Mild Gold-Catalyzed Three-Component Dehydrogenative Coupling of Terminal Alkynes to Amines and Indole-2-carboxaldehyde

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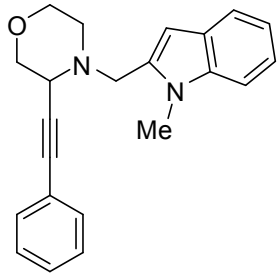
Contents: Pages

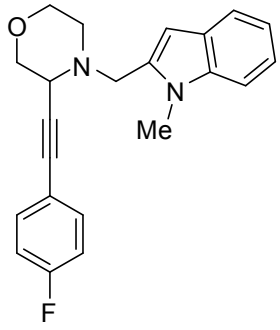
X-Ray Crystallographic Data: CIF in separate file.

Crystallographic data **5b** (CCDC: 973071), has been deposited vat the Cambridge Crystallographic Database Centre and is available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (http//www.ccdc.cam.ac.uk).



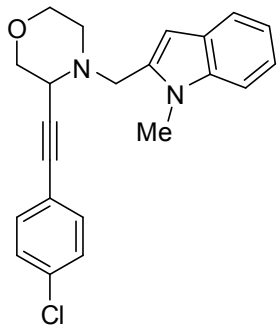
4a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.57-7.54 (m, 2H), 7.38-7.35 (m, 4H), 7.27-7.24 (m, 1H), 7.12 (t, J = 7.8 Hz, 1H), 6.78 (s, 1H), 4.98 (s, 1H), 3.89 (s, 3H), 3.77-3.72 (m, 4H), 2.72-2.67 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 135.8, 131.9, 128.4, 126.8, 122.8, 121.8, 120.7, 119.5, 109.1, 103.4, 87.5, 83.4, 67.2, 55.9, 49.6, 30.2. HRMS (ESI) $([M+H])^+$: calcd for $C_{22}H_{23}N_2O$: 331.1811, found 331.1808.



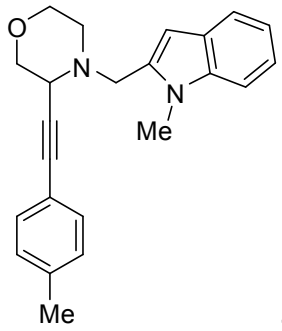
4b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.54-7.50 (m, 2H), 7.35-7.33 (m, 1H), 7.24-7.22 (m, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.05 (t, J = 8.5 Hz, 2H), 6.74 (s, 1H), 4.96 (s, 1H), 3.88 (s, 3H), 3.72-3.69 (m, 4H), 2.67-2.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 161.6, 138.4, 135.6, 133.8, 133.7, 126.8, 121.8, 120.7, 119.5, 118.8, 115.6, 109.1, 103.4, 86.4, 83.1, 67.2, 55.9, 49.6, 30.2, 29.7. HRMS (ESI) $([M+H])^+$ calcd for $C_{22}H_{22}FN_2O$: 349.1717, found 349.1712.



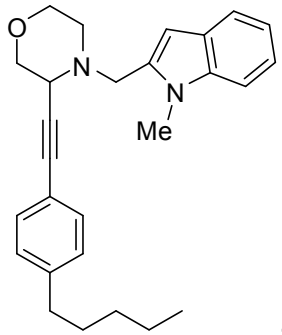
4c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.47-7.45 (m, 2H), 7.34-7.31 (m, 3H), 7.24-7.22 (m, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.73 (s, 1H), 4.96 (s, 1H), 3.88 (s, 3H), 3.71-3.69 (m, 4H), 2.67-2.63 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 135.5, 134.5, 133.1, 128.7, 126.8, 121.8, 121.2, 120.7, 119.5, 109.1, 103.4, 86.4, 84.5, 67.2, 55.9, 49.6, 30.2, 29.7. HRMS (ESI) $([M+H])^+$ calcd for $C_{22}H_{22}ClN_2O$: 365.1421, found 365.1426.



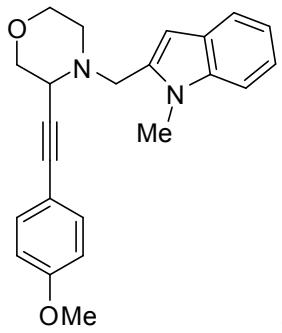
4d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.35-7.33 (m, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.17-7.15 (m, 2H), 7.10 (t, J = 7.8 Hz, 1H), 6.75 (s, 1H), 4.96 (s, 1H), 3.88 (s, 3H), 3.72-3.70 (m, 4H), 2.68-2.64 (m, 4H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.3, 135.9, 131.7, 129.1, 126.8, 121.7, 120.7, 119.4, 109.0, 103.3, 87.6, 67.2, 55.9, 49.6, 30.2, 21.5. HRMS (ESI) $([M+H])^+$ calcd for $C_{23}H_{25}N_2O$: 345.1968, found 345.1962.



4e

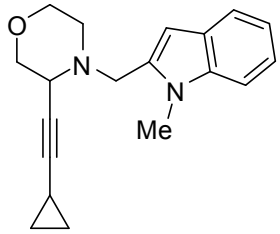
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 5.9 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.36-7.34 (m, 1H), 7.24-7.22 (m,1H), 7.17 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.76 (s, 1H), 3.88 (s, 3H), 3.74-3.71 (m, 4H), 2.69-2.61 (m, 6H), 1.63 (t, J = 7.2 Hz, 1H), 1.36-1.33 (m, 4H), 0.91 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 138.4, 135.9, 131.8, 128.5, 126.8, 121.7, 120.7, 119.4, 109.0, 103.4, 87.6, 67.3, 55.9, 49.6, 35.9, 31.4, 31.0, 30.1, 22.5, 14.1. HRMS (ESI) $([M+H])^+$ calcd for $C_{27}H_{33}N_2O$: 401.2594, found 401.2590.



4f

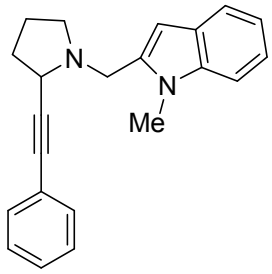
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.37-7.35 (m, 1H), 7.27-7.23 (M, 1H), 7.12 (t, J = 7.7Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.76 (s, 1H), 4.96 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.74-3.70 (m, 4H), 2.70-2.65 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 138.4, 136.0, 133.3, 126.8, 121.7, 120.7, 119.4, 114.9, 113.9, 109.1, 103.4, 87.3, 81.8,

67.3, 55.9, 55.4, 49.6, 30.2. HRMS (ESI) ([M+H])$^+$ calcd for $C_{23}H_{25}N_2O_2$: 361.1917, found 361.1912.



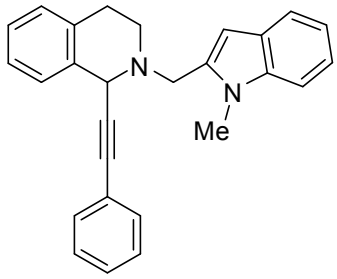
4g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 1H), 7.32-7.30 (m, 1H), 7.19 (t, J = 7.1 Hz, 1H), 7.07 (t, J = 7.0 Hz, 1H), 6.62 (s, 1H), 4.67 (s, 1H), 3.82 (s, 3H), 3.68-3.66 (m, 4H), 2.56-2.51 (m, 4H), 1.38-1.34 (m, 1H), 0.86-0.83 (m, 2H), 0.78-0.75 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 136.9, 127.3, 122.0, 121.1, 119.8, 109.4, 103.6, 91.5, 69.4, 67.7, 55.9, 49.9, 30.6, 8.9. HRMS (ESI) ([M+H])$^+$ calcd for $C_{19}H_{23}N_2O$: 295.1811, found 295.1805.



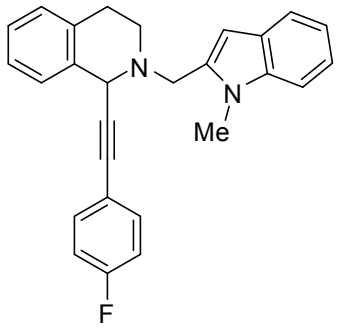
4h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.7 Hz, 1H), 7.52-7.51 (m, 2H), 7.34-7.30 (m, 4H), 7.21 (t, J = 7.2 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.68 (s, 1H), 5.09 (s, 1H), 3.89 (s, 3H), 2.72-2.68 (m, 4H), 1.78 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.8, 131.8, 128.3, 128.1, 127.0, 121.6, 121.5, 120.6, 119.3, 108.9, 101.6, 88.6, 87.6, 52.6, 49.9, 30.2, 23.7. HRMS (ESI) ([M+H])$^+$ calcd for $C_{19}H_{23}N_2$: 315.1861, found 315.1860.



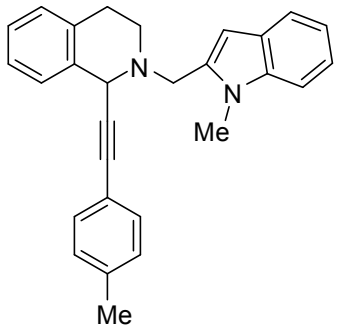
5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1H),7.58-7.55 (m, 2H), 7.40-7.36 (m, 5H), 7.30-7.24 (m, 3H), 7.22-7.20 (m, 2H), 6.64 (s, 1H), 4.23-4.20 (m, 1H), 4.23-4.20 (m, 1H), 4.12-4.08 (m, 1H), 3.89 (s, 3H), 4.90 (s, 1H), 3.23-3.17 (m, 1H), 3.08-3.00 (m, 1H), 2.94-2.88 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 136.2, 135.3, 134.1, 131.7, 128.9, 128.2, 128.1, 127.8, 127.4, 126.9, 125.9, 123.1, 121.3, 120.3, 119.2, 108.9, 102.9, 87.4, 86.9, 54.5, 51.7, 45.4, 29.9, 29.1, 26.9. HRMS (ESI) ([M+H])$^+$ calcd for $C_{27}H_{25}N_2$: 372.2018, found 372.2013.



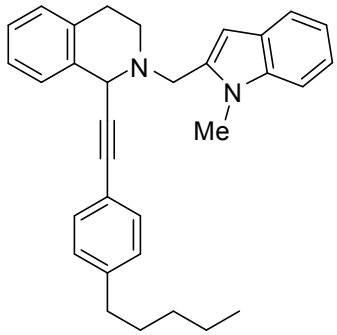
5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.47-7.43 (m, 2H), 7.34-7.31 (m, 1H), 7.23-7.19 (m, 4H), 7.15-7.12 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 6.55 (s, 1H), 4.81 (s, 1H), 4.14-4.00 (m, 2H), 3.83 (s, 3H), 3.13-3.07 (m, 1H), 3.02-2.94 (m, 1H), 2.89-2.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ163.4, 161.4, 138.1, 136.2, 135.3, 134.2, 133.7, 133.6, 128.9, 127.7, 127.3, 127.0, 125.9, 121.3, 120.3, 119.3, 115.6, 115.4, 109.0, 102.9, 87.0, 85.9, 54.5, 51.8, 45.4, 29.9, 29.1. HRMS (ESI) $([M+H])^+$ calcd for $C_{27}H_{24}NF$:395.1924, found: 395.1930.



5c

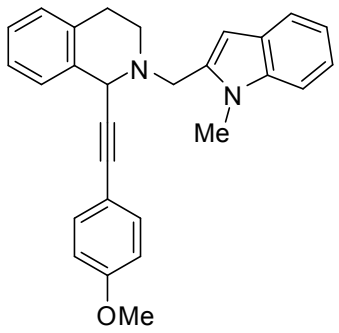
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.16 (m, 3H), 7.14-7.10 (m, 4H), 6.54 (s, 1H), 4.80 (s, 1H), 4.16-4.12 (m, 1H), 4.03-3.99 (m, 1H), 3.83 (s, 3H), 3.14-3.08 (m, 1H), 2.98-2.91 (m, 1H), 2.86-2.76 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 138.1, 136.4, 135.4, 134.2, 131.6, 129.0, 128.9, 127.8, 127.7, 127.4, 126.9, 125.9, 121.2, 120.3, 120.1, 119.2, 109.0, 102.9, 86.9, 86.6, 54.7, 51.8, 45.4, 29.9, 29.2, 21.5. HRMS (ESI) $([M+H])^+$ calcd for $C_{28}H_{27}N_2$: 391.2175, found: 391.2180.



5d

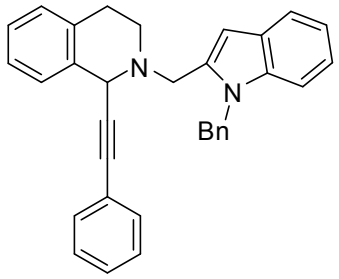
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.39-7.37 (m, 2H), 7.32-7.27 (m, 2H), 7.22-7.20 (m, 1H), 7.18-7.15 (m, 2H), 7.13-7.08 (m, 4H), 6.54 (s, 1H), 4.79 (s, 1H), 4.15-3.98 (m, 2H), 3.82 (s, 3H), 3.13-3.07 (m, 1H), 2.97-2.91 (m, 1H), 2.85-2.75 (m, 2H), 2.61-2.58 (m, 2H), 1.62-1.56 (m, 2H), 1.34-1.30 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 143.3, 138.1, 136.4, 135.5, 134.2, 131.7, 128.9, 128.4, 127.8, 127.4, 126.9, 125.8, 121.2, 120.3,

119.2, 109.0, 102.8, 87.0, 86.6, 54.7, 51.8, 45.4, 35.8, 31.4, 30.9, 30.0, 29.1, 22.5, 14.0. HRMS (ESI) $([M+H])^+$ calcd for $C_{32}H_{35}N_2$: 447.2801, found: 447.2807.



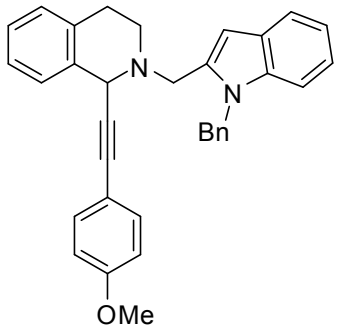
5e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.34-7.30 (m, 2H), 7.25-7.23 (m, 1H), 7.20-7.18 (m, 2H), 7.14-7.10 (m, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.56 (s, 1H), 4.81 (s, 1H), 4.17-4.14 (m, 1H), 4.03-4.00 (m, 1H), 3.84-3.83 (m, 6H), 3.15-3.08 (m, 1H), 2.99-2.90 (m, 1H), 2.87-2.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 138.1, 136.4, 135.6, 134.1, 133.2, 128.9, 127.8, 127.4, 126.9, 125.8, 121.2, 120.3, 119.2, 115.3, 113.9, 109.0, 102.9, 86.7, 85.9, 55.3, 54.7, 51.8, 45.4, 29.9, 29.1. HRMS (ESI) $([M+H])^+$ calcd for $C_{28}H_{27}N_2O$: 407.2124, found: 407.2118.



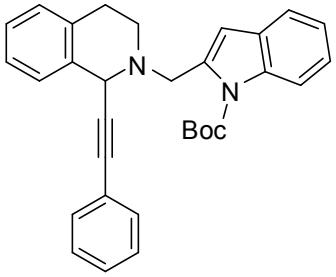
5f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 1H), 7.43-7.40 (m, 2H), 7.32-7.28 (m, 4H), 7.27-7.26 (m, 1H), 7.21-7.17 (m, 6H), 7.15-7.13 (m, 2H), 7.01-6.98 (m, 2H), 6.67 (s, 1H), 5.70-5.66 (m, 1H), 5.57-5.52 (m, 1H), 4.80 (s, 1H), 4.10-3.97 (m, 2H), 3.14-3.09 (m, 1H), 2.97-2.94 (m, 1H), 2.85-2.74 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.1, 136.2, 135.3, 134.2, 131.8, 128.9, 128.6, 128.2, 128.1, 127.8, 127.6, 126.9, 126.1, 125.9, 123.1, 121.7, 120.4, 119.6, 109.7, 103.8, 87.2, 54.6, 51.9, 46.9, 45.5, 29.0, 26.9. HRMS (ESI) $([M+H])^+$ calcd for $C_{33}H_{29}N_2$: 453.2331, found: 453.2328.



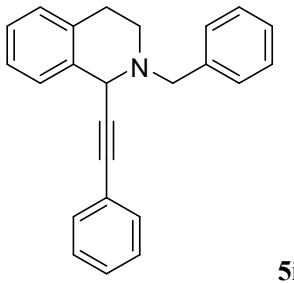
5g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 1H), 7.32-7.30 (m, 2H),7.25-7.23 (m, 2H), 7.17-7.13 (m, 6H), 7.19-7.09 (m, 2H), 6.97-6.95 (m, 2H), 6.82-6.80 (m, 2H), 6.62 (s, 1H), 5.67-5.63 (m, 1H), 5.54-5.49 (m, 1H), 4.75 (s, 1H), 4.06-3.91 (m, 2H), 3.81(s, 3H), 3.11-3.05 (m, 1H), 2.91-2.85 (m, 1H), 2.80-2.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 138.6, 138.0, 136.3, 135.5, 134.1, 133.2, 128.9, 128.6, 127.8, 127.6, 126.9, 126.8, 121.6, 120.4, 119.5, 115.2, 113.8, 109.7, 103.7, 86.8, 85.7, 55.3, 54.7, 51.9, 46.9, 45.4, 29.7, 29.0. HRMS (ESI) $([M+H])^+$ calcd for $C_{34}H_{31}N_2O$: 483.2437, found 483.2432.



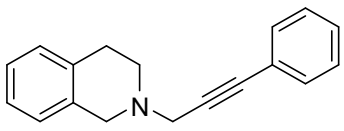
5h

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2Hz, 1H), 7.43-7.40 (m, 2H), 7.35-7.32 (m, 2H), 7.19-7.17 (m, 4H), 7.11-7.10 (m, 1H), 7.08-7.06 (m, 3H), 6.63 (s, 1H), 4.87 (s, 1H), 4.27-4.12 (m, 2H), 3.05-2.89 (m, 3H), 2.73-2.71 (m, 1H), 1.54 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 138.4, 137.2, 135.6, 134.1, 132.1, 131.6, 129.2, 129.0, 128.8, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6,127.2, 126.7, 126.1, 125.6, 123.9, 123.4, 122.8, 122.4, 120.5, 119.9, 115.4, 115.1, 108.9, 108.8, 87.7, 86.7, 83.8, 54.8, 54.6, 54.1, 45.8, 28.3, 28.1. HRMS (ESI) $([M+H])^+$ calcd for $C_{31}H_{31}N_2O_2$: 463.2386, found: 463.2383.



5i (*endo*-yne-THIQ and *exo*-yne-THIQ products **5i**/**6a** = 4.8/1**)**

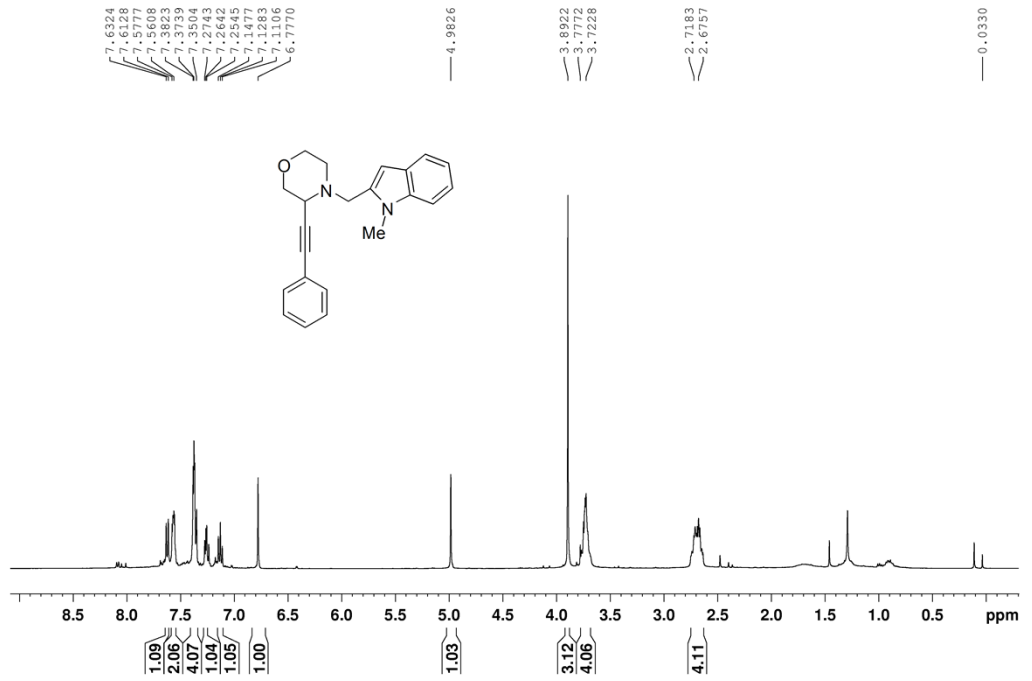
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.4 Hz, 2H), 7.59-7.57 (m, 2H), 7.45-7.43 (m, 2H), 7.38-7.37 (m, 4H), 7.18-7.12 (m, 3H), 7.08-7.06 (m, 1H), 5.14 (s, 0.97H), 4.87 (s, 0.21H), 4.01-4.00 (m, 0.30H), 3.93 (s, 1.76 H), 2.98-2.96 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 135.4, 134.5, 131.9, 129.3, 129.1, 128.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.2, 126.9, 126.8, 126.0, 125.9, 125.6, 123.1, 88.6, 87.6, 86.9, 85.1, 61.7, 59.7, 54.4, 52.3, 45.8, 29.7, 29.1.



6b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.33-7.32 (m, 3H), 7.16-7.14 (m, 3H), 7.10-7.08 (m, 1H), 3.88 (s, 2H), 3.76 (s, 2H), 3.02-2.99 (m, 2H), 2.96-2.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 133.8, 131.8, 128.7, 128.3, 128.1, 126.7, 126.2, 125.7, 123.2, 85.5, 84.5, 54.6, 49.9, 47.7, 29.3.

4a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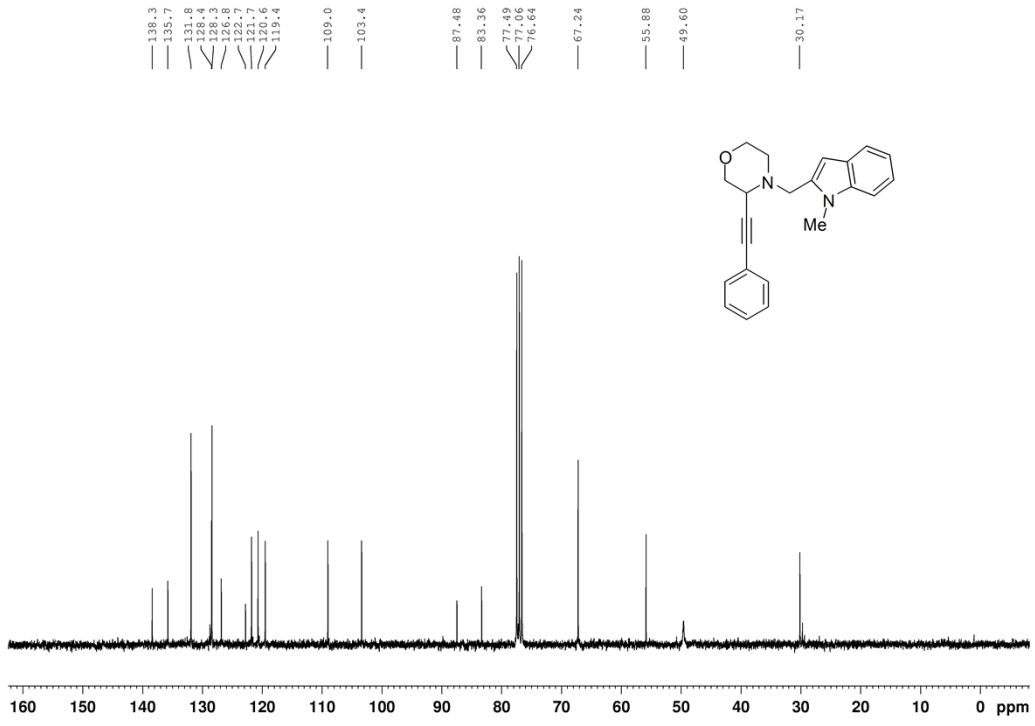
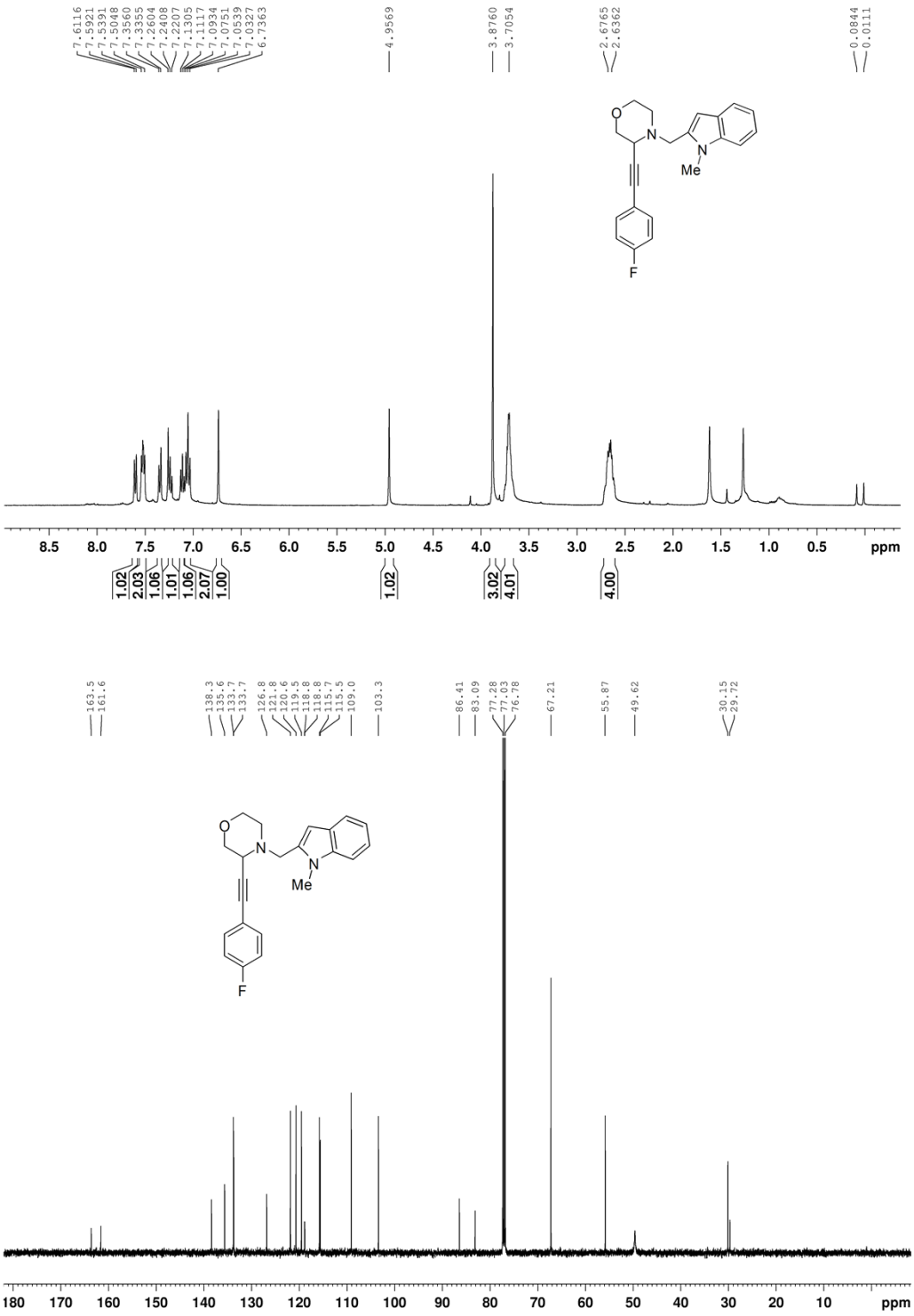
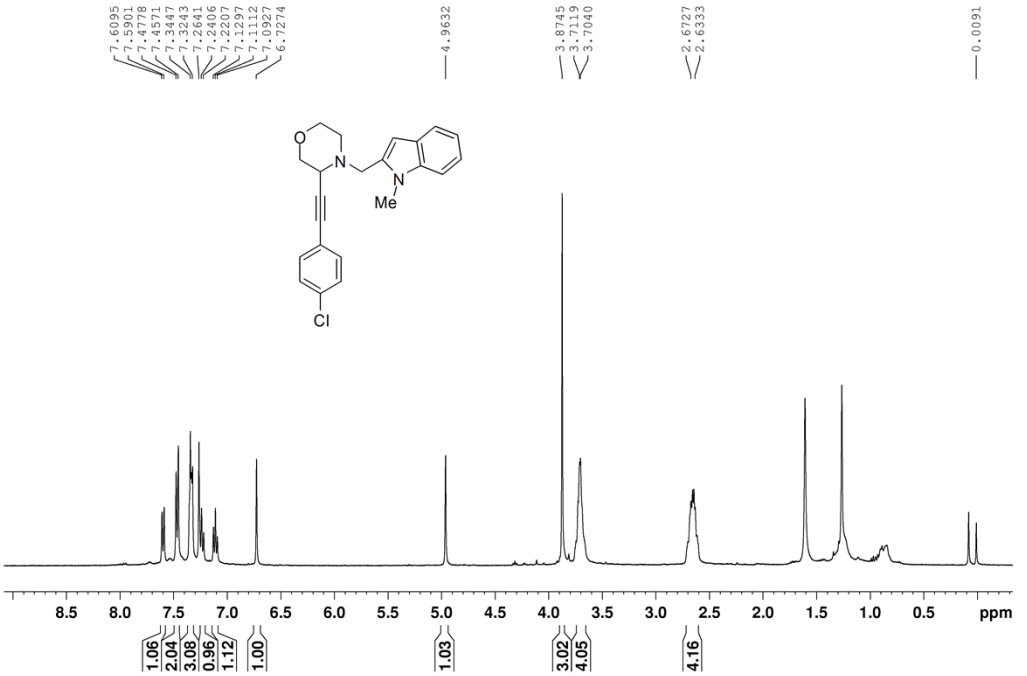
7.6128
7.5777
7.5608
7.3823
7.3739
7.3504
7.2743
7.2642
7.2545
7.1477
7.1283
7.1106
6.7770
4.9826
3.8922
3.7772
3.7228
2.7183
2.6757
0.0330
O
N
N
Me
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.09
2.06
4.07
1.04
1.05
1.00
1.03
3.12
4.06
4.11

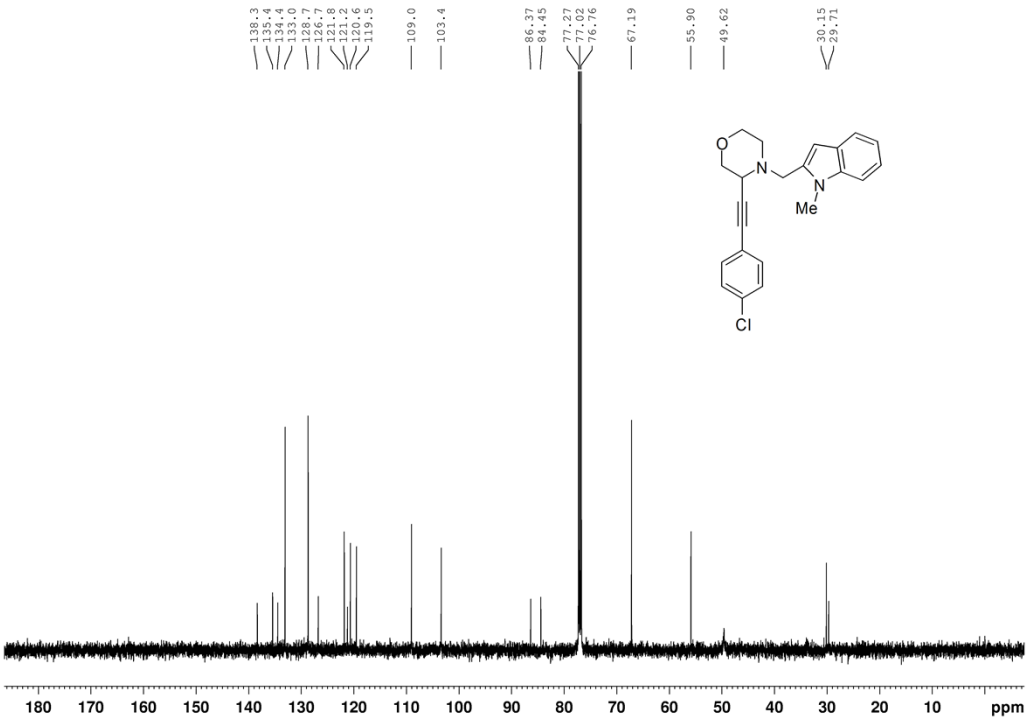

138.3
135.7
131.8
128.4
128.3
126.8
122.7
121.7
120.6
119.4
109.0
103.4
87.48
83.36
77.49
77.06
76.64
67.24
55.88
49.60
30.17
O
N
N
Me
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4b

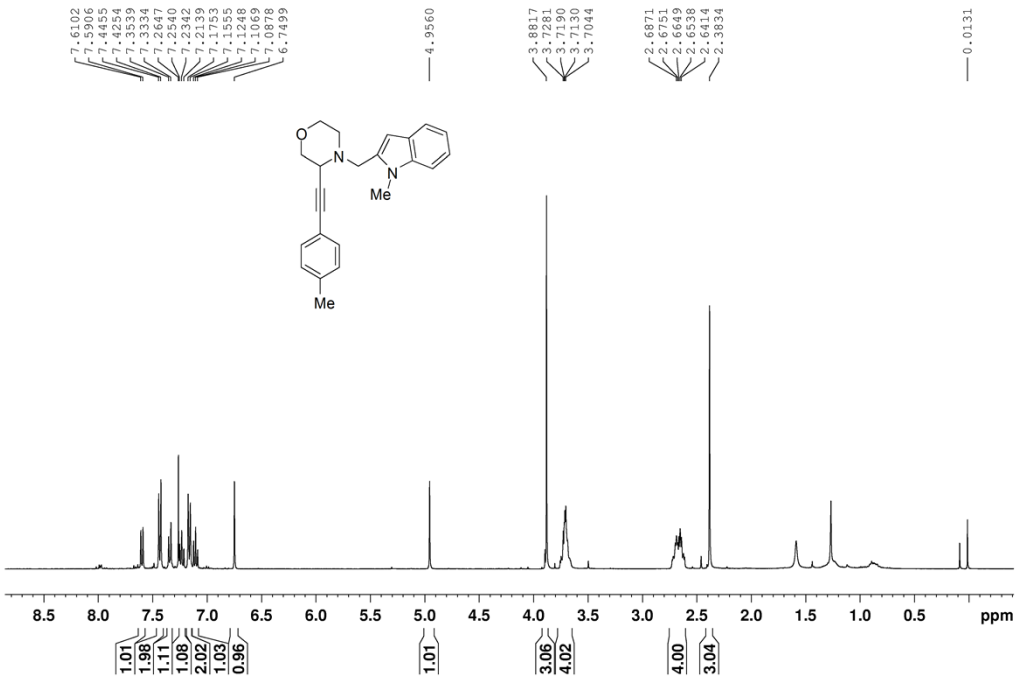

7.6116
7.5921
7.5391
7.5048
7.3560
7.3355
7.2604
7.2408
7.2207
7.1305
7.1117
7.0934
7.0751
7.0539
7.0327
6.7363
4.9569
3.8760
3.7054
2.6765
2.6362
0.0844
0.0111
O
N
N
Me
F
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02 2.03 1.06 1.01 1.06 2.07 1.00 1.02 3.02 4.01 4.00
163.5
161.6
138.3
135.6
133.7
133.7
126.8
121.8
120.6
119.5
118.8
118.8
115.7
115.5
109.0
103.3
86.41
83.09
77.28
77.03
76.78
67.21
55.87
49.62
30.15
29.72
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

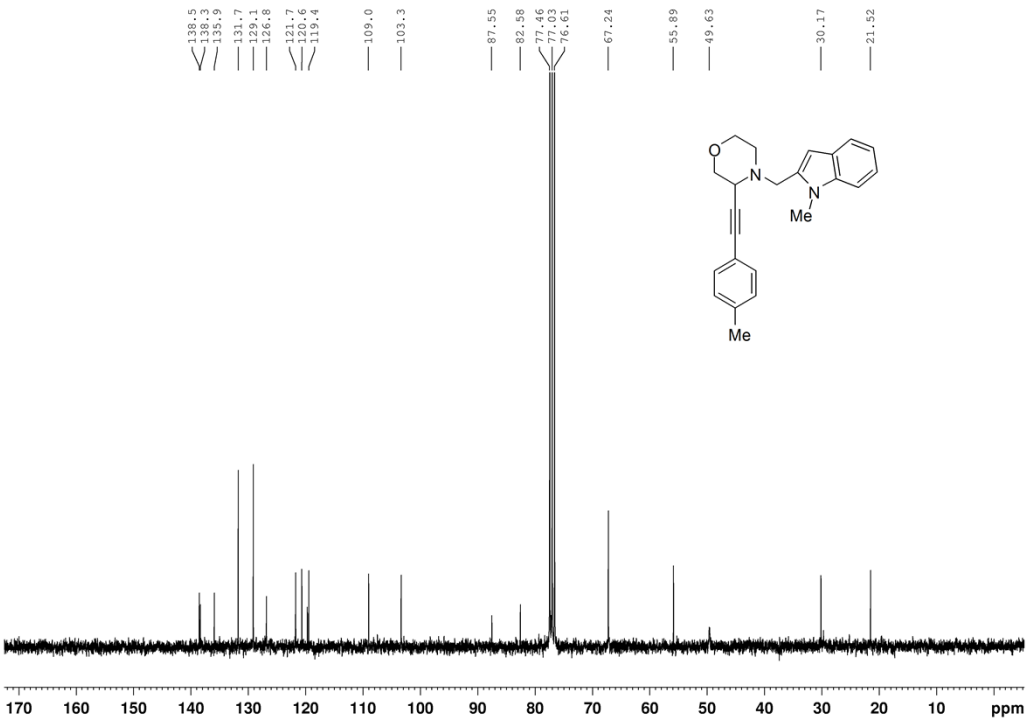
4c


7.6095
7.5901
7.4778
7.4571
7.3447
7.3243
7.2641
7.2406
7.2207
7.1297
7.1112
7.0927
6.7274
4.9632
3.8745
3.7119
3.7040
2.6727
2.6333
0.0091
O
N
N
Me
Cl
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 ppm
1.06
2.04
3.08
0.96
1.12
1.00
1.03
3.02
4.05
4.16

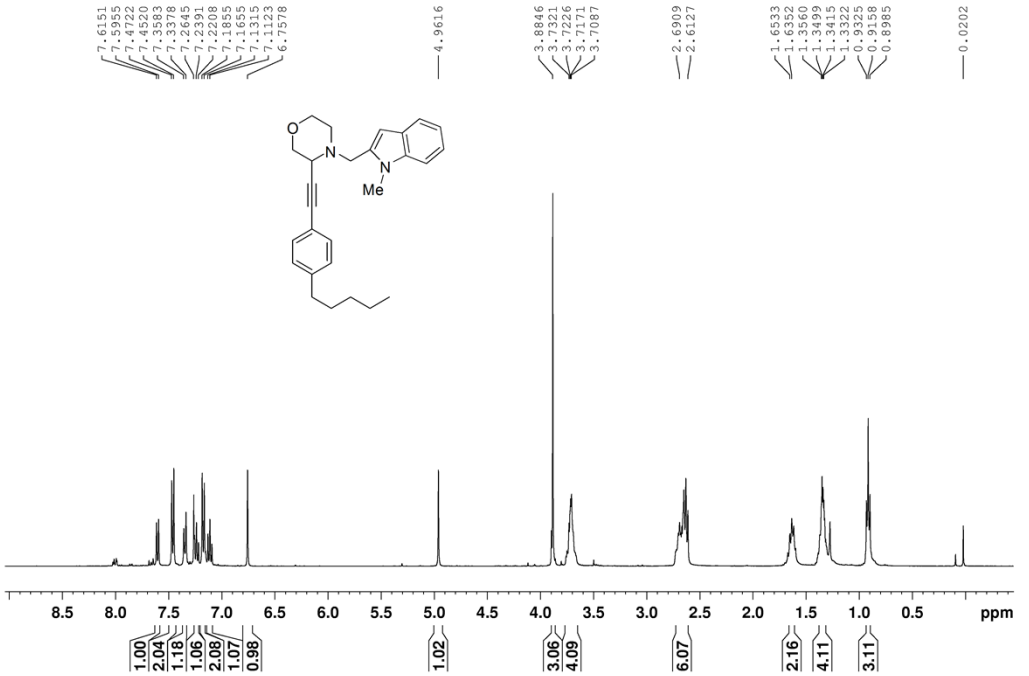

138.3
135.4
134.4
133.0
128.7
126.7
121.8
121.2
120.6
119.5
109.0
103.4
86.37
84.45
77.27
77.02
76.76
67.19
55.90
49.62
30.15
29.71
O
N
N
Me
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

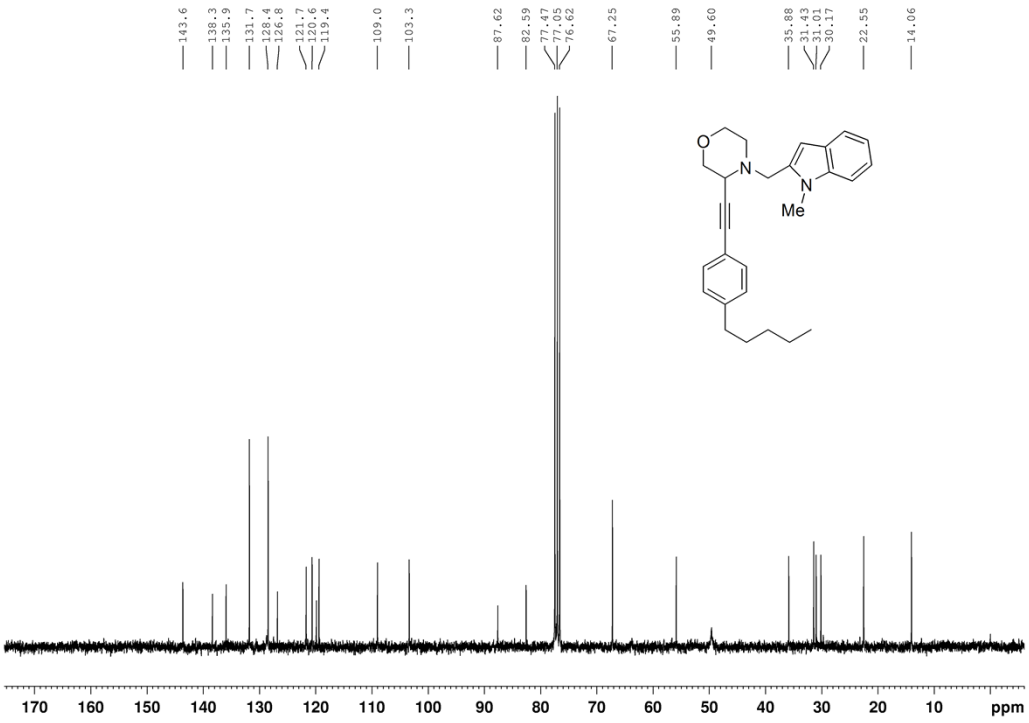
4d


7.6102
7.5906
7.4455
7.4254
7.3539
7.3334
7.2647
7.2540
7.2342
7.2139
7.1753
7.1555
7.1248
7.1069
7.0878
6.7499
4.9560
3.8817
3.7281
3.7190
3.7130
3.7044
2.6871
2.6751
2.6649
2.6538
2.6414
2.3834
0.0131
O
N
N
Me
Me
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 ppm
1.01
1.98
1.11
1.08
2.02
1.03
0.96
1.01
3.06
4.02
4.00
3.04

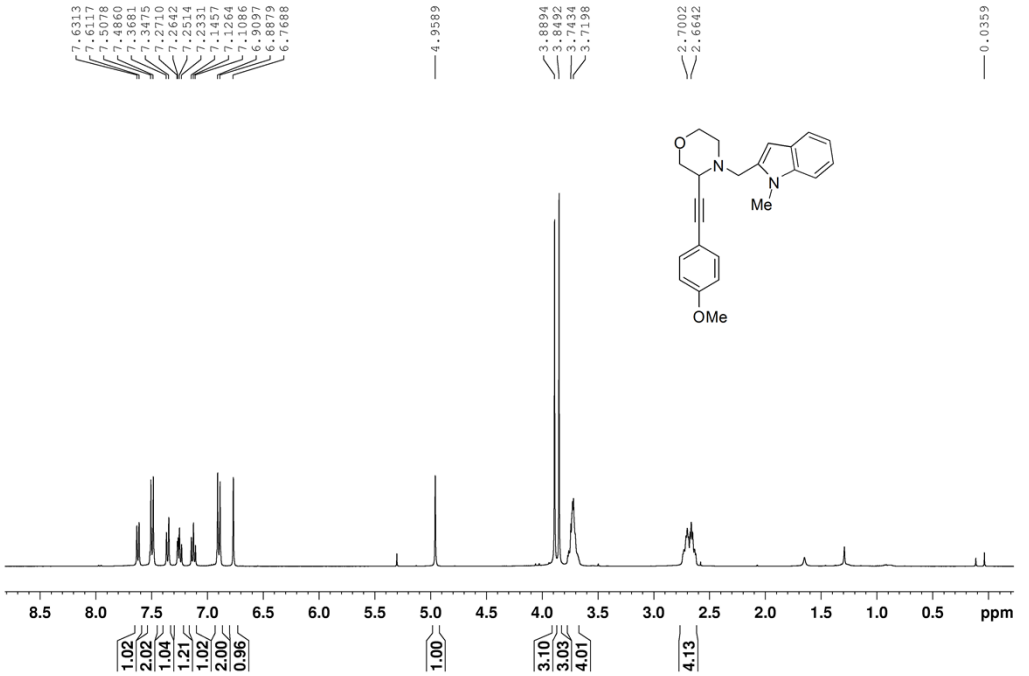

138.5
138.3
135.9
131.7
129.1
126.8
121.7
120.6
119.4
109.0
103.3
87.55
82.58
77.46
77.03
76.61
67.24
55.89
49.63
30.17
21.52
O
N
N
Me
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

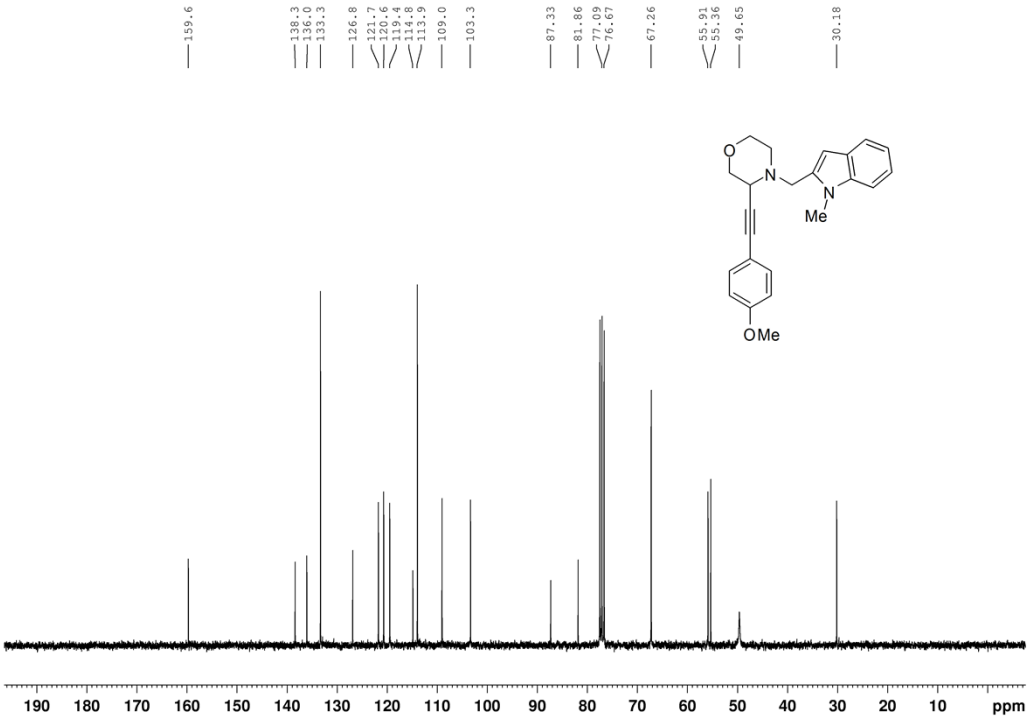
4e


7.6151
7.5955
7.4722
7.4520
7.3583
7.3378
7.2645
7.2391
7.2208
7.1855
7.1655
7.1315
7.1123
6.7578
4.9616
3.8846
3.7321
3.7226
3.7171
3.7087
2.6909
2.6127
1.6533
1.6352
1.3560
1.3499
1.3415
1.3322
0.9325
0.9158
0.8985
0.0202
Me
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 ppm
1.00 2.04 1.18 1.06 2.08 1.07 0.98 1.02 3.06 4.09 6.07 2.16 4.11 3.11

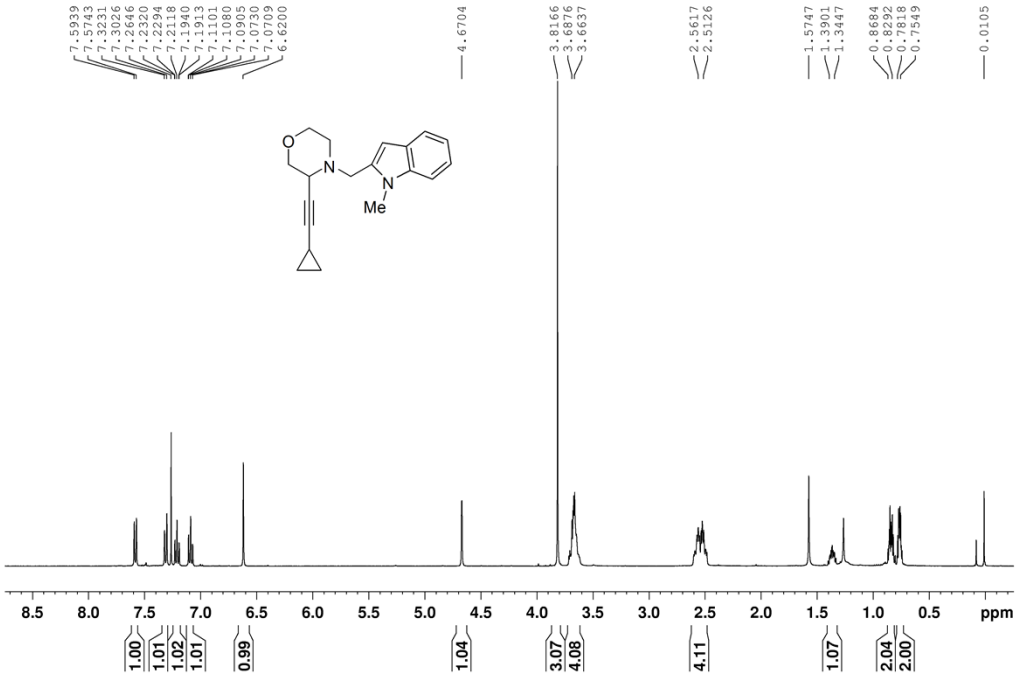

143.6
138.3
135.9
131.7
128.4
126.8
121.7
120.6
119.4
109.0
103.3
87.62
82.59
77.47
77.05
76.62
67.25
55.89
49.60
35.88
31.43
31.01
30.17
22.55
14.06
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

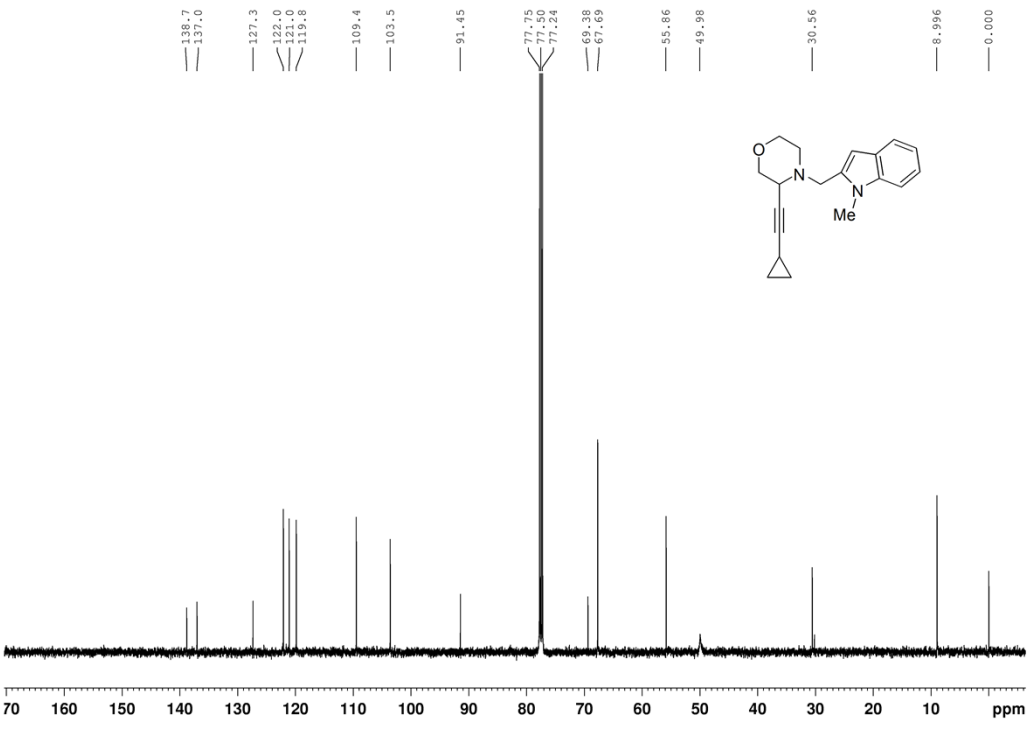
4f


7.6313
7.6117
7.5078
7.4860
7.3681
7.3475
7.2710
7.2642
7.2514
7.2331
7.1457
7.1264
7.1086
6.9097
6.8879
6.7688
4.9589
3.8894
3.8492
3.7434
3.7198
2.7002
2.6642
0.0359
O
N
N
Me
OMe
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 ppm
1.02
2.02
1.04
1.21
1.02
2.00
0.96
1.00
3.10
3.03
4.01
4.13

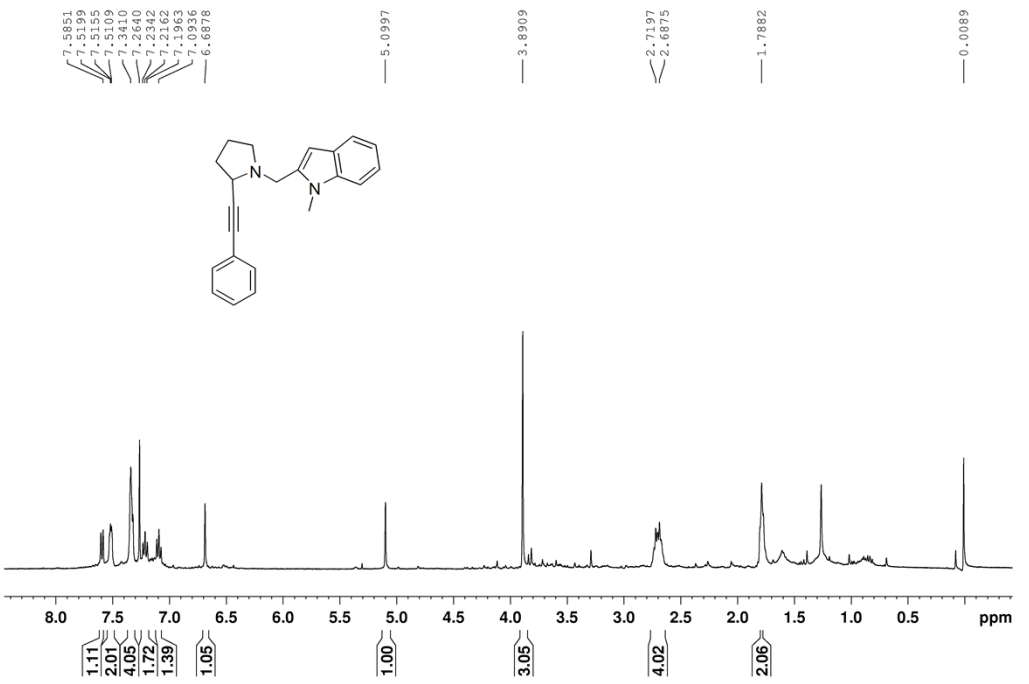

159.6
138.3
136.0
133.3
126.8
121.7
120.6
119.4
114.8
113.9
109.0
103.3
87.33
81.86
77.09
76.67
67.26
55.91
55.36
49.65
30.18
O
N
N
Me
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

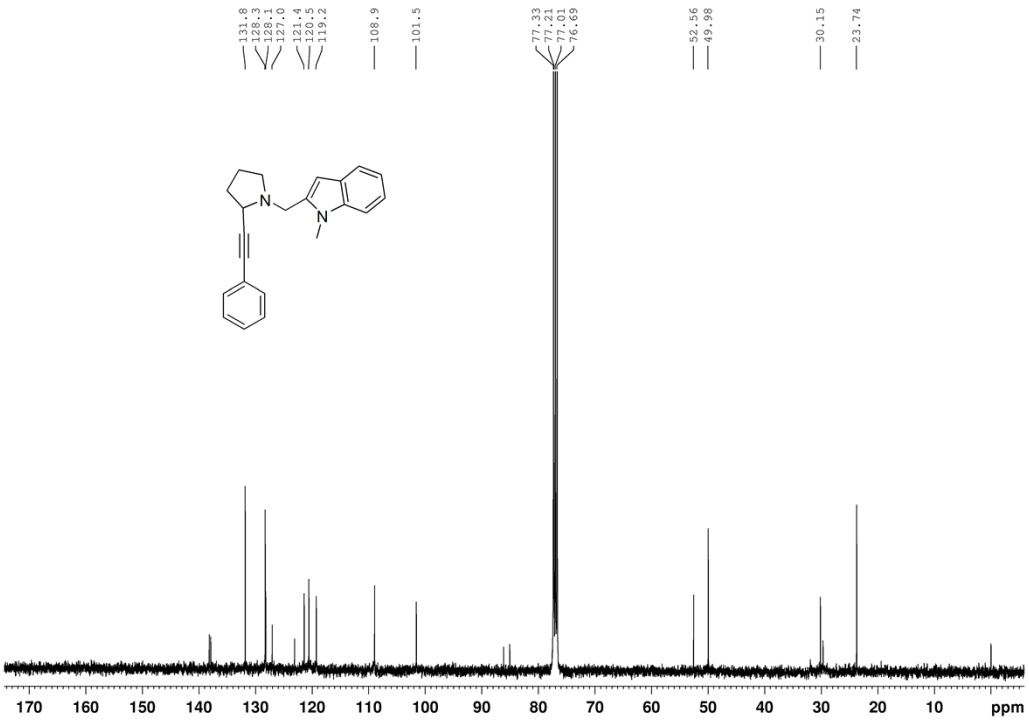
4g


7.5939
7.5743
7.3231
7.3026
7.2646
7.2320
7.2294
7.2118
7.1940
7.1913
7.1101
7.1080
7.0905
7.0730
7.0709
6.6200
4.6704
3.8166
3.6876
3.6637
2.5617
2.5126
1.5747
1.3901
1.3447
0.8684
0.8292
0.7818
0.7549
0.0105
O
N
N
Me
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 ppm
1.00 1.01 1.02 1.01 0.99 1.04 3.07 4.08 4.11 1.07 2.04 2.00

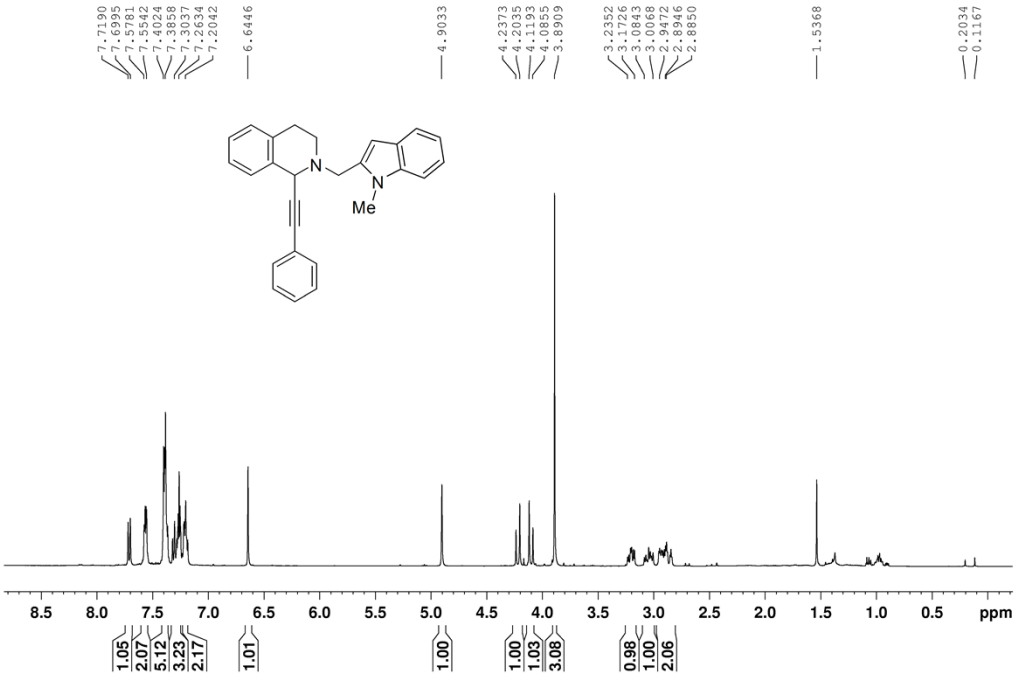

138.7
137.0
127.3
122.0
121.0
119.8
109.4
103.5
91.45
77.75
77.50
77.24
69.38
67.69
55.86
49.98
30.56
8.996
0.000
O
N
N
Me
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

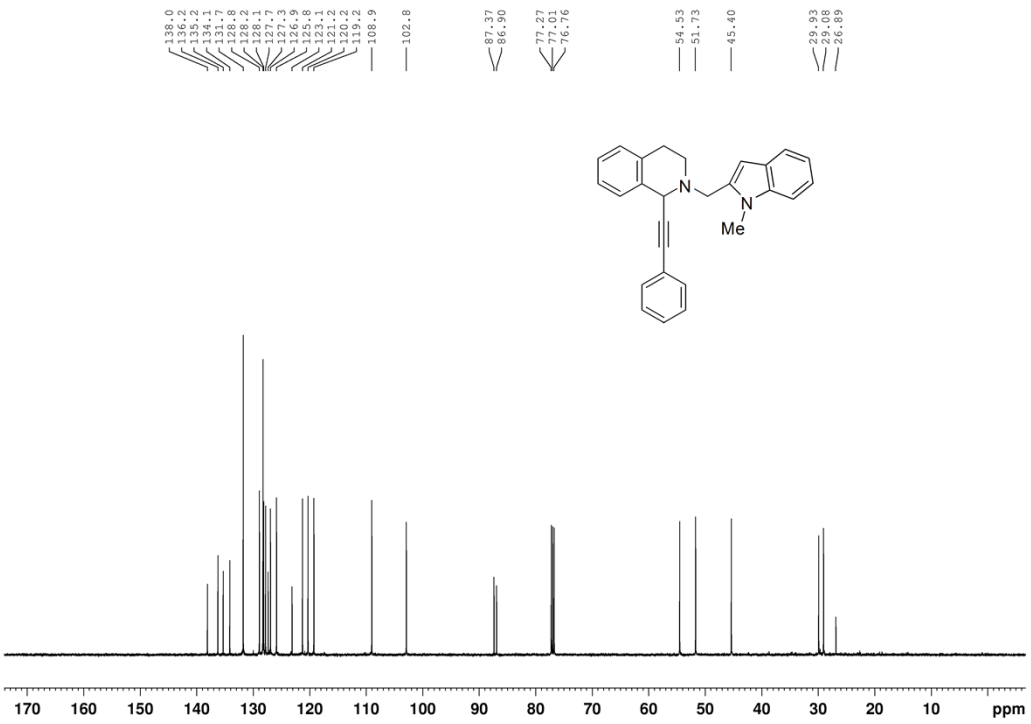
4h


7.5851
7.5199
7.5155
7.5109
7.3410
7.2640
7.2342
7.2162
7.1963
7.0936
6.6878
5.0997
3.8909
2.7197
2.6875
1.7882
0.0089
ppm
1.11
2.01
4.05
1.72
1.39
1.05
1.00
3.05
4.02
2.06

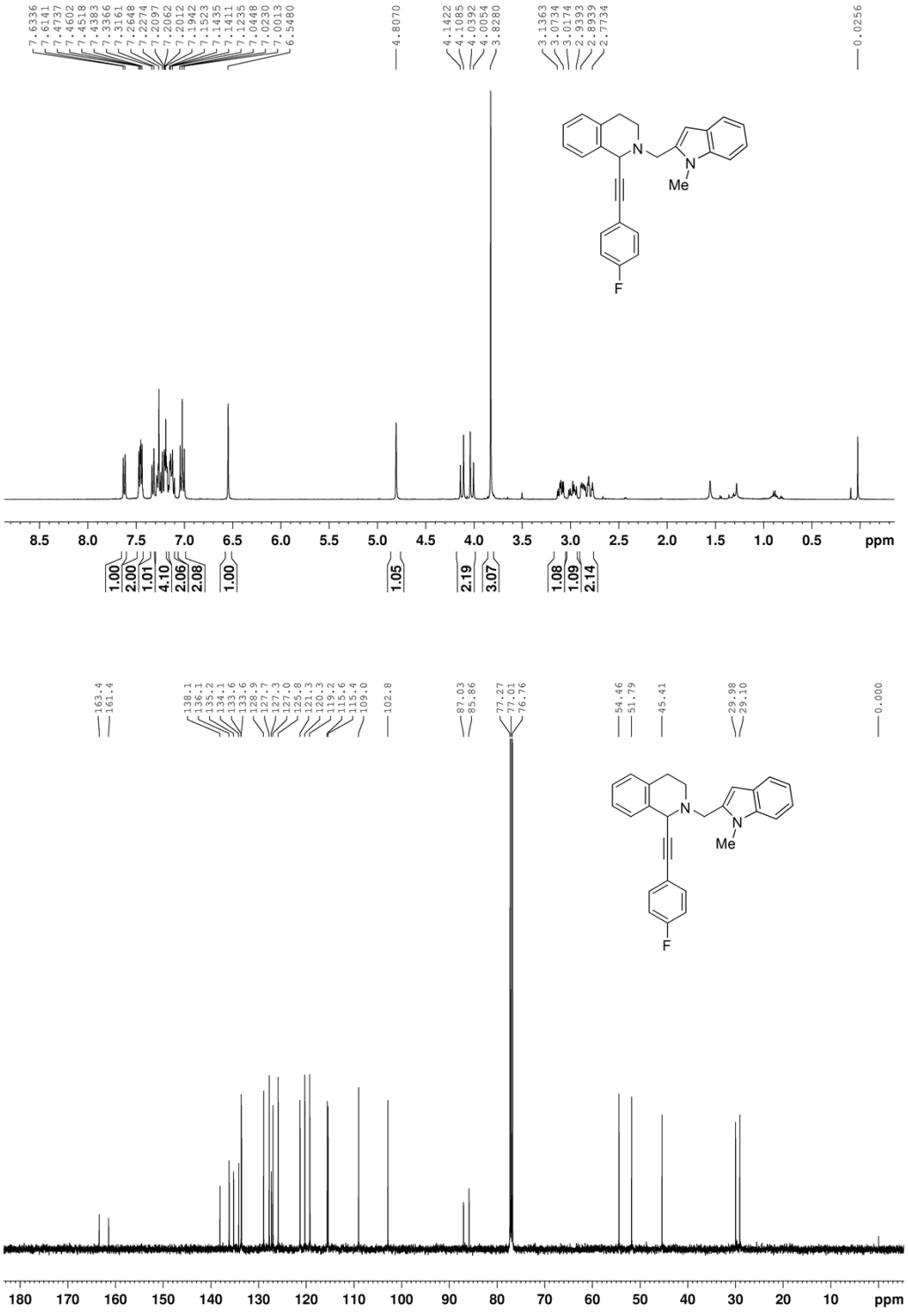

131.8
128.3
128.1
127.0
121.4
120.5
119.2
108.9
101.5
77.33
77.21
77.01
76.69
52.56
49.98
30.15
23.74
ppm

5a

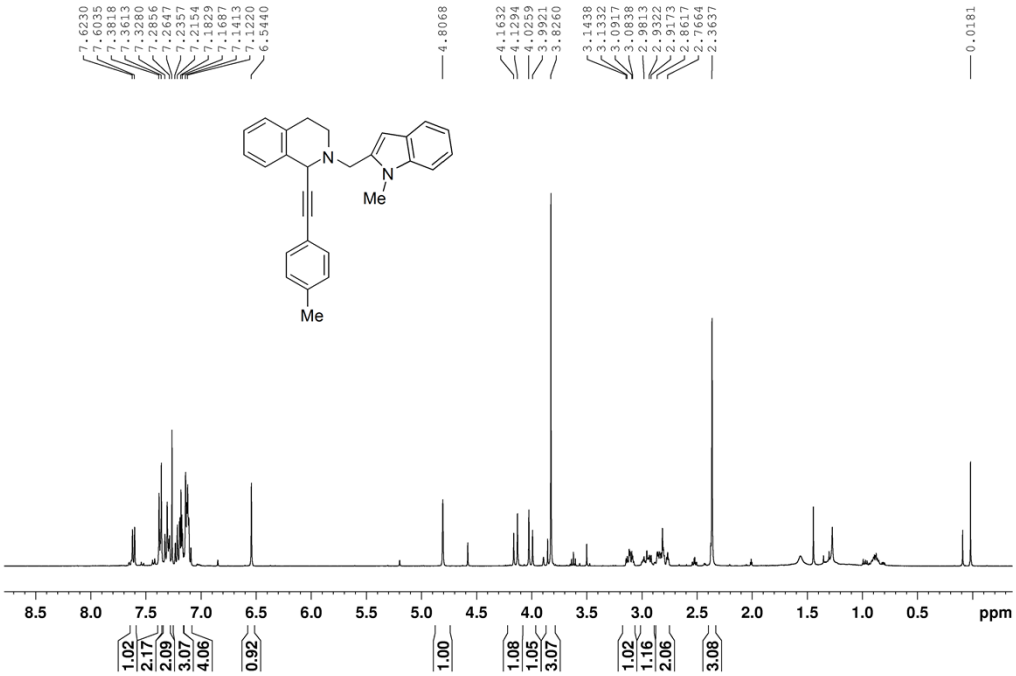

7.7190
7.6995
7.5781
7.5542
7.4024
7.3858
7.3037
7.2634
7.2042
6.6446
4.9033
4.2373
4.2035
4.1193
4.0855
3.8909
3.2352
3.1726
3.0843
3.0068
2.9472
2.8946
2.8850
1.5368
0.2034
0.1167
N
N
Me
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.05 2.07 5.12 3.23 2.17 1.01 1.00 1.00 1.03 3.08 0.98 1.00 2.06

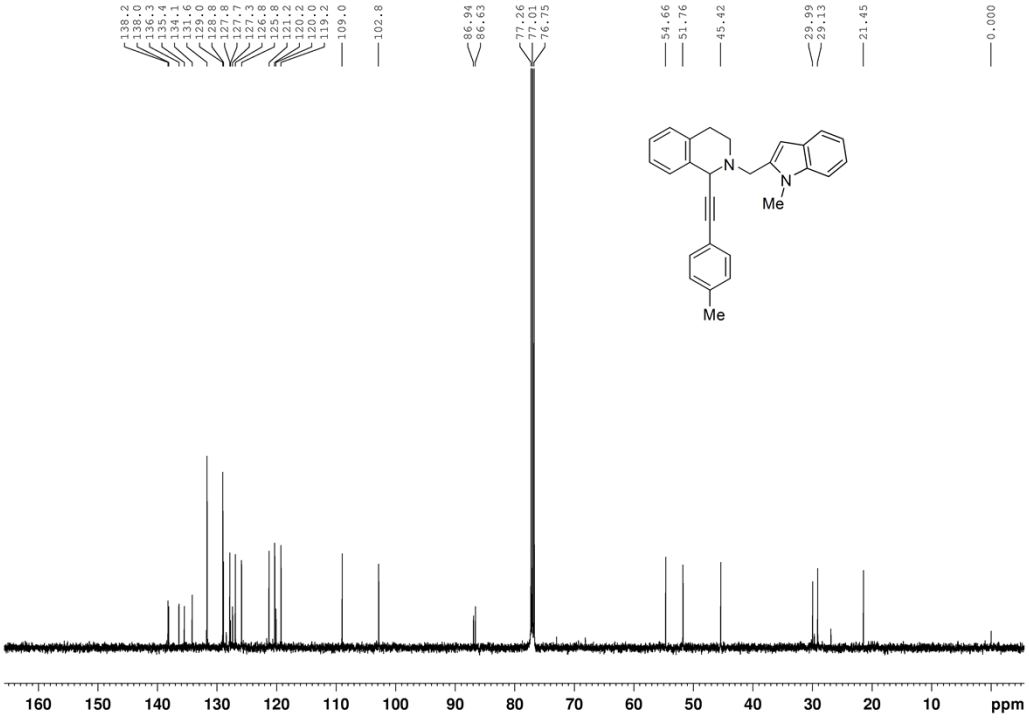

138.0
136.2
135.2
134.1
131.7
128.8
128.2
128.1
127.7
127.3
126.9
125.8
123.1
121.2
120.2
119.2
108.9
102.8
87.37
86.90
77.27
77.01
76.76
54.53
51.73
45.40
29.93
29.08
26.89
N
N
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

5b

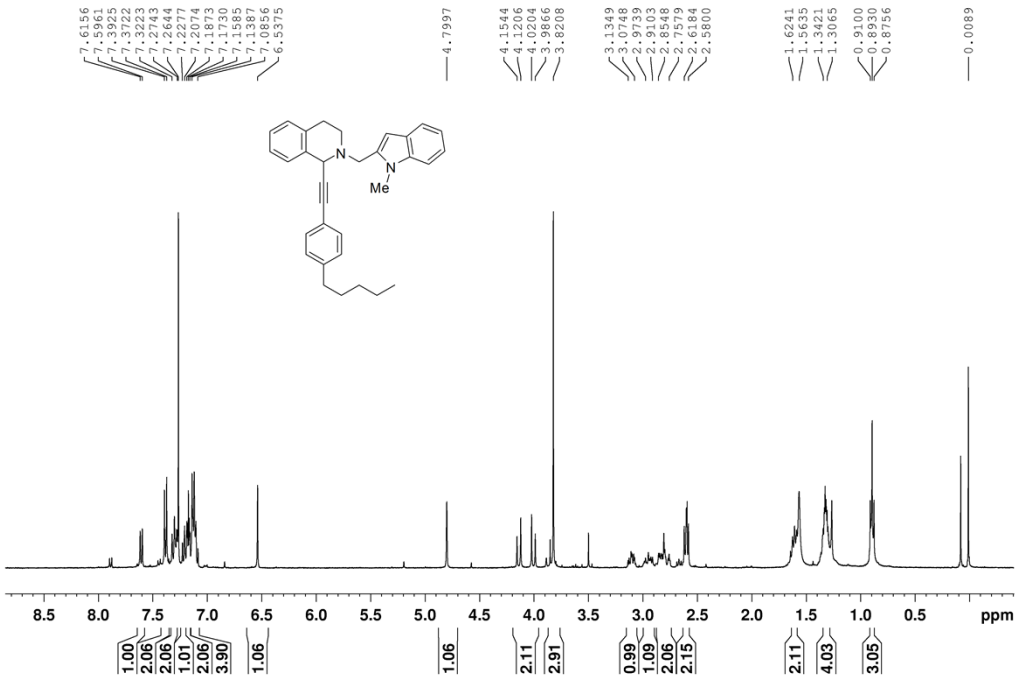

7.6336
7.6141
7.4737
7.4602
7.4518
7.4383
7.3366
7.3161
7.2648
7.2274
7.2097
7.2062
7.2012
7.1942
7.1523
7.1435
7.1411
7.1235
7.0438
7.0230
7.0033
6.5480
4.8070
4.1422
4.1085
4.0392
4.0054
3.8280
3.1363
3.0734
3.0174
2.9393
2.8939
2.7734
0.0256
N
N
Me
F
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 2.00 1.01 4.10 2.06 2.08 1.00 1.05 2.19 3.07 1.08 1.09 2.14
163.4
161.4
138.1
136.1
135.2
134.1
133.6
133.6
128.9
128.7
127.3
127.0
125.8
121.3
120.3
119.2
115.6
115.4
109.0
102.8
87.03
85.86
77.27
77.01
76.76
54.46
51.79
45.41
29.98
29.10
0.000
N
N
Me
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

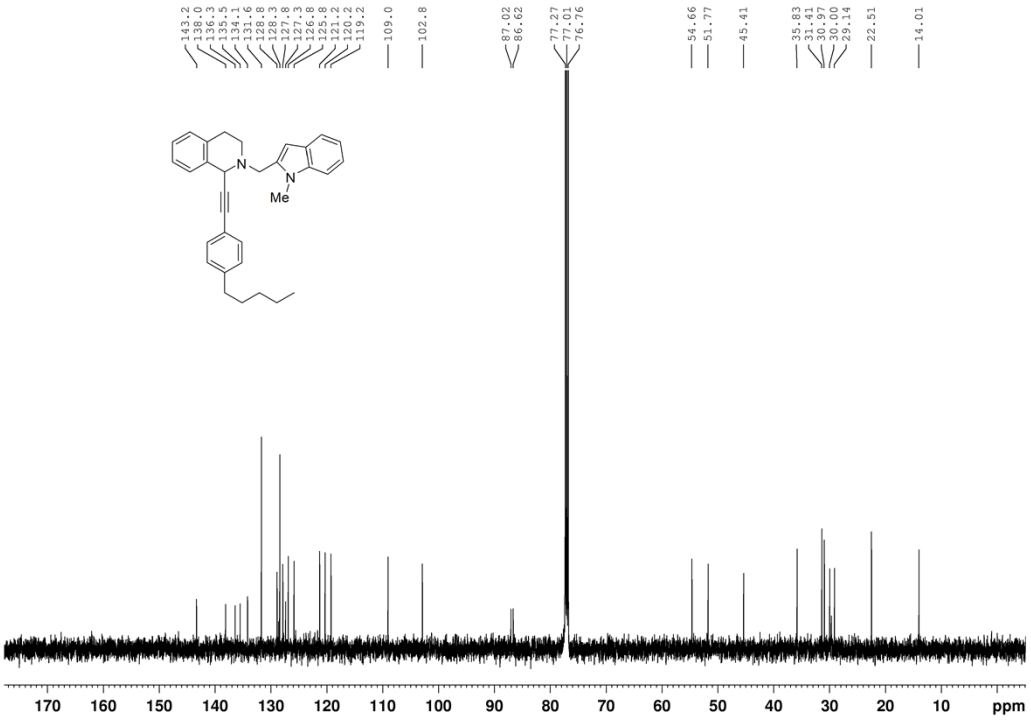
5c


7.6230
7.6035
7.3818
7.3613
7.3280
7.2856
7.2647
7.2357
7.2154
7.1829
7.1687
7.1413
7.1220
6.5440
4.8068
4.1632
4.1294
4.0259
3.9921
3.8260
3.1438
3.1332
3.0917
3.0838
2.9813
2.9322
2.9173
2.8617
2.7664
2.3637
0.0181
N
N
Me
Me
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 ppm
1.02
2.17
2.09
3.07
4.06
0.92
1.00
1.08
1.05
3.07
1.02
1.16
2.06
3.08

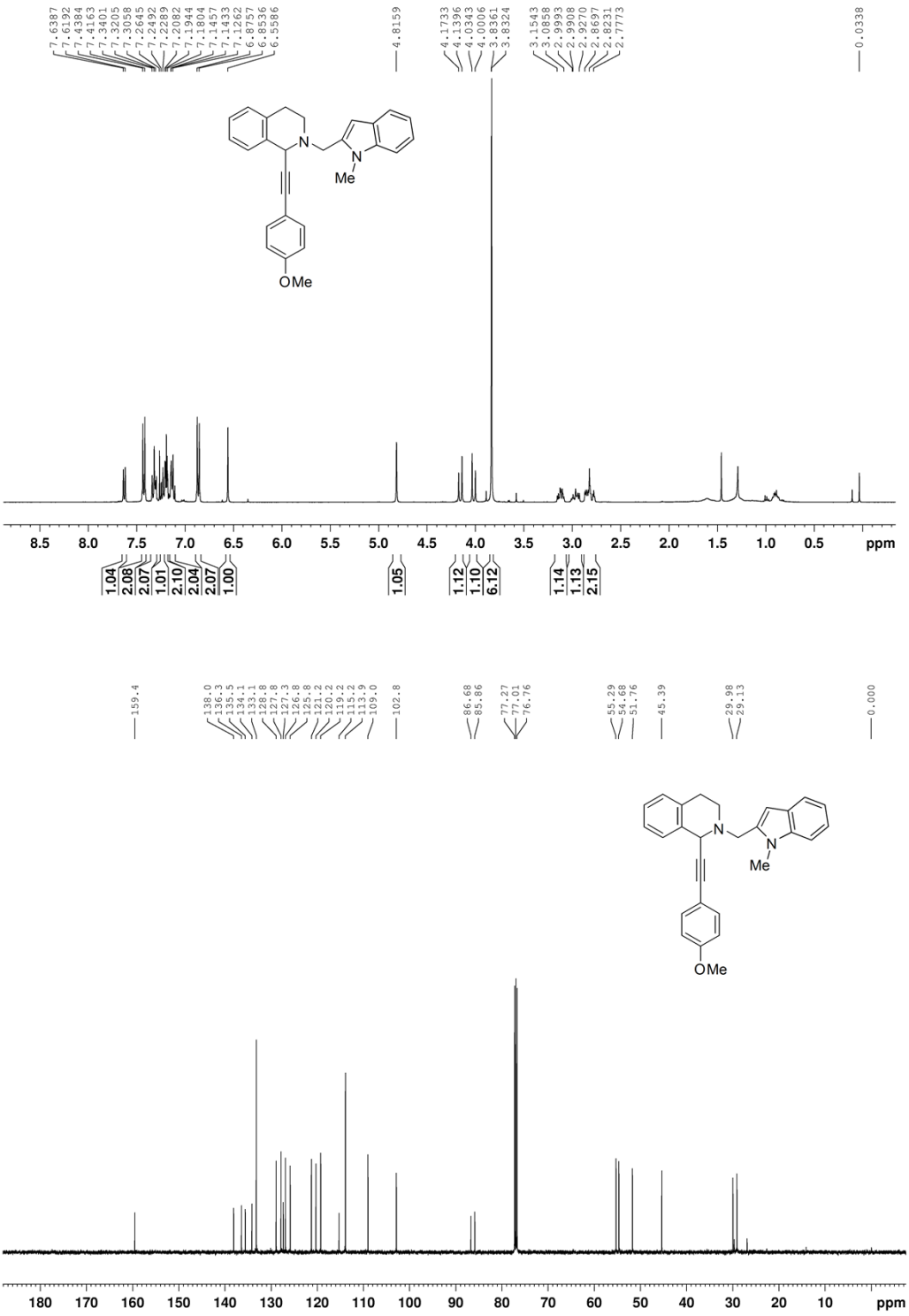

138.2
138.0
136.3
135.4
134.1
131.6
129.0
128.8
127.8
127.7
127.3
126.8
125.8
121.2
120.2
120.0
119.2
109.0
102.8
86.94
86.63
77.26
77.01
76.75
54.66
51.76
45.42
29.99
29.13
21.45
0.000
N
N
Me
Me
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

5d

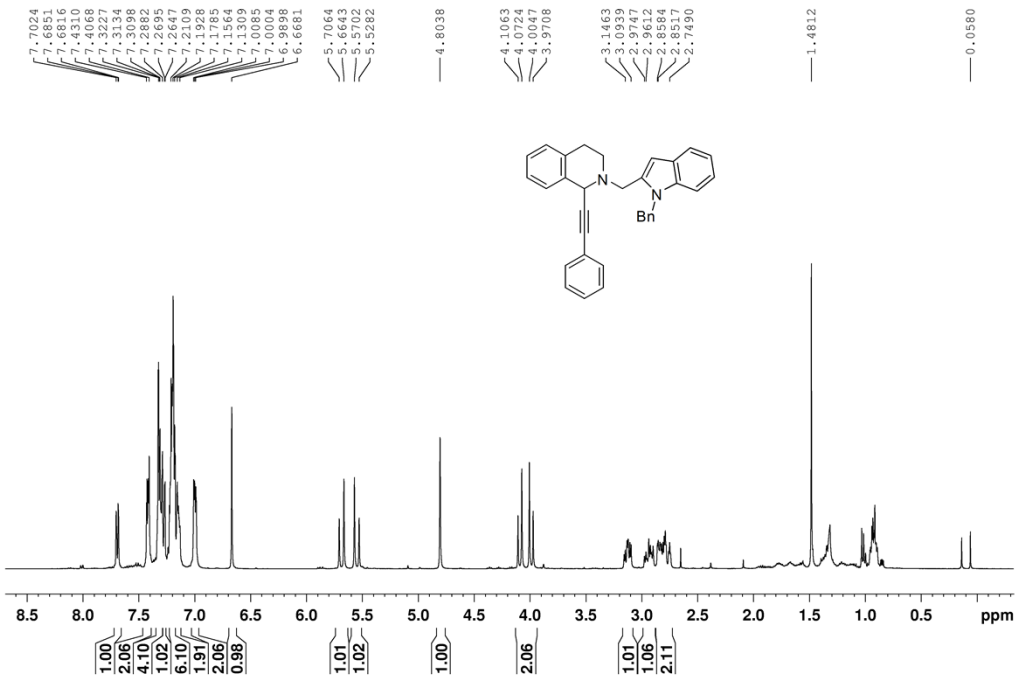

7.6156
7.5961
7.3925
7.3722
7.3223
7.2743
7.2644
7.2277
7.2074
7.1873
7.1730
7.1585
7.1387
7.0856
6.5375
4.7997
4.1544
4.1206
4.0204
3.9866
3.8208
3.1349
3.0748
2.9739
2.9103
2.8548
2.7579
2.6184
2.5800
1.6241
1.5635
1.3421
1.3065
0.9100
0.8930
0.8756
0.0089
Me
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 2.06 2.06 1.01 2.06 3.90 1.06 1.06 2.11 2.91 0.99 1.09 2.06 2.15 2.11 4.03 3.05

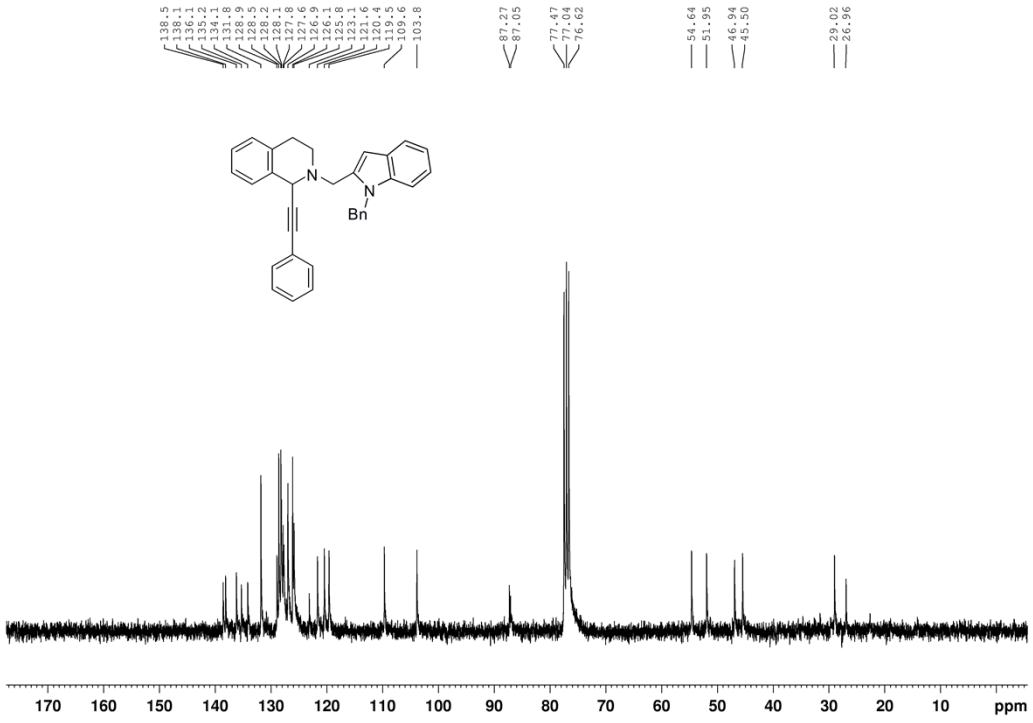

143.2
138.0
136.3
135.5
134.1
131.6
128.8
128.3
127.3
126.8
125.8
121.2
120.2
119.2
109.0
102.8
87.02
86.62
77.27
77.01
76.76
54.66
51.77
45.41
35.83
31.41
30.97
30.00
29.14
22.51
14.01
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

5e

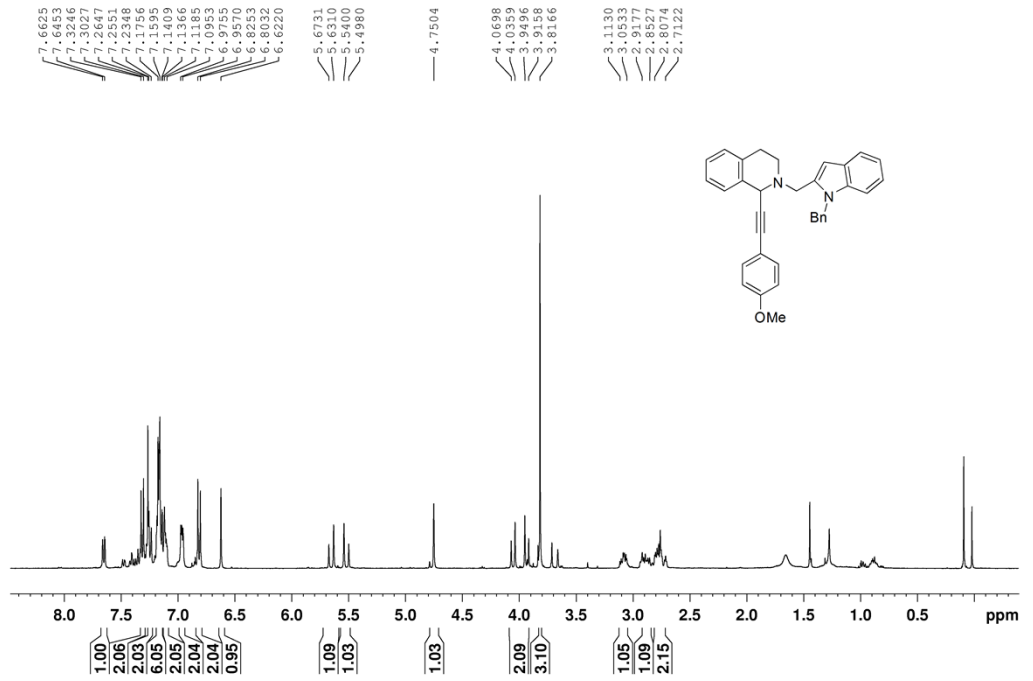

7.6387
7.6192
7.4384
7.4163
7.3401
7.3205
7.3058
7.2645
7.2492
7.2289
7.2082
7.1944
7.1804
7.1457
7.1433
7.1262
6.8757
6.8536
6.5586
4.8159
4.1733
4.1396
4.0343
4.0006
3.8361
3.8324
3.1543
3.0858
2.9993
2.9908
2.9270
2.8697
2.8231
2.7773
0.0338
N
N
Me
OMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.04 2.08 2.07 1.01 2.10 2.04 2.07 1.00 1.05 1.12 1.10 6.12 1.14 1.13 2.15
159.4
138.0
136.3
135.5
134.1
133.1
128.8
127.8
127.3
126.8
125.8
121.2
120.2
119.2
115.2
113.9
109.0
102.8
86.68
85.86
77.27
77.01
76.76
55.29
54.68
51.76
45.39
29.98
29.13
0.000
N
N
Me
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

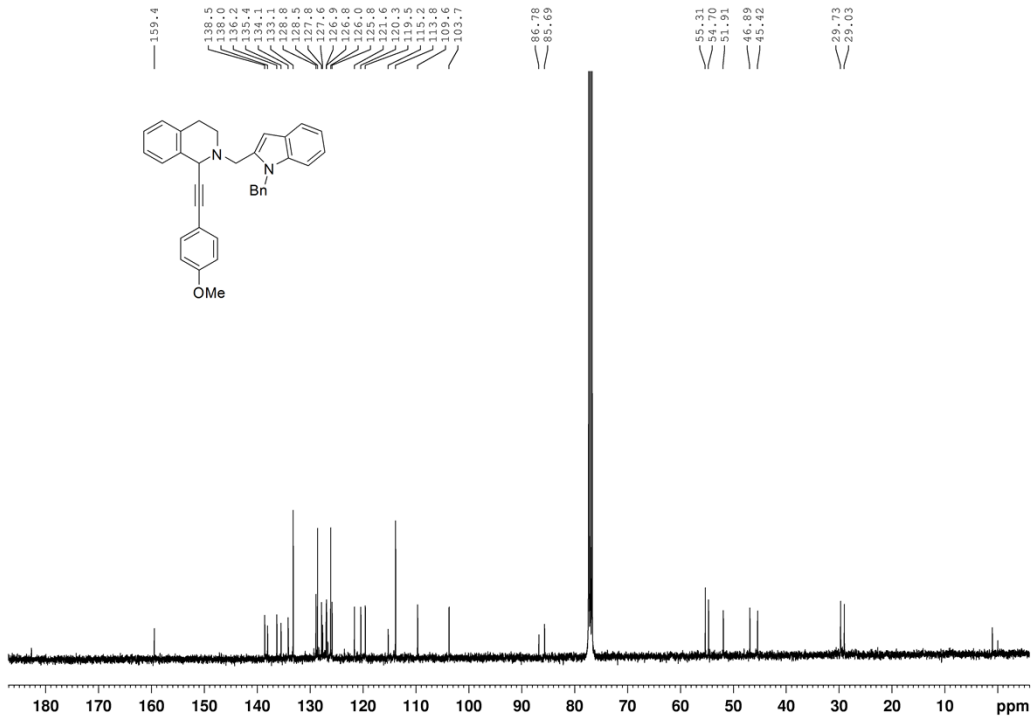
5f


7.7024
7.6851
7.6816
7.4316
7.4068
7.3227
7.3134
7.3098
7.2882
7.2695
7.2647
7.2109
7.1928
7.1785
7.1564
7.1309
7.0085
7.0004
6.9898
6.6681
5.7064
5.6643
5.5702
5.5282
4.8038
4.1063
4.0724
4.0047
3.9708
3.1463
3.0939
2.9747
2.9612
2.8584
2.8517
2.7490
1.4812
0.0580
Bn
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 ppm
1.00 2.06 4.10 1.02 6.10 1.91 2.06 0.98 1.01 1.02 1.00 2.06 1.01 1.06 2.11

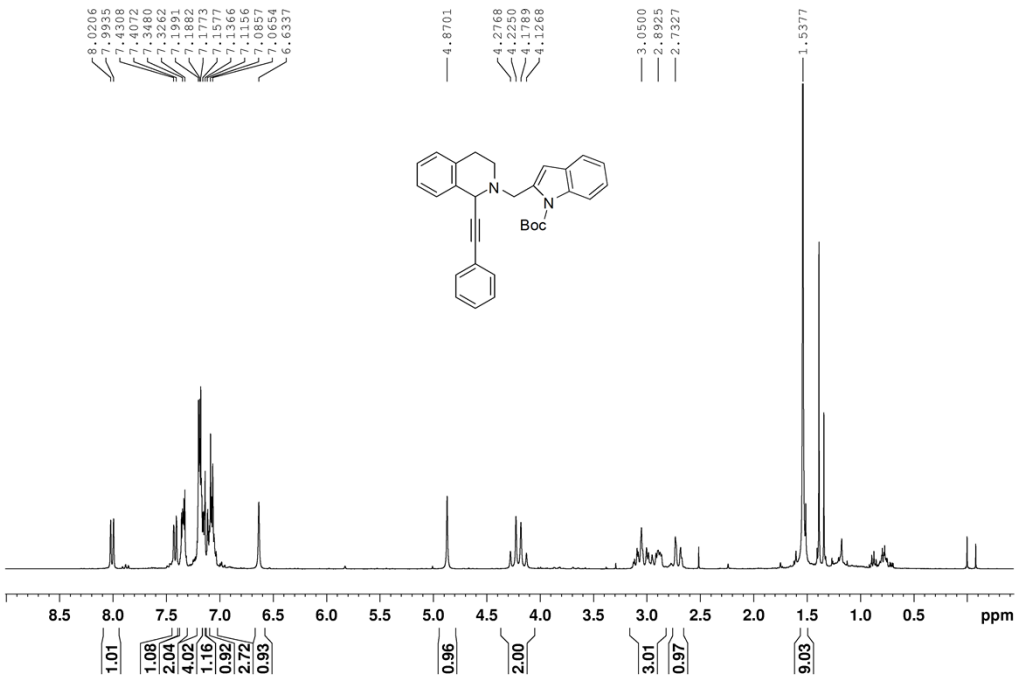

138.5
136.1
135.2
134.1
131.8
128.9
128.5
128.2
128.1
127.8
127.6
126.9
126.1
125.8
123.1
121.6
120.4
119.5
109.6
103.8
87.27
87.05
77.47
77.04
76.62
54.64
51.95
46.94
45.50
29.02
26.96
Bn
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

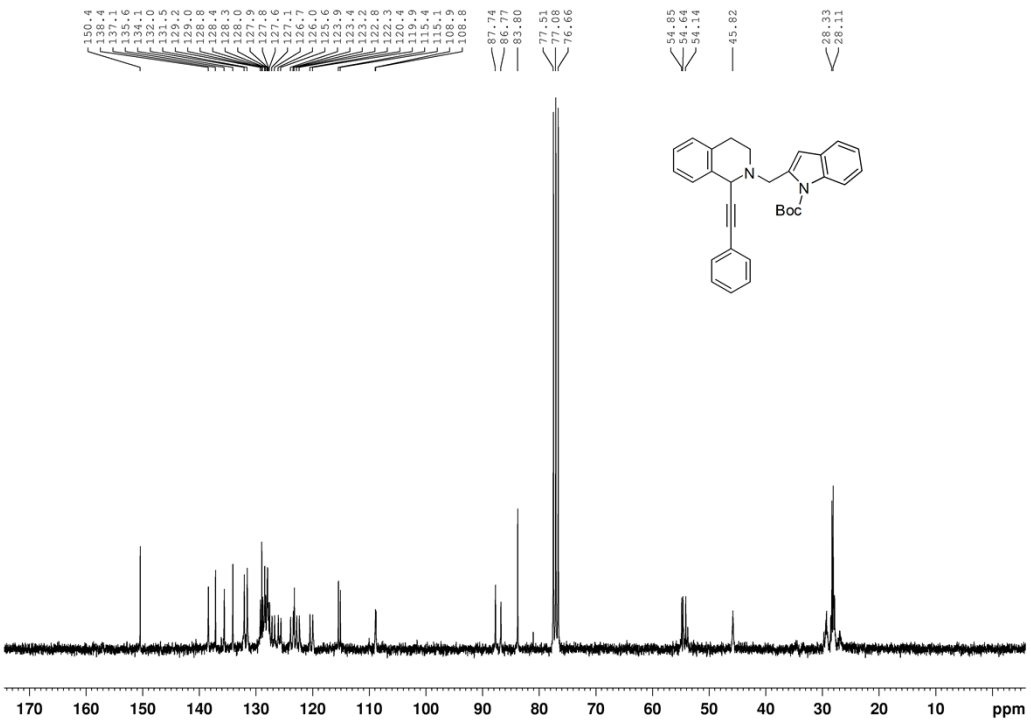
5g


7.6625
7.6453
7.3246
7.3027
7.2647
7.2551
7.2348
7.1756
7.1595
7.1409
7.1366
7.1185
7.0953
6.9755
6.9570
6.8253
6.8032
6.6220
5.6731
5.6310
5.5400
5.4980
4.7504
4.0698
4.0359
3.9496
3.9158
3.8166
3.1130
3.0533
2.9177
2.8527
2.8074
2.7122
N
N
Bn
OMe
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
ppm
1.00
2.06
2.03
6.05
2.05
2.04
2.04
0.95
1.09
1.03
1.03
2.09
3.10
1.05
1.09
2.15

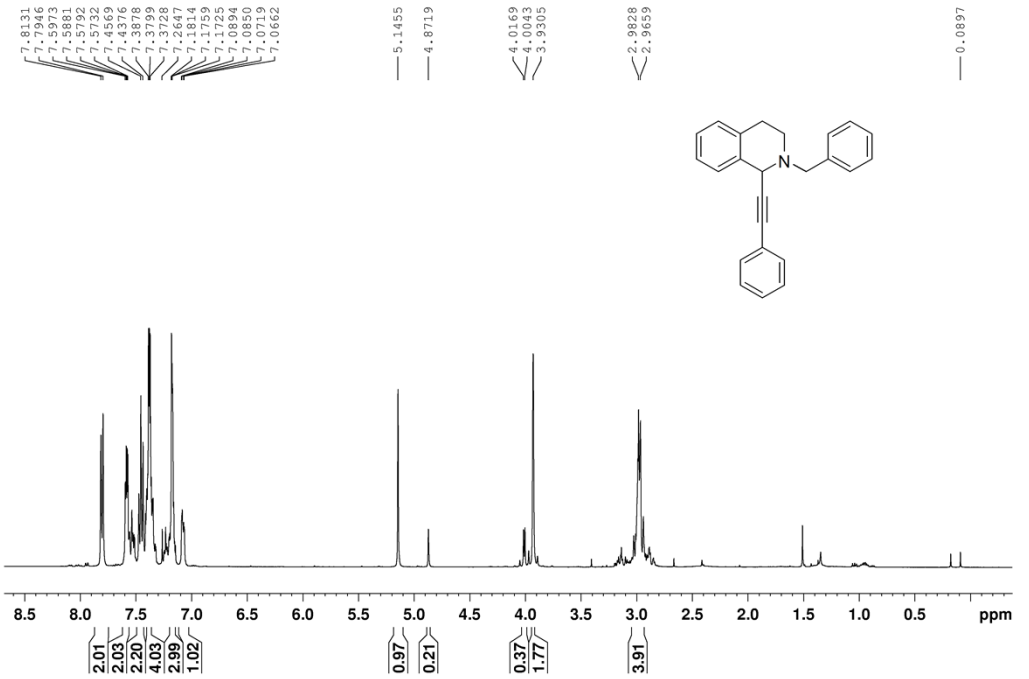

159.4
138.5
138.0
136.2
135.4
134.1
133.1
128.8
128.5
127.8
127.6
126.9
126.8
126.0
125.8
121.6
120.3
119.5
115.2
113.8
109.6
103.7
86.78
85.69
55.31
54.70
51.91
46.89
45.42
29.73
29.03
N
N
Bn
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

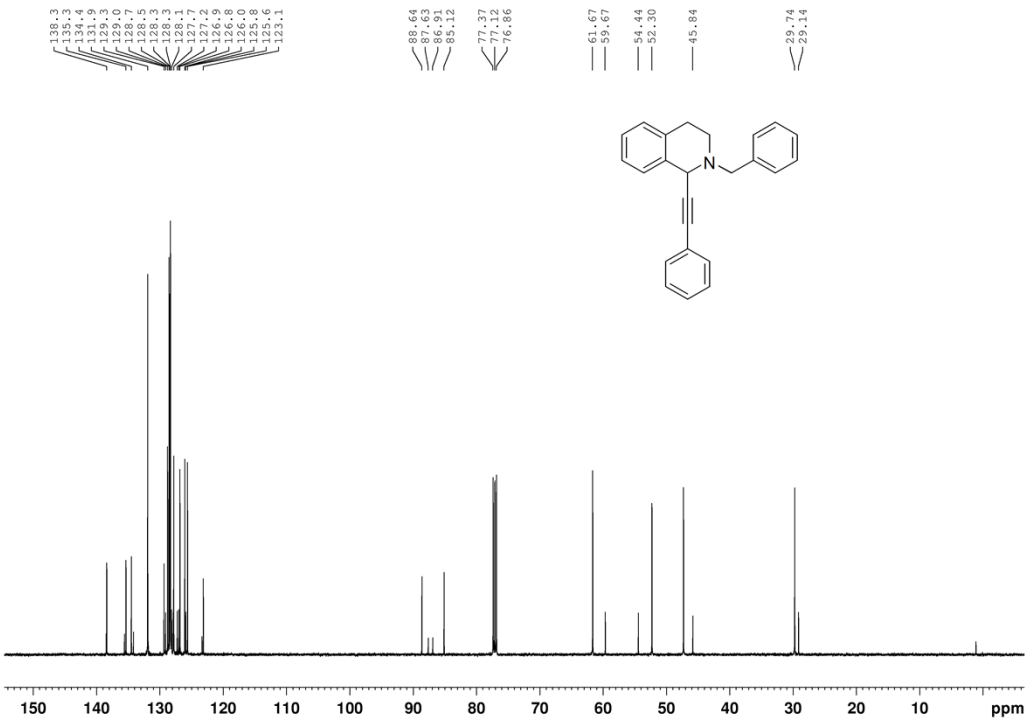
5h


8.0206
7.9935
7.4308
7.4072
7.3480
7.3262
7.1991
7.1882
7.1773
7.1577
7.1366
7.1156
7.0857
7.0654
6.6337
4.8701
4.2768
4.2250
4.1789
4.1268
3.0500
2.8925
2.7327
1.5377
Boc
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 ppm
1.01 1.08 2.04 4.02 1.16 0.92 2.72 0.93 0.96 2.00 3.01 0.97 9.03

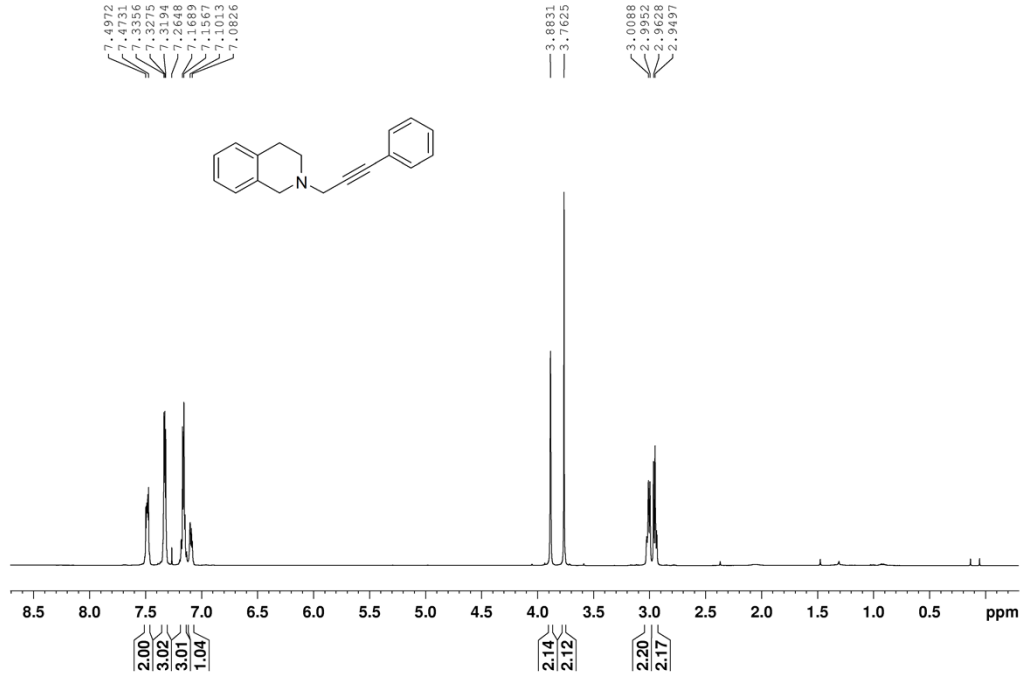

150.4
138.4
137.1
135.6
134.1
132.0
131.5
129.2
129.0
128.8
128.4
128.3
128.0
127.9
127.8
127.6
127.1
126.7
126.0
125.6
123.9
123.4
123.2
122.8
122.3
120.4
119.9
115.4
115.1
108.9
108.8
87.74
86.77
83.80
77.51
77.08
76.66
54.85
54.64
54.14
45.82
28.33
28.11
Boc
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

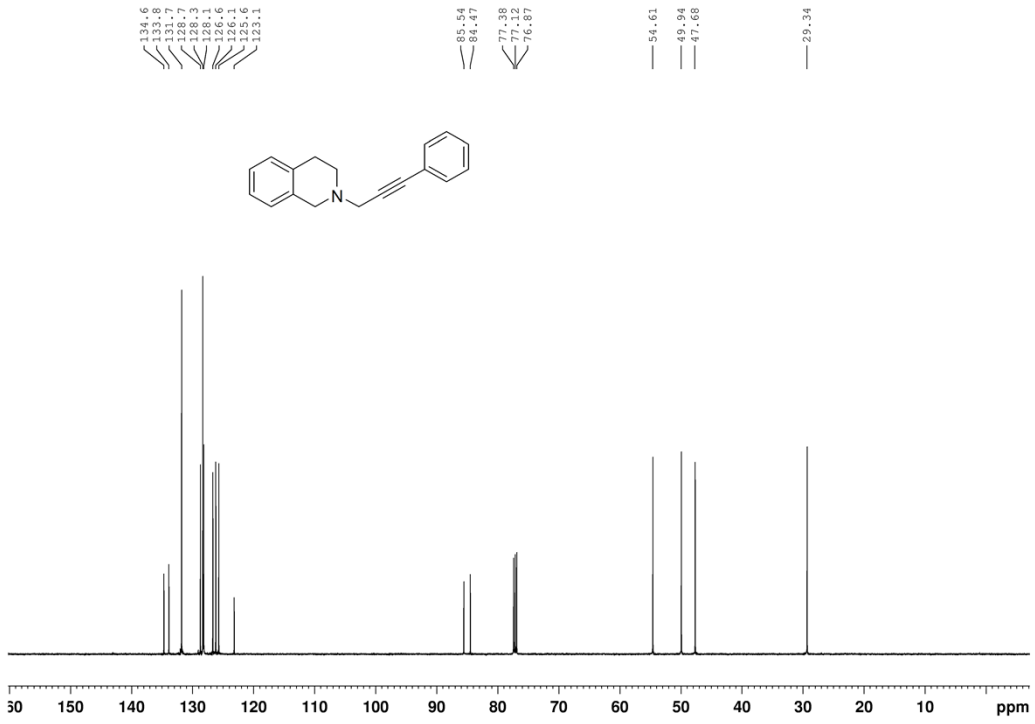
5i (major **5i** and minor **6a**, **5i**/**6a** = 4.8/1)





6b


7.4972
7.4731
7.3356
7.3275
7.3194
7.2648
7.1689
7.1567
7.1013
7.0826
3.8831
3.7625
3.0088
2.9952
2.9628
2.9497
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 ppm
2.00
3.02
3.01
1.04
2.14
2.12
2.20
2.17


134.6
133.8
131.7
128.7
128.3
128.1
126.6
126.1
125.6
123.1
85.54
84.47
77.38
77.12
76.87
54.61
49.94
47.68
29.34
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm