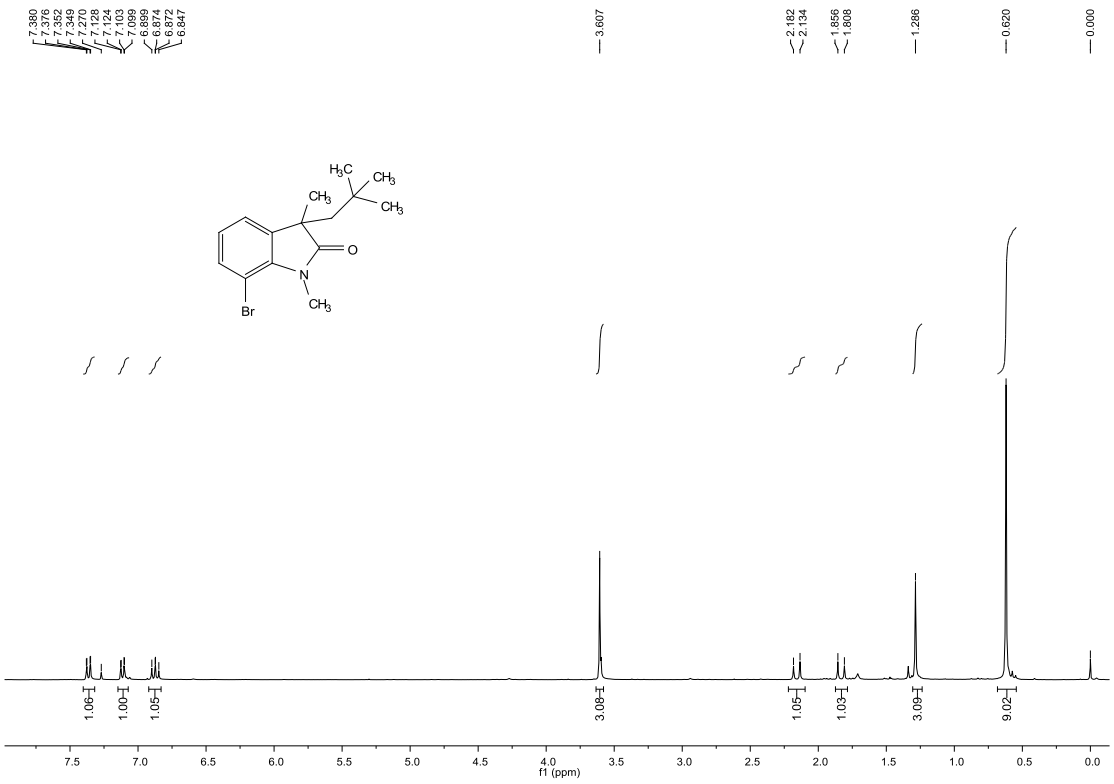


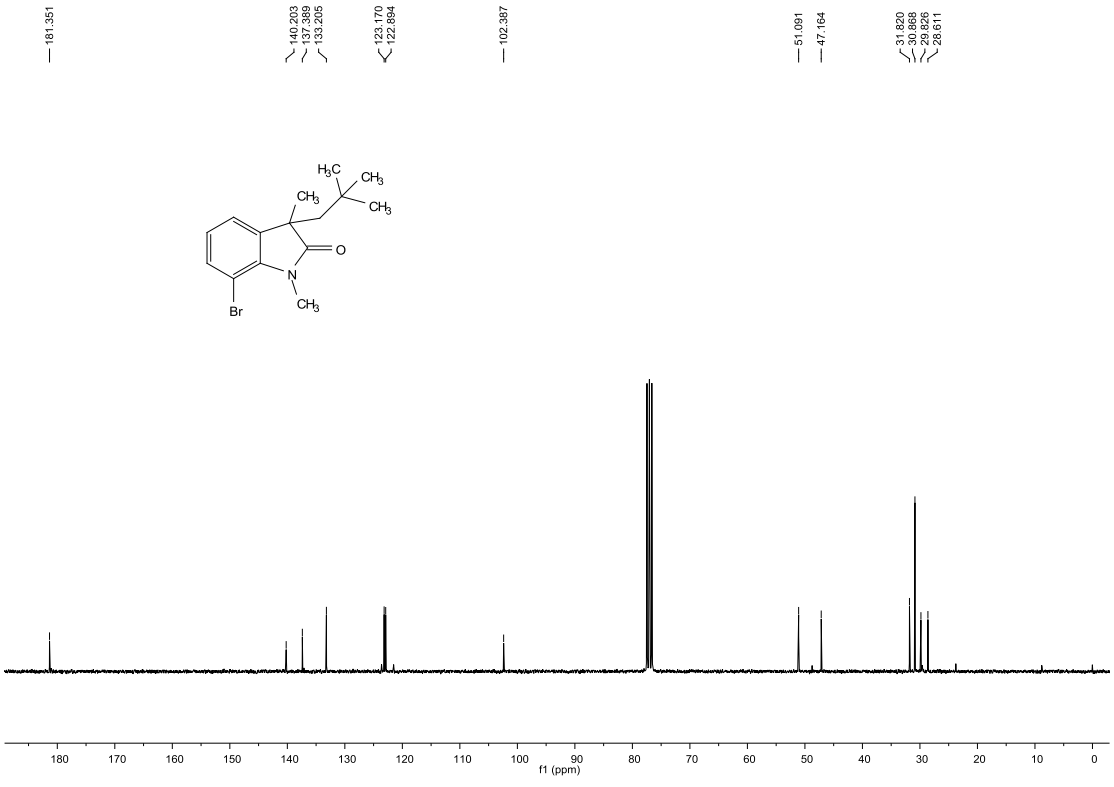
^{1}H and ^{13}C-NMR of 3f′

^{1}H and ^{13}C-NMR of 3g

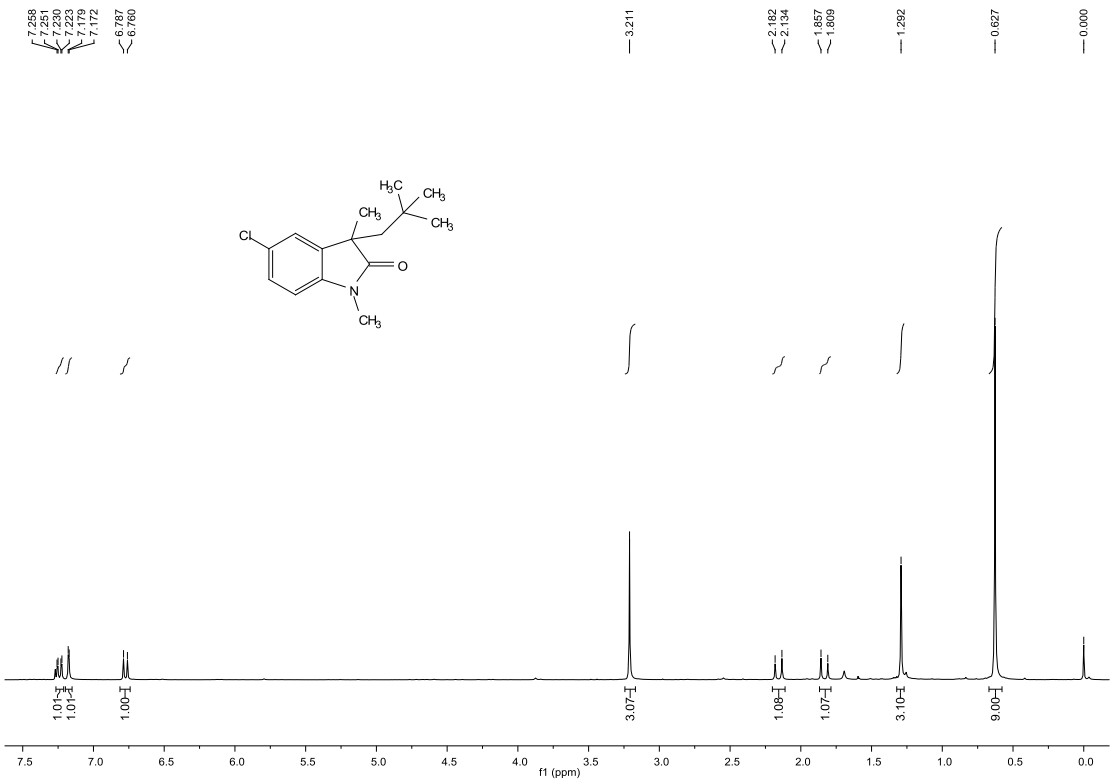


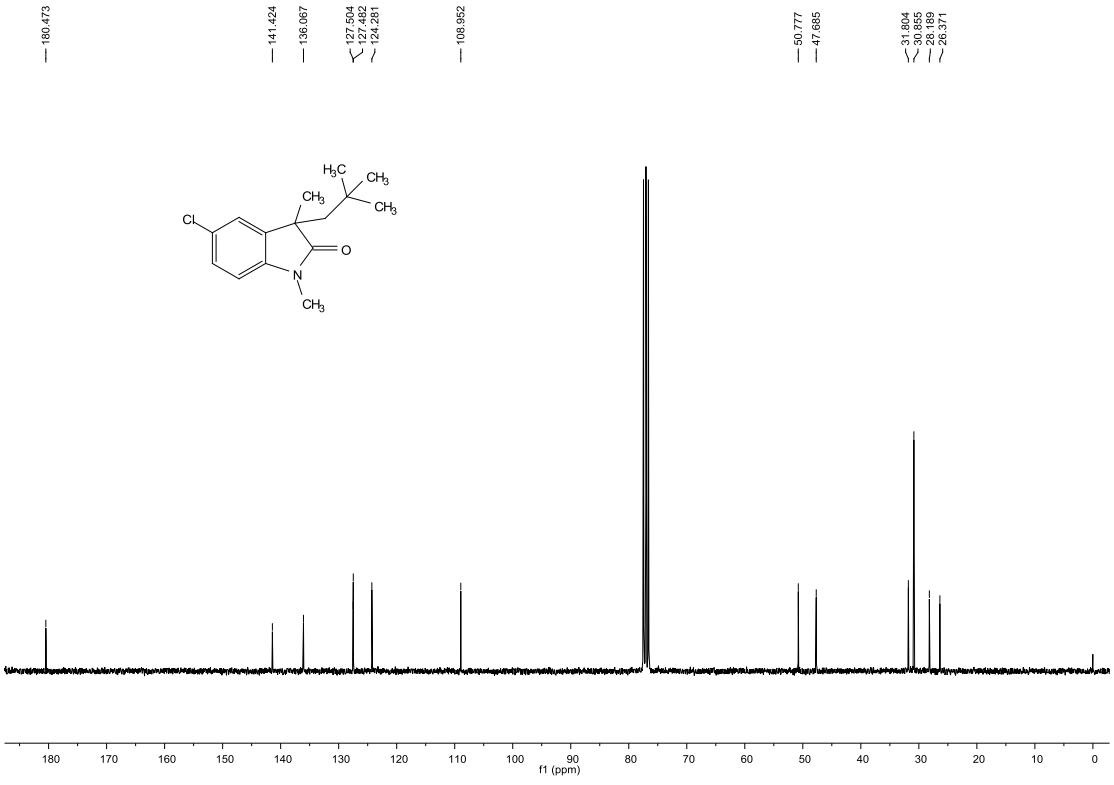
^{1}H and ^{13}C-NMR of 3h



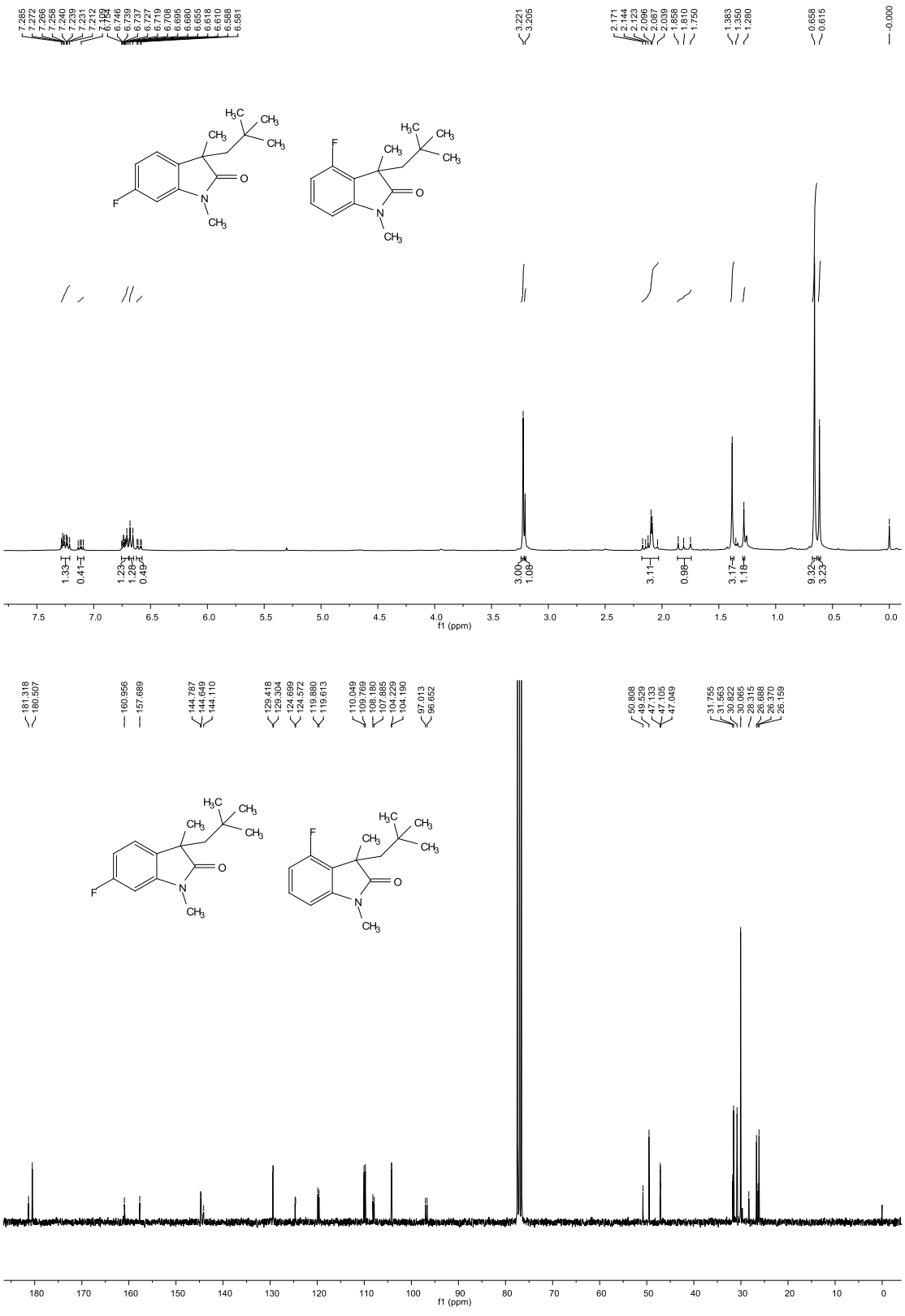


^{1}H and ^{13}C-NMR of 3i

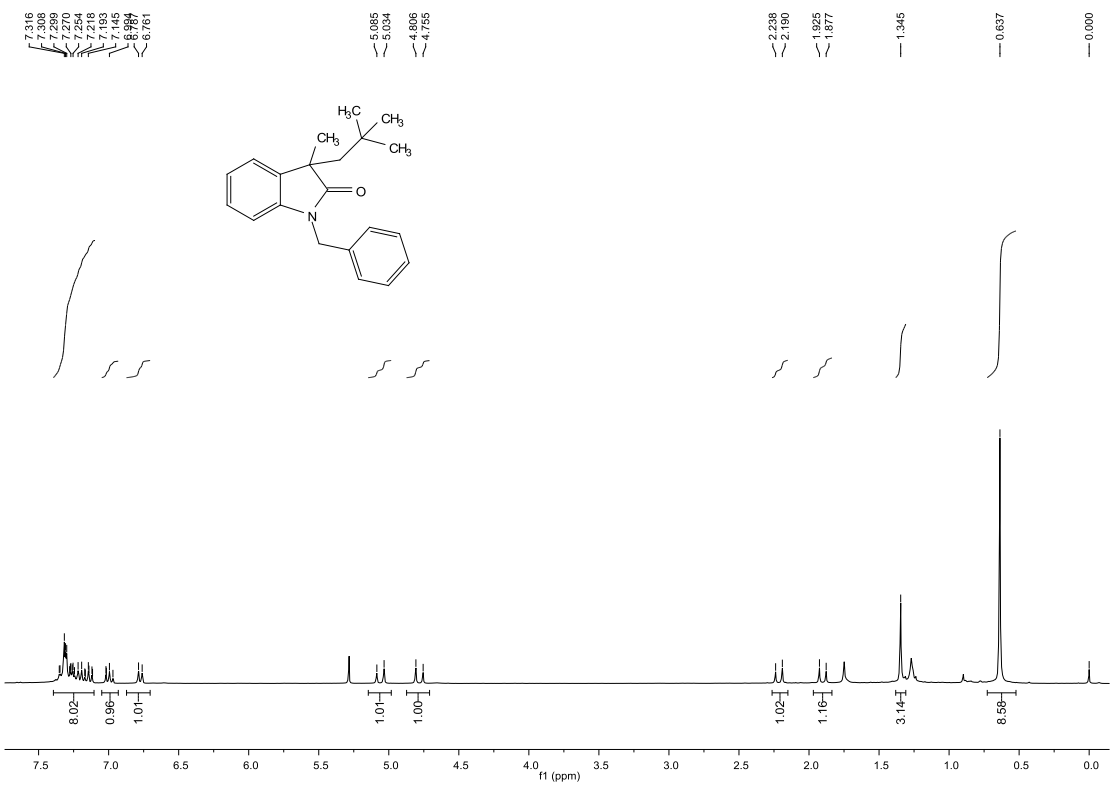


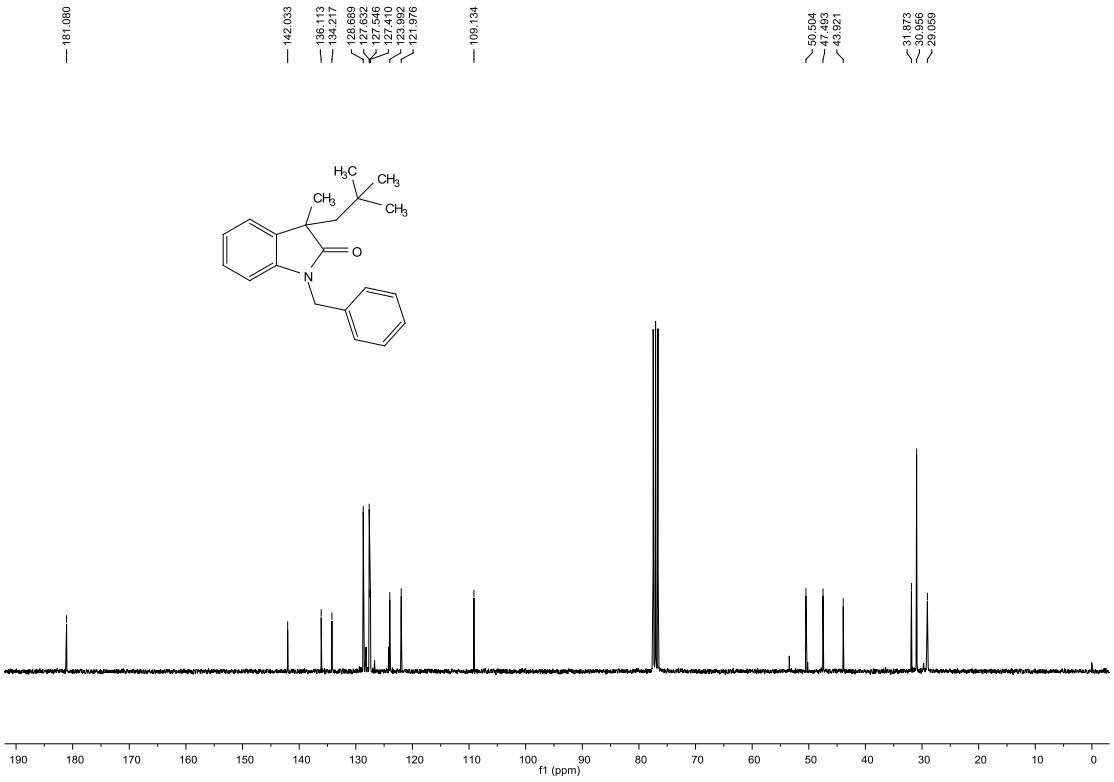


^{1}H and ^{13}C-NMR of 3j

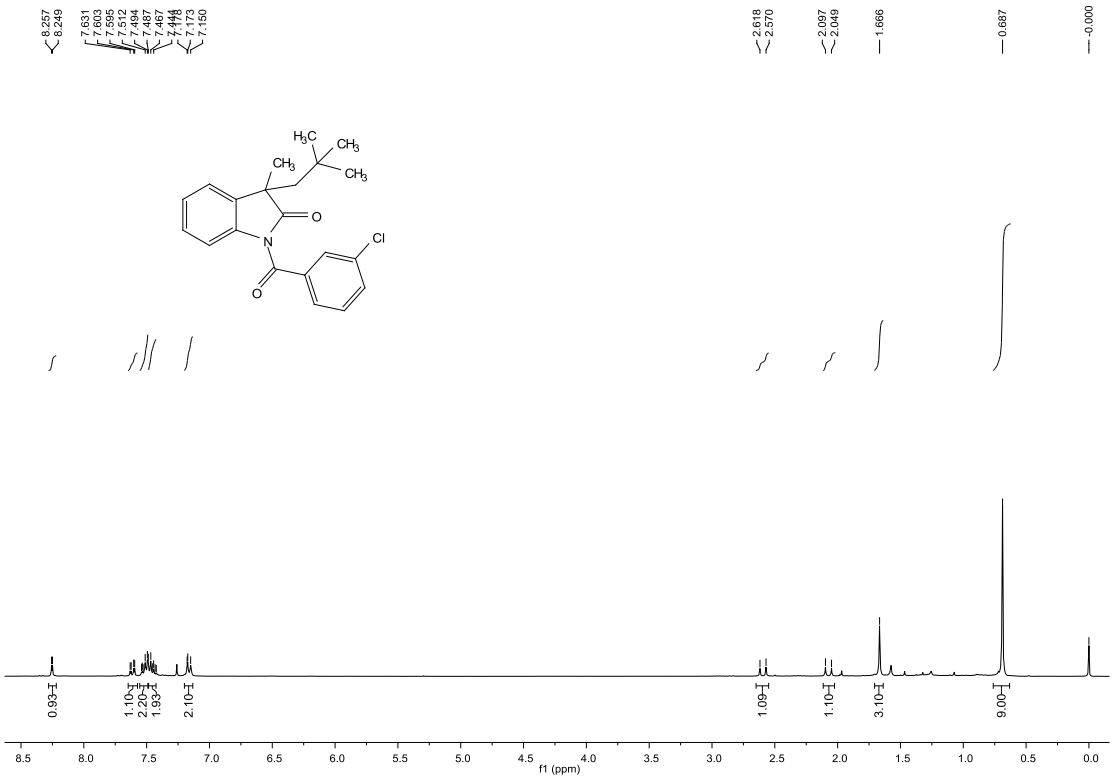


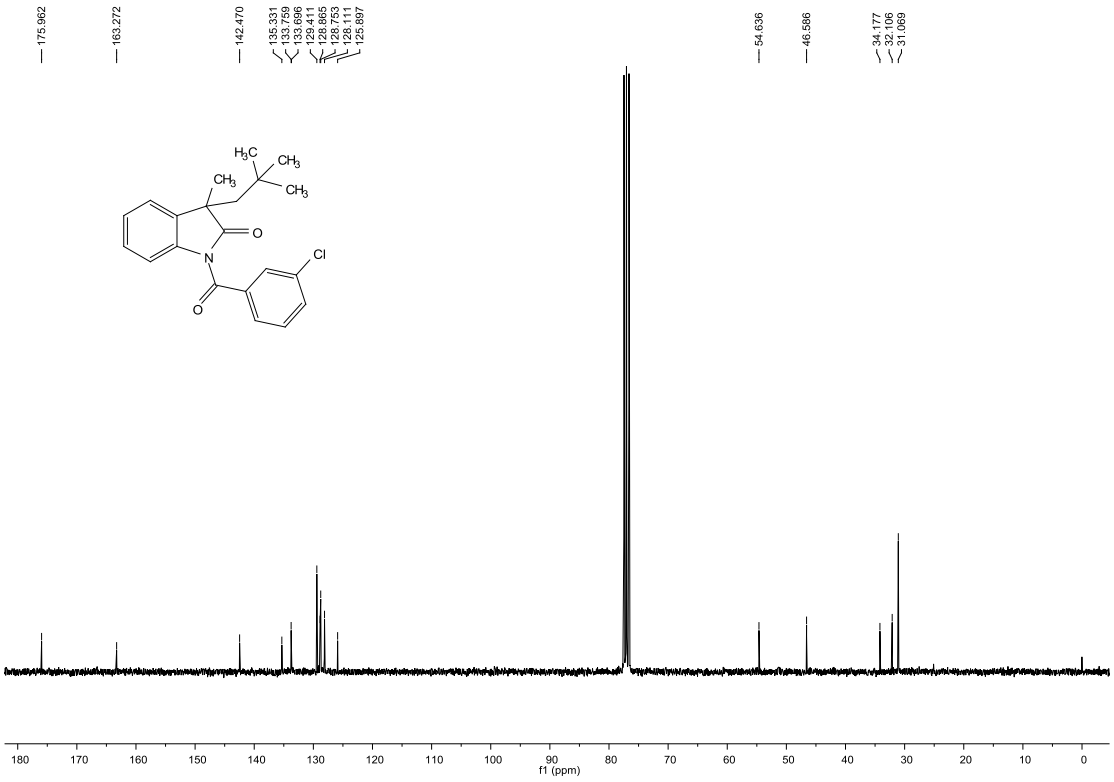
^{1}H and ^{13}C-NMR of 3l



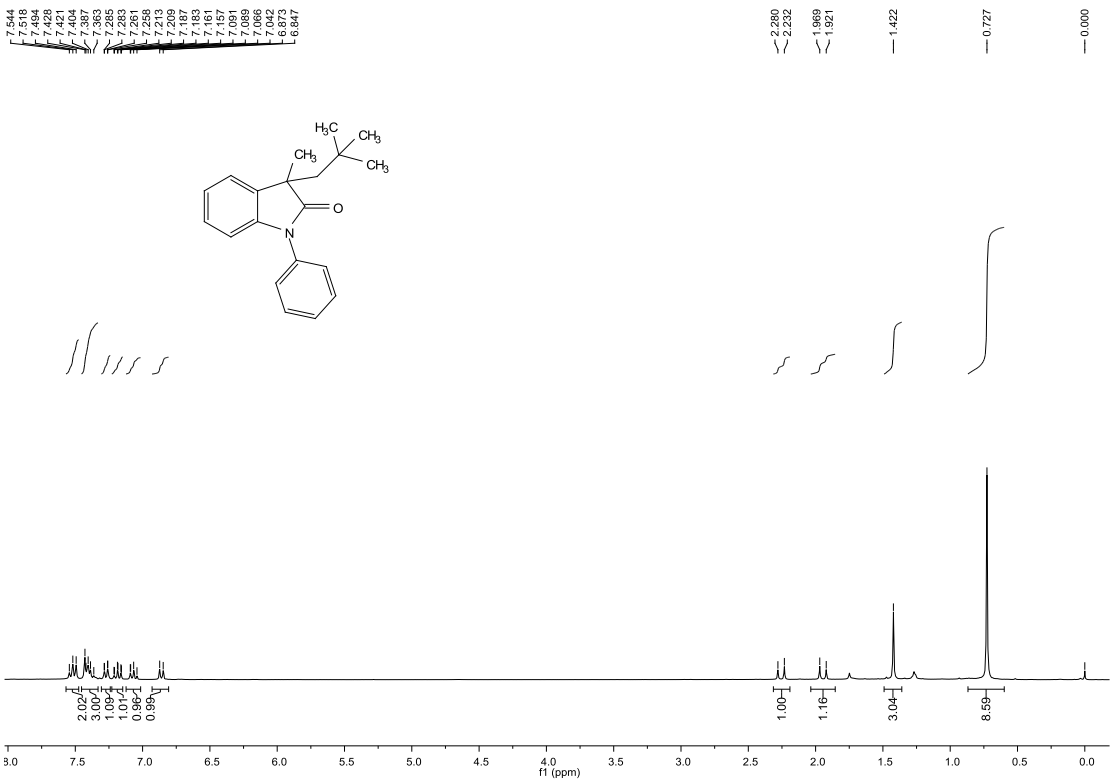


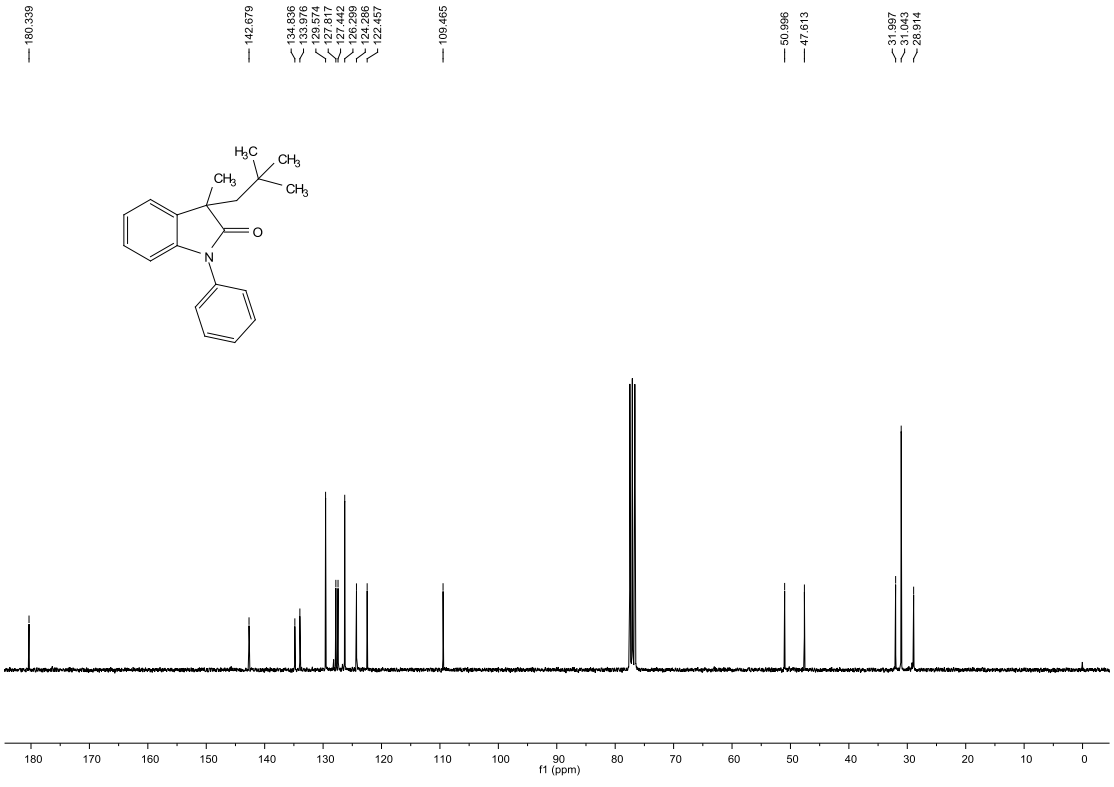
^{1}H and ^{13}C-NMR of 3m



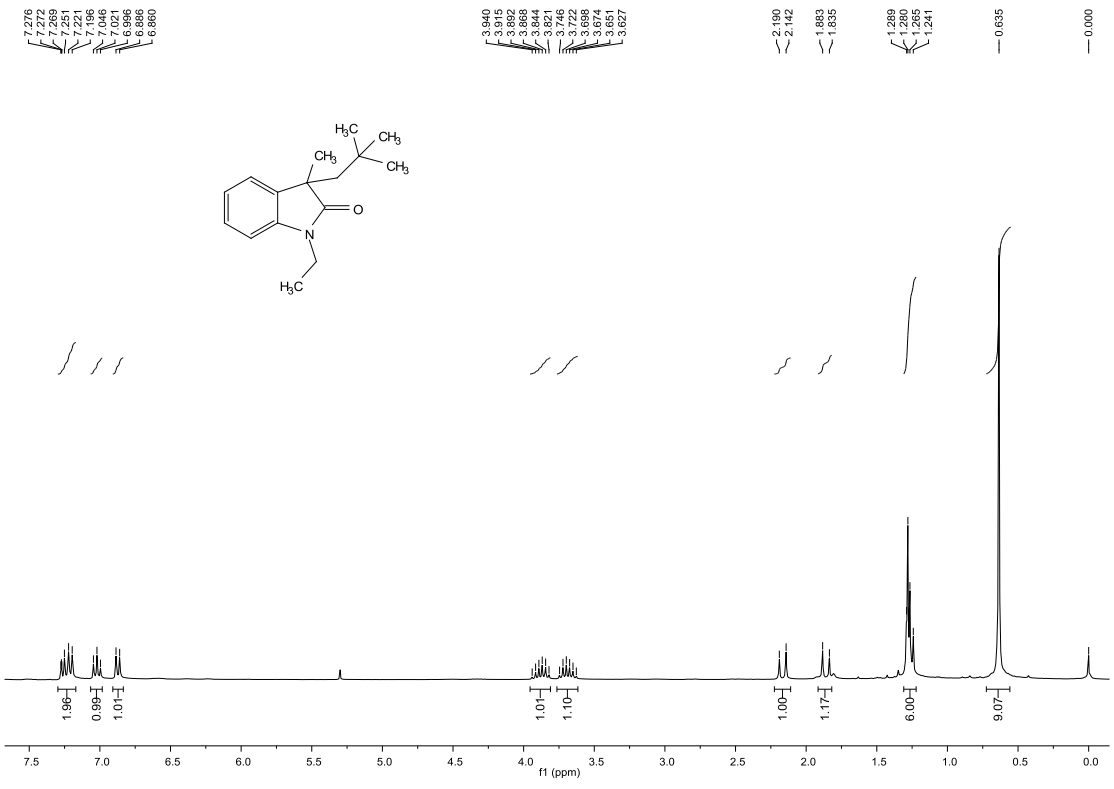


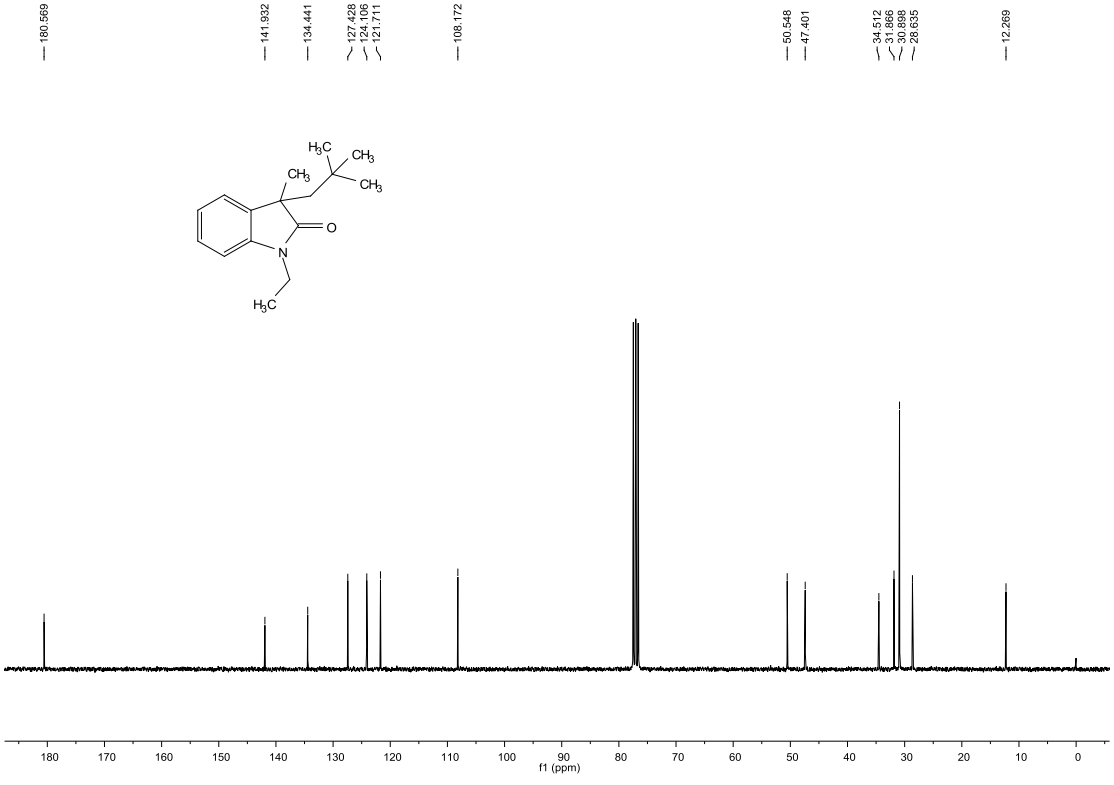
^{1}H and ^{13}C-NMR of 3n



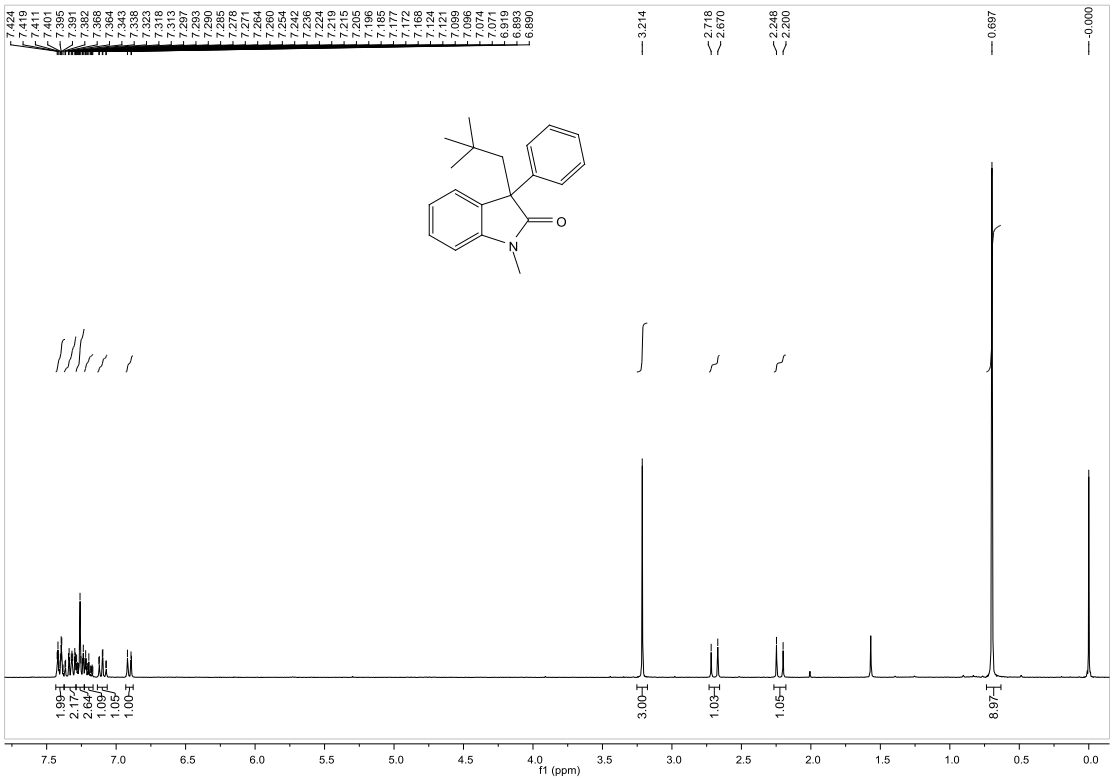


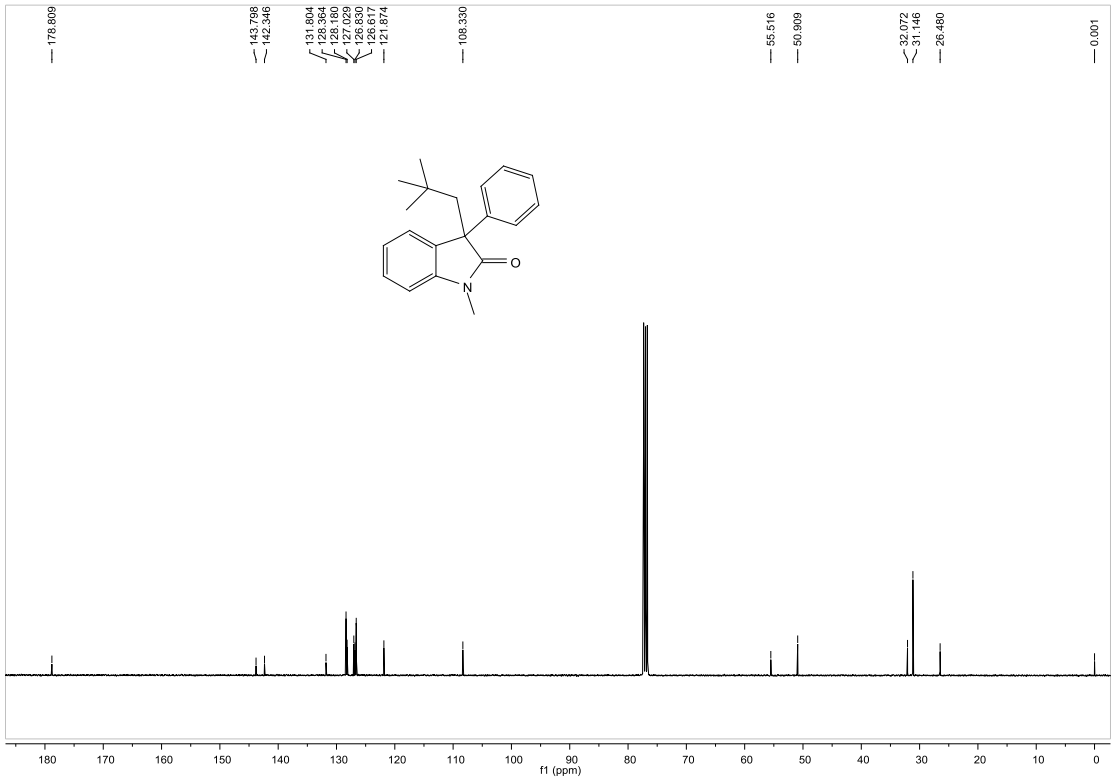
^{1}H and ^{13}C-NMR of 3o



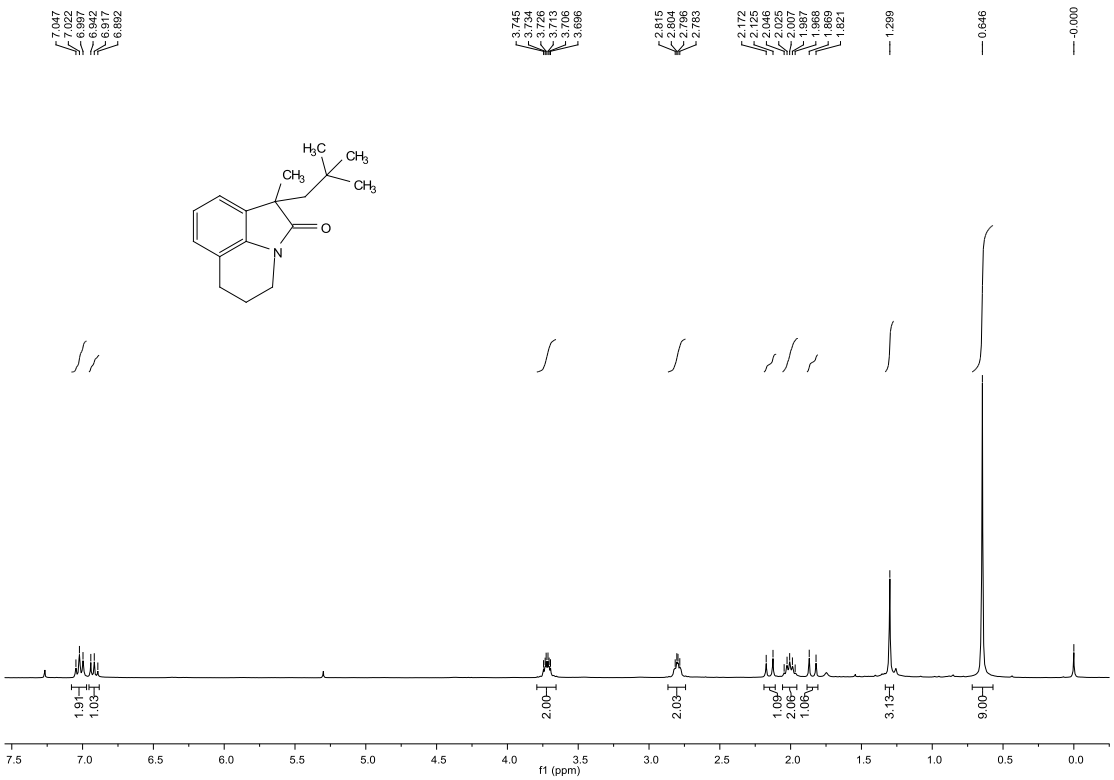


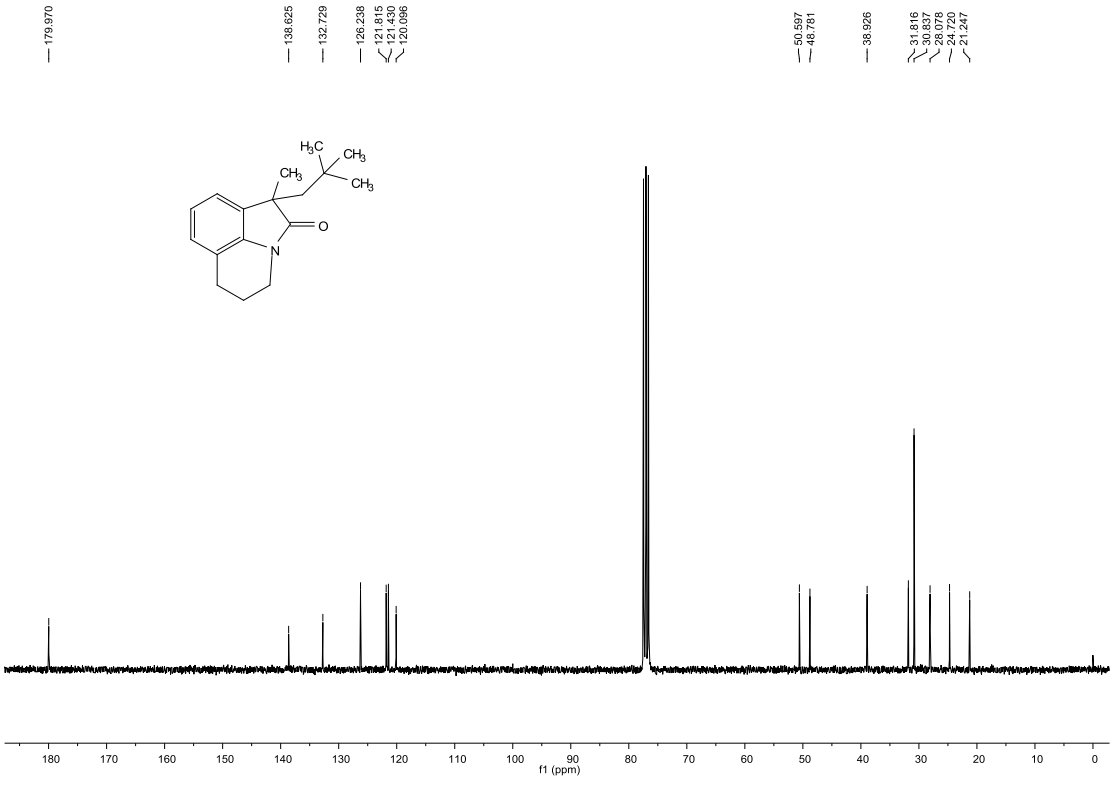
^{1}H and ^{13}C-NMR of 3p



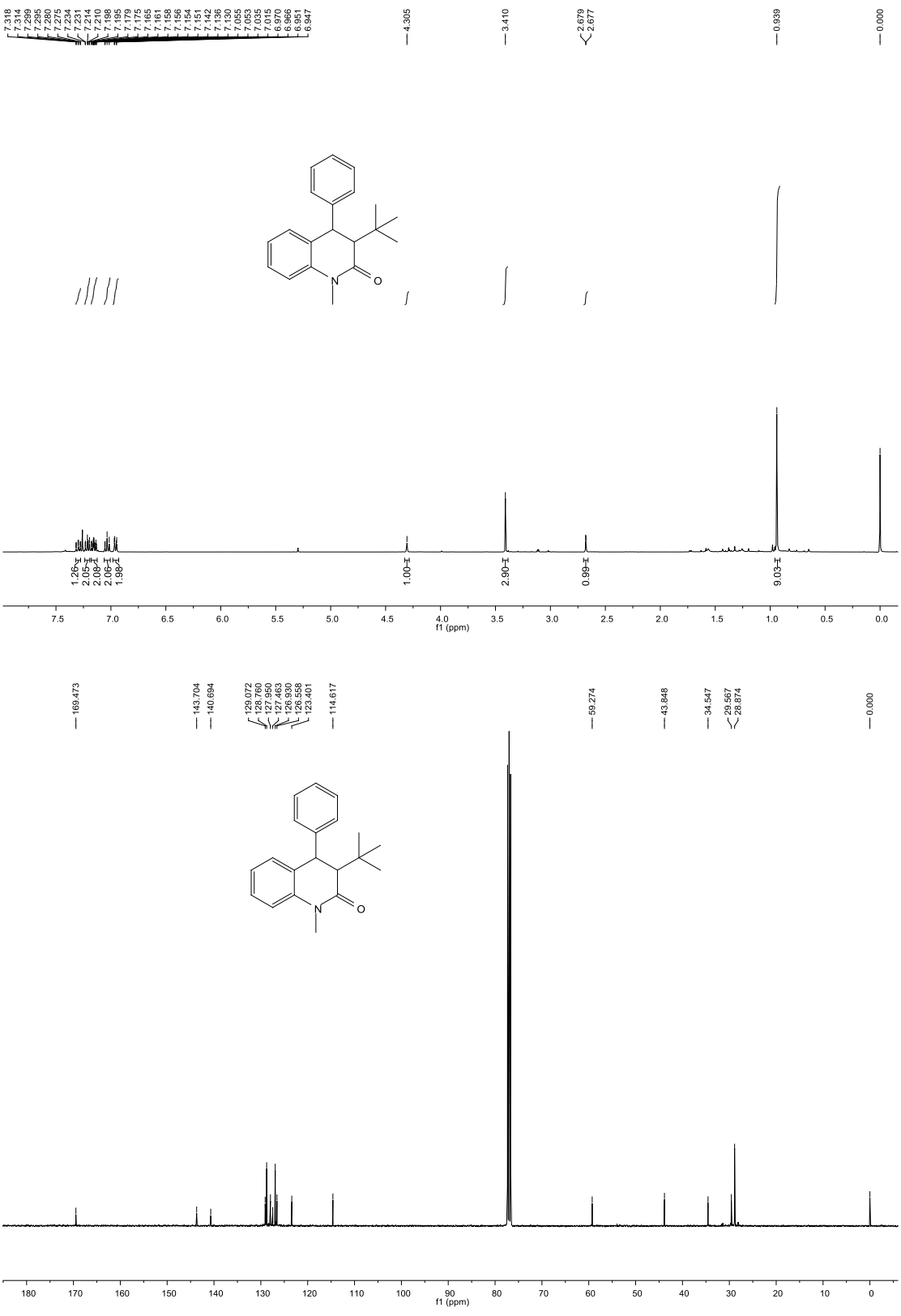


^{1}H and ^{13}C-NMR of 3s

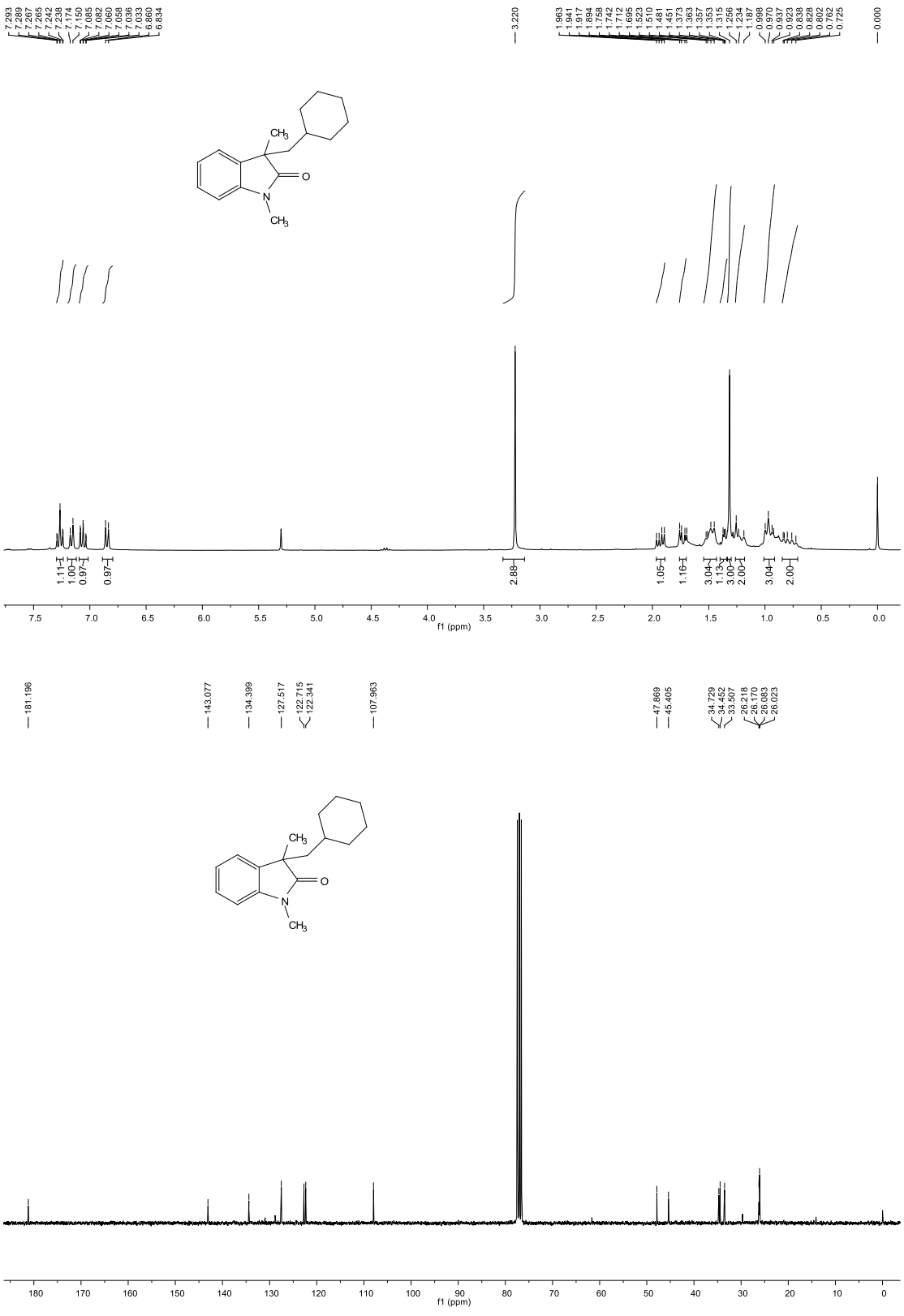




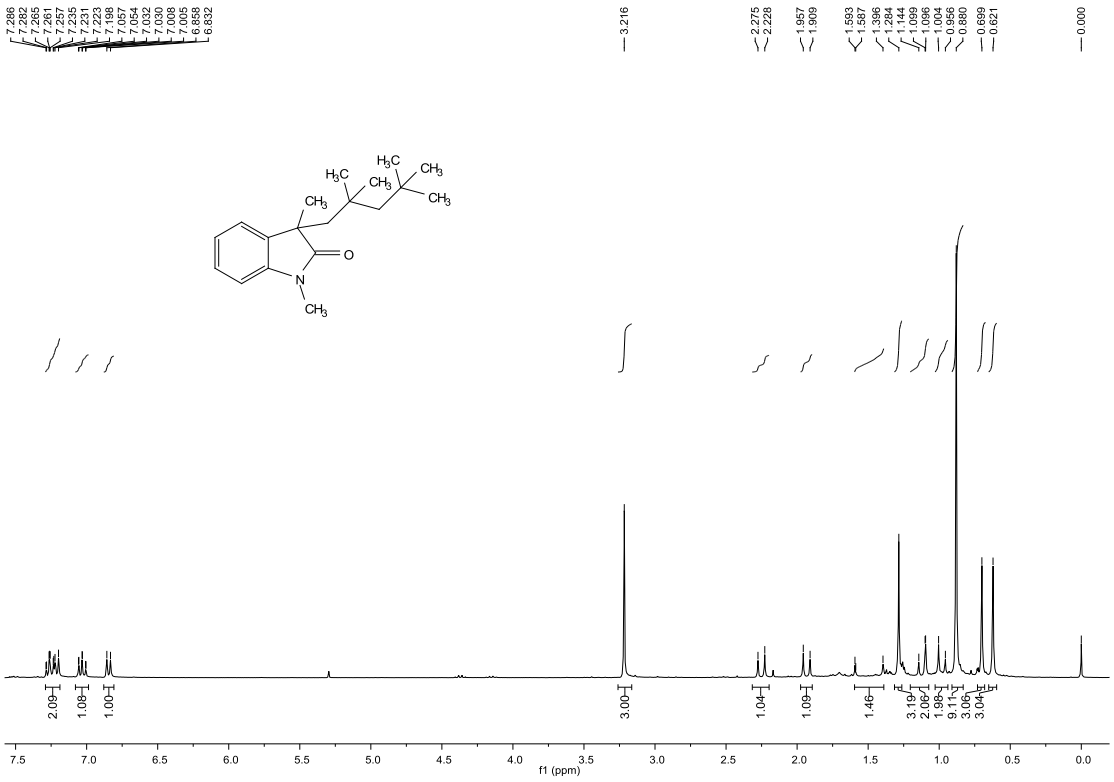
^{1}H and ^{13}C-NMR of 5a

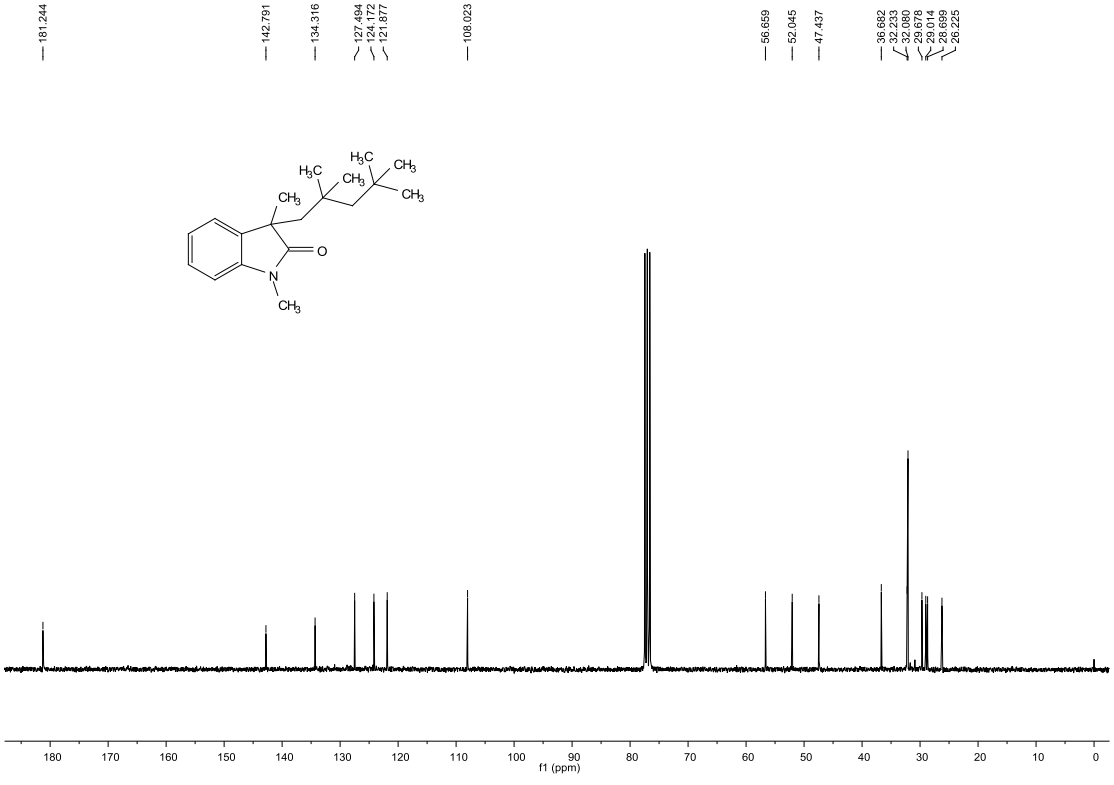


^{1}H and ^{13}C-NMR of 5b

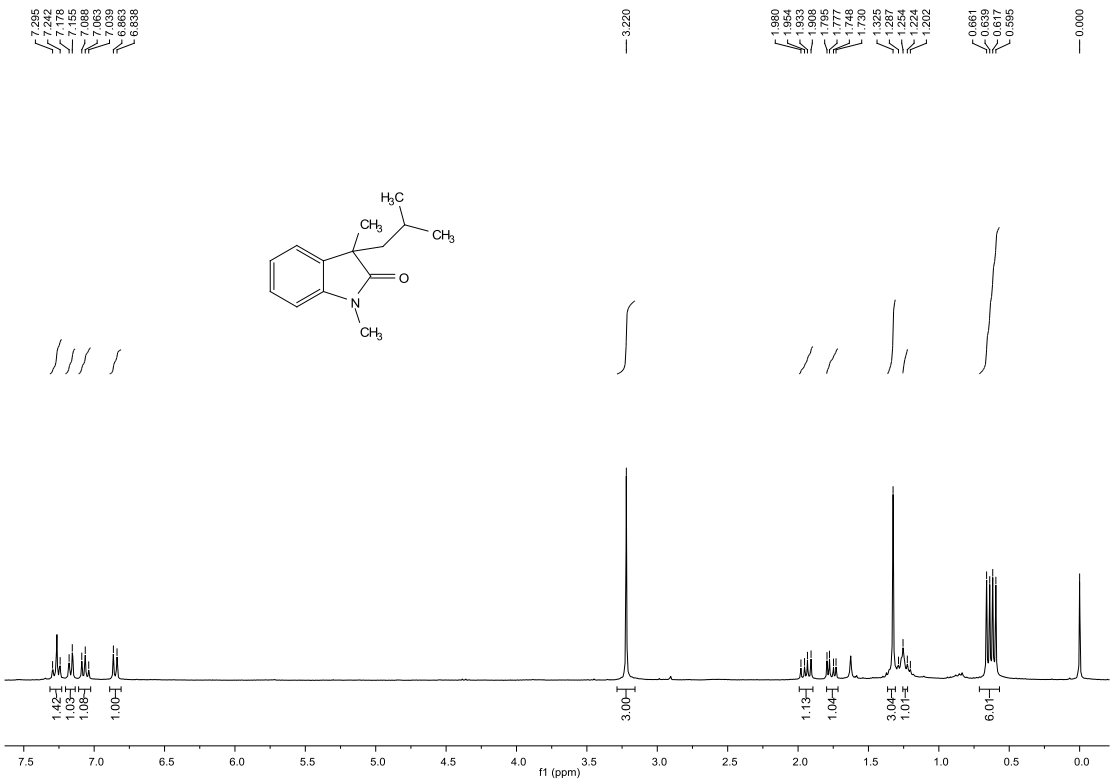


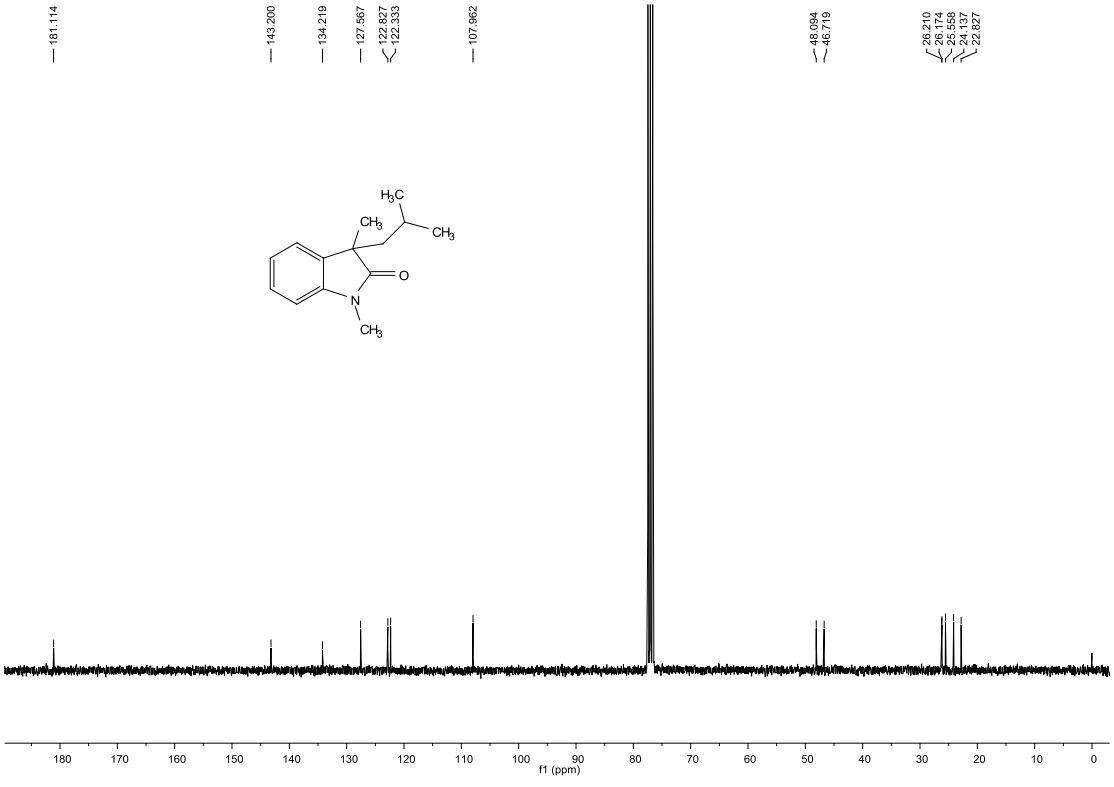
^{1}H and ^{13}C-NMR of 3t



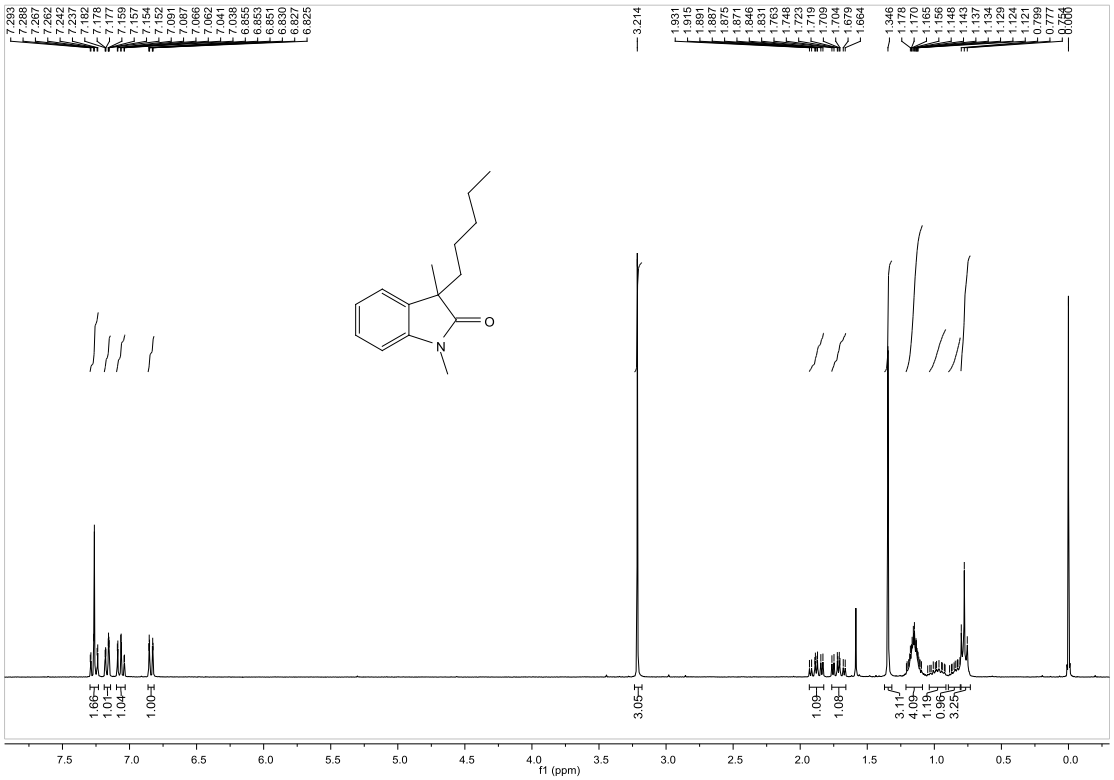


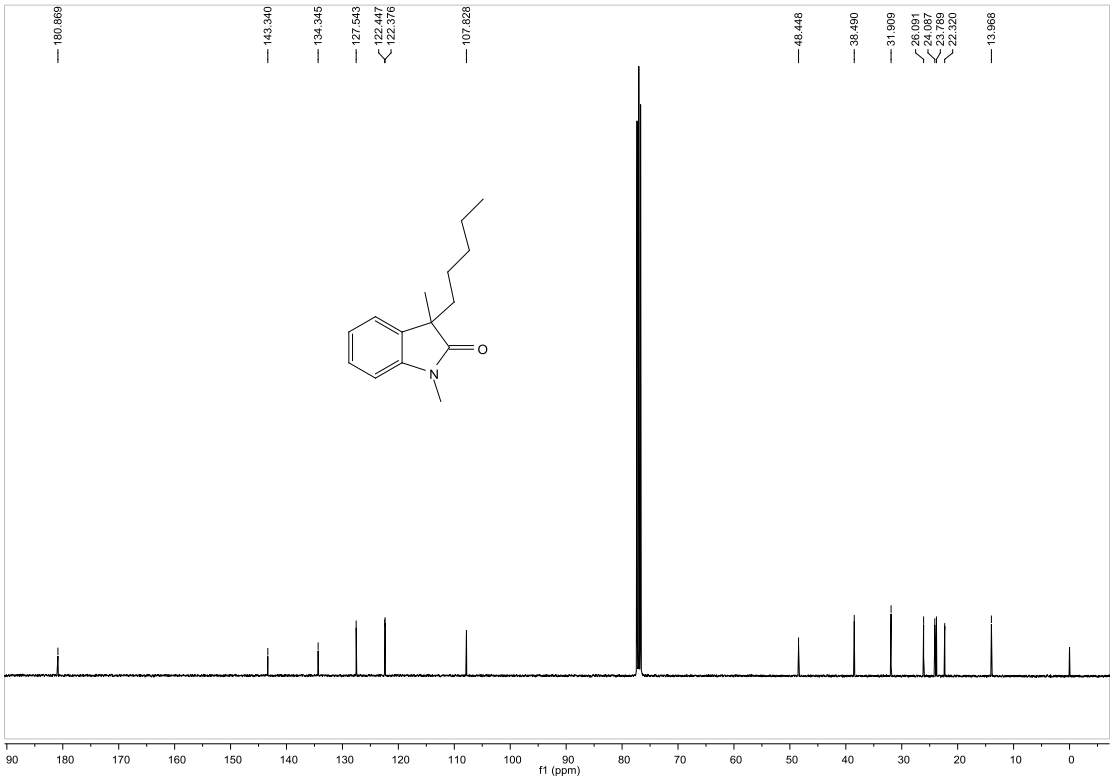
^{1}H and ^{13}C-NMR of 3u



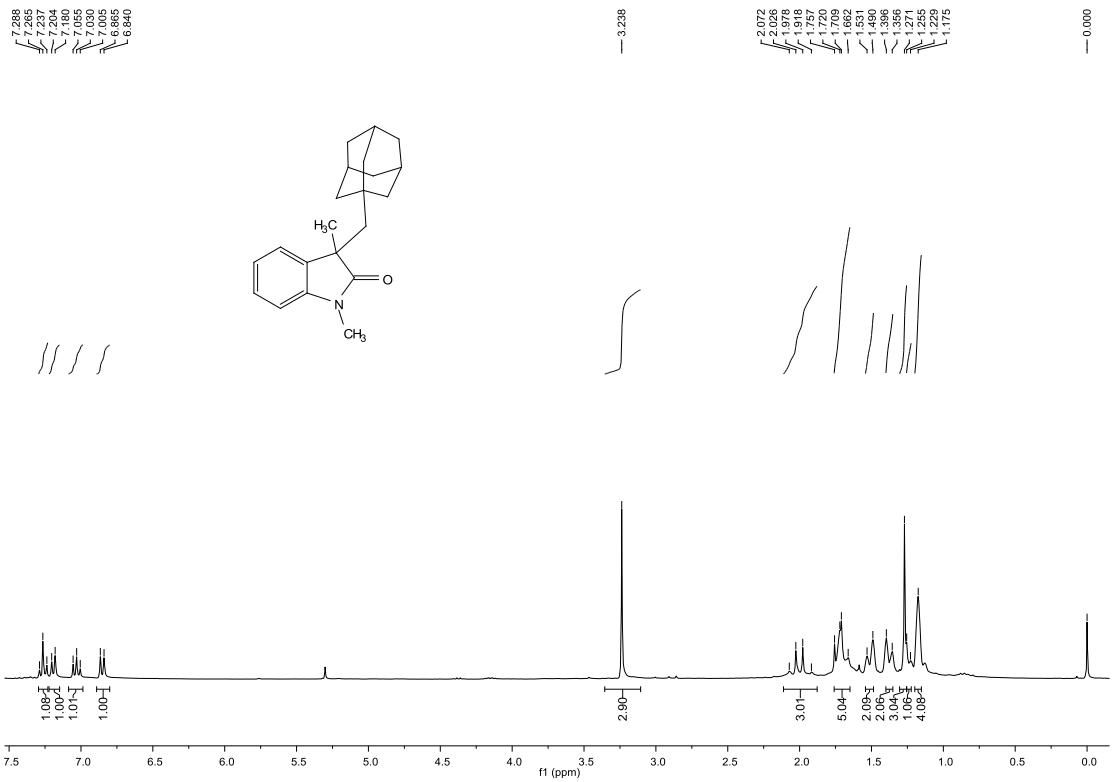


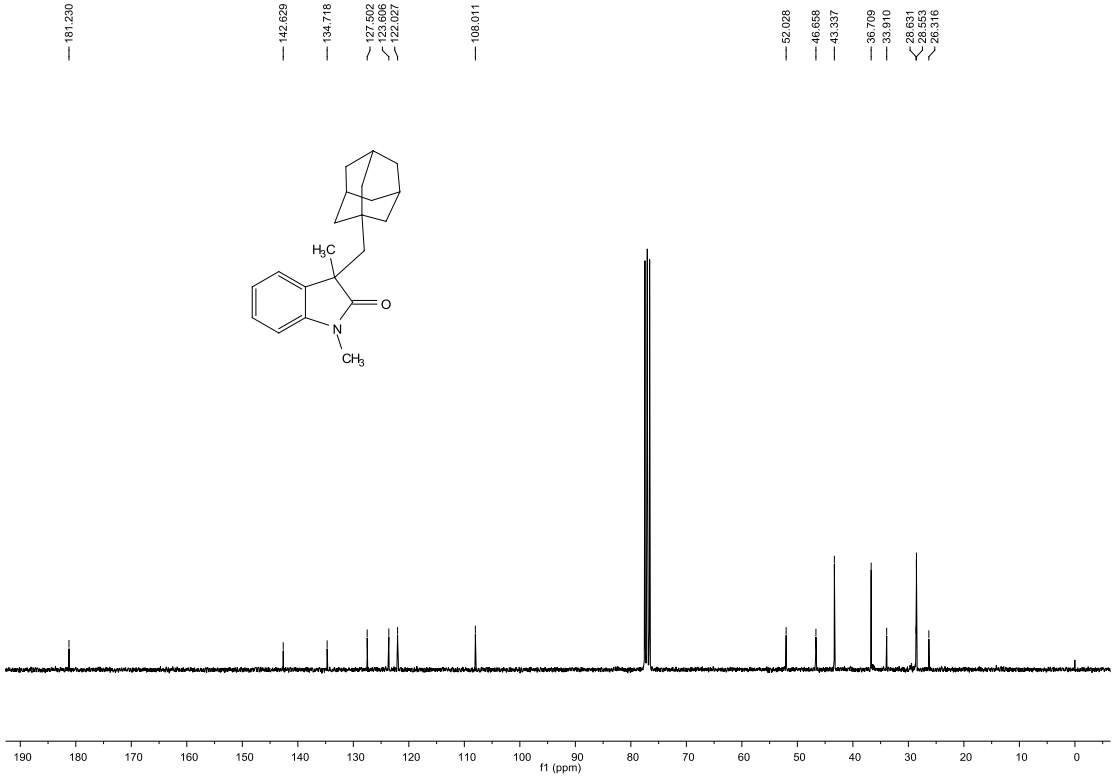
^{1}H and ^{13}C-NMR of 3v



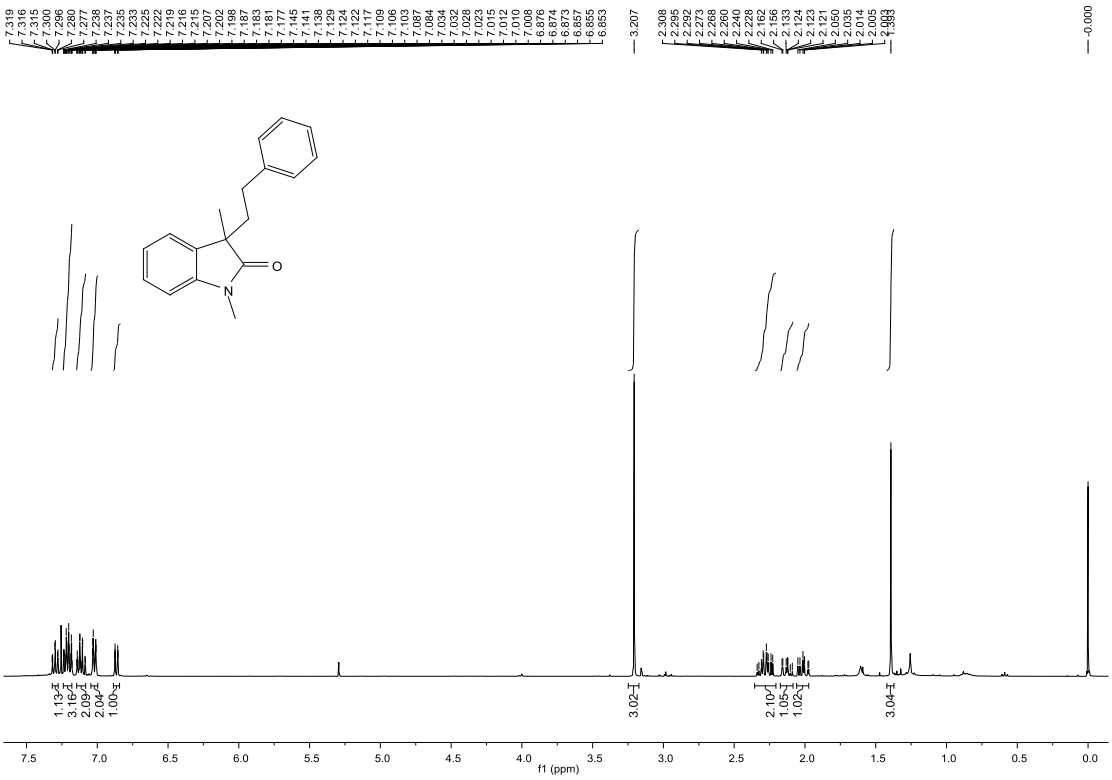


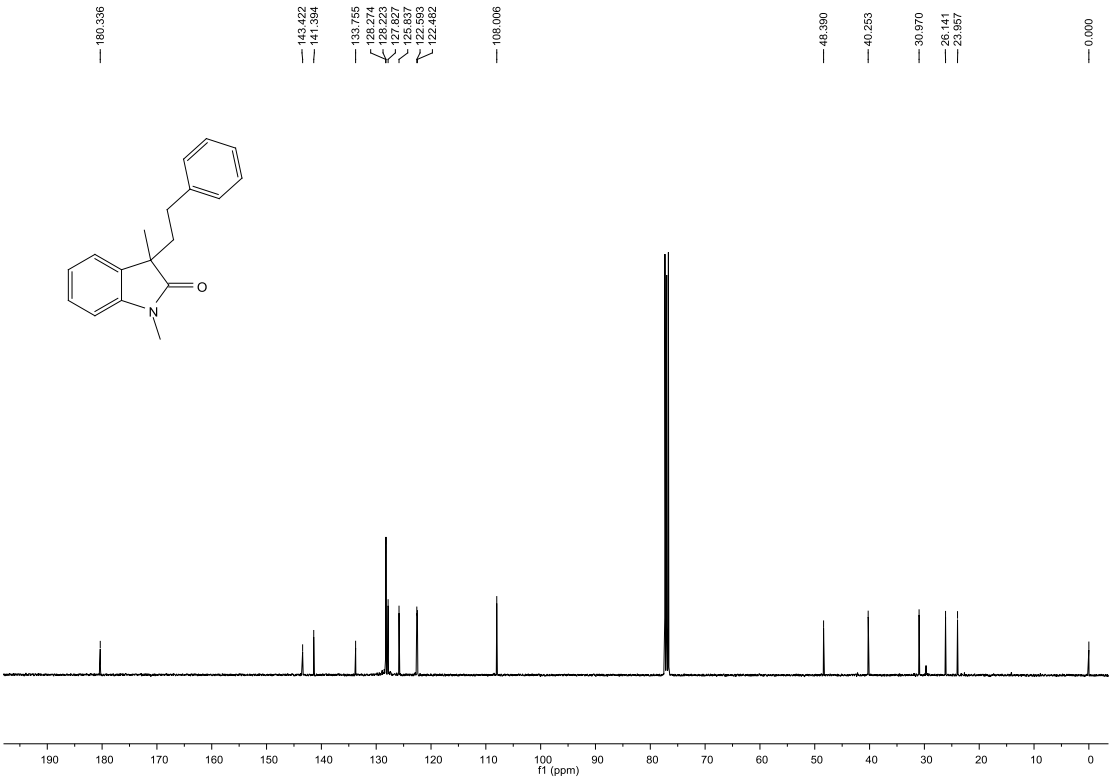
^{1}H and ^{13}C-NMR of 3w



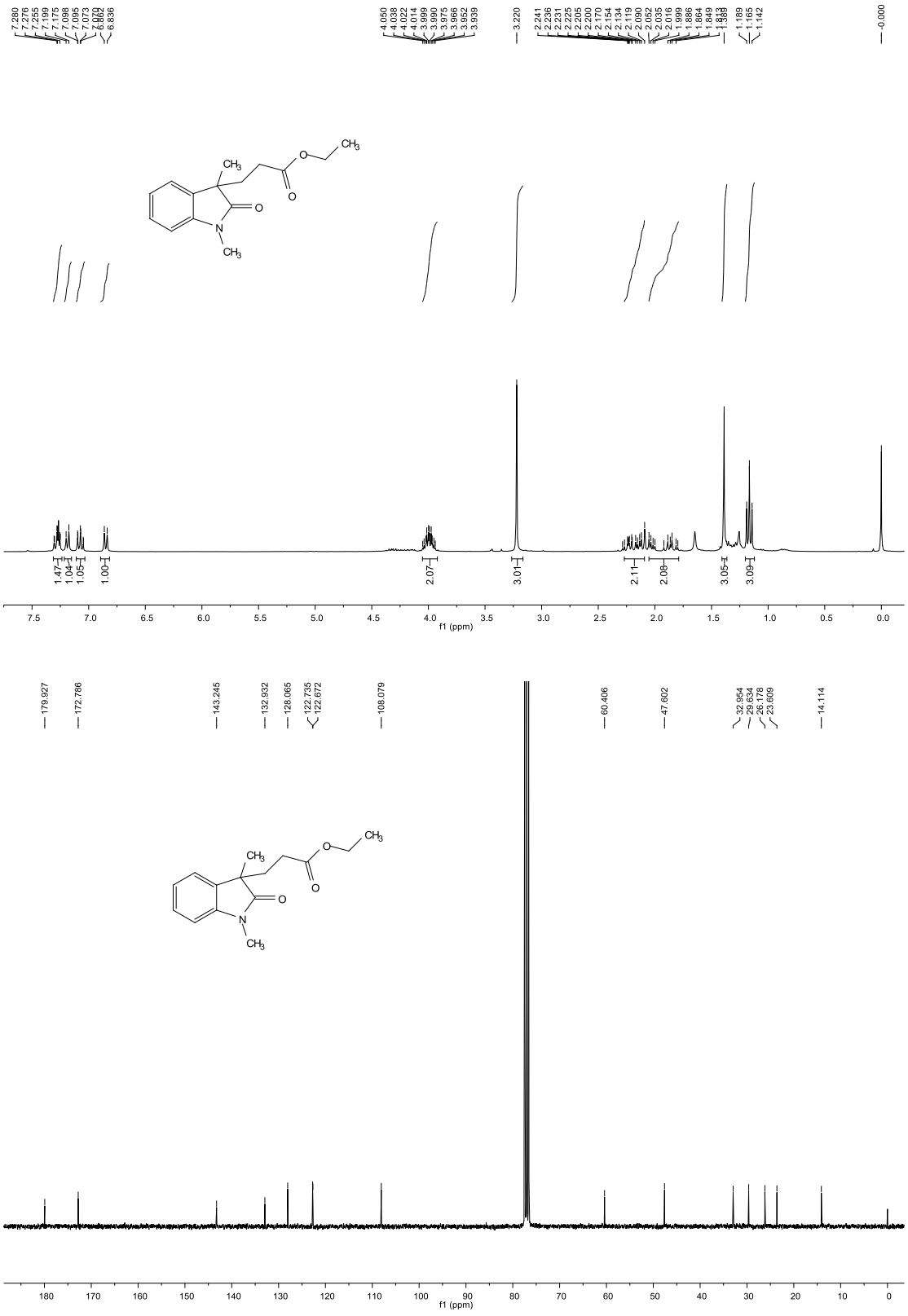


^{1}H and ^{13}C-NMR of 3x





^{1}H and ^{13}C-NMR of 3y



^{1}H and ^{13}C-NMR of 3z