Supporting Information for

Pd^{II}-Catalyzed di-*o*-Olefination of Carbazoles Directed by the Protecting *N*-(2-Pyridyl)sulfonyl Group

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Contents

1. Experimental Section

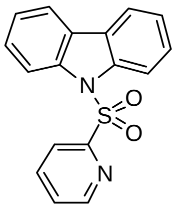
1.1. General methods

All the reactions were carried out in anhydrous solvents and under a nitrogen atmosphere with exclusion of moisture from reagents, solvents and glassware using standard techniques. Melting points were taken in open-end capillary tubes. NMR spectra were recorded at 25 ºC using a 300 MHz spectrometer [300 MHz (^{1}H), 75 MHz (^{13}C)], unless otherwise specified. Chemical shifts (δ) are represented in parts per million, referenced to residual protons in the NMR solvent [$CDCl_3$ (unless otherwise specified): ^{1}H NMR δ = 7.26 ppm (singlet); ^{13}C NMR δ = 77.16 ppm (triplet)]. Data are reported as follows: chemical shift, multiplicity, coupling constant (*J*, in Hz) and integration. All ^{13}C NMR spectra were obtained with complete proton decoupling. MS spectra were recorded on a VG *AutoSpec* mass spectrometer. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (230-400 mesh). Flash column chromatography was performed using 230-400 mesh ultra-pure silica gel. All commercially available compounds were used as provided without further purification.

1.2. Synthesis of the starting carbazoles and derivatives

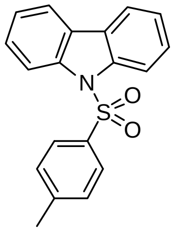
1.2.1. *N*-Protection of commercially available carbazoles and derivatives

Typical procedure: synthesis of *N*-(2-pyridyl)sulfonyl-9H-carbazole (**5**). To a suspension of NaH (1.2 equiv, 103 mg, 7.17 mmol) in THF (60 mL) at 0 ºC, the 9H-carbazole (1.0 g, 5.98 mmol) was added portion wise. The mixture was stirred at 0 ºC for 5 min before 2-pyridylsulfonyl chloride[1](1.3 equiv, 2.68 g, 7.77 mmol) was added drop wise. The solution was allowed to reach room temperature and it was stirred overnight. The mixture was diluted with ethyl acetate and washed with a saturated aqueous solution of ammonium chloride. The aqueous phase was then extracted three times with ethyl acetate. The combined organic phase was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane-EtOAc 6:1) affording **5** as a pale yellow solid; yield: 1.7 g (92%); mp = 126-127 ºC. **^{1}H NMR** δ 8.43 (d, *J*=4.7, 1H), 8.32 (d, *J*=8.3, 2H), 8.05 (d, *J*=7.9, 1H), 7.92 (d, *J*=7.6, 2H), 7.79 (td, *J*=7.7, 1.6, 1H), 7.52 – 7.42 (m, 2H), 7.41 – 7.31 (m, 3H). **^{13}C NMR** δ 155.6, 150.4, 138.8, 138.0, 127.6, 127.5, 126.3, 124.0, 122.2, 120.0, 115.3. **EI$^+$**: calcd for $C_{17}H_{12}N_2O_2S$ $(M)^+$: 308,0619. Found: 308,0615.



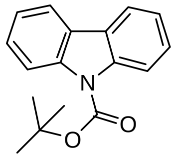
[1] García Rubia, A.; Urones, B.; Gómez Arrayás, R.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2011**, *50*, 10927.

N-(2-p-Toluene)sulfonyl-9H-carbazole (4).[2] Following the typical procedure but using



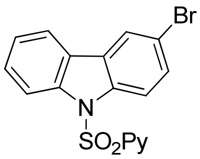
the commercially available *p*-toluenesulfonyl chloride (1.5 equiv), compound **4** was obtained after column chromatography (*n*-hexane-EtOAc 20:1) as a pale grey solid; yield: 87%; mp = 134 ºC. **^{1}H NMR** δ 8.34 (d, *J*=8.3, 2H), 7.98 – 7.83 (m, 2H), 7.70 (d, *J*=8.0, 2H), 7.60 – 7.43 (m, 2H), 7.41 – 7.31 (m, 2H), 7.09 (d, *J*=8.0, 2H), 2.25 (s, 3H). **^{13}C NMR** δ 145.0, 138.5, 135.2, 129.8, 127.5, 126.6, 126.5, 124.0, 120.1, 115.3, 21.6. **FB$^+$**: calcd for $C_{19}H_{15}NO_2S$ $(M)^+$: 321,0824. Found: 321,0836.

***N*-(*tert*-Butyl)-9H-carbazole-9-carboxylate (2)** was prepared according to literature



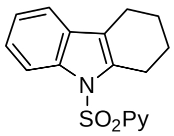
procedure.[3] Colourless oil. **^{1}H NMR** δ 8.31 (d, *J*=8.3, 1H), 7.99 (d, *J*=7.4, 1H), 7.47 (ddd, *J*=8.5, 7.3, 1.5, 1H), 7.35 (td, *J*=7.4, 1.1, 1H), 1.77 (s, 5H).

3-Bromo-*N*-(2-pyridyl)sulfonyl carbazole (13). Following the typical procedure, 3-



bromo-9H-carbazole[4] was protected with 2-pyridylsulfonyl chloride. After column chromatography (*n*-hexane-EtOAc 10:1), the titled compound was obtained as a white solid; yield: 89%; mp = 212–213 ºC. **^{1}H NMR** δ 8.44 (d, *J*=4.7, 1H), 8.28 (d, *J*=8.3, 1H), 8.22 (d, *J*=8.8, 1H), 8.10 – 7.99 (m, 2H), 7.91 – 7.77 (m, 2H), 7.57 (dd, *J*=8.9, 2.1, 1H), 7.53 – 7.44 (m, 1H), 7.43 – 7.31 (m, 2H). **^{13}C NMR** δ 155.5, 150.5, 139.1, 138.1, 137.7, 130.2, 128.2, 128.1, 127.8, 125.1, 124.3, 122.9, 122.3, 120.2, 117.4, 117.0, 115.4. **ESI$^+$**: calcd for $C_{17}H_{12}N_2O_2SBr$ $(M+H)^+$: 386,9797. Found: 386,9801.

2,3,4,9-Tetrahydro-*N*-(2-pyridyl)sulfonyl-1H-carbazole (17). Following the typical



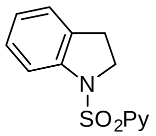
procedure, 2,3,4,9-tetrahydro-1H-carbazole was protected with 2-pyridylsulfonyl chloride. After column chromatography (*n*-hexane-EtOAc 8:1), the titled compound was obtained as a yellow solid; yield: 92%; mp = 137-138 ºC. **^{1}H NMR** δ 8.51 (d, *J*=5.9, 1H), 8.12 (d, *J*=8.7, 1H), 7.99 (d, *J*=7.9, 1H), 7.76 (td, *J*=7.8, 1.7, 1H), 7.39 – 7.28 (m, 2H), 7.22 (ddd, *J*=6.4, 4.1, 1.8, 2H), 3.19 (s, 2H), 2.59 (s, 2H), 1.91 (d, *J*=5.8, 4H), 1.83 (d, *J*=4.5, 2H). **^{13}C NMR** δ 156.0, 150.3, 1378.0, 136.6, 136.0, 130.4, 127.3, 123.7, 123.3, 121.8, 118.2, 117.9, 114.2, 24.4, 23.2, 22.1, 21.1. **FB$^+$**: calcd for $C_{17}H_{16}N_2O_2S$ $(M)^+$: 312,0932. Found: 312,0928.

[2] Youn, S. W.; Bihn, J. H.; Kim, B. S. *Org. Lett.* **2011**, *13*, 3738.

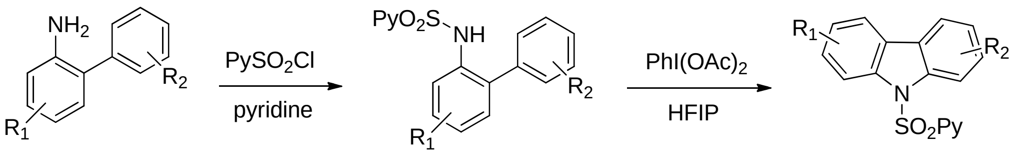
[3] Diep, V.; Dannenberg, J. J.; Franck, R. W. *J. Org. Chem.*, **2003**, *68*, 7907.

[4] Midya, A.; Xie, Z.; Yang, J.-X.; Chen, Z.-K.; Blackwood, D. J.; Wang, J.; Adams, S.; Ping Loh, K. *Chem. Commun.*, **2010**,*46*, 2091.

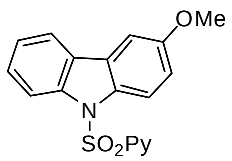
***N*-(2-Pyridyl)sulfonyl indoline 24.** Following the typical procedure, indoline was protected with 2-pyridylsulfonyl chloride. After column chromatography (*n*-hexane-EtOAc 8:1), the titled compound was obtained as a white solid; yield: 93%; mp = 126-127 ºC. **^{1}H NMR** δ 8.61 (ddd, *J*=4.7, 1.6, 0.8, 1H), 7.97 (dt, *J*=7.9, 1.0, 1H), 7.83 (td, *J*=7.8, 1.7, 1H), 7.53 – 7.41 (m, 1H), 7.42 (ddd, *J*=7.6, 4.7, 1.2, 1H), 7.14 – 7.05 (m, 2H), 6.98 – 6.89 (m, 1H), 4.33 (t, *J*=8.5, 2H), 3.05 (t, *J*=8.5, 2H). **^{13}C NMR** δ 156.5, 150.3, 141.7, 137.8, 132.1, 127.6, 127.0, 125.2, 123.8, 123.2, 114.6, 51.5, 28.2. **FB$^+$**: calcd for $C_{13}H_{12}N_2O_2S$ $(M)^+$: 260,0619. Found: 260,0621.



1.2.2. Oxidative cyclization of *N*-(2-pyridyl)sulfonyl 2-aminobiphenyl derivatives



Typical procedure: synthesis of 3-methoxy-*N*-(2-pyridyl)sulfonyl-9H-carbazole (12). To a solution of 2-amino-3'-methoxybiphenyl[5] (370 mg, 1.86 mmol, 1 equiv), in pyridine (9 mL, 0.2 M), cooled at 0 ºC under nitrogen atmosphere, was added 2-pyridylsulfonyl chloride (495 mg, 2.78 mmol, 1.5 equiv).[6] The resulting mixture was stirred at room temperature for 12 h before it was poured into water. The mixture was extracted with CH_2Cl_2 (3 times) and the combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was crystallized in a mixture of *n*-hexane-CH_2Cl_2 to give the *N*-(2-pyridyl)sulfonyl-2-amino-3’-methoxybiphenyl.



To a solution of *N*-(2-pyridyl)sulfonyl 2-amino-3'-methoxybiphenyl (400 mg, 1.17 mmol, 1 equiv) in 1,1,1,3,3,3-hexafluoropropan-2-ol (6 mL, 0.05 M) was added $PhI(OAc)_2$ (454 mg, 1.41 mmol, 1.2 equiv) at room temperature.[7] The reaction mixture was stirred for 12 h at room temperature before it was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane-CH_2Cl_2 1:1) to afford the titled product as a white solid; yield: 146 mg (37%); mp = 171-172 ºC. **^{1}H**

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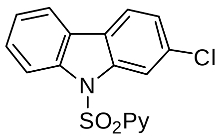
[5] The corresponding 2-aminobiphenyl derivatives were prepared via Suzuki coupling between 2-bromoanilines and arylboronic acids following a reported procedure: Cho, S. H.; Yoon, J.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 5996.

[6] For the synthesis of analogous *N*-(2-*p*-toluene)sulfonyl-2-aminobiaryls, see: Youn, S. W.; Bihn, J. H.; Kim, B. S. *Org. Lett.*, **2011**, *13*, 3738.

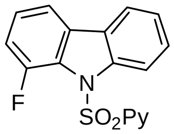
[7] For the oxidative cyclization of analogous *N*-(2-*p*-toluene)sulfonyl-2-aminobiaryls, see: Antonchick, A. P.; Samanta, R.; Kulikov, K.; Lategahn, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 8605.

NMR δ 8.41 (d, *J*=4.0, 1H), 8.29 (d, *J*=8.4, 1H), 8.21 (d, *J*=9.1, 1H), 7.99 (d, *J*=7.9, 1H), 7.85 (d, *J*=7.7, 1H), 7.75 (td, *J*=7.8, 1.7, 1H), 7.45 (t, *J*=7.2, 1H), 7.39 – 7.28 (m, 3H), 7.05 (dd, *J*=9.1, 2.6, 1H), 3.88 (s, 3H). **^{13}C NMR** δ 157.0, 155.5, 150.3, 139.4, 137.9, 133.0, 127.6, 127.5, 127.3, 126.4, 123.9, 122.2, 120.0, 116.3, 115.5, 115.3, 103.3, 55.9. **FB$^+$**: calcd for $C_{18}H_{14}N_2O_3S$ $(M)^+$: 338,0725. Found: 338,0723..

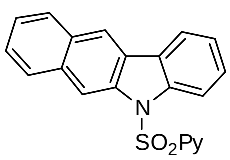
2-Chloro-*N*-2(pyridyl)sulfonyl-9H-carbazole (14). Chromatography: *n*-hexane-CH_2Cl_2 3:1. White solid; yield: 50%; mp =165-166 ºC. **^{1}H NMR** (500 MHz) δ 8.47 (ddd, *J*=4.6, 1.6, 0.8, 1H), 8.35 (d, *J*=1.9, 1H), 8.27 (d, *J*=8.3, 1H), 8.10 (d, *J*=7.9, 1H), 7.89 (d, *J*=7.7, 1H), 7.88 – 7.85 (m, 1H), 7.83 (d, *J*=8.4, 1H), 7.47 (ddd, *J*=8.5, 7.4, 1.3, 1H), 7.43 – 7.38 (m, 1H), 7.36 (ddd, *J*=8.3, 6.5, 1.4, 2H). **^{13}C NMR** (125 MHz) δ 155.5, 150.6, 139.4, 139.0, 138.2, 133.2, 127.9, 127.7, 125.4, 124.8, 124.6, 124.3, 122.3, 120.7, 120.0, 115.7, 115.3. **FB$^+$**: calcd for $C_{17}H_{11}N_2O_2SCl$ $(M)^+$: 342,0230. Found: 342,0231.



1-Fluoro-*N*-(2-pyridyl)sulfonyl-9H-carbazole (15). Chromatography: *n*-hexane-CH_2Cl_2 1:1. White solid; yield: 49%; mp =134-135 ºC. **^{1}H NMR** δ 8.44 – 8.38 (m, 1H), 8.35 (d, *J*=8.5, 1H), 8.10 (ddt, *J*=7.9, 1.8, 1.0, 1H), 7.87 – 7.74 (m, 2H), 7.59 (dd, *J*=7.7, 1.0, 1H), 7.42 (ddd, *J*=8.6, 7.3, 1.3, 1H), 7.35 – 7.30 (m, 1H), 7.30 – 7.23 (m, 1H), 7.19 – 7.08 (m, 1H), 6.96 (ddd, *J*=12.2, 8.1, 1.0, 1H). **^{13}C NMR** δ 156.5, 156.4, 151.8, 150.2, 148.5, 140.6, 137.9, 130.4, 130.3, 128.2, 127.4, 125.6, 125.6, 125.4, 124.8, 124.7, 124.0, 122.7, 122.6, 120.0, 116.4, 115.7, 115.7, 114.6, 114.3. **FB$^+$**: calcd for $C_{17}H_{11}N_2O_2SF$ $(M)^+$: 326,0525. Found: 326,0523.

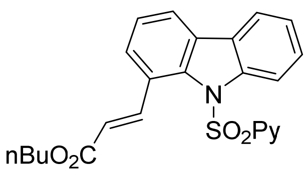


***N*-2(Pyridyl)sulfonyl-5H-benzo[b]carbazole (16).** Chromatography: *n*-hexane-CH_2Cl_2 1:1. White solid; yield: 68%; mp = 170-171 ºC. **^{1}H NMR** δ 8.98 (dd, *J*=8.7, 1.1, 1H), 8.28 (d, *J*=8.2, 1H), 8.14 (ddd, *J*=4.8, 1.6, 1.0, 1H), 7.92 (d, *J*=8.7, 1H), 7.86 – 7.78 (m, 2H), 7.76 – 7.71 (m, 1H), 7.63 (ddd, *J*=8.5, 6.9, 1.4, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.37 (m, 3H), 7.35 – 7.29 (m, 1H), 7.14 (ddd, *J*=7.1, 4.7, 1.5, 1H).**^{13}C NMR** δ 153.7, 149.4, 141.2, 137.1, 137.1, 134.2, 129.4, 128.5, 127.5, 127.1, 127.0, 126.7, 126.2, 125.9, 125.8, 125.4, 122.5, 119.4, 119.1, 117.4. **FB$^+$**: calcd for $C_{21}H_{14}N_2O_2S$ $(M)^+$: 358,0776. Found: 358,0787.



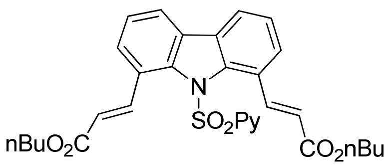
1.4. C–H alkenylation reaction

Butyl (*E*)-3-[*N*-(2-pyridyl)sulfonyl-9H-carbazol-1-yl]acrylate (6)



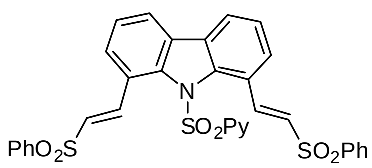
A screw-capped test tube was charged with the carbazole derivative **5** (46.2 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 10 mol%) and $Ce(SO_4)_2$ (96.6 mg, 0.3 mmol, 2.0 equiv). The mixture was placed under nitrogen atmosphere before DCE (1.5 mL) and *n*-butyl acrylate (43 μL, 0.3 mmol, 2.0 equiv) were successively added. The mixture was heated to 110 ºC for 12 h, and then it was allowed to reach room temperature, diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (*n*-hexane-EtOAc 6:1) to afford **6** as a pale yellow solid; yield: 16.8 mg (26%); mp = 151-152 ºC. **^{1}H NMR** δ 8.39 (d, *J* = 15.9 Hz, 1H), 8.34 (d, *J* = 3.9 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.80 – 7.70 (m, 2H), 7.67 (d, *J* = 6.5 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.36 – 7.27 (m, 2H), 6.46 (d, *J* = 15.8 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.72 (tt, *J* = 8.4, 6.4 Hz, 2H), 1.55 – 1.40 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** δ 167.3, 154.8, 149.9, 143.8, 140.9, 139.4, 137.7, 130.1, 128.0, 127.7, 127.4, 127.1, 126.3, 125.4, 125.2, 123.0, 121.1, 119.8, 118.7, 117.9, 64.5, 31.0, 19.4, 13.9. **ESI$^+$**: calcd for $C_{24}H_{23}N_2O_4S$ $(M+H)^+$: 435,1373. Found: 435,1384.

Typical procedure for di-*ortho*-olefination: synthesis of (*E*,*E*)-dibutyl 3,3'-[*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (7).



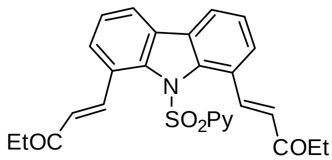
A screw-capped test tube was charged with the carbazole derivative **5** (46.2 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 10 mol%) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv). The mixture was placed under nitrogen atmosphere before DCE (1.5 mL) and *n*-butyl acrylate (86 μL, 0.6 mmol, 4.0 equiv) were successively added. The mixture was heated to 110 ºC for 18 h, and then it was allowed to reach room temperature, diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (CH_2Cl_2-EtOAc 40:1) to afford **7** as a pale yellow solid; yield: 53.8 mg (64%); mp = 175-177 ºC. **^{1}H NMR** δ 8.48 (d, *J*=16.0, 2H), 8.22 (dd, *J*=4.7, 1.6, 1H), 7.69 (d, *J*=7.8, 2H), 7.61 (d, *J*=7.5, 2H), 7.57 – 7.50 (m, 1H), 7.43 – 7.29 (m, 3H), 7.24 – 7.20 (m, 1H), 6.55 (d, *J*=16.0, 2H), 4.27 (t, *J*=6.7, 4H), 1.82 – 1.69 (m, 4H), 1.49 (q, *J*=7.5, 4H), 1.00 (t, *J*=7.4, 6H). **^{13}C NMR** δ 167.0, 152.8, 149.2, 141.8, 141.5, 137.1, 131.8, 128.2, 127.2, 126.8, 126.3, 123.3, 121.0, 118.7, 64.6, 31.0, 19.3, 13.9. **ESI$^+$**: calcd for $C_{31}H_{33}N_2O_6S$ $(M+H)^+$: 561,2053. Found: 561,2071.

1,8-Bis[(*E*)-2-(phenylsulfonyl)vinyl]- *N*-(2-pyridyl)sulfonyl-9H-carbazole (8).



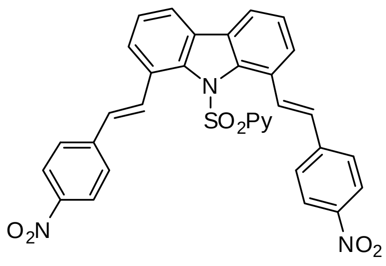
Following the typical procedure, carbazole **5** (46.2 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), phenyl vinyl sulfone (101.0 mg, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: CH_2Cl_2-EtOAc 20:1. Pale yellow solid; yield: 64%; mp = 253-254 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 15.4 Hz, 2H), 8.23 (d, *J* = 3.3 Hz, 1H), 8.08 (d, *J* = 6.9 Hz, 4H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.67 – 7.50 (m, 10H), 7.42 – 7.30 (m, 2H), 6.95 (d, *J* = 15.3 Hz, 2H). **^{13}C NMR** (125 MHz, acetone-d_6) δ 153.2, 150.3, 142.6, 142.4, 140.6, 138.8, 134.2, 132.7, 130.2, 128.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.8, 126.8, 124.2, 123.2. **ESI$^+$**: calcd for $C_{33}H_{25}N_2O_6S_3$ $(M+H)^+$: 641,0869. Found: 641,0847.

(*E*,*E*)-1,1'-[*N*-(2-Pyridyl)sulfonyl-9H-carbazole-1,8-diyl]bis(pent-1-en-3-one) (9).



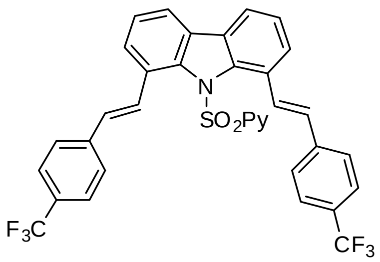
Following the typical procedure, carbazole **5** (46.2 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), ethyl vinyl ketone (60 μL, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: CH_2Cl_2-EtOAc 20:1; yellow solid; yield: 80%; mp = 142-143 ºC; **^{1}H NMR** δ 8.29 (d, *J*=16.3, 2H), 8.08 (d, *J*=3.4, 1H), 7.64 (d, *J*=7.7, 2H), 7.53 (dd, *J*=7.5, 1.1, 2H), 7.44 (t, *J*=7.7, 1H), 7.30 (t, *J*=7.4, 2H), 7.21 – 7.11 (m, 2H), 6.73 (dd, *J*=16.4, 1.2, 2H), 2.85 (qd, *J*=7.3, 1.2, 4H), 1.17 (td, *J*=7.3, 1.3, 6H).**^{13}C NMR** δ 201.88, 152.41, 149.28, 141.67, 139.92, 137.16, 131.93, 128.41, 127.36, 127.09, 126.93, 126.18, 123.35, 121.15, 32.96, 8.36. **ESI$^+$**: calcd for $C_{27}H_{25}N_2O_4S$ $(M+H)^+$: 473,1529. Found: 473,1538.

1,8-Bis[(*E*)-4-nitrostyryl]- *N*-(2-pyridyl)sulfonyl-9H-carbazole (10). Following the



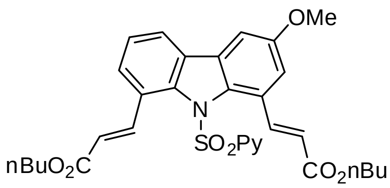
typical procedure, carbazole **5** (46.2 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), 4-nitrostyrene (78 μL, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: *n*-hexane-CH_2Cl_2 1:2; yellow solid; yield: 80%; mp = 235-236 ºC. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.46 (d, *J* = 3.8 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 4H), 8.03 (d, *J* = 16.3 Hz, 2H), 7.93 (dd, *J* = 7.7, 1.6 Hz, 4H), 7.84 – 7.73 (m, 5H), 7.62 – 7.45 (m, 6H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.0, 149.7, 146.4, 144.1, 140.3, 138.5, 131.2, 130.4, 128.9, 128.4, 127.4, 126.9, 126.5, 125.3, 124.1, 123.3, 120.5. **ESI$^+$**: calcd for $C_{33}H_{25}N_2O_4S$ $(M+H)^+$: 603,1332. Found: 603,1351.

1,8-Bis[(*E*)-4-(trifluoromethyl)styryl]-*N*-(2-pyridyl)sulfonyl-9H-carbazole (11).



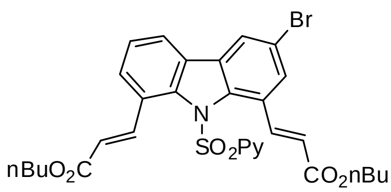
Following the typical procedure, carbazole **5** (46.2 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), 4-(trifluoromethyl)styrene (89 μL, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: *n*-hexane-CH_2Cl_2 1:3. Yellow solid; yield: 91%; mp = 217-218 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.23 (dt, *J*=4.7, 0.9, 1H), 8.07 (d, *J*=16.3, 2H), 7.78 – 7.73 (m, 6H), 7.66 (d, *J*=8.0, 4H), 7.53 (dd, *J*=7.5, 1.1, 2H), 7.44 (td, *J*=7.8, 1.7, 1H), 7.40 – 7.31 (m, 3H), 7.28 – 7.20 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.0, 149.1, 141.1, 141.0, 136.8, 132.1, 130.2, 129.5, 129.3, 128.9, 127.2, 127.1, 127.0, 126.8, 125.7, 125.7, 125.6, 125.6, 125.4, 124.8, 123.5, 123.2, 119.2. **ESI$^+$**: calcd for $C_{35}H_{23}N_2O_2F_6S$ $(M+H)^+$: 649,1378. Found: 649, 1399.

(*E,E*)-Dibutyl 3,3'-[3-methoxy-*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (18).



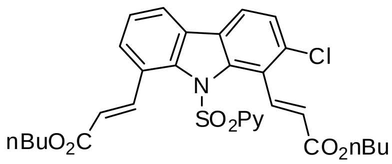
Following the typical procedure, carbazole **12** (50.7 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (86 μL, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: CH_2Cl_2-EtOAc 100:1. Yellow solid; yield: 48%; mp = 145-146ºC. **^{1}H NMR:** δ 8.45 (dd, *J*=16.0, 5.3, 2H), 8.19 (d, *J*=5.1, 1H), 7.67 (d, *J*=7.8, 1H), 7.59 – 7.45 (m, 2H), 7.33 (t, *J*=7.7, 1H), 7.28 – 7.17 (m, 3H), 7.07 (d, *J*=2.5, 1H), 6.54 (dd, *J*=16.0, 5.4, 2H), 4.28 (t, *J*=6.7, 4H), 3.88 (s, 3H), 1.76 (p, *J*=6.9, 4H), 1.49 (q, *J*=7.4, 4H), 1.00 (t, *J*=7.3, 6H). **^{13}C NMR**: δ 167.1, 167.0, 158.7, 152.6, 149.2, 142.3, 141.7, 141.6, 137.0, 135.5, 133.2, 132.1, 129.1, 128.4, 127.1, 126.8, 126.4, 123.5, 120.9, 118.9, 118.7, 111.8, 106.2, 64.7, 64.7, 56.0, 31.0, 19.4, 13.9. **ESI$^+$**: calcd for $C_{32}H_{35}N_2O_7S$ $(M+H)^+$: 591,2140. Found: 591,2143.

(*E,E*)-Dibutyl 3,3'-[3-bromo-*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (19).



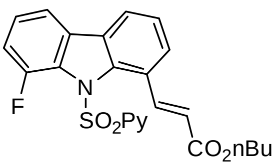
Following the typical procedure, carbazole **13** (58.1 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (86 μL, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: CH_2Cl_2; pale yellow solid; yield: 59%; mp = 163-165 ºC. **^{1}H NMR**: δ 8.40 (dd, *J*=16.0, 5.7, 2H), 8.26 (d, *J*=4.4, 1H), 7.76 (dd, *J*=15.9, 1.9, 2H), 7.71 – 7.64 (m, 1H), 7.63 – 7.53 (m, 2H), 7.45 – 7.27 (m, 3H), 6.52 (d, *J*=16.0, 2H), 4.26 (t, *J*=6.7, 4H), 1.90 – 1.62 (m, 4H), 1.56 – 1.38 (m, 4H), 0.99 (t, *J*=7.3, 6H). **^{13}C NMR**: δ 166.9, 166.6, 153.0, 149.4, 141.7, 141.5, 140.6, 140.5, 137.4, 133.4, 130.6, 129.8, 128.9, 128.2, 127.5, 127.0, 127.0, 123.7, 123.0, 121.1, 120.4, 119.8, 119.1, 64.7, 64.7, 30.9, 30.9, 19.3, 13.9. **ESI$^+$**: calcd for $C_{31}H_{32}N_2O_6SBr$ $(M+H)^+$: 639,1158. Found: 639,1148.

(*E,E*)-Dibutyl 3,3'-[2-chloro-*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate



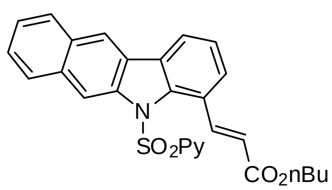
(20). Following the typical procedure, carbazole **14** (51.4 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (86 μL, 0.6 mmol, 4.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (130.2 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: CH_2Cl_2. Yellow oil; yield: 58%. This compound could not be completely purified from minor alkenylated side products. **^{1}H NMR**: δ 8.67 (d, *J*=15.9, 1H), 8.36 (ddd, *J*=4.6, 1.8, 1.0, 1H), 8.05 (d, *J*=16.4, 1H), 7.65 (d, *J*=7.8, 3H), 7.61 – 7.50 (m, 2H), 7.49 – 7.40 (m, 1H), 7.38 – 7.35 (m, 1H), 7.34 – 7.28 (m, 1H), 6.49 (d, *J*=15.9, 1H), 6.41 (d, *J*=16.4, 1H), 4.19 (dt, *J*=13.8, 6.7, 4H), 1.83 – 1.62 (m, 4H), 1.56 – 1.37 (m, 4H), 0.98 (td, *J*=7.3, 2.6, 6H). **^{13}C NMR**: δ 167.0, 166.3, 154.3, 149.5, 142.3, 142.0, 141.3, 140.2, 137.5, 133.4, 130.8, 129.9, 128.2, 127.9, 127.5, 127.3, 126.6, 126.4, 124.9, 123.2, 121.0, 120.3, 119.0, 64.7, 64.6, 30.9, 30.8, 19.4, 19.3, 13.9, 13.9. **ESI$^+$**: calcd for $C_{31}H_{32}N_2O_6SCl$ $(M+H)^+$: 595,1664. Found: 595,1627.

(*E*)-Butyl 3-[8-fluoro-*N*-(2-pyridyl)sulfonyl-9H-carbazol-1-yl]acrylate (21).



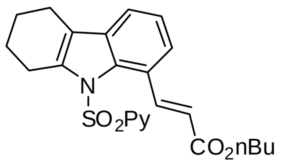
Following the typical procedure, carbazole **15** (48.9 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (43 μL, 0.3 mmol, 2.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (86.8 mg, 0.3 mmol, 2.0 equiv) were used. Chromatography eluent: *n*-hexane-CH_2Cl_2 1:10. Pale yellow solid; yield: 66%; mp = 158-159 ºC. **^{1}H NMR** δ 9.00 (d, *J*=15.8, 1H), 8.71 (dt, *J*=5.2, 1.2, 1H), 8.17 – 8.08 (m, 1H), 7.92 (td, *J*=7.8, 1.7, 1H), 7.85 (dd, *J*=7.6, 1.3, 1H), 7.74 (dd, *J*=7.9, 1.4, 1H), 7.61 (dd, *J*=7.7, 1.1, 1H), 7.51 (ddd, *J*=7.6, 4.7, 1.2, 1H), 7.42 (t, *J*=7.7, 1H), 7.30 (dt, *J*=8.0, 4.0, 1H), 7.08 (ddd, *J*=11.1, 8.2, 1.0, 1H), 6.52 (d, *J*=15.8, 1H), 4.19 (t, *J*=6.7, 2H), 1.65 (dq, *J*=8.5, 6.7, 2H), 1.51 – 1.33 (m, 2H), 0.94 (t, *J*=7.4, 3H). **^{13}C NMR** δ 167.2, 155.9, 155.9, 153.8, 150.5, 150.0, 143.1, 140.1, 137.8, 132.0, 132.0, 130.0, 129.9, 128.8, 128.6, 127.6, 126.9, 126.9, 126.6, 126.5, 125.8, 123.3, 123.3, 121.5, 118.0, 115.9, 115.8, 115.0, 114.7, 64.4, 30.9, 19.3, 13.9. **ESI$^+$**: calcd for $C_{24}H_{22}N_2O_4FS$ $(M+H)^+$:453,1278. Found: 453,1284.

(*E*)-Butyl 3-{*N*-(2-pyridyl)sulfonyl-5H-benzo[b]carbazol-4-yl}acrylate (22).



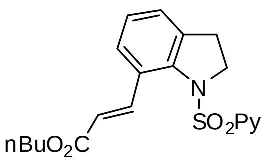
Following the typical procedure, carbazole **16** (53.8 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (43 μL, 0.3 mmol, 2.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (86.8 mg, 0.3 mmol, 2.0 equiv) were used. Chromatography eluent: CH_2Cl_2. Brown solid; yield: 64%; mp = 160-162 ºC. **^{1}H NMR** δ 8.87 (d, *J*=8.6, 1H), 8.56 (d, *J*=16.0, 1H), 8.06 (ddd, *J*=4.7, 1.8, 0.9, 1H), 7.87 (dd, *J*=8.2, 1.5, 1H), 7.78 – 7.74 (m, 1H), 7.69 (dt, *J*=8.6, 1.4, 2H), 7.66 – 7.61 (m, 1H), 7.61 – 7.57 (m, 1H), 7.54 (ddd, *J*=8.2, 6.9, 1.2, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.30 (m, 1H), 7.12 (ddd, *J*=7.7, 4.7, 1.1, 1H), 7.00 (dt, *J*=7.9, 1.0, 1H), 6.63 (d, *J*=16.0, 1H), 4.29 (t, *J*=6.7, 2H), 1.86 – 1.70 (m, 2H), 1.59 – 1.43 (m, 2H), 1.01 (t, *J*=7.4, 3H). **^{13}C NMR** δ 167.2, 152.1, 148.9, 142.2, 138.8, 136.6, 133.8, 132.8, 128.4, 128.3, 128.2, 128.2, 127.0, 126.8, 126.7, 126.5, 126.4, 126.3, 125.4, 123.2, 120.7, 118.3, 117.1, 64.6, 31.0, 19.4, 14.0. **ESI$^+$**: calcd for $C_{28}H_{25}N_2O_4S$ $(M+H)^+$:485,1529. Found: 485,1530.

(*E*)-Butyl 3-*N*-(2-pyridyl)sulfonyl-2,3,4,9-tetrahydro-1H-carbazol-8-yl]acrylate (23).



Following the typical procedure, carbazole **17** (46.8 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (86 μL, 0.6 mmol, 4.0 equiv) and $PhI(OAc)_2$ (144.9 mg, 0.45 mmol, 3.0 equiv) were used. Chromatography eluent: *n*-hexane-EtOAc 6:1. Yellow solid; yield: 84%; mp = 104-105 ºC. **^{1}H NMR** δ 8.57 (ddd, *J*=4.7, 1.7, 0.8, 1H), 8.37 (d, *J*=15.6, 1H), 7.90 (dt, *J*=8.0, 1.1, 1H), 7.87 – 7.80 (m, 1H), 7.48 – 7.37 (m, 2H), 7.31 (dd, *J*=7.6, 1.4, 1H), 7.28 – 7.20 (m, 1H), 6.30 (d, *J*=15.7, 1H), 4.22 (t, *J*=6.7, 2H), 3.21 – 3.05 (m, 2H), 2.68 – 2.40 (m, 2H), 1.99 – 1.76 (m, 4H), 1.77 – 1.64 (m, 2H), 1.58 – 1.37 (m, 2H), 0.97 (t, *J*=7.3, 3H). **^{13}C NMR** δ 167.3, 155.9, 150.0, 145.1, 139.6, 138.0, 136.4, 133.5, 127.4, 124.6, 124.5, 124.4, 122.6, 120.7, 119.5, 117.7, 64.4, 31.0, 25.7, 23.6, 22.1, 21.3, 19.3, 13.9. **ESI$^+$**: calcd for $C_{24}H_{27}N_2O_4S$ $(M+H)^+$:439,1692. Found: 439,1695.

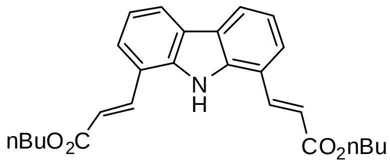
(*E*)-Butyl 3-[*N*-(2-pyridyl)sulfonyl)indolin-7-yl]acrylate (25). Following the typical procedure, indoline **24** (39.0 mg, 0.15 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *n*-butyl acrylate (43 μL, 0.3 mmol, 2.0 equiv) and 1-fluoro-2,4,6-trimethylpyridinium triflate (86.8 mg, 0.3 mmol, 2.0 equiv) were used. Chromatography eluent: CH_2Cl_2. Yellow solid; yield: 80%; mp = 107-108 ºC. **^{1}H NMR** δ 8.63 (d, *J*=4.6, 1H), 8.14 (d, *J*=16.1, 1H), 7.75 (t, *J*=7.7, 1H), 7.61 (d, *J*=7.9, 1H), 7.52 – 7.40 (m, 2H), 7.18 – 7.02 (m, 2H), 6.40 (d, *J*=16.1, 1H), 4.29 (t, *J*=7.5, 2H), 4.21 (t, *J*=6.7, 2H), 2.55 (t, *J*=7.3, 2H), 1.70 (p, *J*=6.9, 2H), 1.45 (h, *J*=7.4, 2H), 0.96 (t, *J*=7.3, 3H). **^{13}C NMR** δ 167.1, 156.2, 150.2, 142.0, 141.6, 137.9, 137.8, 128.0, 127.2, 126.8, 126.0, 125.6, 123.5, 118.1, 64.5, 53.4,



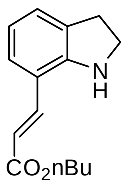
30.9, 29.4, 19.3, 13.9. **ESI**$^+$: calcd for $C_{20}H_{23}N_2O_4S$ $(M+H)^+$:387,1373. Found: 387,1354.

1.5. Zn-promoted reductive *N*-desulfonylation

Typical procedure: synthesis of (*E*,*E*)-dibutyl 3,3'-(9H-carbazole-1,8-diyl)diacrylate (26). A suspension of diolefinated adduct **7** (56,1 mg, 0.1 mmol) and activated Zn powder (327 mg, 5 mmol, 50 equiv) in a 1:1 mixture of THF and sat aq. NH_4Cl solution (5 mL) was stirred at room temperature until consumption of the starting material (TLC monitoring). The mixture was diluted with EtOAc (15 mL) and filtered over a pad of celite to remove the Zn. The filtrate was washed with a saturated aqueous solution of ammonium chloride (10 mL) and brine (10 mL). The combined organic phase was dried ($MgSO_4$) and concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane-EtOAc 3:1) to afford **26** as a yellow oil; yield: 39 mg (93%). **^{1}H NMR** δ 8.95 (s, 1H), 8.12 (d, *J*=15.9, 2H), 8.04 (d, *J*=7.7, 2H), 7.63 (d, *J*=7.5, 2H), 7.25 – 7.19 (m, 2H), 6.56 (d, *J*=15.9, 2H), 4.21 (t, *J*=6.8, 4H), 1.74 – 1.60 (m, 4H), 1.39 (dtd, *J*=16.6, 8.6, 8.0, 5.5, 4H), 0.91 (t, *J*=7.3, 6H). **^{13}C NMR** δ 167.3, 139.6, 138.5, 125.0, 124.5, 122.5, 120.5, 119.1, 118.3, 64.9, 30.8, 19.4, 13.6. **ESI**$^+$: calcd for $C_{26}H_{30}NO_4$ $(M+H)^+$:420,2169. Found: 420,2187.

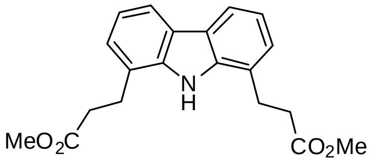


(*E*)-Butyl 3-(indolin-7-yl)acrylate (28). Chromatography eluent: *n*-hexane- CH_2Cl_2 1:2. Dark yellow solid; yield: 63 %; mp = 61-62 ºC. **^{1}H NMR** δ 7.70 (d, *J*=16.0, 1H), 7.16 (d, *J*=7.9, 1H), 7.09 (d, *J*=7.1, 1H), 6.69 (t, *J*=7.5, 1H), 6.28 (d, *J*=16.0, 1H), 4.48 (s, 1H), 4.19 (t, *J*=6.7, 2H), 3.62 (t, *J*=8.5, 2H), 3.05 (t, *J*=8.4, 2H), 1.68 (dt, *J*=14.3, 6.8, 2H), 1.43 (h, *J*=7.4, 2H), 0.96 (t, *J*=7.3, 3H). **^{13}C NMR** δ 167.6, 150.9, 141.5, 130.8, 127.0, 126.3, 119.0, 116.7, 116.3, 64.3, 47.1, 30.9, 29.4, 19.3, 13.8. **FB**$^+$: calcd for $C_{15}H_{19}NO_2$ $(M)^+$: 245,1416. Found: 245,1418.



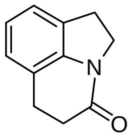
1.6. Mg-promoted reductive *N*-desulfonylation

Typical procedure: synthesis of dimethyl 3,3'-(9H-carbazole-1,8-diyl)dipropanoate (27). The diolefinated adduct **7** (0.1 mmol) was dissolved in MeOH (5 mL) and treated with magnesium turnings (51 mg, 2 mmol, 20 equiv). The mixture was sonicated at room temperature until consumption of the starting



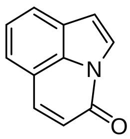
material (TLC monitoring, 2h), then diluted with EtOAc (10 mL) and filtered (celite) to remove excess of Mg. The filtrate was washed with sat. aq NH_4Cl (10 mL) and brine (10 mL). The combined organic phase was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography (*n*-hexane-EtOAc 3:1) to afford **27** as a yellow solid; yield: 22 mg (75%); mp = 136-138 ºC. **^{1}H NMR** δ 9.32 (s, 1H), 7.94 (d, *J*=7.6, 2H), 7.27 – 7.11 (m, 4H), 3.69 (s, 6H), 3.31 (t, *J*=7.1, 4H), 2.85 (t, *J*=7.1, 4H). **^{13}C NMR** δ 174.8, 138.8, 125.7, 123.9, 123.4, 119.6, 118.8, 52.0, 34.6, 26.6. **FB$^+$**: calcd for $C_{20}H_{21}NO_4$ $(M)^+$: 339,1471. Found: 339,1472.

1,2,5,6-Tetrahydropyrrolo[3,2,1-ij]quinolin-4-one (29).[8] The crude product was purified by trituration in a mixture of ether and hexane, obtaining a pale yellow solid; yield: 43 mg (99%); mp = 80-81 ºC **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.07 (d, *J*=7.4, 1H), 6.99 (m, 1H), 6.92 (t, *J*=7.4, 1H), 4.08 (t, *J*=8.4, 2H), 3.19 (t, *J*=8.4, 2H), 2.97 (t, *J*=7.8, 2H), 2.68 (t, *J*=7.8, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.8, 141.4, 129.1, 125.5, 123.4, 123.4, 120.4, 45.3, 31.8, 27.9, 24.6. **ESI$^+$**: calcd for $C_{11}H_{11}NO$ $(M)^+$:173,0841. Found: 173,0842.



1.7. Oxidative aromatization

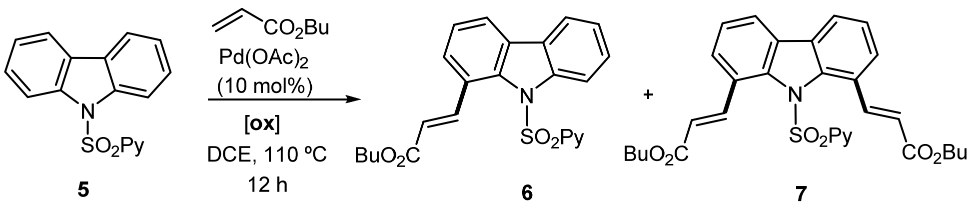
Pyrrolo[3,2,1-ij]quinolin-4-one (30).[9] To a solution of 1,2,5,6-tetrahydropyrrolo[3,2,1-ij]quinolin-4-one (38,4 mg, 0.22 mmol) in DCE (1.5 mL) at room temperature was added DDQ (149.8 mg, 0.66 mmol, 3.0 equiv). The mixture was heated at 80 ºC overnight before it was allowed to reach room temperature and quenched with sat aq. $NaHCO_3$ solution (5 mL). The mixture was extracted with EtOAc (5 mL) and the organic phase washed with brine (5 mL), then dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (*n*-hexane-CH_2Cl_2 1:1) to afford the indole derivative as a light brown solid; yield: 26,4 mg (71%); mp = 110-112 ºC [mp$^{lit(8)}$ = 113 ºC]. **^{1}H NMR** δ 7.96 (d, *J*=3.6, 1H), 7.91 – 7.81 (m, 2H), 7.61 (d, *J*=7.6, 1H), 7.43 (t, *J*=7.6, 1H), 6.90 (d, *J*=3.6, 1H), 6.72 (d, *J*=9.5, 1H). **^{13}C NMR** δ 159.4, 139.0, 132.6, 127.9, 125.5, 124.4, 124.2, 123.8, 117.2, 110.9. **ESI$^+$**: calcd for $C_{11}H_7NO$ $(M)^+$:169,0528. Found: 169,0526.



[8] Yin, L.; Lucas, S.; Maurer, F.; Kazmaier, U.; Hu, Q.; Hartmann, R. W. *J. Med. Chem.* **2012**, *55*, 6629.

[9] McNab, H.; Nelson, D. J.; Rozgowska, E. J. *Synthesis*, **2009**, *13*, 2171.

2. Optimization studies: effect of other oxidants



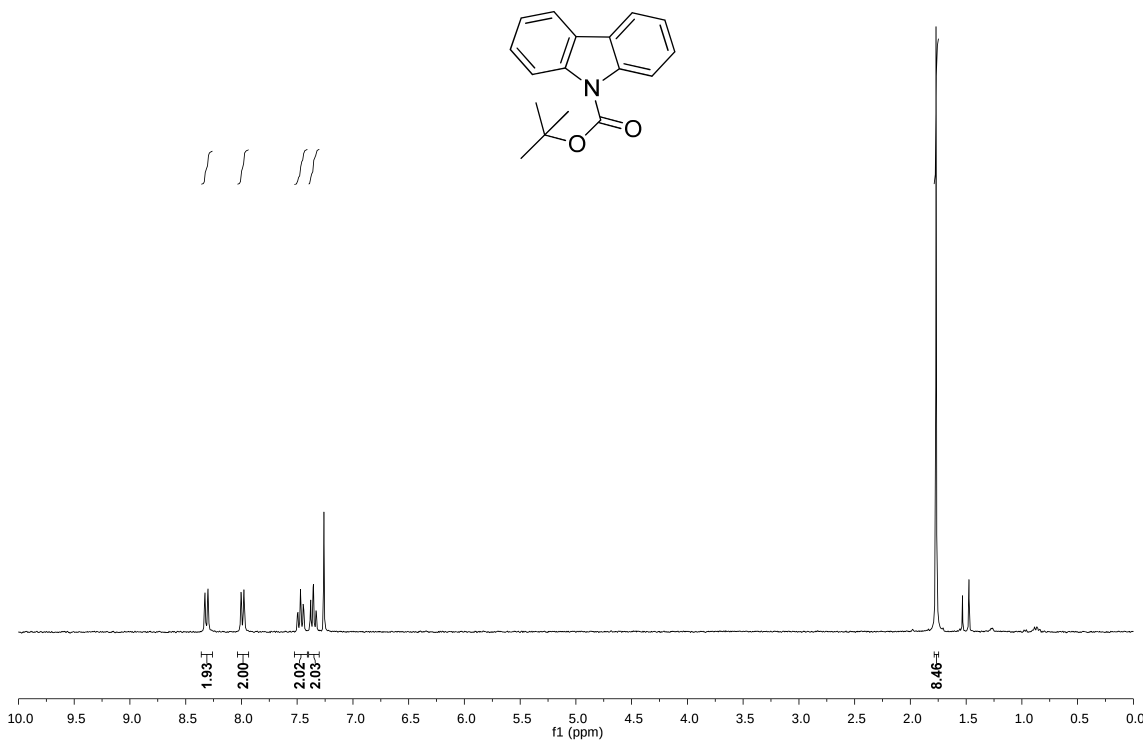
entry	equiv. of butyl acrylate	[**ox**]	equiv. of oxidant	conv. (%)[a]	yield [**6**/**7**, (%)][b]
1	2	$Ce(SO_4)_2$	2	45	26 / 3
2	2	$K_2S_2O_8$	2	<10	--
3	2	AgOAc	2	57	35 / 10
4	2	$AgCO_3$	2	<10	--
5	2	AgOTf	2	<10	--
6	2	AgF	2	<10	--
7	2	$AgNO_3$	2	77	37 / 30
8	2	$Ce(SO_4)_2$	2	61	40 / 10
9	2	$Cu(OAc)_2$	2	0	--
10	2	CAN[d]	1.2	<10	--
11	2	1,4-Benzoquinone	2	<10	--
12	2	Tempo	2	<10	--
13	2	Oxone	2	<10	--
14	2	$PhI(OAc)_2$	1	60	36 / 11
15	2	$PhI(OAc)_2$	2	95	26 / 43
16	4	$PhI(OAc)_2$	3	95	16 / 58

[a] Based on starting material recovered after chromatographic purification. [b] Isolated yield after chromatography. [c] $[F^+]$ = *N*-fluoro-2,4,6-trimethylpyridinium triflate. [d] CAN: ceric ammonium nitrate.

3. Copies of ^{1}H and ^{13}C NMR spectra

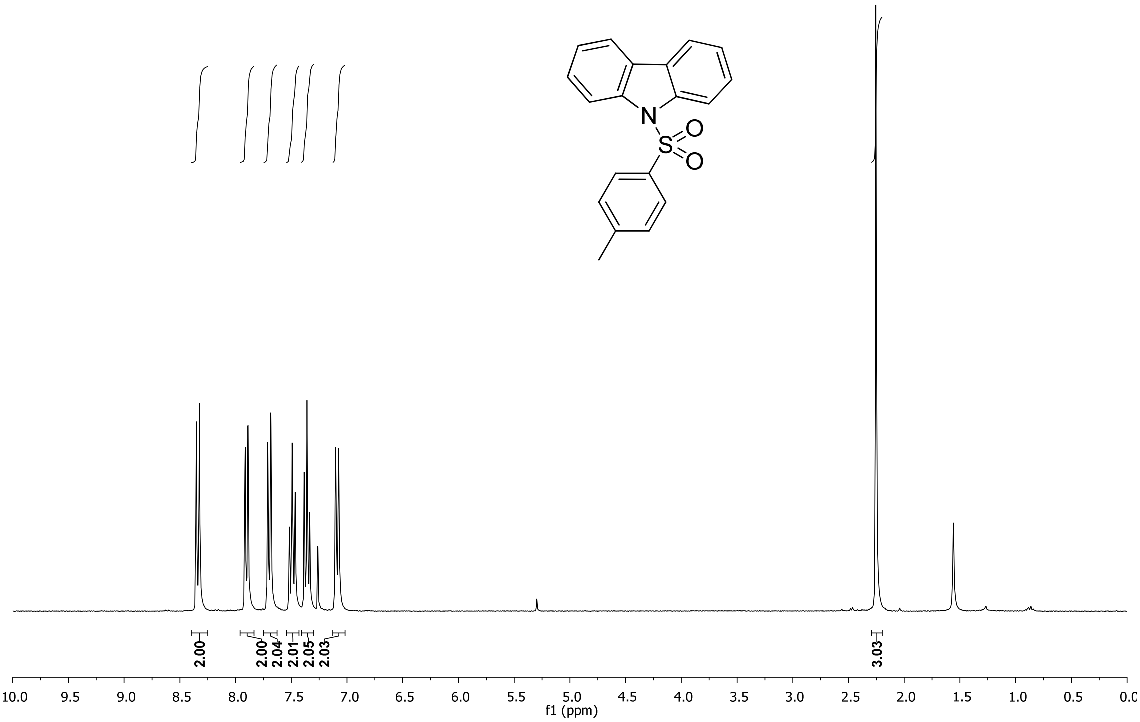
N-(*tert*-Butyl)-9H-carbazole-9-carboxylate (2)

^{1}H NMR (300 MHz, $CDCl_3$)

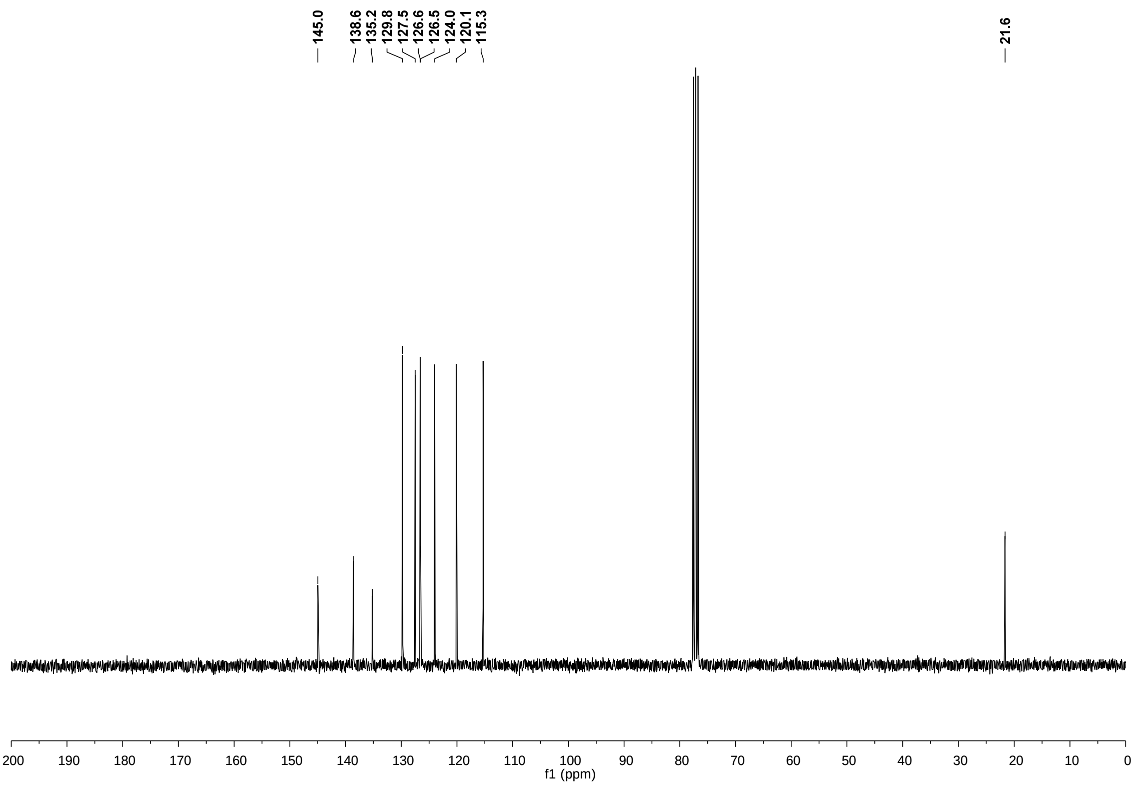


_N_-(2-_p_-Toluene)sulfonyl-9H-carbazole (4)

^{1}H NMR (300 MHz, $CDCl_3$)

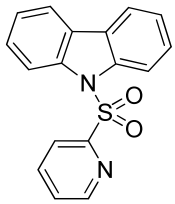


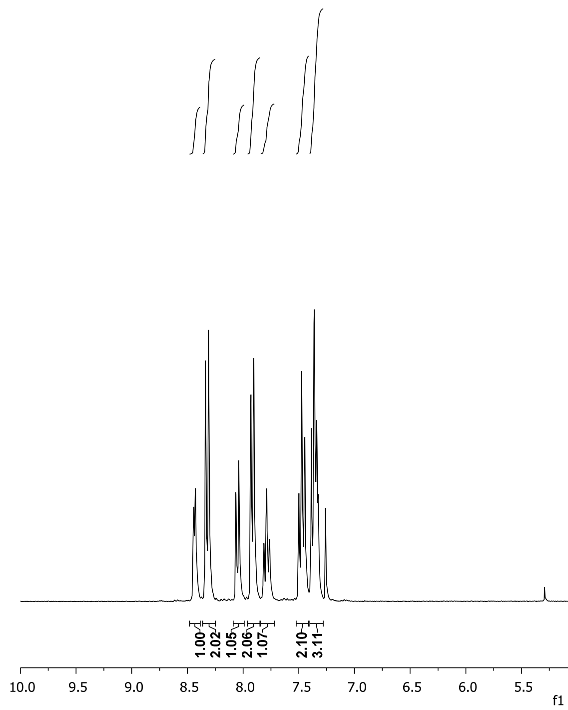
^{13} C NMR (75 MHz, $CDCl_3$)



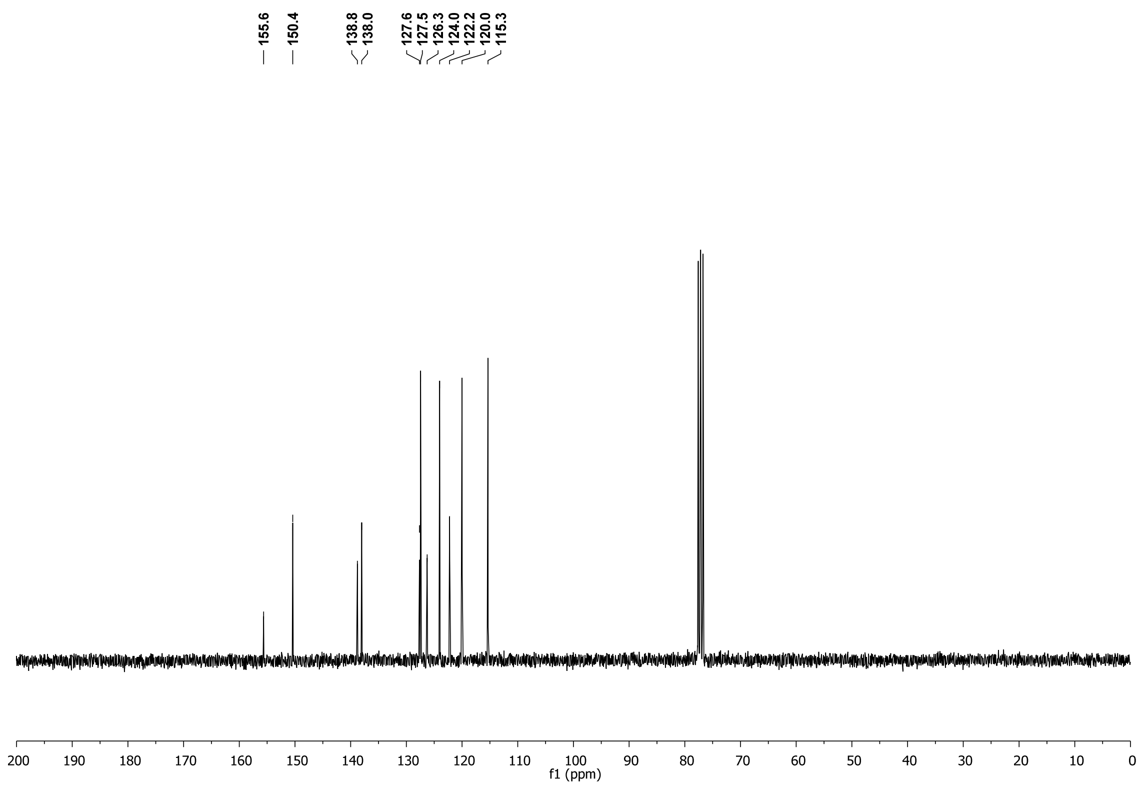
***N*-(2-pyridyl)sulfonyl-9H-carbazole (5)**

^{1}H NMR (300 MHz, $CDCl_3$)



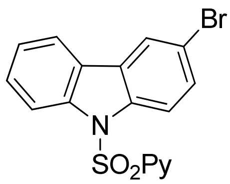


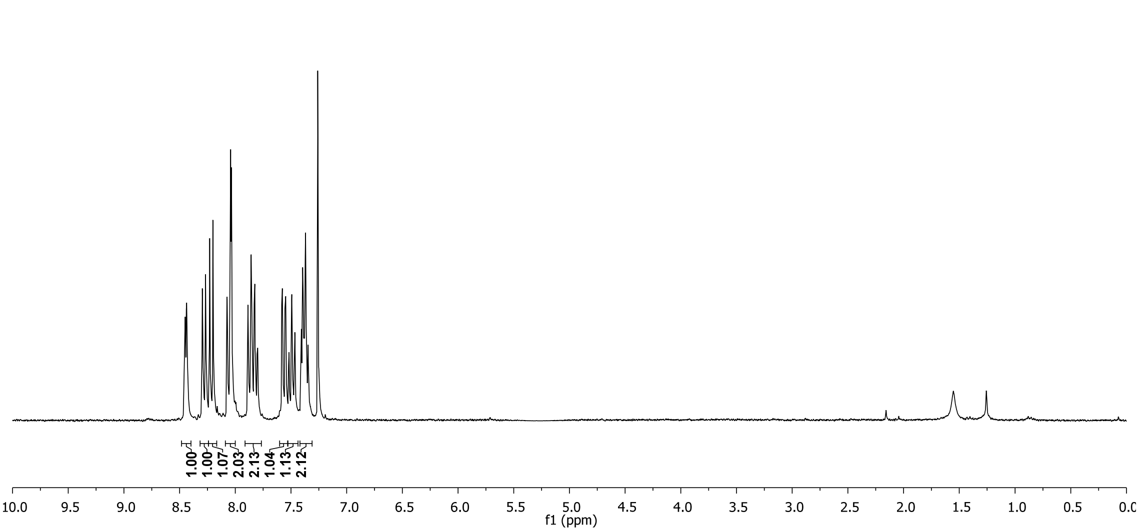
^{13}C NMR (75 MHz, $CDCl_3$)



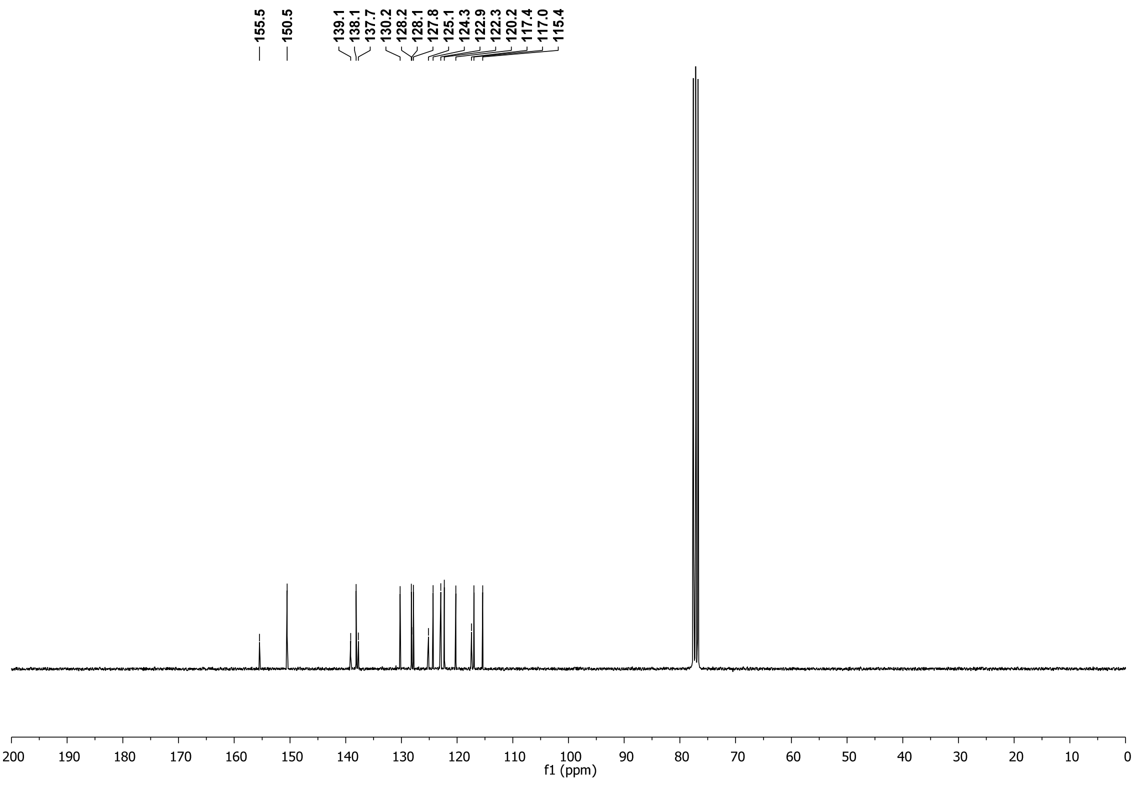
3-Bromo-*N*-(2-pyridyl)sulfonyl carbazole (13)

^{1}H NMR (300 MHz, $CDCl_3$)



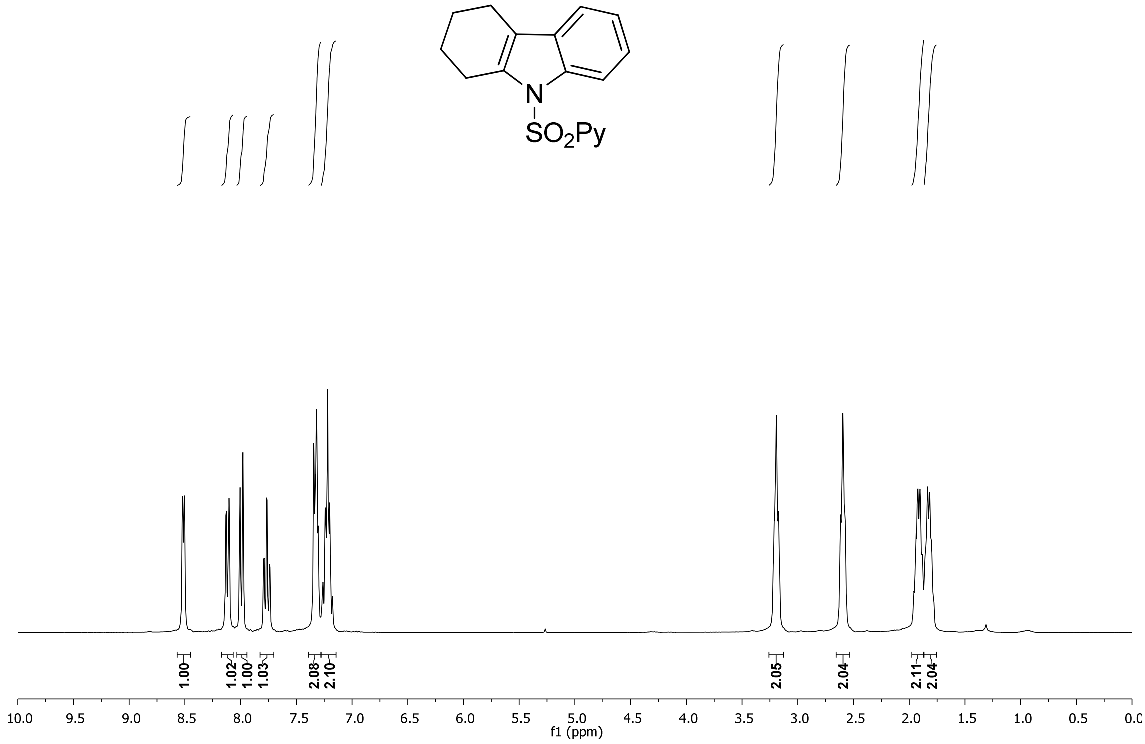


^{13}C NMR (75 MHz, $CDCl_3$)

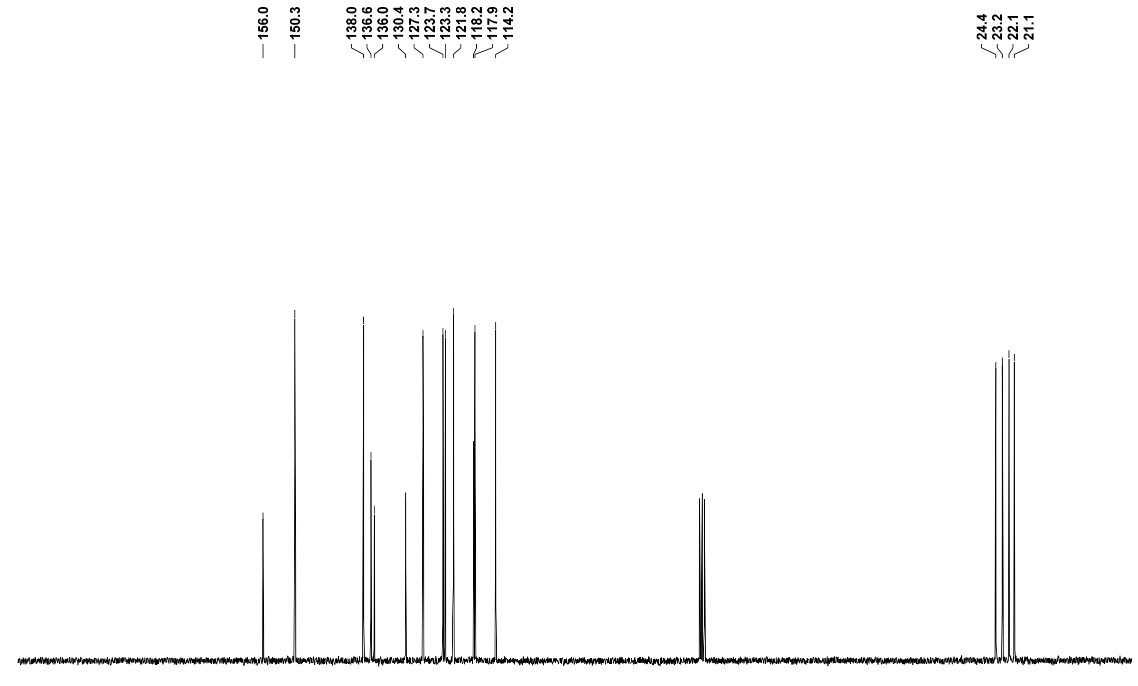


2,3,4,9-Tetrahydro-*N*-(2-pyridyl)sulfonyl-1H-carbazole (17)

^{1}H NMR (300 MHz, $CDCl_3$)

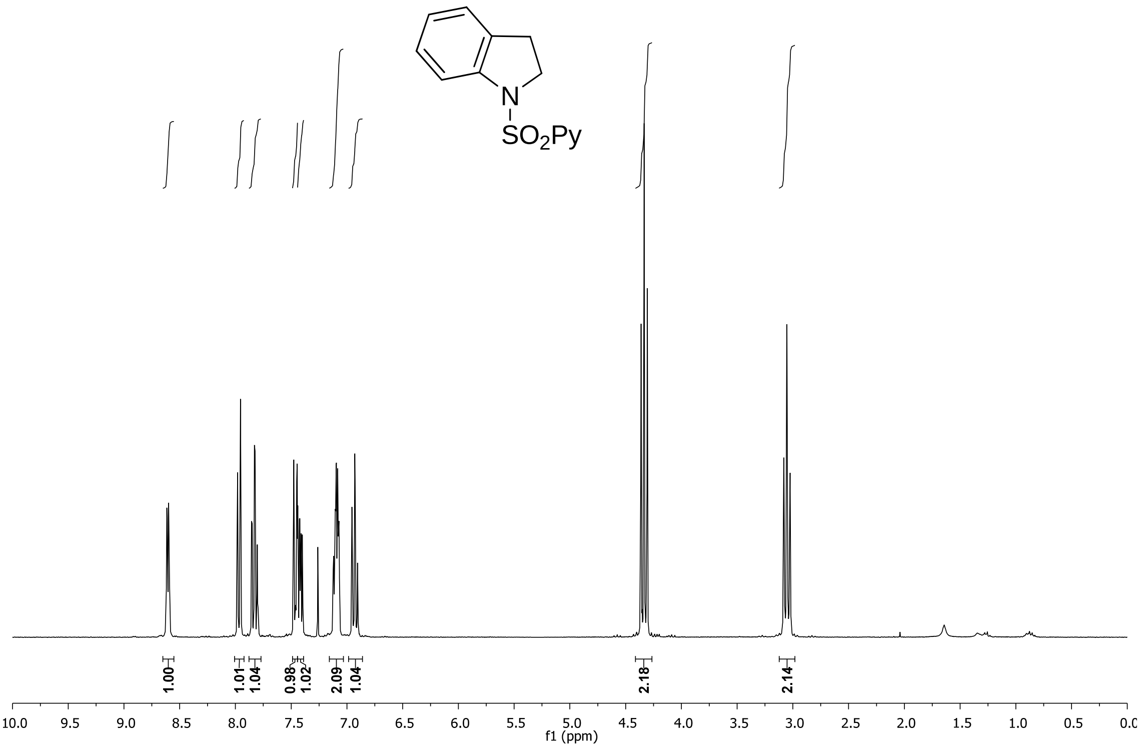


^{13}C NMR (75 MHz, $CDCl_3$)

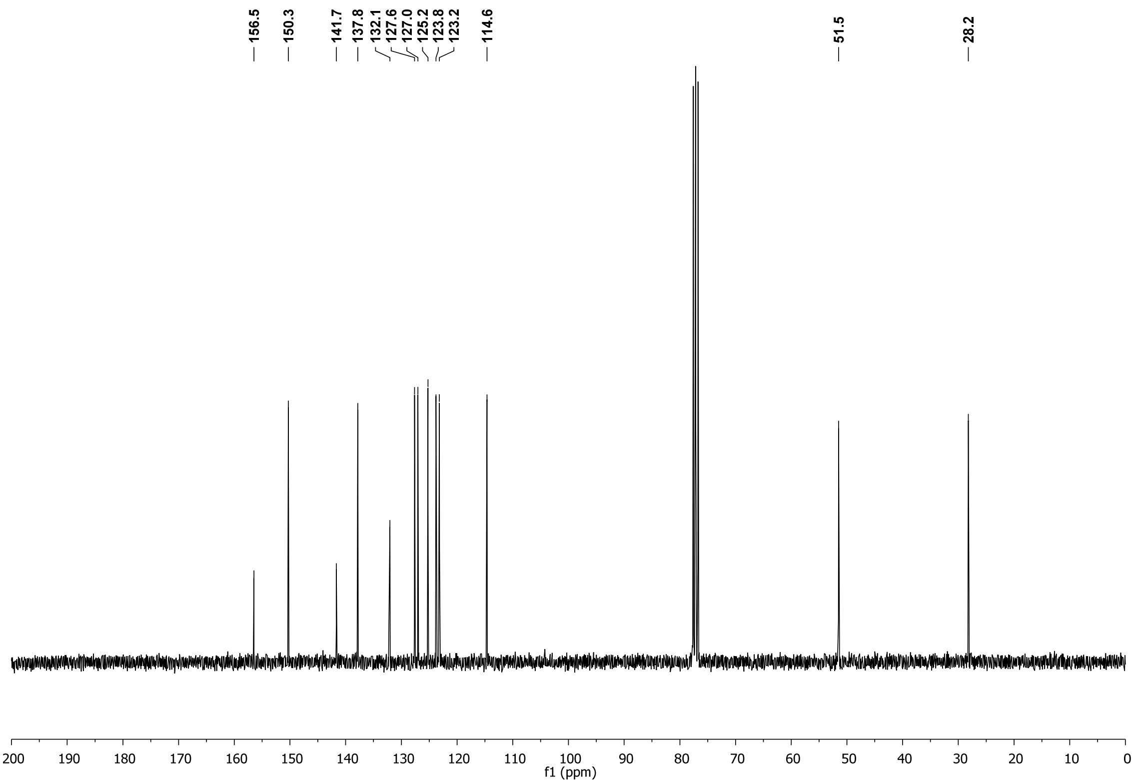


_N_-(2-Pyridyl)sulfonyl indoline (24)

^{1}H NMR (300 MHz, $CDCl_3$)

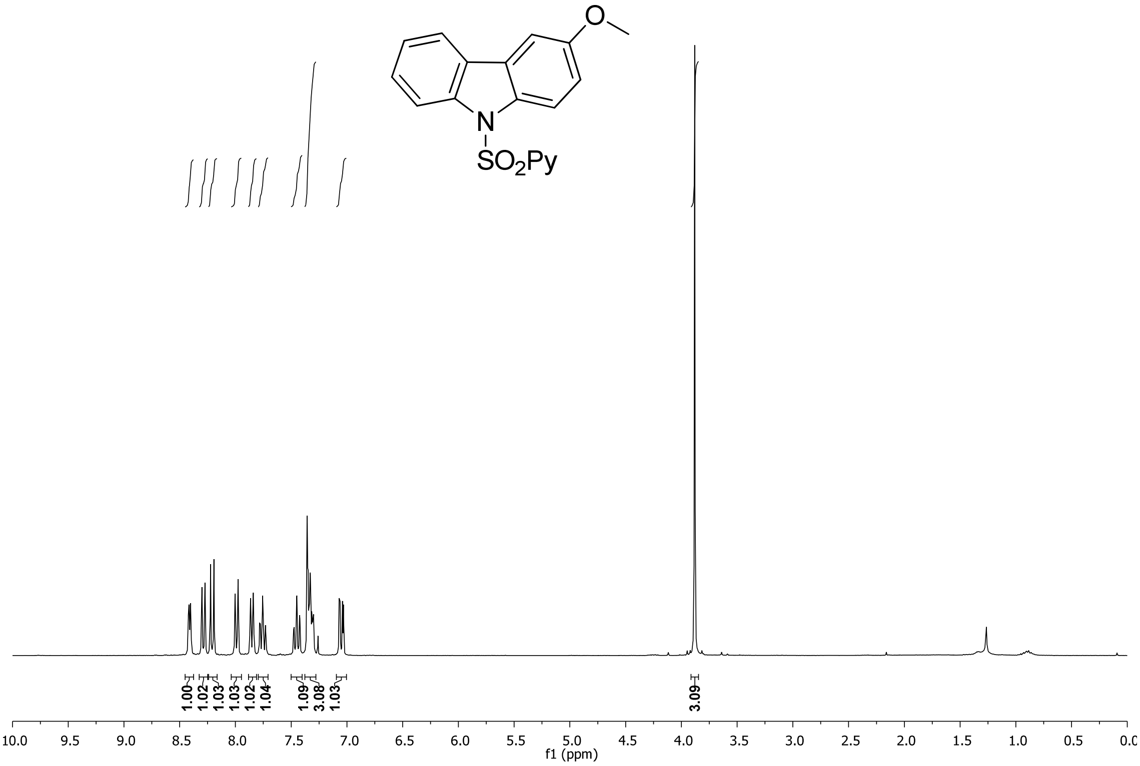


^{13}C NMR (75 MHz, $CDCl_3$)

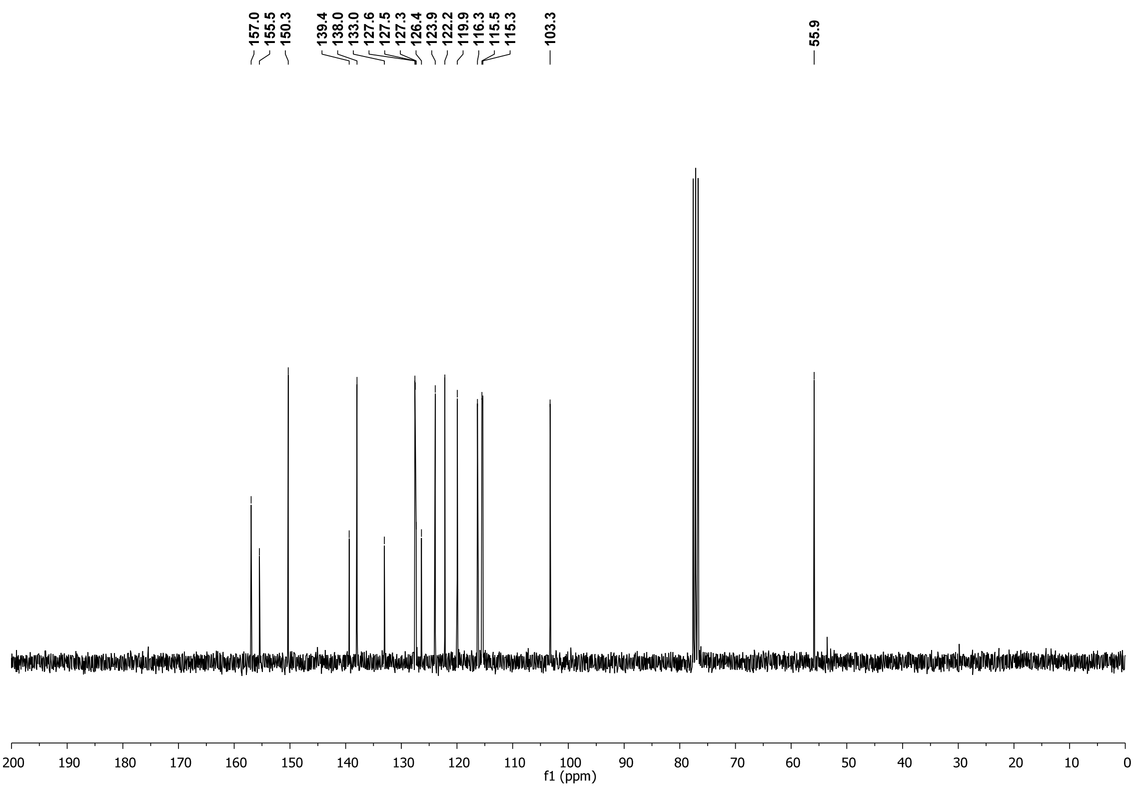


3-methoxy-*N*-(2-pyridyl)sulfonyl-9H-carbazole (12)

^{1}H NMR (300 MHz, $CDCl_3$)

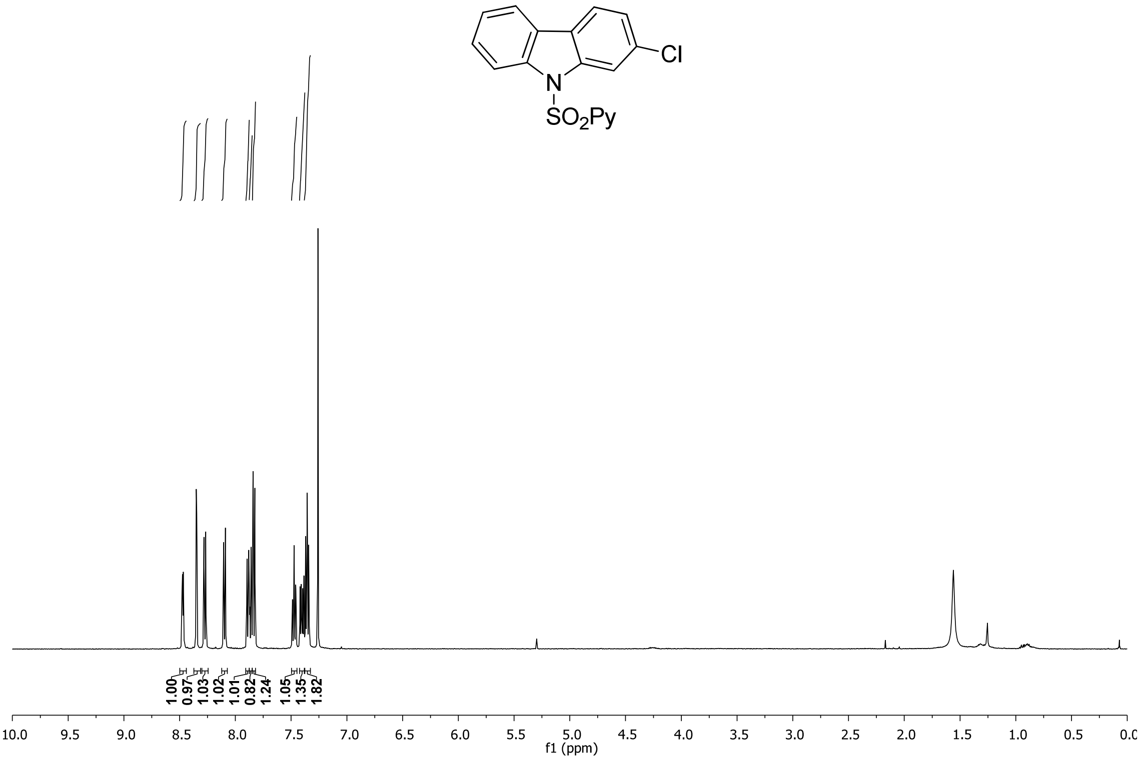


^{13}C NMR (75 MHz, $CDCl_3$)

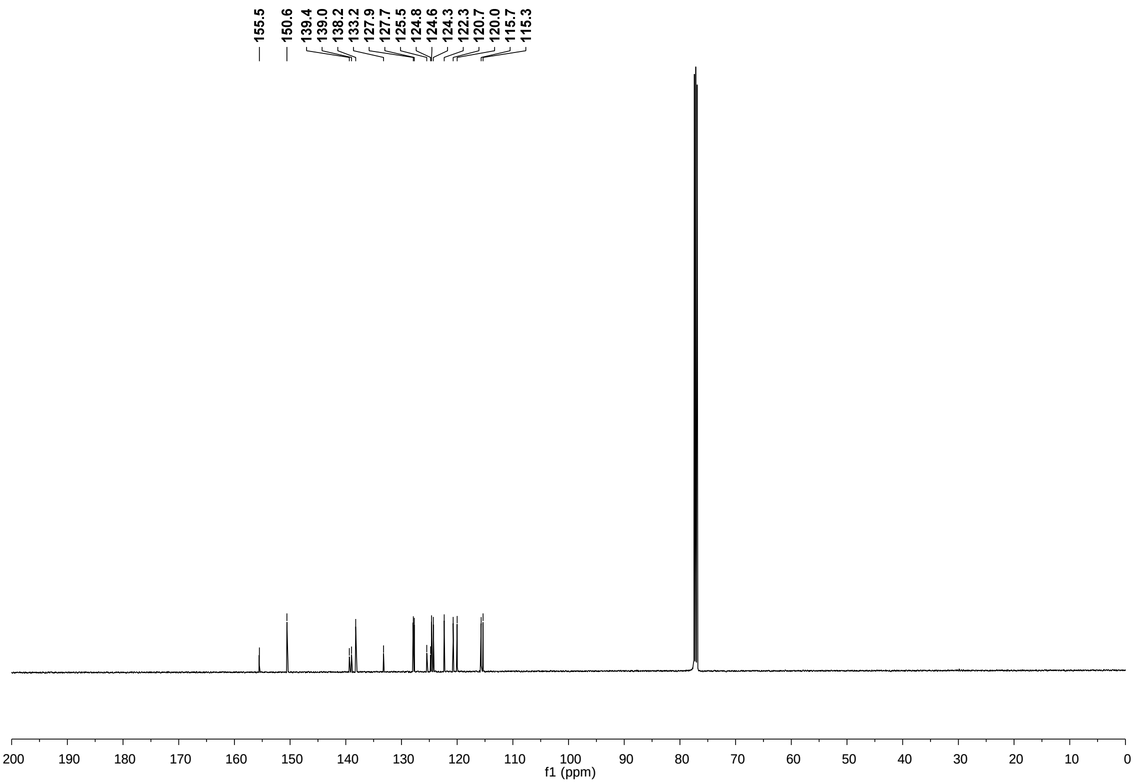


2-Chloro-*N*-2(pyridyl)sulfonyl-9H-carbazole (14)

^{1}H NMR (500 MHz, $CDCl_3$)

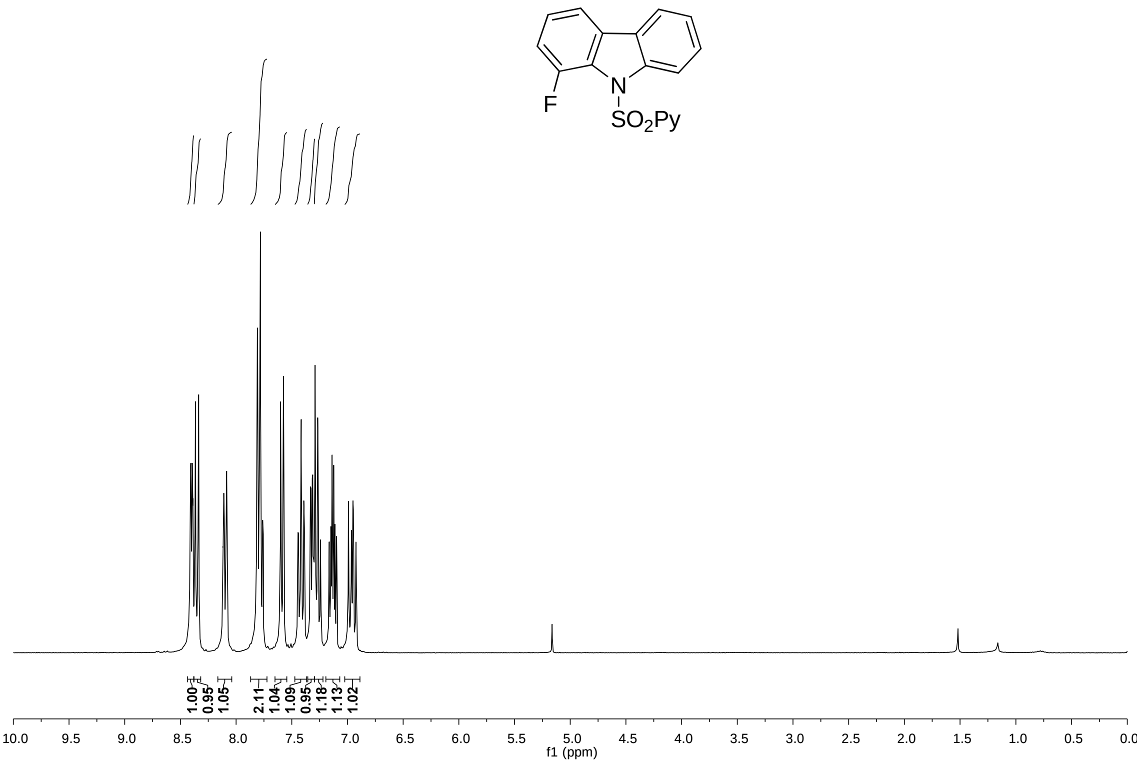


^{13}C NMR (125 MHz, $CDCl_3$)

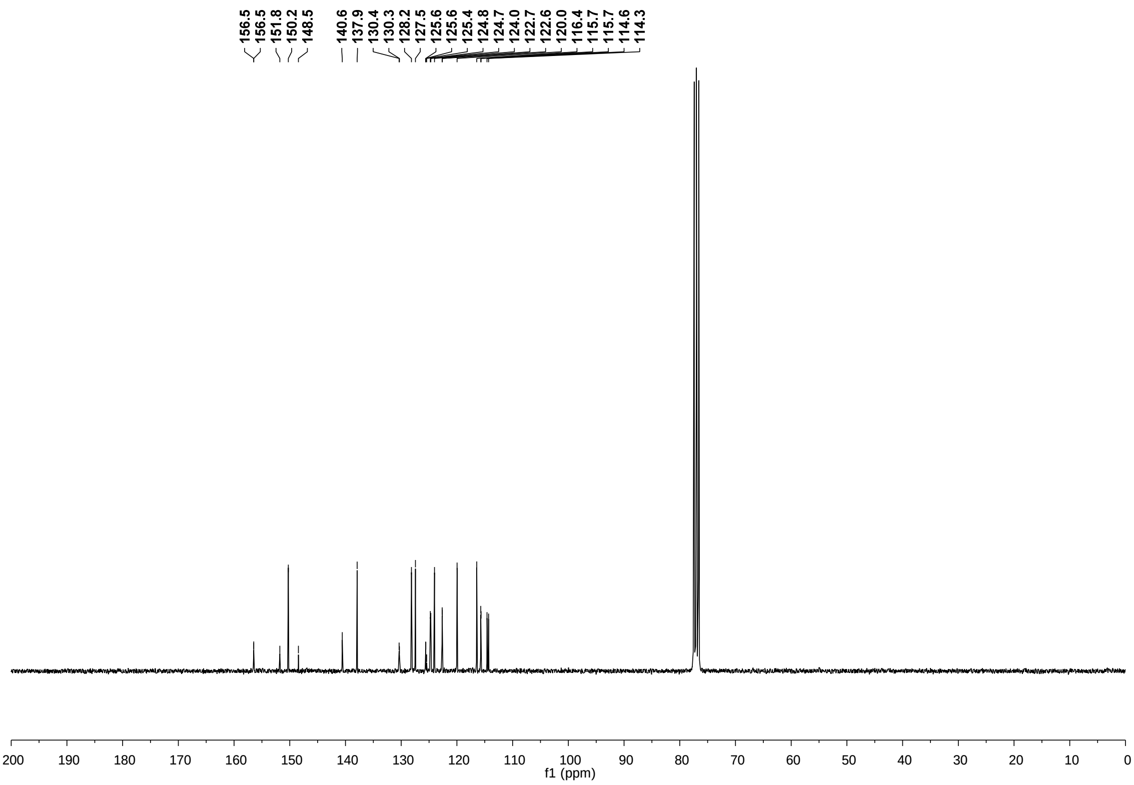


1-Fluoro-*N*-(2-pyridyl)sulfonyl-9H-carbazole (15)

^{1}H NMR (300 MHz, $CDCl_3$)

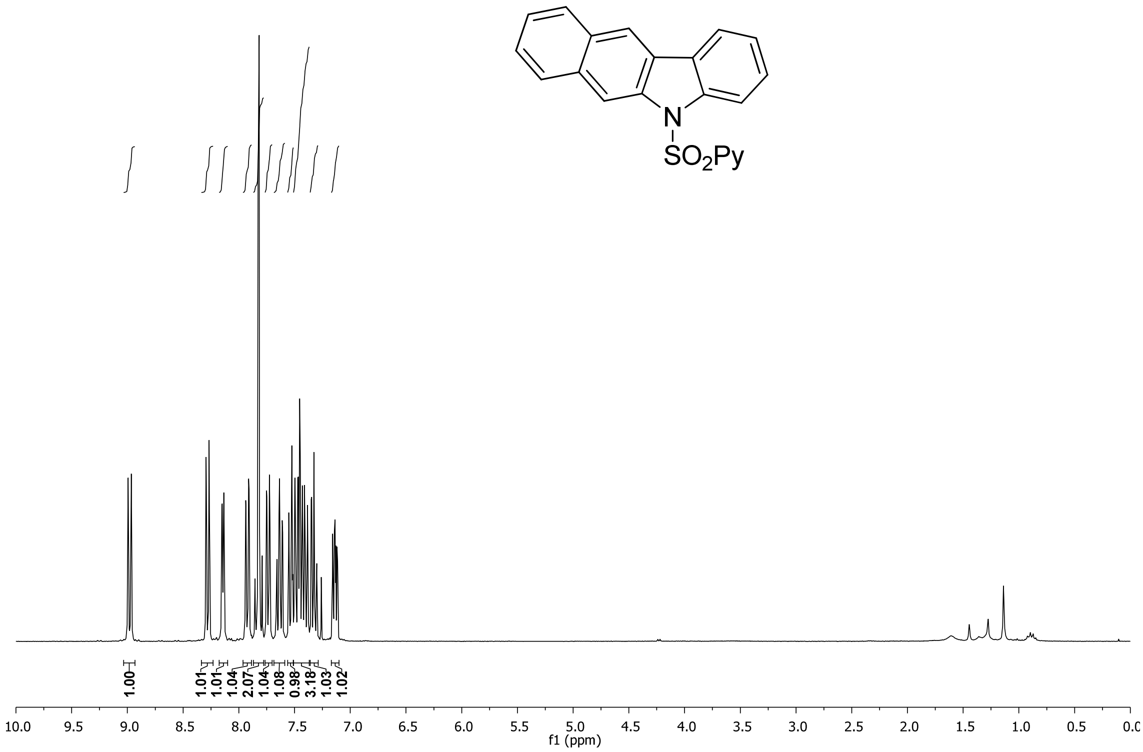


^{13}C NMR (75 MHz, $CDCl_3$)

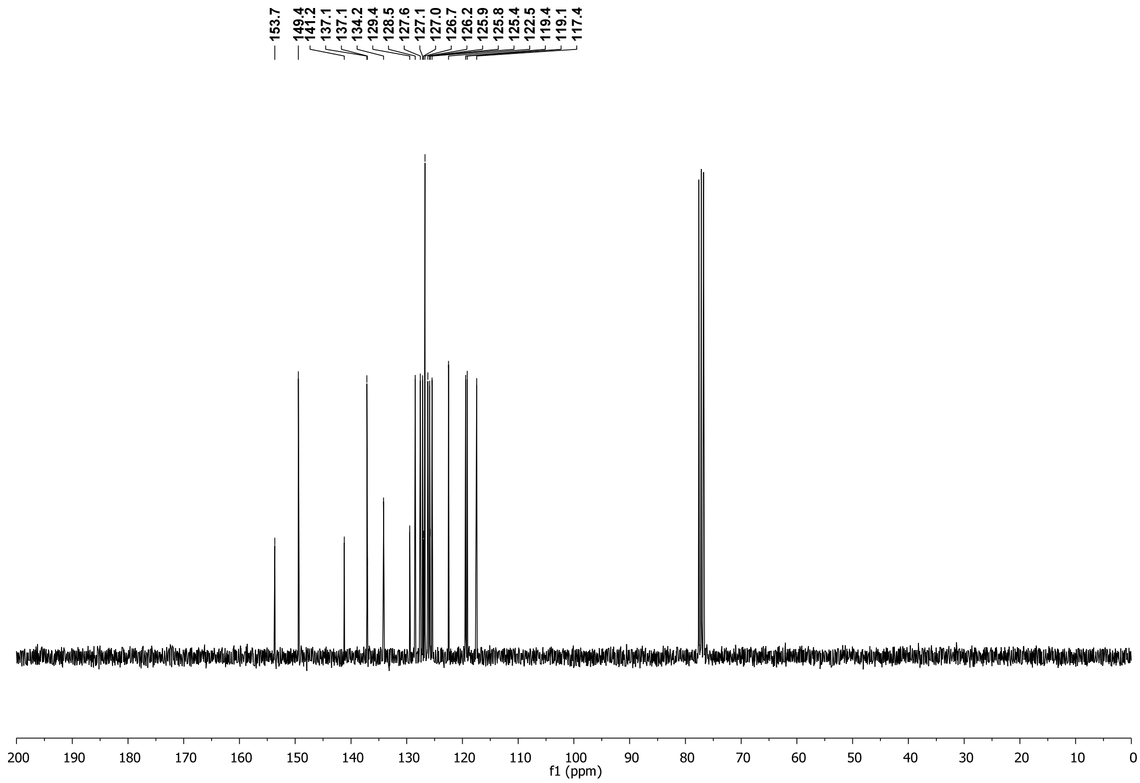


_N_-2(Pyridyl)sulfonyl-5H-benzo[b]carbazole (16)

^{1}H NMR (300 MHz, $CDCl_3$)

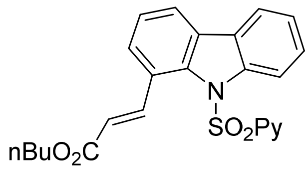


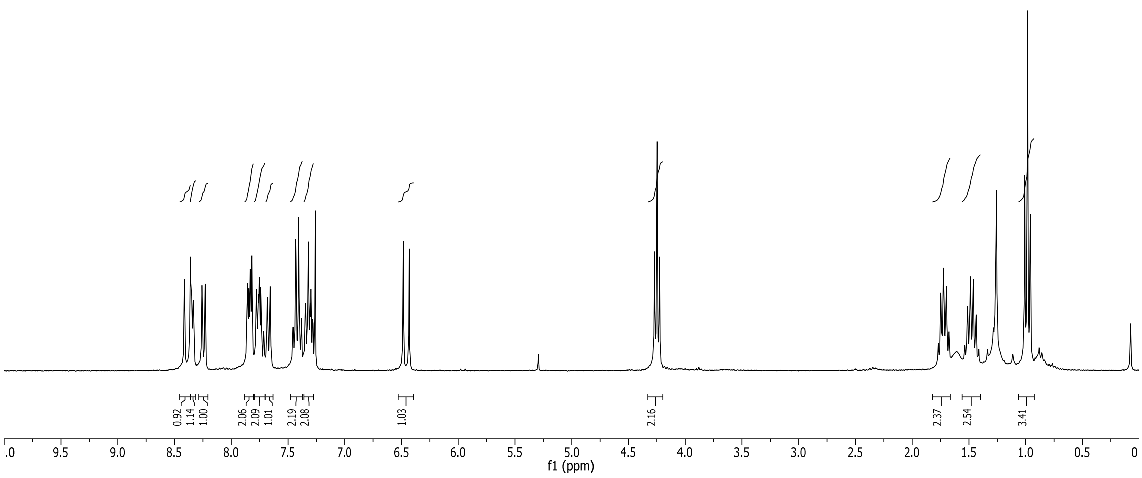
^{13}C NMR (75 MHz, $CDCl_3$)



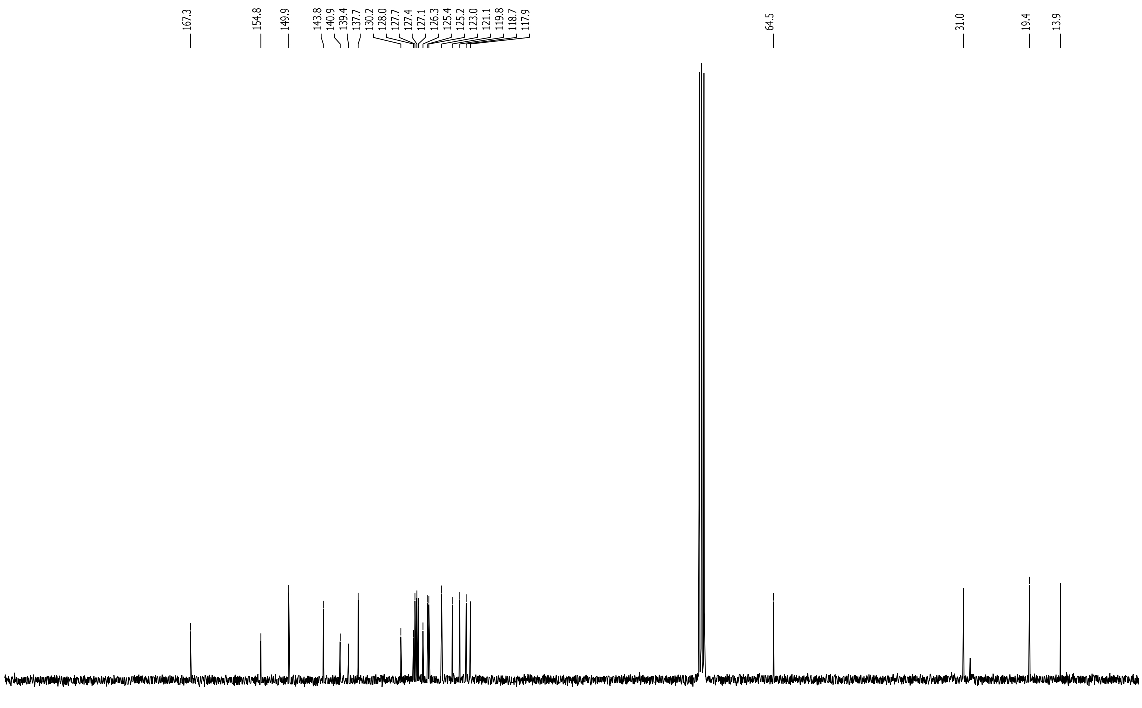
Butyl (*E*)-3-[*N*-(2-pyridyl)sulfonyl-9H-carbazol-1-yl]acrylate (6)

^{1}H NMR (300 MHz, $CDCl_3$)



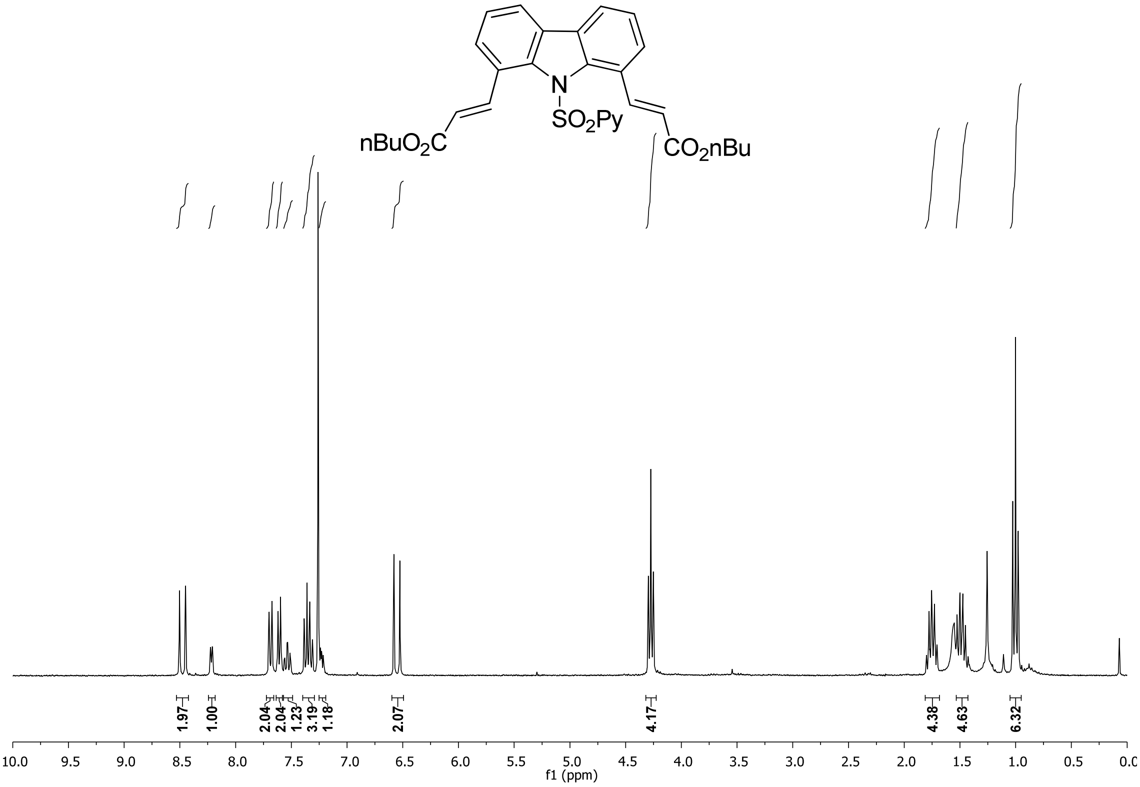


^{13}C NMR (75 MHz, $CDCl_3$)

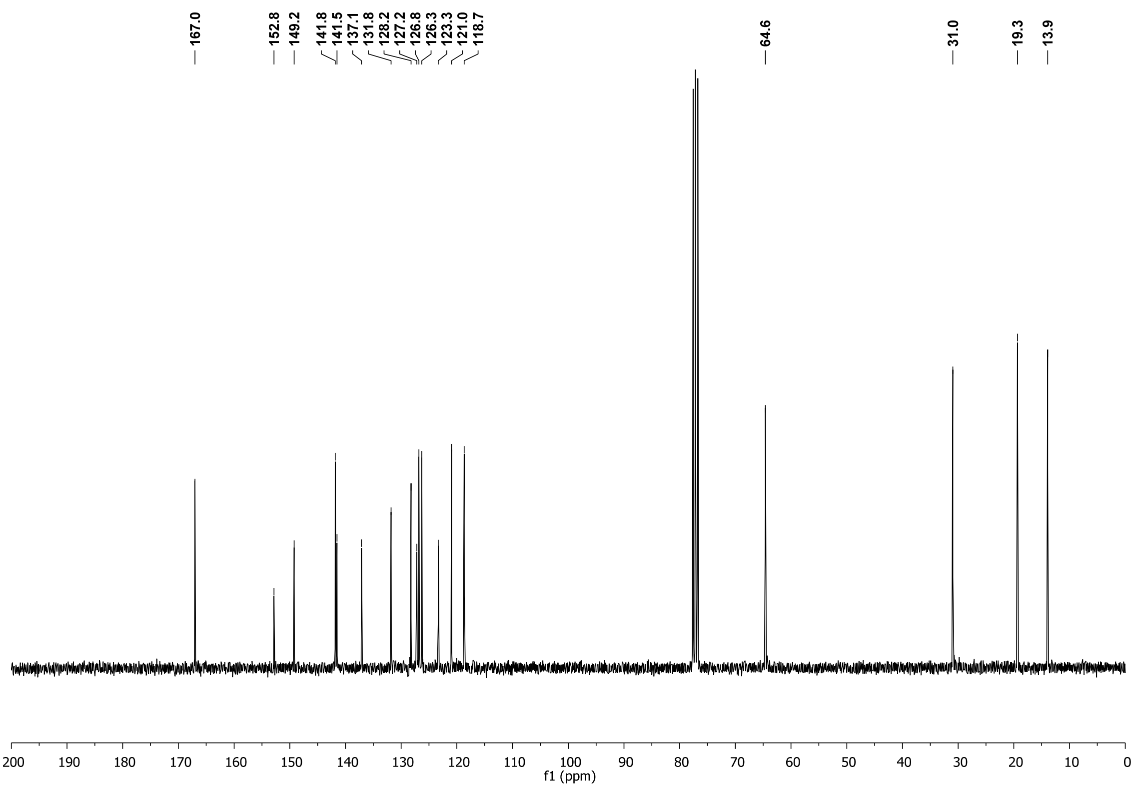


(*E*,*E*)-Dibutyl 3,3'-[*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (7)

^{1}H NMR (300 MHz, $CDCl_3$)

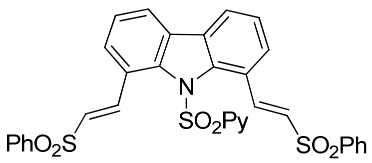


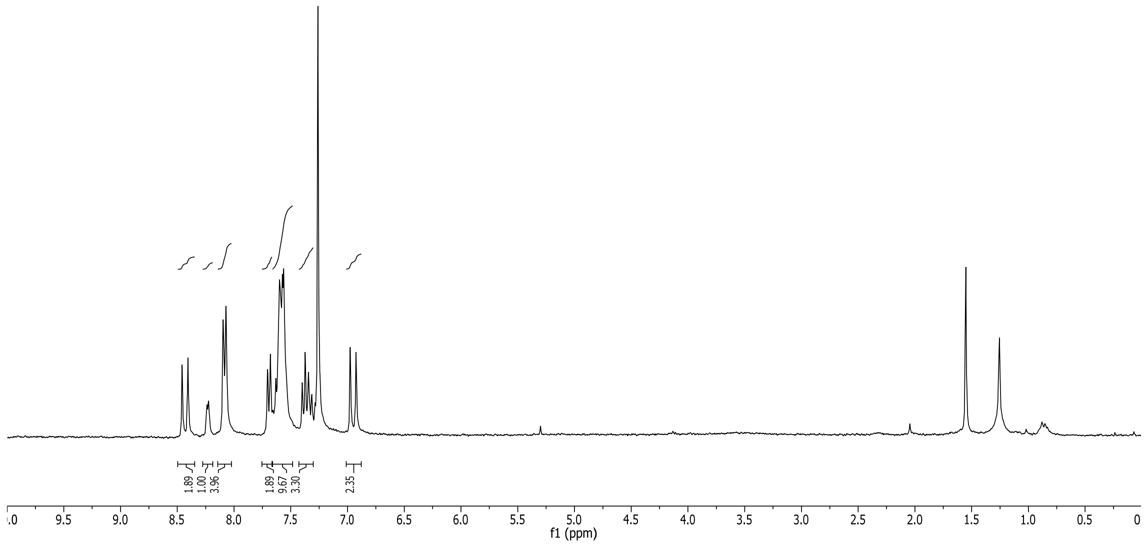
^{13}C NMR (75 MHz, $CDCl_3$)



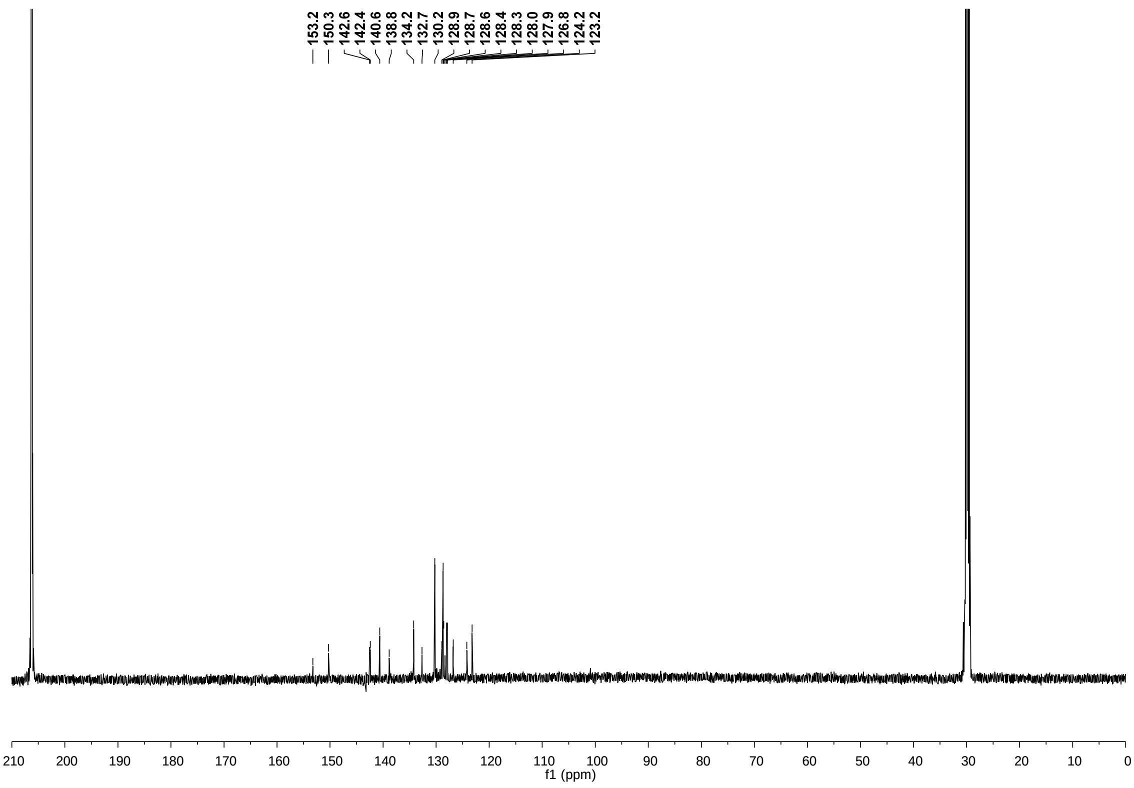
1,8-Bis[(*E*)-2-(phenylsulfonyl)vinyl]- *N*-(2-pyridyl)sulfonyl-9H-carbazole (8)

^{1}H NMR (300 MHz, $CDCl_3$)



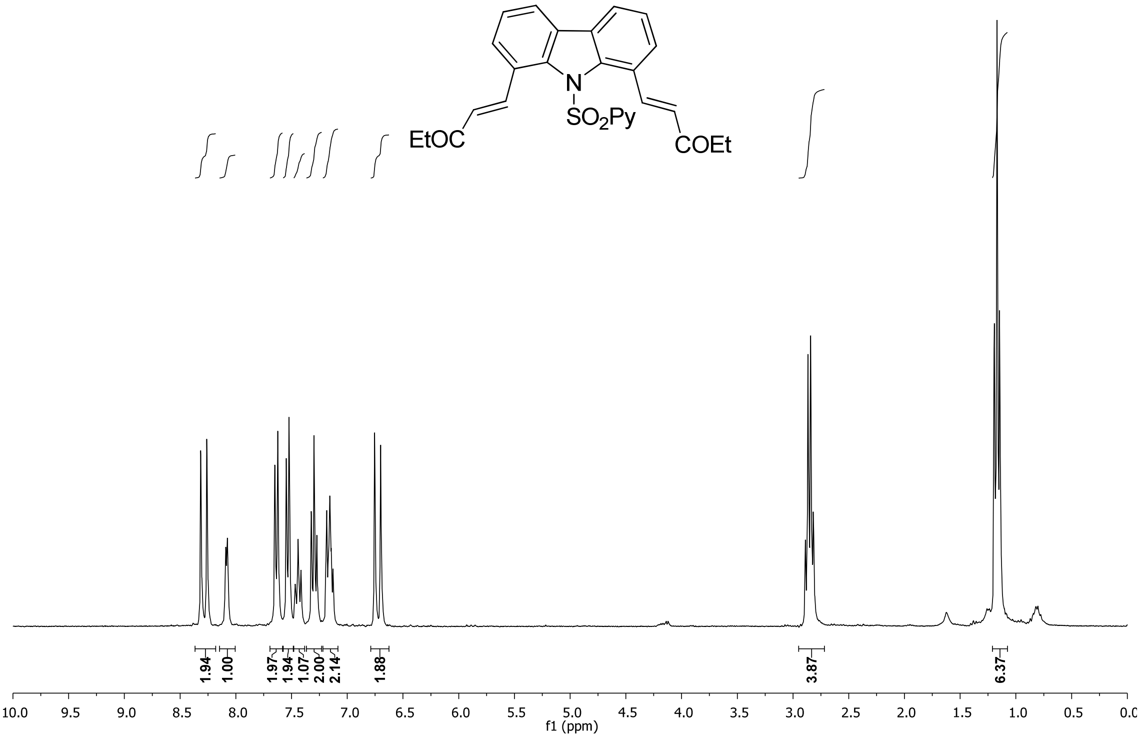


^{13}C NMR (125 MHz, acetone-d_6)

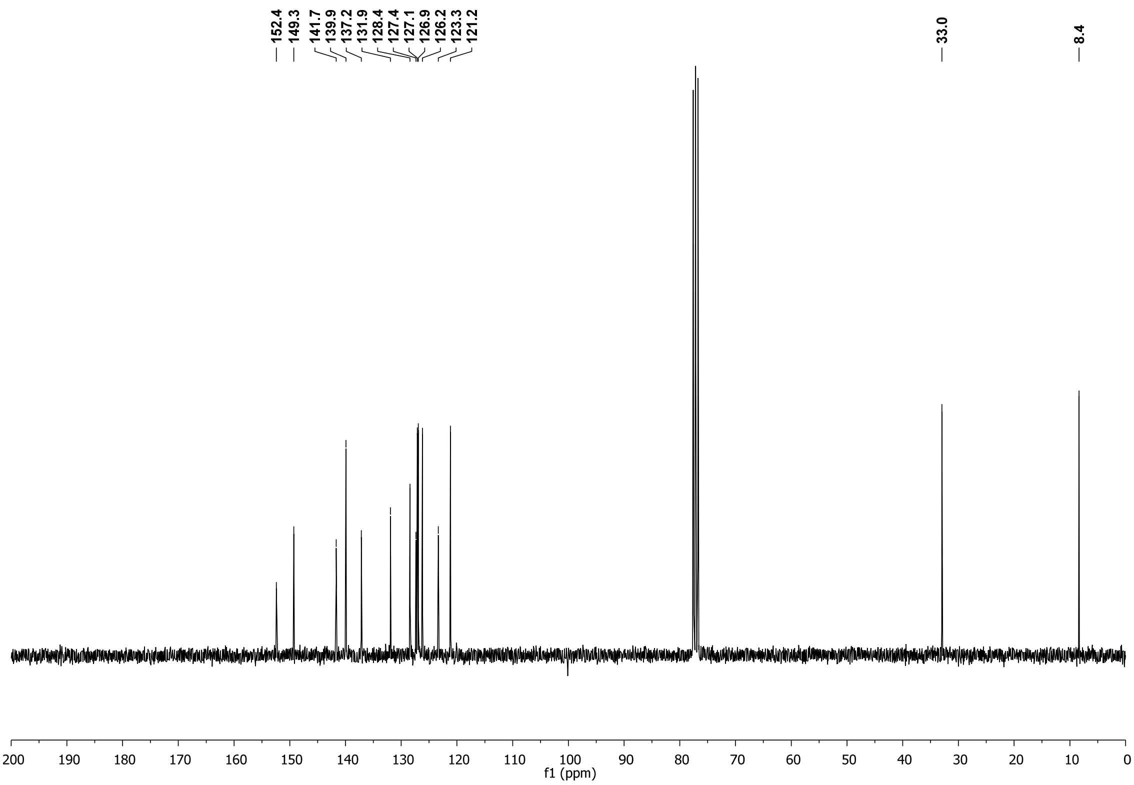


(*E*,*E*)-1,1'-[*N*-(2-Pyridyl)sulfonyl-9H-carbazole-1,8-diyl]bis(pent-1-en-3-one) (9)

^{1}H NMR (300 MHz, $CDCl_3$)

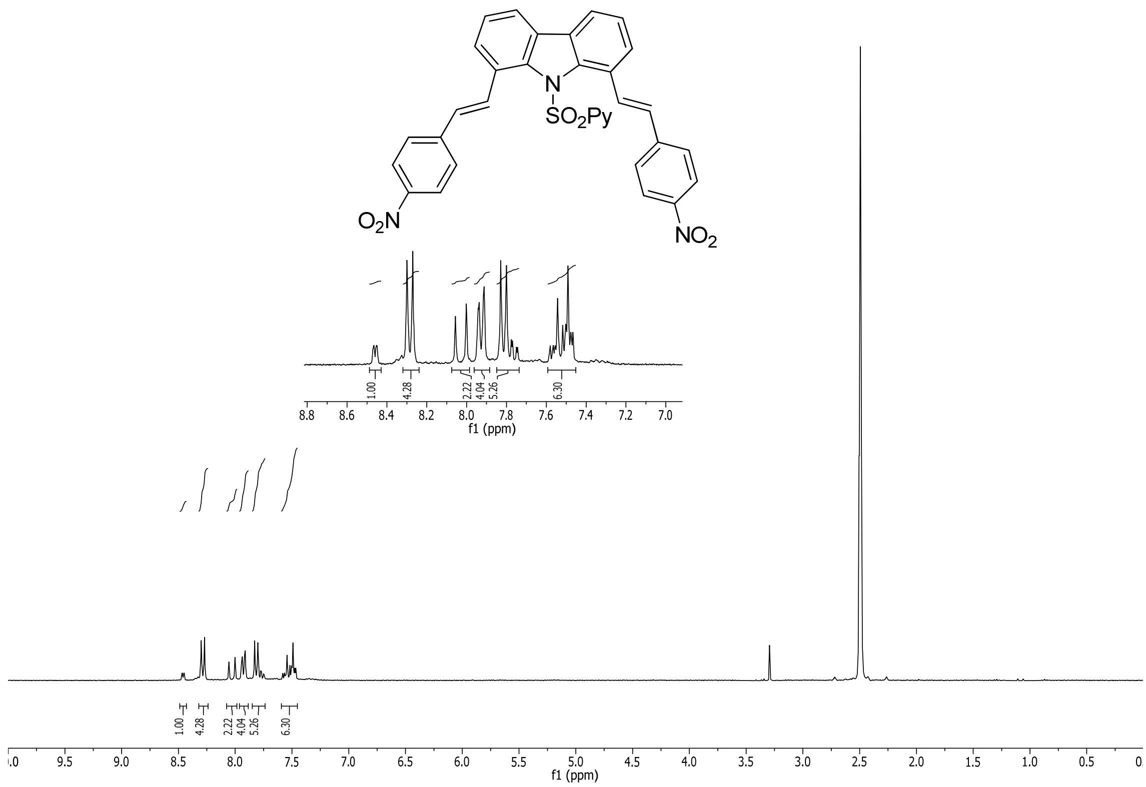


^{13}C NMR (75 MHz, $CDCl_3$)

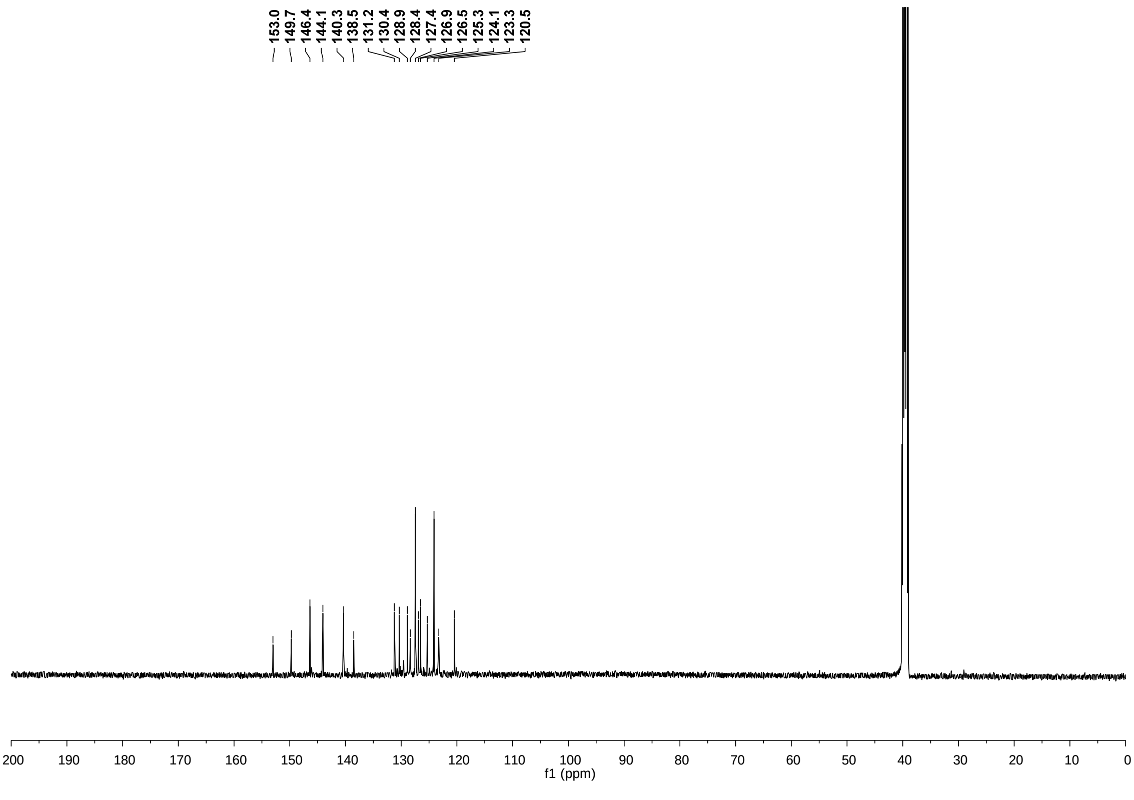


1,8-Bis[(*E*)-4-nitrostyryl]- *N*-(2-pyridyl)sulfonyl-9H-carbazole (10)

^{1}H NMR (300 MHz, DMSO-d_6)

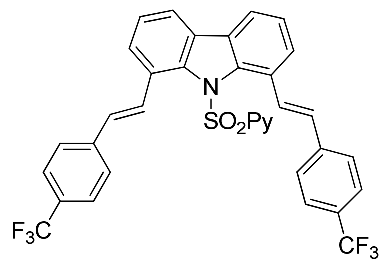


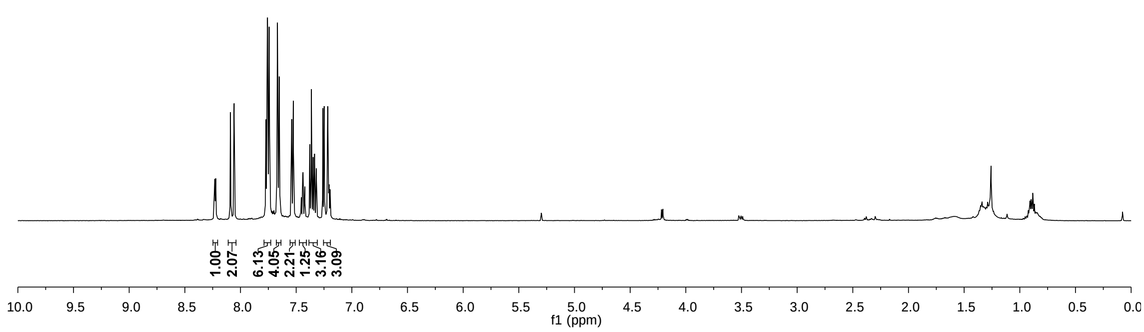
^{13}C NMR (125 MHz, DMSO-d_6)



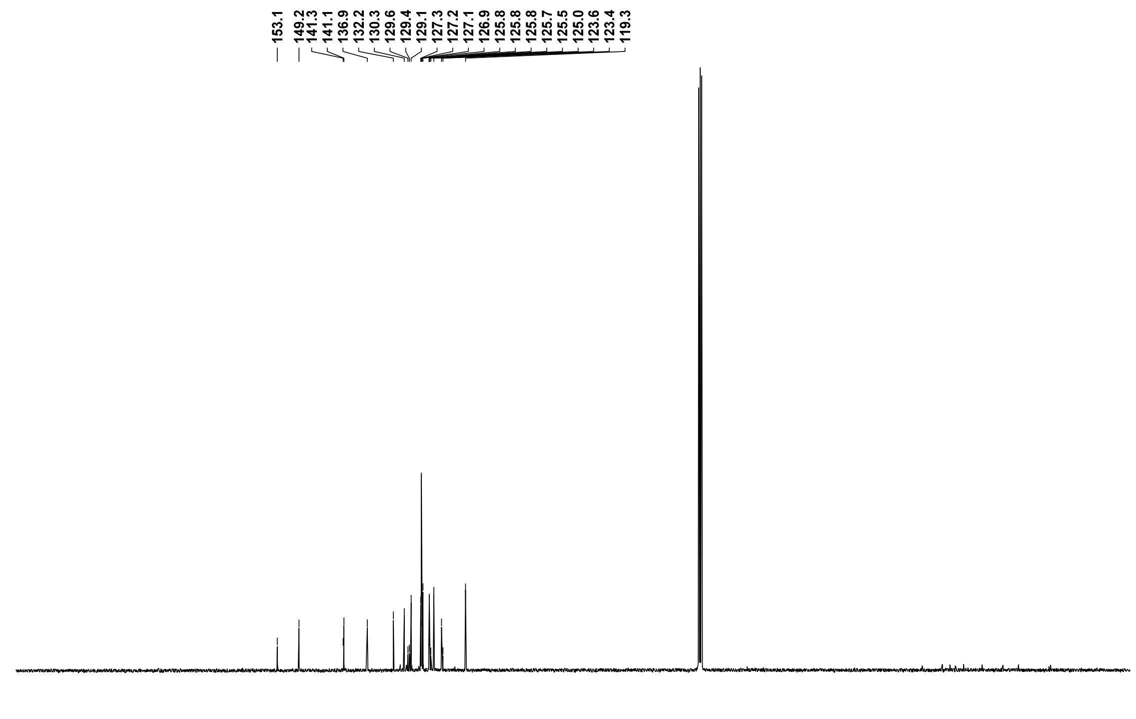
1,8-Bis[(*E*)-4-(trifluoromethyl)styryl]-*N*-(2-pyridyl)sulfonyl-9H-carbazole (11)

^{1}H NMR (500 MHz, $CDCl_3$)



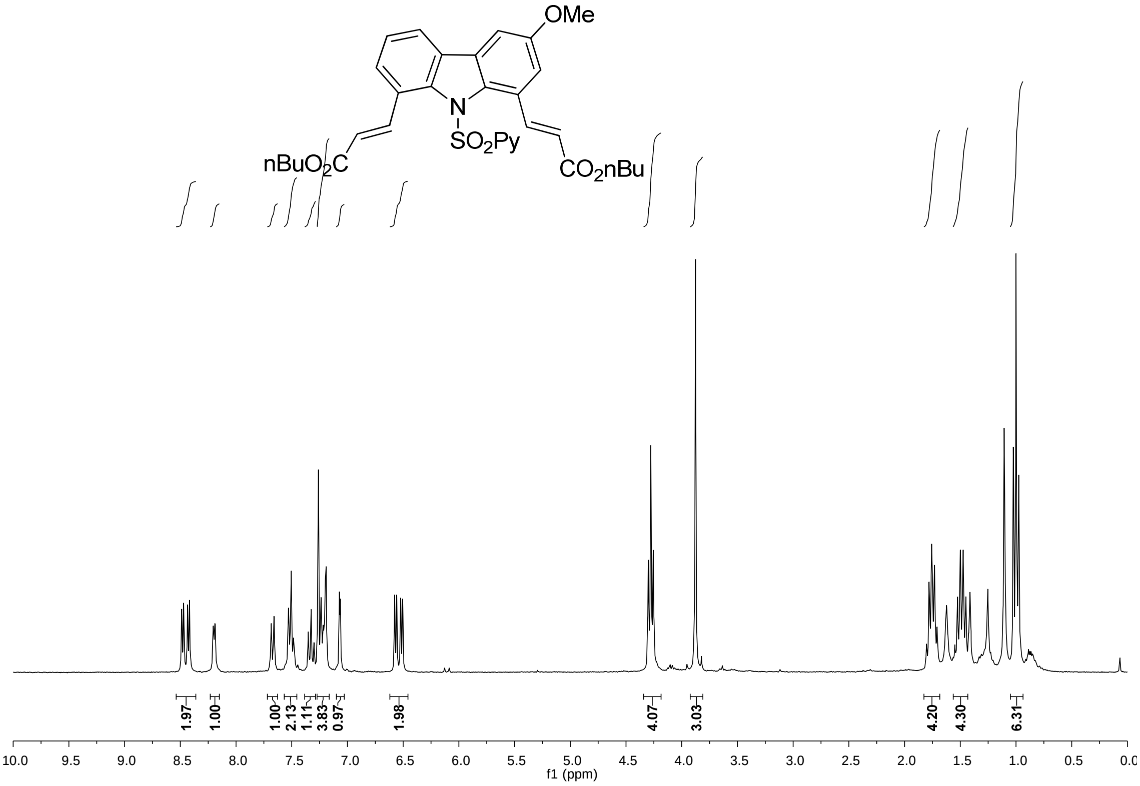


^{13}C NMR (125 MHz, $CDCl_3$)

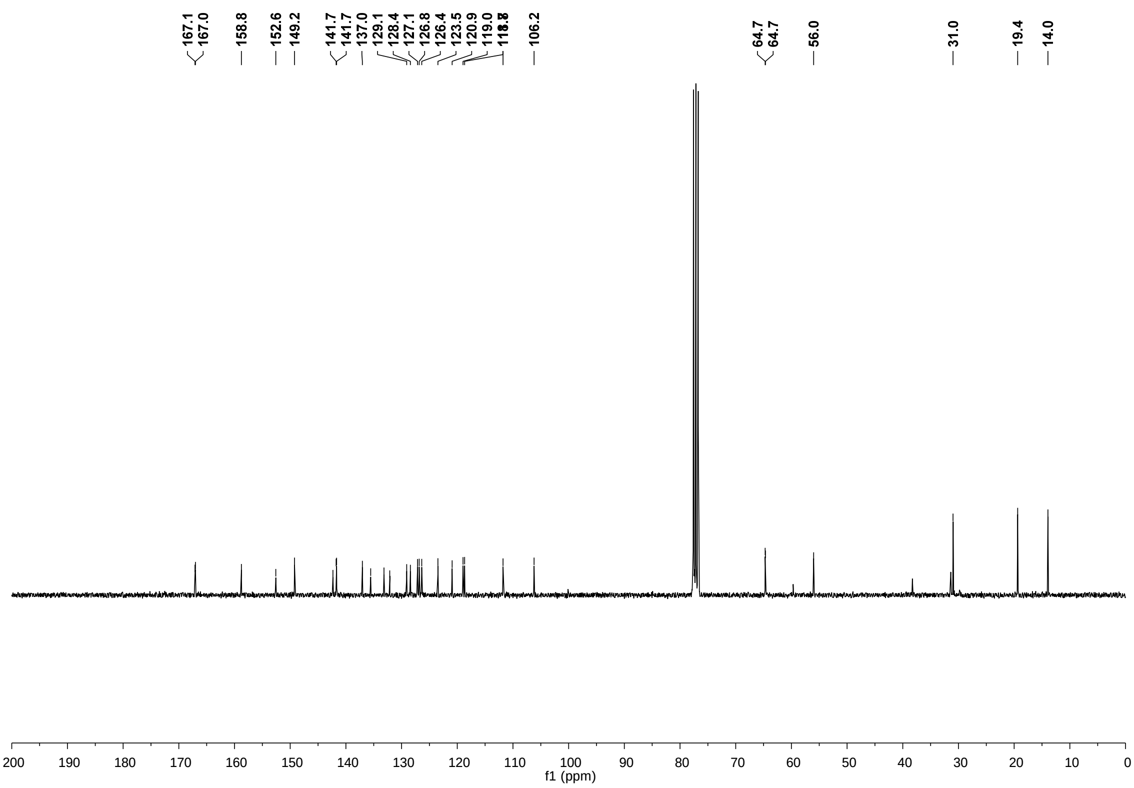


(*E*,*E*)-Dibutyl 3,3'-[3-methoxy-*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (18)

^{1}H NMR (300 MHz, $CDCl_3$)

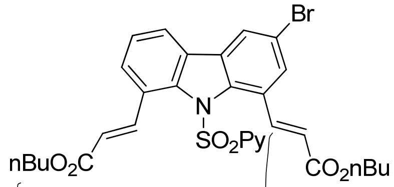


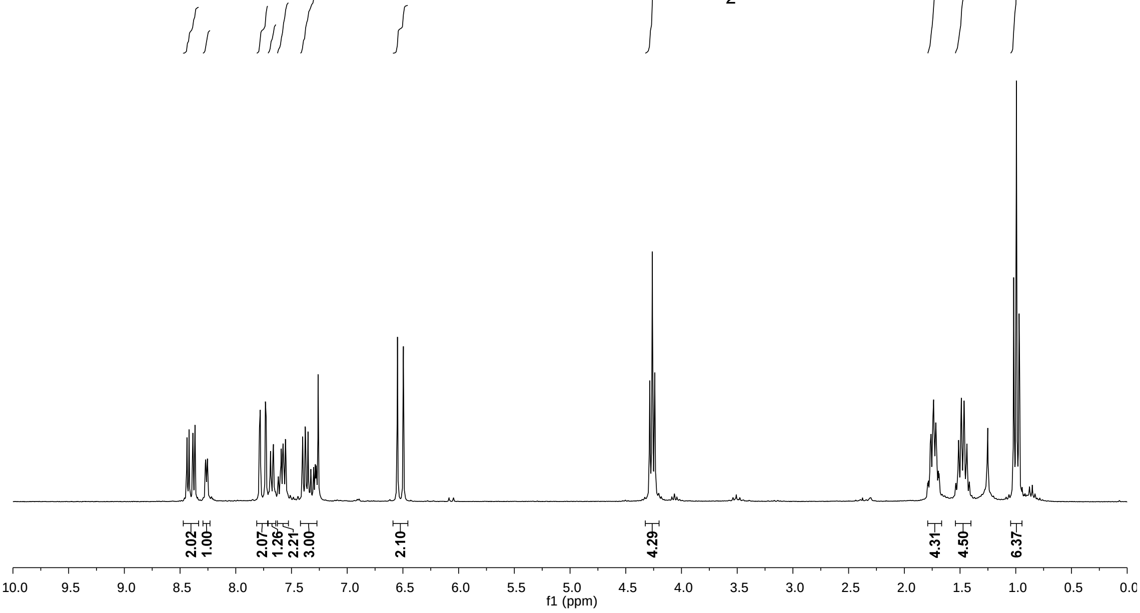
^{13}C NMR (75 MHz, $CDCl_3$)



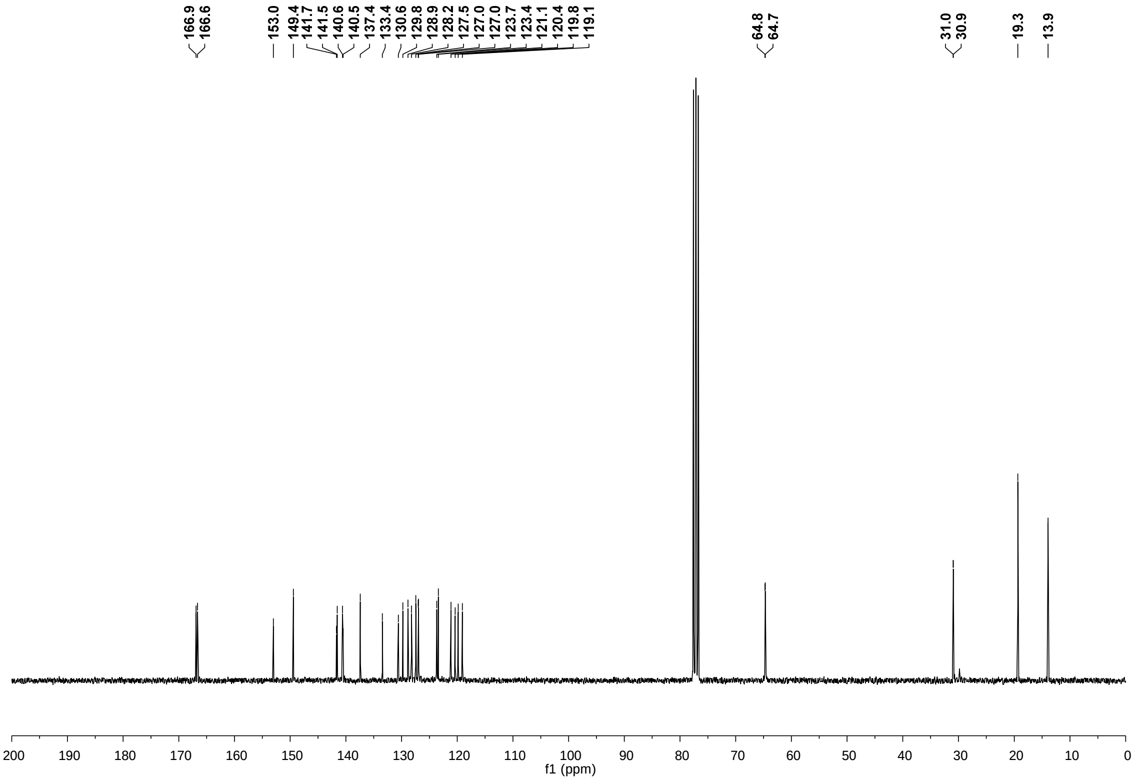
(*E*,*E*)-Dibutyl 3,3'-[3-bromo-*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (19)

^{1}H NMR (300 MHz, $CDCl_3$)



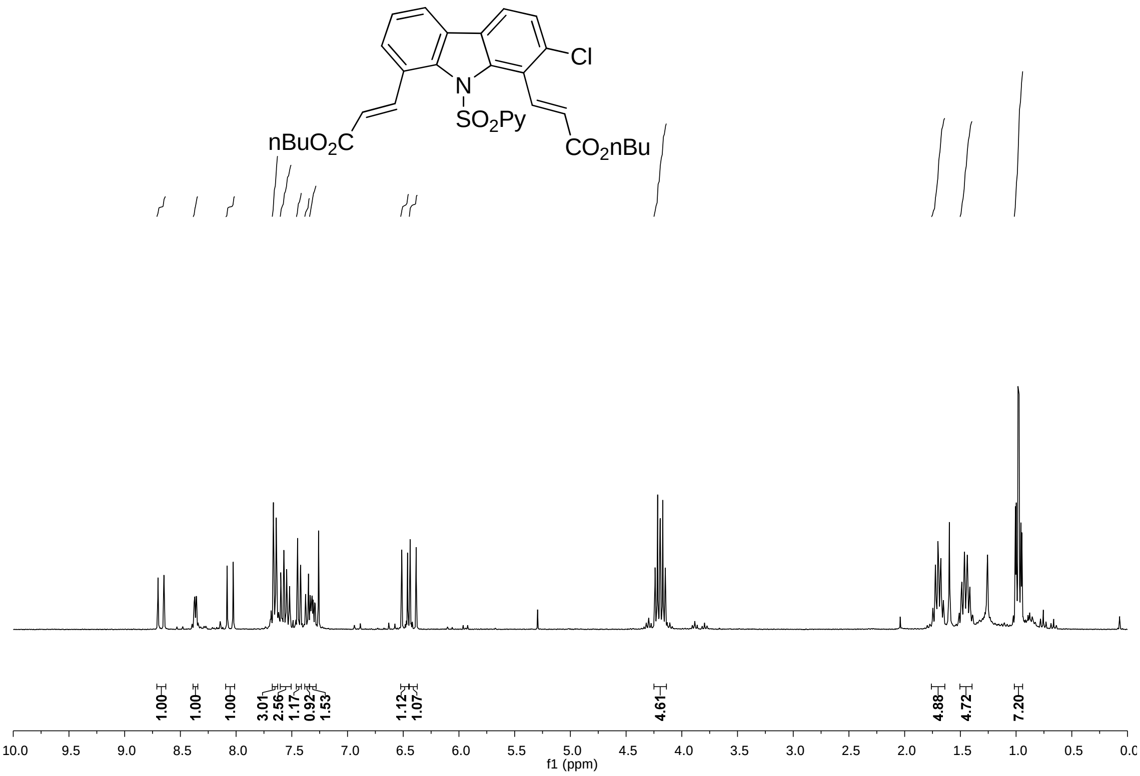


^{13}C NMR (75 MHz, $CDCl_3$)

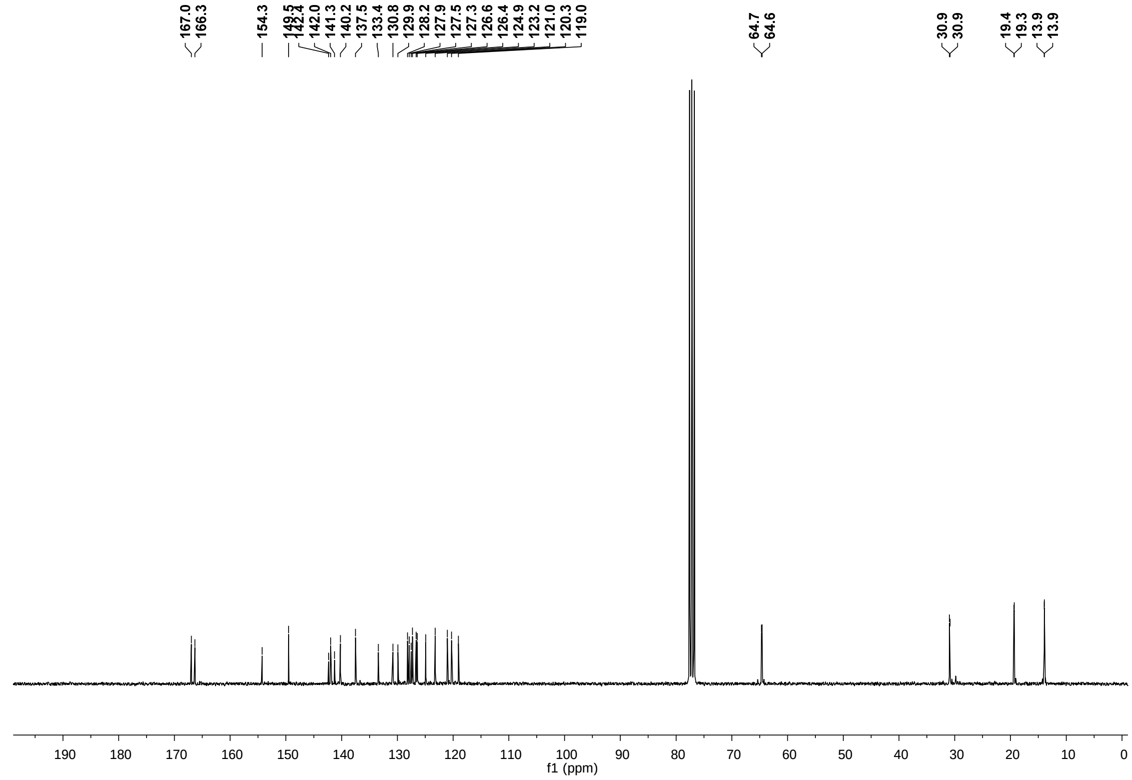


(*E*,*E*)-Dibutyl 3,3'-[2-chloro-*N*-(2-pyridyl)sulfonyl-9H-carbazole-1,8-diyl]diacrylate (20)

^{1}H NMR (300 MHz, $CDCl_3$)

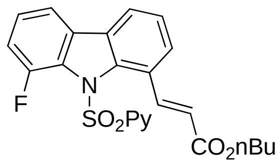


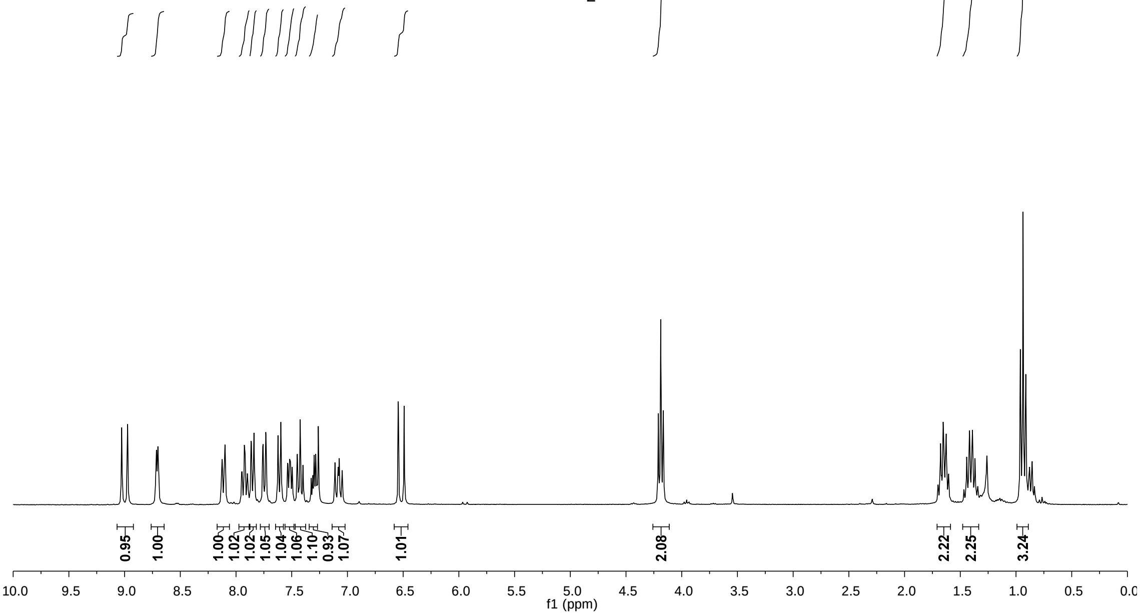
^{13}C NMR (75 MHz, $CDCl_3$)



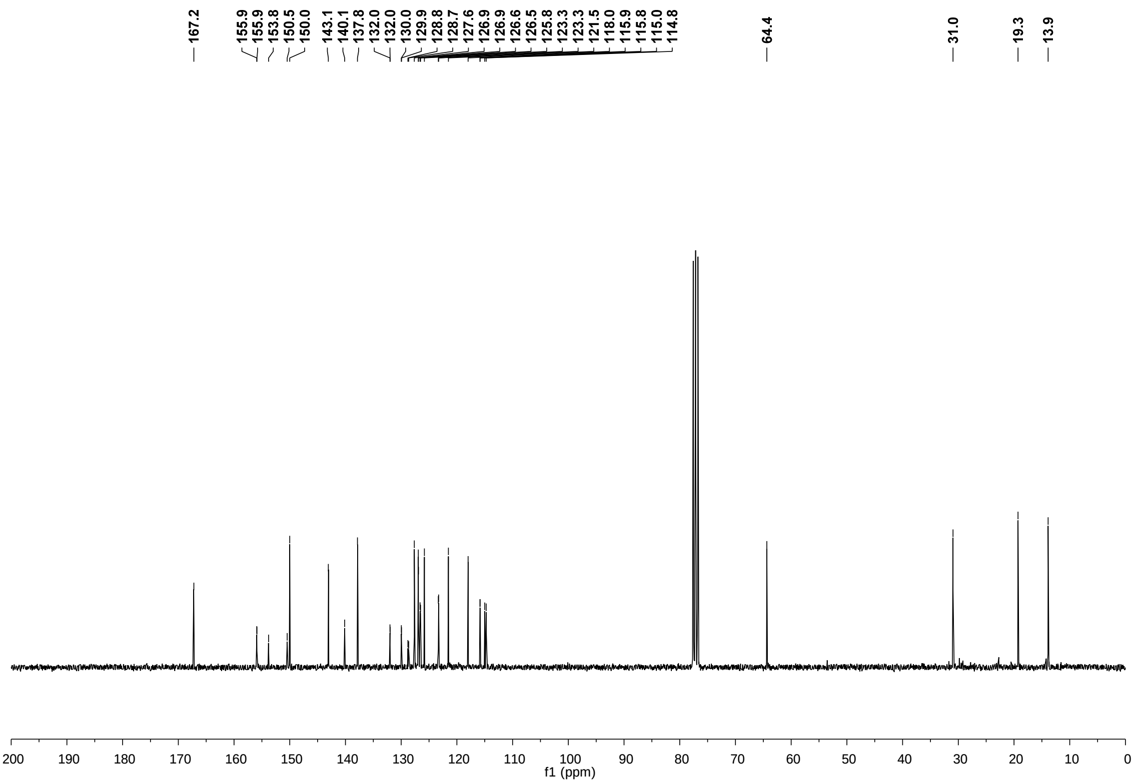
(*E*)-Butyl 3-[8-fluoro-*N*-(2-pyridyl)sulfonyl-9H-carbazol-1-yl]acrylate (21)

^{1}H NMR (300 MHz, $CDCl_3$)



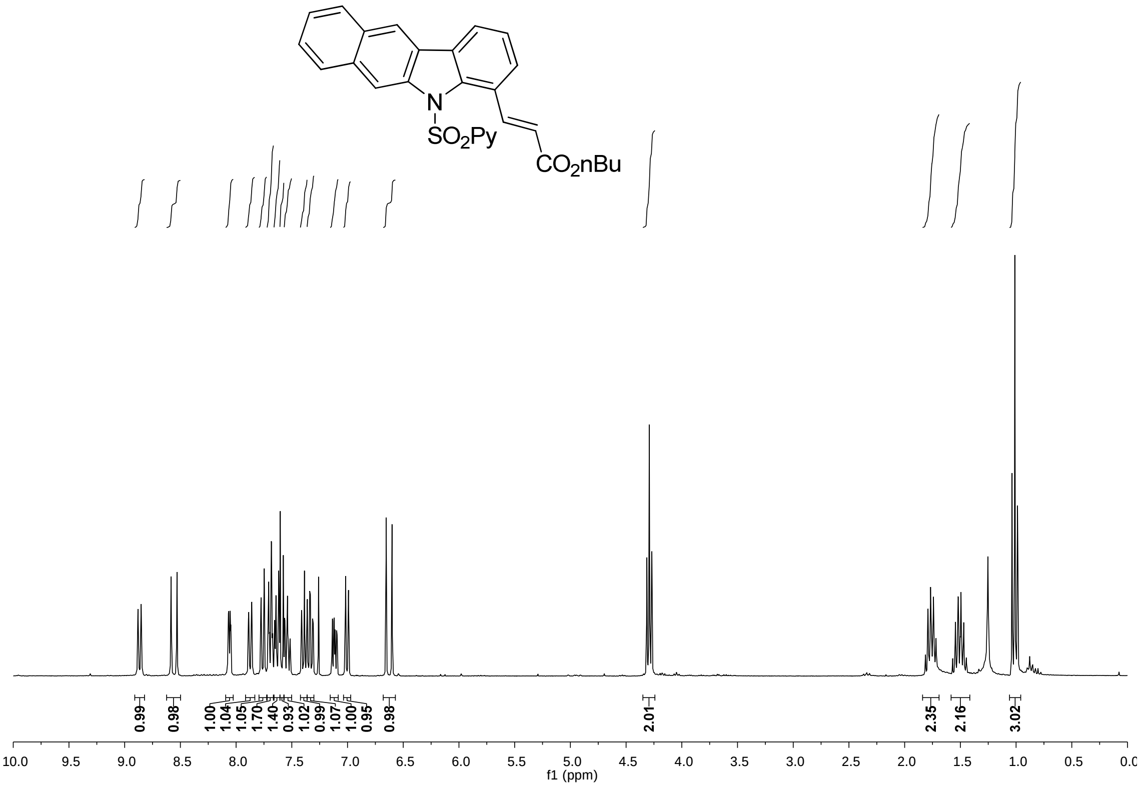


^{13}C NMR (75 MHz, $CDCl_3$)

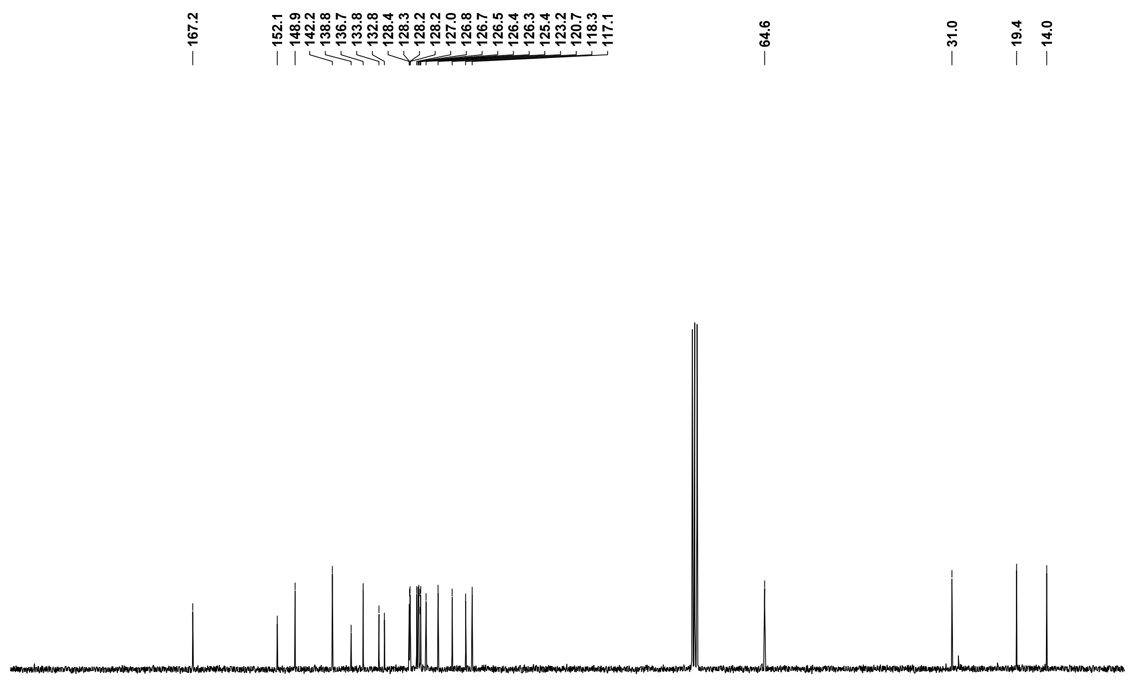


(*E*)-Butyl 3-{*N*-(2-pyridyl)sulfonyl-5H-benzo[b]carbazol-4-yl}acrylate (22)

^{1}H NMR (300 MHz, $CDCl_3$)

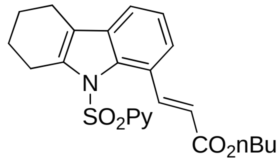


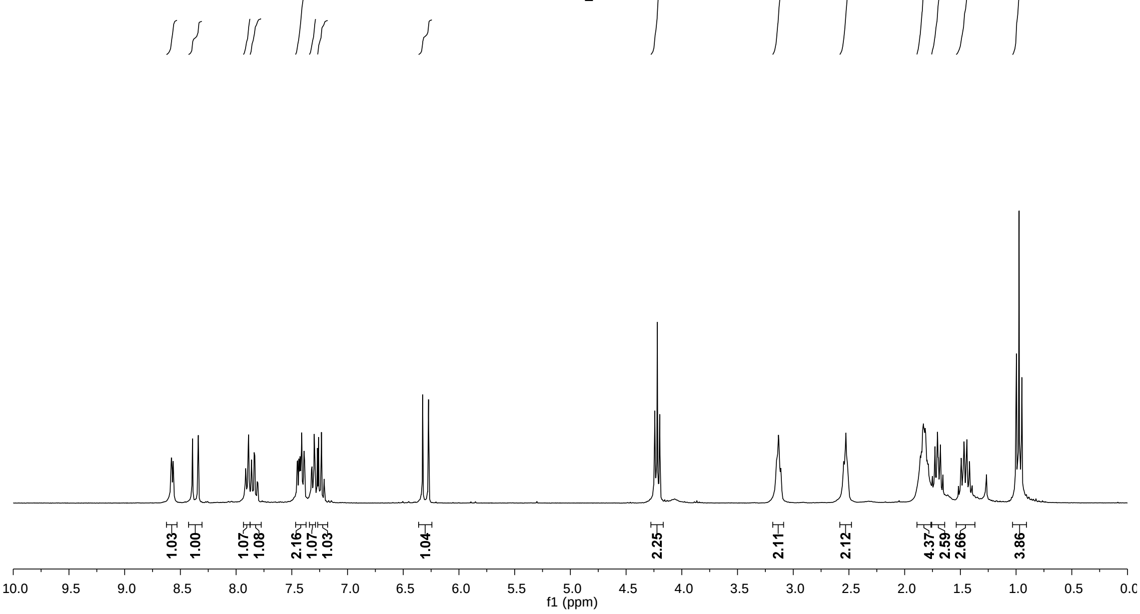
^{13}C NMR (75 MHz, $CDCl_3$)



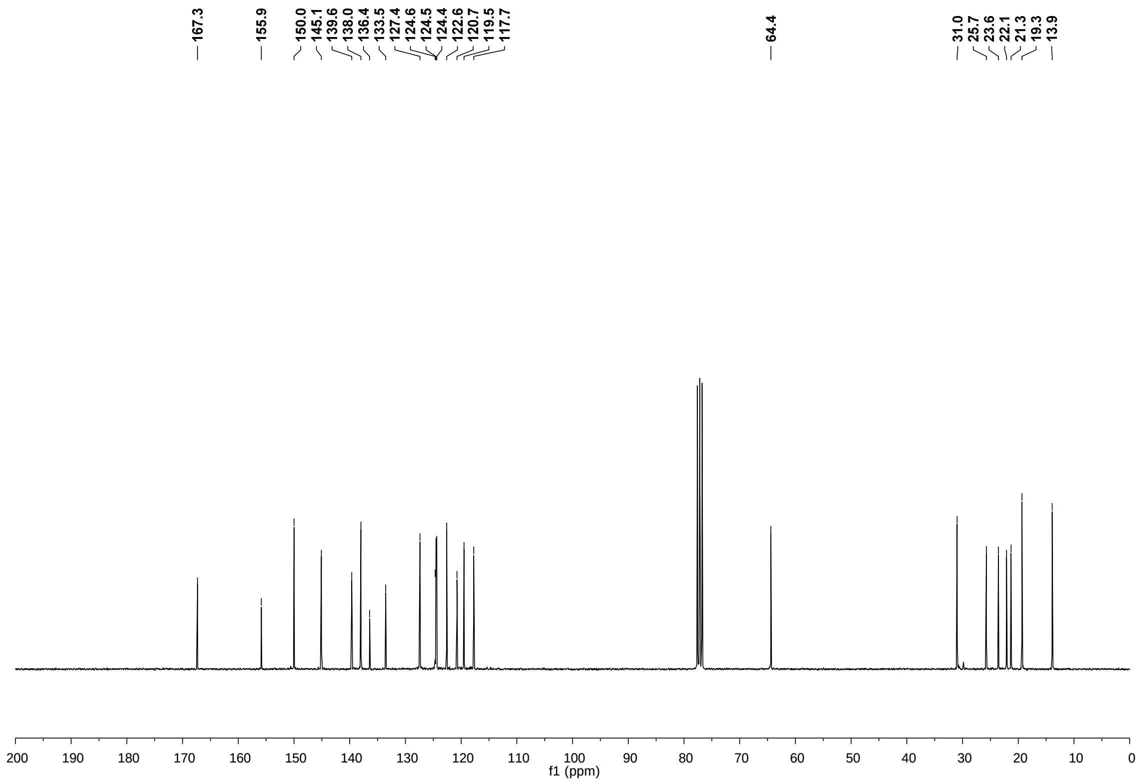
(*E*)-Butyl 3-*N*-(2-pyridyl)sulfonyl-2,3,4,9-tetrahydro-1H-carbazol-8-yl]acrylate (23)

^{1}H NMR (300 MHz, $CDCl_3$)



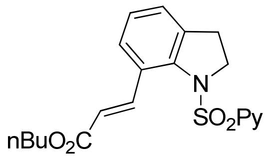


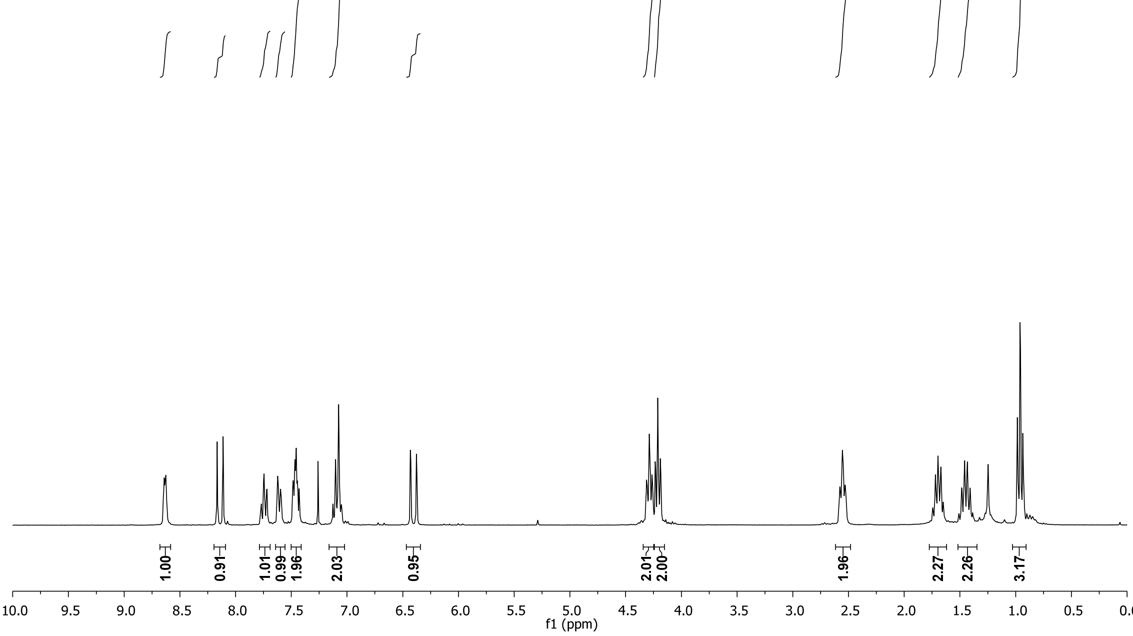
^{13}C NMR (75 MHz, $CDCl_3$)



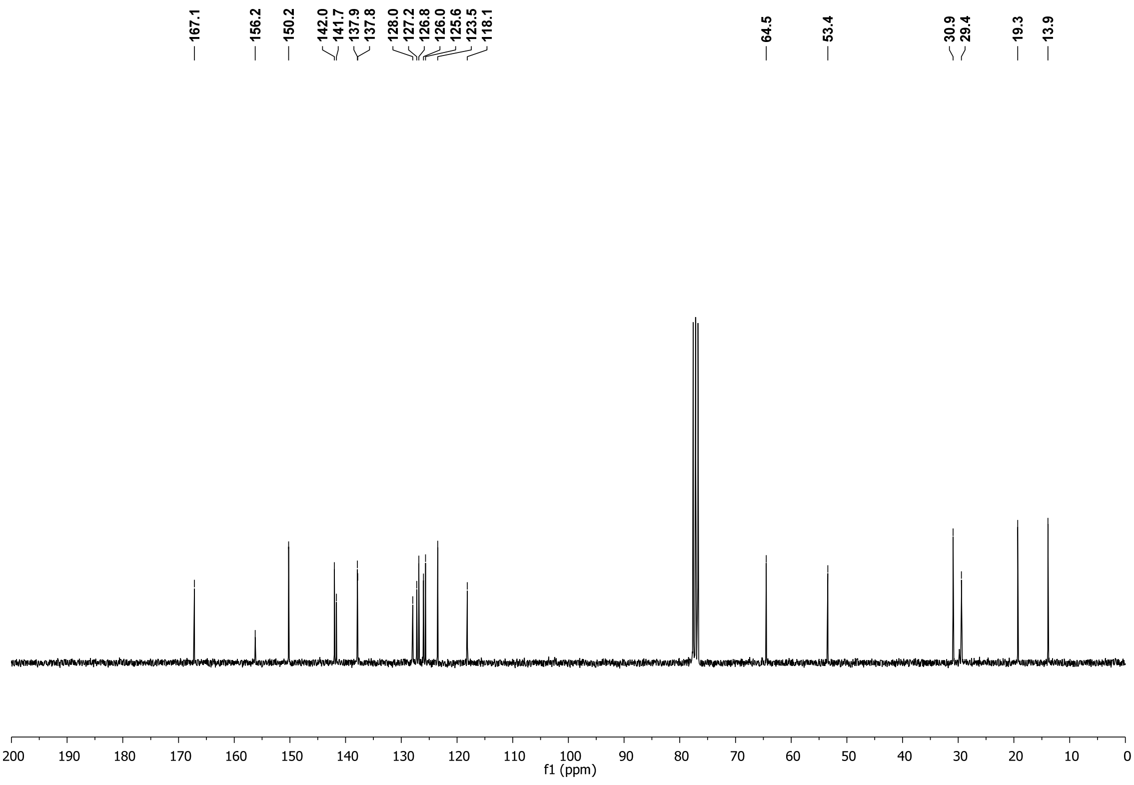
(*E*)-Butyl 3-[*N*-(2-pyridyl)sulfonyl)indolin-7-yl]acrylate (25)

^{1}H NMR (300 MHz, $CDCl_3$)



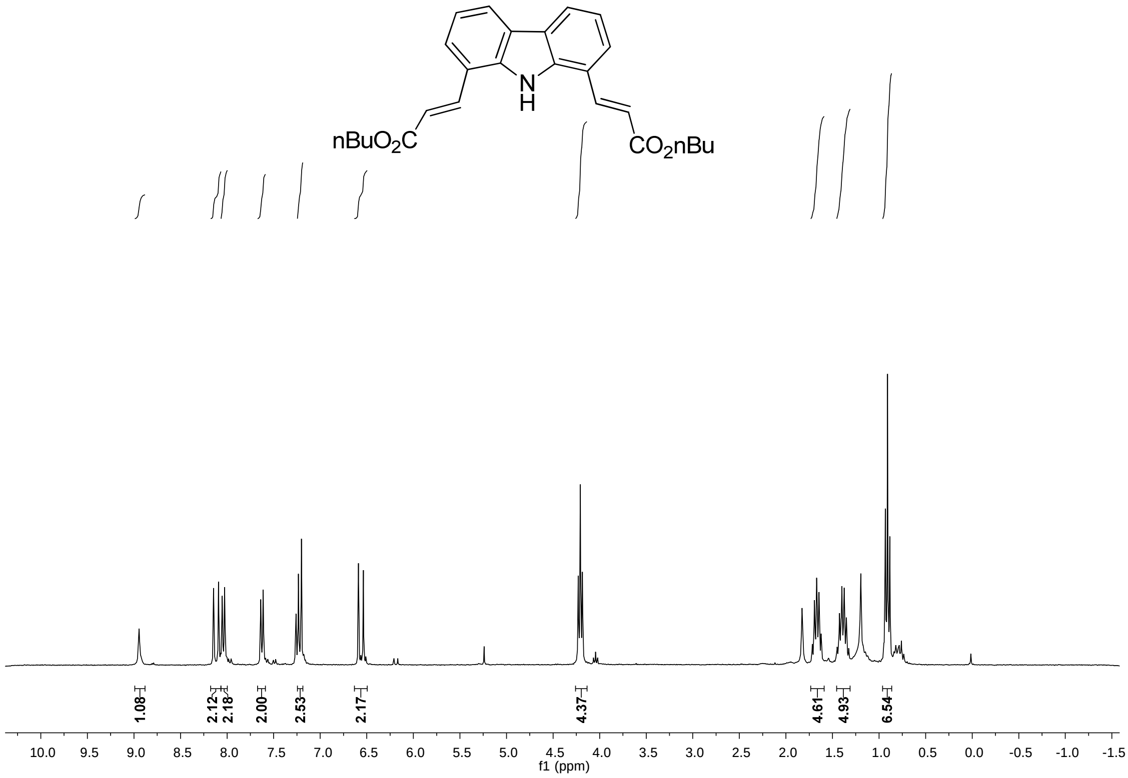


^{13}C NMR (75 MHz, $CDCl_3$)

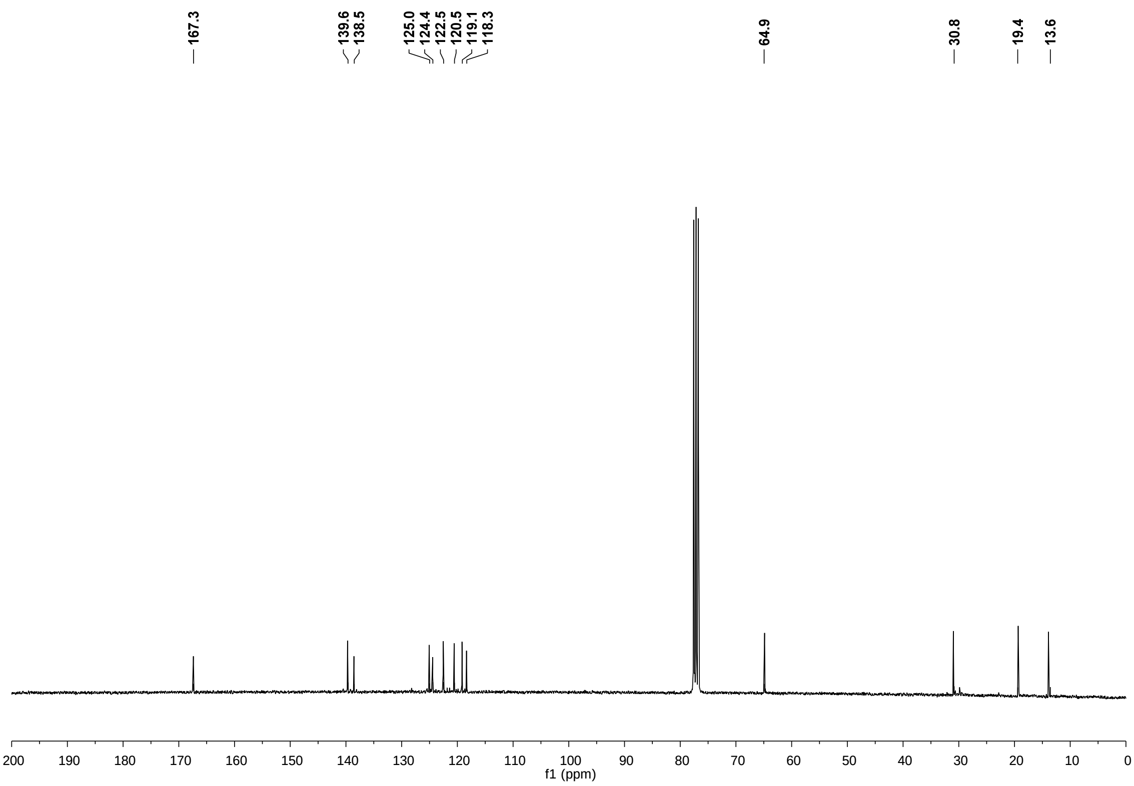


(*E*,*E*)-dibutyl 3,3'-(9H-carbazole-1,8-diyl)diacrylate (26)

^{1}H NMR (300 MHz, $CDCl_3$)

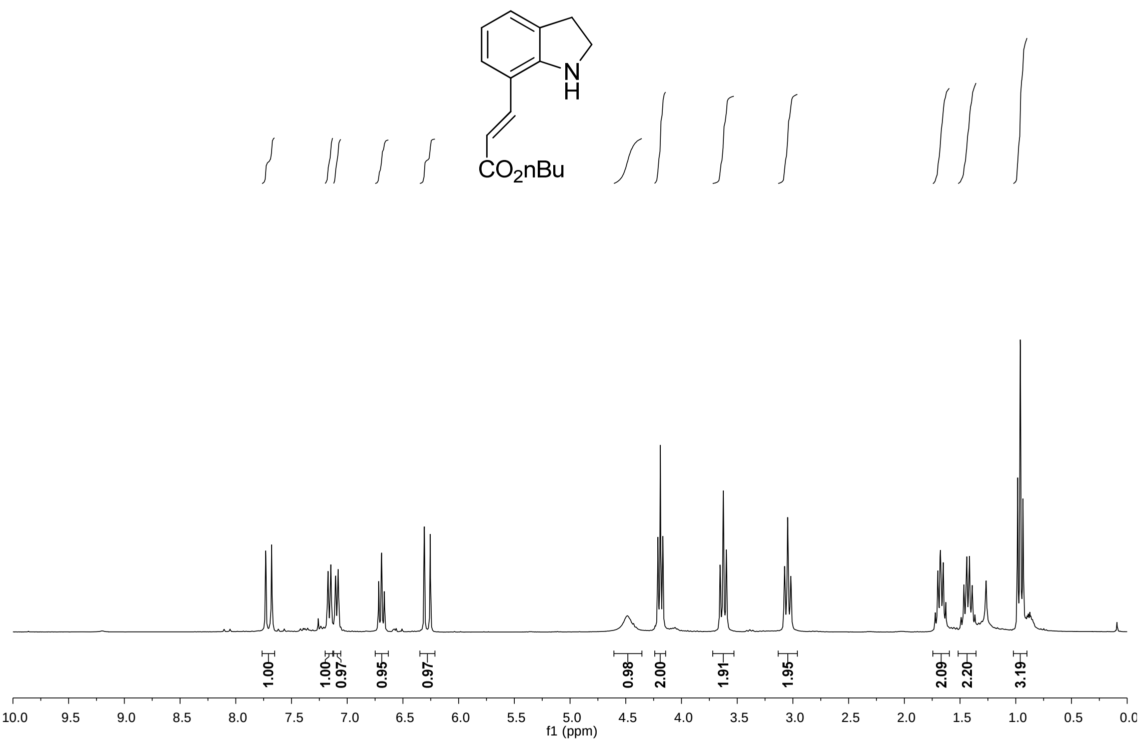


^{13}C NMR (75 MHz, $CDCl_3$)

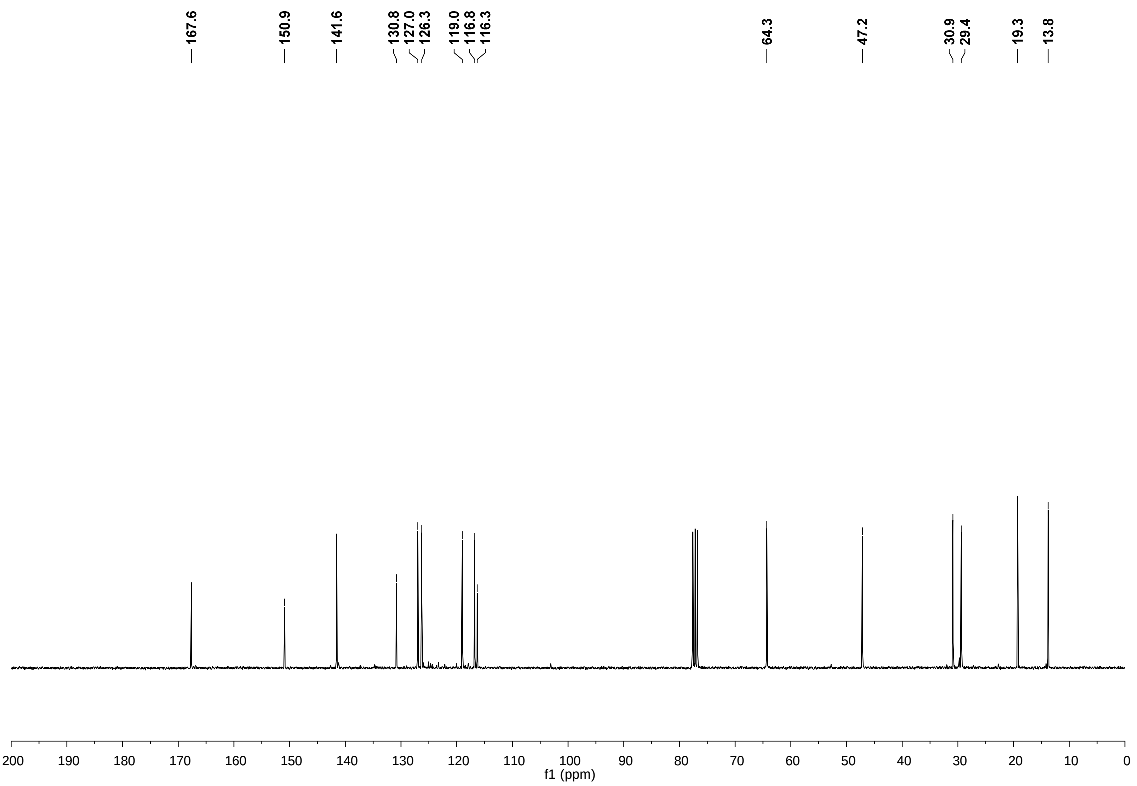


(*E*)-Butyl 3-(indolin-7-yl)acrylate (28)

^{1}H NMR (300 MHz, $CDCl_3$)

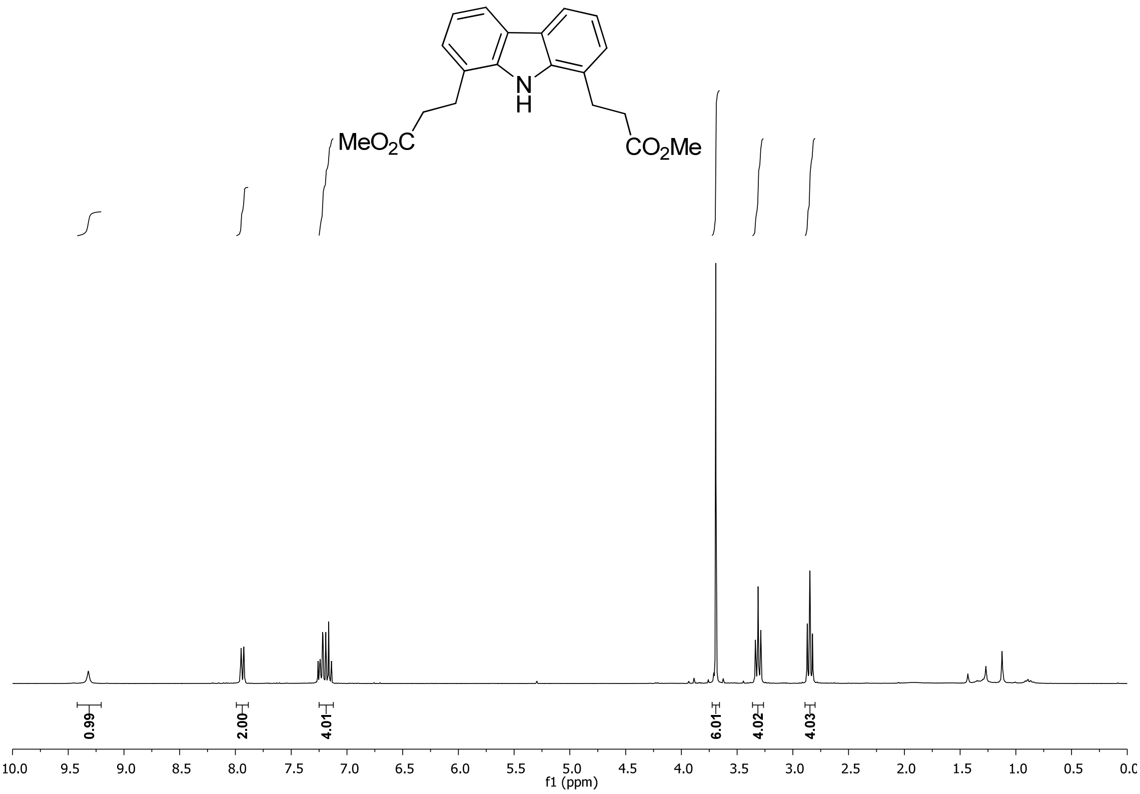


^{13}C NMR (75 MHz, $CDCl_3$)

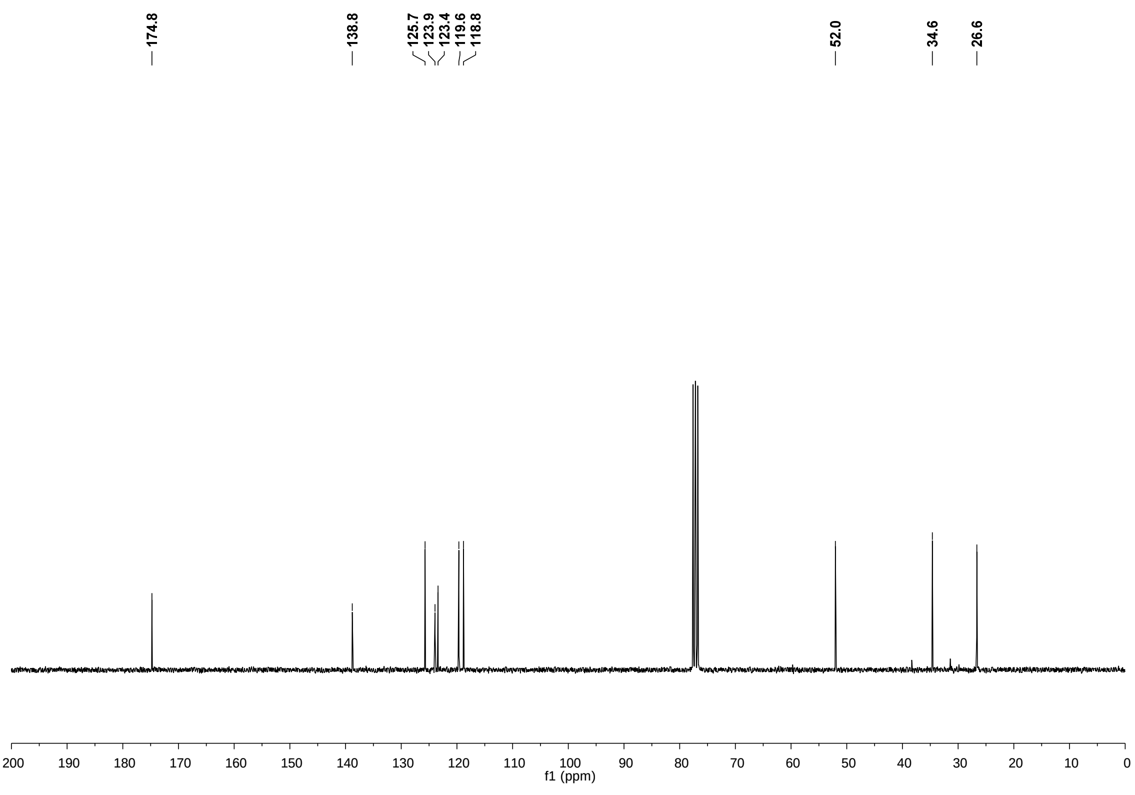


Dimethyl 3,3'-(9H-carbazole-1,8-diyl)dipropanoate (27)

^{1}H NMR (300 MHz, $CDCl_3$)

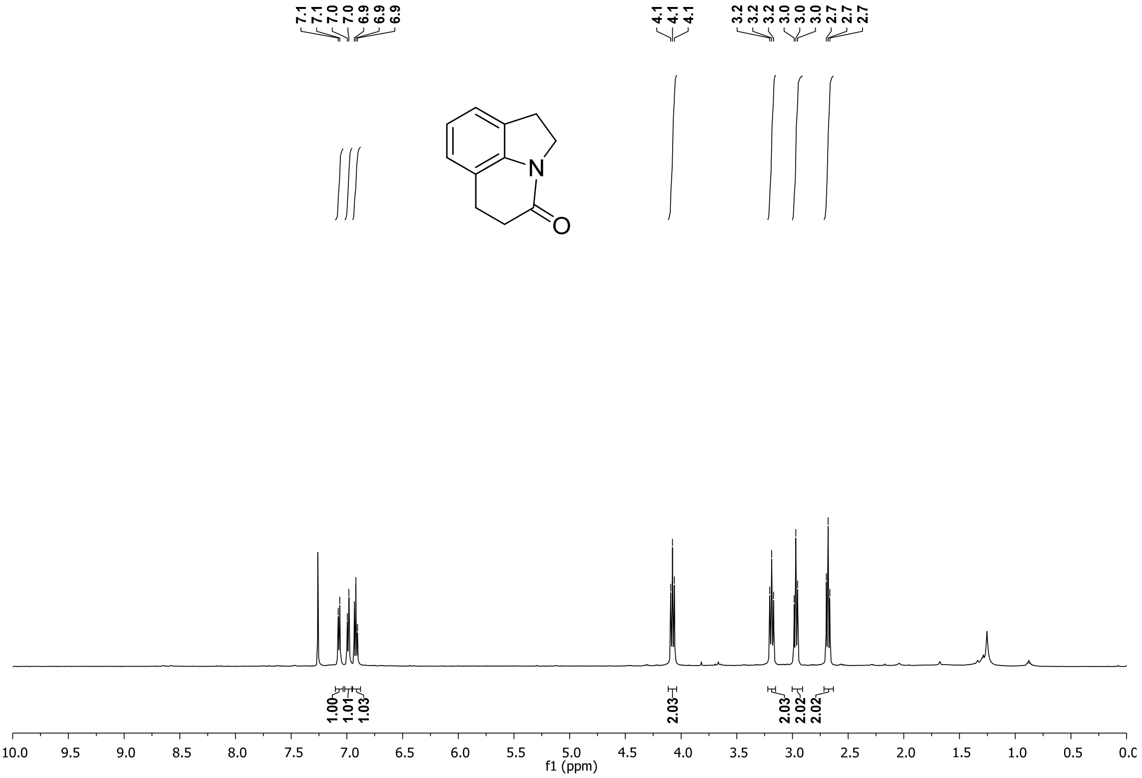


^{13}C NMR (75 MHz, $CDCl_3$)

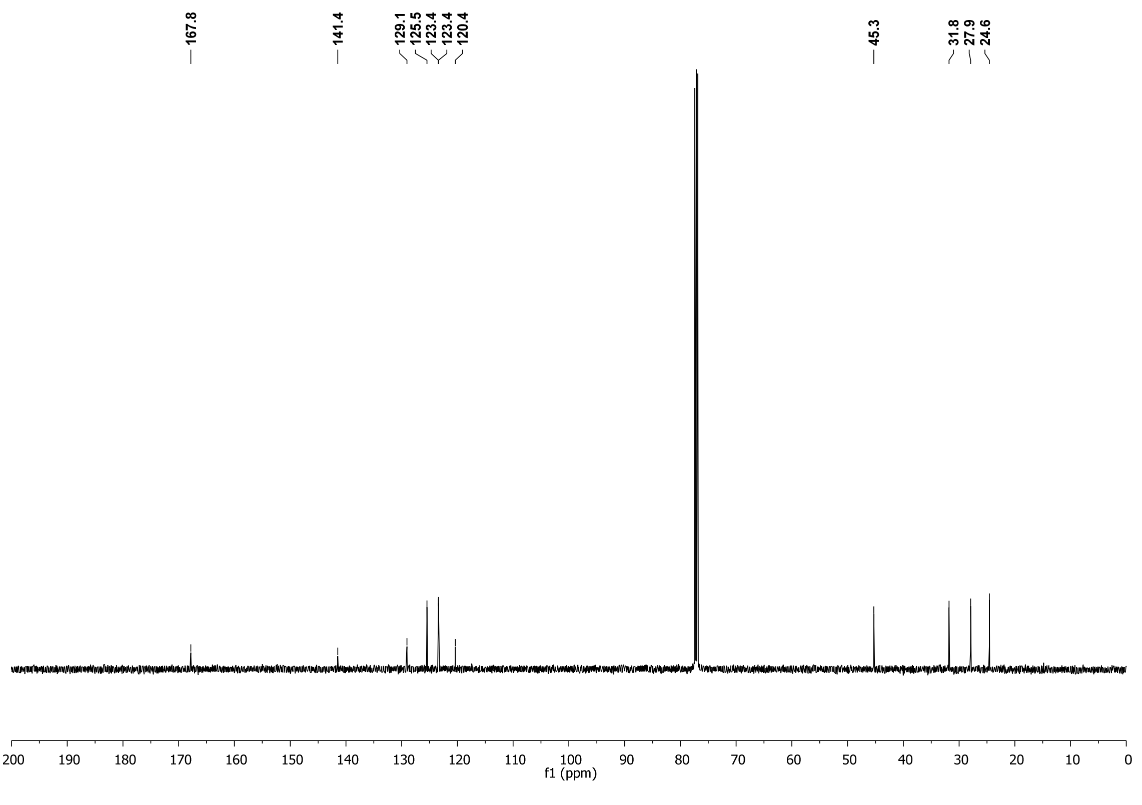


1,2,5,6-Tetrahydropyrrolo[3,2,1-ij]quinolin-4-one (29)

^{1}H NMR (500 MHz, $CDCl_3$)

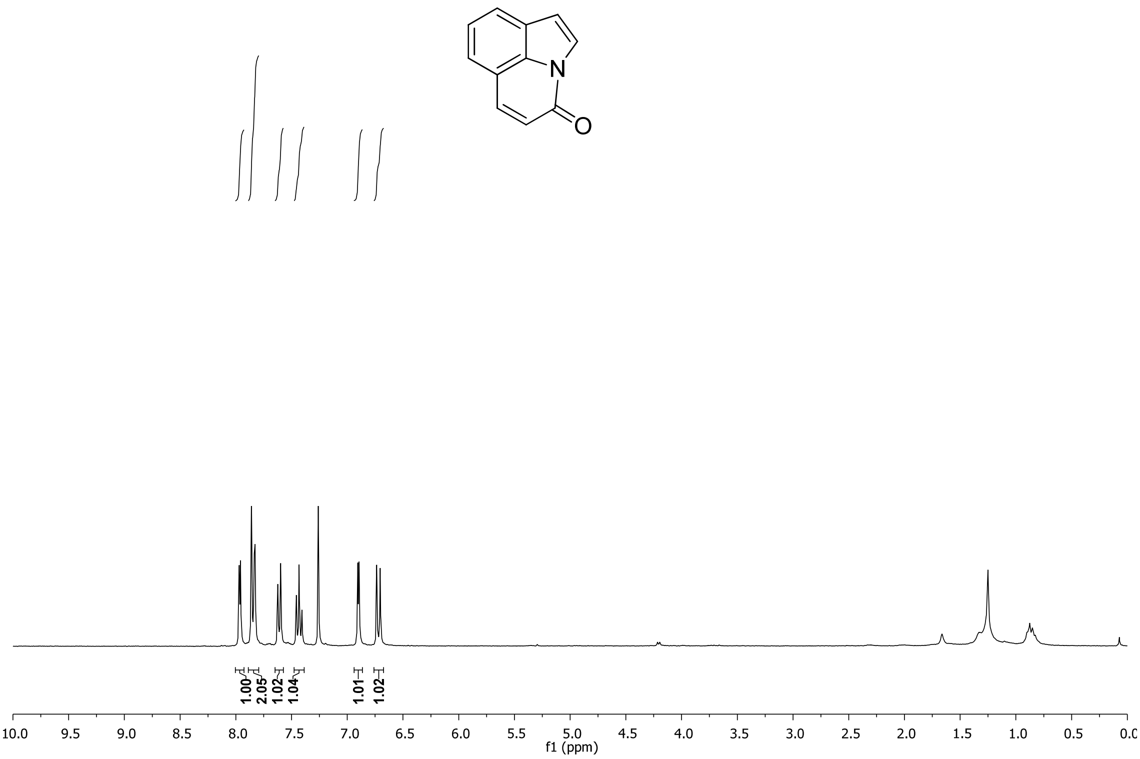


^{13}C NMR (125 MHz, $CDCl_3$)



Pyrrolo[3,2,1-ij]quinolin-4-one (30)

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)