Supporting Information

Direct Palladium-Catalyzed Alkynylation of N-Fused Heterocycles

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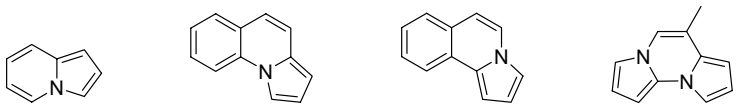
General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz), instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle silica gel (43-60 μm). HRMS (EI) analysis was performed on a JEOL GCmate II instrument. All manipulations with transition metal catalysts were conducted under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous toluene, tetrahydrofuran, and dichloromethane, purchased from Aldrich, were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system. All other chemicals and solvents were purchased from Aldrich, Fisher, Acros Organics, TCI, and Alfa Aesar and used without additional purification.

Preparation of Starting Materials

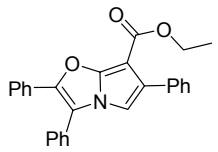
Indolizine, pyrrolo[1,2-*a*]quinoline, pyrrolo[2,1-*a*]isoquinoline and 6-methyl-dipyrrolo[1,2-*a*:1',2'-*c*]pyrimidine



Compounds were prepared using copper-catalyzed cycloizomerization methodology developed by Gevorgyan *et al.*[1] NMR spectra matched those found in literature: indolizine,[2] pyrrolo[1,2-*a*]quinoline,[3] pyrrolo[2,1-*a*]isoquinoline[4] and 6-methyl- dipyrrolo[1,2-*a*:1',2'-*c*]pyrimidine.[5]

(1) Kel'in A. V.; Sromek A. W.; Gevorgyan V. *J. Am. Chem. Soc.* **2001**, *123*, 2074.
(2) Ohsawa, A.; Kawaguchi, T.; Igeta, H. *J. Org. Chem*. **1982**, 47, 3497.
(3) Mamane V.; Hannen P.; Fürstner A. *Chem. Eur. J*. **2004**, *10*, 4556.
(4) Hosomi, A.; et al. *J. Heterocyclic Chem*. **1989**, *26*, 477 (and references therein).
(5) Kim, J. T.; Gevorgyan, V. *Org. Lett*. **2002**, *4*, 4697.

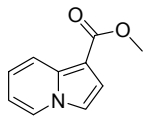
1-carboethoxy-2,6,7-triphenylpyrrolo[2,1-*b*]oxazole



1-Carboethoxy-2,6,7-triphenylpyrrolo[2,1-*b*]oxazole was prepared *via* cyclopropene isomerization protocol developed by Gevorgyan *et al*.[6]

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.59 - 7.69 (4 H, m), 7.48 - 7.59 (5 H, m), 7.32 - 7.43 (5 H, m), 7.27 - 7.33 (1 H, m), 6.65 (1 H, s), 4.33 (2 H, q, *J*=7.15 Hz), 1.35 (3 H, t, *J*=7.15 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 163.31, 150.00, 145.27, 134.84, 130.84, 129.98 (+), 129.57 (+, 2C), 129.48 (+, 2C), 128.96 (+, 3C), 128.73 (+, 2C), 128.05, 127.70 (+, 2C), 126.95 (+), 126.59, 125.95 (+, 2C), 119.72, 101.72 (+), 59.45 (-), 14.55 (+).

1-carbomethoxyindolizine



1-Carbomethoxyindolizine was prepared according to the procedure reported by Zhang *et al*.[7]

Bromoalkynes and 1-iodo-2-phenylacetylene

All compounds were prepared from commercially available corresponding terminal alkynes *via* conventional procedures using *N*-bromosuccinamide (or *N*-iodosuccinamide), and $AgNO_3$ in acetone.[8]

1-Chloro-2-cyclohexenylacetylene

1-Chloro-2-cyclohexenylacetylene was prepared *via* published procedure,[9] NMR data matched those reported in literature.[10]

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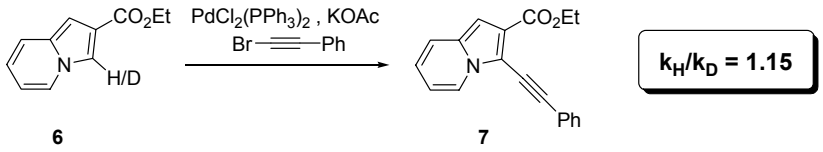
(6) Chuprakov, S.; Hwang, F; Gevorgyan V. *Angew. Chem. Int. Ed.,* **2007**, *46*, ASAP.
(7) Zhang, L.; Liang, F.; Sun, L.; Hu, Y.; Hu, H. *Synthesis* **2000**, *12*, 1733.
(8) For exact procedures, see for example: Villeneuve, K.; Riddell, N.; Jordan, R. W.; Tsui, G. C.; Tam, W. *Org. Lett*. **2004**, *6*, 4543 (and references therein).
(9) Martins, M. A. P.; Emmerich, D. J.; Pereira, C. M. P.; Cunico, W.; Rossato, M.; Zanatta, N.; Bonacorso, H. G. *Tetrahedron Lett*. **2004**, *45*, 4935.
(10) Murray, R. E.; *Synth. Comm.* **1980**, *10*, 345.

General procedure for C-H alkynylation of heterocycles

In a glovebox under nitrogen atmosphere, to a 5.0 mL Wheaton microreactor equipped with a spin vane and screw cap with a PTFE faced silicone septum under nitrogen atmosphere were added heterocyclic substrate, 3-5 mol% of $PdCl_2(PPh_3)_2$ and 2 equiv. of KOAc. The microreactor was removed from the glovebox, bromoalkyne (1.3 - 1.8 equiv) and anhydrous toluene (0.001M-0.010M) were successively added and the mixture was stirred until completion (as monitored by TLC and/or GC/MS). The solvent was removed under reduced pressure and the residue was purified using flash-column chromatography using hexane or hexane/ethylacetate combination as eluent to afford pure alkynyl-heterocycles **3a-q**.

Compound-specific experimental details are summarized in **Table S1**.

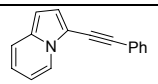
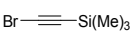
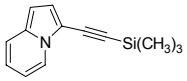
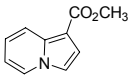
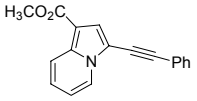
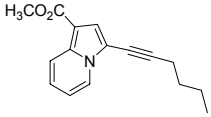
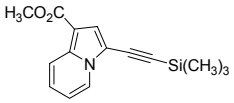
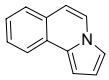
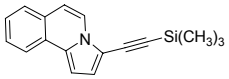
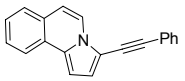
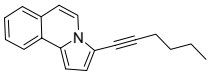
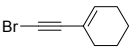
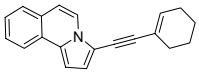
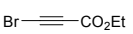
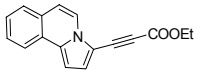
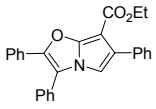
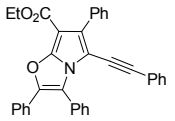
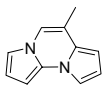
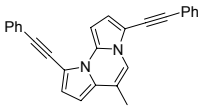
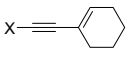
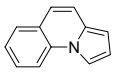
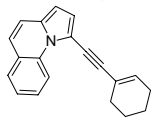
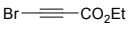
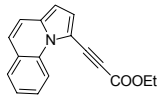
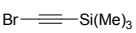
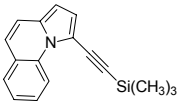
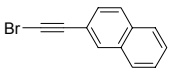
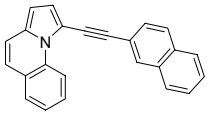
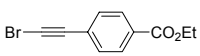
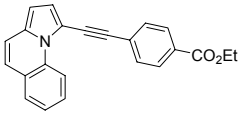
Notes on KIE experiment



6 **7**

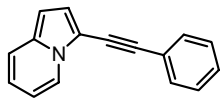
Reactions were run at 70°C in toluene and stopped at nearly 50% conversion. The product-starting material ratios were determined by NMR versus an internal standard (CH_2Br_2). KIE value provided is an average of three experiments. Reference experiment with isotopically pure indolizine **6** indicated no observable deuterium scrambling at the reaction conditions.

Table S1. Direct C-H alkynylation of N-fused heterocycles (experimental details).

#	Haloalkyne	Heterocyclic substrate	Product		T°C, time, rection scale	Yield, %[a]
1				**3a**	60°C, 12 hrs 0.90 mmol	51 (59)
2		-		**3b**	60°C, 12 hrs 0.90 mmol	62 (71)
3				**3c**	X=Br, 60°C, 8h X=I, 80°C, 24h 0.14 mmol	76 (97) *Trace*
4		-		**3d**	60°C, 8 hrs 0.30 mmol	64 (88)
5		-		**3e**	60°C, 8 hrs 0.30 mmol	90 (98)
6	-			**3f**	60°C, 12 hrs 0.30 mmol	87 (98)
7		-		**3g**	80°C, 8 hrs 0.47 mmol	73 (83)
8		-		**3h**	80°C, 8 hrs 0.30 mmol	72 (89)
9		-		**3i**	80°C, 5 hrs 0.30 mmol	65 (76)
10		-		**3j**	30°C, 20 hrs 0.10 mmol	64 (75)
11				**3k**	60°C, 12 hrs 0.12 mmol	76 (97)
12	-			**3l**	60°C, 12 hrs 0.30 mmol	51 (64)[b]
13				**3m**	X=Br, 80°C, 5h X=Cl,80°C, 24h 0.28 mmol	71 (85) *Trace*
14		-		**3n**	40°C, 12 hrs 0.27 mmol	63 (74)
15		-		**3o**	60°C, 12 hrs 0.30 mmol	59 (71)
16		-		**3p**	70°C, 12 hrs 0.30 mmol	58 (67)
17		-		**3q**	75°C, 36 hrs 0.24 mmol	50 (56)[c]

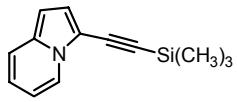
[a] Isolated yields, NMR yields are in brackets. [b] Bromoalkyne was used in the amount of 2.5 equiv. [c] Yield based on recovery of starting material. The reaction was stopped at 60% conversion to avoid thermal decomposition of the product.

3-(phenylethynyl)indolizine, 3a



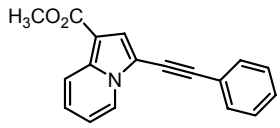
3a (0.90 mmol, 60°C, 51% isolated yield, 59% NMR yield)**:** ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.44 (1 H, d, *J*=8.07 Hz) 7.61 (2 H, d, *J*=6.97 Hz) 7.52 (1 H, d, *J*=8.99 Hz) 7.32 - 7.46 (3 H, m) 7.09 (1 H, d, *J*=4.22 Hz) 6.89 (1 H, dd, *J*=9.44, 5.96 Hz) 6.79 (1 H, dd, *J*=8.50, 3.40 Hz) 6.50 (1 H, d, *J*=4.77 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 134.24, 131.00, 130.99, 128.42, 127.89, 124.67, 123.49, 119.15, 118.80, 111.31, 106.78, 99.94, 96.78, 80.56. HR EI MS m/z 217.08915, Calcd for $C_{16}H_{11}N$ 217.089149.

3-(trimethylsilyl(ethynyl))indolizine, 3b



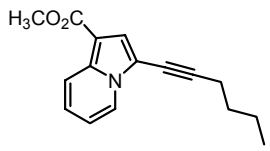
3b (0.90 mmol, 60°C, 62% isolated yield, 71% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.27 (1 H, d, *J*=7.15 Hz) 7.51 (1 H, d, *J*=8.99 Hz) 7.03 (1 H, d, *J*=4.03 Hz) 6.88 (1 H, dd *J*=6.59, 2,01) 6.78 (1 H, dd, *J*=7.99, 1,73) 6.44 (1 H, d, *J*=4.22 Hz) 0.30 (9 H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 124.80, 121.86, 119.49, 119.07, 118.91, 111.27, 102.20, 100.33, 99.54, 95.89, 0.23. HR EI MS m/z 213.09747, Calcd for $C_{13}H_{15}NSi$ 213.09738.

1-carbomethoxy-3-(phenylethynyl)indolizine, 3c



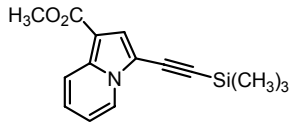
3c (0.14 mmol, 60°C, 76% isolated yield, 97% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.38 (1 H, d, *J*=7.02 Hz), 8.24 (1 H, d, *J*=9.06 Hz), 7.58 (1 H, d, *J*=1.90 Hz), 7.56 (1 H, d, *J*=2.92 Hz), 7.52 (1 H, s), 7.34 - 7.43 (3 H, m), 7.18 (1 H, dd, *J*=8.48, 7.31 Hz), 6.89 (1 H, dd, *J*=6.80, 1.32 Hz), 3.91 (3 H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 164.74, 136.34, 131.27, 128.50, 125.38, 125.35, 123.86, 122.71, 121.14, 121.11, 119.82, 113.29, 108.23, 104.09, 97.01, 78.92, 51.08. HR EI MS m/z 275.09463, Calcd for $C_{18}H_{13}NO_2$ 275.095298.

1-carbomethoxy-3-(hexyn-1-yl)indolizine, 3d



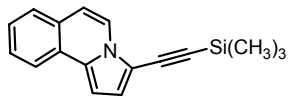
3d (0.30 mmol, 60°C, 64% isolated yield, 88% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.26 (1 H, d, *J*=6.87 Hz), 8.18 (1H, d, 9.06 Hz), 7.34 (1H, s), 7.11 (1 H, dd, *J*=8.33, 7.31 Hz), 6.82 (1 H, dd, *J*=6.80, 5.51 Hz), 3.88 (3 H, s), 2.55 (2 H, t, *J*=7.02 Hz), 1.64 (2 H, d, *J*=7.31 Hz), 1.65 (2 H, m), 1.53 (2 H, m), 0.97 (3 H, t, *J*=7.31 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 164.87, 135.70, 125.12, 123.26, 119.98, 119.64, 112.88, 103.28, 98.10, 70.09, 50.97, 30.84, 22.08, 19.50, 13.65. HR EI MS m/z 255.12509, Calcd for $C_{16}H_{17}NO_2$ 255.12593.

1-carbomethoxy-3-(trimethylsilyl(ethynyl))indolizine, 3e



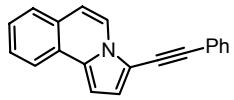
3e (0.30 mmol, 60°C, 90% isolated yield, 98% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.26 (1 H, d, *J*=6.79 Hz), 8.20 (1 H, d, *J*=8.99 Hz), 7.45 (1 H, s), 7.15 (1 H, dd, *J*=8.99, 6.79 Hz), 6.86 (1 H, dd, *J*=6.79, 1.28 Hz), 3.88 (3 H, s), 0.30 (9 H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 164.67, 136.17, 125.45, 123.91, 121.49, 119.73, 113.26, 108.33, 103.69, 103.08, 94.13, 51.03, 0.01. HR EI MS m/z 271.10294, Calcd for $C_{15}H_{17}NO_2Si$ 271.10286.

3-((trimethylsilyl)ethynyl)pyrrolo[2,1-*a*]isoquinoline, 3f



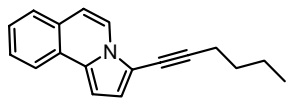
3f (0.30 mmol, 60°C, 87% isolated yield, 98% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.03 (2 H, d, *J*=7.70 Hz), 7.60 (1 H, d, *J*=7.70 Hz), 7.49 (1 H, dd, *J*=7.32, 5.98 Hz), 7.40 (1 H, dd, *J*=8.01, 1,49), 7.00 (1 H, d, *J*=4.03 Hz), 6.90 (1 H, d, *J*=0.55 Hz), 6.87 (1 H, d, *J*=0.87), 0.33 (9 H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 131.16, 127.58, 127.35, 126.96, 126.30, 125.86, 123.20, 122.49, 118.20, 111.57, 109.49, 101.54, 100.10, 95.67, 0.17. HR EI MS m/z 263.11230, Calcd for $C_{17}H_{17}NSi$ 263.11303.

3-(phenylethynyl)pyrrolo[2,1-*a*]isoquinoline, 3g



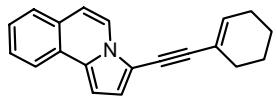
3g (0.47 mmol, 80°C, 73% isolated yield, 83% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.15 (1 H, d, *J*=7.52 Hz), 8.07 (1 H, d, *J*=8.07 Hz), 7.58-7.63 (3 H, m), 7.32 - 7.45 (5 H, m), 7.06 (1 H, d, *J*=4.03 Hz), 6.97 (1 H, dd, *J*=4.03, 0.73 Hz), 6.91 (1 H, d, *J*=7.34 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 132.48, 131.97, 131.26, 131.09, 128.41, 128.05, 127.59, 127.29, 126.95, 126.25, 125.90, 123.11, 122.40, 117.77, 111.57, 100.46, 95.96, 80.37. HR EI MS m/z 267.10415, Calcd for $C_{20}H_{13}N$ 267.10480.

3-(hexyn-1-yl)pyrrolo[2,1-*a*]isoquinoline, 3h



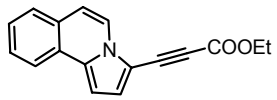
3h (0.30 mmol, 80°C, 72% isolated yield, 89% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.03 (2 H, d, *J*=7.34 Hz), 7.58 (1 H, d, *J*=7.70 Hz), 7.47 (1 H, dd,), 7.37 (1 H, dd, *J*=5.11, 1.32 Hz), 6.89 (2 H, d, *J*=6.81 Hz), 6.83 (1 H, d, *J*=7.34 Hz), 2.58 (2 H, t, *J*=7.15 Hz), 1.63 - 1.74 (2 H, m), 1.48 - 1.61 (2 H, m), 1.00 (3 H, t, *J*=7.34 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 130.25, 127.44, 127.13, 126.87, 126.04, 125.90, 123.09, 122.25, 116.52, 111.14, 110.09, 99.73, 96.72, 71.29, 31.02, 22.12, 19.58, 13.68. HR EI MS m/z 247.13528, Calcd for $C_{18}H_{17}N$ 247.13610.

3-((cyclohex-1-enyl)ethynyl) pyrrolo[2,1-*a*]isoquinoline, 3i



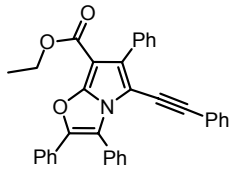
3i (0.30 mmol, 80°C, 65% isolated yield, 76% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.03 (2 H, d, *J*=7.31 Hz), 7.59 (1 H, d, *J*=7.60 Hz), 7.48 (1 H, dd, *J* = 6.53, 2.04), 7.38 (1 H, dd, *J*=7.90, 1.79 Hz), 6.93 (2 H, d, *J*=4.09 Hz), 6.84 (1 H, d, *J*=7.31 Hz), 6.22 - 6.32 (1 H, m), 2.27 - 2.36 (2 H, m), 2.13 - 2.25 (2 H, m), 1.70 - 1.79 (2 H, m), 1.57 - 1.70 (2 H, m); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.51, 134.64, 127.51, 127.24, 126.91, 126.07, 123.15, 122.33, 122.12, 120.66, 117.11, 111.31, 110.32, 100.22, 97.66, 77.51, 29.35, 25.85, 22.40, 21.58. HR EI MS m/z 271.13634, Calcd for $C_{20}H_{17}N$ 271.13610.

3-(ethylpropynoyl)pyrrolo[2,1-*a*]isoquinoline, 3j



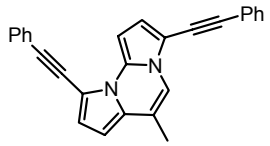
3j (0.10 mmol, 30°C, 64% isolated yield, 75% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.16 (1 H, d, *J*=7.34 Hz), 8.07 (1 H, d, *J*=7.89 Hz), 7.65 (1 H, d, *J*=7.89 Hz), 7.55 (1 H, dd, *J*=5.57, 0.97), 7.47 (1 H, d, *J*=6.87), 7.25 (1 H, d, *J*=4.22 Hz), 6.99 (1 H, d, *J*=7.34 Hz), 6.96 (1 H, dd, *J*=4.31, 0.64 Hz), 4.34 (2 H, q, *J*=7.09 Hz), 1.39 (3 H, t, *J*=7.15 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.51, 133.80, 127.98, 127.92, 127.32, 127.15, 125.40, 123.23, 122.93, 122.60, 112.69, 106.33, 101.60, 90.48, 79.63, 61.84, 14.25. HR EI MS m/z 263.09441, Calcd for $C_{17}H_{13}NO_2$ 263.09463.

7-carboethoxy-5-phenylethynyl-2,3,6-triphenyl-pyrrolo[2,1-*b*][1,3]oxazole, 3k



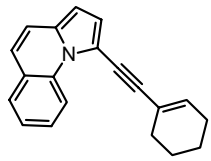
3k (0.12 mmol, 60°C, 76% isolated yield, 97% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.64 - 7.75 (4 H, m), 7.59 (1 H, d, *J*=7.52 Hz), 7.50 - 7.56 (4 H, m), 7.42 (2 H, d, *J*=6.47), 7.29 - 7.38 (4 H, m), 7.14 - 7.21 (3 H, m), 6.77 - 6.85 (2 H, m), 4.33 (2 H, q, *J*=7.15 Hz), 1.35 (3 H, t, *J*=7.06 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 162.67, 149.48, 146.06, 135.41, 133.23, 131.23, 130.66, 130.47, 130.21, 128.97, 128.87, 128.69, 127.94, 127.75, 127.50, 127.42, 127.29, 125.57, 125.50, 123.03, 121.09, 95.61, 80.00, 59.68, 14.48.

6-methyl-3,9-bis(phenylethynyl)dipyrrolo[1,2-*a*:1',2'-*c*]pyrimidine, 3l



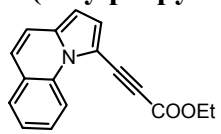
3l (0.30 mmol, 60°C, 51% isolated yield, 64% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.53 - 7.63 (2 H, m) 7.45 - 7.52 (3 H, m) 7.32 - 7.44 (4 H, m) 7.27 (1 H, s) 7.23 (1 H, d, *J*=4.22 Hz) 6.87 - 6.90 (2 H, m) 6.36 (1 H, d, *J*=1.10 Hz) 6.25 (1 H, d, *J*=4.03 Hz) 2.97 (3 H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 131.33, 131.06, 130.89, 130.49, 130.40, 128.56, 128.50, 128.47, 128.44, 128.34, 128.15, 127.88, 119.80, 119.40, 103.40, 102.06, 92.68, 92.25, 83.78, 82.71, 20.65. HR EI MS m/z 370.145974, Calcd for $C_{27}H_{18}N_2$ 370.14700.

1-((cyclohex-1-enyl)ethynyl)pyrrolo[1,2-*a*]quinoline, 3m



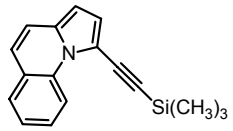
3m (0.28 mmol, 80°C, 71% isolated yield, 85% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.53 (1 H, d, *J*=8.48 Hz), 7.63 (1 H, d, *J*=7.89 Hz), 7.48 (1 H, dd, *J*=6.51, 4.22 Hz), 7.34 (1 H, dd, *J*=7.14, 1.70 Hz), 7.27 (1 H, d, *J*=9.06 Hz), 7.03 (1 H, d, *J*=9.06 Hz), 7.00 (1 H, d, *J*=4.09 Hz), 6.49 (1 H, d, *J*=3.80 Hz), 6.24 - 6.34 (1 H, m), 2.31 - 2.41 (2 H, m), 2.18 - 2.26 (2 H, m), 1.71 - 1.82 (2 H, m), 1.61 - 1.71 (2 H, m); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 135.71, 134.74, 134.11, 132.73, 128.26, 126.88, 125.00, 123.88, 121.72, 121.00, 120.44, 118.74, 116.29, 103.40, 97.32, 82.12, 28.78, 25.85, 22.38, 21.61. HR EI MS m/z 271.13713, Calcd for $C_{20}H_{17}N$ 271.13610.

1-(ethylpropynoyl)pyrrolo[1,2-*a*]quinoline, 3n



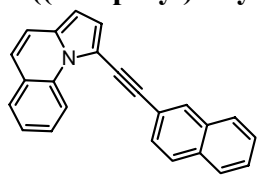
3n (0.27 mmol, 40°C, 63% isolated yield, 74% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.37 (1 H, d, *J*=8.48 Hz), 7.70 (1 H, d, *J*=7.75 Hz), 7.61 (1 H, dd, *J*=8.01, 1.22 Hz), 7.42 (1 H, dd, *J*=7.17, 3.90 Hz), 7.32 (2 H, d, *J*=8.48 Hz), 7.22 (1 H, d, *J*=9.35 Hz), 6.53 (1 H, d, *J*=4.38 Hz), 4.36 (2 H, q, *J*=7.02 Hz), 1.41 (3 H, t, *J*=7.16 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.69, 135.51, 135.37, 128.82, 128.33, 126.59, 124.74, 124.72, 123.28, 118.30, 116.36, 109.57, 104.61, 89.69, 83.54, 61.78, 14.28. HR EI MS m/z 263.0939, Calcd for $C_{17}H_{13}NO_2$ 263.09463.

1-((trimethylsilyl)ethynyl)pyrrolo[1,2-*a*]quinoline, 3o



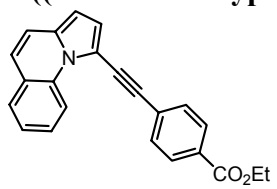
3o (0.30 mmol, 60°C, 59% isolated yield, 71% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.63 (1 H, d, *J*=8.80 Hz), 7.64 (1 H, d, *J*=7.79 Hz), 7.47 (1 H, dd *J*=8.01, 1.55 Hz), 7.36 (1 H, dd, *J*=7.39, 2.99 Hz), 7.28 (1 H, d, *J*=9.17 Hz), 7.08 (1 H, d, *J*=4.22 Hz), 7.06 (1 H, d, *J*=9.17 Hz), 6.47 (1 H, d, *J*=4.03 Hz), 0.37 (9 H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 135.73, 132.96, 128.34, 126.75, 124.92, 124.02, 122.24, 121.04, 118.64, 116.47, 116.42, 110.14, 103.23, 101.57, 100.30, -0.16. HR EI MS m/z 263.11228, Calcd for $C_{17}H_{17}NSi$ 263.11303.

1-((2-naphtyl)ethynyl)pyrrolo[1,2-*a*]quinoline, 3p

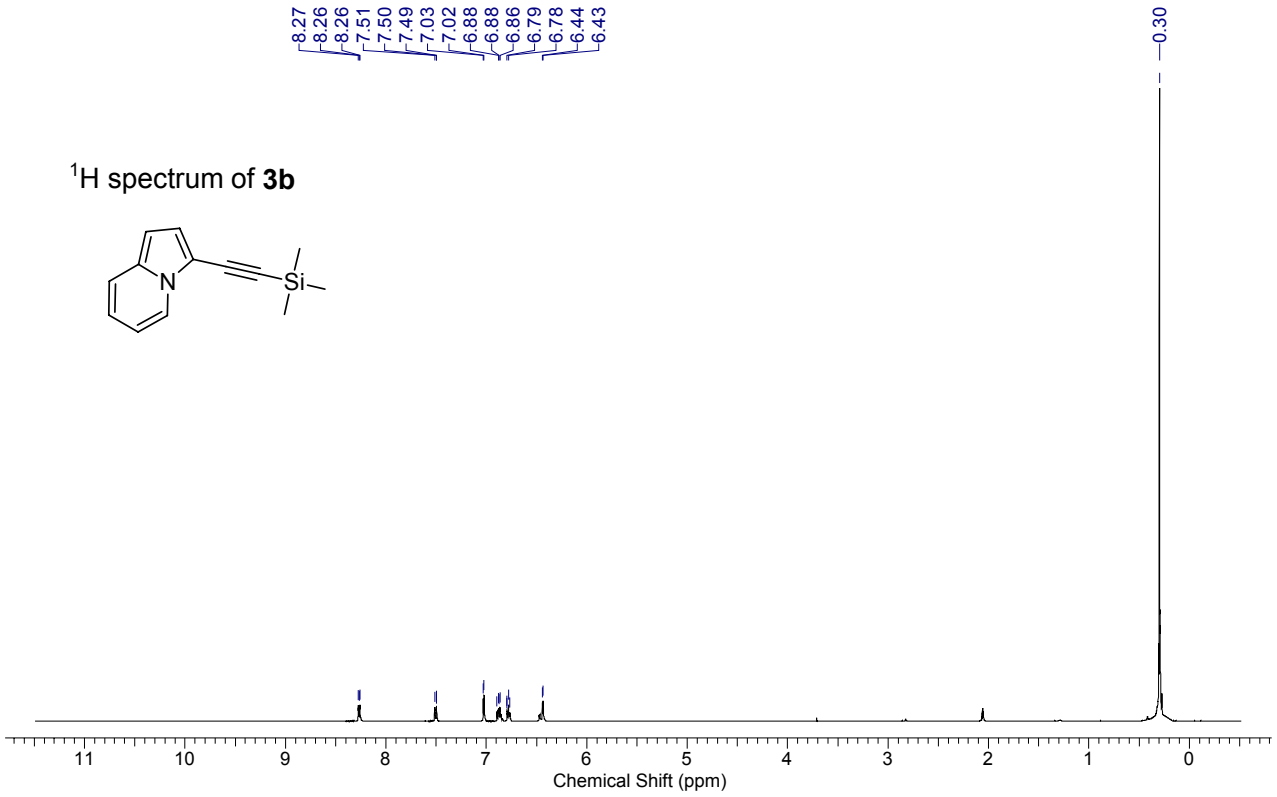


3p (0.30 mmol, 80°C, 58% isolated yield, 67% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.68 (1 H, d, *J*=8.62 Hz) 8.12 (1 H, s) 7.77 - 7.94 (3 H, m) 7.68 (2 H, d, *J*=8.25 Hz) 7.48 - 7.61 (3 H, m) 7.40 (1 H, dd, *J*=7.52, 1.05 Hz) 7.33 (1 H, d, *J*=9.35 Hz) 7.19 (1 H, d, *J*=4.03 Hz) 7.10 (1 H, d, *J*=9.17 Hz) 6.57 (1 H, d, *J*=4.03 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 135.70, 133.28, 133.20, 132.73, 130.33, 128.46, 128.21, 127.86, 127.78, 127.67, 127.22, 126.69, 126.62, 125.07, 124.11, 121.91, 120.99, 120.96, 118.74, 116.32, 110.12, 103.76, 96.12, 85.30. HR EI MS m/z 317.120961, Calcd for $C_{24}H_{15}N$ 317.12045.

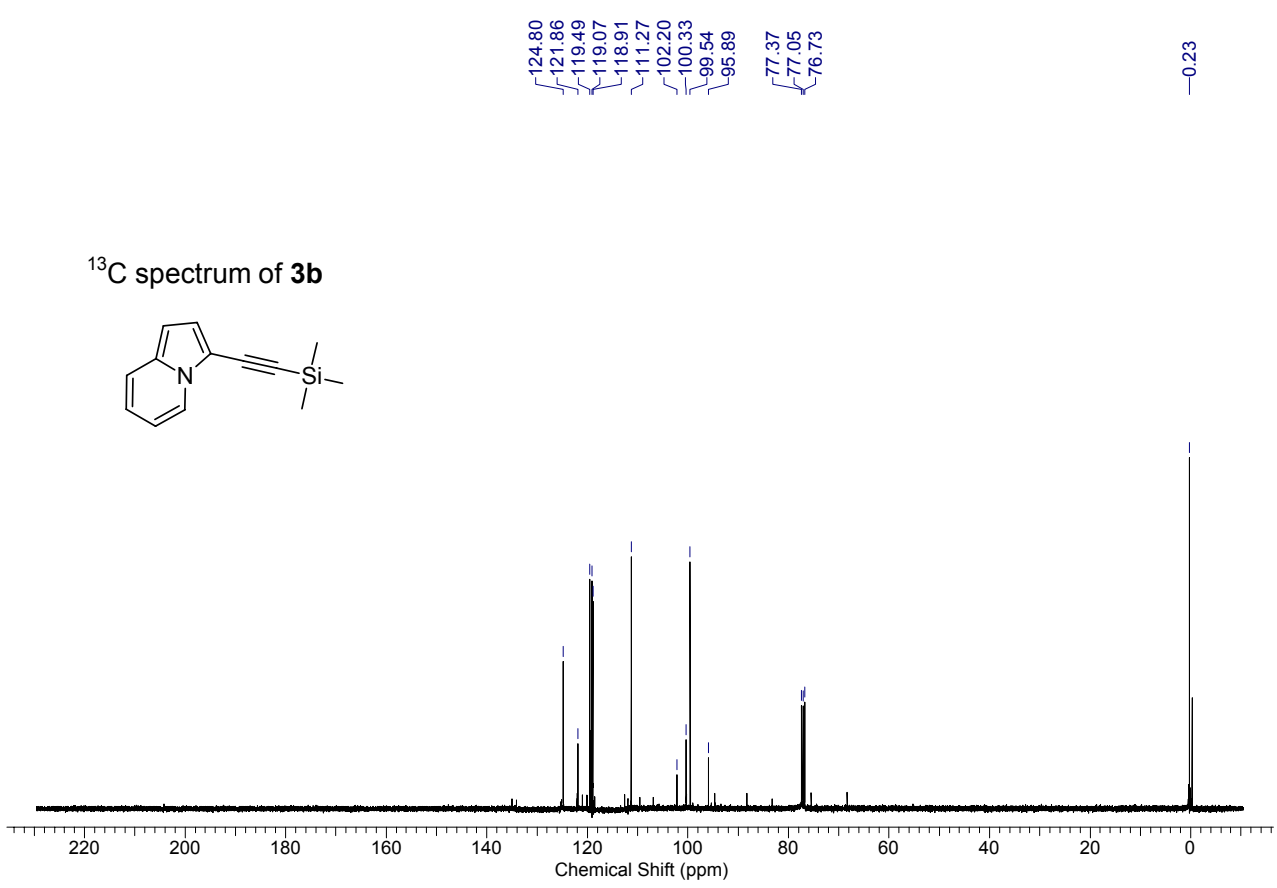
1-((4-carboethoxyphenyl)ethynyl)pyrrolo[1,2-*a*]quinoline, 3q



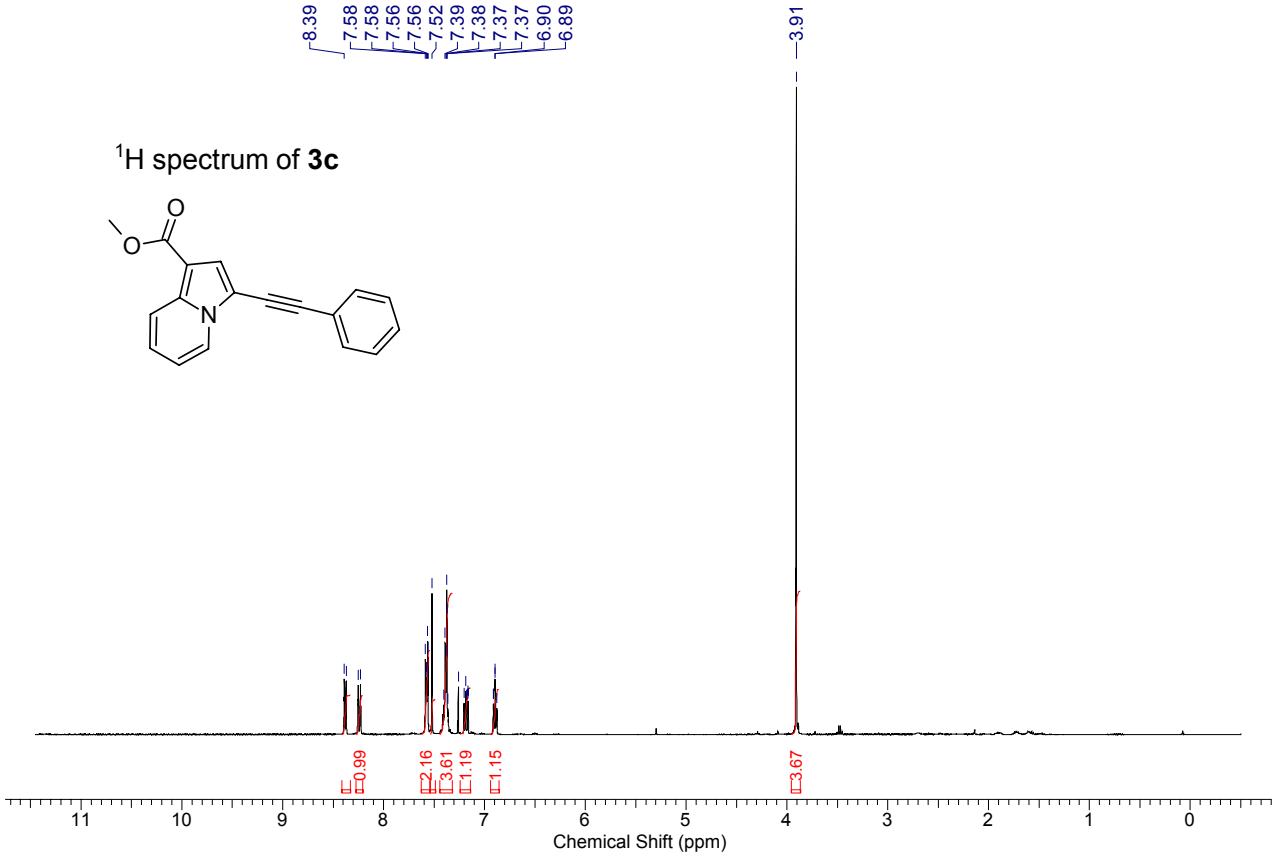
3q (0.24 mmol, 80°C, 50% isolated yield, 56% NMR yield): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.55 (1 H, d, *J*=8.44 Hz) 8.08 (2 H, d, *J*=8.62 Hz) 7.68 (1 H, d, *J*=7.70 Hz) 7.64 (2 H, d, *J*=8.80 Hz) 7.56 (1 H, dd, *J*=6.74, 0.89 Hz) 7.39 (1 H, dd, *J*=7.98, 1.05 Hz) 7.32 (1 H, d, *J*=9.17 Hz) 7.16 (1 H, d, *J*=4.03 Hz) 7.12 (1 H, d, *J*=9.17 Hz) 6.55 (1 H, d, *J*=4.22 Hz) 4.41 (2 H, q, *J*=7.15 Hz) 1.43 (3 H, t, *J*=7.15 Hz); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.09, 135.57, 133.68, 130.23, 129.67, 129.39, 128.56, 128.25, 127.31, 125.03, 124.23, 122.54, 121.36, 118.67, 116.18, 109.53, 103.98, 95.37, 88.13, 61.13, 14.36. HR EI MS m/z 339.125021, Calcd for $C_{23}H_{17}NO_2$ 339.12593.



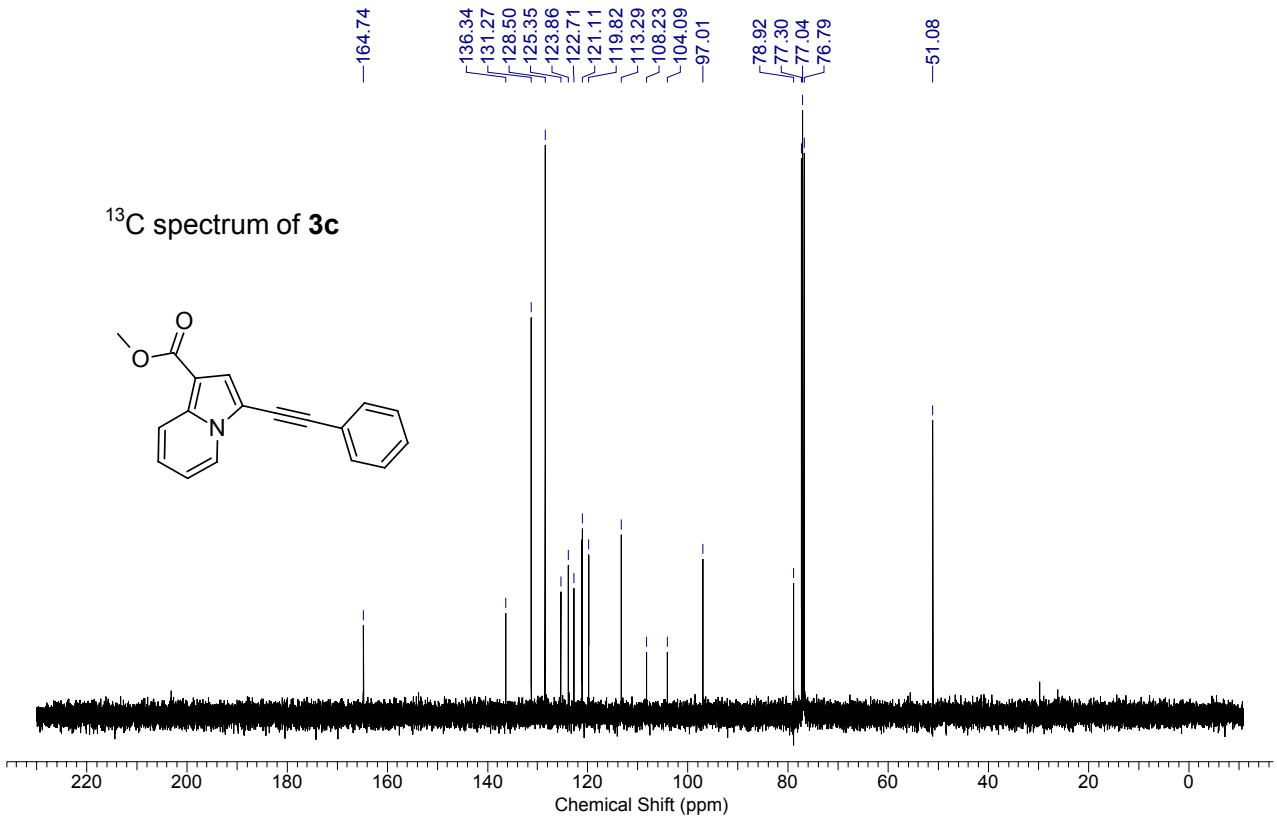
^{1}H spectrum of **3b**



^{13}C spectrum of **3b**

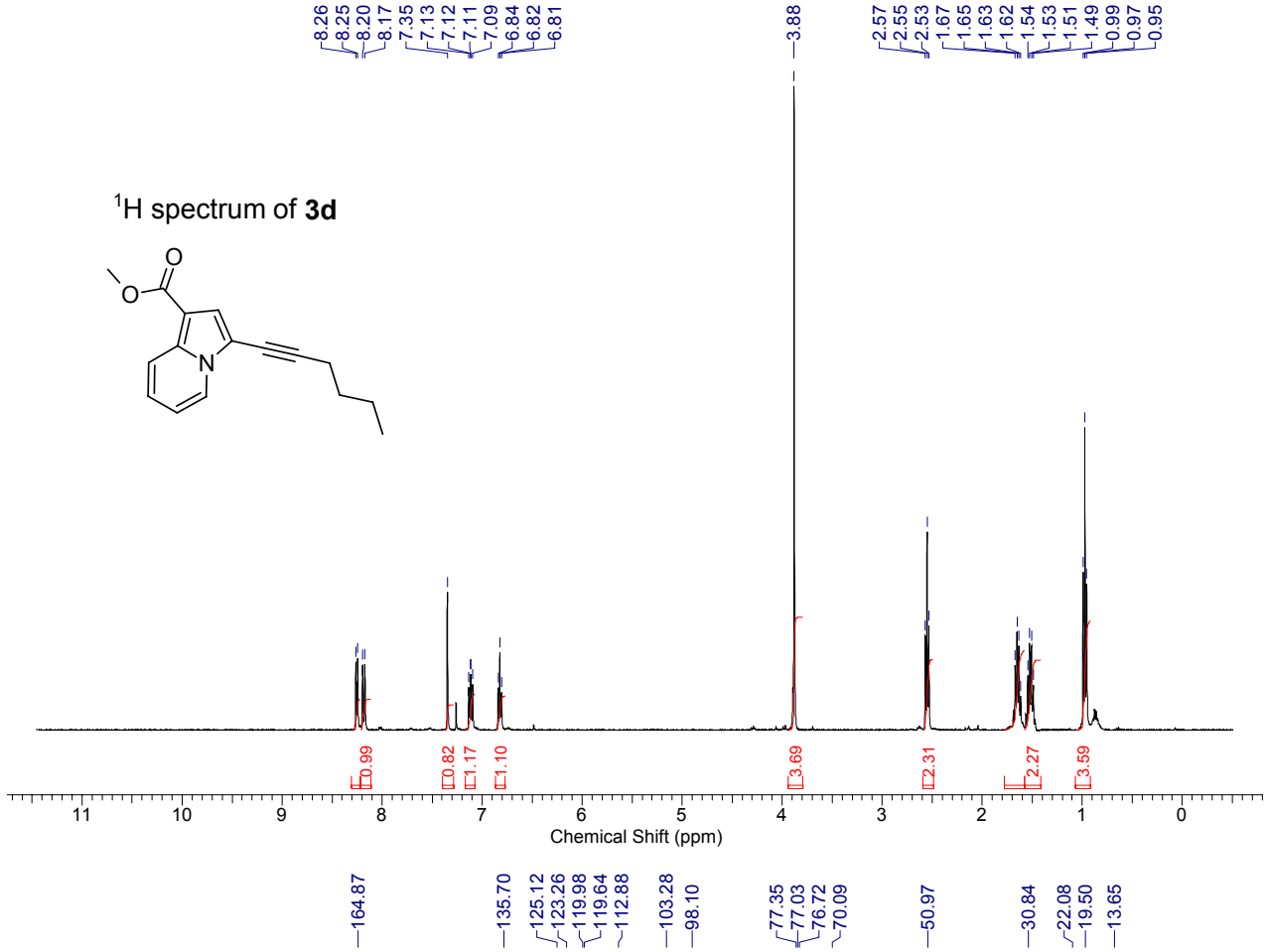


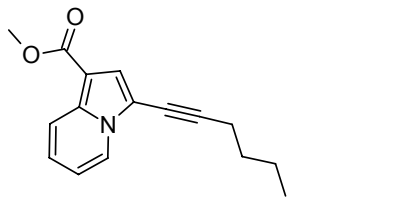
^{1}H spectrum of **3c**



^{13}C spectrum of **3c**

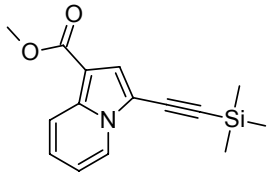
^{1}H spectrum of **3d**



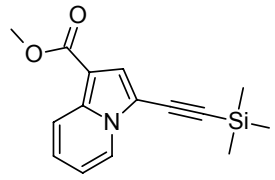


^{13}C spectrum of **3d**

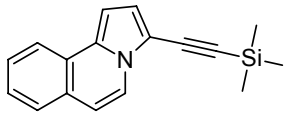
^{1}H spectrum of **3e**



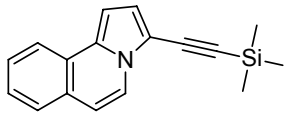
^{13}C spectrum of **3e**



^{1}H spectrum of **3f**

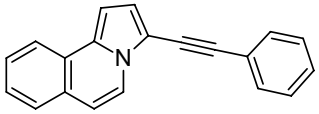


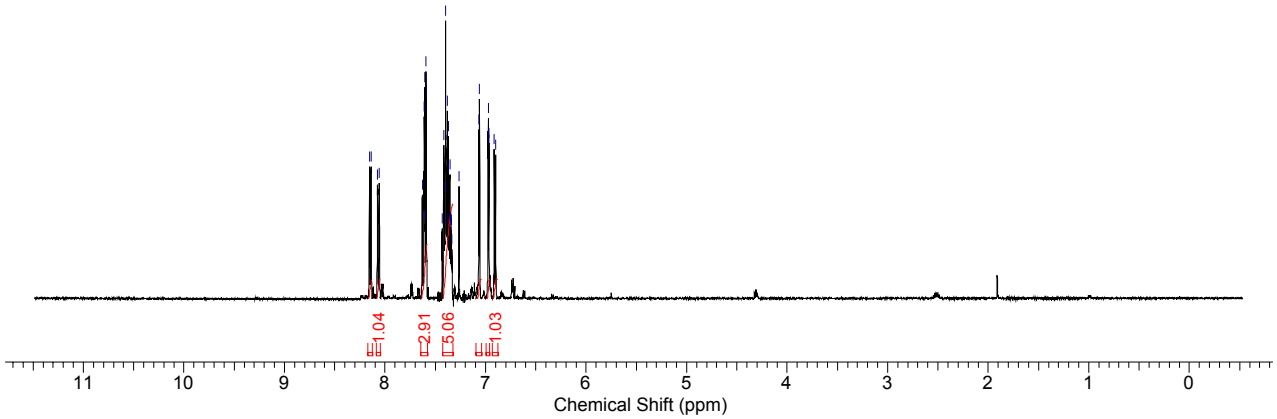
^{13}C spectrum of **3f**



8.15
8.14
7.61
7.60
7.59
7.59
7.40
7.38
7.37
7.07
7.06
6.97
6.97

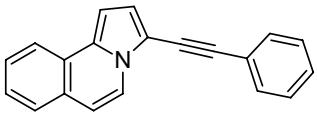
^{1}H spectrum of **3g**

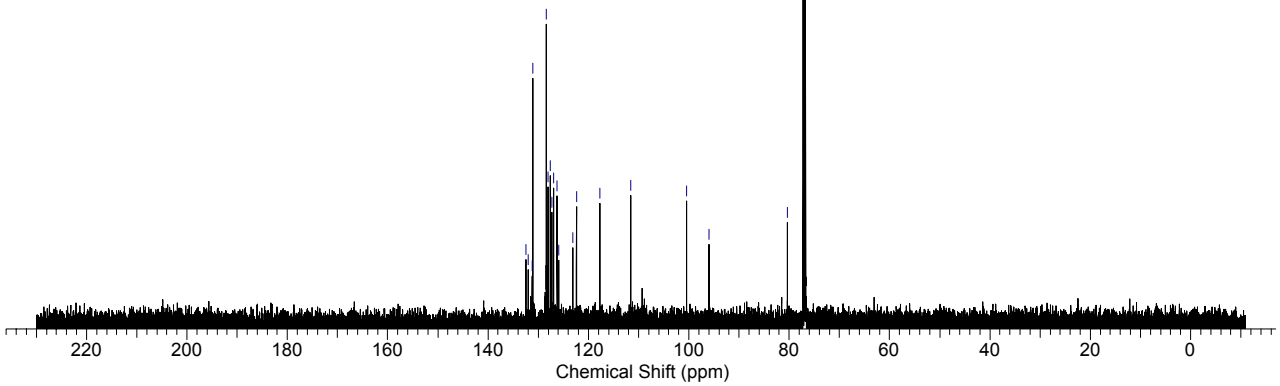


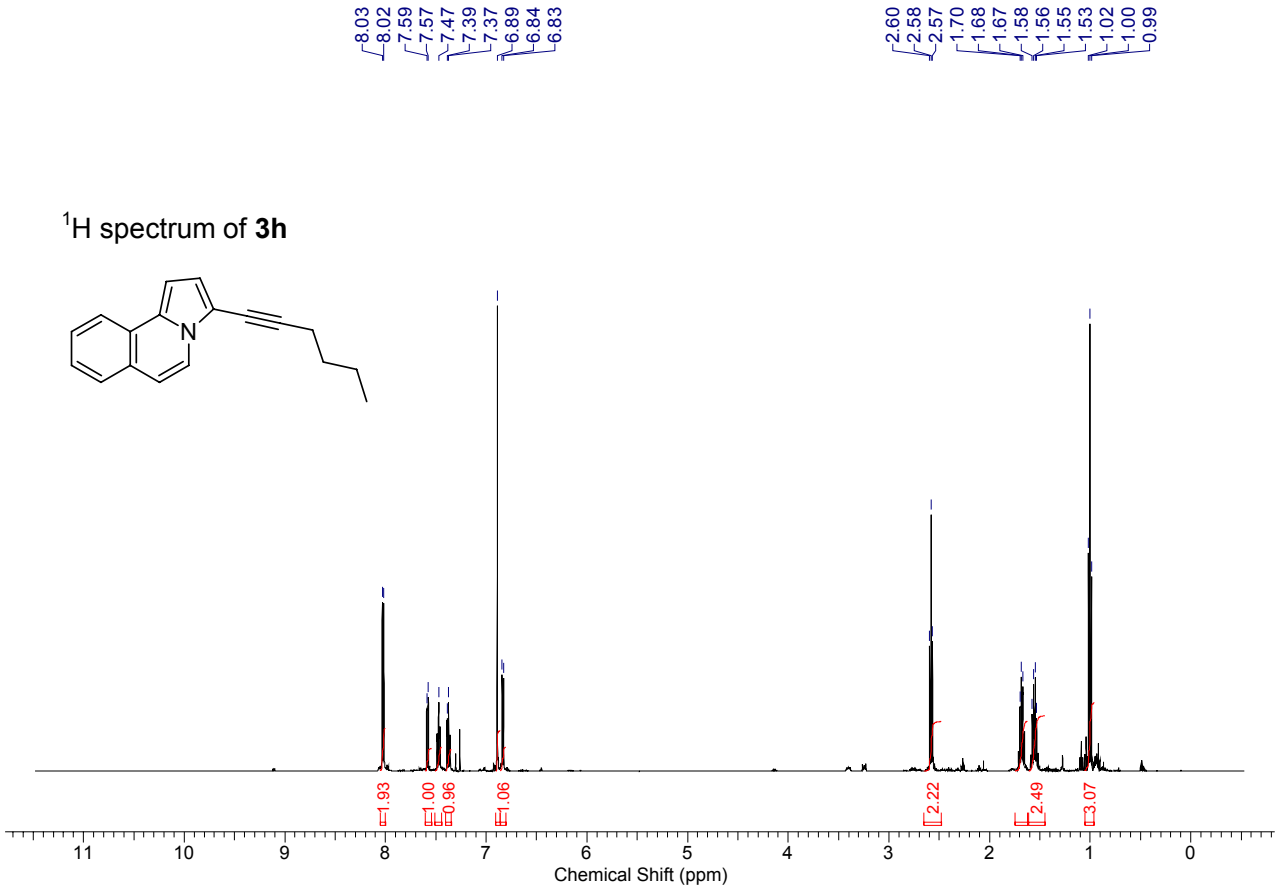


132.48
131.09
128.41
128.05
127.59
127.29
126.95
126.25
123.11
122.40
117.77
111.57
100.46
95.96
80.37
77.25
77.00
76.74

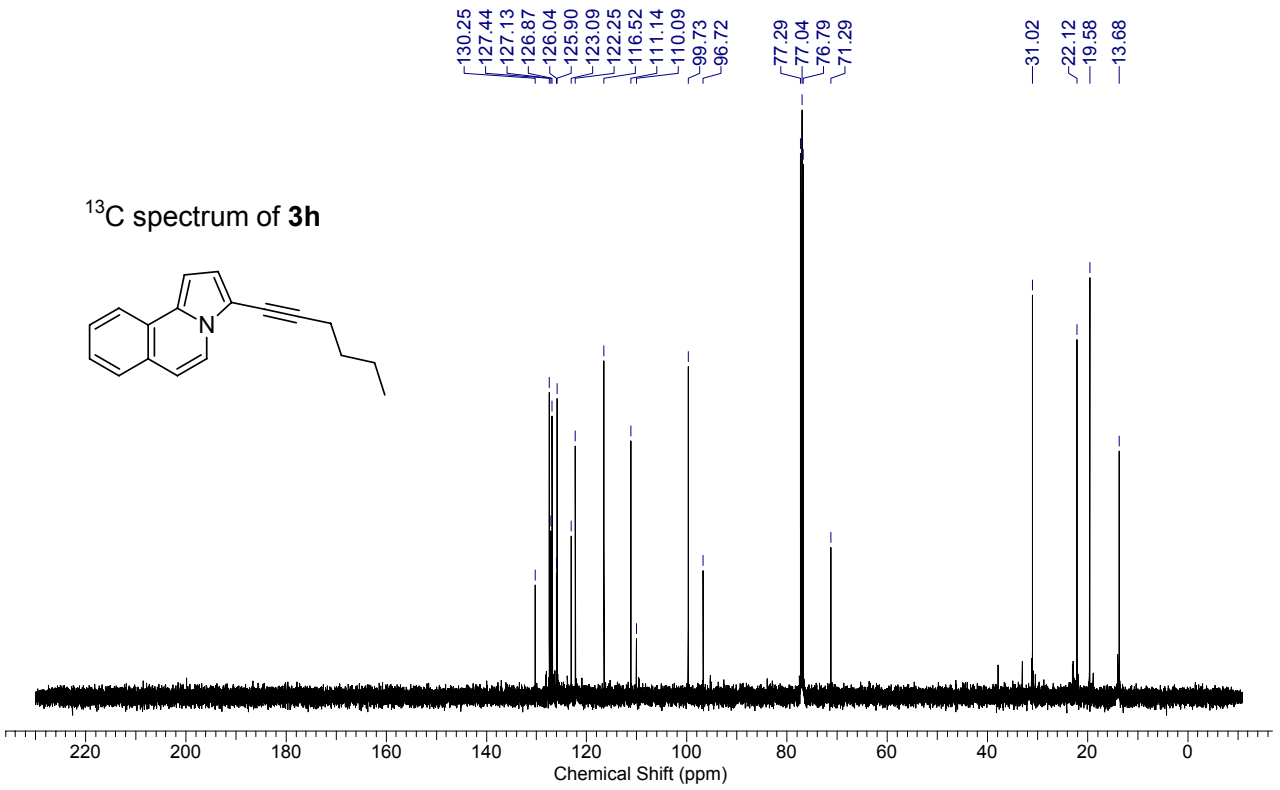
^{13}C spectrum of **3g**





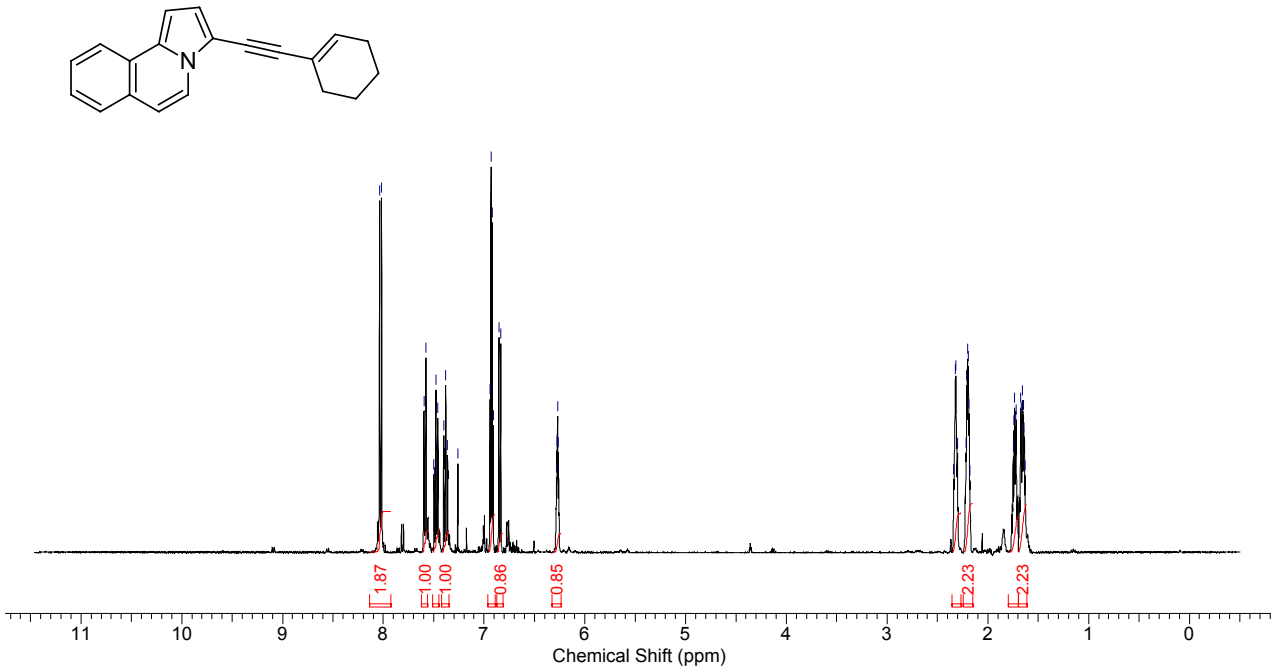


^{1}H spectrum of **3h**

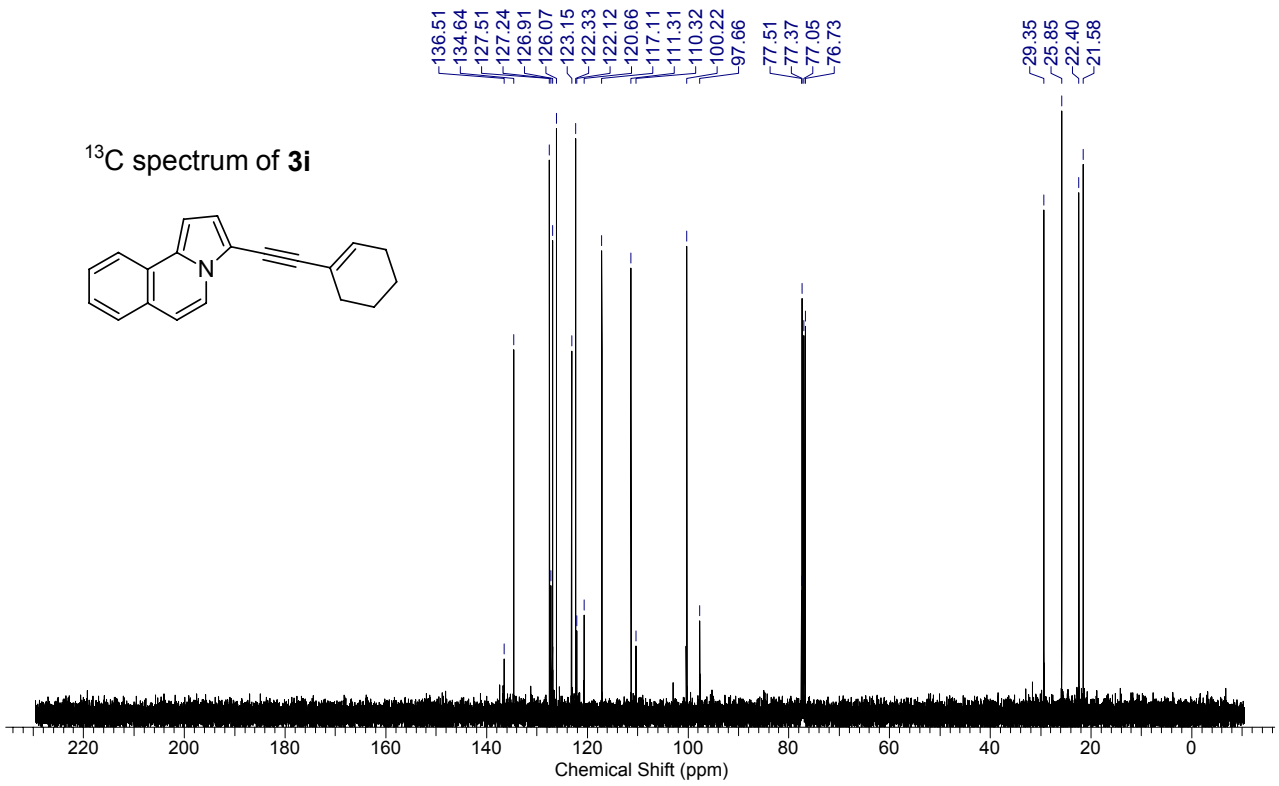


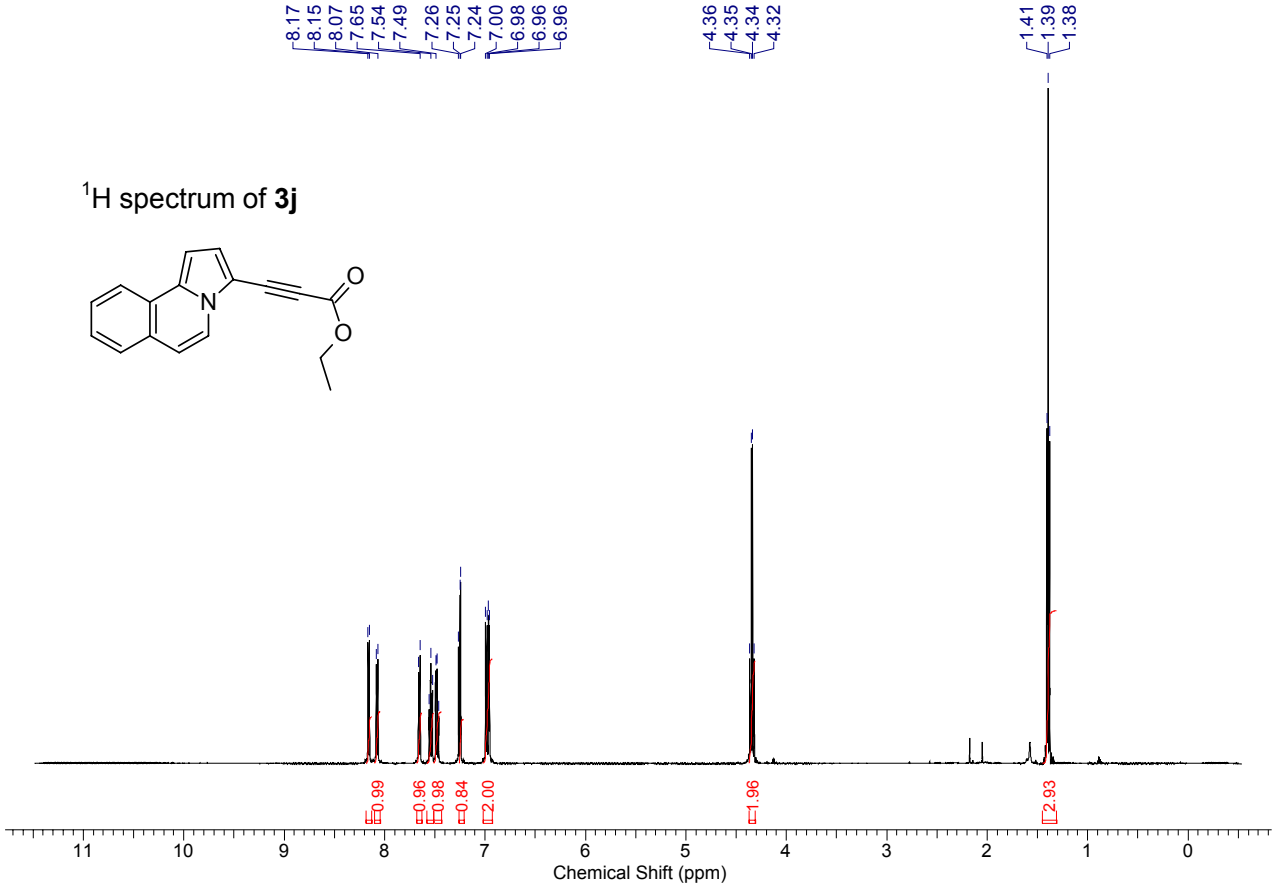
^{13}C spectrum of **3h**

^{1}H spectrum of **3i**

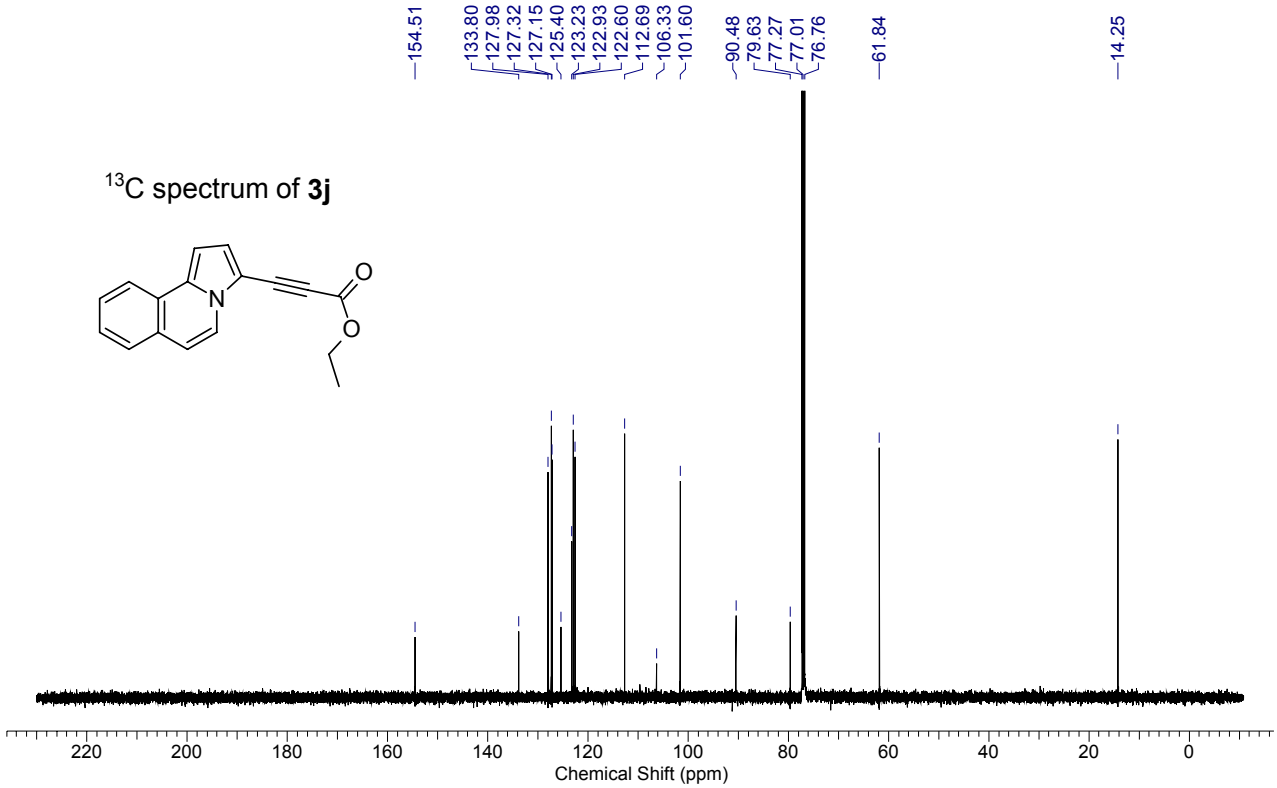


^{13}C spectrum of **3i**

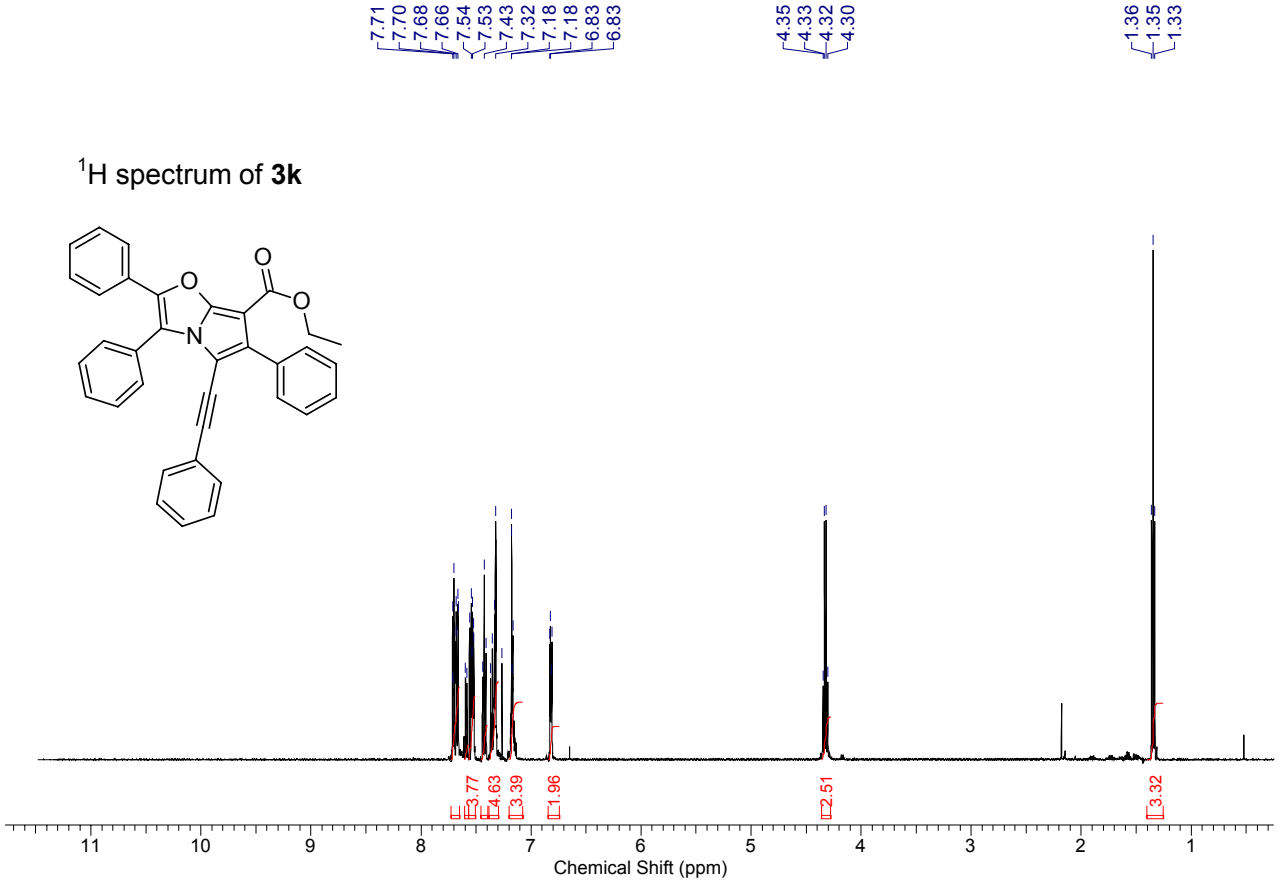




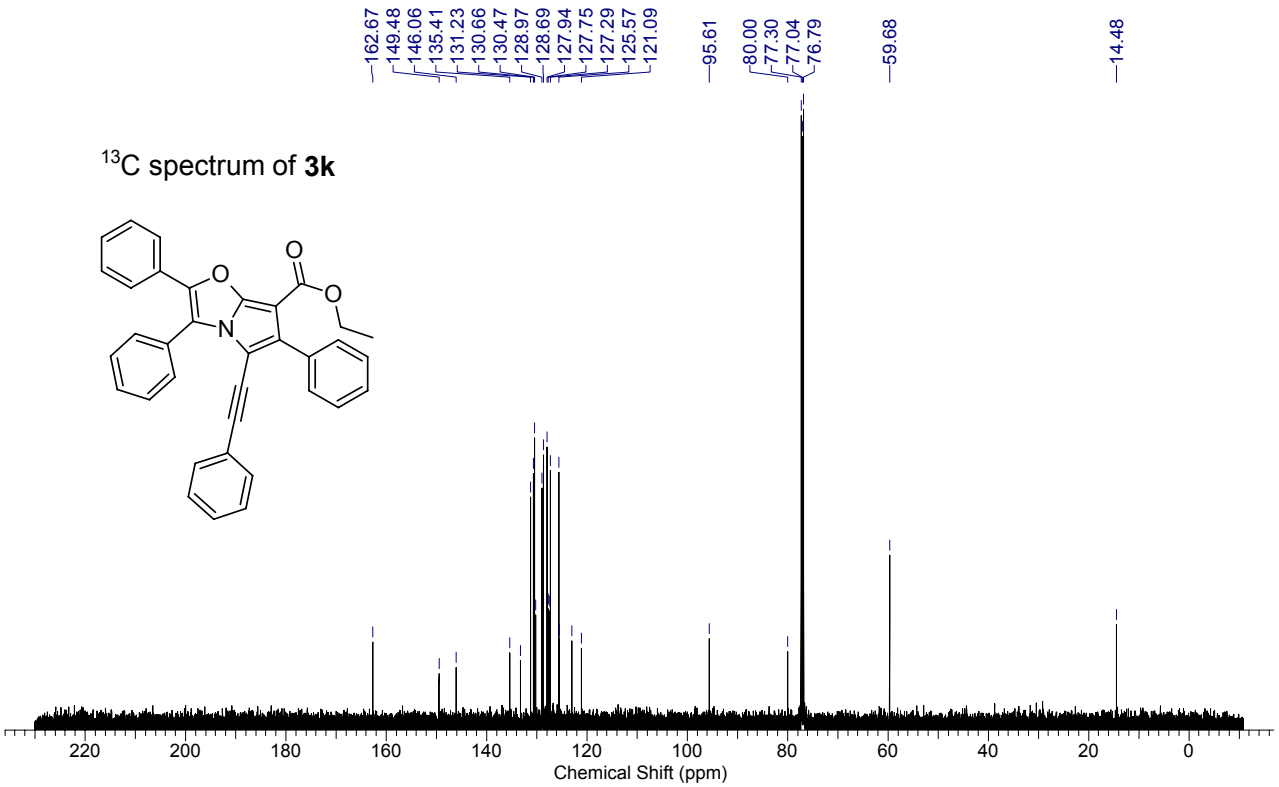
^{1}H spectrum of **3j**



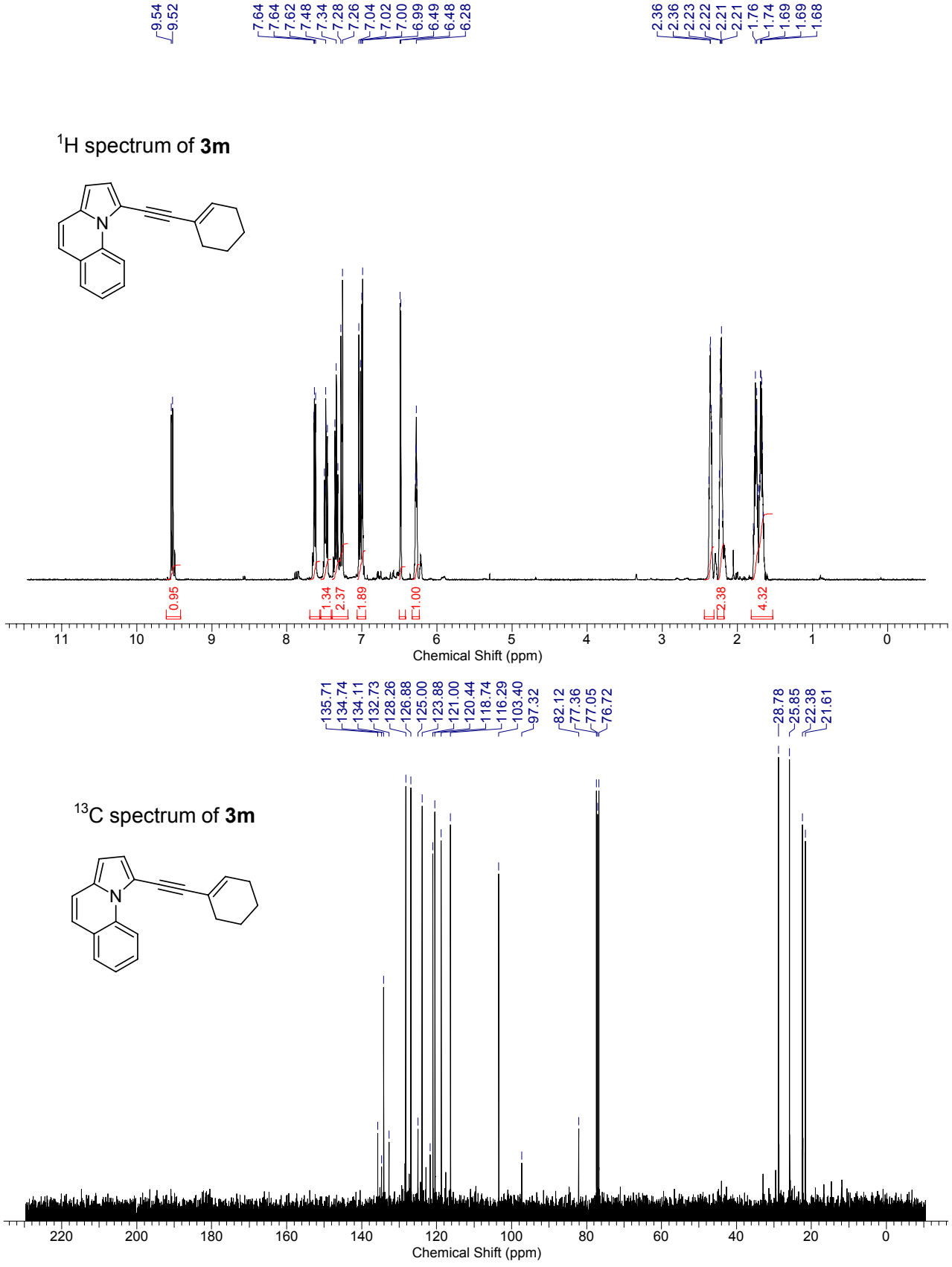
^{13}C spectrum of **3j**

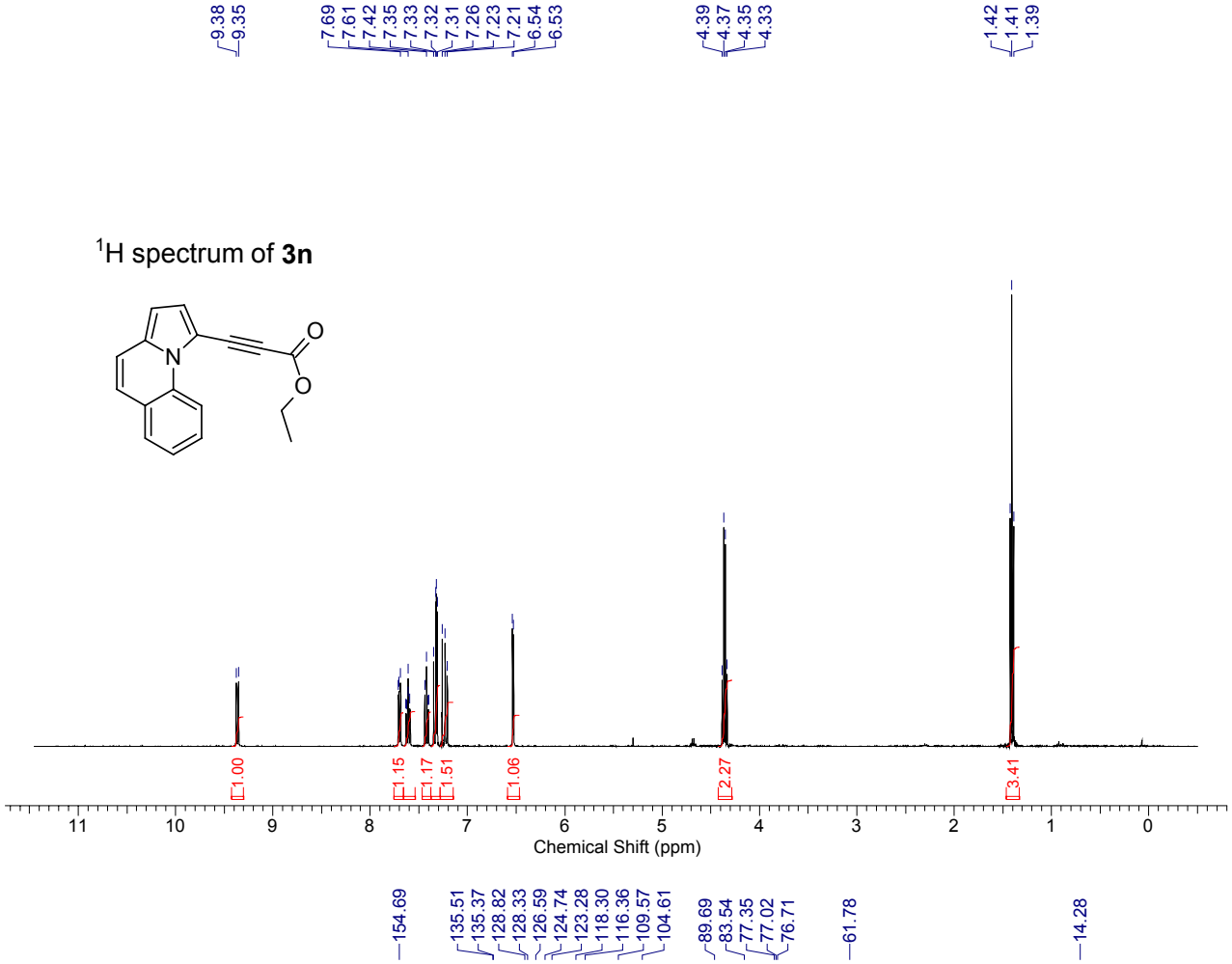


^{1}H spectrum of **3k**

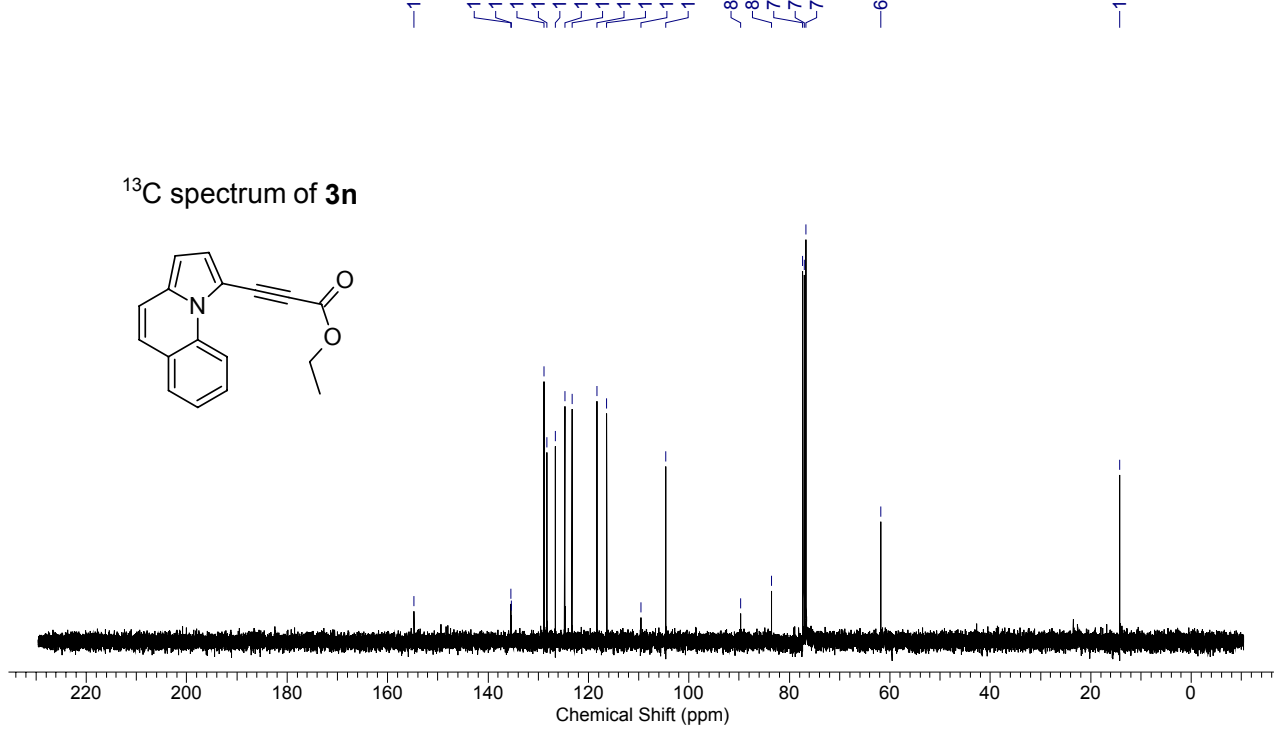


^{13}C spectrum of **3k**


9.54
9.52
7.64
7.64
7.62
7.48
7.34
7.28
7.26
7.04
7.02
7.00
6.99
6.49
6.48
6.28
2.36
2.36
2.23
2.22
2.21
2.21
1.76
1.74
1.69
1.69
1.68
1H spectrum of 3m
N
0.95
1.34
2.37
1.89
1.00
2.38
4.32
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
135.71
134.74
134.11
132.73
128.26
126.88
125.00
123.88
121.00
120.44
118.74
116.29
103.40
97.32
82.12
77.36
77.05
76.72
28.78
25.85
22.38
21.61
13C spectrum of 3m
N
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

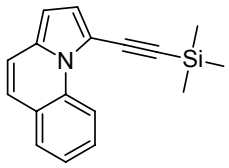


^{1}H spectrum of **3n**

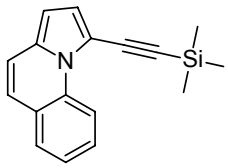


^{13}C spectrum of **3n**

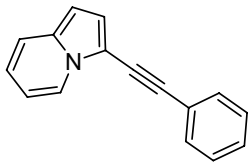
^{1}H spectrum of **3o**

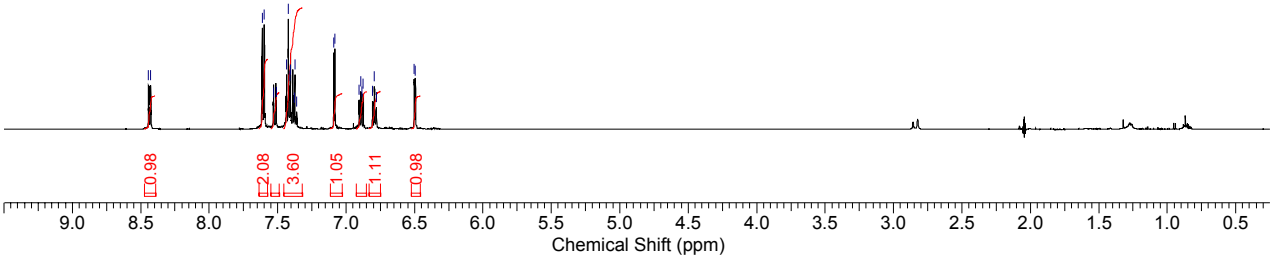


^{13}C spectrum of **3o**

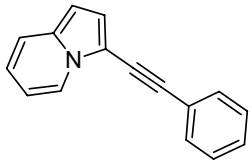


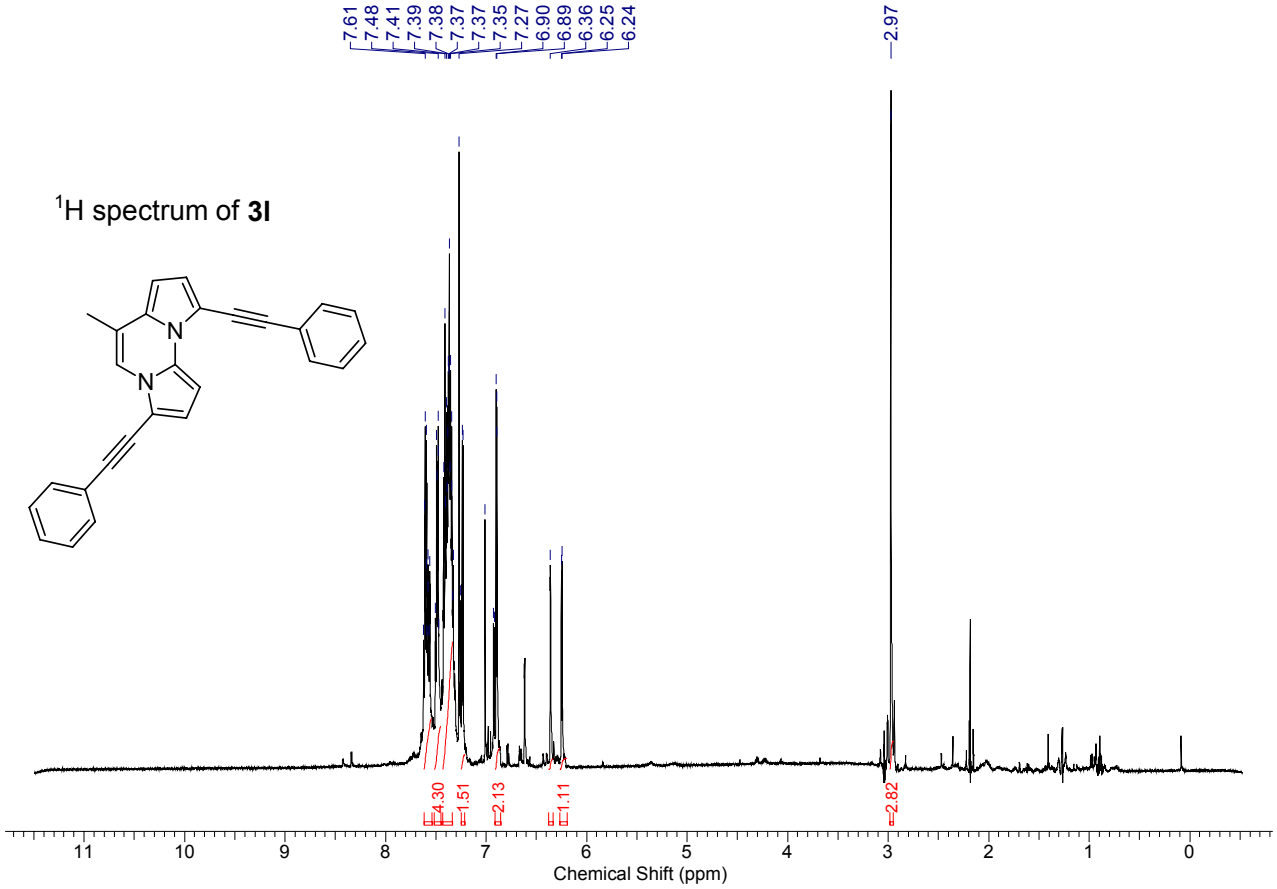
^{1}H spectrum of **3a**



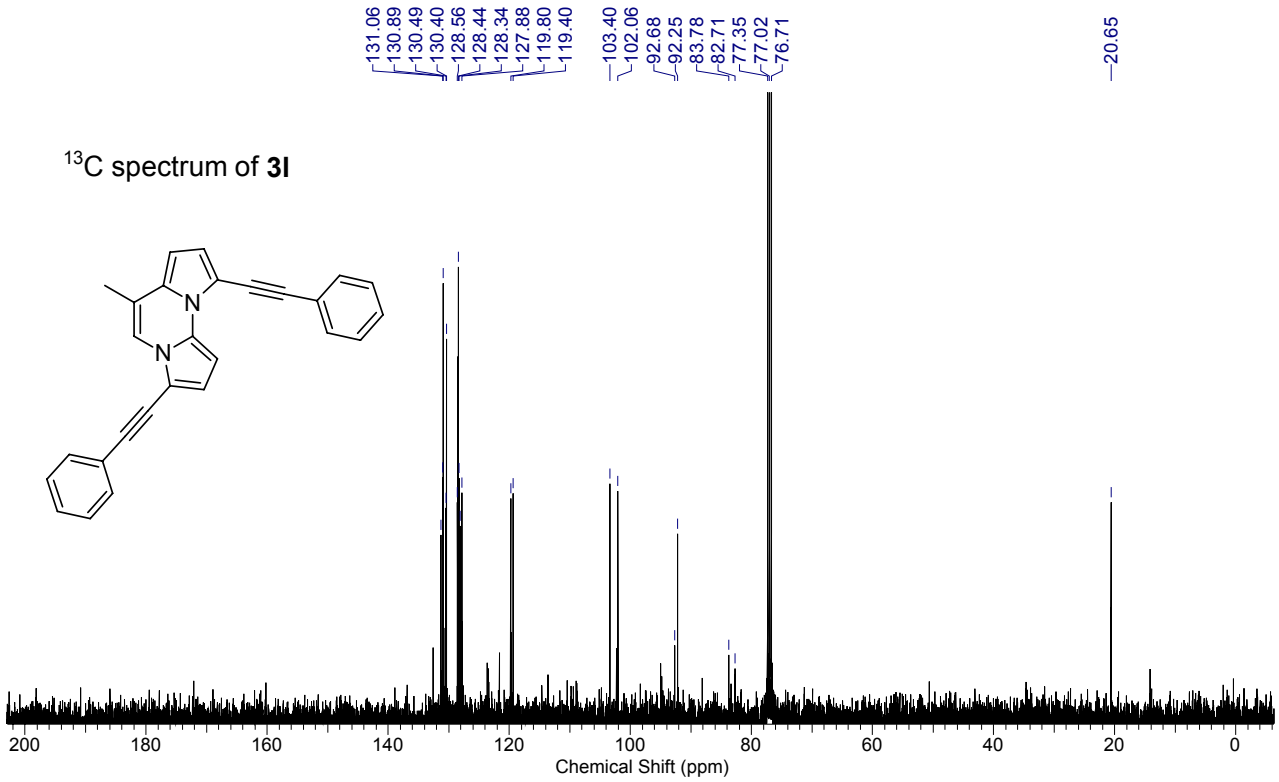


^{13}C spectrum of **3a**

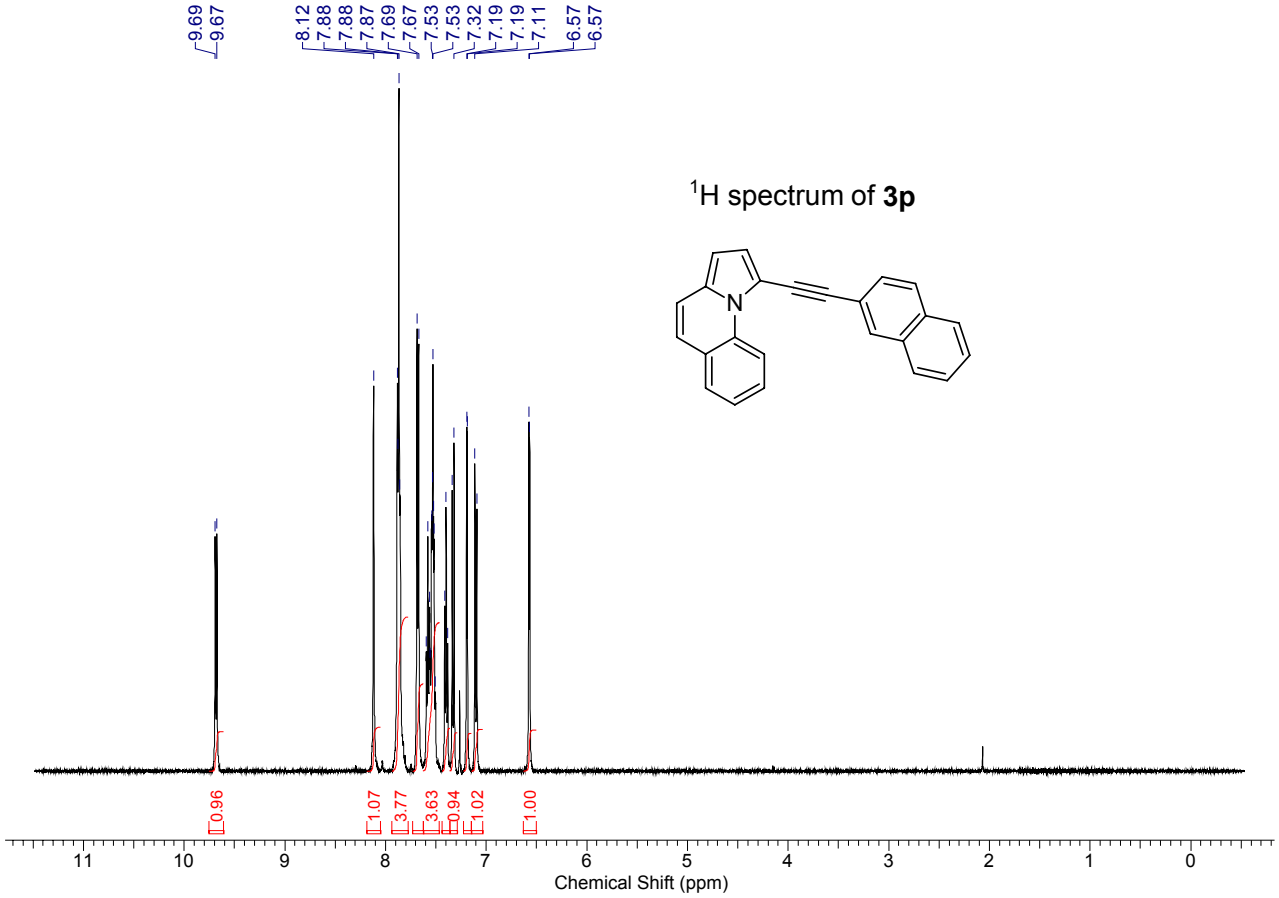




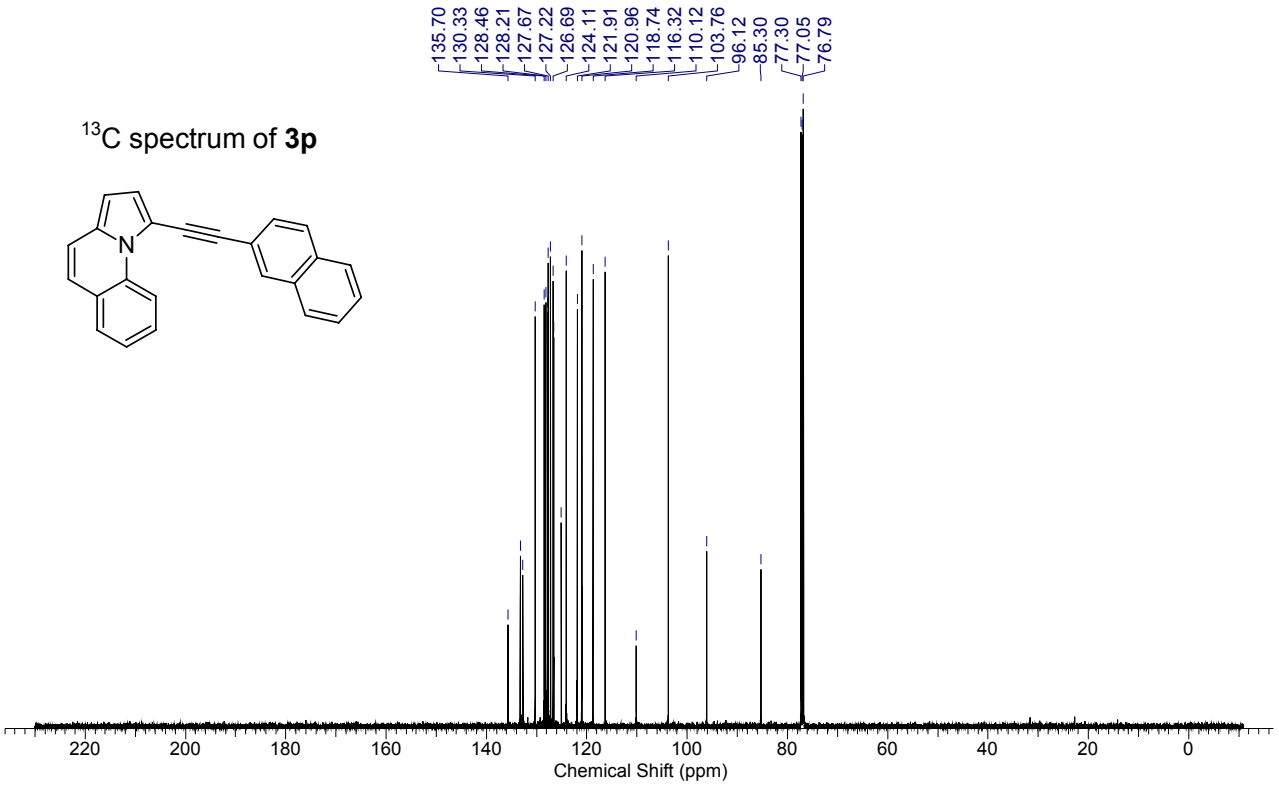
^{1}H spectrum of **3l**



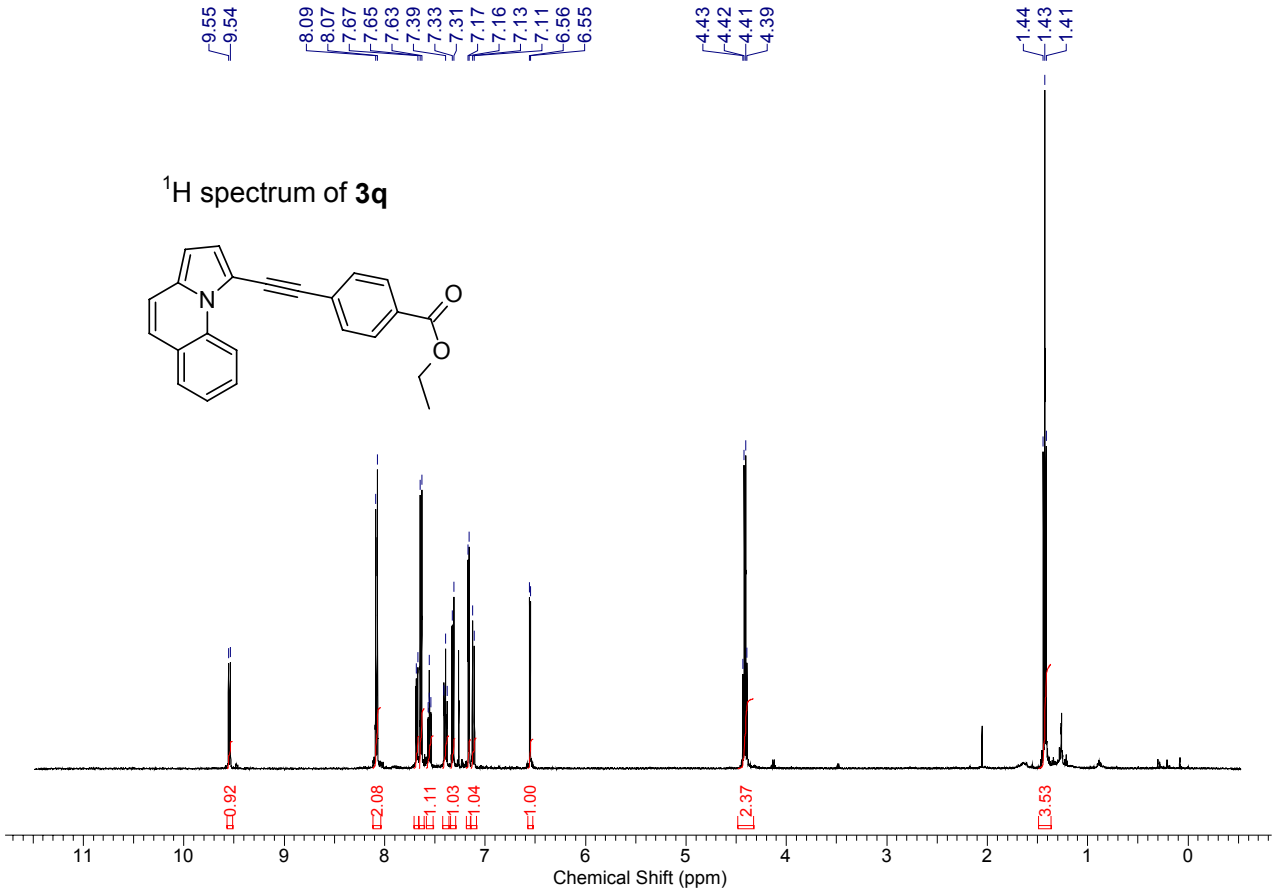
^{13}C spectrum of **3l**



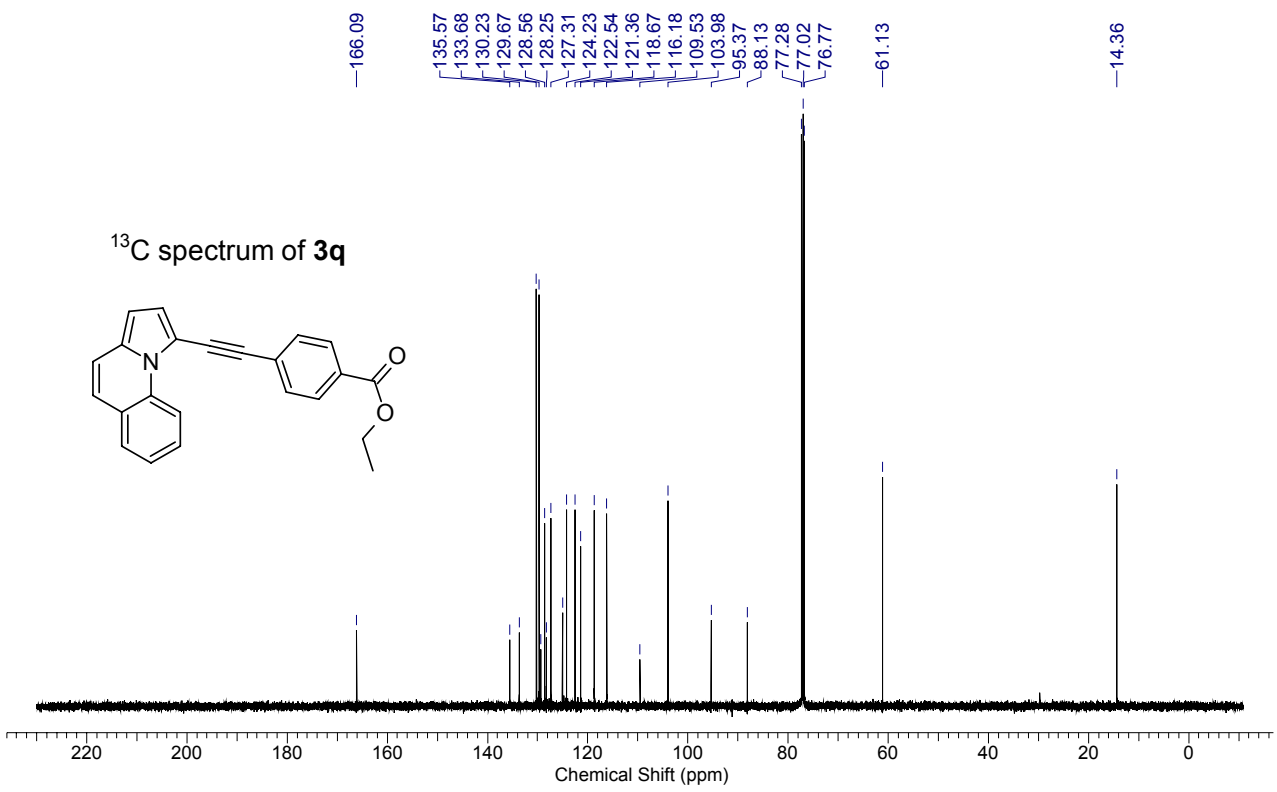
^{1}H spectrum of **3p**



^{13}C spectrum of **3p**

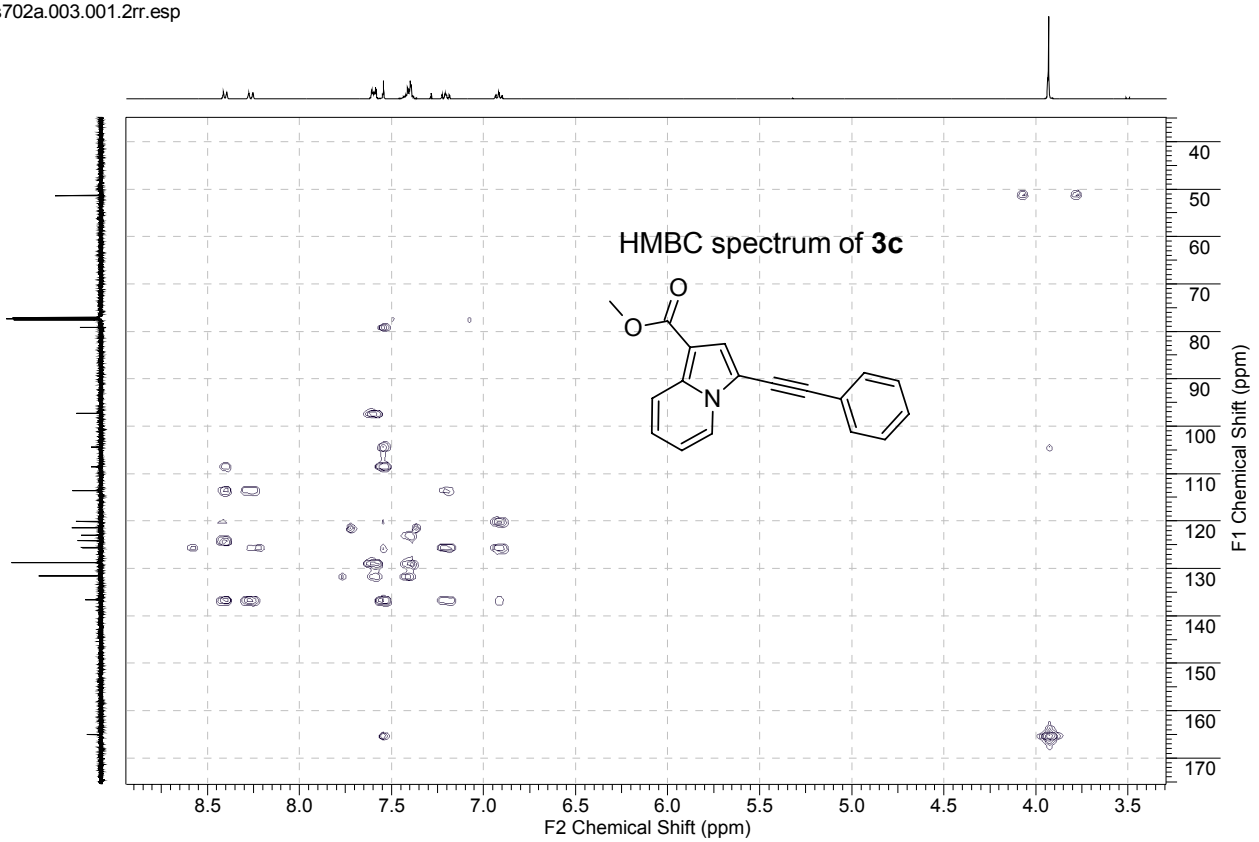


^{1}H spectrum of **3q**



^{13}C spectrum of **3q**

is702a.003.001.2rr.esp



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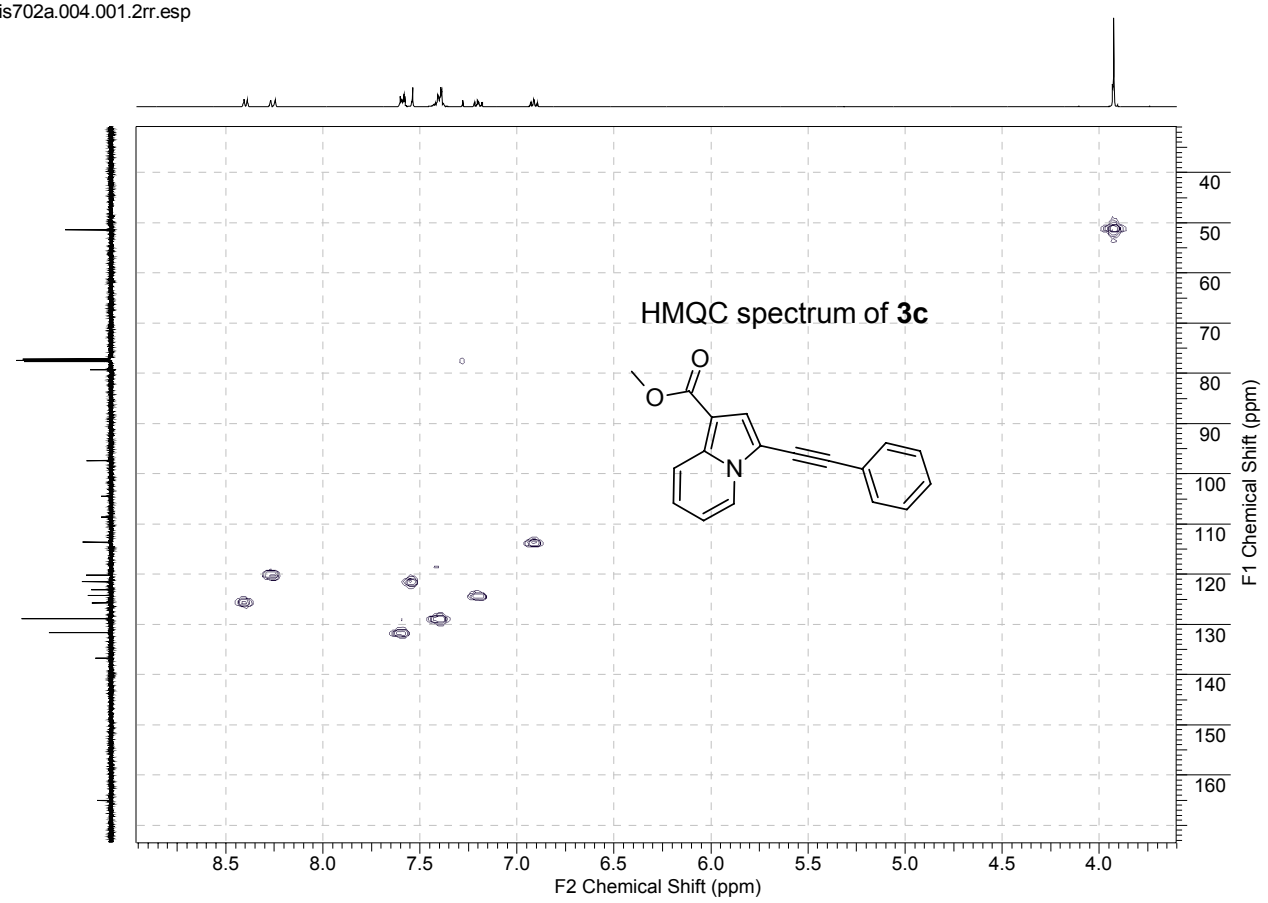
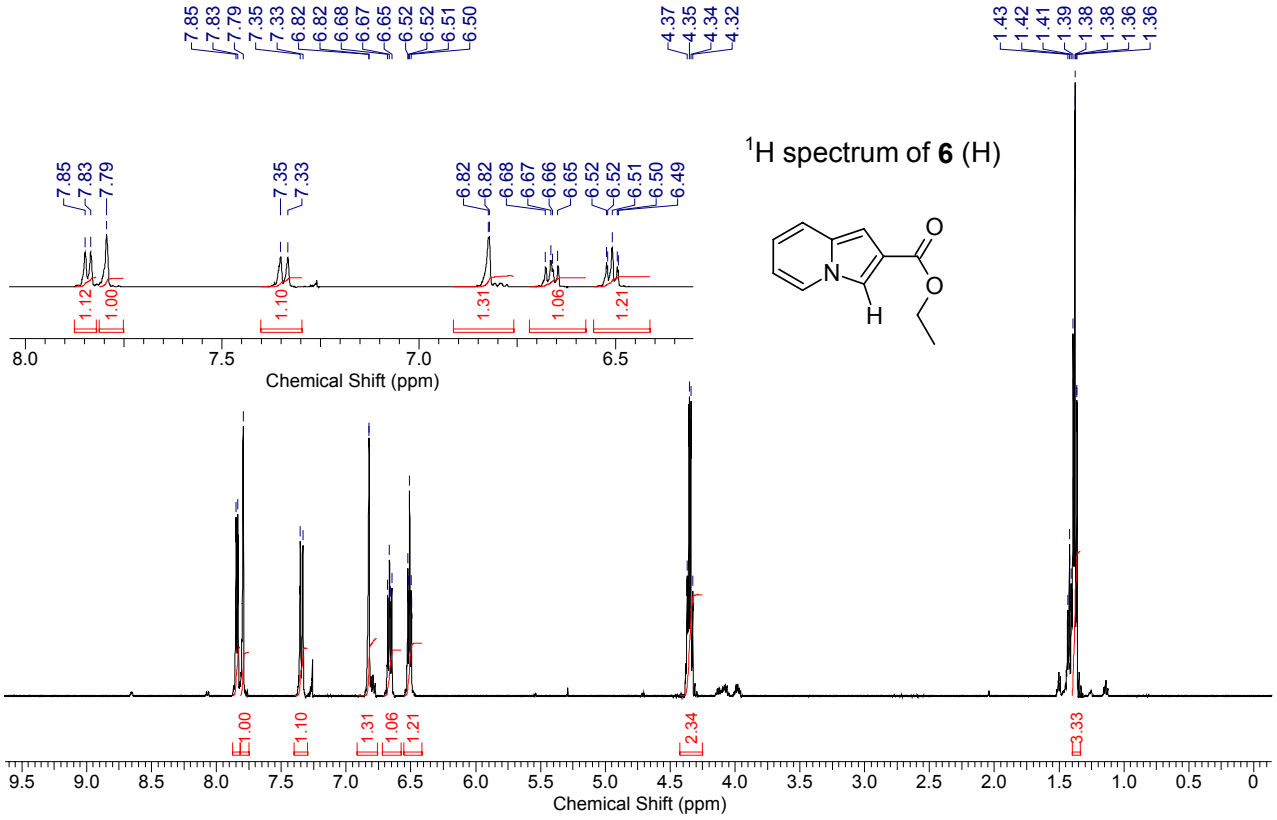
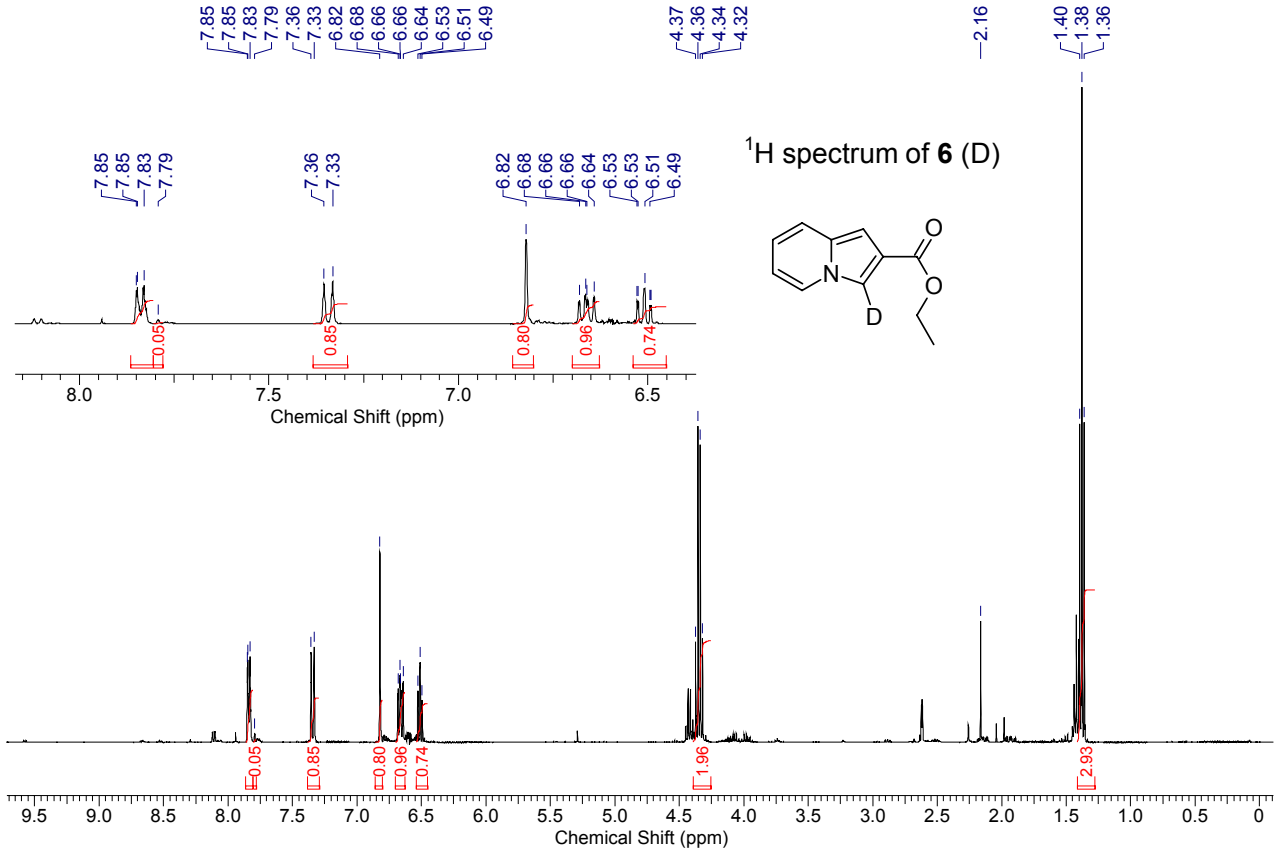



^{1}H spectrum of **6** (H)
Chemical Shift (ppm)


^{1}H spectrum of **6** (D)
Chemical Shift (ppm)