Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Gold-catalyzed benzannulations of 2-alkenylindoles with alkynes: a protecting-group-free regioselective approach to carbazoles

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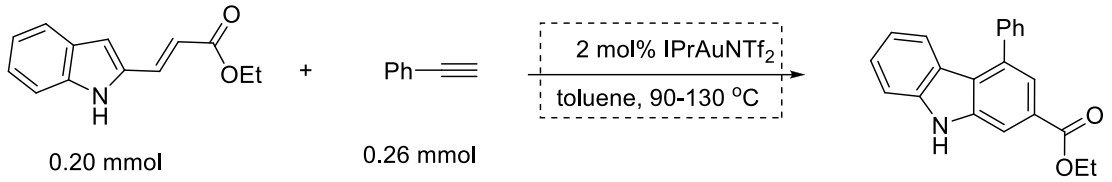
General

NMR spectra were recorded on a Bruker-400 MHz or JEOL-400 MHz. ^{1}H NMR spectra were recorded at 400 MHz or JEOL-400 MHz and data are reported as follows: chemical shift in ppm using residue solvent peak as internal standard ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration. ^{13}C NMR spectra were recorded at 101 MHz and data are reported as follows: chemical shift in ppm using solvent residue peak as internal indicator ($CDCl_3$ δ 77.15 ppm). ^{19}F NMR spectra were recorded at 376 MHz. High resolution mass spectra were performed on a WATERS I-Class VION IMS QTof at the Instrumental Analysis Center of Xi'an Jiaotong University and are given in m/z. All reactions were carried out in flame dried glasswares. Commercial reagents and solvents were purchased from Energy Chemicals, China (purities ranging from 97% to 99.5%) and are used without further purification unless stated otherwise. TLC was performed on pre-coated glass plates visualized either with a UV lamp (254 nm), or using solutions of $KMnO_4$–K_2CO_3 in water followed by heating. Flash chromatography was performed on silica gel (230-400 mesh).

Scope of the 2-alkenylindole substrate

Ethyl 4-phenyl-9*H*-carbazole-2-carboxylate (3a)



0.20 mmol 0.26 mmol

(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (51.9 mg, 81% yield).

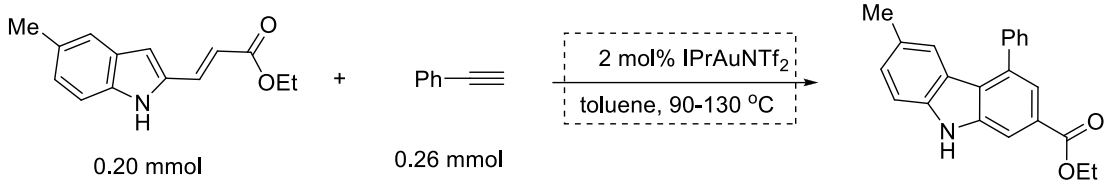
R_f 0.50 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.19 (s, 1H), 7.83 (s, 1H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.57 – 7.41 (m, 6H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.45 (q, *J* = 6.8 Hz, 2H), 1.44 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 141.1, 140.7, 139.4, 137.5, 129.3, 128.6, 128.0, 127.6, 127.1, 124.6, 123.2, 122.4, 122.1, 119.6, 111.4, 110.9, 61.2, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}NO_2^+$ 316.1332; Found 316.1343.

Ethyl 6-methyl-4-phenyl-9*H*-carbazole-2-carboxylate (3b)



(*E*)-Ethyl 3-(5-methyl-1*H*-indol-2-yl)acrylate (45.8 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (48.8 mg, 74% yield).

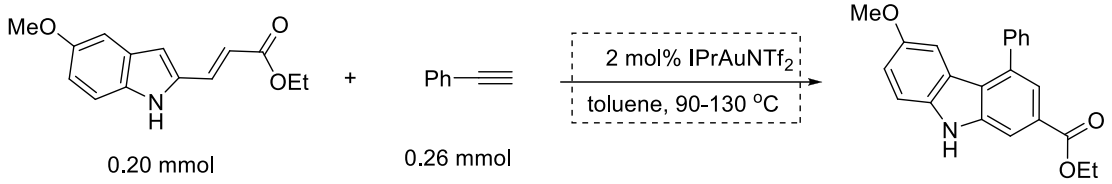
R_f 0.55 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.19 (s, 1H), 7.83 (s, 1H), 7.66 (d, *J* = 6.5 Hz, 2H), 7.57 – 7.55 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.30 -7.25 (m, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 140.7, 139.7, 139.4, 137.4, 129.3, 128.8, 128.6, 128.5, 127.9, 127.3, 124.4, 123.0, 122.5, 121.9, 111.4, 110.6, 61.2, 21.6, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_2^+$ 330.1489; Found 330.1499.

Ethyl 6-methoxy-4-phenyl-9*H*-carbazole-2-carboxylate (3c)



(*E*)-Ethyl 3-(5-methoxy-1*H*-indol-2-yl)acrylate (49.0 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol)) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (51.5 mg, 75% yield).

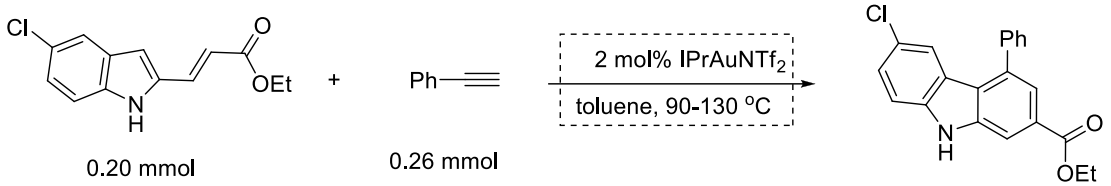
R_f 0.6 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.17 (s, 1H), 7.81 (s, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.59 – 7.43 (m, 3H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.92 (s, 1H), 4.45 (q, *J* = 6.6 Hz, 2H), 3.61 (s, 3H), 1.44 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 153.5, 140.5, 140.1, 137.3, 136.1, 129.4, 128.5, 128.0, 127.3, 124.4, 122.7, 121.4, 116.7, 111.7, 111.6, 105.4, 61.2, 55.6, 14.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_3^+$ 346.1438; Found 346.1447.

Ethyl 6-chloro-4-phenyl-9*H*-carbazole-2-carboxylate (3d)



(*E*)-Ethyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (49.9 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (48.8 mg, 70% yield).

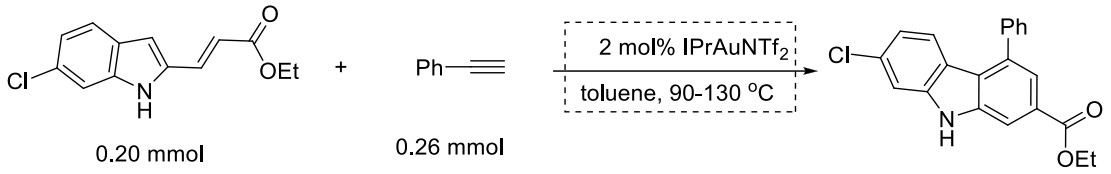
R_f 0.45 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, Chloroform-*d*) 8.52 (s, 1H), 8.17 (s, 1H), 7.82 (s, 1H), 7.73 – 7.47 (m, 5H), 7.44 (s, 1H), 7.37 (s, 2H), 4.45 (q, *J* = 6.7 Hz, 2H), 1.44 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 140.1, 140.0, 139.3, 137.8, 129.1, 128.8, 128.3, 128.2, 127.2, 125.0, 123.7, 123.5, 122.7, 122.3, 111.9, 111.6, 61.3, 14.5.

HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{20}ClN_2O_2^+$ 367.1208; Found 367.1172.

Ethyl 7-chloro-4-phenyl-9*H*-carbazole-2-carboxylate (3e)



(*E*)-Ethyl 3-(6-chloro-1*H*-indol-2-yl)acrylate (49.9 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (52.6 mg, 75% yield).

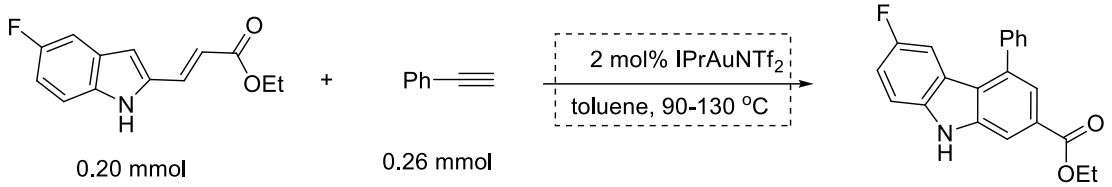
R_f 0.45 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.17 (s, 1H), 7.83 (s, 1H), 7.61 – 7.53 (m, 5H), 7.44 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.64 – 4.37 (m, 2H), 1.44 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 141.6, 140.3, 139.7, 137.4, 132.9, 129.2, 128.8, 128.1, 127.9, 124.0, 123.8, 122.6, 121.1, 120.3, 111.5, 110.9, 61.3, 14.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}ClNO_2^+$ 350.0942; Found 350.0961.

Ethyl 6-fluoro-4-phenyl-9*H*-carbazole-2-carboxylate (3f)



(*E*)-Ethyl 3-(5-fluoro-1*H*-indol-2-yl)acrylate (46.6 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (54.0 mg, 81% yield).

R_f 0.45 (Petroleum ether/EtOAc = 10/2).

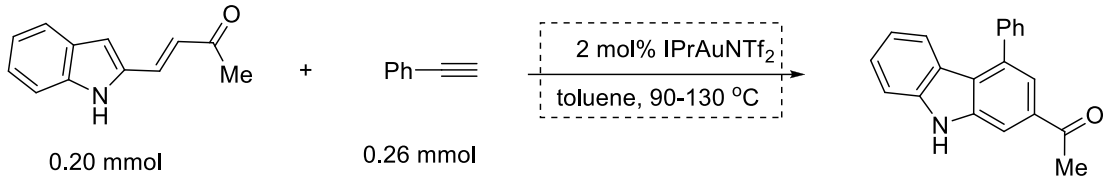
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 8.18 (s, 1H), 7.81 (s, 1H), 7.73 – 7.45 (m, 5H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.15 (t, *J* = 11.7 Hz, 2H), 4.44 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 140.4, 140.1, 137.8, 137.4, 129.2, 128.8, 128.2, 128.1, 122.0, 115.3, 115.0, 111.7, 111.4, 108.8, 108.6, 61.3, 14.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.96 (dd, *J* = 8.4, 3.7, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}CNFO_2^+$ 334.1238; Found 334.1246.

1-(4-Phenyl-9*H*-carbazol-2-yl)ethanone (3g)



(*E*)-4-(1*H*-indol-2-yl)but-3-en-2-one (37 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (40.4 mg, 71% yield).

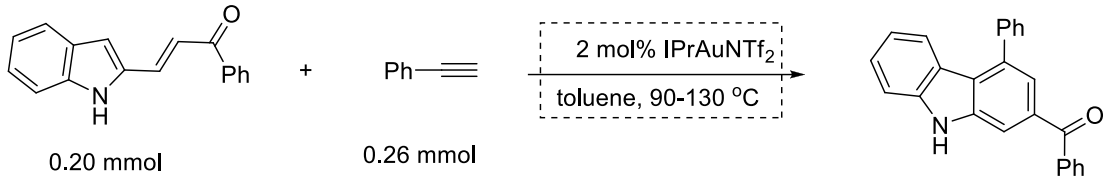
R_f 0.30 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.10 (s, 1H), 7.71 (s, 1H), 7.63 (d, *J* = 6.7 Hz, 2H), 7.58 – 7.42 (m, 6H), 7.01(t, *J* = 7.4 Hz, 1H), 2.72 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.5, 141.4, 140.5, 139.5, 137.5, 134.5, 129.3, 128.7, 128.1, 127.3, 124.9, 123.3, 122.3, 121.6, 119.7, 110.9, 109.8, 27.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{16}NO^+$ 286.1226; Found 286.1239.

Phenyl(4-phenyl-9*H*-carbazol-2-yl)methanone (3h)



(*E*)-3-(1*H*-indol-2-yl)-1-phenylprop-2-en-1-one (49.4 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 ºC until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (48.3 mg, 70% yield).

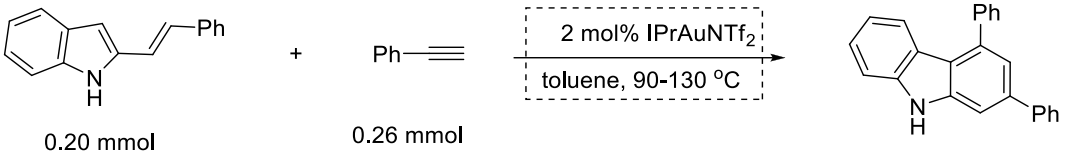
R_f 0.30 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.09 – 7.79 (m, 3H), 7.76 – 7.34 (m, 12H), 7.05 (t, *J* = 7.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.2, 141.3, 140.5, 139.4, 138.4, 137.4, 134.7, 132.3, 130.2, 129.3, 128.7, 128.4, 128.0, 127.2, 124.4, 123.2, 122.4, 119.7, 112.0, 111.0.

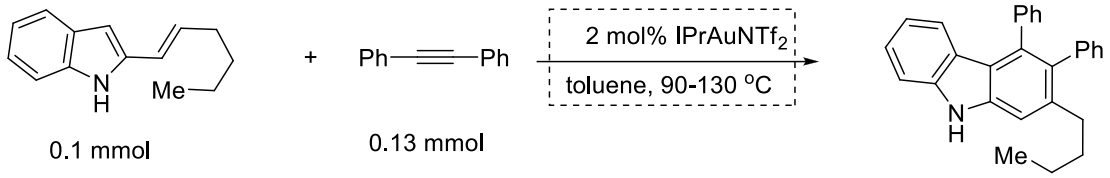
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{18}NO^+$ 348.1383; Found 348.1389.

2,4-Diphenyl-9*H*-carbazole (3i)



(*E*)-2-Styryl-1*H*-indole (43.8 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (50.1 mg, 79% yield). The titled compound is known. Its ^{1}H NMR is in accordance with the known literature: Lijun Shi, Xiang Zhong, Houde She, Ziqiang Lei and Fuwei Li. Manganese catalyzed C–H functionalization of indoles with alkynes to synthesize bis/trisubstituted indolylalkenes and carbazoles: the acid is the key to control selectivity. *Chem. Commun*., **2015**, *51*, 7136.

2-Butyl-3,4-diphenyl-9*H*-carbazole (3j)



(*E*)-2-(hex-1-enyl)-1*H*-indole (19.9 mg, 0.1 mmol), 1,2-diphenylethyne (23.0 mg, 0.13 mmol) and $IPrAuNTf_2$ (1.74 mg, 0.002 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.1 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (27.3 mg, 72% yield).

R_f 0.35 (Petroleum ether/EtOAc = 10/2).

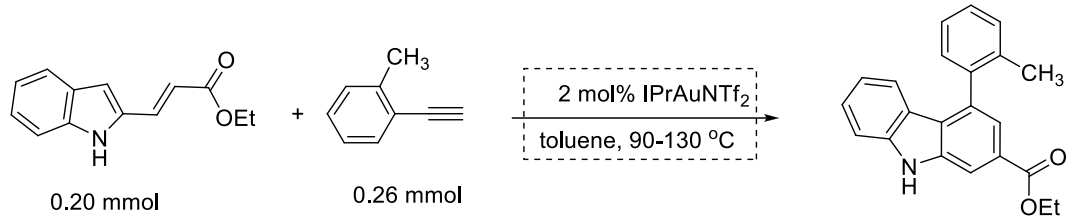
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.38 (d, *J* = 8.7, 2H), 7.29 (d, *J* = 7.8, 1H), 7.26 – 7.14 (m, 7H), 7.10 (t, *J* = 7.7, 3H), 6.86 (t, *J* = 7.5, 1H), 6.72 (d, *J* = 7.9, 1H), 2.71 – 2.33 (m, 2H), 1.51 (dd, *J* = 15.4, 7.9, 2H), 1.27 – 1.23 (m, 2H), 0.79 (t, *J* = 7.3, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.3, 140.1, 139.7, 139.0, 136.4, 133.4, 131.4, 130.2, 127.9, 127.3, 126.6, 126.0, 125.2, 123.7, 122.1, 120.0, 119.1, 110.3, 109.6, 34.3, 33.9, 22.7, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{25}N^+$ 376.2059; Found 376.2061.

Scope of the alkyne substrate

Ethyl 4-m-tolyl-9*H*-carbazole-2-carboxylate (3k)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-ethynyl-2-methylbenzene (30.0 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (40.2 mg, 60% yield).

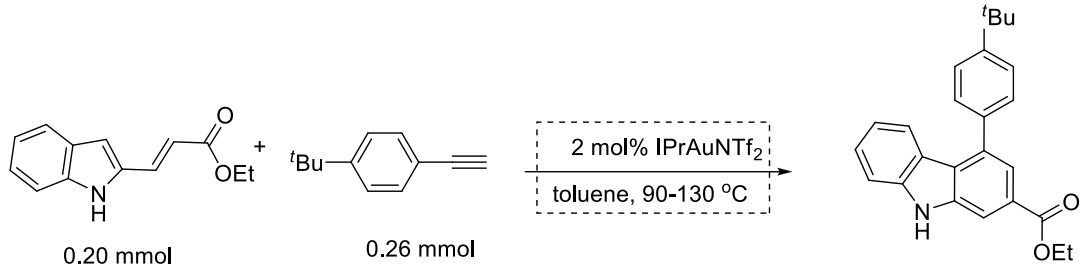
R_f 0.6 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.21 (dd, *J* = 1.7 Hz, 0.8 Hz, 1H), 7.78 (dd, *J* = 1.4 Hz, 0.8 Hz, 1H), 7.46 – 7.35 (m, 6H), 7.02 – 6.95 (m, 2H), 4.51 – 4.38 (m, 2H), 2.08 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 141.0, 140.1, 139.0, 136.6, 136.5, 130.2, 129.6, 128.2, 127.5, 127.0, 126.2, 125.2, 122.7, 122.5, 121.6, 120.0, 111.3, 110.8, 61.2, 19.9, 14.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_2^+$ 330.1489; Found 330.1496.

Ethyl 4-(4-tert-butylphenyl)-9*H*-carbazole-2-carboxylate (3l)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-tert-butyl-4-ethynylbenzene (41.1 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 ºC until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (54.4 mg, 72% yield).

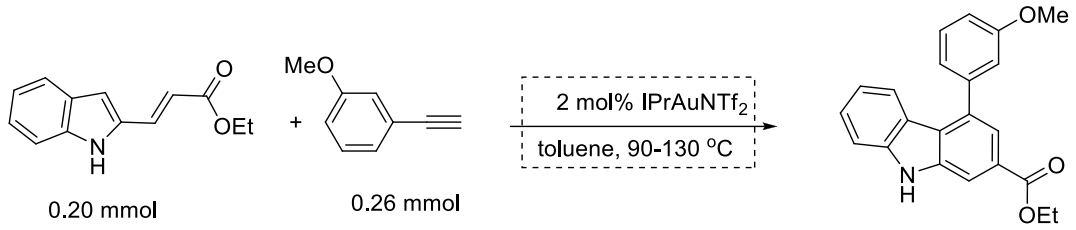
R_f 0.60 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.17 (s, 1H), 7.83 (s, 1H), 7.59-7.57 (m, 5H), 7.47 – 7.41 (m, 2H), 7.03 (s, 1H), 4.44 (q, *J* = 6.9 Hz, 2H), 1.60 – 1.36 (m, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 150.9, 141.1, 139.5, 137.6, 137.5, 128.9, 127.5, 127.0, 125.5, 124.6, 123.3, 122.5, 122.3, 119.5, 111.2, 110.9, 61.2, 34.9, 31.6, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NO_2^+$ 372.1958; Found 372.1957.

Ethyl 4-(3-methoxyphenyl)-9*H*-carbazole-2-carboxylate (3m)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-ethynyl-3-methoxybenzene (34.3 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (48.9 mg, 70% yield).

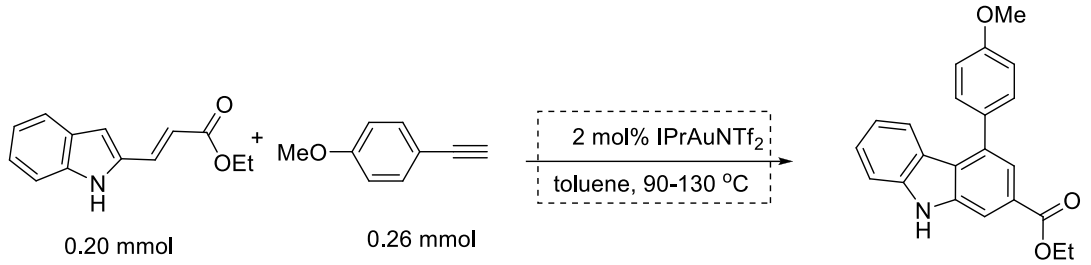
R_f 0.55 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.28 (s, 1H), 7.93 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.36 – 7.28 (m, 2H), 7.21 – 7.01 (m, 2H), 4.54 (q, *J* = 5.8 Hz, 2H), 3.95 (s, 3H), 1.52 (t, *J* = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 159.8, 142.0, 141.1, 139.4, 137.3, 129.7, 127.4, 127.1, 124.5, 123.3, 122.3, 121.9, 121.7, 119.6, 114.4, 113.9, 111.5, 110.9, 61.2, 55.5, 14.5.

HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{23}N_2O_3^+$ 363.1703; Found 363.1731.

Ethyl 4-(4-methoxyphenyl)-9*H*-carbazole-2-carboxylate (3n)



0.20 mmol 0.26 mmol

(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-ethynyl-4-methoxybenzene (34.0 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 ºC until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (59.1 mg, 84% yield).

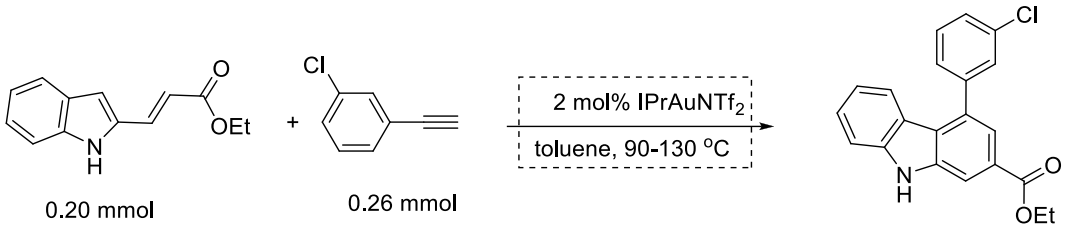
R_f 0.55 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.16 (s, 1H), 7.81 (s, 1H), 7.57 – 7.56 (m, 3H), 7.46 – 7.41 (m, 2H), 7.17 – 6.93 (m, 3H), 4.72 – 4.28 (m, 2H), 3.94 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 159.5, 141.1, 139.5, 137.2, 131.3, 130.4, 127.5, 127.0, 124.7, 123.2, 122.5, 122.2, 119.6, 114.1, 111.1, 110.9, 61.2, 55.5, 14.6.

HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{23}N_2O_3^+$ 363.1703; Found 363.1731.

Ethyl 4-(3-chlorophenyl)-9*H*-carbazole-2-carboxylate (3o)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-chloro-3-ethynylbenzene (35.4 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (53.9 mg, 76% yield).

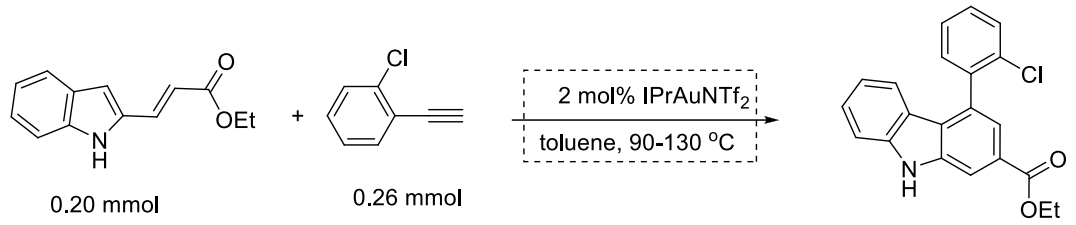
R_f 0.45 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.19 (d, *J* = 1.4 Hz, 1H), 7.79 (d, *J*=1.4 Hz, 1H), 7.63 (dd, *J* = 2.9 Hz, 1.0 Hz, 1H), 7.59 – 7.37 (m, 6H), 7.05 (ddd, *J* = 8.1 Hz, 6.9 Hz, 1.3 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 142.4, 141.1, 139.4, 135.8, 134.5, 129.9, 129.4, 128.1, 127.6, 127.5, 124.3, 123.0, 122.0, 121.9, 119.8, 111.9, 111.1, 61.3, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}ClNO_2^+$ 350.0942; Found 350.0941.

4-(2-Chlorophenyl)-2-phenyl-9*H*-carbazole (3p)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-chloro-2-ethynylbenzene (35.4 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (43.1 mg, 61% yield).

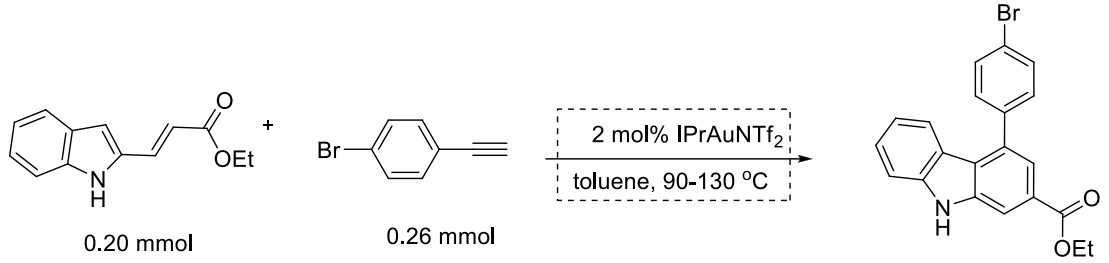
R_f 0.45 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) 8.47 (s, 1H), 8.23 (s, 1H), 7.81 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.35 (m, 5H), 7.07 (d, *J* = 7.8, 1H), 7.01 (d, *J* = 7.7, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 141.0, 139.2, 139.0, 134.0, 133.8, 131.5, 129.8, 129.5, 127.4, 127.2, 127.1, 125.2, 122.6, 122.3, 121.9, 120.0, 112.1, 110.9, 61.2, 14.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{16}NO_2Cl^+$ 372.7612; Found 372.7847.

Ethyl 4-(4-bromophenyl)-9*H*-carbazole-2-carboxylate (3q)



0.20 mmol 0.26 mmol

(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1-bromo-4-ethynylbenzene (47.1 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (51.3 mg, 64% yield).

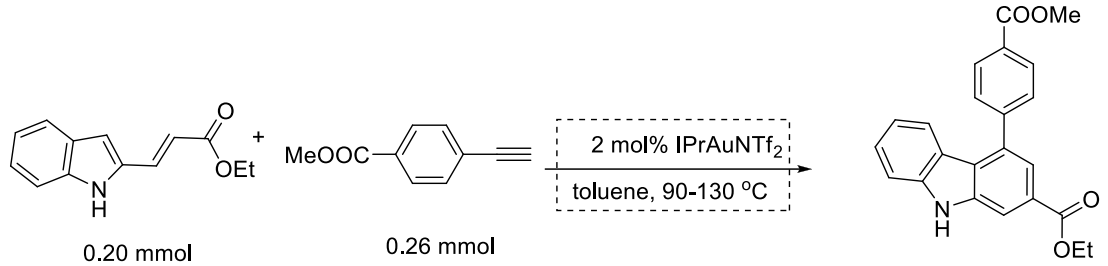
R_f 0.45 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.19 (s, 1H), 7.80 (s, 1H), 7.68 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.38 (m, 5H), 7.05 (t, *J* = 7.2 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 141.1, 139.6, 139.4, 136.1, 131.8, 131.0, 127.6, 127.3, 124.3, 123.0, 122.2, 122.0, 119.8, 111.8, 111.0, 61.3, 14.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{16}BrNNaO_2^+$ 416.0257; Found 416.0262.

Ethyl 4-(4-(methoxycarbonyl)phenyl)-9*H*-carbazole-2-carboxylate (3r)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), methyl 4-ethynylbenzoate (41.7 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (46.2 mg, 61% yield).

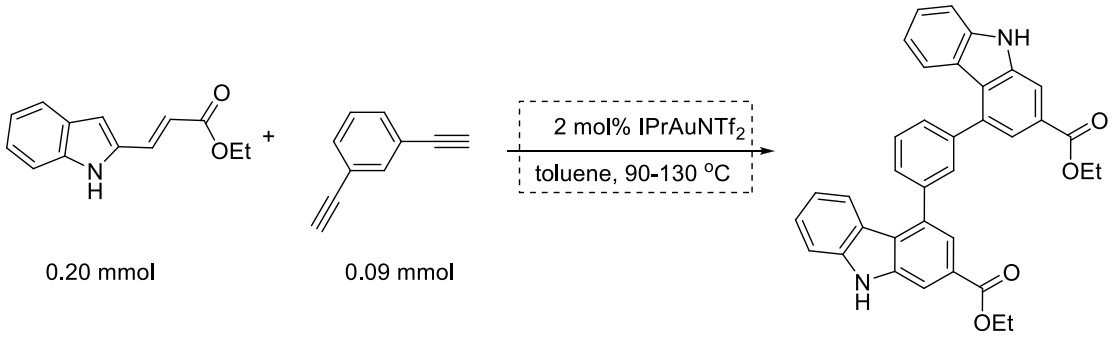
R_f 0.35 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 8.22 – 8.20 (m, 3H), 7.80 (d, *J* = 1.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.00 (dd, *J* = 8.0 Hz, 7.0 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.24, 167.19, 145.4, 141.1, 139.4, 136.3, 130.0, 129.7, 129.5, 127.6, 127.3, 124.2, 123.0, 122.1, 121.9, 119.8, 112.0, 111.1, 61.3, 52.4, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO_4^+$ 374.1387; Found 374.1387.

Diethyl 4,4'-(1,3-phenylene)bis(9*H*-carbazole-2-carboxylate) (3s)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 1,3-diethynylbenzene (11.4 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (26.1 mg, 52% yield).

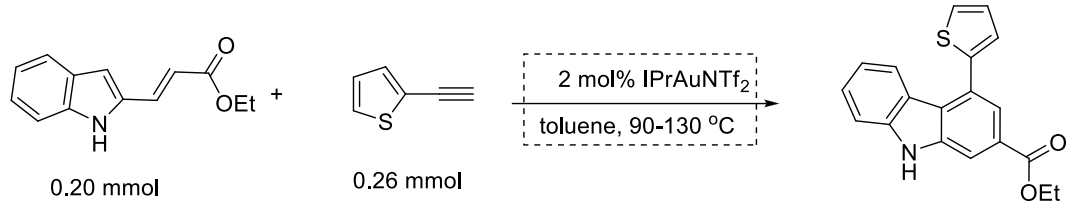
R_f 0.30 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 2H), 8.19 (s, 2H), 7.91 (d, J =13.5, 2H), 7.80 - 7.72 (m, 5H), 7.47 - 7.41 (m, 5H), 7.01 (s, 2H), 4.44 (dd, *J* = 12.9, 6.2, 4H), 1.43 (t, *J* = 6.8, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 141.1, 139.4, 137.2, 130.1, 128.8, 127.6, 127.1, 124.7, 123.2, 122.4, 122.1, 119.7, 111.6, 111.0, 61.2, 14.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2NaO_4^+$ 575.1941; Found 575.1958.

Ethyl 4-(thiophen-2-yl)-9*H*-carbazole-2-carboxylate (3t)



0.20 mmol 0.26 mmol

(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 2-ethynylthiophene (28.1 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 ºC until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (61.1 mg, 94% yield).

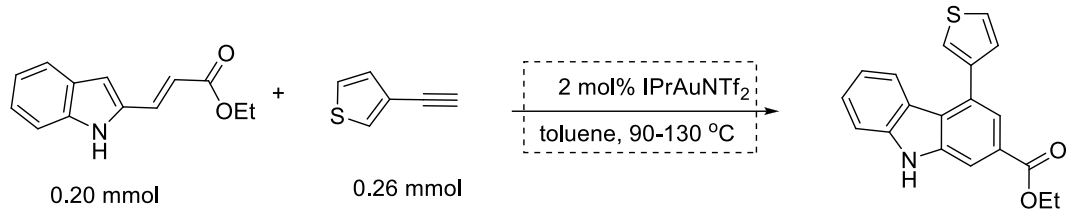
R_f 0.55 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.19 (d, *J* = 1.4 Hz, 1H), 7.93 (d, *J* = 1.4 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.35 (dd, *J* = 3.5 Hz, 1.2 Hz, 1H), 7.24 (dd, *J* = 5.1 Hz, 3.5 Hz, 1H), 7.08 (ddd, *J* = 8.1 Hz, 6.6 Hz, 1.6 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 141.5, 141.1, 139.3, 129.6, 127.4, 127.3, 127.1, 126.1, 125.4, 123.4, 123.1, 122.3, 119.8, 112.2, 111.0, 61.3, 14.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O_2S^+$ 339.1162; Found 339.1163.

Ethyl 4-(thiophen-3-yl)-9*H*-carbazole-2-carboxylate (3u)



0.20 mmol 0.26 mmol

(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), 3-ethynylthiophene (28.1 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (59.9 mg, 92% yield).

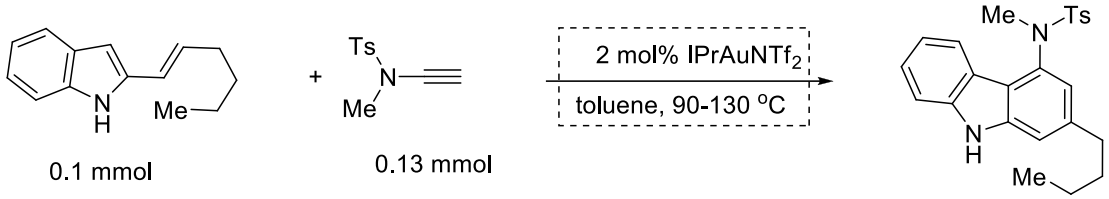
R_f 0.55 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) 8.44 (s, 1H), 8.16 (s, 1H), 7.86 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.28 (m, 5H), 7.07 (t, *J* = 6.6 Hz, 1H), 4.80 – 4.32 (m, 2H), 1.44 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 141.1, 139.4, 132.2, 129.1, 127.5, 127.2, 125.8, 124.9, 123.4, 123.1, 122.4, 122.2, 119.8, 111.6, 110.9, 61.2, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O_2S^+$ 339.1162; Found 339.1163.

***N*-(2-butyl-9H-carbazol-4-yl)-*N*,4-dimethylbenzenesulfonamide (3v)**



(*E*)-2-(hex-1-enyl)-1*H*-indole (19.9 mg, 0.1 mmol), *N*-ethynyl-*N*,4-dimethylbenzenesulfonamide (27.0 mg, 0.13 mmol) and $IPrAuNTf_2$ (1.74 mg, 0.002 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.1 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:4) to get the target product (37.1 mg, 91% yield).

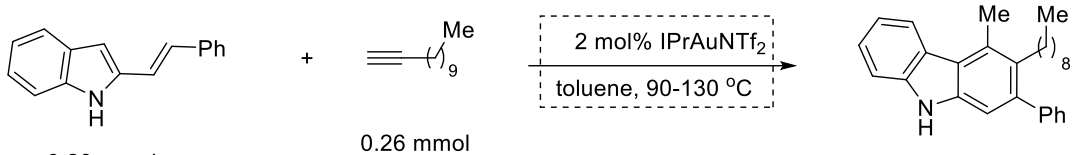
R_f 0.40 (Petroleum ether/EtOAc = 10/3).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 7.9, 1H), 8.05 (s, 1H), 7.69 (d, *J* = 8.2, 2H), 7.41 – 7.34 (m, 2H), 7.30 (d, *J* = 8.0, 2H), 7.25 – 7.21 (m, 1H), 7.13 (s, 1H), 6.32 (d, *J* = 1.0, 1H), 3.34 (s, 3H), 2.70 – 2.52 (m, 2H), 2.46 (s, 3H), 1.57 – 1.47 (m, 2H), 1.32 (d, *J* = 7.7, 2H), 0.93 (t, *J* = 7.3, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.3, 140.1, 139.7, 139.0, 136.4, 133.4, 131.4, 130.2, 127.9, 127.3, 126.6, 126.0, 125.2, 123.7, 122.1, 120.0, 119.1, 110.3, 109.6, 34.3, 33.9, 22.7, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}N_2S_2^+$ 407.1787; Found 407.1786.

3-Ethyl-4-methyl-2-phenyl-9*H*-carbazole (3w)



(*E*)-2-styryl-1*H*-indole (43.8 mg, 0.2 mmol), 1-dodecyne (46.3 mg, 0.26 mmol) and $IPrNTf_2$ (3.5 mg) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 ºC until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (54.1 mg, 71% yield).

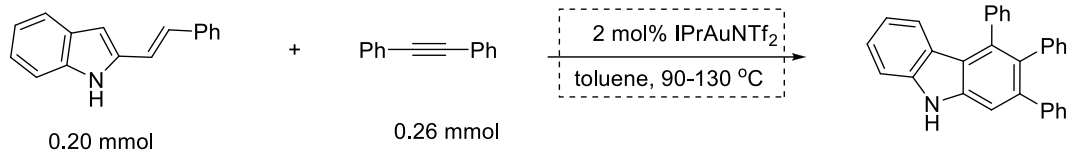
R_f 0.40 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) 8.27 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.72 – 7.27 (m, 8H), 7.13 (s, 1H), 2.92 (s, 3H), 2.80 – 2.53 (m, 2H), 1.44 (m, 2H), 1.29 – 1.15 (m, 12H), 0.88 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.9, 141.1, 140.2, 137.4, 131.6, 130.6, 129.7, 127.9, 126.7, 125.1, 124.3, 123.0, 119.4, 110.5, 109.7, 32.0, 31.5, 29.9, 29.6, 29.4, 29.3, 22.8, 17.1, 14.3.

HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{28}H_{37}N_2^+$ 401.2951; Found 401.2960.

2,3,4-Triphenyl-9*H*-carbazole (3x)



(*E*)-2-Styryl-1*H*-indole (43.8 mg, 0.2 mmol), 1,2-diphenylethyne (46.3 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the target product (54.5 mg, 65% yield).

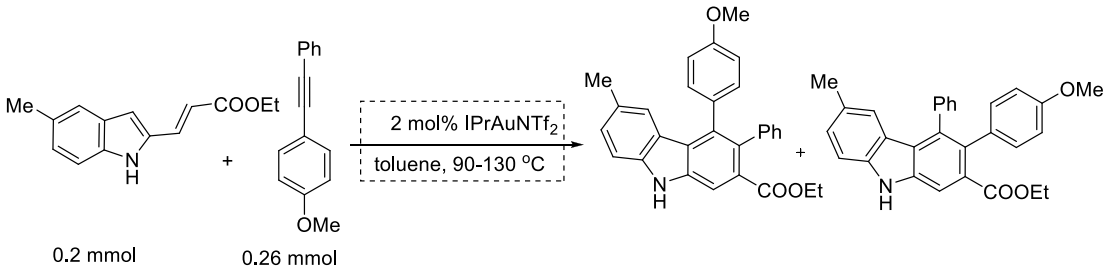
R_f 0.40 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.51 – 7.48 (m, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.25 (m, 6H), 7.22 – 7.13 (m, 5H), 6.98 – 6.85 (m, 6H), 6.81 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9, 140.4, 140.2, 140.1, 140.0, 138.7, 136.7, 132.4, 132.2, 130.4, 130.3, 128.1, 127.6, 126.9, 126.2, 125.7, 125.4, 123.5, 122.5, 121.3, 119.4, 111.3, 110.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{22}N^+$ 396.1747; Found 396.1753.

Ethyl4-(4-methoxyphenyl)-6-methyl-3-phenyl-9*H*-carbazole-2-carboxylate (3y)



(*E*)-ethyl 3-(5-methyl-1*H*-indol-2-yl)acrylate (45.8 mg, 0.2 mmol), 1-methoxy-4-(phenylethynyl)benzene (54.0 mg, 0.26 mmol) and $IPrNTf_2$ (3.67 mg, 0.004 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:3) to get the regioisomeric mixture of product (55.1 mg, 63% yield, regioselectivity 7.5/1). (Regioselectivity was determined by ^{1}H NMR.)

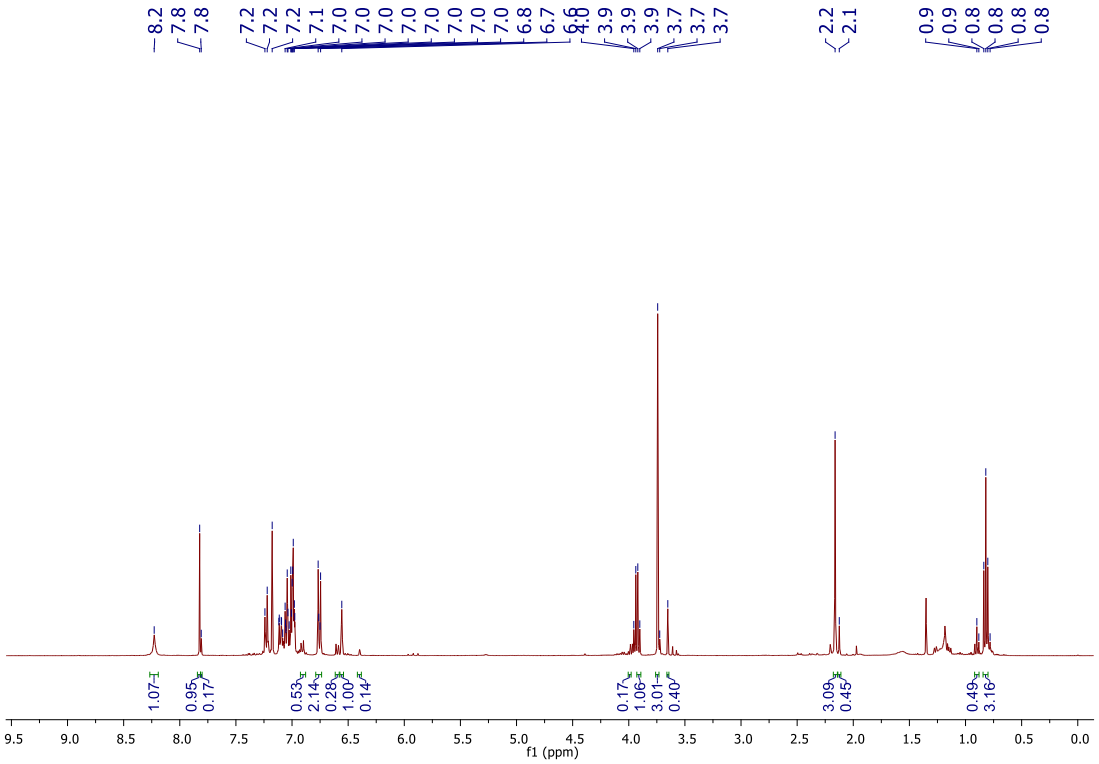
R_f 0.35 (Petroleum ether/EtOAc = 10/3).

^{1}H NMR (400 MHz, Chloroform-*d*) 8.21 (s, 1H), 7.91 (s, 1H), 7.33 (d, *J* = 8.3, 1H), 7.24 – 7.16 (m, 1H), 7.14 – 7.05 (m, 7H), 6.91 – 6.78 (m, 2H), 6.64 (s, 1H), 4.00 (q, *J* = 7.1, 2H), 3.83 (s, 3H), 2.24 (s, 3H), 0.89 (t, *J* = 7.2, 3H).

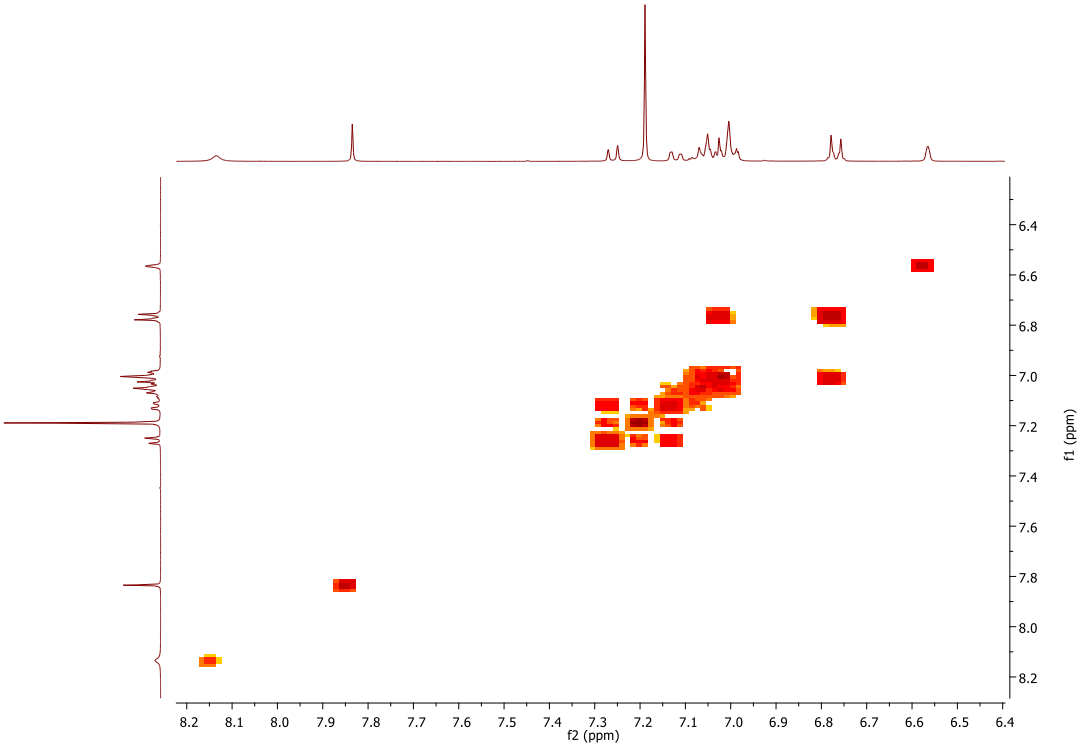
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 158.6, 140.6, 139.3, 138.2, 136.7, 132.7, 131.6, 131.3, 130.7, 130.0, 128.8, 128.1, 127.1, 125.9, 124.5, 123.3, 122.9, 113.5, 111.0, 110.4, 61.0, 55.4, 21.7, 13.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}NO_3^+$ 435.1907; Found 435.1905.

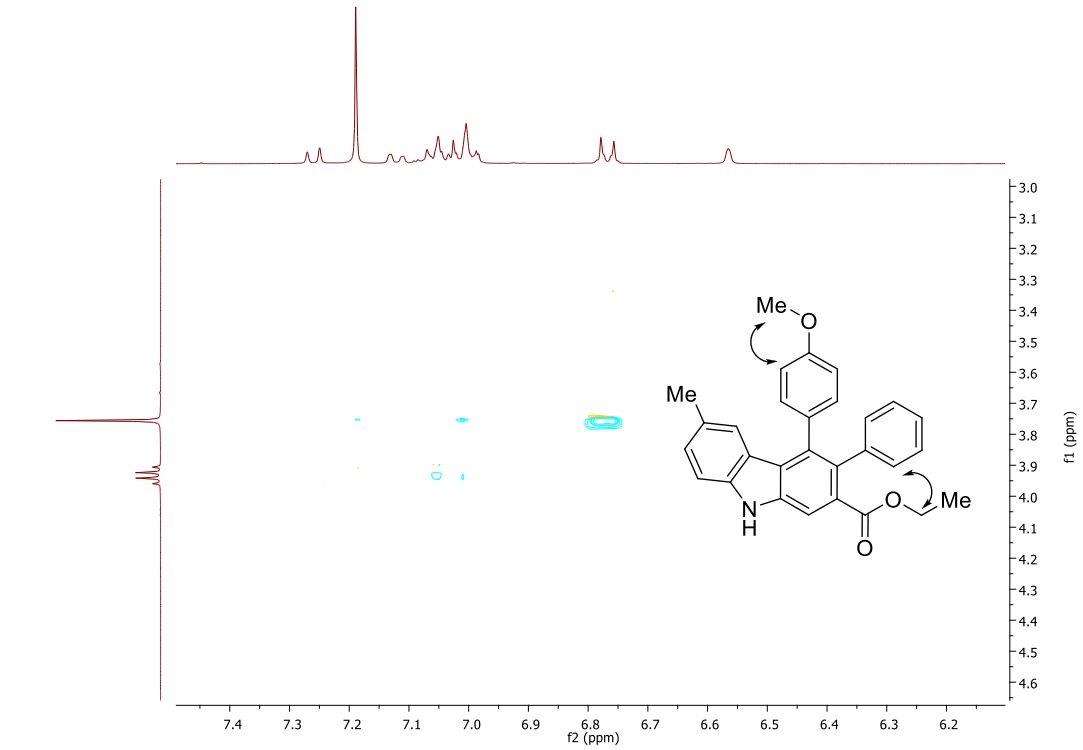
^{1}H NMR of **3y**

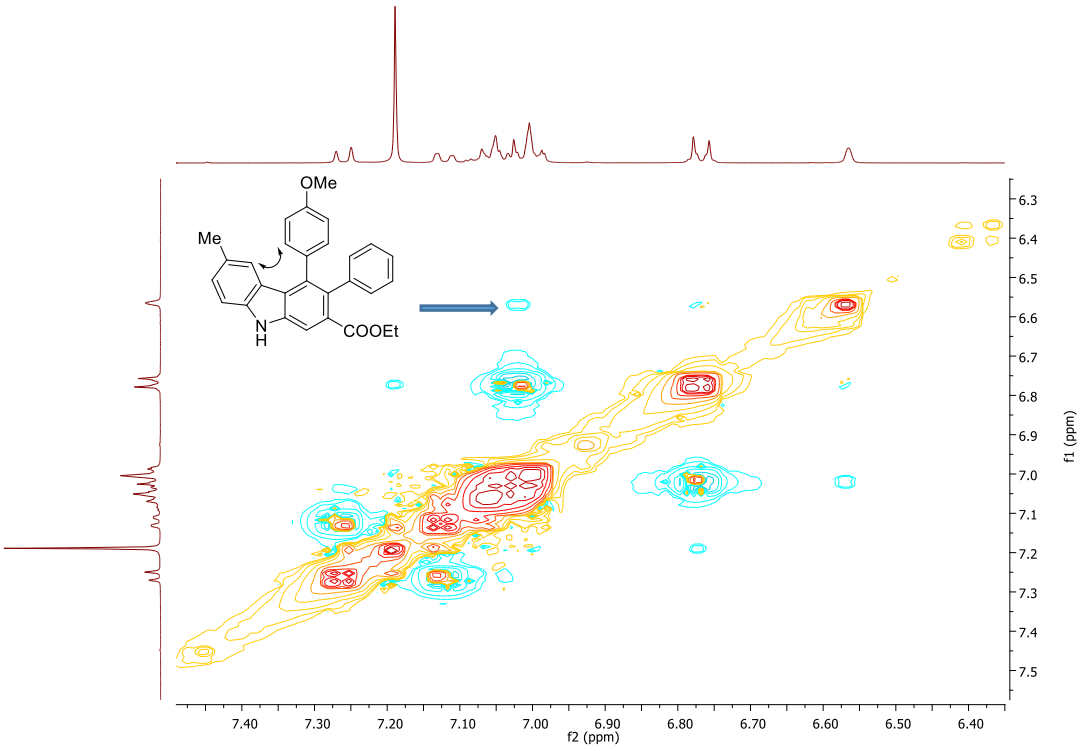


COSY experiment:

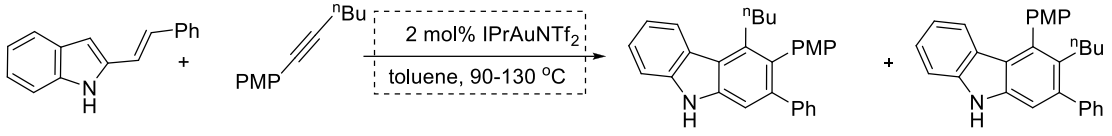


NOESY experiment:





4-Butyl-3-(4-methoxyphenyl)-2-phenyl-9*H*-carbazole (3z)



0.1 mmol 0.13 mmol

(*E*)-2-styryl-1*H*-indole (21.9 mg, 0.1 mmol), 1-(hex-1-ynyl)-4-methoxybenzene (27.0 mg, 0.13 mmol) and $IPrNTf_2$ (1.74 mg, 0.002 mmol) were added to a dried vial under air in dry toluene (1 mL, 0.1 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:2) to get the regioisomeric mixture of product (25.1 mg, 62% yield, regioselectivity 2.5/1). (Regioselectivity was determined by ^{1}H NMR.)

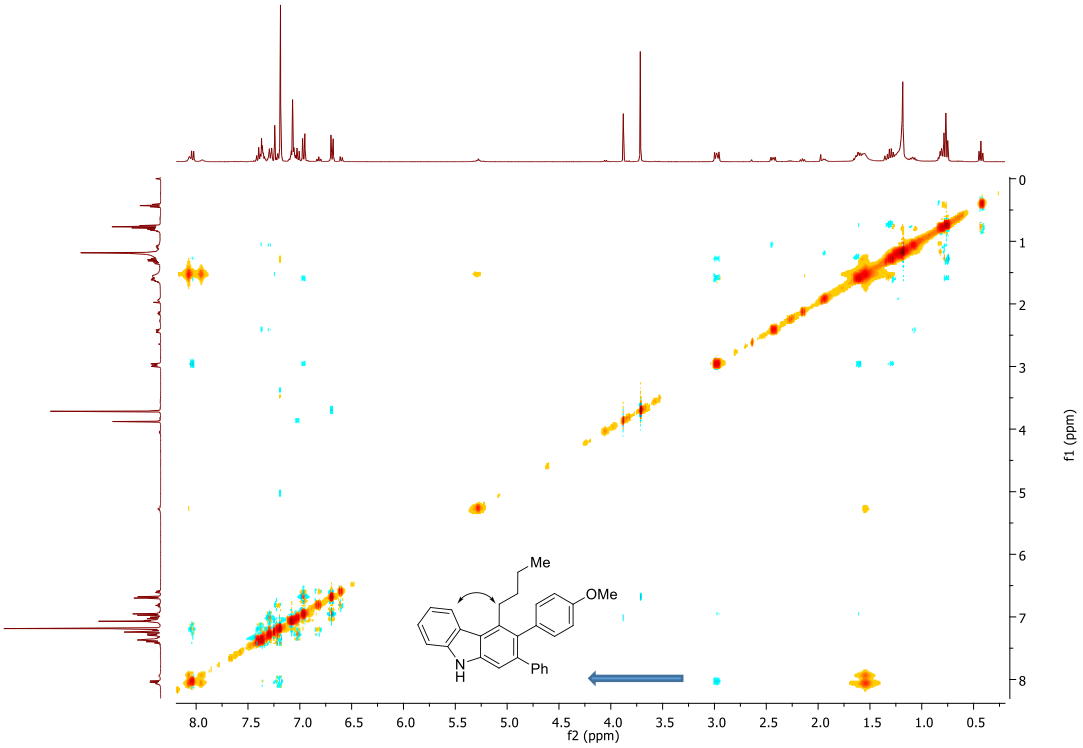
R_f 0.40 (Petroleum ether/EtOAc = 10/3).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (*s*, 1H), 8.05 (d, *J* =8.0, 1H), 7.39 (dd, *J* = 6.2, 3.7, 2H), 7.21 (d, *J* =3.9, 3H), 7.12 – 7.06 (m, 4H), 7.01 – 6.96 (m, 2H), 6.76 – 6.66 (m, 2H), 3.73 (s, 3H), 3.22 – 2.78 (m, 2H), 1.63 (d, *J* = 7.6, 2H), 1.35 – 1.30 (m, 2H), 0.79 (t, *J* = 7.4, 3H).

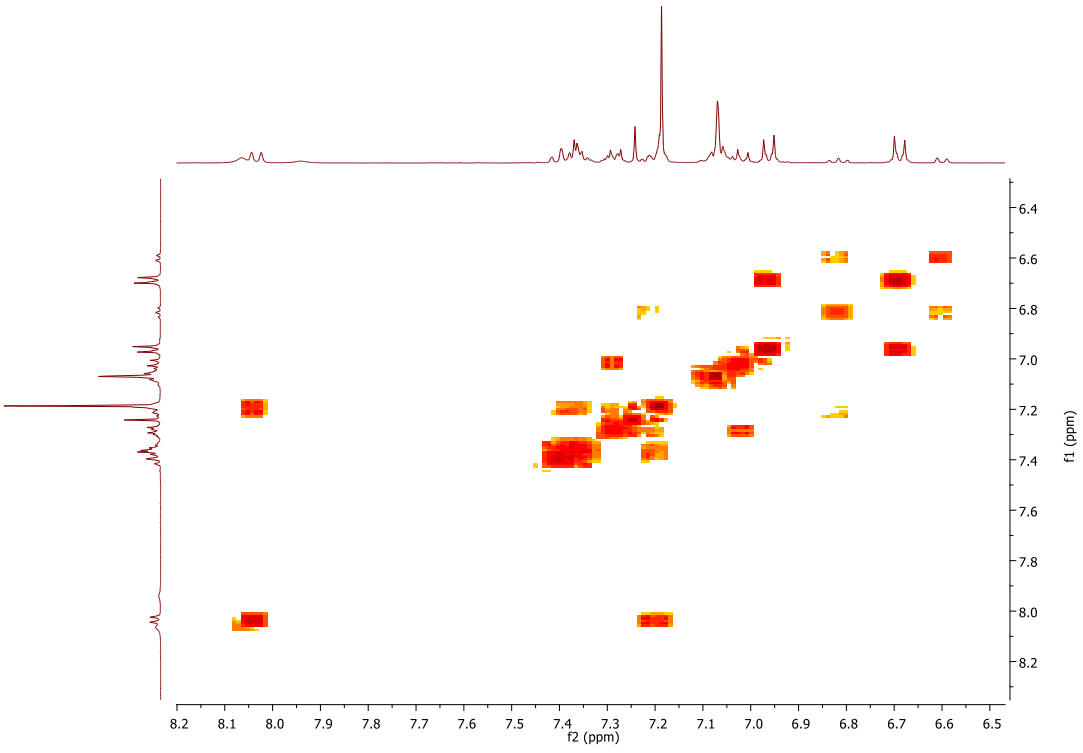
^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9, 143.5, 140.9, 140.2, 137.3, 136.4, 133.0, 130.9, 130.7, 129.8, 127.9, 126.7, 125.3, 123.7, 122.3, 122.1, 119.2, 114.1, 111.4, 110.3, 55.5, 33.8, 29.3, 22.7, 13.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{27}NO^+$ 406.2165; Found 406.2149.

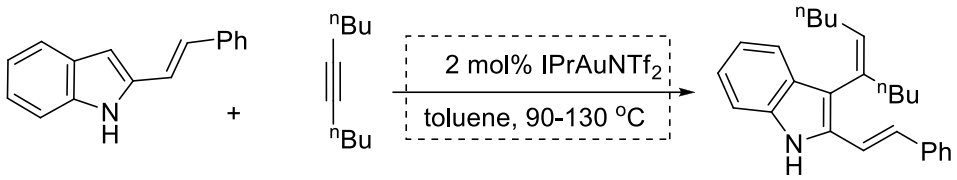
NOESY experiment：



COSY experiment:



3-((*Z*)-dec-5-en-5-yl)-2-styryl-1*H*-indole (3aa)



0.1 mmol 0.13 mmol

(*E*)- (*E*)-2-styryl-1*H*-indole (21.9 mg, 0.1 mmol), dec-5-yne (18.0 mg, 0.13 mmol) and $IPrNTf_2$ (1.74 mg, 0.002 mmol) were added to a dried vial under air sequentially in dry toluene (1 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (21.9 mg, 61% yield).

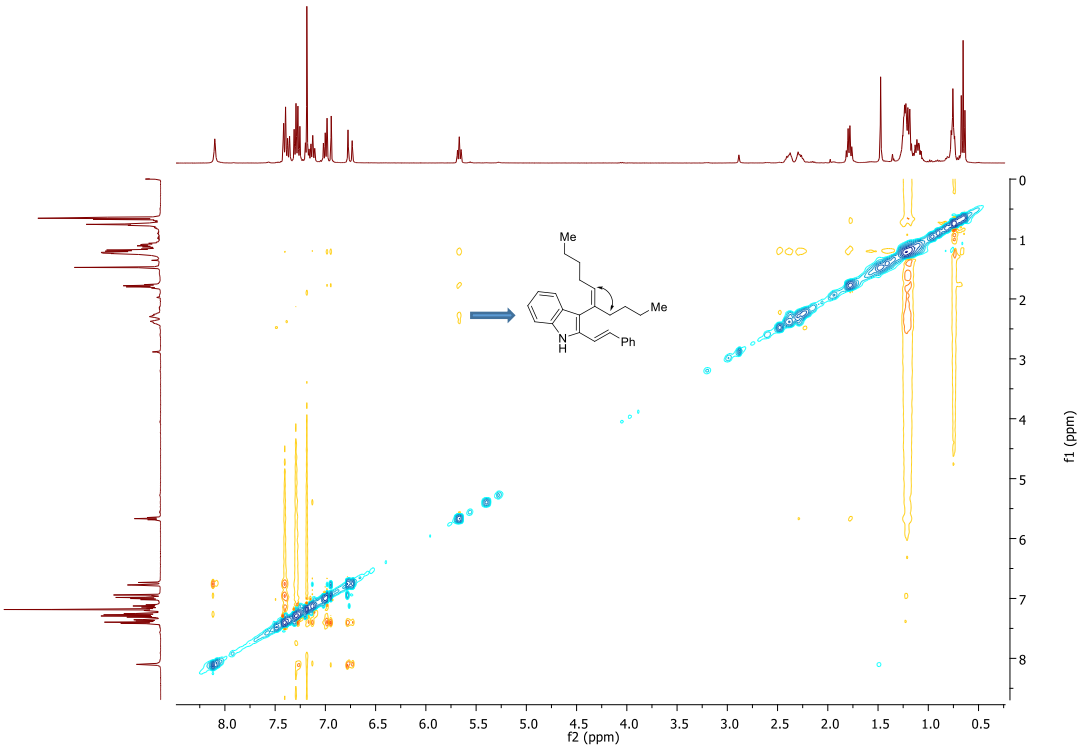
R_f 0.40 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, Chloroform-*d*) 8.18 (s, 1H), 7.46 (dd, *J* =15.8, 7.7, 3H), 7.36 (dd, *J* = 15.3, 7.6, 3H), 7.21 (dd, *J* = 14.9, 7.7, 2H), 7.06 (dd, *J* = 19.1, 11.9, 2H), 6.83 (d, *J* = 16.7, 1H), 5.74 (t, *J* = 7.1, 1H), 2.37 (s, 2H), 1.86 (dd, *J* = 14.5, 7.2, 2H), 1.33 – 1.18 (m, 8H), 0.83 (t, *J* = 6.9, 3H), 0.73 (t, *J* = 7.2, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.4, 136.8, 133.1, 132.4, 131.2, 131.0, 128.9, 127.6, 126.3, 125.9, 123.2, 123.1, 120.2, 119.8, 118.4, 110.6, 39.4, 39.2, 32.2, 31.0, 22.6, 22.42, 14.3, 14.1.

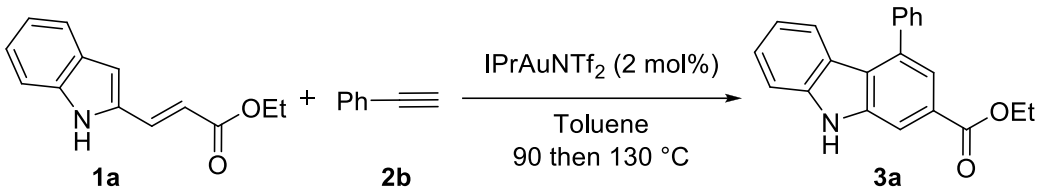
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{31}N^+$ 358.2529; Found 358.2530.

NOESY experiment:



Scale up reaction

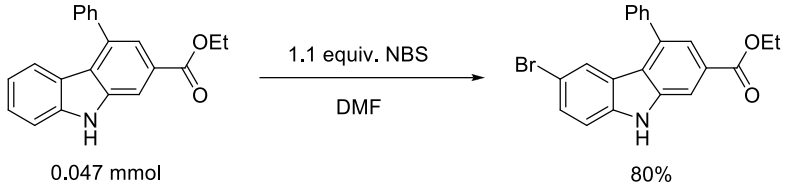
Ethyl 4-phenyl-9*H*-carbazole-2-carboxylate (3a)



(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (215 mg, 1 mmol), phenylacetylene (132.0 mg, 1.3 mmol) and $IPrAuNTf_2$ (17.3 mg, 0.02 mmol) were added to a dried vial under air sequentially in dry toluene (10 mL, 0.2 M). The reaction was stirred at 90 °C for 12 h and then 130 °C until complete consumption of the intermediate was observed by TLC. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (261.0 mg, 83% yield).

Synthetic applications

Ethyl 6-bromo-4-phenyl-9*H*-carbazole-2-carboxylate (5)



0.047 mmol 80%

A solution of *N*-bromosuccinimide (9.35 mg, 0.053 mmol, 1.1 equiv.) in 0.25 mL DMF was slowly added to a solution of 4-phenyl-9*H*-carbazole-2-carboxylate (15.0 mg, 0.047 mmol, 1.0 equiv.) in DMF (0.75 mL) in a dry vial under nitrogen. The reaction mixture was stirred at room temperature until complete consumption of starting material was observed by TLC. To the reaction mixture was then added water and extracted with ethyl acetate for three times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was separated on silica gel by PE/EA gradient (10:1) to get the target product (15.0 mg, 80%).

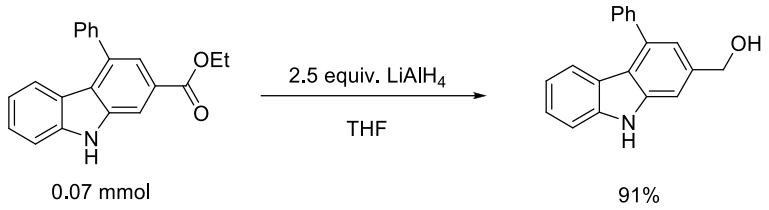
R_f 0.4 (Petroleum ether/EtOAc = 10/2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.17 (d, *J* = 1.4 Hz, 1H), 7.83 (d, *J* = 1.4 Hz, 1H), 7.63 – 7.47 (m, 7H), 7.34 (d, *J* = 8.6 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 140.0, 139.7, 137.8, 129.8, 129.1, 128.8, 128.4, 125.7, 124.2, 123.6, 122.4, 112.4, 112.3, 111.6, 61.3, 14.5.

HRMS (ESI) m/z: $[M + Li]^+$ Calcd for $C_{21}H_{16}BrLiNO_2^+$ 400.0519; Found 400.0566.

(4-Phenyl-9*H*-carbazol-2-yl)methanol (6)



0.07 mmol 91%

In a dry Schlenk tube charged with nitrogen ethyl 4-phenyl-9*H*-carbazole-2-carboxylate (22.0 mg, 0.07 mmol, 1.0 equiv.) was taken in THF (1 mL). To this was added $LiAlH_4$ (65.0 mg, 1.75 mmol, 2.5 equiv.) at 0°C. The rection mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was quenched with 0.2 mL aq KOH (3 M) at 0°C.The reaction mixture was extracted with ethyl acetate for three times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was separated on silica gel by PE/EA gradient (10:3) to get the target product (17.0 mg, 91%).

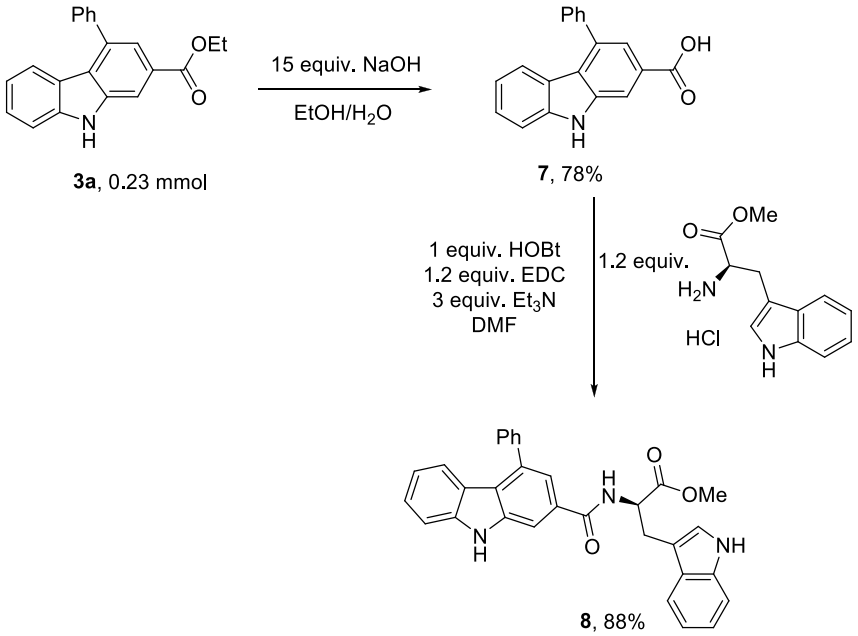
R_f 0.25 (Petroleum ether/EtOAc = 10/4).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.54 (d, *J* = 6.3 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.29 – 7.19 (m, 3H), 7.01 (s, 1H), 6.93 (d, *J* = 5.5 Hz, 1H), 4.76 (s, 2H), 1.94 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.1, 140.2, 140.1, 138.8, 137.9, 129.2, 128.6, 127.7, 125.8, 122.8, 122.4, 120.3, 119.2, 110.6, 108.1, 65.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}NO^+$ 274.1226; Found 274.1228.

(*R*)-Methyl 3-(1*H*-indol-3-yl)-2-(4-phenyl-9*H*-carbazole-2-carboxamido)propanoate (8)



To a solution of ethyl 4-phenyl-9*H*-carbazole-2-carboxylate (73.0 mg, 0.23 mmol, 1 equiv.) in ethanol (5 mL) and H_2O (1 mL) was added NaOH (136.0 mg, 3.48 mmol, 15 equiv.). The reaction mixture was refluxed under air until complete consumption of starting material was observed by TLC. The pH was adjusted to 4 with 6 N HCl. The ethanol was evaporated and resulting precipitate was filtered. The residue was washed with H_2O (5 mL) to obtain 4-phenyl-9*H*-carbazole-2-carboxylic acid **7** which is used without further purification (52.0 mg, 78%).

HOBt (8.5 mg, 0.063 mmol, 1.2 equiv.), EDCI (12.1 mg, 0.063 mmol, 1.2 equiv.), Et_3N (15.8 mg, 0.156 mmol, 3 equiv.) and D-Tryptophan methyl ester hydrochloride (16.1 mg, 0.063 mmol, 1.2 equiv.) were added to a solution of 4-phenyl-9*H*-carbazole-2-carboxylic acid **7** (15.0 mg, 0.052 mmol, 1 equiv.) in DMF (1 mL). The reaction mixture was stirred under nitrogen at room temperature until complete consumption of starting material was observed by TLC. To the reaction mixture was then added water and extracted with ethyl acetate for three times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was separated on silica gel by PE/EA gradient (10:4) to get the target product (22.0 mg, 88%).

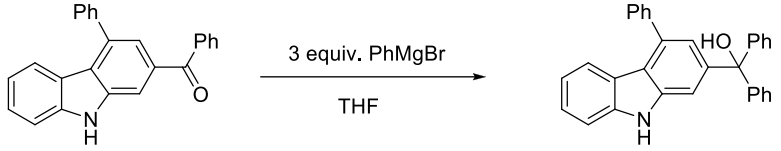
R_f 0.2 (Petroleum ether/EtOAc = 10/4).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.40 (s, 1H), 7.88 (s, 1H), 7.62 (d, *J* = 7.2, 1H), 7.57 – 7.44 (m, 6H), 7.41 – 7.28 (m, 4H), 7.16 (s, 1H), 7.10 - 6.89 (m, 4H), 5.26 (s, 1H), 3.74 (s, 3H), 3.51 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 167.9, 141.1, 140.5, 139.7, 137.6, 136.2, 130.6, 129.3, 128.6, 127.9, 127.7, 126.8, 123.6, 123.1, 122.9, 122.4, 122.2 120.0, 119.4, 119.0, 118.6, 111.5, 111.0, 110.0, 109.6, 53.8, 52.5, 27.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{25}N_3NaO_3^+$ 510.1788; Found 510.1800.

Diphenyl(4-phenyl-9*H*-carbazol-2-yl)methanol (9)



0.057 mmol 78%

To a solution of phenyl(4-phenyl-9*H*-carbazol-2-yl)methanone (20.0 mg, 0.057 mmol, 1 equiv.) in THF (2 mL) at 0°C was added phenylmagnesium bromide (1.3 equiv.) under nitrogen. The resulting solution was allowed to stir at 60 ºC for 2 h. The reaction mixture was then cooled to 0°C and quenched with saturated aqueous ammonium chloride solution. The aqueous layer is extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was separated on silica gel by PE/EA gradient (30:1) to get the target product as a colourless liquid (19.0 mg, 78% yield).

R_f 0.48 (Petroleum ether/EtOAc = 30/1).

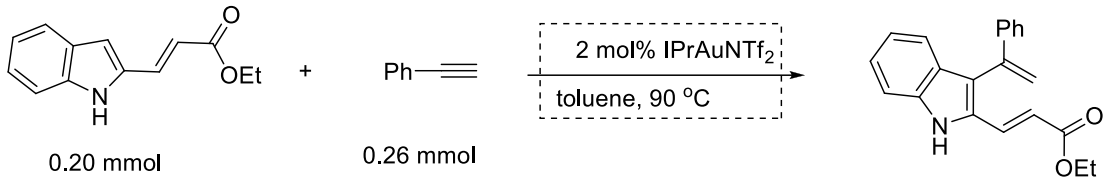
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.62 – 7.55 (m, 2H), 7.51 – 7.42 (m, 4H), 7.38 – 7.28 (m, 12H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 6.97 (ddd, *J* = 8.1 Hz, 6.4 Hz, 1.8 Hz, 1H), 2.94 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.2, 145.0, 141.2, 140.3, 139.6, 137.2, 129.4, 128.5, 128.15, 128.07, 127.6, 127.4, 125.8, 122.7, 122.5, 121.5, 119.9, 119.3, 110.6, 109.6, 82.6.

HRMS (ESI) m/z: $[M + Li]^+$ Calcd for $C_{31}H_{23}NO^+$ 432.1934; Found 432.2016.

Control experiments

(*E*)-ethyl 3-(3-(1-phenylvinyl)-1*H*-indol-2-yl)acrylate (10)



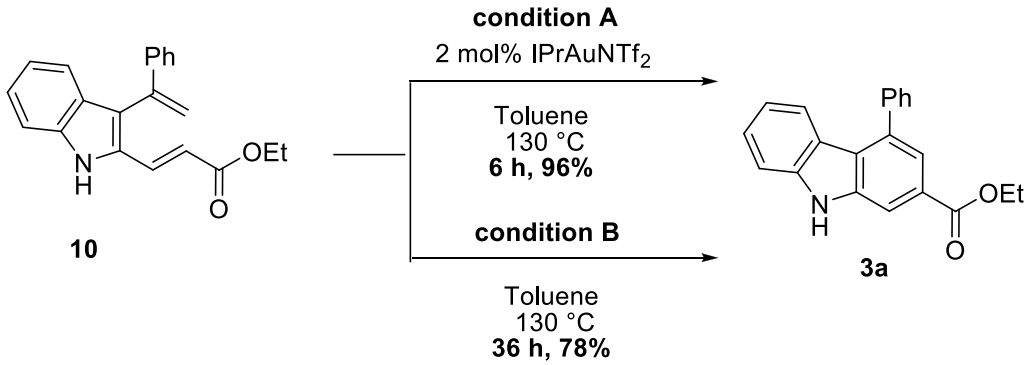
(*E*)-ethyl 3-(1*H*-indol-2-yl)acrylate (43.5 mg, 0.2 mmol), phenylacetylene (26.6 mg, 0.26 mmol) and $IPrAuNTf_2$ (3.5 mg, 0.004 mmol) were added to a dried vial sequentially in dry toluene (1 mL, 0.2 M) under air. The reaction was stirred at 90 ℃ for 12 h. Then the reaction mixture was concentrated under reduced pressure with the aid of a rotary evaporator and separated on silica gel by PE/EA gradient (10:1) to get the target product (61.0 mg, 95% yield).

R_f 0.50 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 7.80 (d, *J* = 16.1 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.34 – 7.30 (m, 3H), 7.25 (ddd, *J* = 8.1 Hz, 5.1 Hz, 1.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.07 – 6.93 (m, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 5.90 (d, *J* = 1.5 Hz, 1H), 5.35 (d, *J* = 1.5 Hz, 1H), 4.29 (q, *J* =7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 141.1, 137.3, 133.3, 131.5, 128.4, 128.0, 127.4, 125.0, 123.6, 121.5, 120.4, 117.9, 115.5, 111.2, 77.4, 60.7, 14.5.

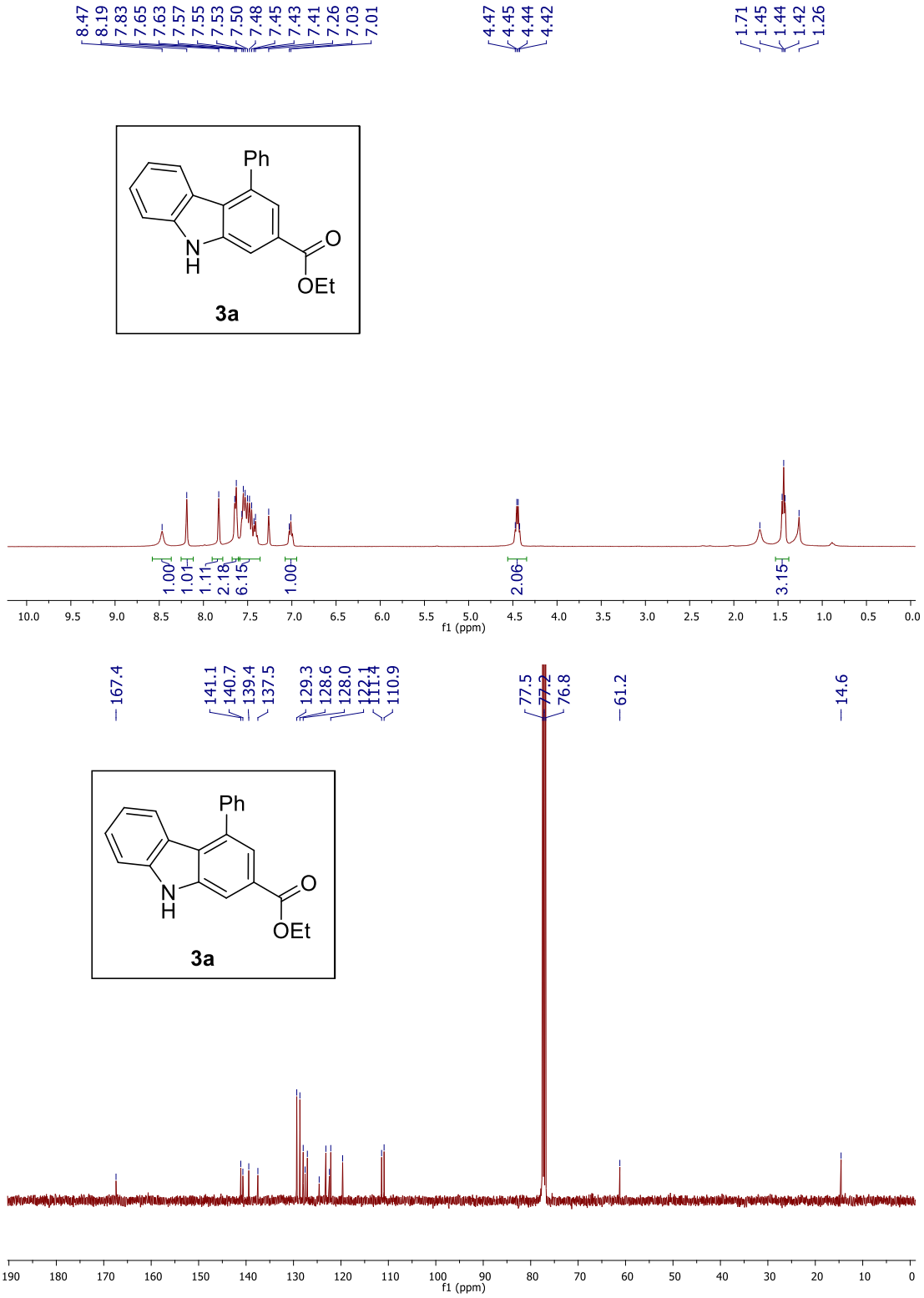
HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{23}N_2O_2^+$ 335.1754; Found 335.1717.

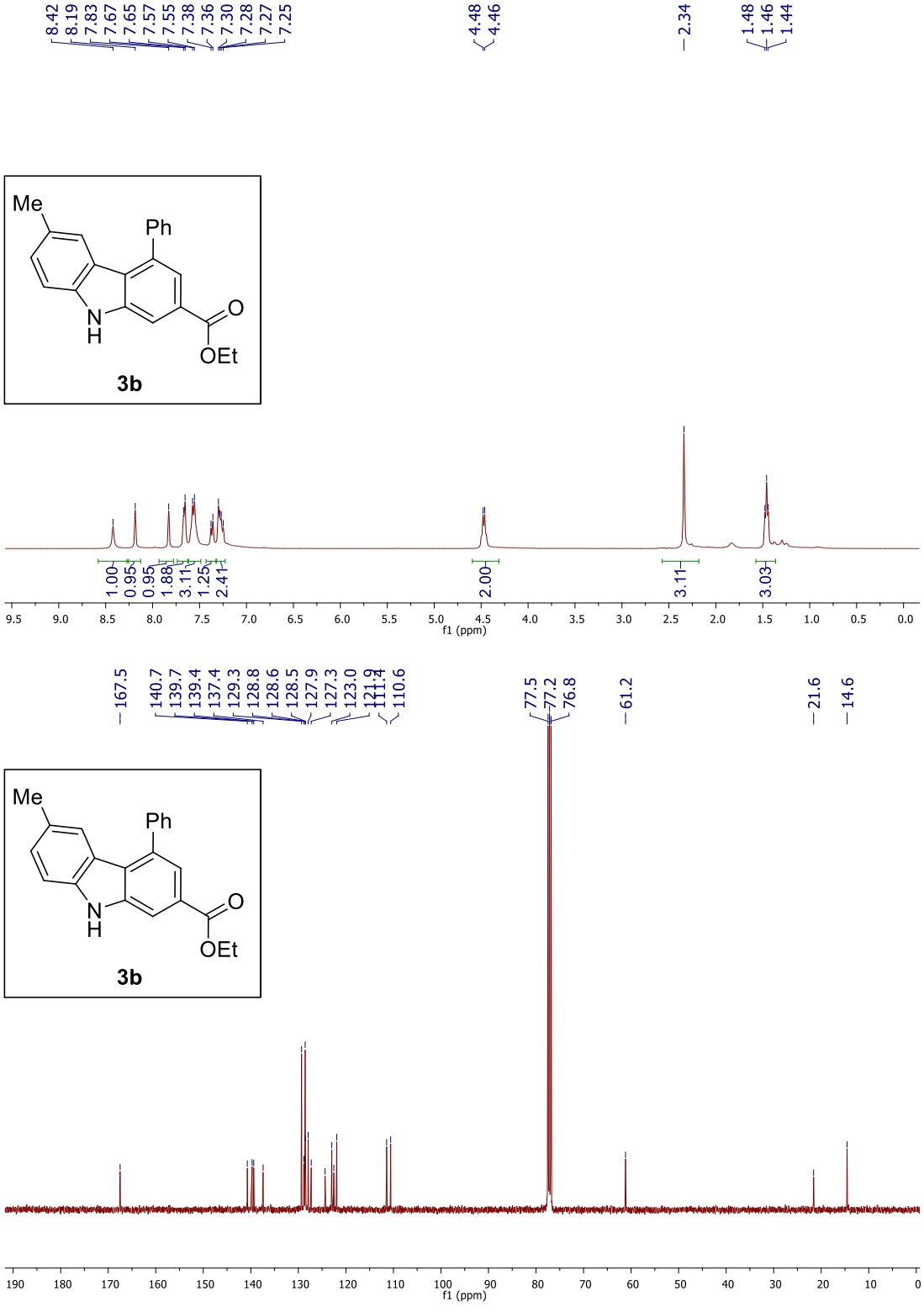


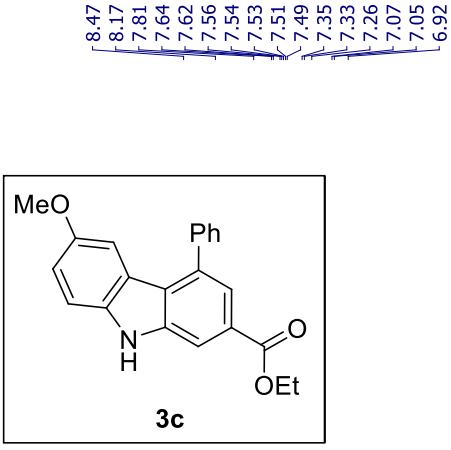
Condition A: To a solution of the intermediate **10** (10.9 mg, 0.05 mmol) in toluene (0.25 mL) was added $IPrAuNTf_2$ (0.9 mg, 0.001 mmol) under air and then the reaction mixture was allowed to stir at 130 °C until complete consumption of the starting material monitored by TLC (6 h). The yield was determined by ^{1}H NMR using dibutyl phthalate as the internal standard (96% yield).

Condition B: The solution of the intermediate **10** (10.9 mg, 0.05 mmol) in toluene (0.25 mL) was allowed to stir under air at 130 ^{o}C until complete consumption of the starting material monitored by TLC (36 h). The yield was determined by ^{1}H NMR using dibutyl phthalate as the internal standard (78% yield).

Spectra


8.47
8.19
7.83
7.65
7.63
7.57
7.55
7.53
7.50
7.48
7.45
7.43
7.41
7.26
7.03
7.01
4.47
4.45
4.44
4.42
1.71
1.45
1.44
1.42
1.26
Ph
N
H
O
OEt
3a
1.00
1.01
1.11
2.18
6.15
1.00
2.06
3.15
f1 (ppm)
167.4
141.1
140.7
139.4
137.5
129.3
128.6
128.0
122.1
111.4
110.9
77.5
77.2
76.8
61.2
14.6
Ph
N
H
O
OEt
3a
f1 (ppm)


8.42
8.19
7.83
7.67
7.65
7.57
7.55
7.38
7.36
7.30
7.28
7.27
7.25
4.48
4.46
2.34
1.48
1.46
1.44
Me
Ph
N
H
O
OEt
3b
1.00
0.95
0.95
1.88
3.11
1.25
2.41
2.00
3.11
3.03
f1 (ppm)
167.5
140.7
139.7
139.4
137.4
129.3
128.8
128.6
128.5
127.9
127.3
123.0
121.9
111.4
110.6
77.5
77.2
76.8
61.2
21.6
14.6
f1 (ppm)


8.47
8.17
7.81
7.64
7.62
7.56
7.54
7.53
7.51
7.49
7.35
7.33
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7.07
7.05
6.92
4.48
4.46
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1.45
1.44
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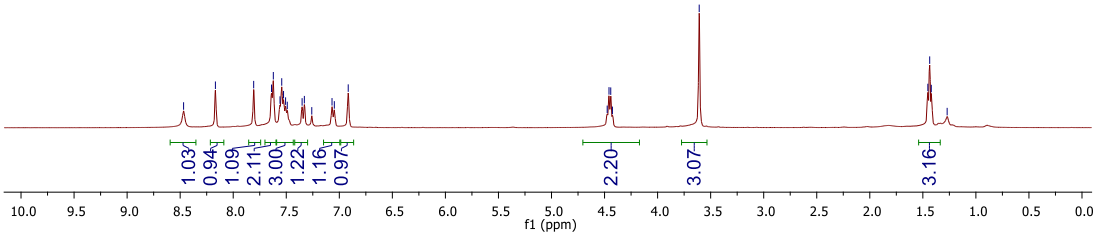
1.27
MeO
Ph
N
H
O
OEt
3c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3.07
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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1.0
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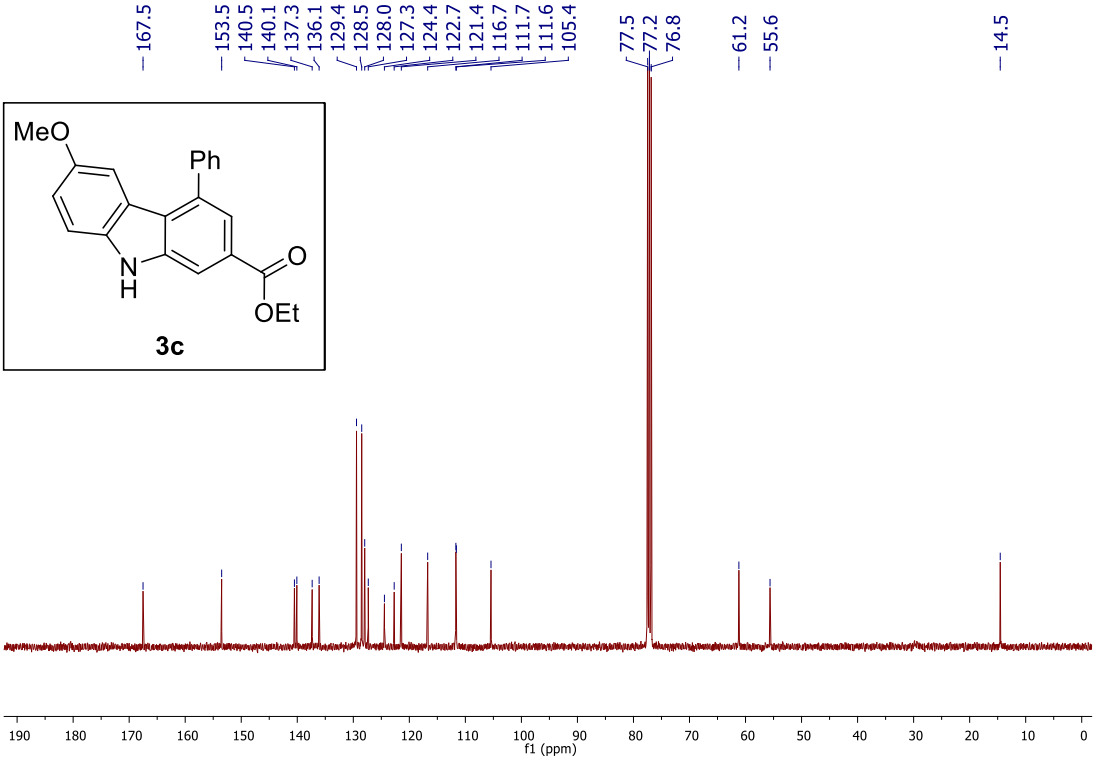
f1 (ppm)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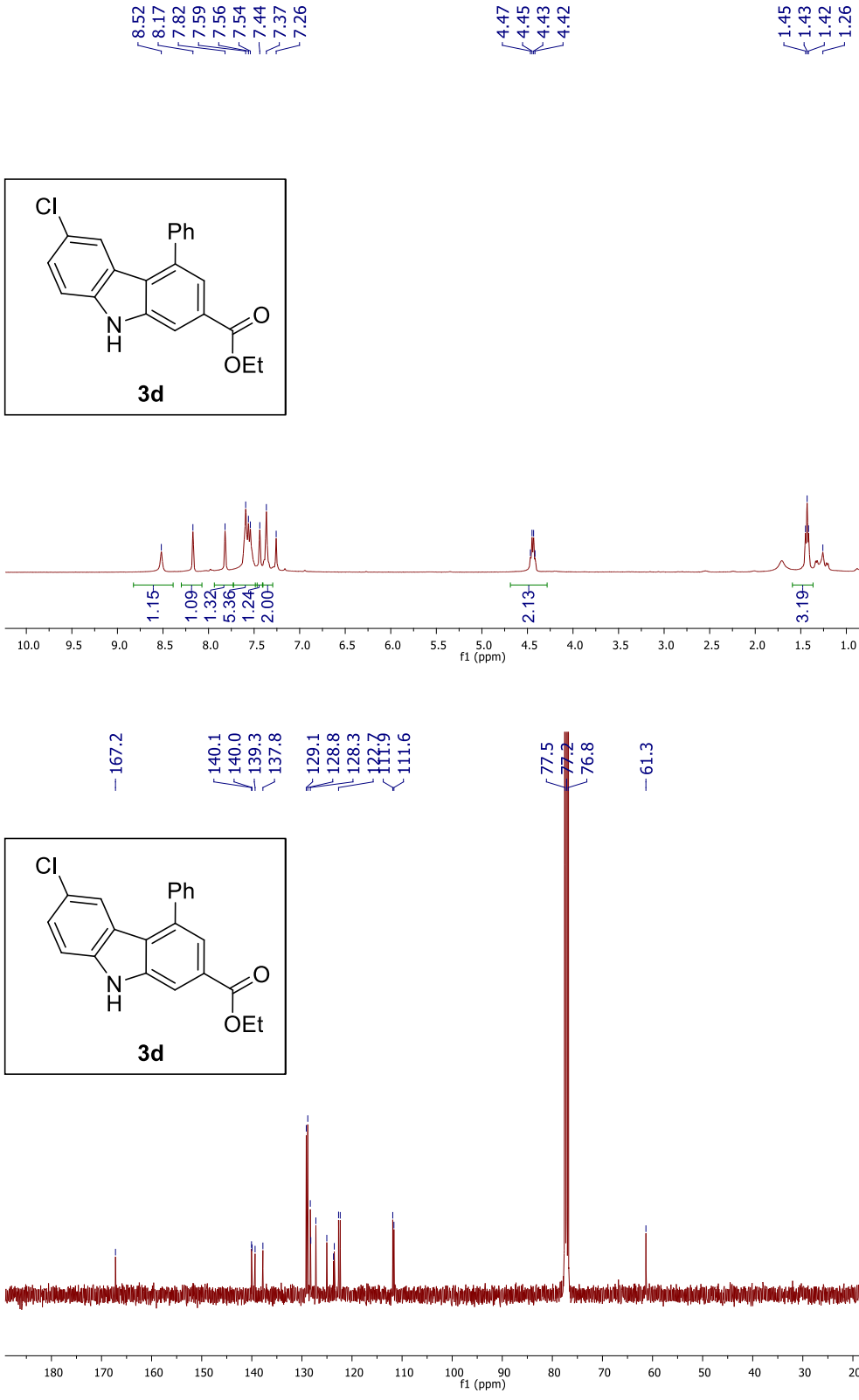
137.3
136.1
129.4
128.5
128.0
127.3
124.4
122.7
121.4
116.7
111.7
111.6
105.4
77.5
77.2
76.8
61.2
55.6
14.5
MeO
Ph
N
H
O
OEt
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.37
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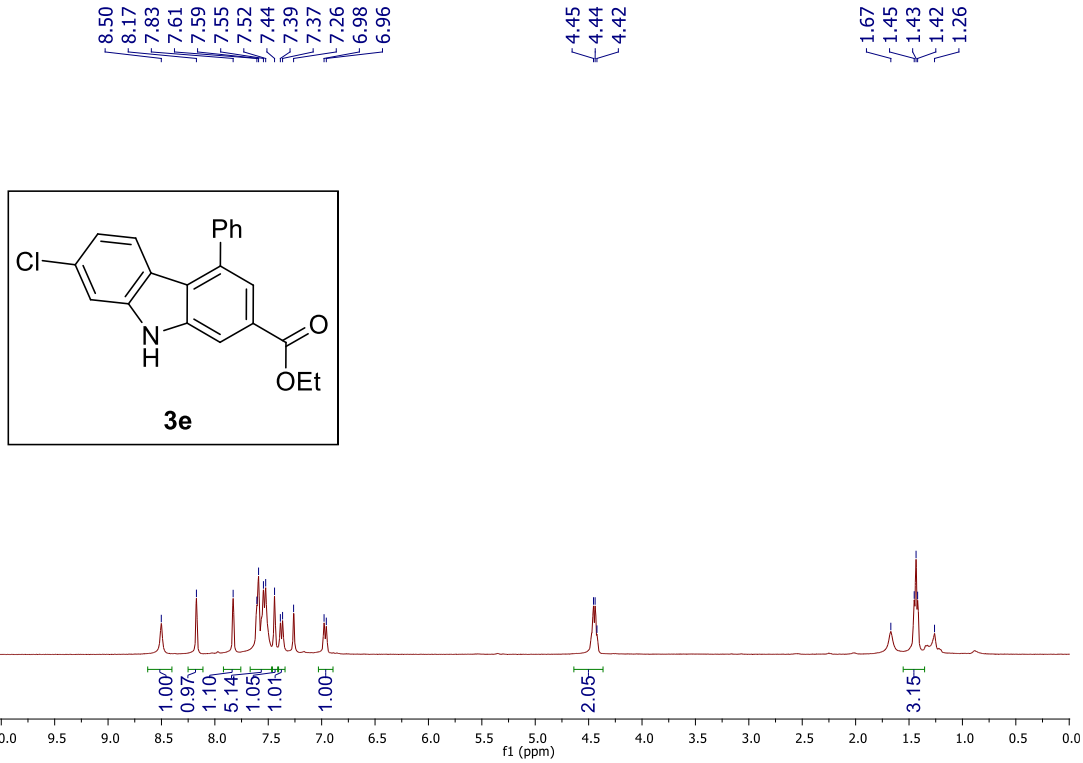
4.45
4.43
4.42
1.45
1.43
1.42
1.26
Cl
Ph
N
H
O
OEt
3d
1.15
1.09
1.32
5.36
1.24
2.00
2.13
3.19
f1 (ppm)
167.2
140.1
140.0
139.3
137.8
129.1
128.8
128.3
122.7
111.9
111.6
77.5
77.2
76.8
61.3
14.5
f1 (ppm)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7.44
7.39
7.37
7.26
6.98
6.96
4.45
4.44
4.42
1.67
1.45
1.43
1.42
1.26
Cl
Ph
N
H
O
OEt
3e
1.00
0.97
1.10
5.14
1.05
1.01
1.00
2.05
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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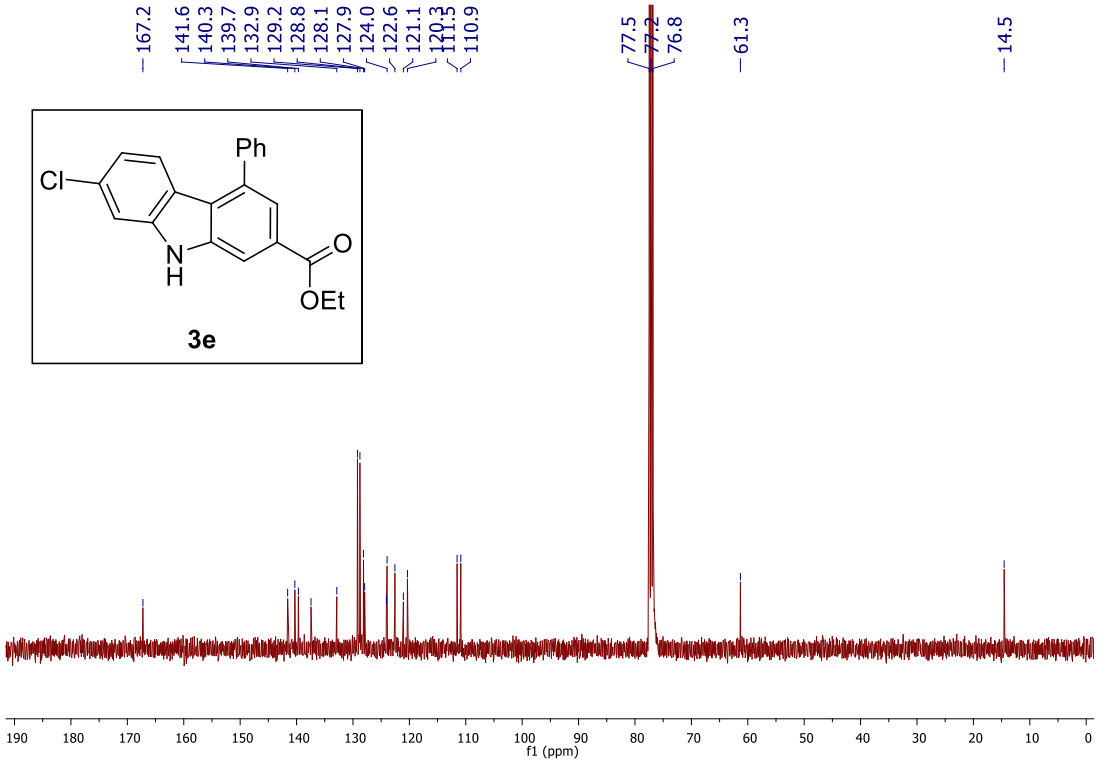
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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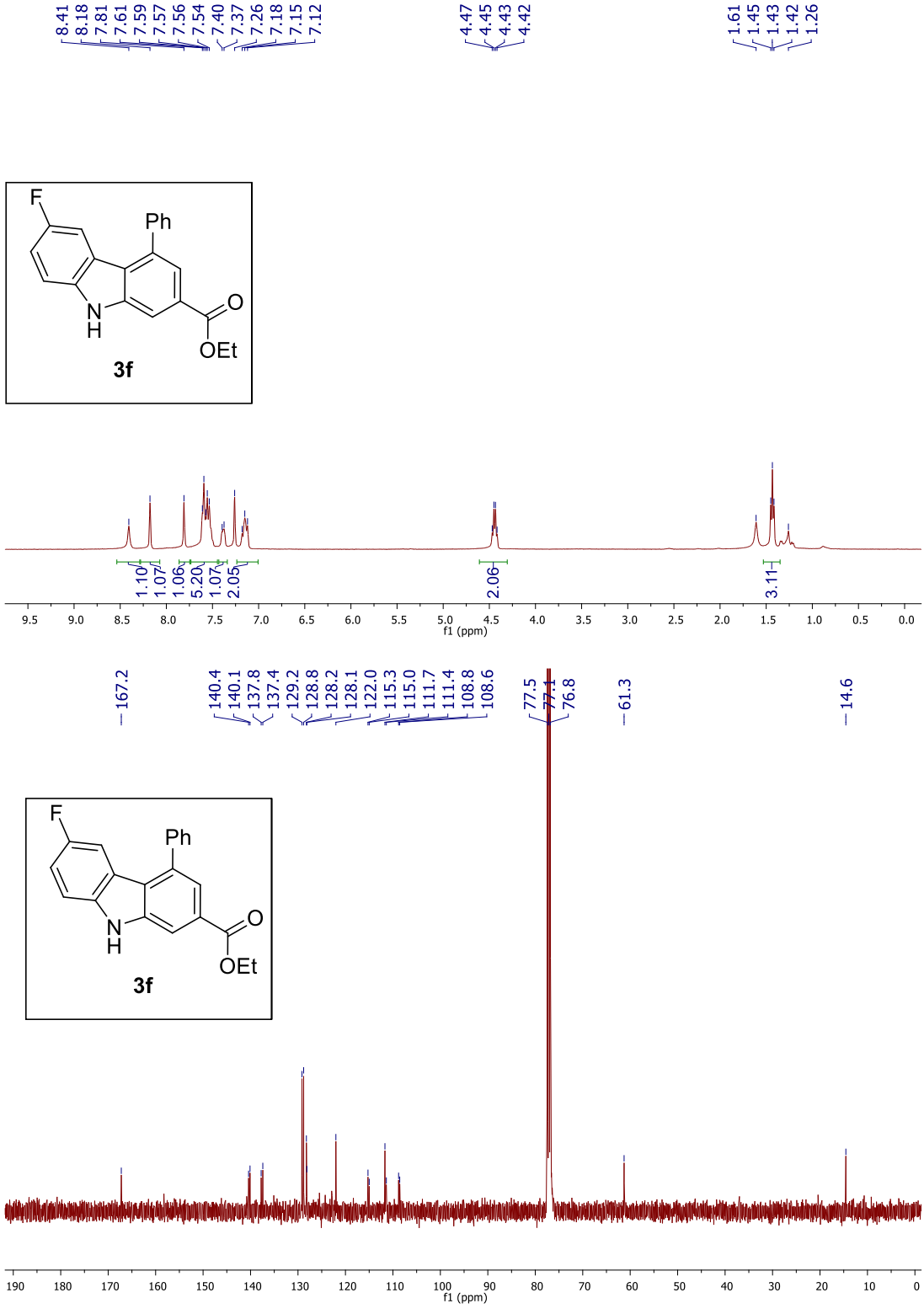
129.2
128.8
128.1
127.9
124.0
122.6
121.1
120.3
111.5
110.9
77.5
77.2
76.8
61.3
14.5
Cl
Ph
N
H
O
OEt
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.18
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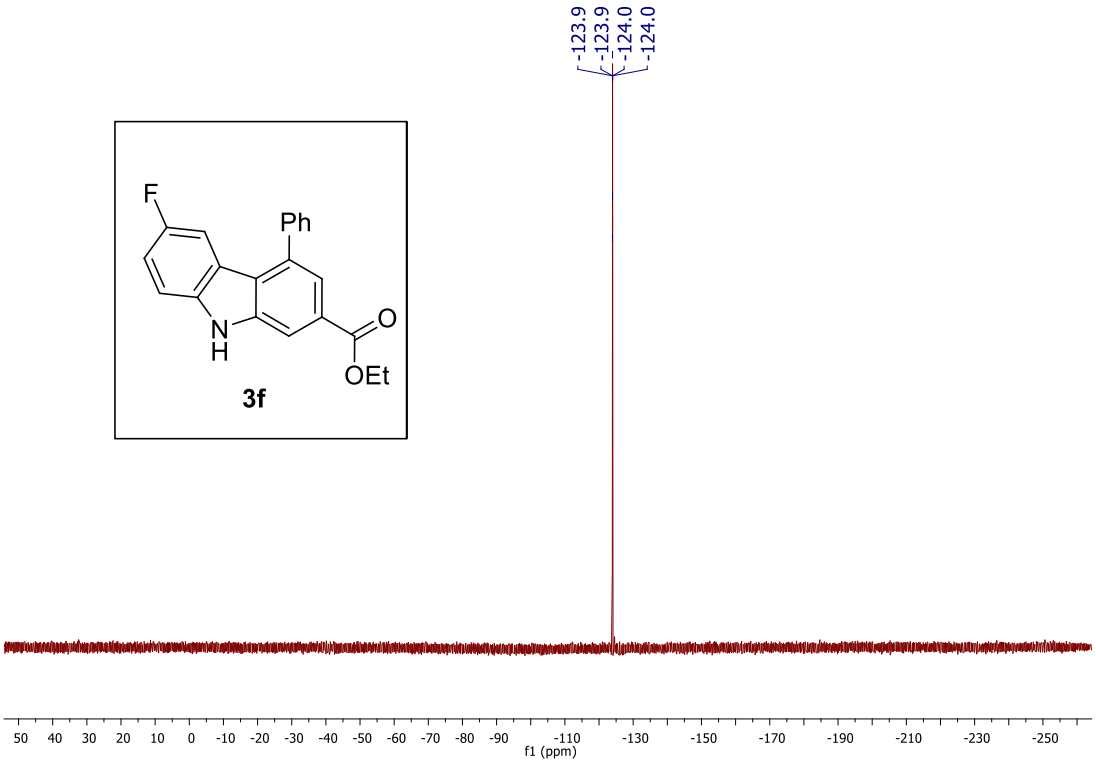
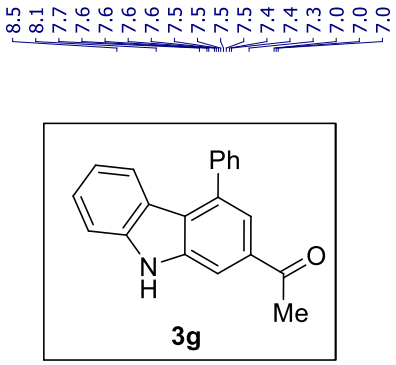
7.37
7.26
7.18
7.15
7.12
4.47
4.45
4.43
4.42
1.61
1.45
1.43
1.42
1.26
F
Ph
N
H
O
OEt
3f
1.10
1.07
1.06
5.20
1.07
2.05
2.06
3.11
f1 (ppm)
167.2
140.4
140.1
137.8
137.4
129.2
128.8
128.2
128.1
122.0
115.3
115.0
111.7
111.4
108.8
108.6
77.5
77.1
76.8
61.3
14.6
f1 (ppm)


-123.9
-123.9
-124.0
-124.0
F
Ph
N
H
O
OEt
3f
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)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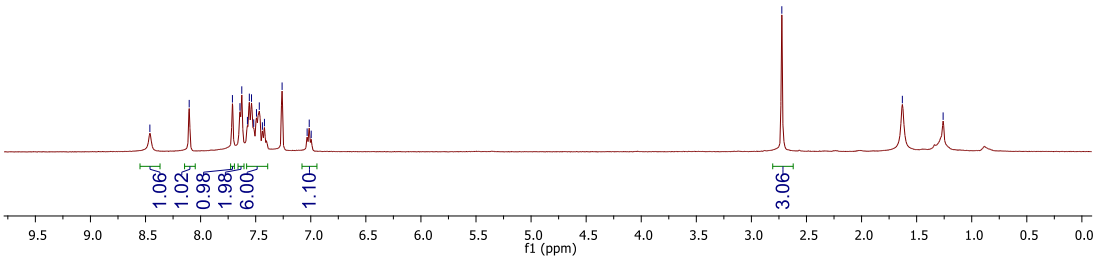
8.1
7.7
7.6
7.6
7.6
7.6
7.5
7.5
7.5
7.5
7.4
7.4
7.3
7.0
7.0
7.0
2.7
1.6
1.3
Ph
N
H
O
Me
3g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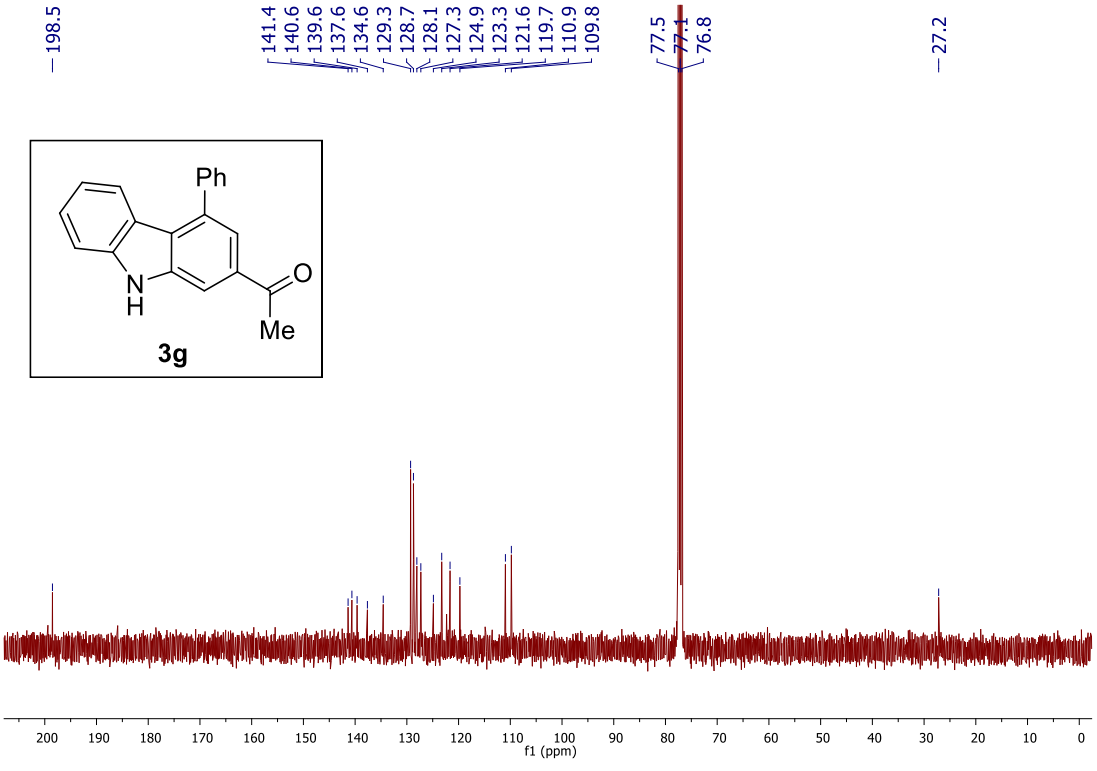
1.02
0.98
1.98
6.00
1.10
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.6
139.6
137.6
134.6
129.3
128.7
128.1
127.3
124.9
123.3
121.6
119.7
110.9
109.8
77.5
77.1
76.8
27.2
Ph
N
H
O
Me
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.96
7.96
7.96
7.91
7.91
7.91
7.91
7.90
7.89
7.89
7.65
7.65
7.64
7.64
7.63
7.63
7.63
7.60
7.59
7.59
7.59
7.58
7.58
7.56
7.56
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7.51
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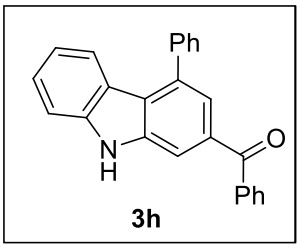
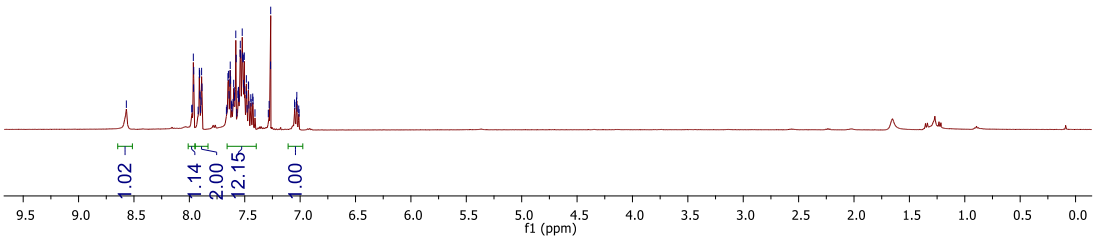
7.27
7.27
7.03


Ph
N
H
O
Ph

3h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1.14
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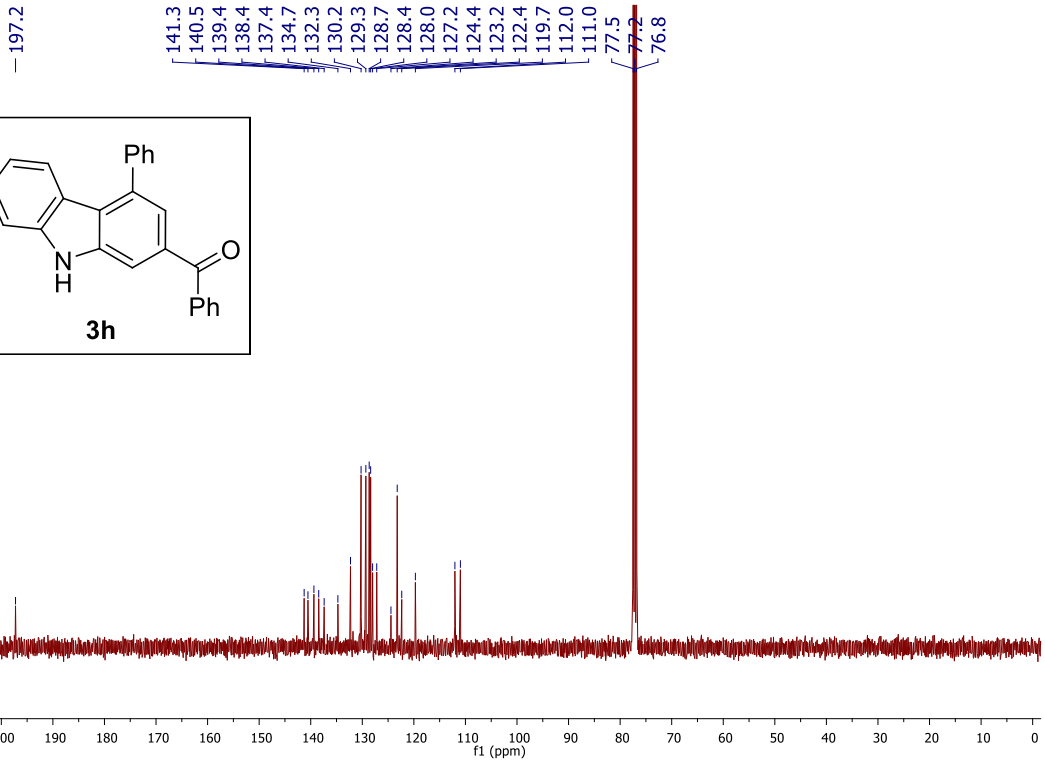
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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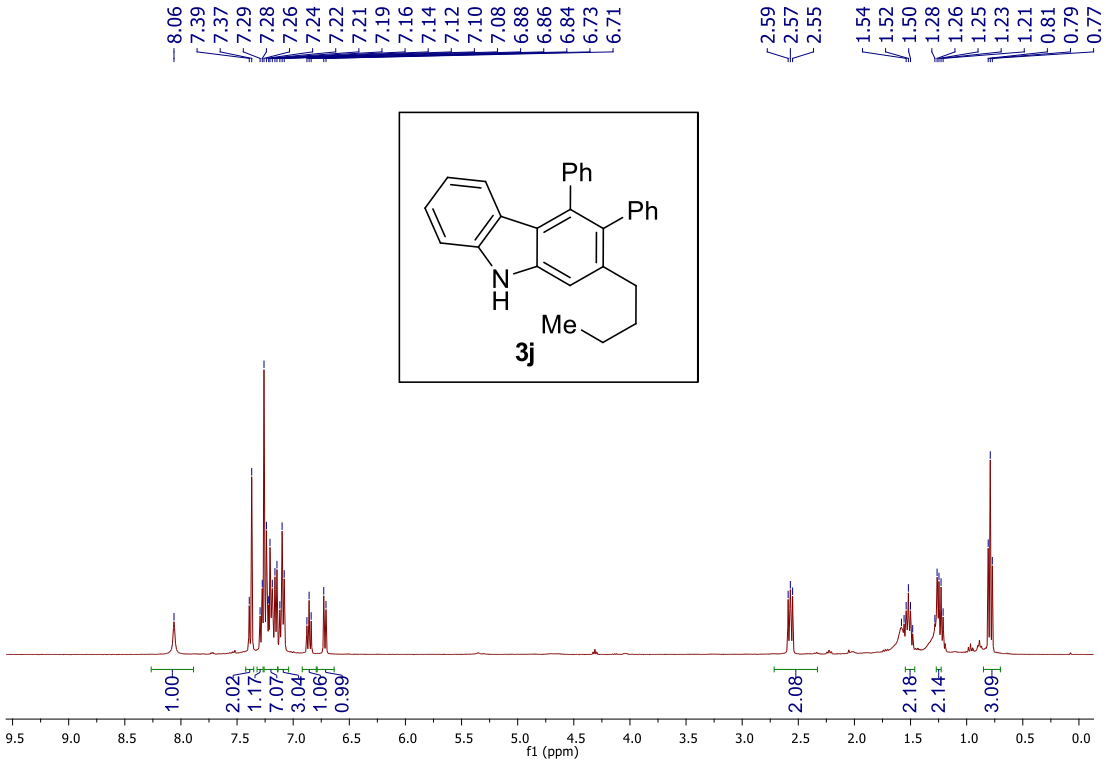
138.4
137.4
134.7
132.3
130.2
129.3
128.7
128.4
128.0
127.2
124.4
123.2
122.4
119.7
112.0
111.0
77.5
77.2
76.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Ph
N
H
O
Ph

3h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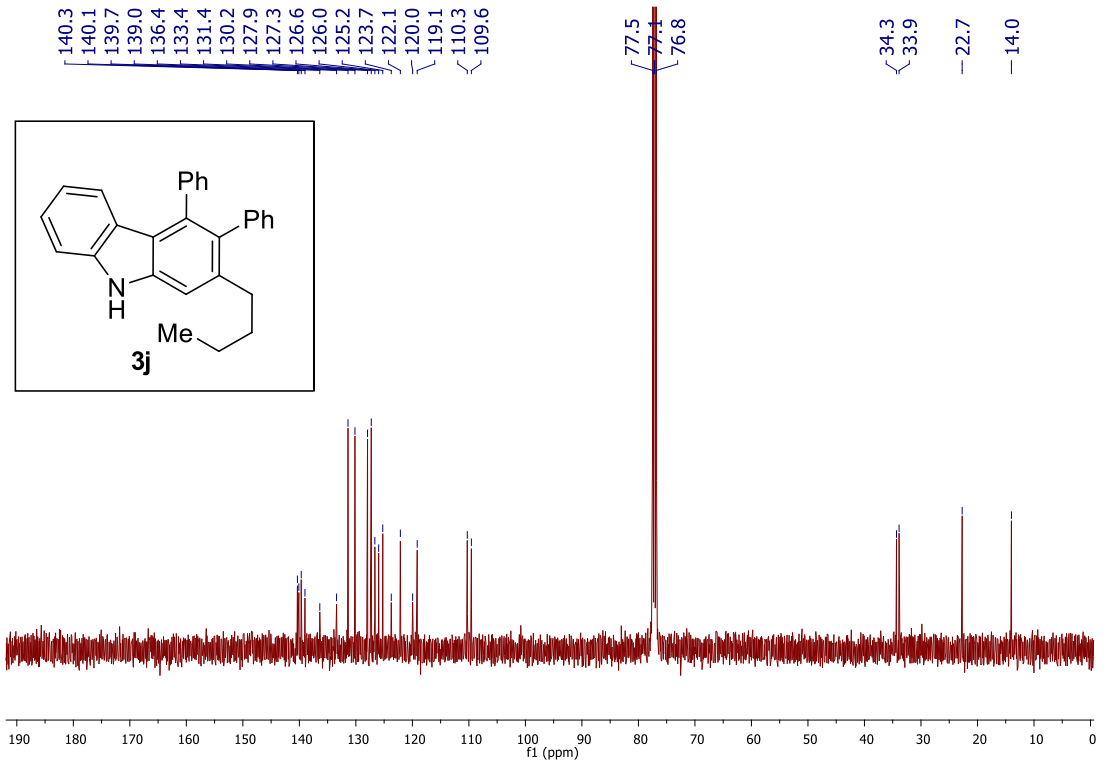
7.19
7.16
7.14
7.12
7.10
7.08
6.88
6.86
6.84
6.73
6.71
2.59
2.57
2.55
1.54
1.52
1.50
1.28
1.26
1.25
1.23
1.21
0.81
0.79
0.77
Ph
Ph
N
H
Me
3j
1.00
2.02
1.17
7.07
3.04
1.06
0.99
2.08
2.18
2.14
3.09
f1 (ppm)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139.7
139.0
136.4
133.4
131.4
130.2
127.9
127.3
126.6
126.0
125.2
123.7
122.1
120.0
119.1
110.3
109.6
77.5
77.1
76.8
34.3
33.9
22.7
14.0
Ph
Ph
N
H
Me
3j
f1 (ppm)


8.22
8.22
8.21
8.21
7.78
7.78
7.78
7.78
7.46
7.46
7.44
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.26
6.99
6.99
6.98
6.98
6.97
6.97
4.46
4.46
4.44
4.44
4.42
2.08
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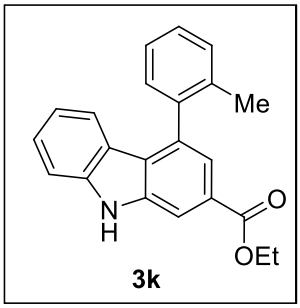
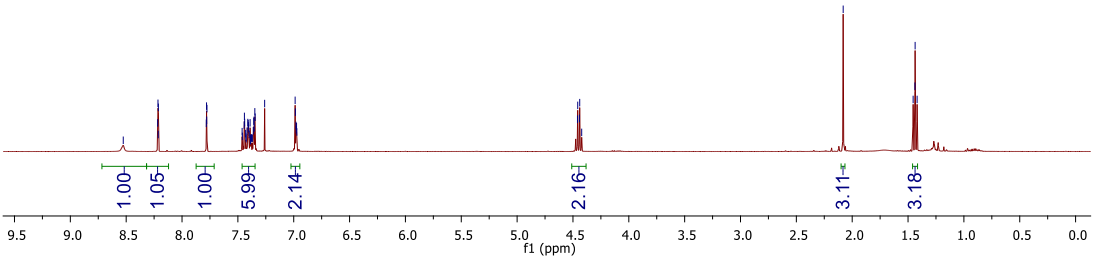
1.44
1.44
1.42


Me
N
H
O
OEt
3k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1.05
1.00
5.99
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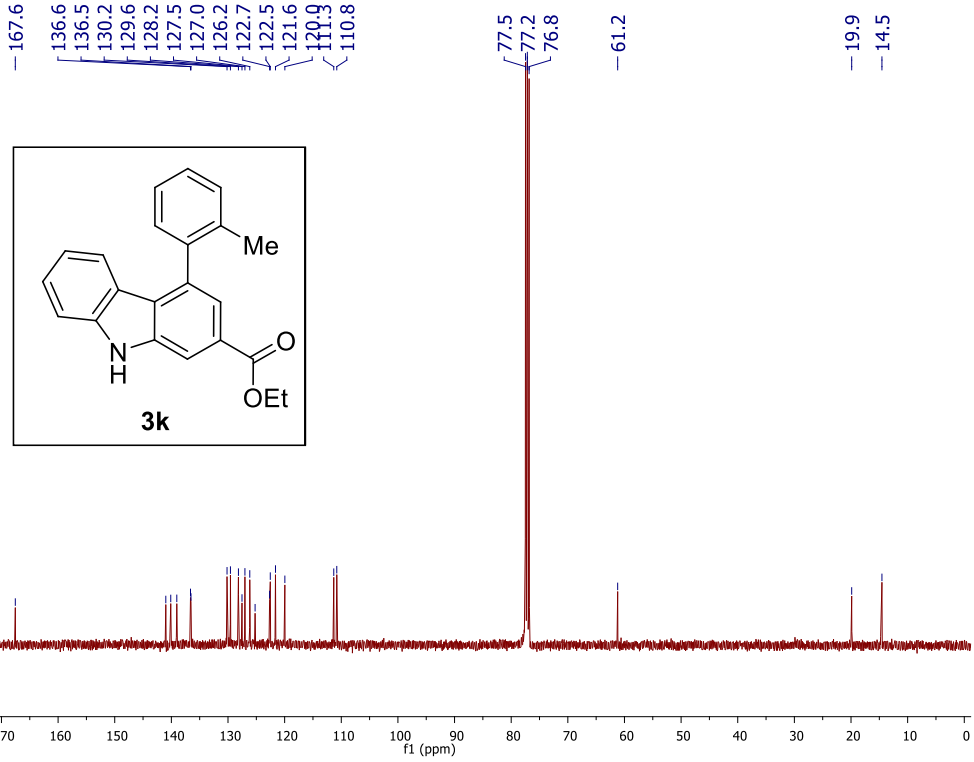
2.16
3.11
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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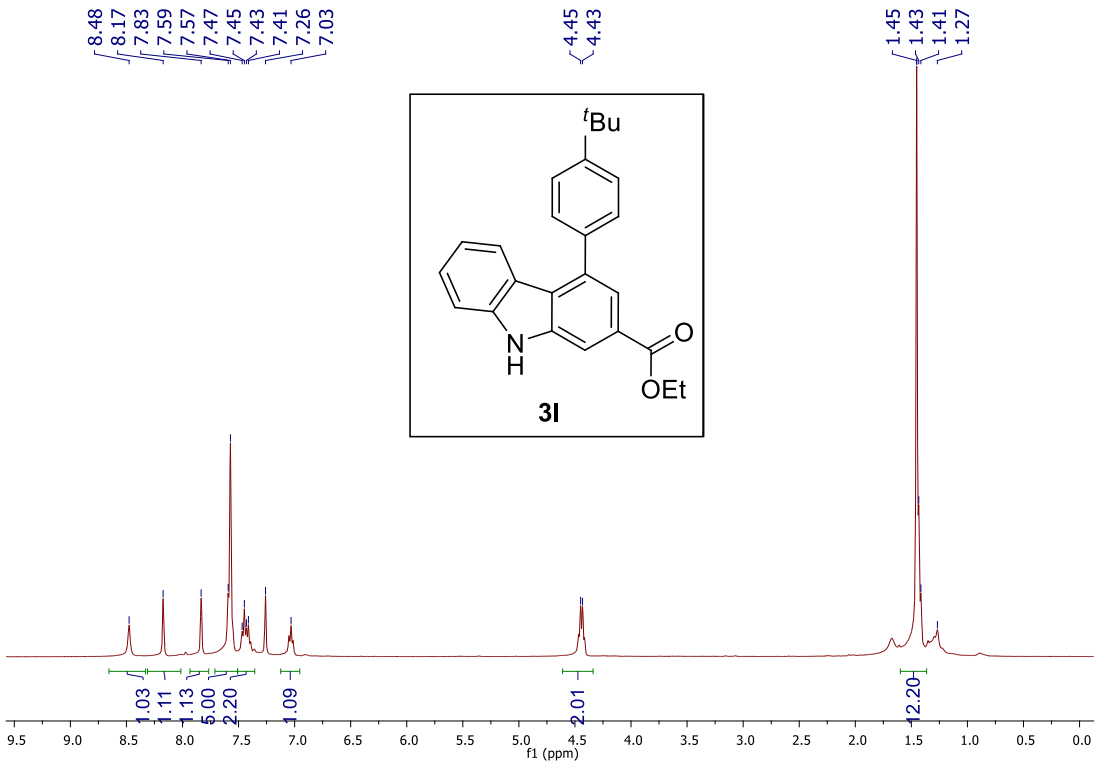
136.6
136.5
130.2
129.6
128.2
127.5
127.0
126.2
122.7
122.5
121.6
120.9
111.3
110.8
77.5
77.2
76.8
61.2
19.9
14.5
Me
N
H
O
OEt
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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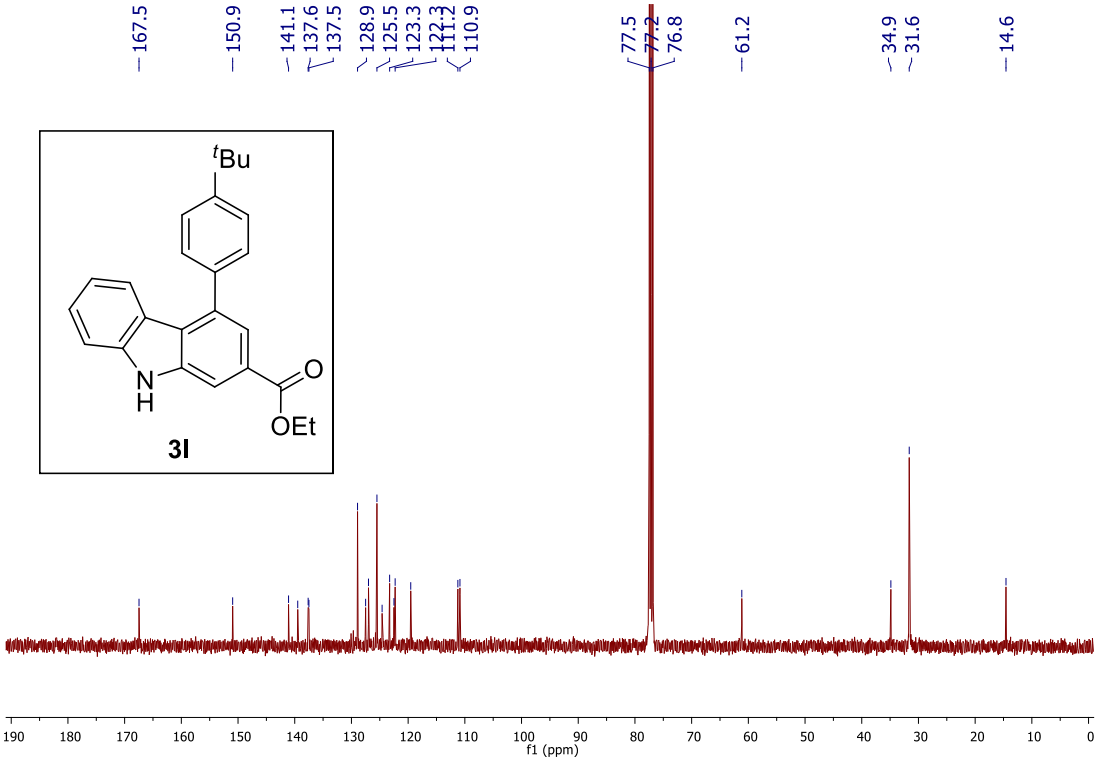
7.43
7.41
7.26
7.03
4.45
4.43
1.45
1.43
1.41
1.27
tBu
N
H
O
OEt
3l
1.03
1.11
1.13
5.00
2.20
1.09
2.01
12.20
f1 (ppm)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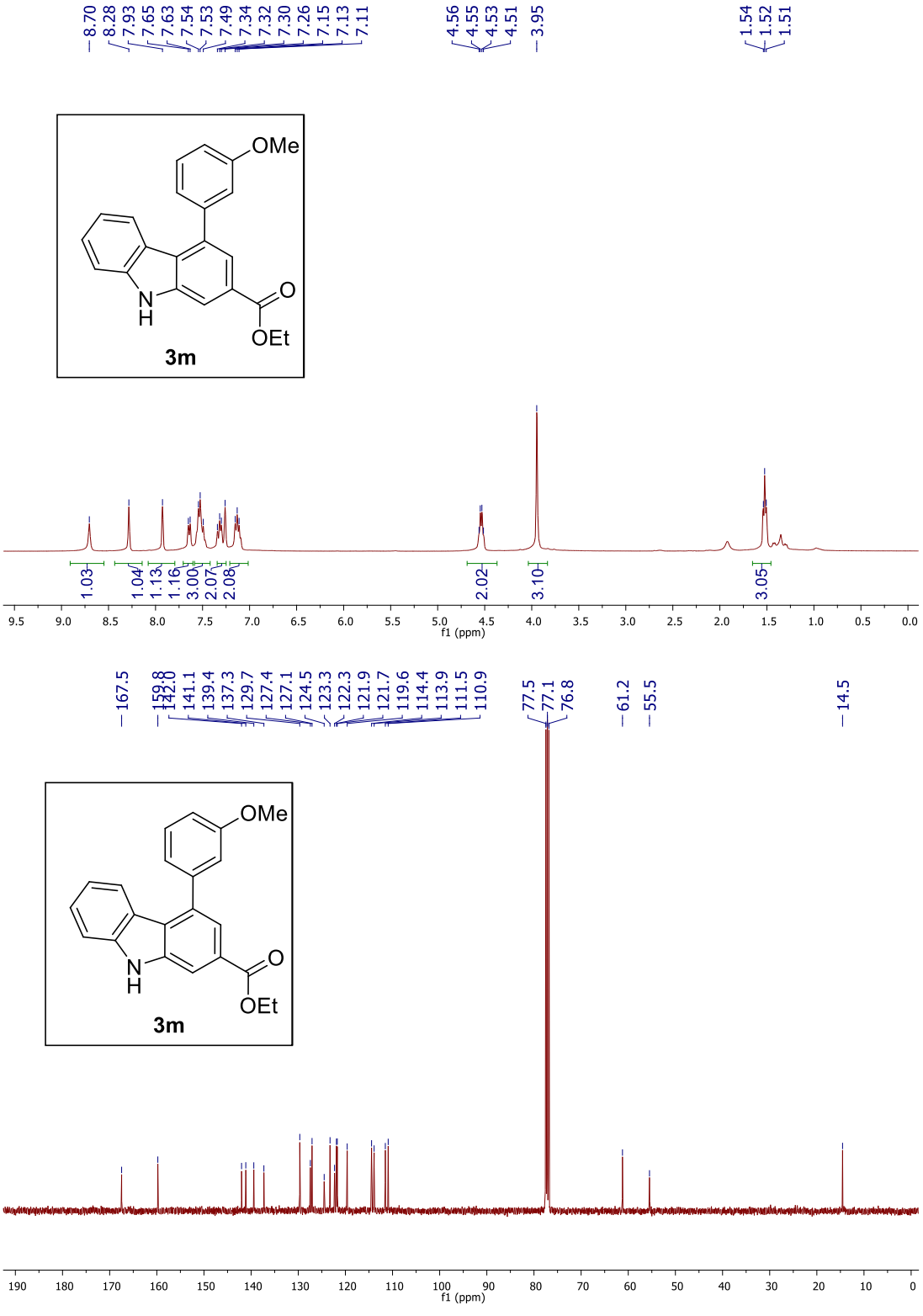
137.6
137.5
128.9
125.5
123.3
122.3
111.2
110.9
77.5
77.2
76.8
61.2
34.9
31.6
14.6
tBu
N
H
O
OEt
3l
f1 (ppm)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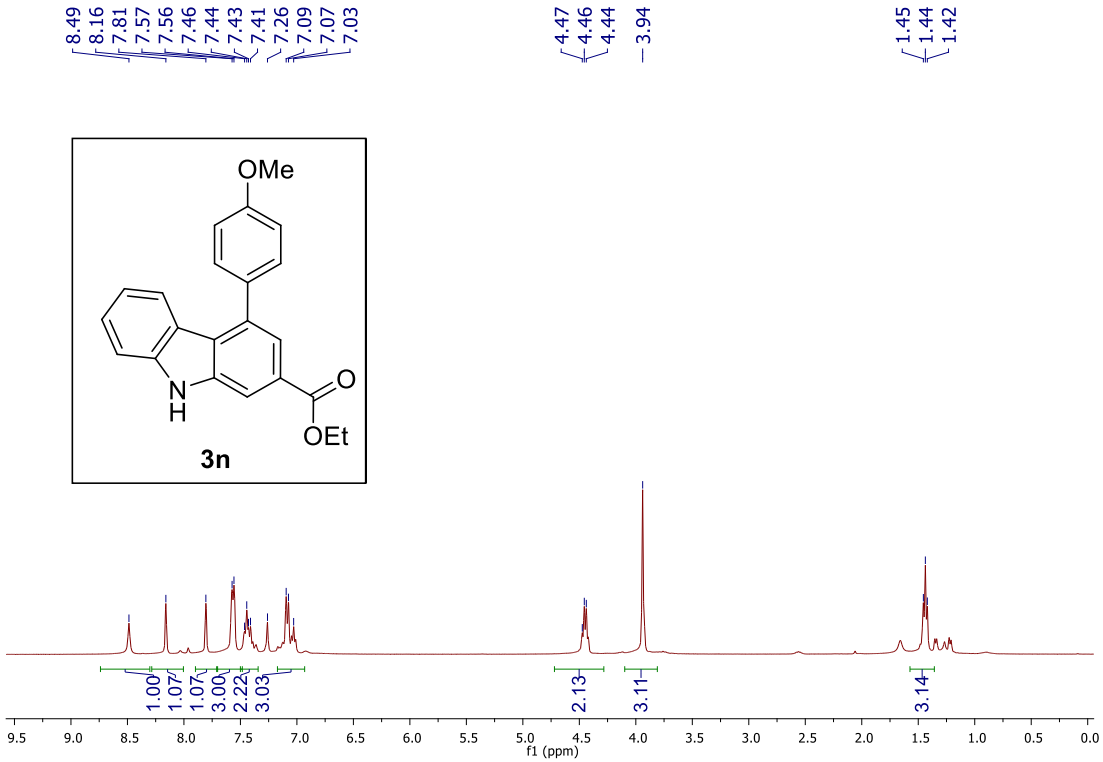
7.32
7.30
7.26
7.15
7.13
7.11
4.56
4.55
4.53
4.51
3.95
1.54
1.52
1.51
OMe
N
H
O
OEt
3m
1.03
1.04
1.13
1.16
3.00
2.07
2.08
2.02
3.10
3.05
f1 (ppm)
167.5
159.8
142.0
141.1
139.4
137.3
129.7
127.4
127.1
124.5
123.3
122.3
121.9
121.7
119.6
114.4
113.9
111.5
110.9
77.5
77.1
76.8
61.2
55.5
14.5
OMe
N
H
O
OEt
3m
f1 (ppm)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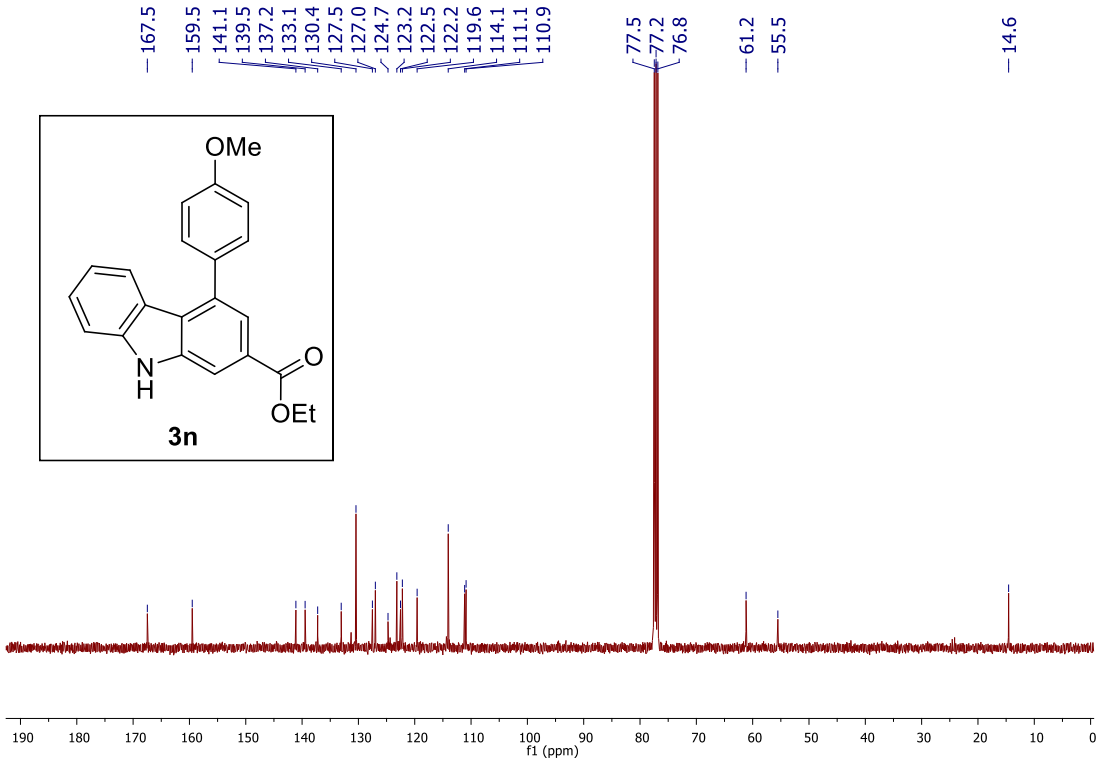
7.26
7.09
7.07
7.03
4.47
4.46
4.44
3.94
1.45
1.44
1.42
OMe
N
H
O
OEt
3n
1.00
1.07
1.07
3.00
2.22
3.03
2.13
3.11
3.14
f1 (ppm)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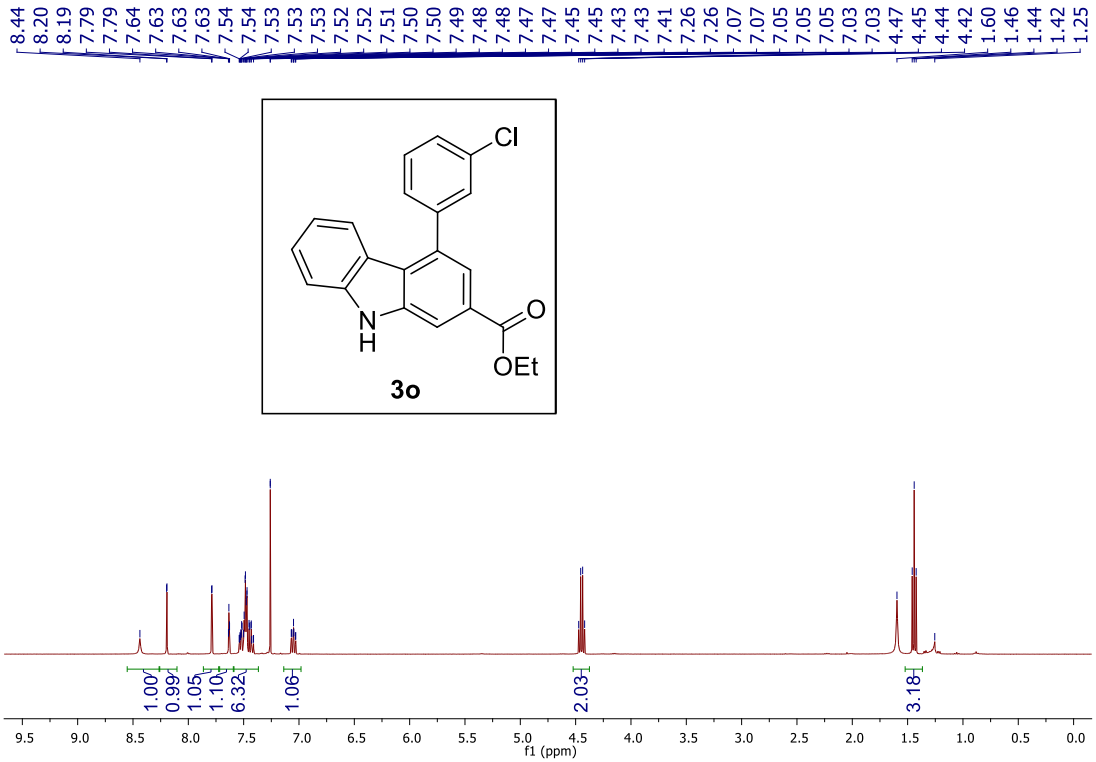
141.1
139.5
137.2
133.1
130.4
127.5
127.0
124.7
123.2
122.5
122.2
119.6
114.1
111.1
110.9
77.5
77.2
76.8
61.2
55.5
14.6
OMe
N
H
O
OEt
3n
f1 (ppm)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7.53
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7.53
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7.43
7.43
7.41
7.26
7.26
7.07
7.07
7.05
7.05
7.05
7.03
7.03
4.47
4.45
4.44
4.42
1.60
1.46
1.44
1.42
1.25
Cl
N
H
O
OEt
3o
1.00
0.99
1.05
1.10
6.32
1.06
2.03
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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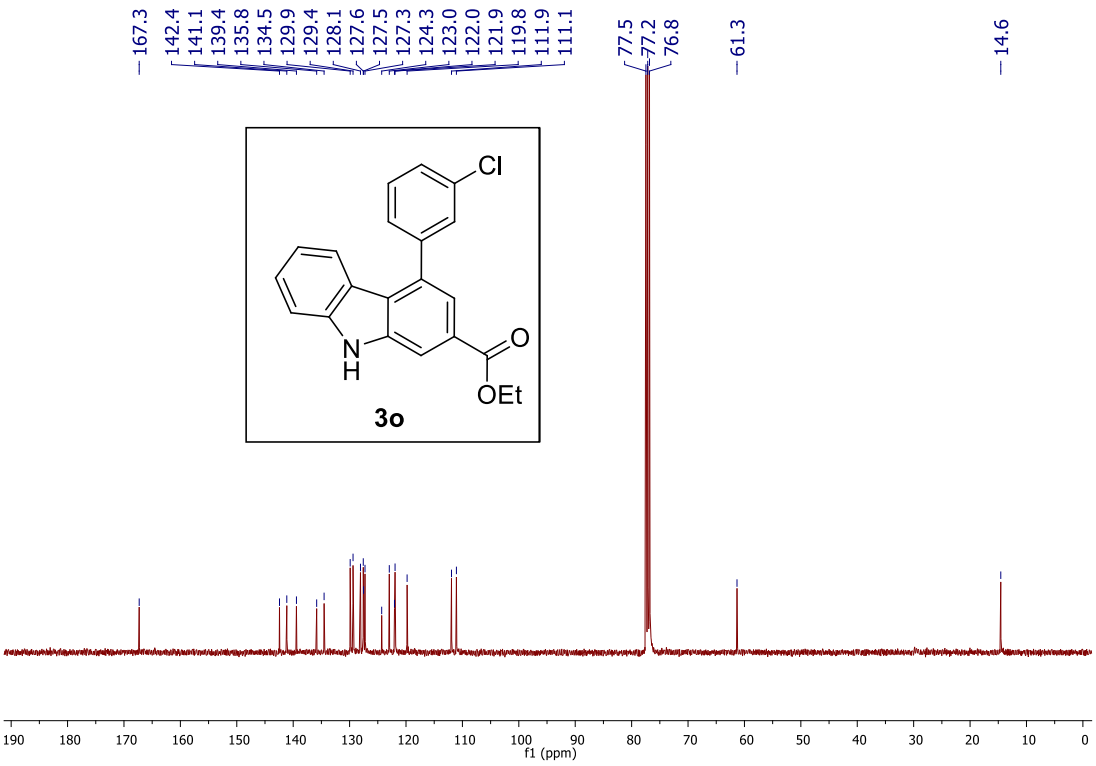
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.4
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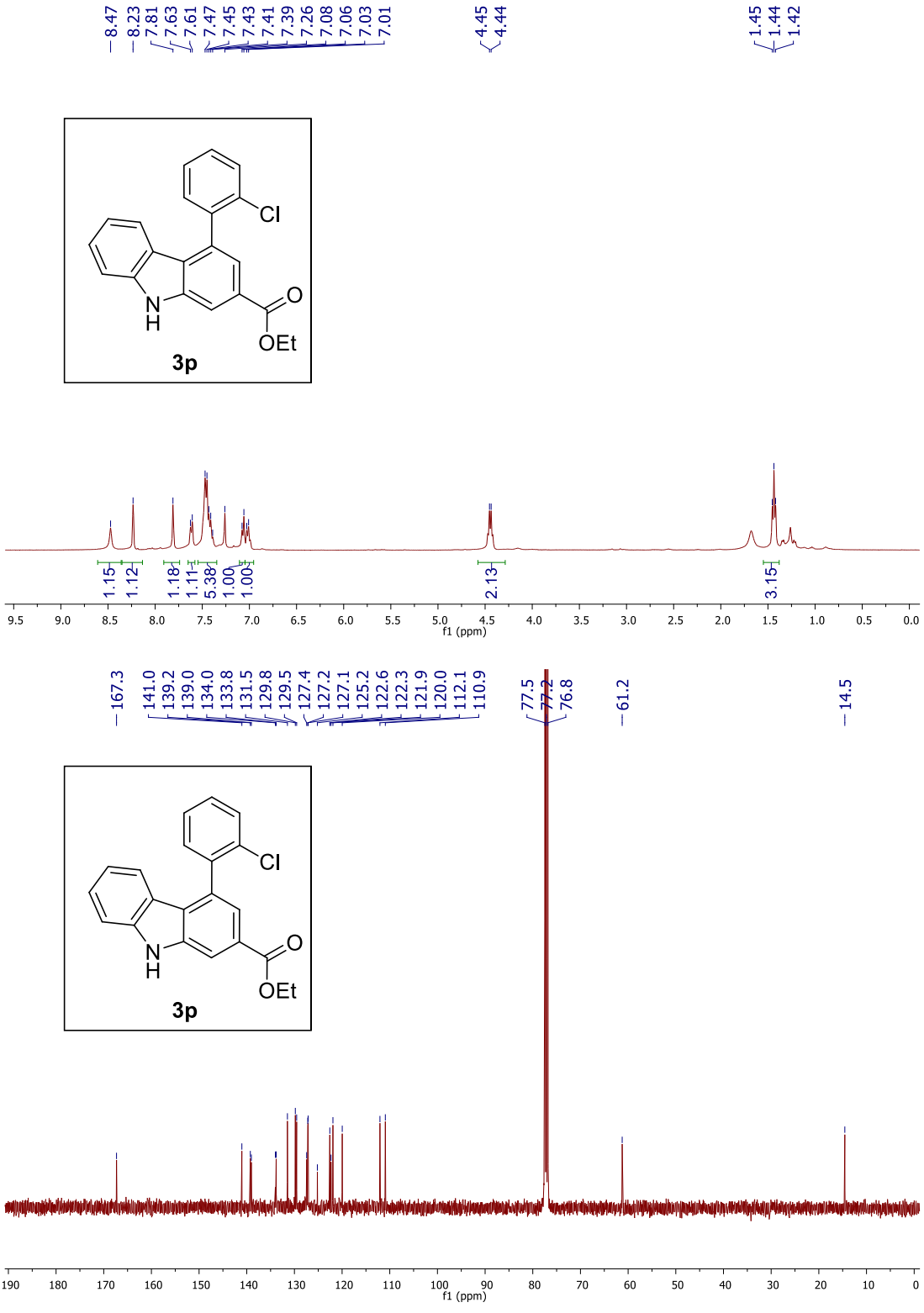
127.6
127.5
127.3
124.3
123.0
122.0
121.9
119.8
111.9
111.1
77.5
77.2
76.8
61.3
14.6
Cl
N
H
O
OEt
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.61
7.47
7.45
7.43
7.41
7.39
7.26
7.08
7.06
7.03
7.01
4.45
4.44
1.45
1.44
1.42
Cl
N
H
O
OEt
3p
1.15
1.12
1.18
1.11
5.38
1.00
1.00
2.13
3.15
f1 (ppm)
167.3
141.0
139.2
139.0
134.0
133.8
131.5
129.8
129.5
127.4
127.2
127.1
125.2
122.6
122.3
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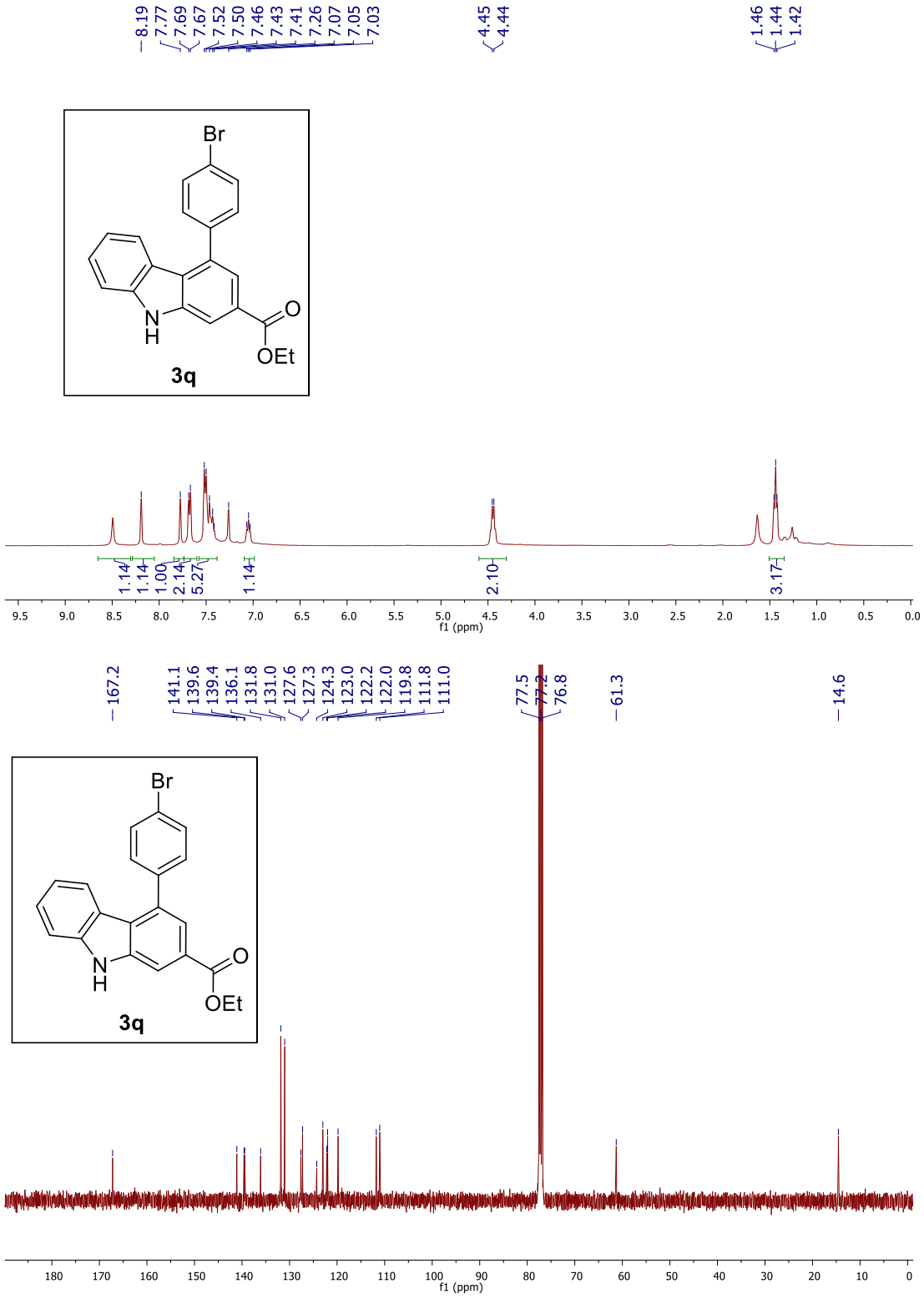
110.9
77.5
77.2
76.8
61.2
14.5
f1 (ppm)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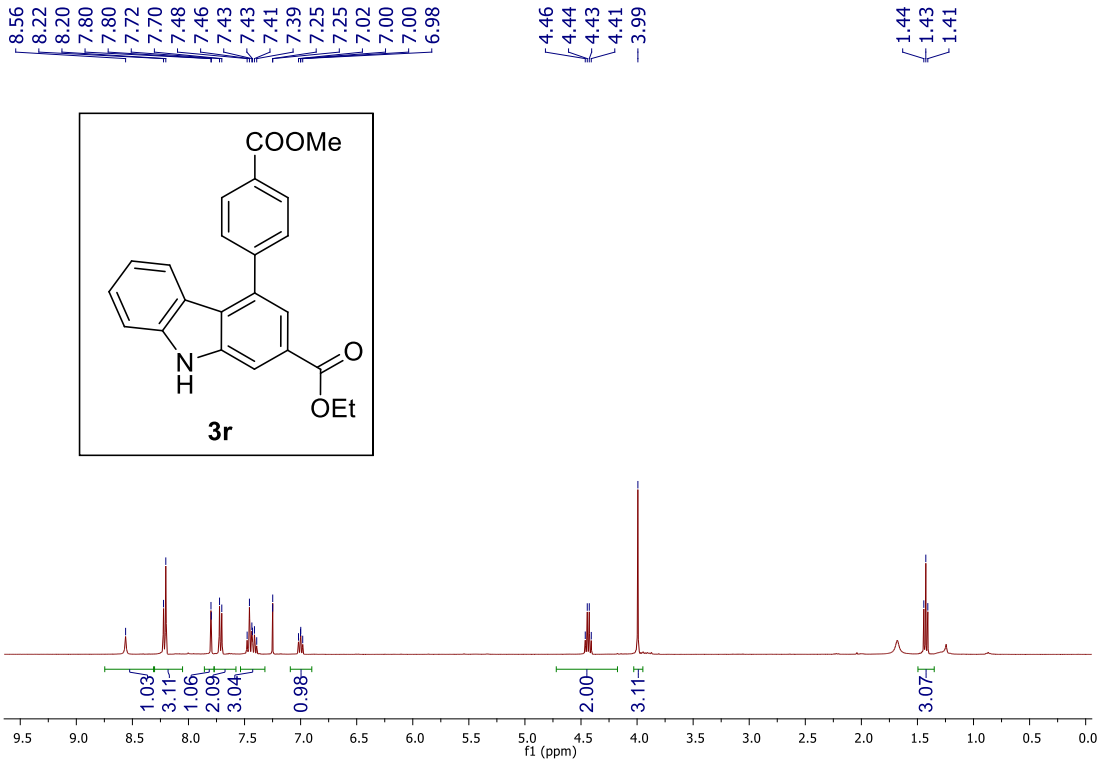
7.43
7.41
7.26
7.07
7.05
7.03
4.45
4.44
1.46
1.44
1.42
Br
N
H
O
OEt
3q
1.14
1.14
1.00
2.14
5.27
1.14
2.10
3.17
f1 (ppm)
167.2
141.1
139.6
139.4
136.1
131.8
131.0
127.6
127.3
124.3
123.0
122.2
122.0
119.8
111.8
111.0
77.5
77.2
76.8
61.3
14.6
Br
N
H
O
OEt
3q
f1 (ppm)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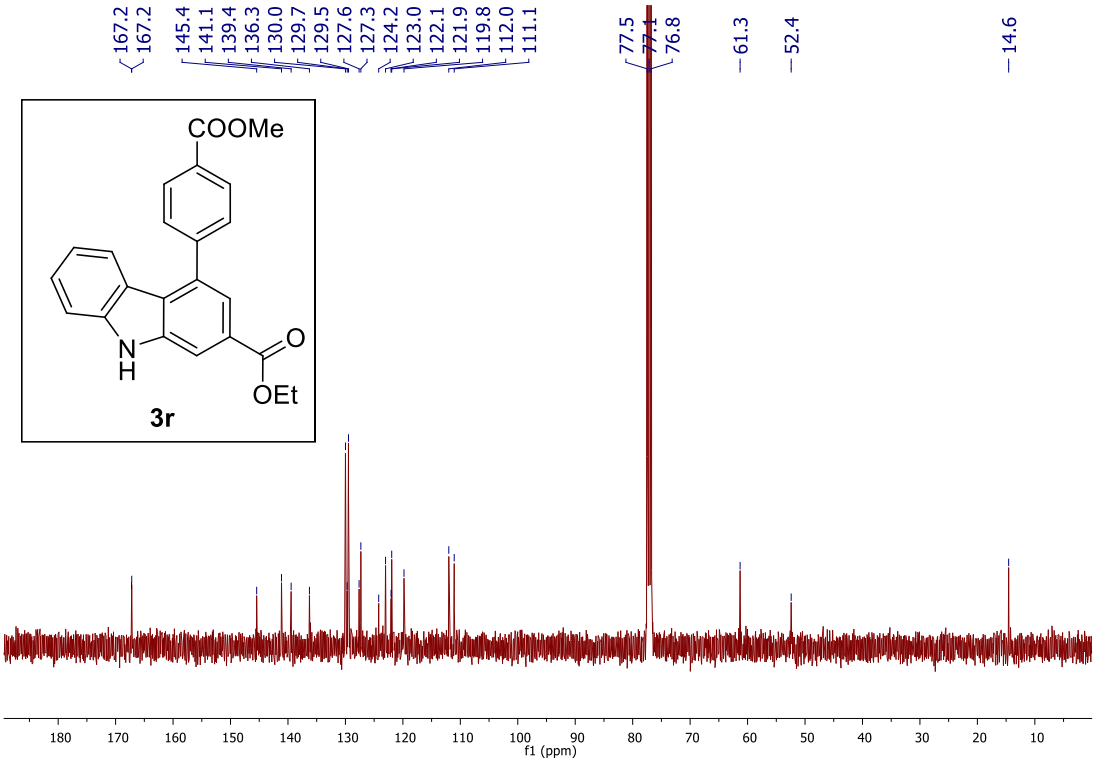
7.70
7.48
7.46
7.43
7.43
7.41
7.39
7.25
7.25
7.02
7.00
7.00
6.98
4.46
4.44
4.43
4.41
3.99
1.44
1.43
1.41
COOMe
N
H
O
OEt
3r
1.03
3.11
1.06
2.09
3.04
0.98
2.00
3.11
3.07
f1 (ppm)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167.2
145.4
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139.4
136.3
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129.7
129.5
127.6
127.3
124.2
123.0
122.1
121.9
119.8
112.0
111.1
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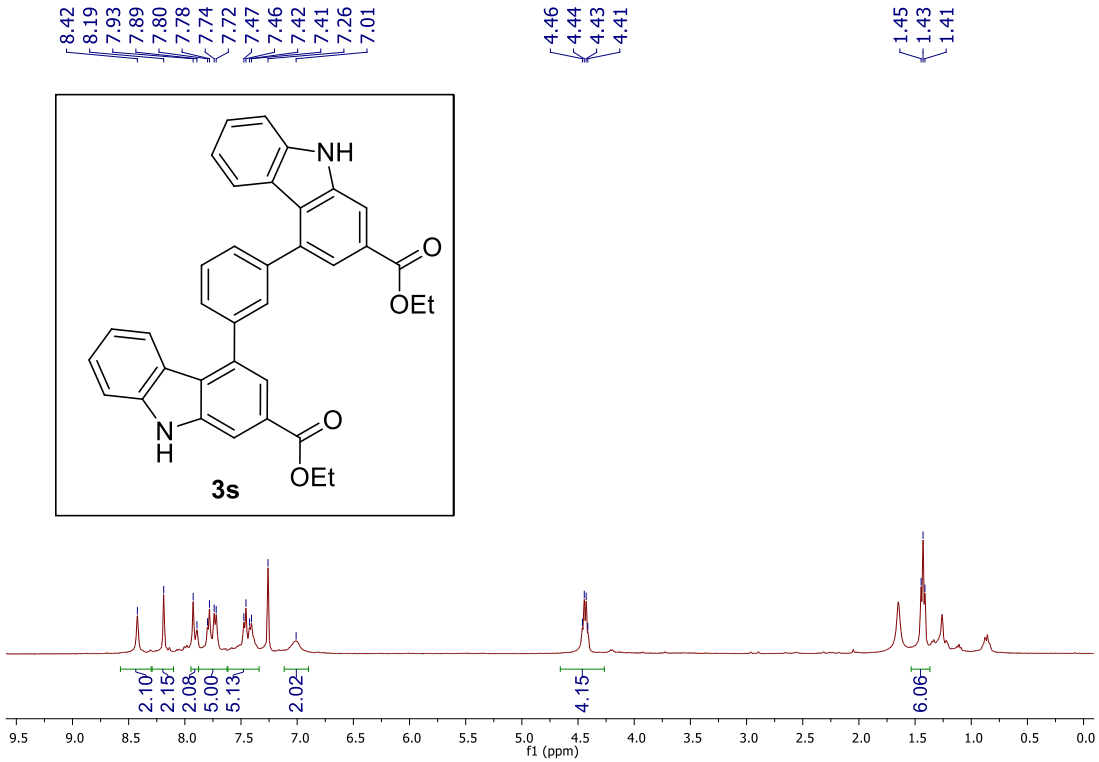
77.1
76.8
61.3
52.4
14.6
COOMe
N
H
O
OEt
3r
f1 (ppm)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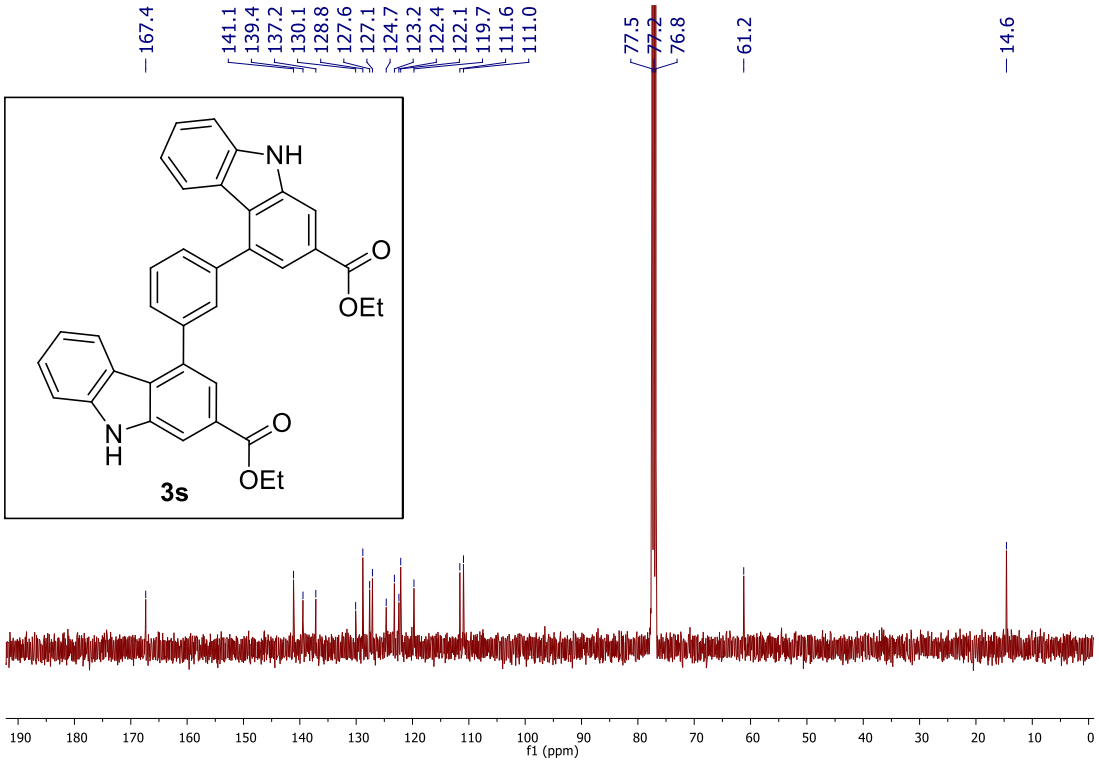
7.74
7.72
7.47
7.46
7.42
7.41
7.26
7.01
4.46
4.44
4.43
4.41
1.45
1.43
1.41
NH
O
OEt
N
H
O
OEt
3s
2.10
2.15
2.08
5.00
5.13
2.02
4.15
6.06
f1 (ppm)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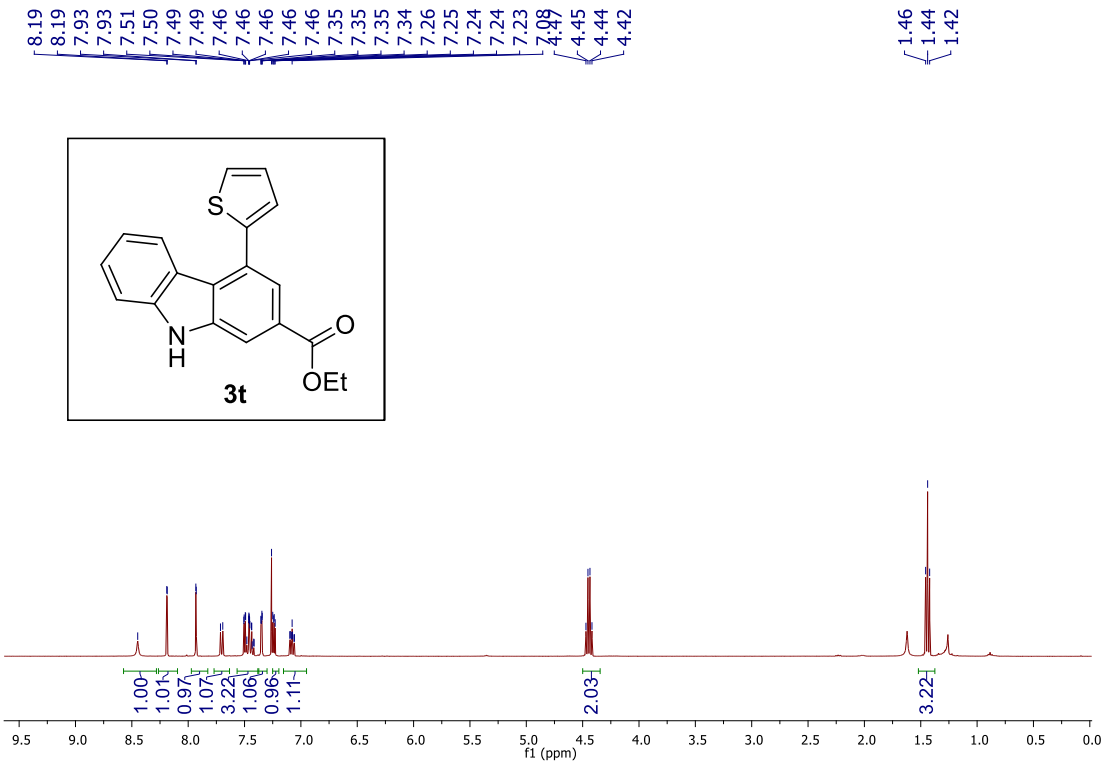
139.4
137.2
130.1
128.8
127.6
127.1
124.7
123.2
122.4
122.1
119.7
111.6
111.0
77.5
77.2
76.8
61.2
14.6
NH
O
OEt
N
H
O
OEt
3s
f1 (ppm)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8.19
7.93
7.93
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7.50
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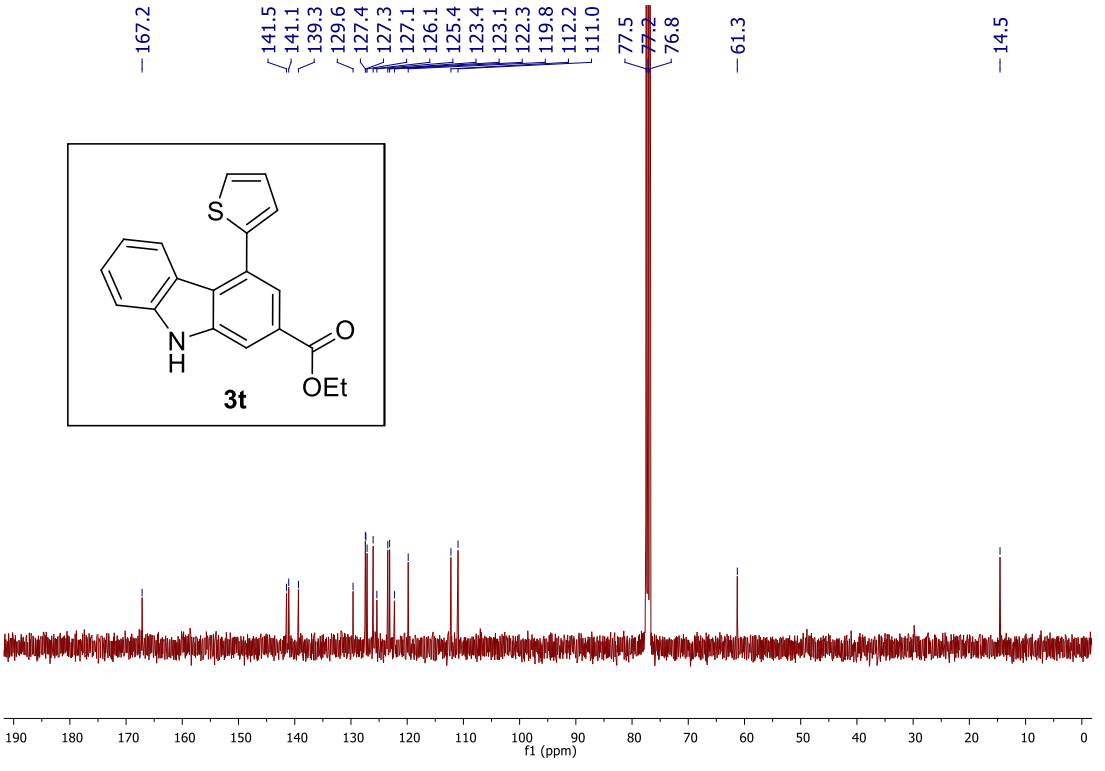
7.49
7.46
7.46
7.46
7.46
7.46
7.35
7.35
7.35
7.34
7.26
7.25
7.24
7.24
7.23
7.08
4.47
4.45
4.44
4.42
1.46
1.44
1.42
S
N
H
O
OEt
3t
1.00
1.01
0.97
1.07
3.22
1.06
0.96
1.11
2.03
3.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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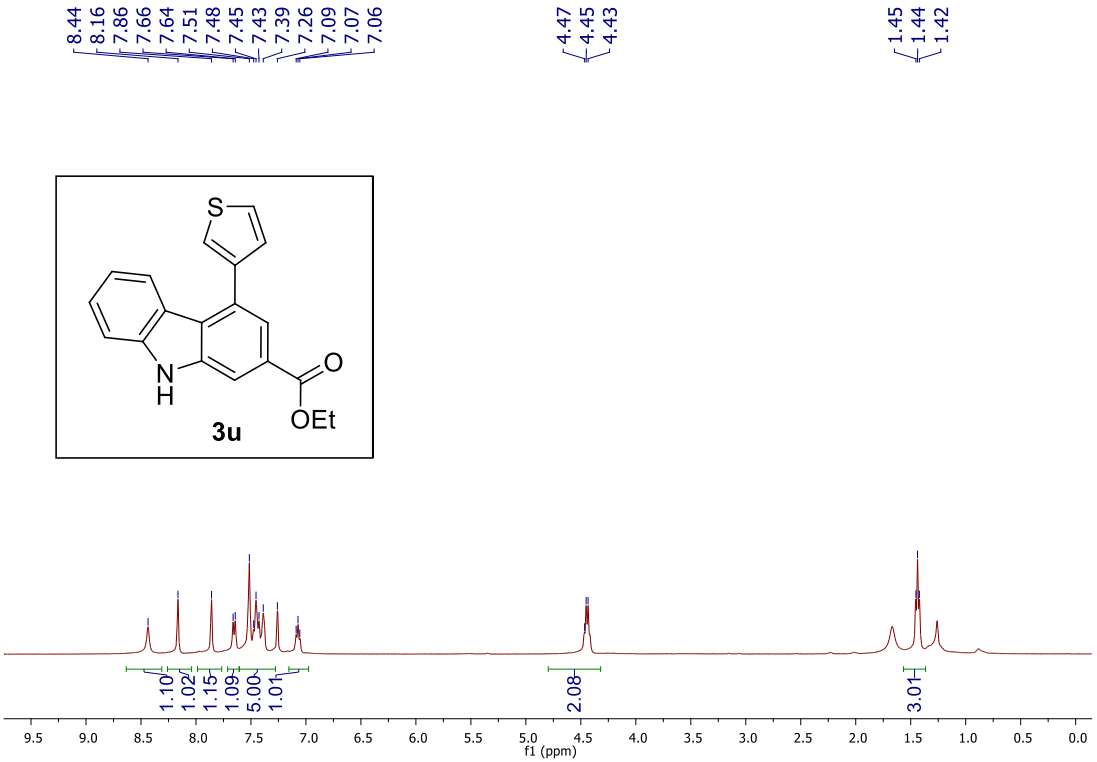
141.5
141.1
139.3
129.6
127.4
127.3
127.1
126.1
125.4
123.4
123.1
122.3
119.8
112.2
111.0
77.5
77.2
76.8
61.3
14.5
S
N
H
O
OEt
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.45
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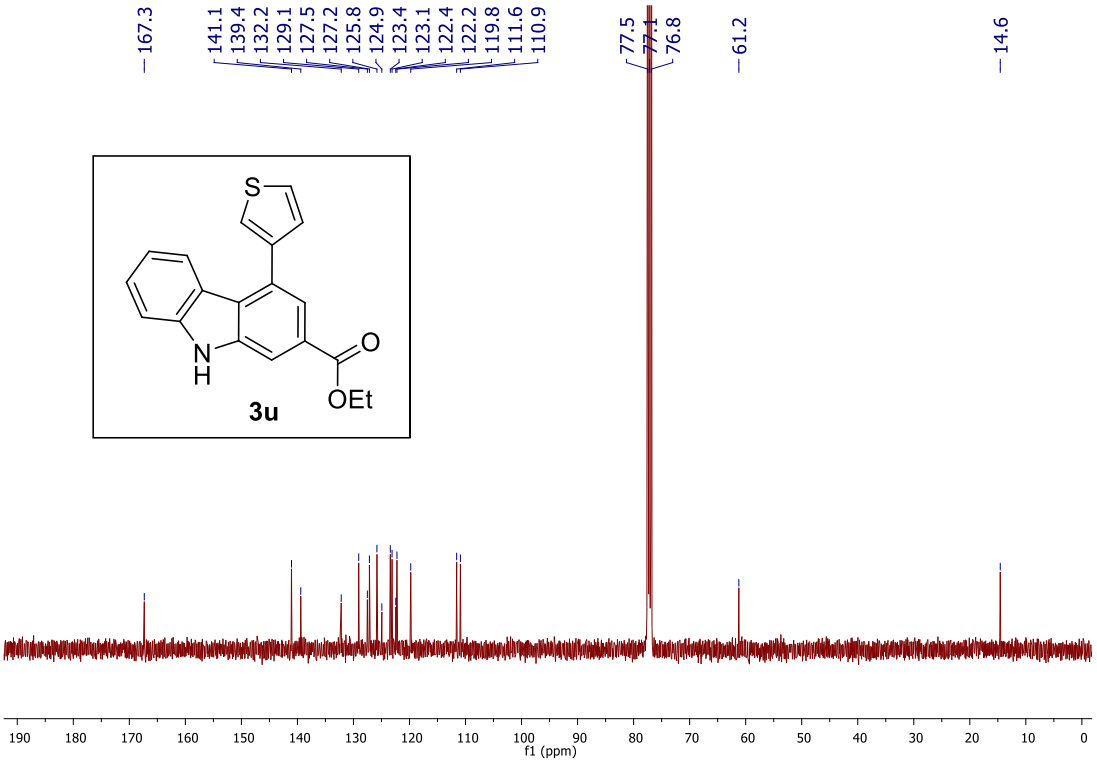
7.39
7.26
7.09
7.07
7.06
4.47
4.45
4.43
1.45
1.44
1.42
S
N
H
O
OEt
3u
1.10
1.02
1.15
1.09
5.00
1.01
2.08
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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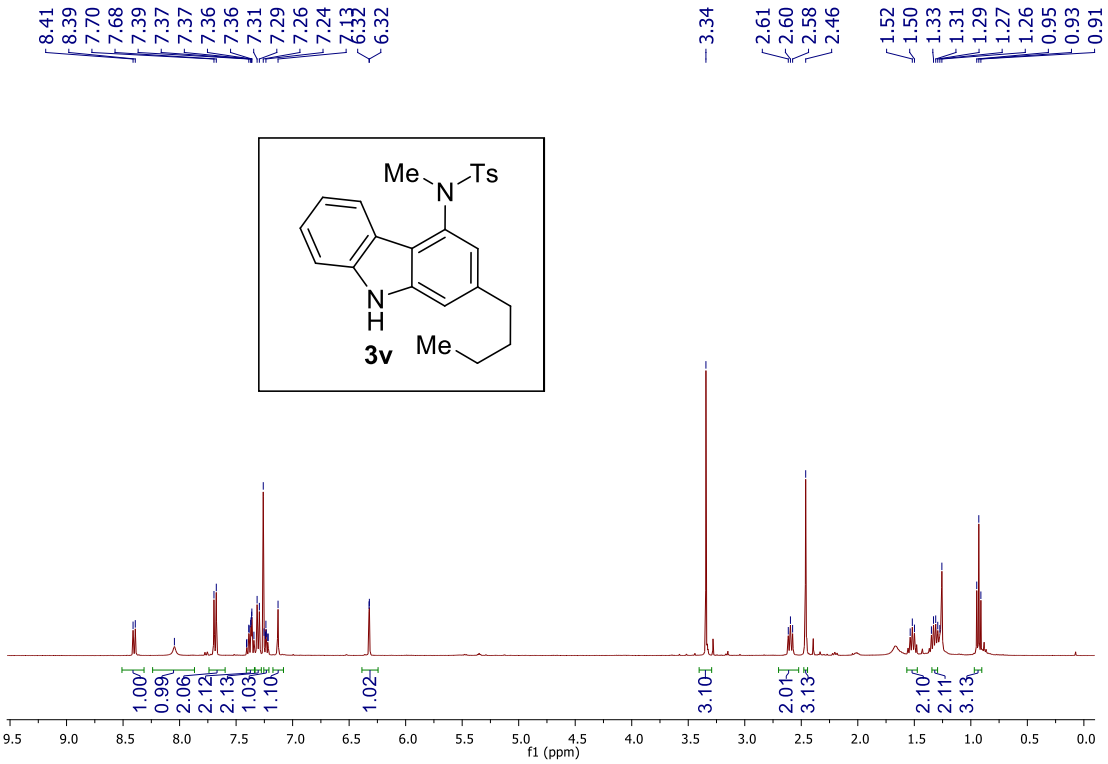
141.1
139.4
132.2
129.1
127.5
127.2
125.8
124.9
123.4
123.1
122.4
122.2
119.8
111.6
110.9
77.5
77.1
76.8
61.2
14.6
S
N
H
O
OEt
3u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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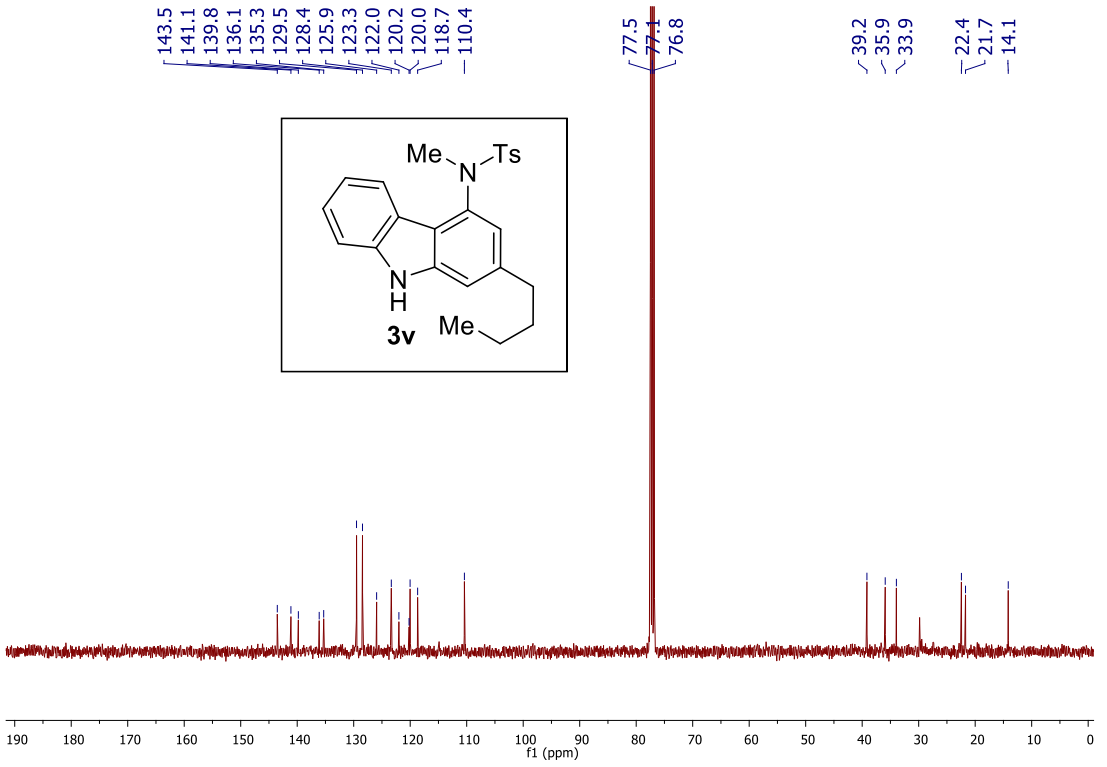
7.36
7.36
7.31
7.29
7.26
7.24
7.13
6.32
6.32
3.34
2.61
2.60
2.58
2.46
1.52
1.50
1.33
1.31
1.29
1.27
1.26
0.95
0.93
0.91
Me
N
Ts
N
H
Me
3v
1.00
0.99
2.06
2.12
2.13
1.03
1.10
1.02
3.10
2.01
3.13
2.10
2.11
3.13
f1 (ppm)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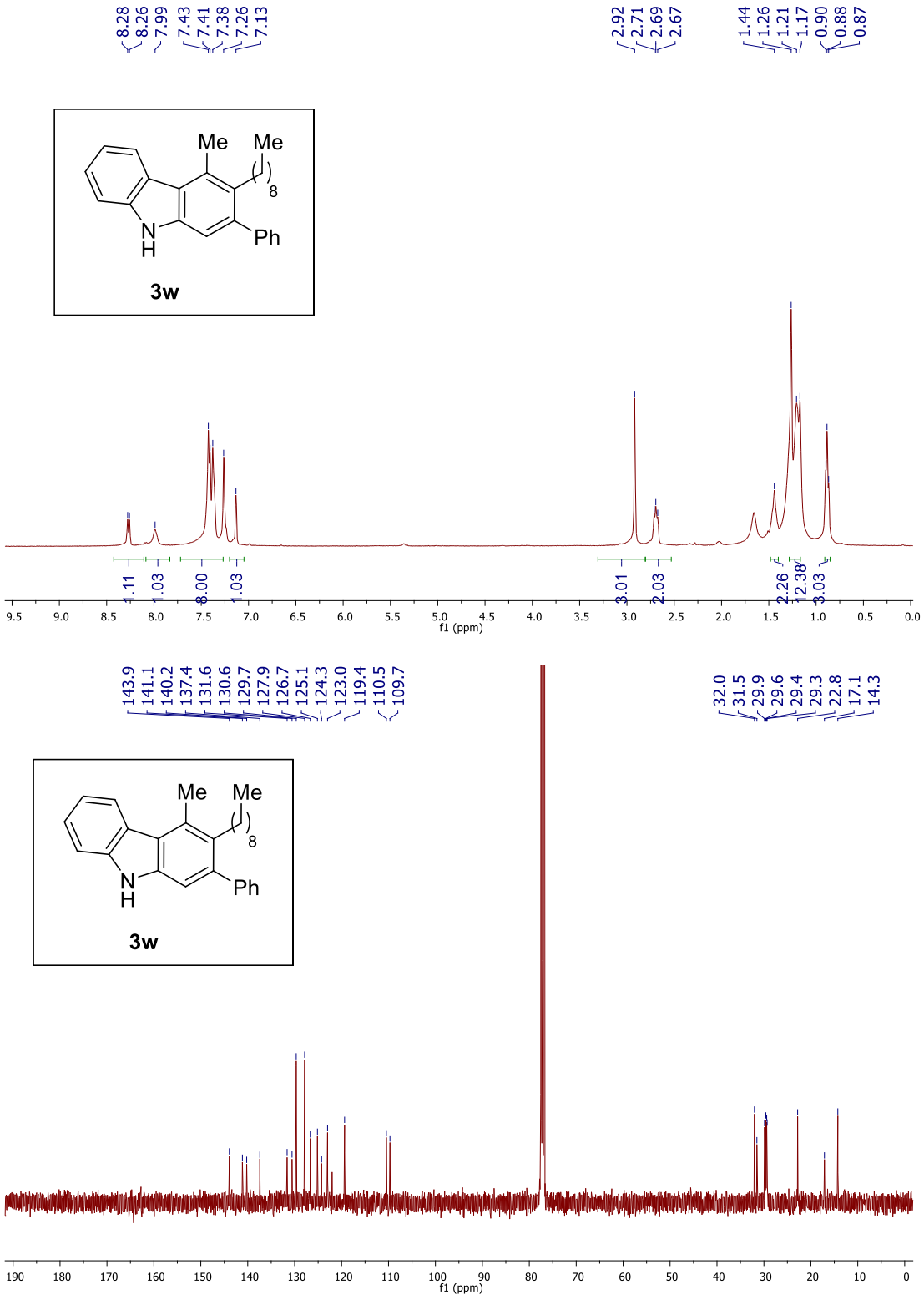
128.4
125.9
123.3
122.0
120.2
120.0
118.7
110.4
77.5
77.1
76.8
39.2
35.9
33.9
22.4
21.7
14.1
Me
N
Ts
N
H
Me
3v
f1 (ppm)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7.38
7.26
7.13
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2.71
2.69
2.67
1.44
1.26
1.21
1.17
0.90
0.88
0.87
Me
Me
8
N
H
Ph
3w
1.11
1.03
8.00
1.03
3.01
2.03
2.26
12.38
3.03
f1 (ppm)
143.9
141.1
140.2
137.4
131.6
130.6
129.7
127.9
126.7
125.1
124.3
123.0
119.4
110.5
109.7
32.0
31.5
29.9
29.6
29.4
29.3
22.8
17.1
14.3
f1 (ppm)


7.49
7.49
7.41
7.39
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.25
7.25
7.20
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.16
7.15
7.15
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6.94
6.93
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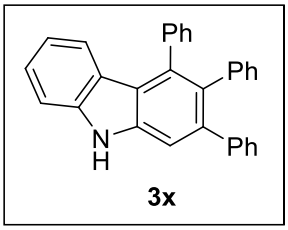
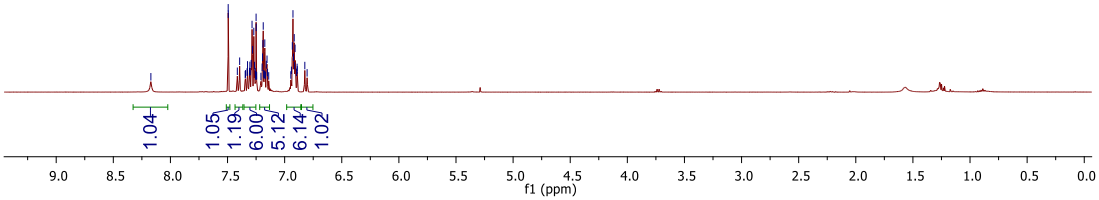
6.91
6.90
6.89
6.89
6.82
6.80


Ph
Ph
Ph
N
H

3x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6.14
1.02
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.9
140.4
140.2
140.1
140.0
138.7
136.7
132.4
132.2
130.4
130.3
128.1
127.6
126.9
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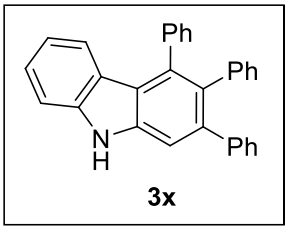
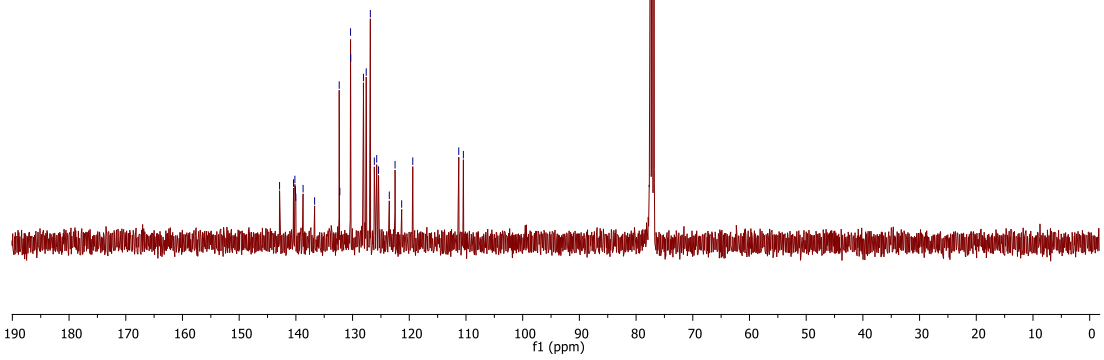
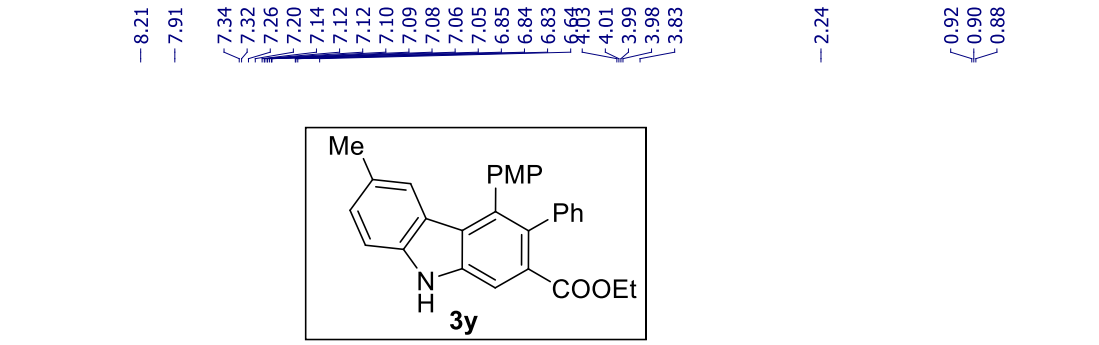
119.4
111.3
110.5
77.5
77.2
76.8


Ph
Ph
Ph
N
H

3x


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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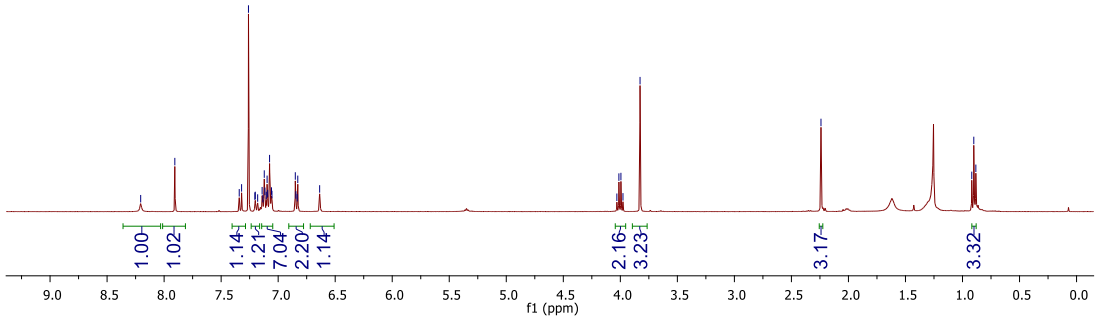
7.12
7.12
7.10
7.09
7.08
7.06
7.05
6.85
6.84
6.83
6.64
4.03
4.01
3.99
3.98
3.83
2.24
0.92
0.90
0.88
Me
PMP
Ph
N
H
COOEt
3y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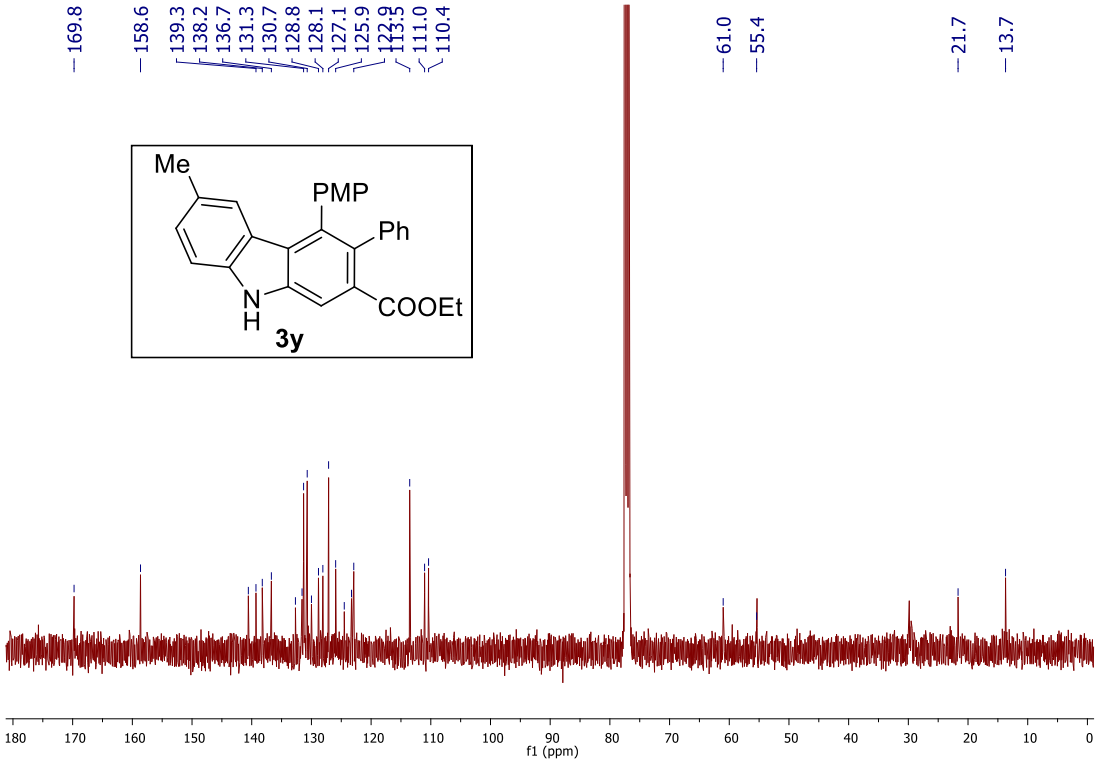
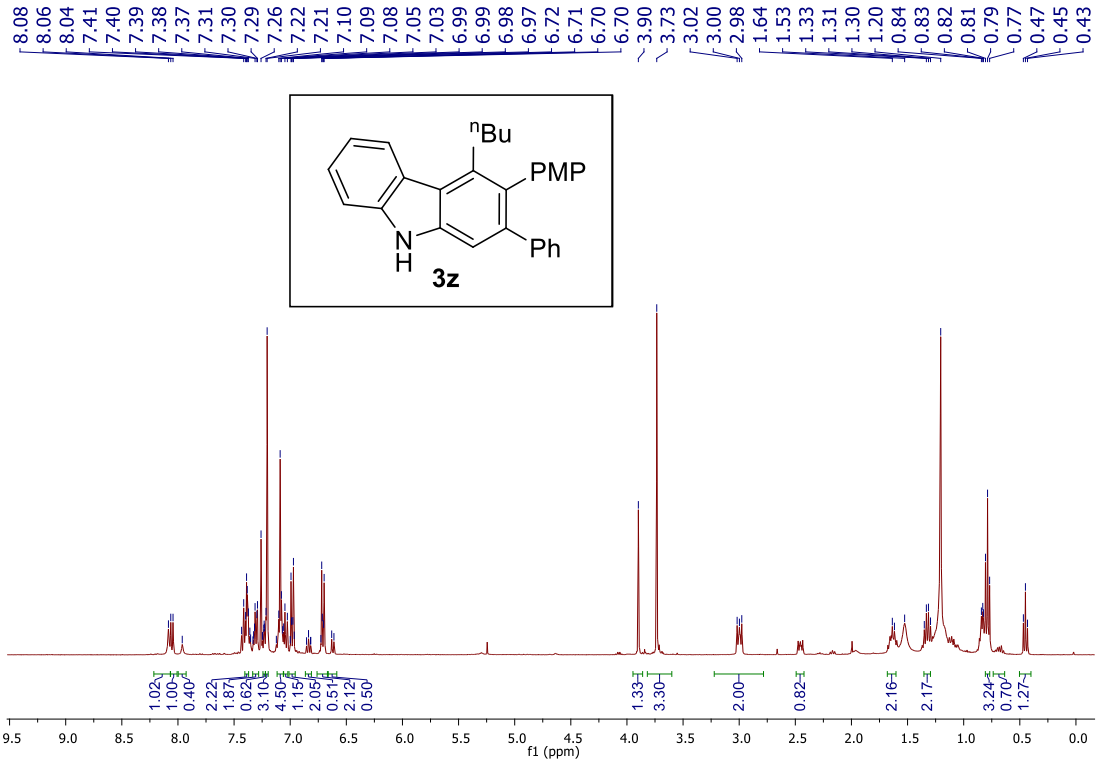
1.21
7.04
2.20
1.14
2.16
3.23
3.17
3.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.8
158.6
139.3
138.2
136.7
131.3
130.7
128.8
128.1
127.1
125.9
122.9
113.5
111.0
110.4
61.0
55.4
21.7
13.7
Me
PMP
Ph
N
H
COOEt
3y
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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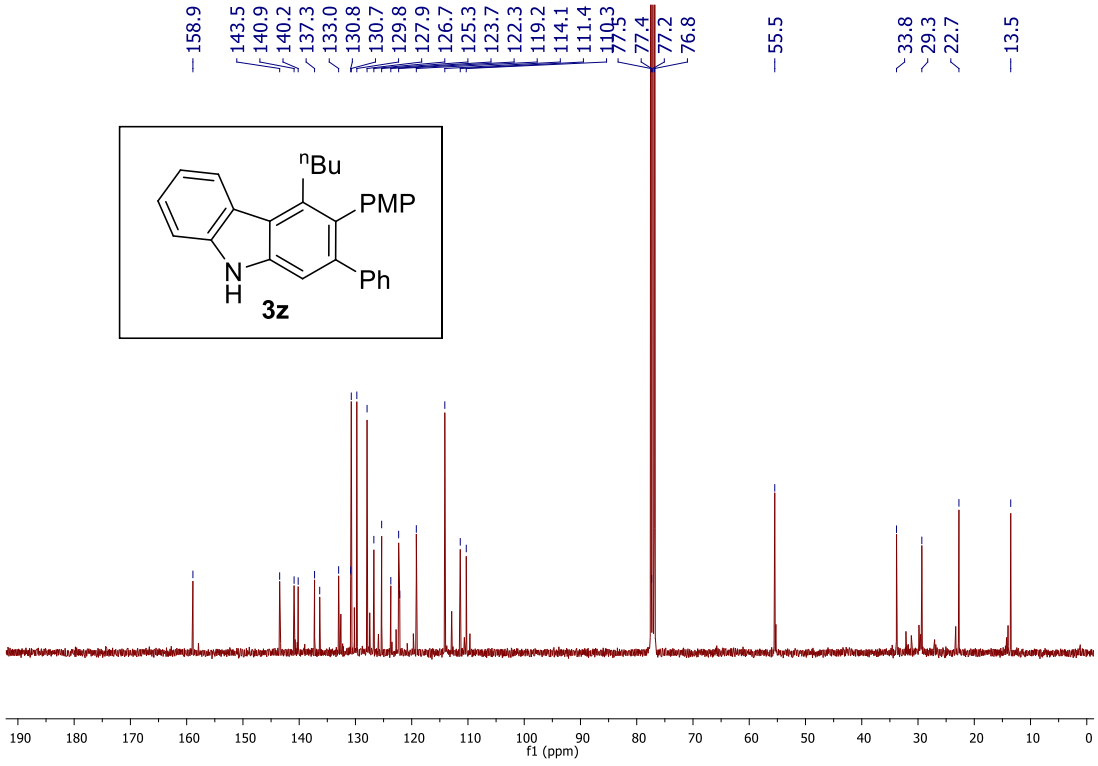
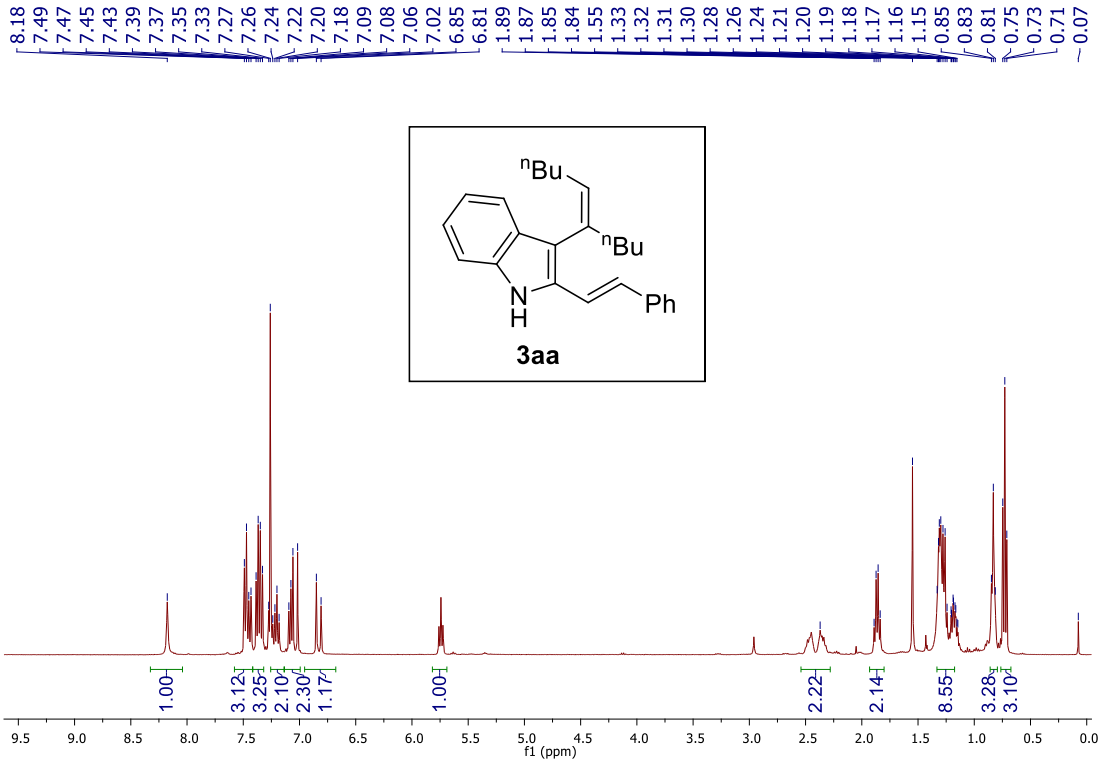
nBu
PMP
Ph
N
H
3z
1.02 1.00 0.40 2.22 1.87 0.62 3.10 4.50 1.15 2.05 0.51 2.12 0.50 1.33 3.30 2.00 0.82 2.16 2.17 3.24 0.70 1.27
f1 (ppm)


158.9 143.5 140.9 140.2 137.3 133.0 130.8 130.7 129.8 127.9 126.7 125.3 123.7 122.3 119.2 114.1 111.4 110.3 77.5 77.4 77.2 76.8 55.5 33.8 29.3 22.7 13.5
nBu
PMP
Ph
N
H
3z
f1 (ppm)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7.26
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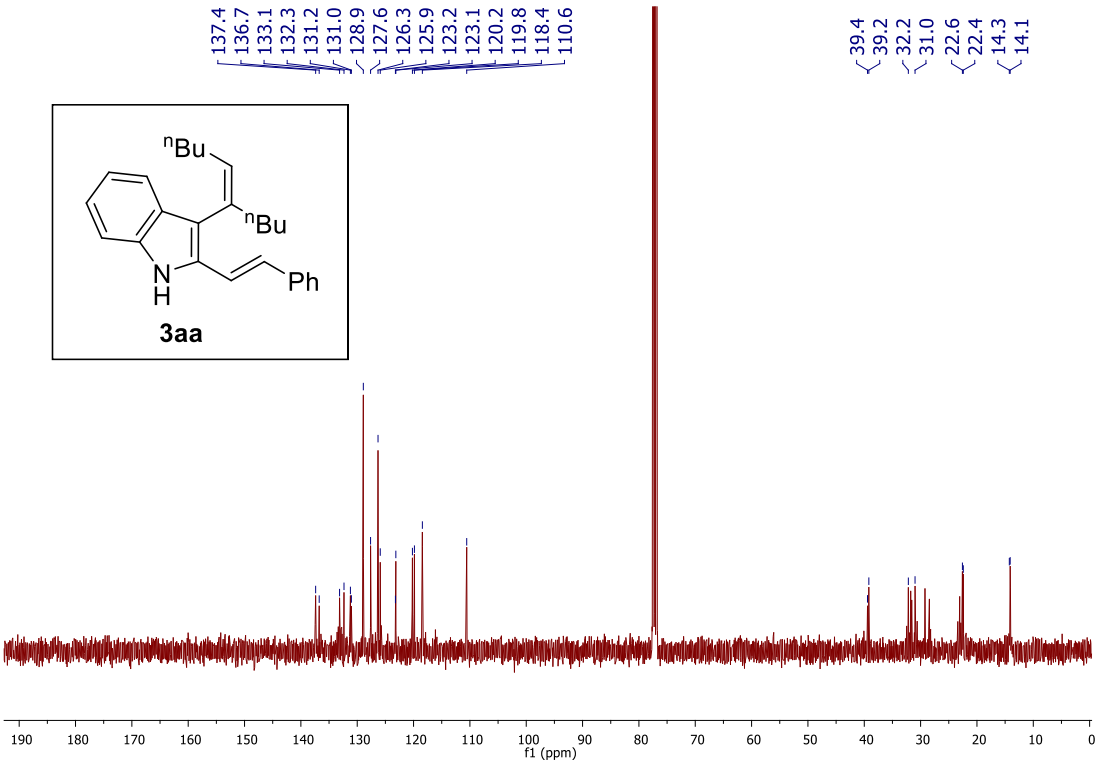
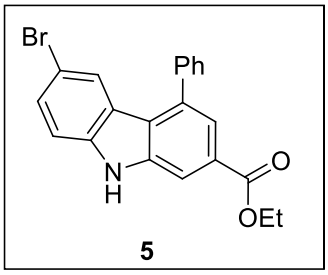
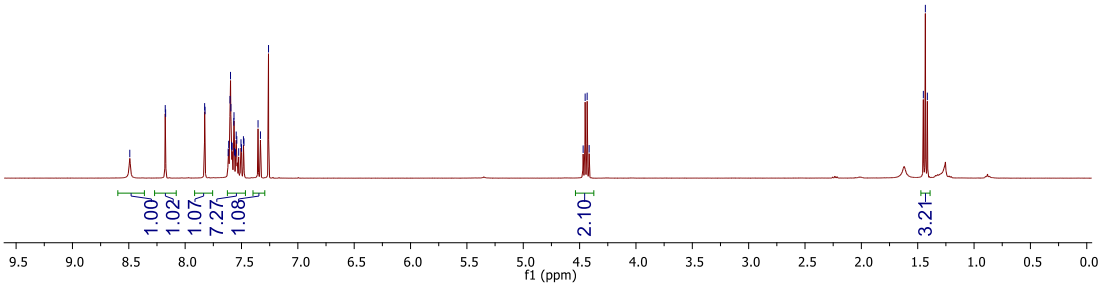
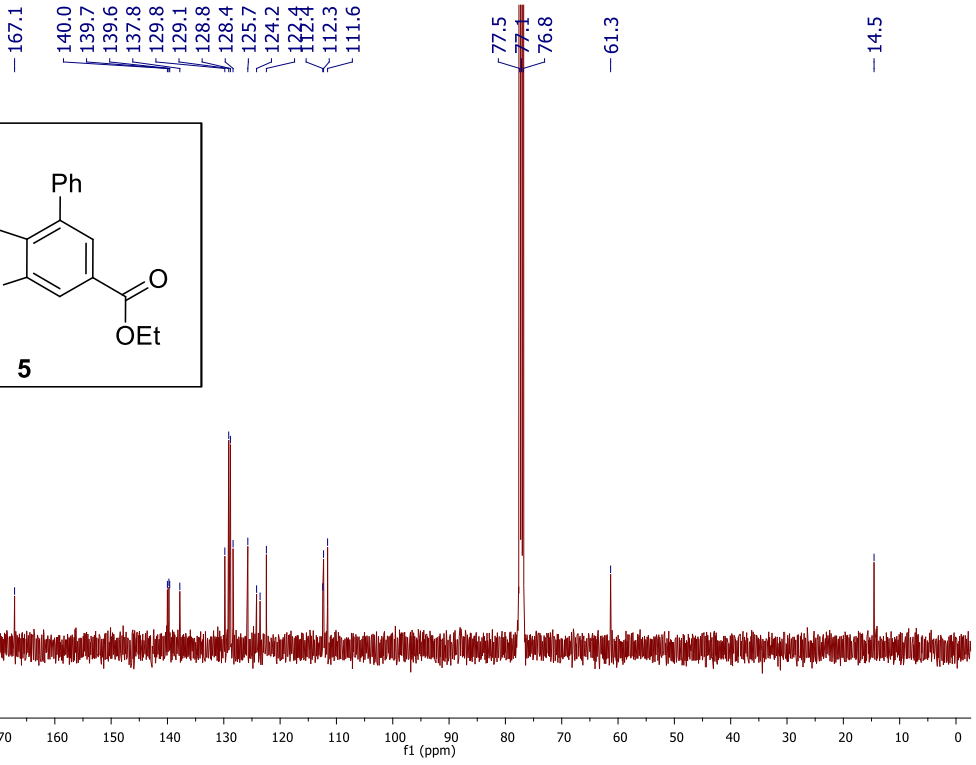
7.22
7.20
7.18
7.09
7.08
7.06
7.02
6.85
6.81
1.89
1.87
1.85
1.84
1.55
1.33
1.32
1.31
1.30
1.28
1.26
1.24
1.21
1.20
1.19
1.18
1.17
1.16
1.15
0.85
0.83
0.81
0.75
0.73
0.71
0.07
nBu
nBu
N
H
Ph
3aa
1.00
3.12
3.25
2.10
2.30
1.17
1.00
2.22
2.14
8.55
3.28
3.10
f1 (ppm)

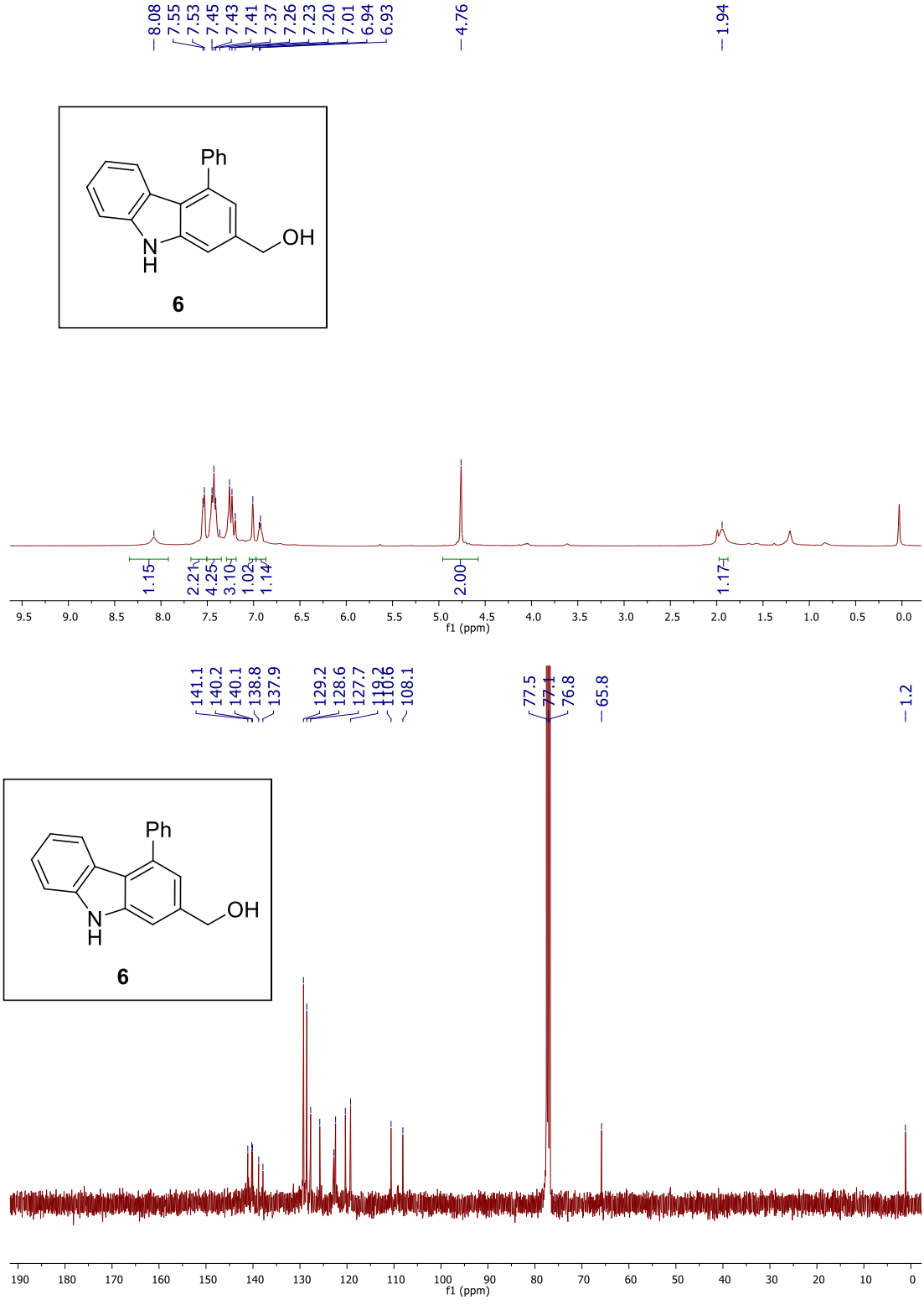

137.4
136.7
133.1
132.3
131.2
131.0
128.9
127.6
126.3
125.9
123.2
123.1
120.2
119.8
118.4
110.6
39.4
39.2
32.2
31.0
22.6
22.4
14.3
14.1
nBu
nBu
N
H
Ph
3aa
f1 (ppm)

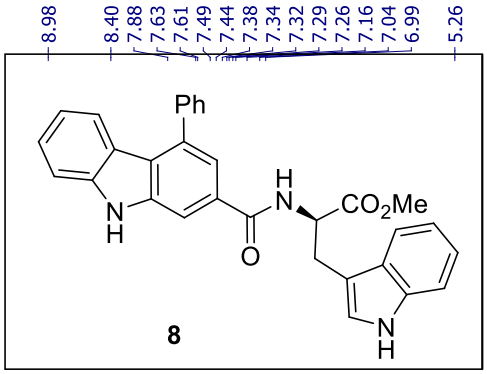

8.18
8.17
7.83
7.82
7.61
7.60
7.60
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.53
7.50
7.50
7.48
7.48
7.35
7.33
4.47
4.45
4.43
4.42
1.45
1.43
1.41


Br
Ph
N
H
O
OEt
5

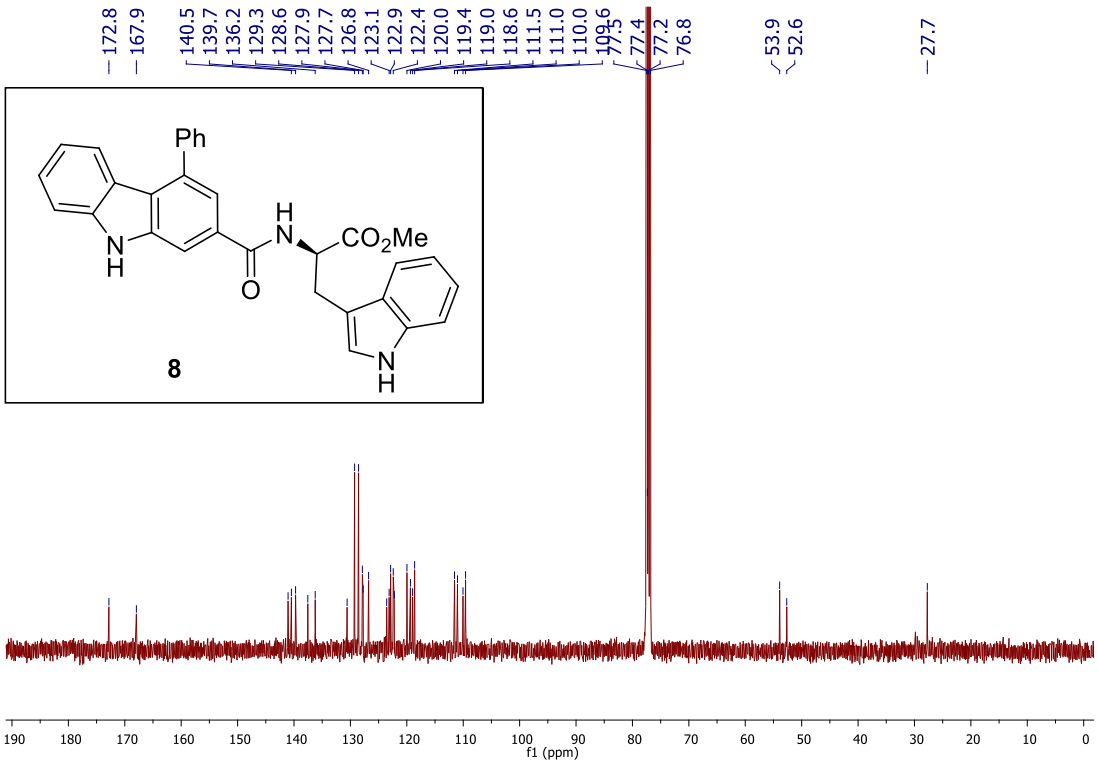

1.00
1.02
1.07
7.27
1.08
2.10
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.1
140.0
139.7
139.6
137.8
129.8
129.1
128.8
128.4
125.7
124.2
112.3
111.6
77.5
77.1
76.8
61.3
14.5
Br
Ph
N
H
O
OEt
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

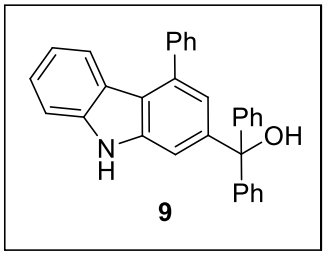

8.08
7.55
7.53
7.45
7.43
7.41
7.37
7.26
7.23
7.20
7.01
6.94
6.93
4.76
1.94
Ph
N
H
OH
6
1.15
2.21
4.25
3.10
1.02
1.14
2.00
1.17
f1 (ppm)
141.1
140.2
140.1
138.8
137.9
129.2
128.6
127.7
110.6
108.1
77.5
77.1
76.8
65.8
1.2
f1 (ppm)

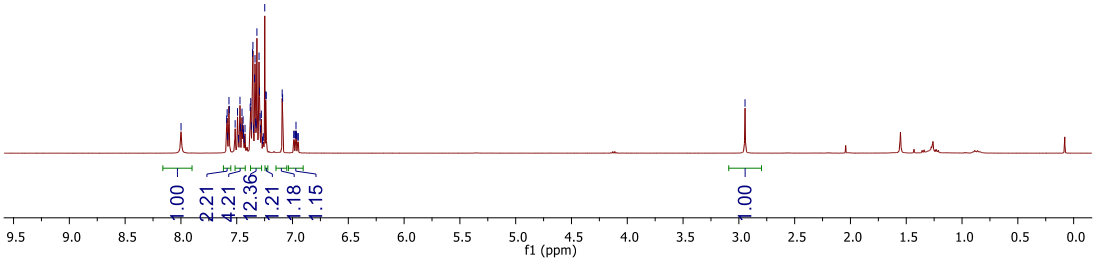

Ph
H
N
CO2Me
O
N
H
8

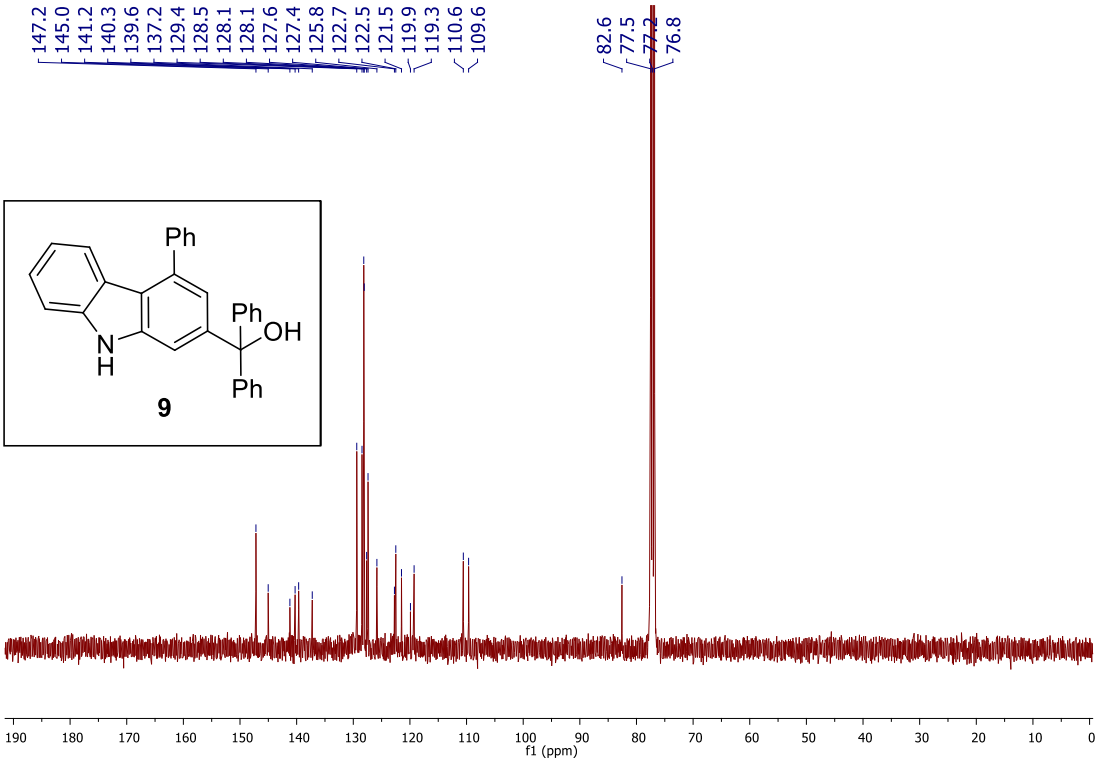
8.98
8.40
7.88
7.63
7.61
7.49
7.44
7.38
7.34
7.32
7.29
7.26
7.16
7.04
6.99
5.26
3.74
3.51
1.00
1.09
1.28
1.15
6.06
4.28
1.32
4.00
1.20
3.09
2.04
f1 (ppm)

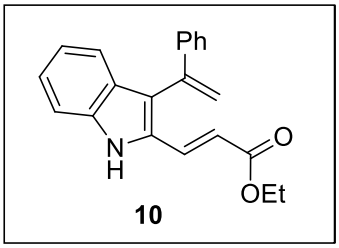

172.8
167.9
140.5
139.7
136.2
129.3
128.6
127.9
127.7
126.8
123.1
122.9
122.4
120.0
119.4
119.0
118.6
111.5
111.0
110.0
109.6
77.5
77.4
77.2
76.8
53.9
52.6
27.7
Ph
H
N
CO2Me
O
N
H
8
f1 (ppm)


8.00
7.59
7.59
7.58
7.57
7.57
7.51
7.49
7.48
7.47
7.47
7.45
7.45
7.44
7.44
7.43
7.43
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.30
7.30
7.29
7.29
7.28
7.26
7.25
7.24
7.24
7.09
7.09
6.99
6.98
6.97
6.97
6.96
6.95
6.95
2.94

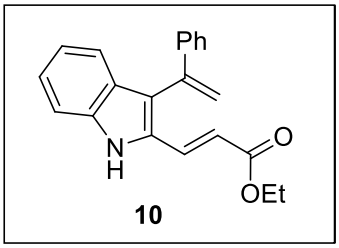

Ph
Ph
OH
N
H
Ph
9


1.00
2.21
4.21
12.36
1.21
1.18
1.15
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.2
145.0
141.2
140.3
139.6
137.2
129.4
128.5
128.1
128.1
127.6
127.4
125.8
122.7
122.5
121.5
119.9
119.3
110.6
109.6
82.6
77.5
77.2
76.8
Ph
Ph
OH
N
H
Ph
9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
N
H
O
OEt
10

8.96
7.82
7.78
7.40
7.40
7.38
7.33
7.32
7.32
7.31
7.26
7.15
6.37
6.33
5.90
5.90
5.36
5.35
4.32
4.30
4.28
4.26
1.35
1.33
1.32
1.00
1.04
2.17
3.12
1.28
1.04
1.09
1.05
1.03
1.05
2.19
3.07
f1 (ppm)


Ph
N
H
O
OEt
10

167.3
141.2
141.0
137.3
133.3
131.5
128.4
128.0
127.9
127.4
125.0
123.6
121.5
120.4
117.9
115.5
111.2
77.4
77.3
77.1
76.8
60.7
14.3
f1 (ppm)