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TBHP mediated oxidation of *N*-2-alkynylphenyl α-amino carbonyl compounds to oxalic amides using visible light photoredox catalysis and its application in synthesis of 2-aryl indoles

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***General*:**

Column chromatography silica gel (200-300 mesh) and TCL plate were purchased from Qingdao Meijin Chemical Inc(Qingdao; China); HRMS data were obtained in the ESI mode on a Agilent 6530 Q-TOF/MS system; ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer and chemical shifts were given in δ with TMS as an internal reference.

Representative experimental procedure for visible light promoted oxidation of N-2-alkynyl glycine esters (1) to N-2-alkynylphenyl oxalic amides (2):

A solution of *N*-2-alkynyl glycine ester **1** (1.0 mmol), 4.0 eq of TBHP (6M in decane), CuBr (20mol%), and $Ru(bpy)_3Cl_2.6H_2O$ (2mol%) in the super dried mixed solvent of MeCN/DMSO (4 mL, V_{MeCN}:V_{DMSO}=4:1) was irradiated with 26W compact fluorescent lamp for 24 h at room temperature. After the reaction was completed, the resulting mixture was washed with water (5 mL×3). The organic layers were washed with brine and dried over $MgSO_4$. The solvent were removed via vacuo and theresidue was purified by flash column chromatography (SiO_2) with hexane/acetone (40:1) to give target compounds **2**.

HPLC-Q-TOF analysis for intermediate 10

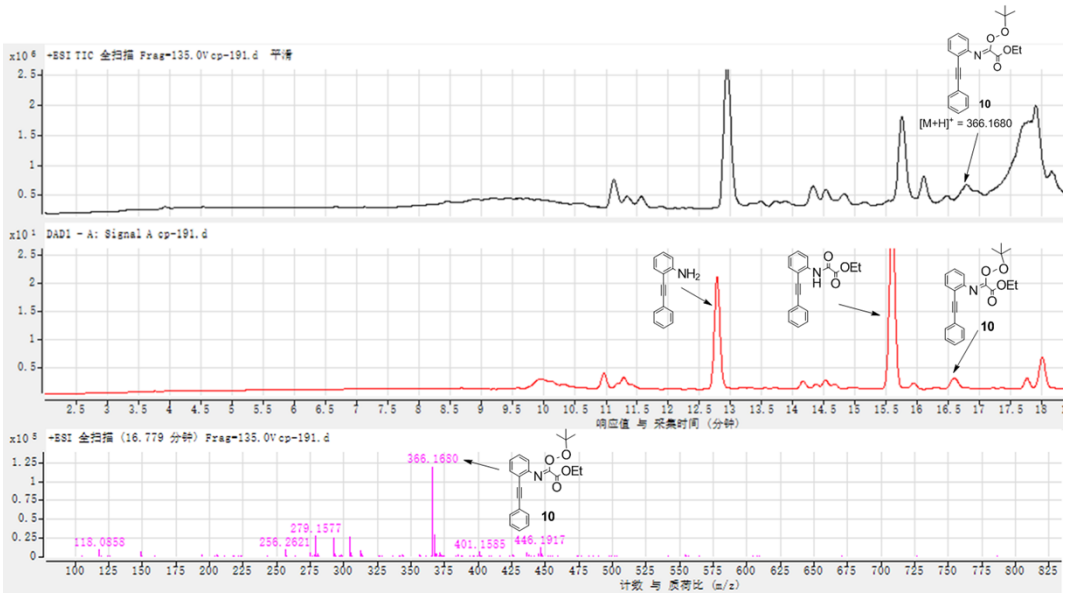
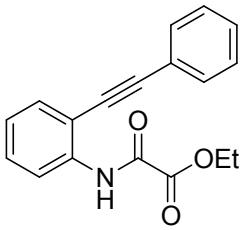


Figure 1s. HPLC-Q-TOF analysis of the photocatalytic reaction (sample from Table 1, entry 4)

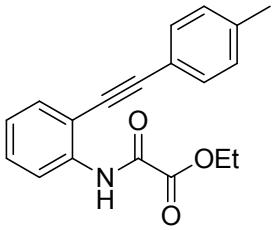
Characterization data of compounds 2

ethyl 2-oxo-2-((2-(phenylethynyl)phenyl)amino)acetate (2a):



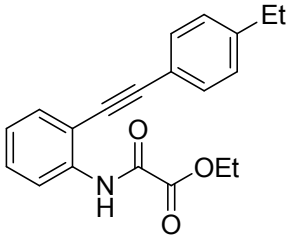
obtained as yellow solid, isolated yield 57%; mp: 84.5-86.0°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.95 (s, 1H), 8.49 (brd, *J* = 8.0 Hz, 1H), 7.66-7.64 (m, 2H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41-7.37 (m, 4H), 7.15 (td, *J* = 8.4, 1.2 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H);□ ^{13}C NMR (100MHz, $CDCl_3$): 160.8, 153.9, 137.5, 131.7, 131.6, 131.6 (overlapped), 129.8, 129.1, 128.7, 128.7 (overlapped), 124.8, 122.3, 119.2, 113.2, 97.8, 83.7, 63.7, 14.1;HRMS (ESI-QTOF) m/z:$[M+H]^+$ calcd for $C_{18}H_{16}NO_3$ 294.1125; found 294.1117.

ethyl 2-oxo-2-((2-(p-tolylethynyl)phenyl)amino)acetate (2b):



obtained as yellow solid, isolated yield 52%; mp: 104.0-106.0 °C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.95 (s, 1H), 8.48 (d, *J* = 8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.38 (brt, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 160.8, 153.9, 139.4, 137.4, 131.6, 131.6 (overlapped), 131.5, 129.6, 129.6 (overlapped), 129.5, 124.8, 119.3 119.2, 113.5, 98.0, 83.1, 63.8, 21.7, 14.1; HRMS (ESI-QTOF) m/z: $[M+H]^+$calcd for $C_{19}H_{18}NO_3$ 308.1281; found 308.1289.

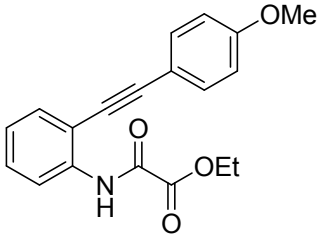
ethyl 2-((2-((4-ethylphenyl)ethynyl)phenyl)amino)-2-oxoacetate (2c)



obtained as yellow viscous oil, isolated yield 49%; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.95 (s, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 756 (d, *J* = 8.0 Hz, 2H), 7.52(d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.7, 153.8, 145.5, 137.3, 131.6, 131.6

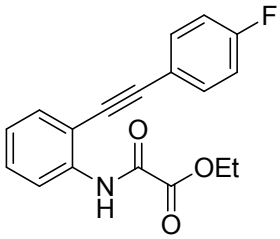
(overlapped), 131.4, 129.5, 128.1, 128.1(overlapped), 124.7, 119.3, 119.1, 113.4, 97.9, 83.0, 63.7, 28.9, 15.3, 14.0; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$ 322.1438; found 322.1446.

ethyl 2-((2-((4-methoxyphenyl)ethynyl)phenyl)amino)-2-oxoacetate (2d)



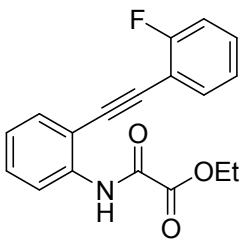
obtained as gray solid, isolated yield 46%; mp: 89.5-91.0°C; ^{1}HNMR (400MHz, $CDCl_3$): δ9.95 (s, 1H), 8.47 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.50, (dd, J = 7.6, 1.2 Hz, 1H), 7.37 (brt, J = 8.4 Hz, 1H) 7.14 (brt, J = 7.6 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.9, 160.3, 153.9, 137.3, 133.3, 133.3 (overlapped), 131.4, 129.4, 124.8, 119.2, 114.4, 114.4,114.4 (overlapped), 113.7, 97.9, 82.5, 63.8, 55.5, 14.2; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$ 324.1230; found 324.1237.

ethyl 2-((2-((4-fluorophenyl)ethynyl)phenyl)amino)-2-oxoacetate (2e)



obtained as gray solid, isolated yield 50 %; mp: 118.0-120.0°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.48 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.51 (dd, J = 7.6, 1.2 Hz, 1H), 7.39 (dt, J = 1.6, 8.8 Hz, 1H), 7.15 (td, J = 1.2, 7.6 Hz, 1H), 7.10 (t, J = 8.8 Hz, 2H), 4.44 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$): δ 163.1 (d, J_{F-C} = 249 Hz), 161.0, 153.7, 137.5, 133.7, 133.6, 131.5, 128.8, 124.9, 119.2, 118.5 (d, J_{F-C} = 3.4 Hz), 116.1, 116.0, 113.1, 96.7, 83.5, 63.9, 14.1;HRMS (ESI-QTOF) m/z: $[M+H]^+$calcd for $C_{18}H_{15}FNO_3$ 312.1030; found 312.1036.

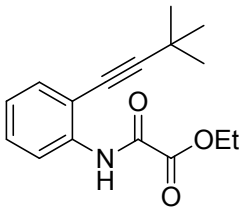
ethyl 2-((2-((2-fluorophenyl)ethynyl)phenyl)amino)-2-oxoacetate (2f)



obtained as yellow solid, isolated yield 54%; mp: 72.3-74.0 °C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.83 (s, 1H), 8.49 (d, J = 8.4 Hz, 1H), 7.62 (td, J = 7.2, 1.6 Hz, 1H), 7.68 (dd, J = 1.2, 7.6 Hz, 1H), 7.42-7.33 (m, 2H), 7.19-7.12 (m, 3H), 4.43 (t, J = 7.2 Hz, 2H),

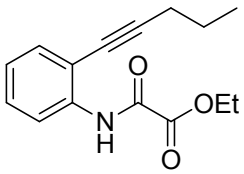
1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.6 (d, $J_{F\text{-}C}$= 251 Hz), 160.6, 154.1, 137.6, 133.4, 131.9, 130.8 (d, $J_{F\text{-}C}$ = 7.8 Hz), 130.2, 124.8, 124.3 ($J_{F\text{-}C}$ = 3.7 Hz), 119.4, 115.7 (d, $J_{F\text{-}C}$ = 20.4 Hz), 112.9, 111.1 (d, $J_{F\text{-}C}$ = 15.5 Hz), 90.8, 88.7 (d, $J_{F\text{-}C}$ = 3.0 Hz), 63.8, 14.1; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{15}FNO_3$ 312.1030; found 312.1035.

ethyl 2-((2-(3,3-dimethylbut-1-yn-1-yl)phenyl)amino)-2-oxoacetate (2g)



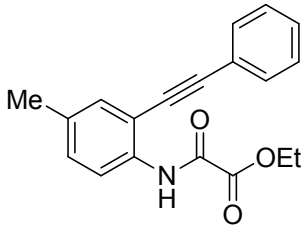
obtained as yellow viscous oid, isolated yield 43%; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.43 (brd, J =8.0 Hz, 1H), 7.34 (dd, J = 7.6, 1.2 Hz, 1H), 7.31 (td, J = 8.8, 1.2 Hz, 1H), 7.07 (td, J = 7.6, 1.2 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.40 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.9, 153.9, 137.5, 131.5, 129.0, 124.6, 119.0, 113.9, 107.3, 73.8, 63.7, 31.0, 31.0 (overlapped), 31.0 (overlapped), 14.2; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_3$ 274.1438; found 274.1447.

ethyl 2-oxo-2-((2-(pent-1-yn-1-yl)phenyl)amino)acetate (2h)



obtained as yellow viscous oil, isolated yield 41%; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.43 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 1.2, 7.6 Hz, 1H), 7.32 (td, J = 1.2, 8.4 Hz, 1H), 7.08 (td, J = 1.2, 7.6 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 1.72 (dt, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.9, 153.9, 137.6, 131.7, 129.0, 124.7, 119.1, 114.0, 99.0, 75.4, 63.7, 22.3, 21.7, 14.2, 13.7; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NO_3$ 260.1281; found 260.1288.

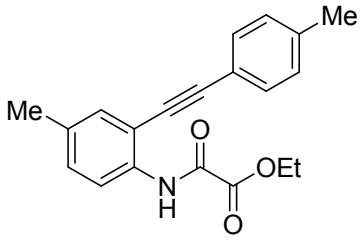
ethyl 2-((4-methyl-2-(phenylethynyl)phenyl)amino)-2-oxoacetate (2i)



obtained as yellow viscous oil, isolated yield 33%;^{1}HNMR (400MHz, $CDCl_3$):δ9.88 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.64-7.62 (m, 2H), 7.40-7.36 (m, 5H) 7.19 (dd, J = 8.4, 1.6

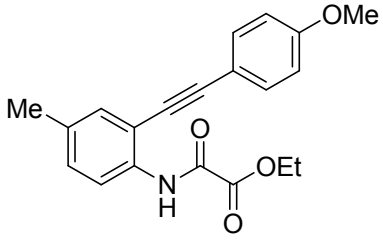
Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$): δ 161.0, 153.8, 135.2, 134.6, 131.7, 131.7 (overlapped), 130.6, 129.0, 128.7, 128.7 (overlapped), 122.4, 119.2, 113.2, 97.4, 83.9, 63.8, 20.9, 14.2;HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}NO_3$ 308.1281; found 308.1291.

ethyl 2-((4-methyl-2-(p-tolylethynyl)phenyl)amino)-2-oxoacetate (2j)



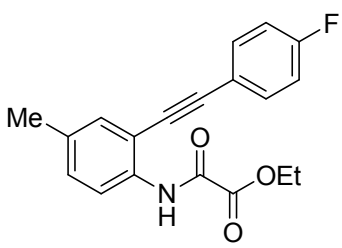
obtained as yellow solid, isolated yield 37%; mp: 125.0-127.0 °C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34 (brs, 1H), 7.20 (d, *J* = 8.0 Hz, 7.17 (brs, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$): δ 160.9, 153.8, 139.3, 135.1, 134.6, 131.8, 131.6, 131.6 (overlapped), 130.4, 129.4, 129.4 (overlapped), 119.4, 119.2, 113.4, 97.6, 83.3, 63.8, 21.7, 20.9, 14.1; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$ 322.1438; found 322.1442.

ethyl 2-((2-((4-methoxyphenyl)ethynyl)-4-methylphenyl)amino)-2-oxoacetate (2k)



obtained as yellow solid, isolated yield 42%; mp: 78.5-80.5°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.88 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 1H), 7.17 (brd, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 2.33 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$): δ 161.0, 160.3, 153.8, 135.0, 134.6, 133.3, 133.3(overlapped), 131.7, 130.2, 119.1, 114.5, 114.4, 114.4 (overlapped), 113.6, 97.5, 82.7, 63.8, 55.5, 21.0, 14.2; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 338.1387; found 338.1394.

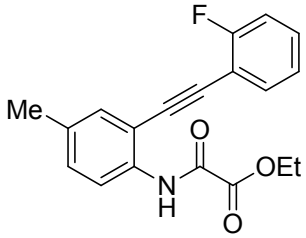
ethyl 2-((2-((4-fluorophenyl)ethynyl)-4-methylphenyl)amino)-2-oxoacetate (2l)



obtained as yellow viscous oil, isolated yield 39%;

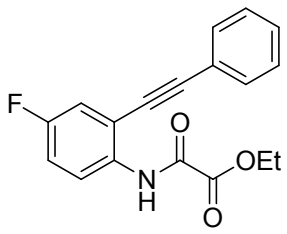
^{1}HNMR (400MHz, $CDCl_3$): δ 9.85 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.63-7.60 (m, 2H), 7.33 (brs, 1H), 7.20 (brd, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.9 (d, J_{F-C} = 249.0 Hz), 160.9, 153.6, 135.0, 134.5, 133.6, 133.5, 131.7, 130.5, 119.1, 118.4 (d, J_{F-C}= 3.5 Hz), 116.0, 115.8, 112.8, 96.1, 83.6, 63.7, 20.8, 14.0; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FNO_3$ 326.1187; found 326.1192.

ethyl 2-((2-((2-fluorophenyl)ethynyl)-4-methylphenyl)amino)-2-oxoacetate (2m)



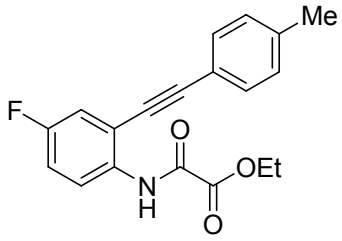
obtained as yellow viscous oil, isolated yield 32%; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.76 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.61 (td, *J* = 1.2, 8.4 Hz, 1H), 7.39-7.35 (m, 2H), 7.23-7.15 (m, 3H),4.44 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.42 (t, *J* = 7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.6 (d, J_{F-C}= 250.8 Hz), 160.7, 154.0, 135.3, 134.7, 133.5, 131.0, 130.7 (d, J_{F-C}= 7.9 Hz), 124.5 (d, J_{F-C} = 2.7 Hz), 119.5, 115.8 (d, J_{F-C}= 30.5 Hz), 112.8, 111.2 (d, J_{F-C}= 5.7 Hz), 90.4, 89.0 (d, J_{F-C} = 3.2 Hz), 63.8, 20.9, 14.1;HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FNO_3$ 326.1187; found 326.1198.

ethyl 2-((4-fluoro-2-(phenylethynyl)phenyl)amino)-2-oxoacetate (2n)



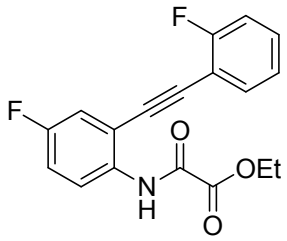
obtained as yellow solid, isolated yield 69%; mp: 84.0-86.0°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.48 (dd, *J* = 4.2, 9.2 Hz, 1H), 7.66-7.3 (m, 2H), 7.42-7.40 (m, 3H) 7.23 (dd, *J* = 0.7, 8.2 Hz, 1H), 7.10 (td, *J* = 0.7, 9.2 Hz, 1H), 4.45 (q, *J* = 7.2Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$): δ 160.8, 159.0 (d, J_{F-C} = 243.9 Hz), 153.8, 134.0, 131.8, 131.8 (overlapped), 129.5, 128.8, 121.8, 120.9 (d, J_{F-C} = 8.2 Hz), 118.0 (d, J_{F-C}= 2.4 Hz), 116.8 (d, J_{F-C}= 22.3 Hz), 114.9 (d, J_{F-C} = 9.8 Hz), 98.6, 82.7 (d, J_{F-C}= 3.2 Hz), 64.0, 14.2;HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{15}FNO_3$ 312.1030; found 312.1031.

ethyl 2-((4-fluoro-2-(p-tolylethynyl)phenyl)amino)-2-oxoacetate (2o)



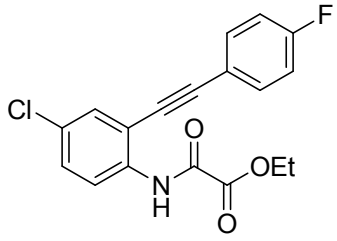
obtained as yellow solid, isolated yield 55%; mp: 107.5-109.5°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.46 (dd, *J* = 5.2, 9.2 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.23-7.20 (m, 3H), 7.08 (td, *J* = 2.8, 8.4 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.42 (t, *J* =7.2 Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$): δ 160.8, 159.0 (d, J_{F-C}= 243.8 Hz), 153.8, 139.8, 133.9, 131.8, 131.8 (overlapped), 129.5, 129.5 (overlapped), 120.8 (d, J_{F-C}= 8.5 Hz, 118.8, 117.9 (d, J_{F-C}= 24.3 Hz), 116.6 (d, J_{F-C}= 22.3 Hz), 115.2 (d, J_{F-C} = 8.7 Hz), 98.9, 82.2, 3.9, 21.8, 14.2; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FNO_3$ 326.1187; found 326.1193.

ethyl 2-((4-fluoro-2-((2-fluorophenyl)ethynyl)phenyl)amino)-2-oxoacetate (2p)



obtained as yellow solid, isolated yield 56%; mp: 93.7-95.0°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.76 (s, 1H), 8.48 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.62 (td, *J* = 7.2, 1.2 Hz, 1H), 7.42-7.36 (m, 1H), 7.27-7.24 (m, 1H), 7.20-7.12 (m, 3H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.7 (d, J_{F-C}= 251.5 Hz), 160.6, 159.0 (d, J_{F-C}= 244 Hz), 154.0, 134.0 (d, J_{F-C}= 2.6 Hz), 133.5, 131.3 (d, J_{F-C}=7.9 Hz), 124.4 (d, J_{F-C}=3.7 Hz), 121.2 (d, J_{F-C}= 8.2 Hz), 118.3 (d, J_{F-C}=24.3 Hz), 117.2 (J_{F-C}=22.1 Hz), 115.8 (d, J_{F-C}= 30.3 Hz), 114.5 (d, J_{F-C}=19.6 Hz), 110.6 (d, J_{F-C}=15.5 Hz), 91.6, 87.7, 63.9, 14.1; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}F_2NO_3$ 330.0936; found 330.0932.

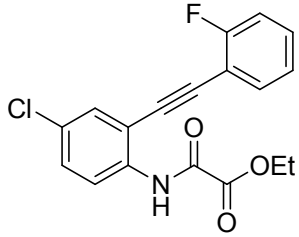
ethyl 2-((4-chloro-2-((4-fluorophenyl)ethynyl)phenyl)amino)-2-oxoacetate (2q)



obtained as yellow solid, isolated yield 49%; mp: 106.0-108.0°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.44 (d, *J* = 8.8 Hz, 1H), 7.63-7.60 (m, 2H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.34 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.10 (t, *J* = 8.8 Hz, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 163.3 (d, J_{F-C} = 250 Hz), 160.8, 153.8, 136.1, 133.9, 133.8, 131.0, 129.9, 120.3, 118.0, 117.9, 116.3, 116.1, 114.7, 97.8, 82.3, 64.0, 14.1; HRMS (ESI-QTOF)

m/z: $[M+H]^+$ calcd for $C_{18}H_{14}ClFNO_3$ 346.0641; found 346.0645.

ethyl 2-((4-chloro-2-((2-fluorophenyl)ethynyl)phenyl)amino)-2-oxoacetate (2r)



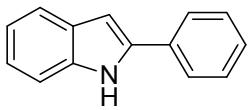
obtained as yellow solid, isolated yield 38%; mp: 112.0-113.8°C; ^{1}HNMR (400MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.56-7.55 (m, 1H), 7.39-7.36 (m, 2H), 7.20-7.16 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.8 (d, *J*= 150 Hz), 160.5, 154.1, 136.2, 133.6, 131.5, 131.3 (d, J_{F-C} = 8.2 Hz), 130.3, 130.0, 124.4 (d, J_{F-C}=3.4 Hz), 120.6, 116.0, 115.8, 114.5, 91.9, 876, 64.0, 14.2; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}ClFNO_3$ 346.0641; found 346.0651.

Representative experimental procedure for synthesis of 2-aryl indoles (12) with N-2-alkynylphenyl oxalic amides (2) as starting materials:

To a 10 mL scintillation flask was charged with **2** (0.5 mmol), $AgNO_3$ (20 mol%), K_2CO_3 (2.0 eq) and MeCN (4 mL). The reaction mixture was stirred at 70^{o}C for 2 h. The resulting mixture was poured into 30 mL water and then extracted with AcOEt (20 mL×3). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent were removed via vacuo and the residue was purified by flash column chromatography (SiO_2) with hexane/acetone (40:1) to give compounds **12** .

Characterization data of compounds 12

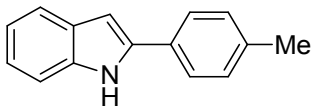
2-phenyl-1H-indole (12a)



obtained as white amorphous powder, isolated yield 95%; ^{1}HNMR (400MHz, $CDCl_3$): δ 8.34(s, 1H), 7.67-7.64 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.21(td, *J* = 7.2, 1.2 Hz, 1H), 7.14 (td, *J* = 8.0, 1.2 Hz, 1H), 6.84 (dd, *J* = 1.5, 0.8 Hz, 1H, NH); ^{13}C NMR (100MHz, $CDCl_3$): δ 138.0, 137.0, 132.5, 129.4, 129.2, 129.2

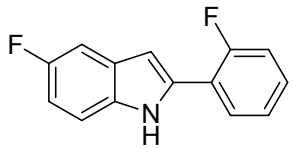
(overlapped), 127.8, 125.3, 125.3 (overlapped), 122.5, 120.8, 120.4, 111.0, 100.1; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}N$ 194.0964; found 194.0960.

2-(p-tolyl)-1H-indole (12b)



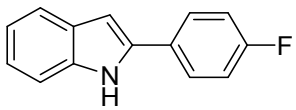
obtained as white amorphous powder, isolated yield 91%; ^{1}HNMR (400MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.62 (d, J = 8.0Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 1.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 138.2, 137.8, 136.8, 129.8, 129.8 (overlapped), 129.7, 129.5, 125.2, 125.2 (overlapped), 122.3, 120.7, 120.3, 110.9, 99.6, 21.4; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}N$ 208.1121; found 208.1113.

5-fluoro-2-(2-fluorophenyl)-1H-indole (12c)



obtained as white amorphous powder, isolated yield 88%; ^{1}HNMR (400MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.71 (brt, J = 8.0 Hz, 1H), 7.34-7.16 (m, 5H), 6.96 (brt, J = 8.8 Hz, 1H), 6.90 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 159.4 (d, J_{F-C} = 245 Hz), 158.3 (d, J = 245.0 Hz), 134.5, 133.3, 129.5 (d, J_{F-C} = 9.0 Hz), 128.6 (d, J_{F-C} = 10.1 Hz), 128.2 (d, J_{F-C} = 4.0 Hz), 125.0(d, J_{F-C} = 3.1 Hz), 119.7 (d, J_{F-C} = 10.1 Hz), 116.7 (d, J_{F-C} = 23.0 Hz), 111.8 (d, J_{F-C} = 9.6 Hz), 111.3 (d, J_{F-C} = 26.4 Hz), 105.4 (d, J_{F-C} = 23.4 Hz), 101.7 (dd, J_{F-C} = 4.7, 4.7 Hz); HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}F_2N$ 230.0776; found 230.0783.

2-(4-fluorophenyl)-1H-indole (12d)



obtained as white amorphous powder, isolated yield 90%; ^{1}HNMR (400MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.64-7.61 (m, 3H), 7.40 (brd, J = 8.0 Hz, 1H), 7.20 (td, J = 8.0, 1.2 Hz, 1H), 7.16-7.12 (m, 3H), 6.76 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.6 (d, J_{F-C} = 246 Hz), 137.2, 137.0, 129.4, 128.8 (J_{F-C} = 3.1 Hz), 127.1, 127.0, 122.6, 120.8, 120.5, 116.3, 116.1, 111.0, 100.1; HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}FN$ 212.0876; found 212.0869.

Table s1. Crystal data and structure refinement for compound **2q**.

Identification code	mo_2q _0m
Empirical formula	C18 H13 Cl F N O3
Formula weight	345.74
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 14.191(2) A alpha = 90 deg.
	b = 4.4973(7) A beta = 95.570(2) deg.
	c = 25.988(4) A gamma = 90 deg.
Volume	1650.7(4) A^3
Z, Calculated density	4, 1.391 Mg/m^3
Absorption coefficient	0.257 mm^-1
F(000)	712
Crystal size	0.70 x 0.06 x 0.05 mm
Theta range for data collection	1.57 to 28.30 deg.
Limiting indices	-18<=h<=18, -5<=k<=5, -34<=l<=34
Reflections collected / unique	15559 / 4056 [R(int) = 0.0691]
Completeness to theta = 28.30	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9873 and 0.8404
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4056 / 0 / 218
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1059
R indices (all data)	R1 = 0.0986, wR2 = 0.1197
Largest diff. peak and hole	0.382 and -0.358 e.A^-3

Table s2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for compound **2q**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	-4050(1)	14864(2)	500(1)	22(1)
F(1)	269(1)	-1630(4)	3316(1)	38(1)
O(1)	2275(1)	9804(4)	848(1)	25(1)
O(2)	1399(1)	7474(5)	1398(1)	54(1)
O(3)	750(1)	12663(6)	448(1)	70(1)
N(1)	-174(1)	10129(5)	966(1)	18(1)
C(1)	-107(2)	394(6)	2966(1)	24(1)
C(2)	-1018(2)	1345(6)	3000(1)	24(1)
C(3)	-1407(2)	3381(5)	2637(1)	19(1)
C(4)	-875(2)	4413(5)	2249(1)	16(1)
C(5)	-1269(2)	6488(5)	1864(1)	17(1)
C(6)	-1572(2)	8183(5)	1536(1)	15(1)
C(7)	-1810(1)	10278(5)	1129(1)	14(1)
C(8)	-1084(2)	11285(5)	835(1)	14(1)
C(9)	646(2)	10870(6)	776(1)	23(1)
C(10)	1480(2)	9127(6)	1046(1)	22(1)
C(11)	3129(2)	8324(7)	1080(1)	31(1)
C(12)	3924(2)	9278(7)	779(1)	30(1)
C(13)	-2727(2)	11387(5)	1017(1)	16(1)
C(14)	-2909(2)	13440(5)	626(1)	16(1)
C(15)	-2198(2)	14425(5)	334(1)	17(1)
C(16)	-1286(2)	13334(5)	440(1)	17(1)
C(17)	55(2)	3401(6)	2230(1)	21(1)
C(18)	441(2)	1358(6)	2591(1)	26(1)

Table s3. Bond lengths [A] and angles [deg] for compound **2q**

Cl(1)-C(14)	1.742(2)
F(1)-C(1)	1.357(3)
O(1)-C(10)	1.320(3)
O(1)-C(11)	1.459(3)
O(2)-C(10)	1.194(3)
O(3)-C(9)	1.192(3)
N(1)-C(9)	1.349(3)
N(1)-C(8)	1.403(3)
N(1)-H(1)	0.8800
C(1)-C(18)	1.376(4)
C(1)-C(2)	1.373(3)
C(2)-C(3)	1.389(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.397(3)
C(3)-H(3A)	0.9500
C(4)-C(17)	1.401(3)
C(4)-C(5)	1.440(3)
C(5)-C(6)	1.192(3)
C(6)-C(7)	1.433(3)
C(7)-C(13)	1.397(3)
C(7)-C(8)	1.416(3)
C(8)-C(16)	1.389(3)
C(9)-C(10)	1.532(3)
C(11)-C(12)	1.496(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.380(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.392(3)
C(15)-C(16)	1.387(3)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-C(18)	1.386(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(10)-O(1)-C(11)	116.24(19)
C(9)-N(1)-C(8)	128.7(2)
C(9)-N(1)-H(1)	115.6

C(8)-N(1)-H(1)	115.6
F(1)-C(1)-C(18)	118.2(2)
F(1)-C(1)-C(2)	118.5(2)
C(18)-C(1)-C(2)	123.2(2)
C(1)-C(2)-C(3)	118.4(2)
C(1)-C(2)-H(2)	120.8
C(3)-C(2)-H(2)	120.8
C(2)-C(3)-C(4)	120.2(2)
C(2)-C(3)-H(3A)	119.9
C(4)-C(3)-H(3A)	119.9
C(3)-C(4)-C(17)	119.5(2)
C(3)-C(4)-C(5)	121.1(2)
C(17)-C(4)-C(5)	119.3(2)
C(6)-C(5)-C(4)	177.9(2)
C(5)-C(6)-C(7)	172.5(2)
C(13)-C(7)-C(8)	119.1(2)
C(13)-C(7)-C(6)	122.41(19)
C(8)-C(7)-C(6)	118.50(19)
C(16)-C(8)-N(1)	122.97(19)
C(16)-C(8)-C(7)	120.2(2)
N(1)-C(8)-C(7)	116.9(2)
O(3)-C(9)-N(1)	126.8(2)
O(3)-C(9)-C(10)	122.0(2)
N(1)-C(9)-C(10)	111.2(2)
O(2)-C(10)-O(1)	126.2(2)
O(2)-C(10)-C(9)	122.9(2)
O(1)-C(10)-C(9)	110.8(2)
O(1)-C(11)-C(12)	107.0(2)
O(1)-C(11)-H(11A)	110.3
C(12)-C(11)-H(11A)	110.3
O(1)-C(11)-H(11B)	110.3
C(12)-C(11)-H(11B)	110.3
H(11A)-C(11)-H(11B)	108.6
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(7)	119.8(2)
C(14)-C(13)-H(13)	120.1
C(7)-C(13)-H(13)	120.1
C(13)-C(14)-C(15)	121.3(2)
C(13)-C(14)-Cl(1)	119.29(17)

C(15)-C(14)-Cl(1)	119.37(18)
C(16)-C(15)-C(14)	119.5(2)
C(16)-C(15)-H(15)	120.3
C(14)-C(15)-H(15)	120.3
C(8)-C(16)-C(15)	120.2(2)
C(8)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(18)-C(17)-C(4)	120.2(2)
C(18)-C(17)-H(17)	119.9
C(4)-C(17)-H(17)	119.9
C(1)-C(18)-C(17)	118.4(2)
C(1)-C(18)-H(18)	120.8
C(17)-C(18)-H(18)	120.8

Symmetry transformations used to generate equivalent atoms:

Table s4. Anisotropic displacement parameters (A^2 x 10^3) for compound **2q**. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	14(1)	31(1)	22(1)	0(1)	-2(1)	6(1)
F(1)	54(1)	31(1)	27(1)	9(1)	-10(1)	9(1)
O(1)	13(1)	36(1)	26(1)	6(1)	3(1)	5(1)
O(2)	21(1)	75(2)	67(2)	54(1)	9(1)	13(1)
O(3)	19(1)	110(2)	82(2)	81(2)	16(1)	18(1)
N(1)	15(1)	22(1)	18(1)	8(1)	3(1)	3(1)
C(1)	38(1)	17(1)	16(1)	3(1)	-10(1)	2(1)
C(2)	36(1)	20(1)	14(1)	0(1)	2(1)	-2(1)
C(3)	24(1)	17(1)	15(1)	-1(1)	0(1)	-2(1)
C(4)	22(1)	12(1)	13(1)	-1(1)	-3(1)	-2(1)
C(5)	18(1)	18(1)	16(1)	-3(1)	3(1)	-4(1)
C(6)	14(1)	17(1)	15(1)	-1(1)	2(1)	-2(1)
C(7)	16(1)	15(1)	11(1)	-2(1)	0(1)	0(1)
C(8)	13(1)	17(1)	12(1)	-1(1)	-2(1)	1(1)
C(9)	16(1)	32(2)	20(1)	10(1)	2(1)	4(1)
C(10)	16(1)	27(1)	24(1)	4(1)	2(1)	2(1)
C(11)	15(1)	36(2)	42(2)	8(1)	0(1)	9(1)
C(12)	15(1)	46(2)	29(2)	-13(1)	0(1)	4(1)
C(13)	14(1)	19(1)	16(1)	-5(1)	2(1)	-2(1)
C(14)	14(1)	21(1)	14(1)	-3(1)	-2(1)	2(1)
C(15)	19(1)	20(1)	12(1)	1(1)	-2(1)	3(1)
C(16)	16(1)	21(1)	14(1)	1(1)	1(1)	0(1)
C(17)	24(1)	22(1)	17(1)	-2(1)	1(1)	-1(1)
C(18)	26(1)	22(1)	27(1)	-2(1)	-6(1)	2(1)

Table s5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for compound **2q**.

	x	y	z	U(eq)
H(1)	-132	8732	1204	22
H(2)	-1374	629	3266	28
H(3A)	-2036	4073	2654	23
H(11A)	3050	6138	1061	38
H(11B)	3260	8905	1447	38
H(12A)	3802	8590	421	45
H(12B)	4518	8417	935	45
H(12C)	3971	11452	784	45
H(13)	-3223	10730	1210	19
H(15)	-2337	15834	65	21
H(16)	-797	13991	241	20
H(17)	423	4118	1970	25
H(18)	1068	641	2579	31

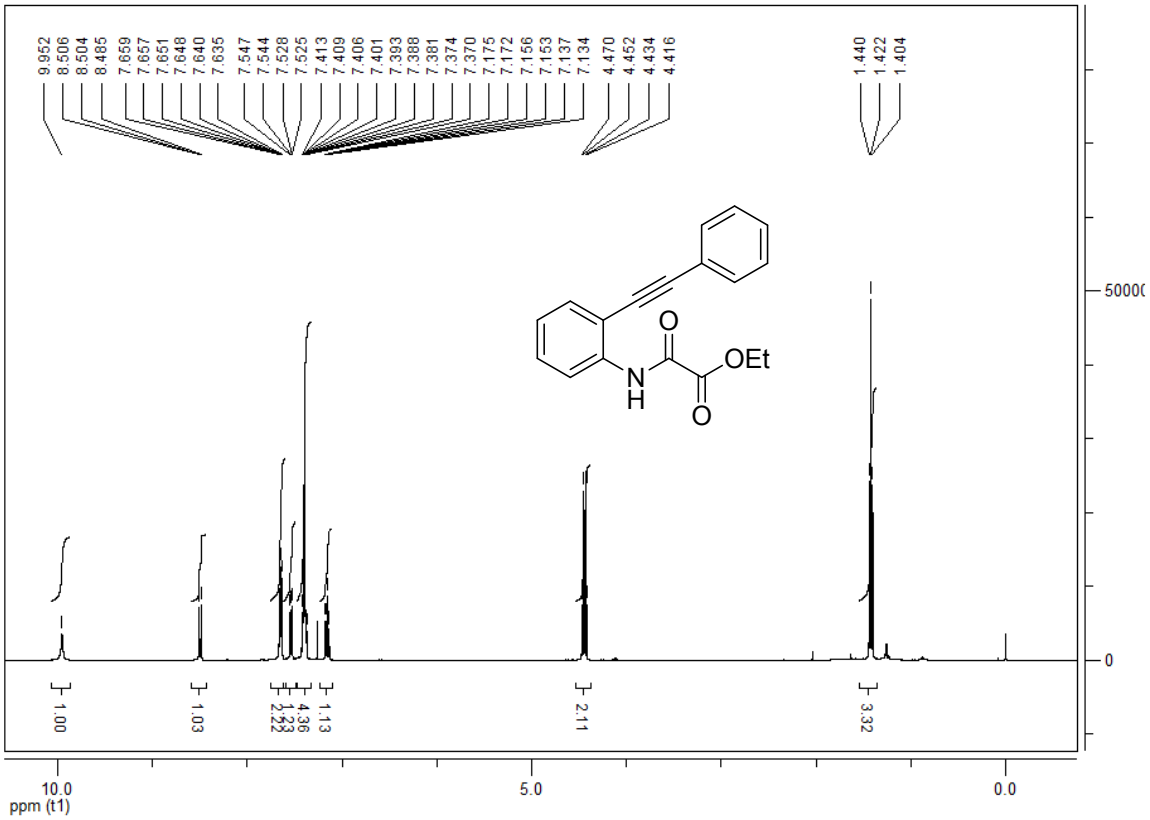
Table s6. Torsion angles [deg] for compound **2q.**

F(1)-C(1)-C(2)-C(3)	-179.0(2)
C(18)-C(1)-C(2)-C(3)	0.0(4)
C(1)-C(2)-C(3)-C(4)	0.1(4)
C(2)-C(3)-C(4)-C(17)	-0.6(3)
C(2)-C(3)-C(4)-C(5)	179.0(2)
C(3)-C(4)-C(5)-C(6)	-163(7)
C(17)-C(4)-C(5)-C(6)	17(7)
C(4)-C(5)-C(6)-C(7)	-33(9)
C(5)-C(6)-C(7)-C(13)	-172.4(18)
C(5)-C(6)-C(7)-C(8)	7(2)
C(9)-N(1)-C(8)-C(16)	5.0(4)
C(9)-N(1)-C(8)-C(7)	-174.6(2)
C(13)-C(7)-C(8)-C(16)	-0.4(3)
C(6)-C(7)-C(8)-C(16)	-179.4(2)
C(13)-C(7)-C(8)-N(1)	179.3(2)
C(6)-C(7)-C(8)-N(1)	0.2(3)
C(8)-N(1)-C(9)-O(3)	-1.1(5)
C(8)-N(1)-C(9)-C(10)	177.7(2)
C(11)-O(1)-C(10)-O(2)	1.5(4)
C(11)-O(1)-C(10)-C(9)	179.0(2)
O(3)-C(9)-C(10)-O(2)	174.7(3)
N(1)-C(9)-C(10)-O(2)	-4.1(4)
O(3)-C(9)-C(10)-O(1)	-2.9(4)
N(1)-C(9)-C(10)-O(1)	178.3(2)
C(10)-O(1)-C(11)-C(12)	176.8(2)
C(8)-C(7)-C(13)-C(14)	-0.2(3)
C(6)-C(7)-C(13)-C(14)	178.9(2)
C(7)-C(13)-C(14)-C(15)	0.5(4)
C(7)-C(13)-C(14)-Cl(1)	-178.66(17)
C(13)-C(14)-C(15)-C(16)	-0.3(4)
Cl(1)-C(14)-C(15)-C(16)	178.87(18)
N(1)-C(8)-C(16)-C(15)	-179.1(2)
C(7)-C(8)-C(16)-C(15)	0.6(3)
C(14)-C(15)-C(16)-C(8)	-0.3(3)
C(3)-C(4)-C(17)-C(18)	0.9(4)
C(5)-C(4)-C(17)-C(18)	-178.7(2)
F(1)-C(1)-C(18)-C(17)	179.3(2)
C(2)-C(1)-C(18)-C(17)	0.3(4)
C(4)-C(17)-C(18)-C(1)	-0.8(4)

Symmetry transformations used to generate equivalent atoms:

Table s7. Hydrogen bonds for compound **2q** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)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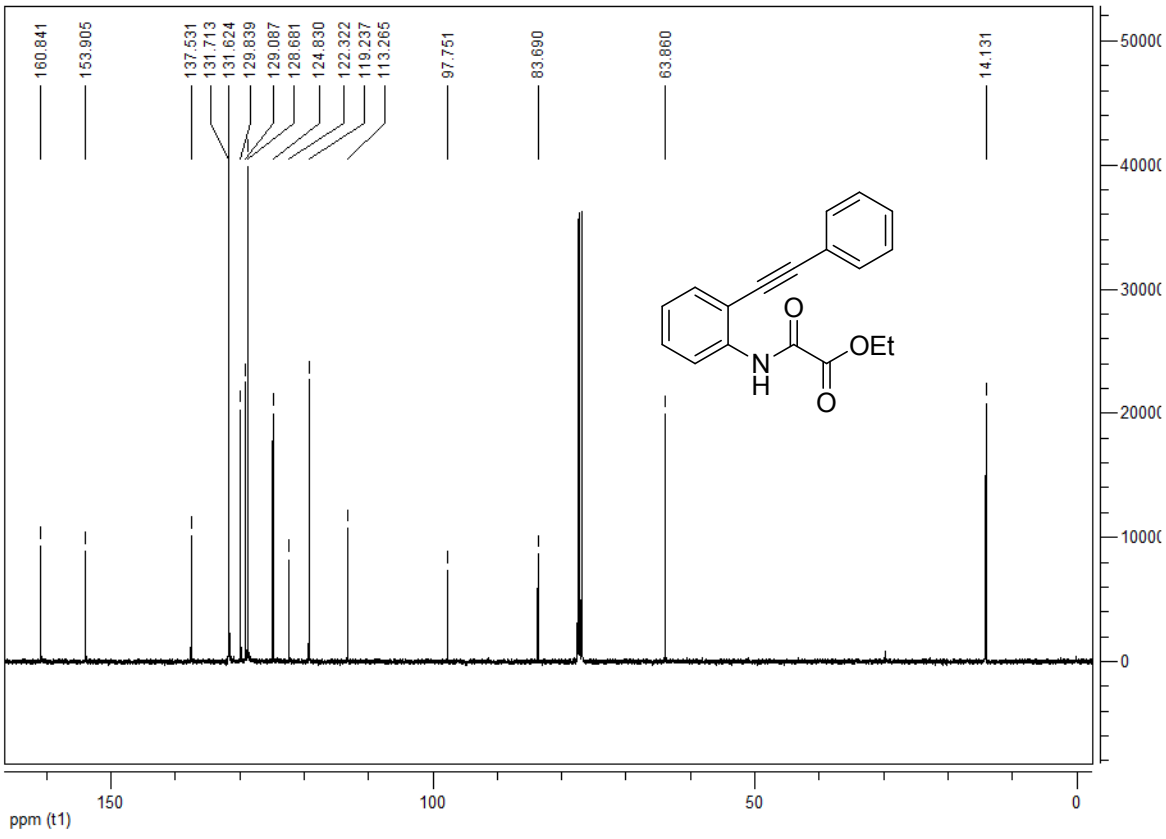
8.506
8.504
8.485
7.659
7.657
7.651
7.648
7.640
7.635
7.547
7.544
7.528
7.525
7.413
7.409
7.406
7.401
7.393
7.388
7.381
7.374
7.370
7.175
7.172
7.156
7.153
7.137
7.134
4.470
4.452
4.434
4.416
1.440
1.422
1.404
O
OEt
N
H
O
1.00
1.03
2.22
1.23
4.96
1.13
2.11
3.32
10.0
5.0
0.0
ppm (t1)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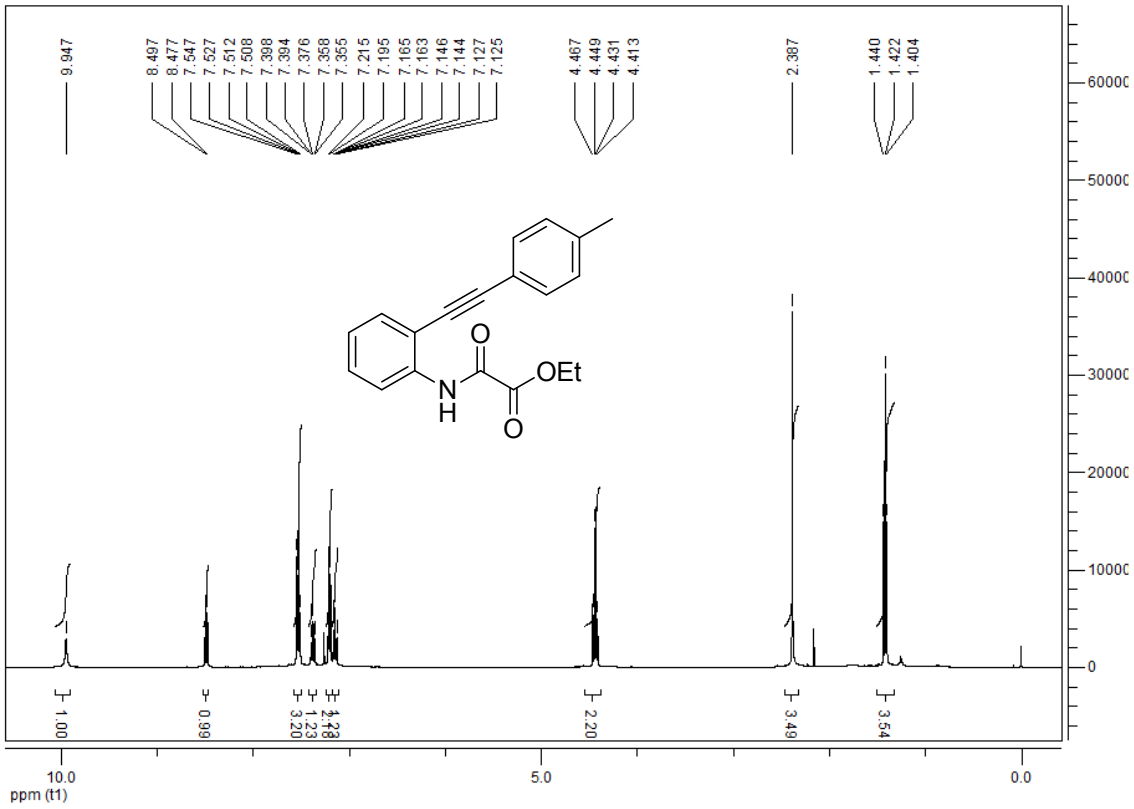
153.905
137.531
131.713
131.624
129.839
129.087
128.681
124.830
122.322
119.237
113.265
97.751
83.690
63.860
14.131
O
OEt
N
H
O
150
100
50
0
ppm (t1)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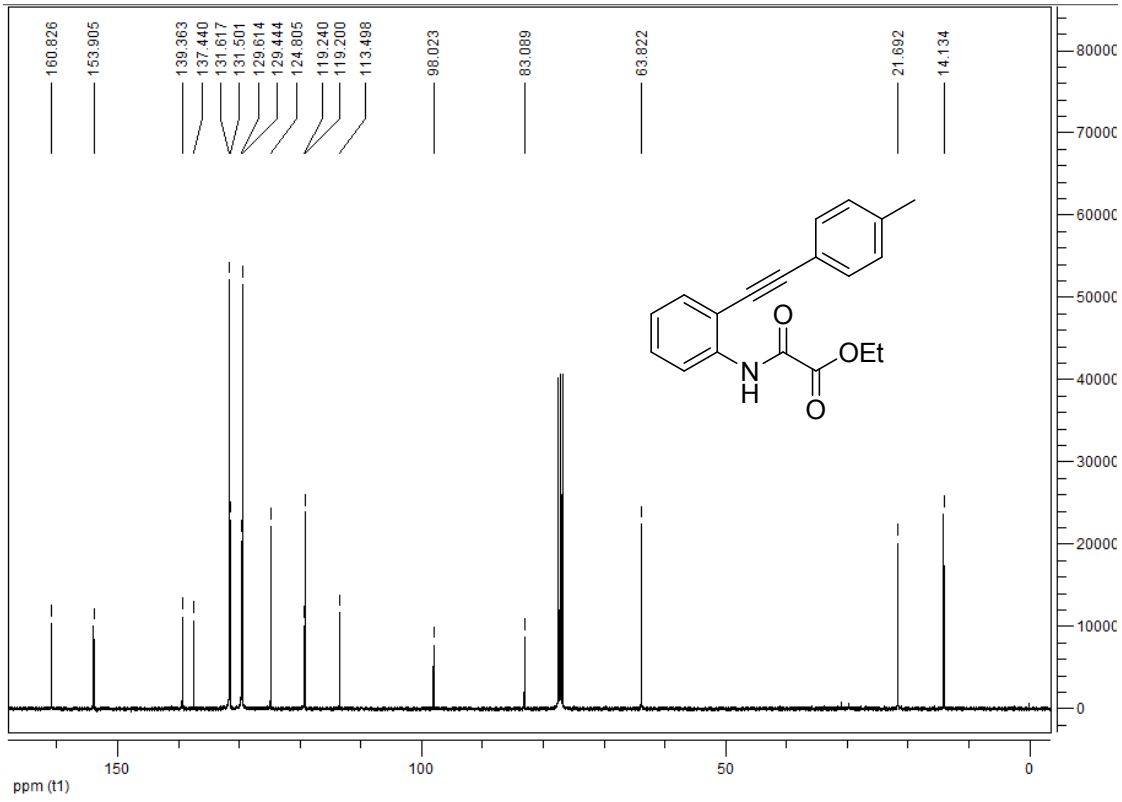
8.497
8.477
7.547
7.527
7.512
7.508
7.398
7.394
7.376
7.358
7.355
7.215
7.195
7.165
7.163
7.146
7.144
7.127
7.125
4.467
4.449
4.431
4.413
2.387
1.440
1.422
1.404
O
OEt
N
H
O
1.00
0.99
3.20
1.23
4.28
2.20
3.49
3.54
10.0
5.0
0.0
ppm (t1)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153.905
139.363
137.440
131.617
131.501
129.614
129.444
124.805
119.240
119.200
113.498
98.023
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21.692
14.134
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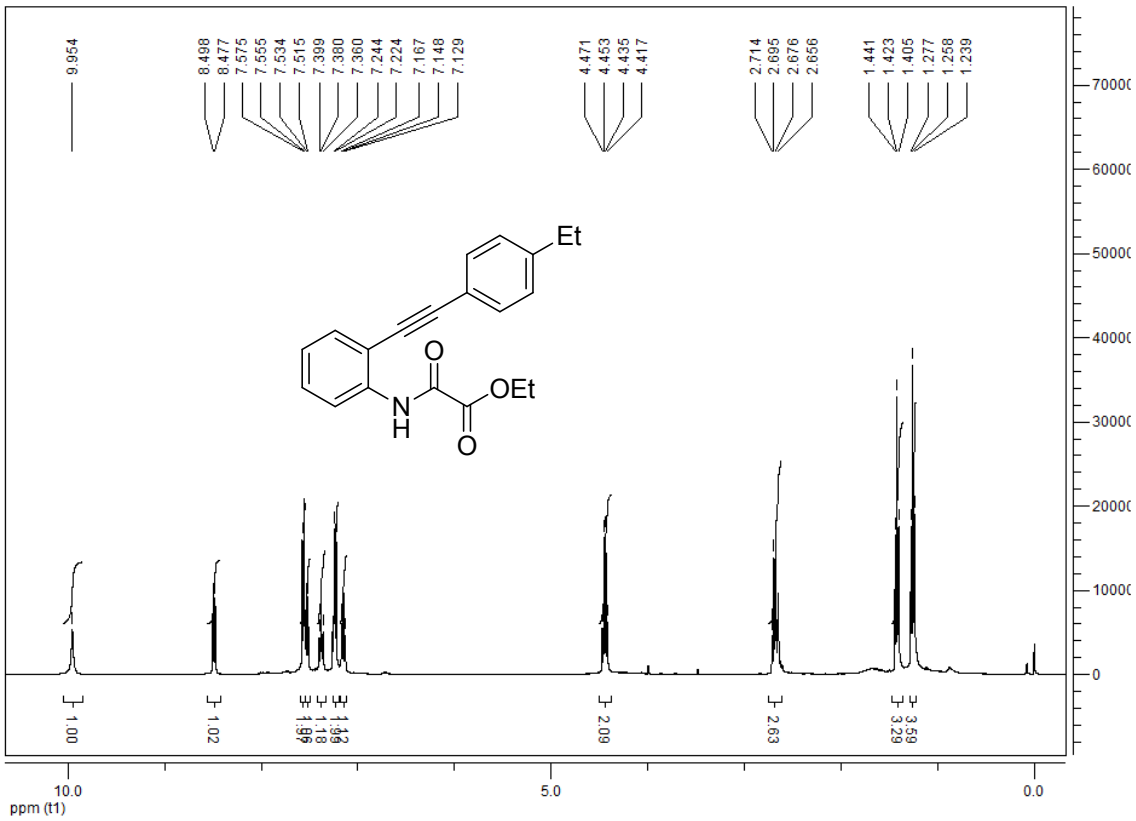
OEt
N
H
O
150
100
50
0
ppm (t1)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8.498
8.477
7.575
7.555
7.534
7.515
7.399
7.380
7.360
7.244
7.224
7.167
7.148
7.129
4.471
4.453
4.435
4.417
2.714
2.695
2.676
2.656
1.441
1.423
1.405
1.277
1.258
1.239
Et
O
N
H
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O
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1.02
2.09
2.93
3.29
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5.0
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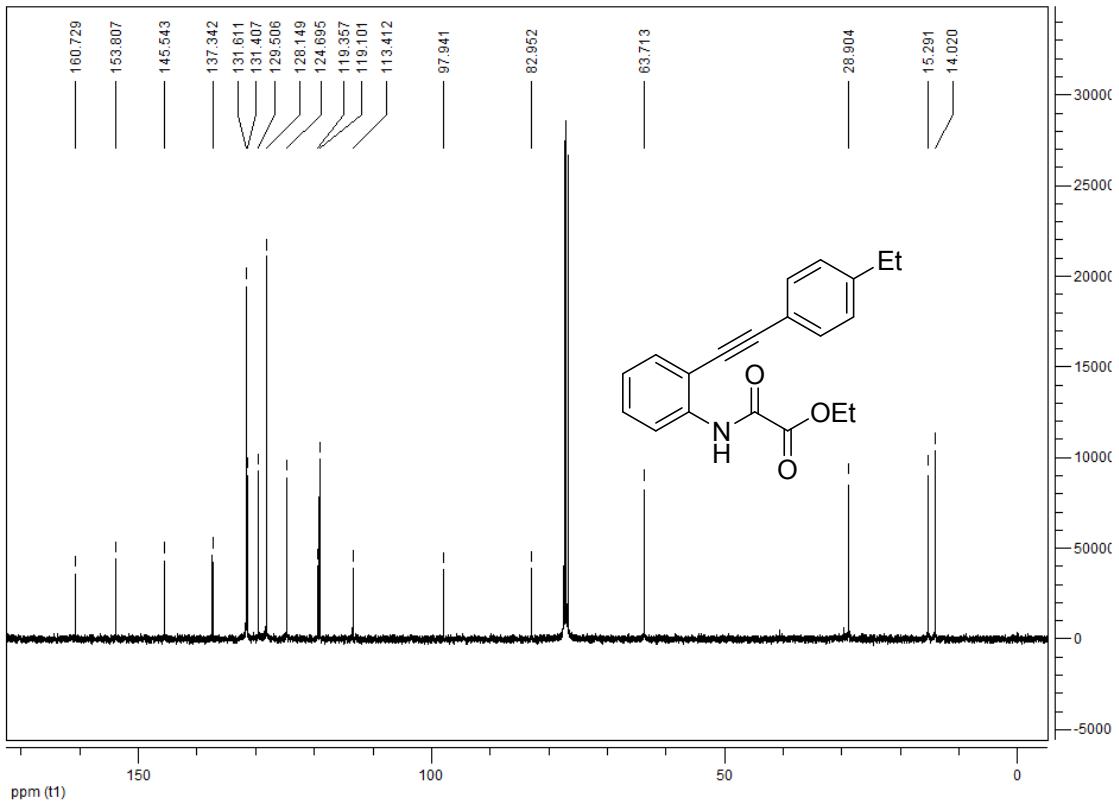
ppm (t1)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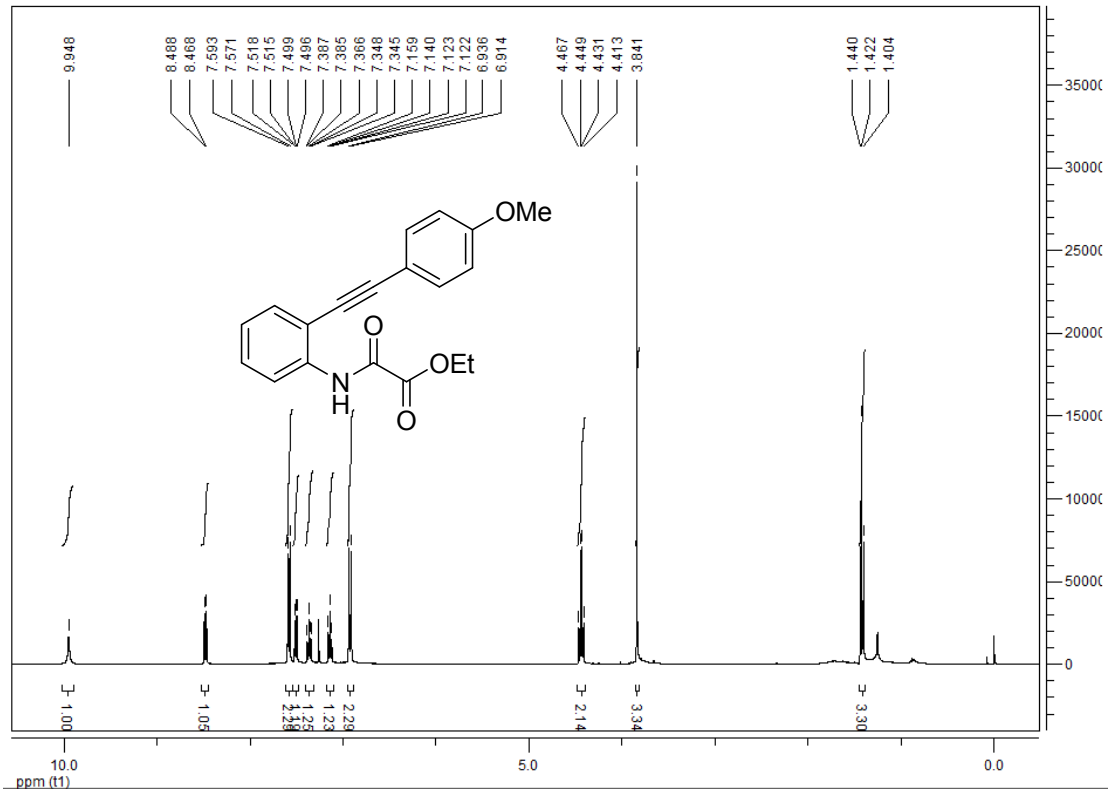
131.611
131.407
129.506
128.149
124.695
119.357
119.101
113.412
97.941
82.952
63.713
28.904
15.291
14.020
Et
O
N
H
OEt
O
150
100
50
0
ppm (t1)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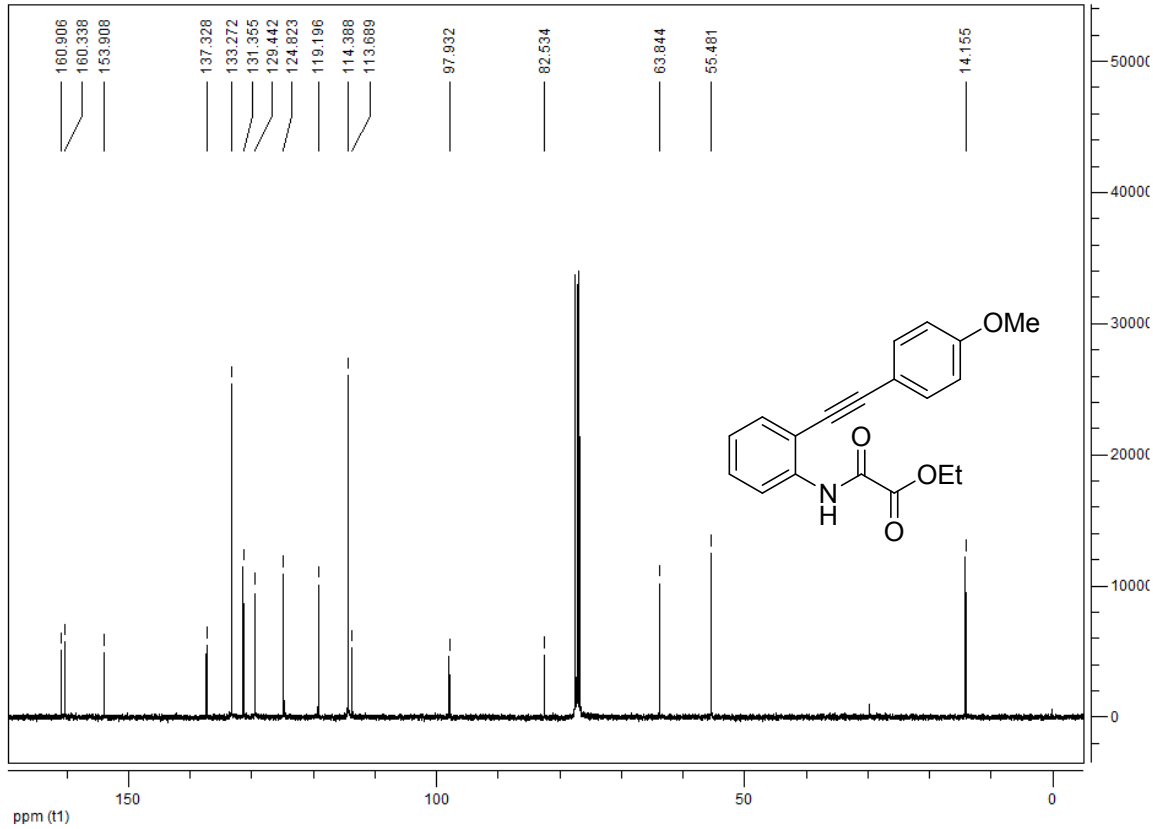
7.518
7.515
7.499
7.496
7.387
7.385
7.366
7.348
7.345
7.159
7.140
7.123
7.122
6.936
6.914
4.467
4.449
4.431
4.413
3.841
1.440
1.422
1.404
OMe
O
OEt
N
H
O
1.00
1.05
2.29
2.14
3.34
3.30
10.0
5.0
0.0
ppm (t1)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137.328
133.272
131.355
129.442
124.823
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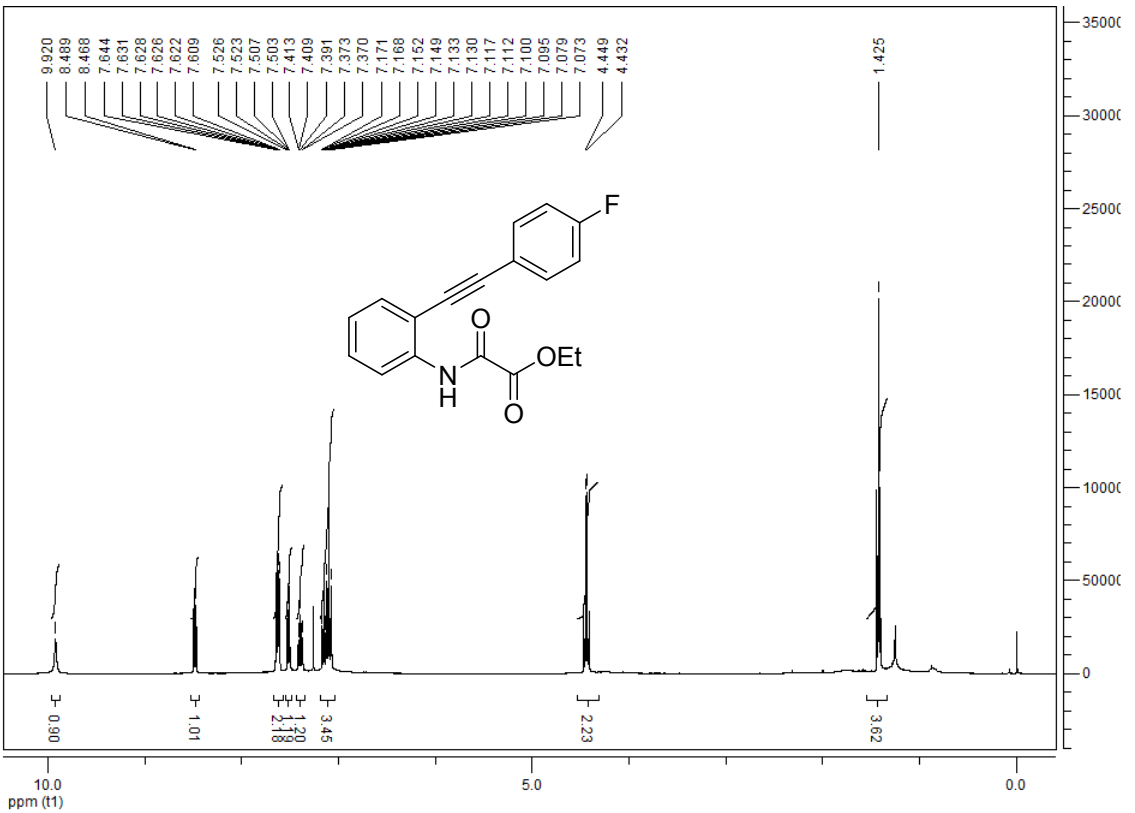
114.388
113.689
97.932
82.534
63.844
55.481
14.155
OMe
O
OEt
N
H
O
150
100
50
0
ppm (t1)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7.622
7.609
7.526
7.523
7.507
7.503
7.413
7.409
7.391
7.373
7.370
7.171
7.168
7.152
7.149
7.133
7.130
7.117
7.112
7.100
7.095
7.079
7.073
4.449
4.432
1.425
F
O
OEt
N
H
O
0.90
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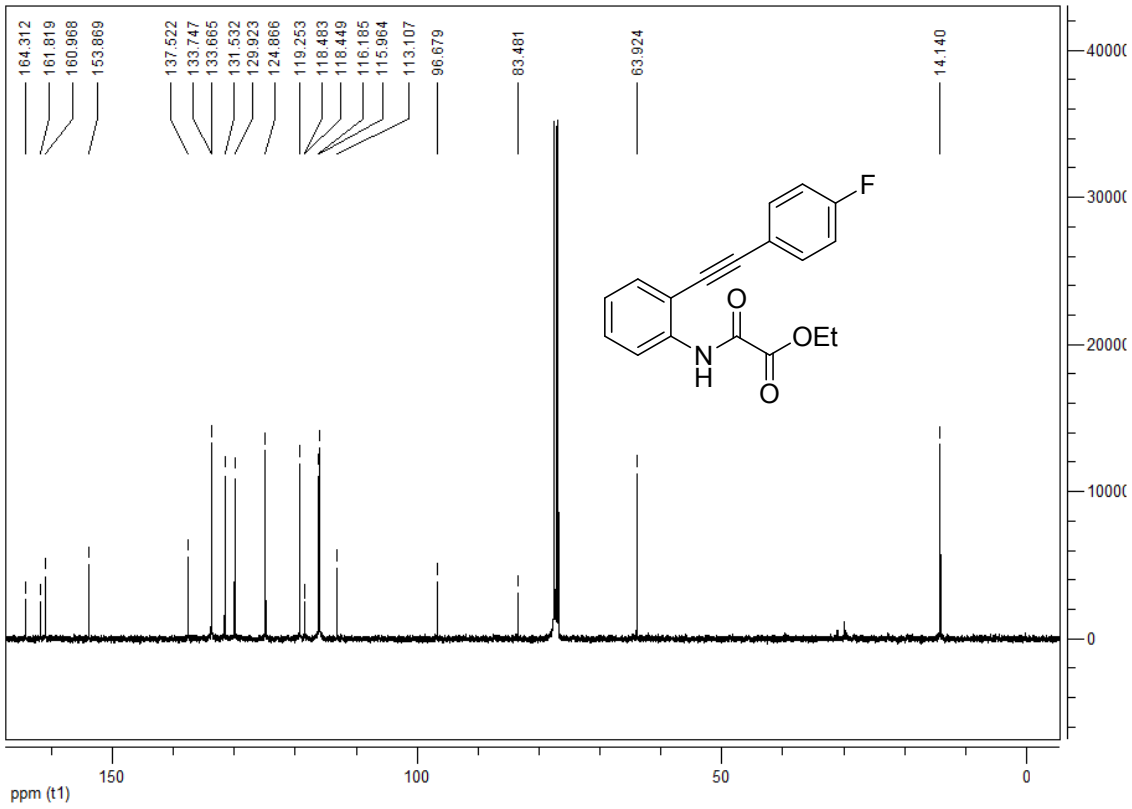
1.20
2.18
3.45
2.23
3.62
10.0
5.0
0.0
ppm (t1)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160.968
153.869
137.522
133.747
133.665
131.532
129.923
124.866
119.253
118.483
118.449
116.185
115.964
113.107
96.679
83.481
63.924
14.140
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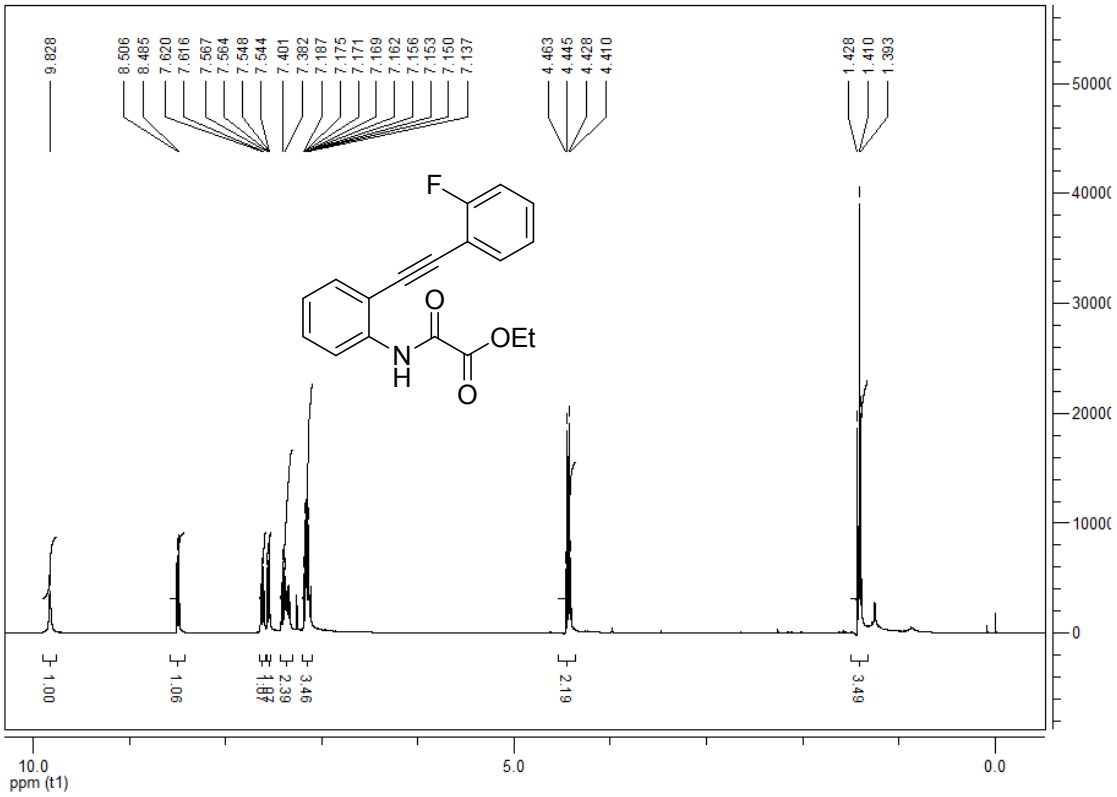
OEt
N
H
O
150
100
50
0
ppm (t1)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8.485
7.620
7.616
7.567
7.564
7.548
7.544
7.401
7.382
7.187
7.175
7.171
7.169
7.162
7.156
7.153
7.150
7.137
4.463
4.445
4.428
4.410
1.428
1.410
1.393
F
O
N
H
OEt
O
1.00
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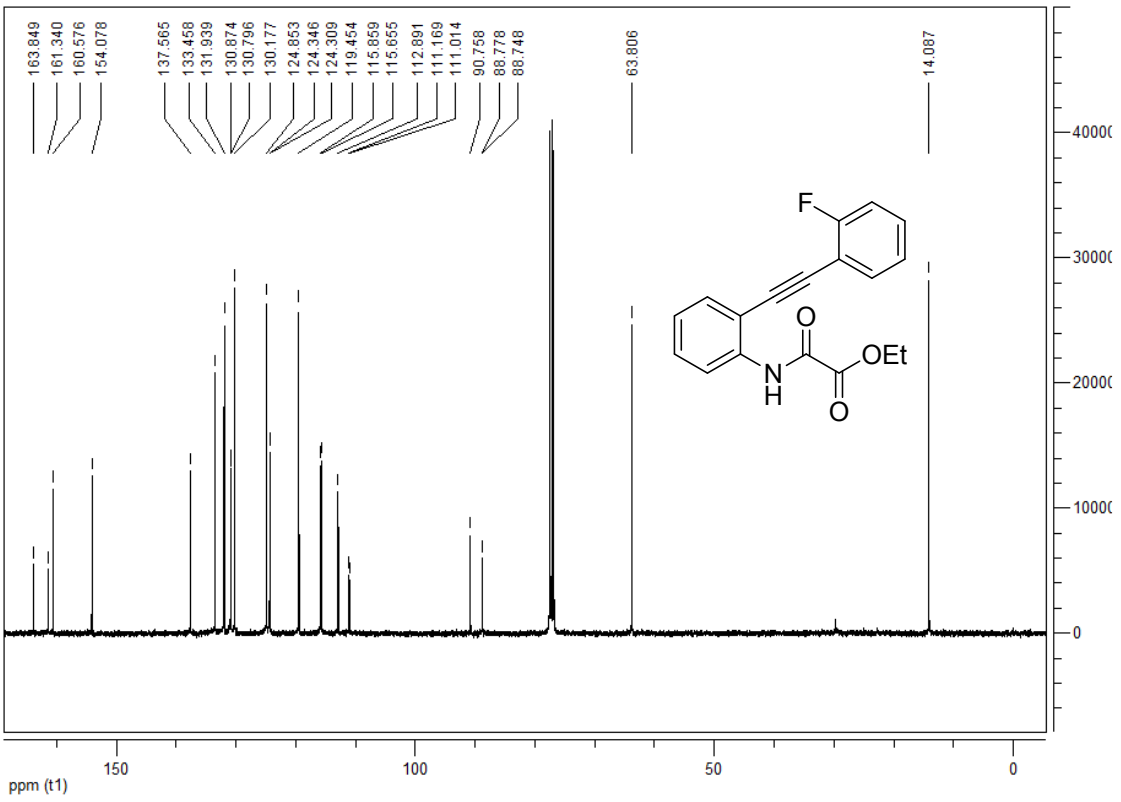
1.87
2.09
3.46
2.19
3.49
10.0
5.0
0.0
ppm (t1)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131.939
130.874
130.796
130.177
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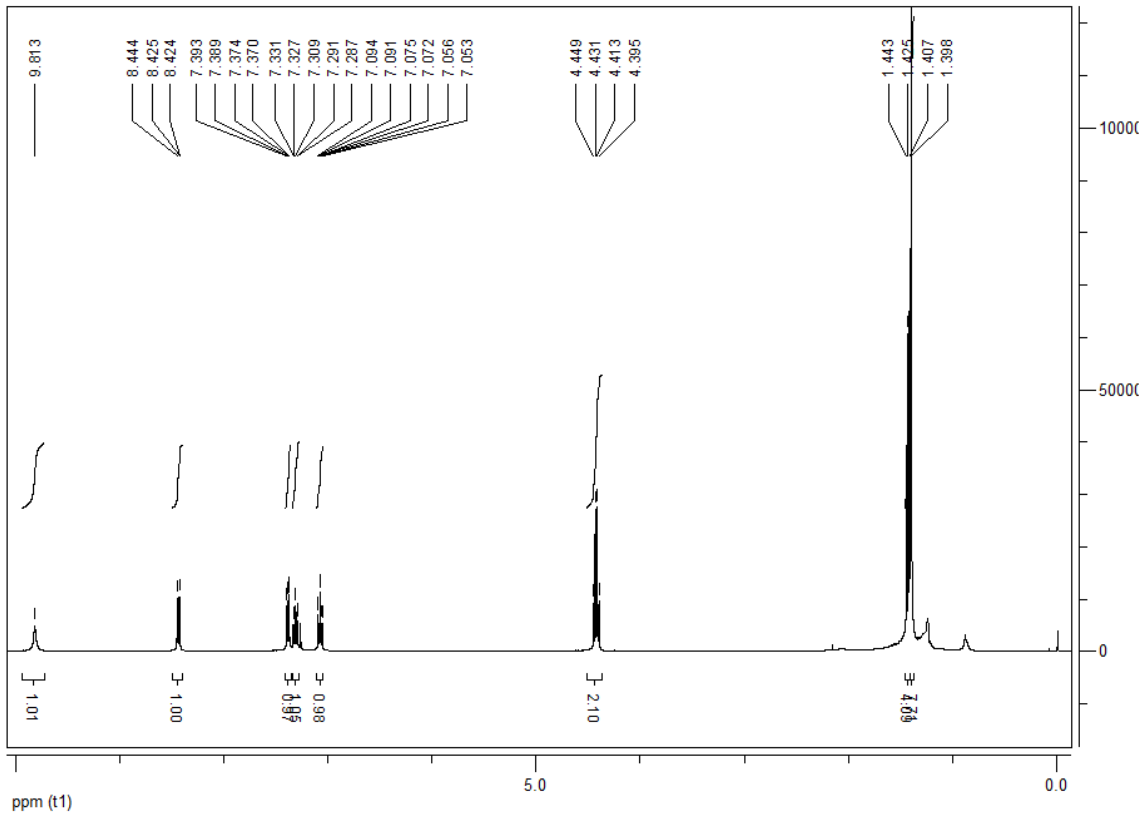
124.346
124.309
119.454
115.859
115.655
112.891
111.169
111.014
90.758
88.778
88.748
63.806
14.087
F
O
N
H
OEt
O
150
100
50
0
ppm (t1)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7.389
7.374
7.370
7.331
7.327
7.309
7.291
7.287
7.094
7.091
7.075
7.072
7.056
7.053
4.449
4.431
4.413
4.395
1.443
1.425
1.407
1.398
1.01
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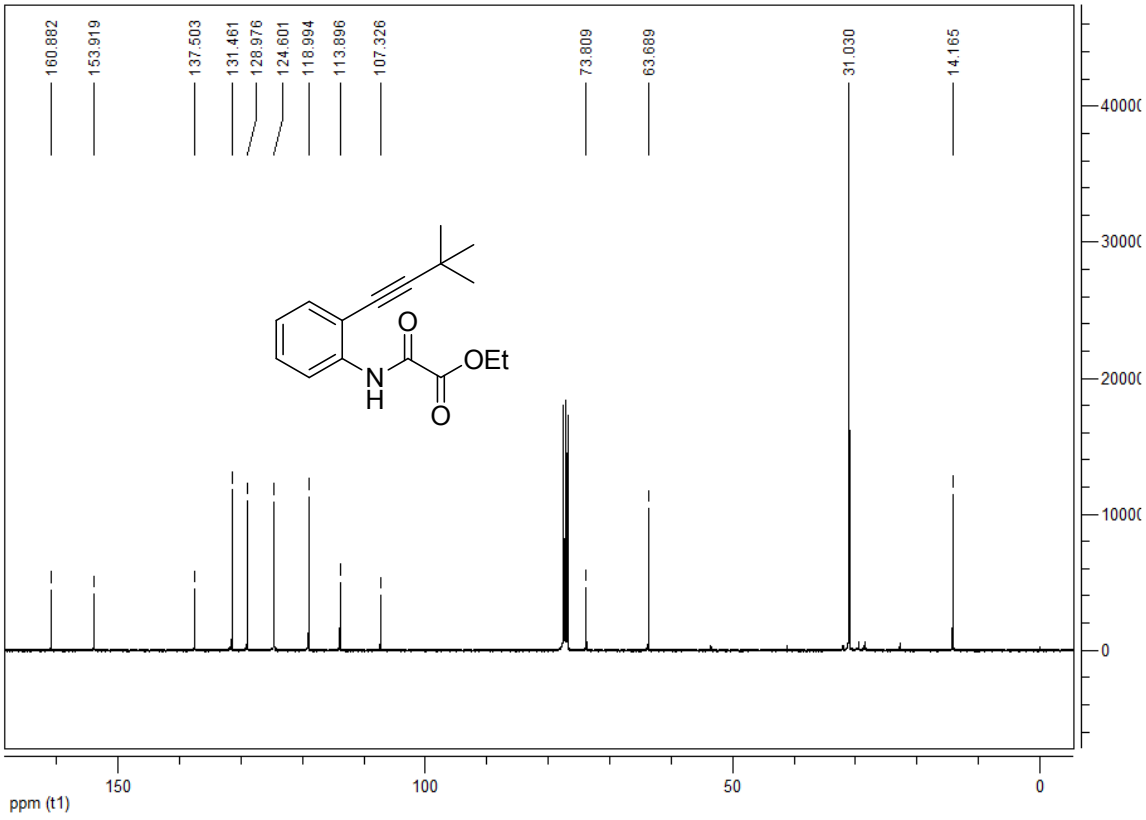
3.09
0.98
2.10
4.69
10000
5000
0
5.0
0.0
ppm (t1)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107.326
73.809
63.689
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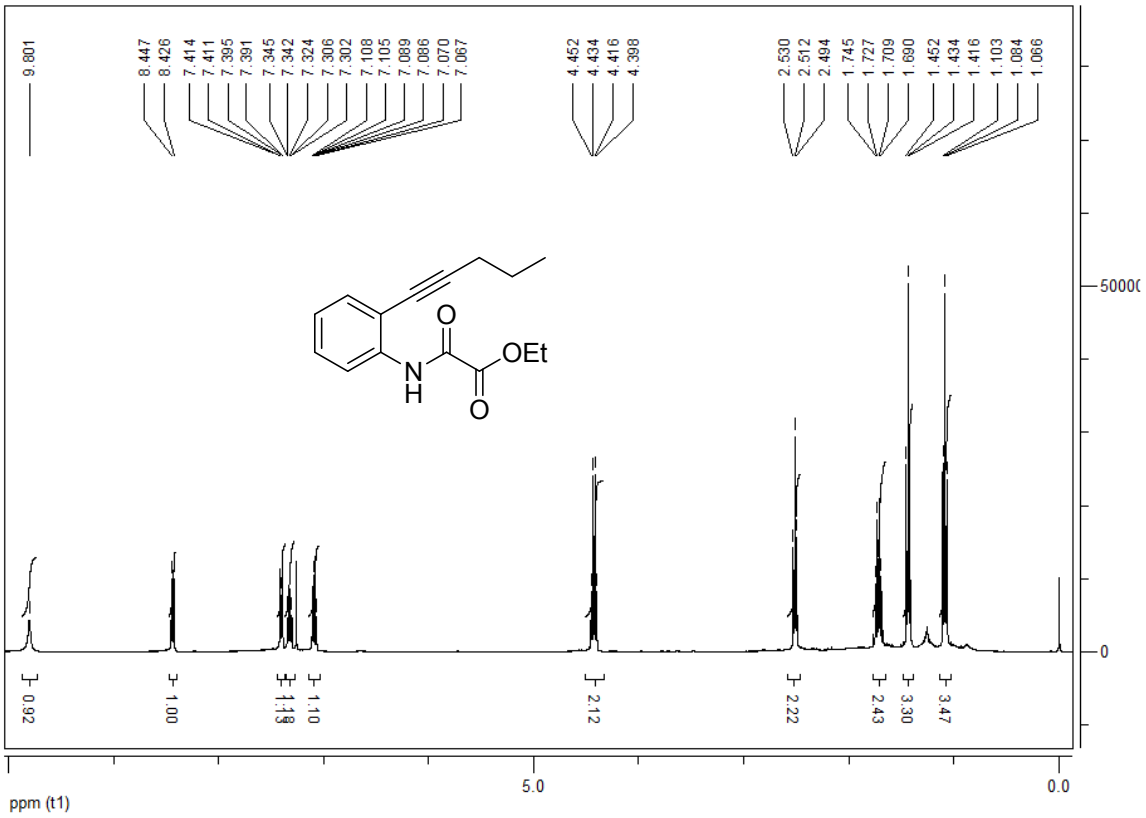
O
OEt
N
H
O
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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7.411
7.395
7.391
7.345
7.342
7.324
7.306
7.302
7.108
7.105
7.089
7.086
7.070
7.067
4.452
4.434
4.416
4.398
2.530
2.512
2.494
1.745
1.727
1.709
1.690
1.452
1.434
1.416
1.103
1.084
1.066
O
N
H
O
OEt
50000
0
0.92
1.00
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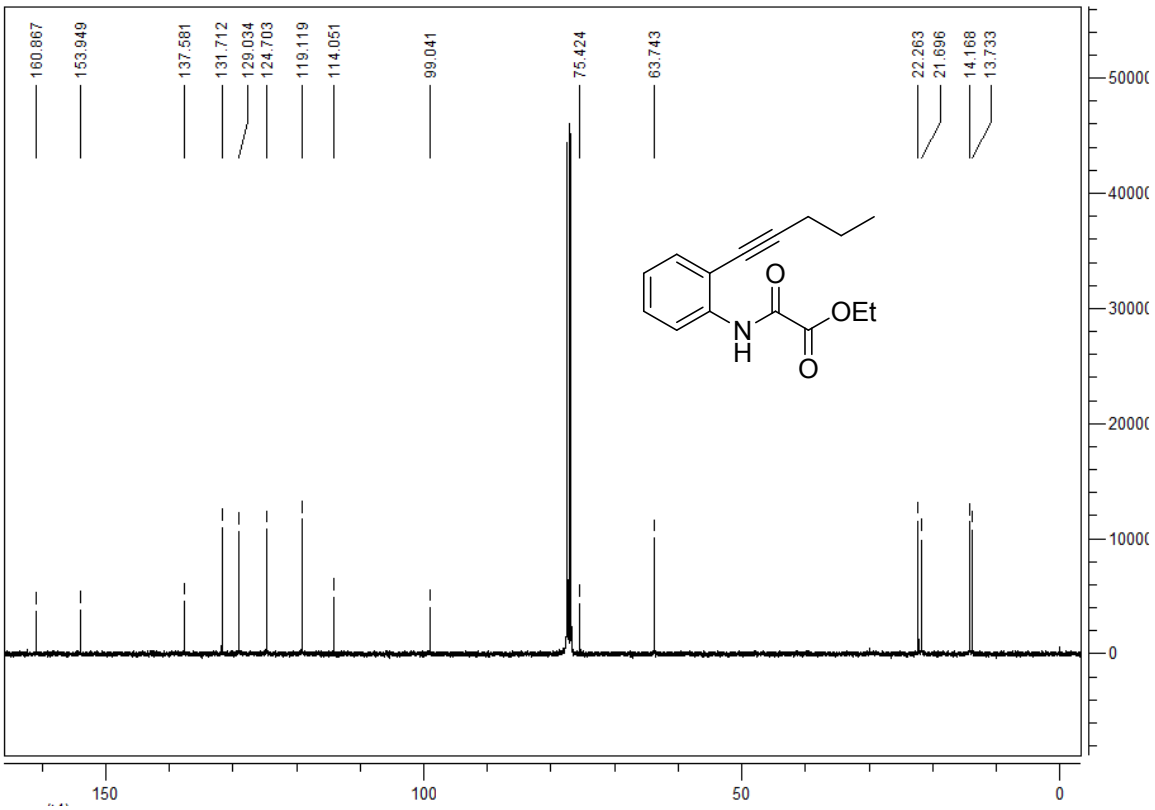
1.10
2.12
2.22
2.43
3.30
3.47
5.0
0.0
ppm (t1)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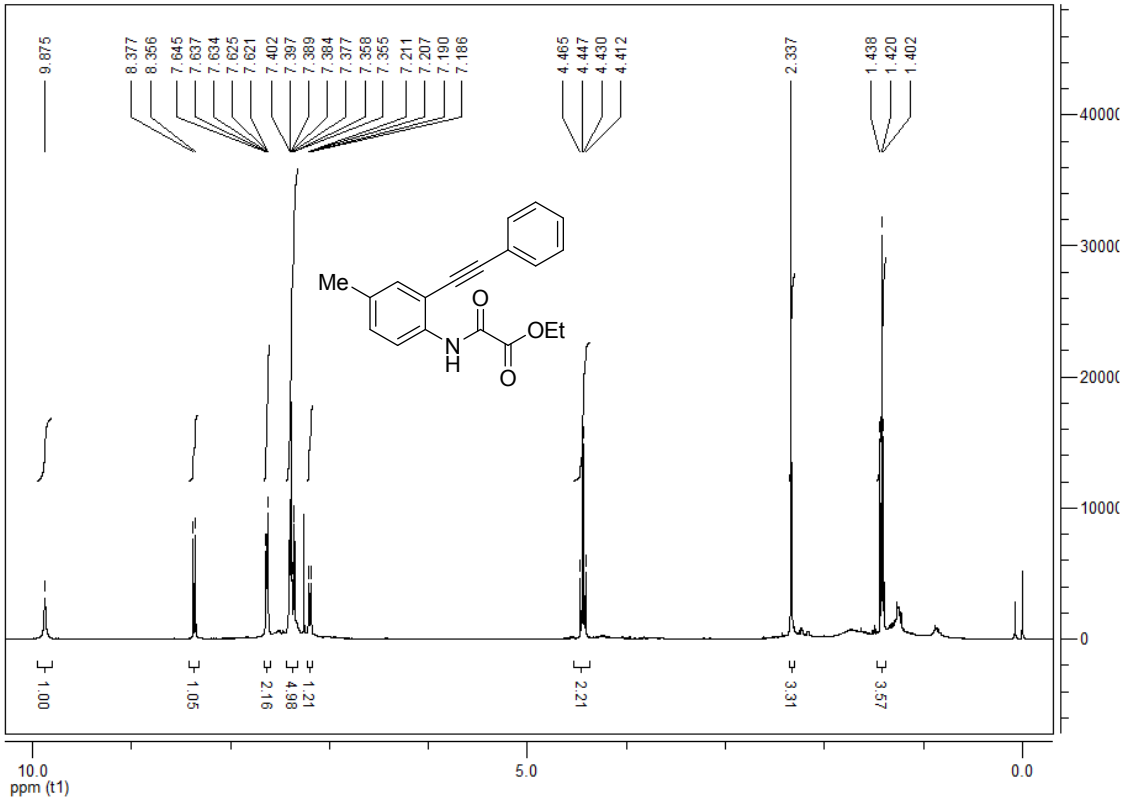
129.034
124.703
119.119
114.051
99.041
75.424
63.743
22.263
21.696
14.168
13.733
O
N
H
O
OEt
50000
40000
30000
20000
10000
0
150
100
50
0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7.621
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7.377
7.358
7.355
7.211
7.207
7.190
7.186
4.465
4.447
4.430
4.412
2.337
1.438
1.420
1.402
Me
O
N
H
OEt
O
1.00
1.05
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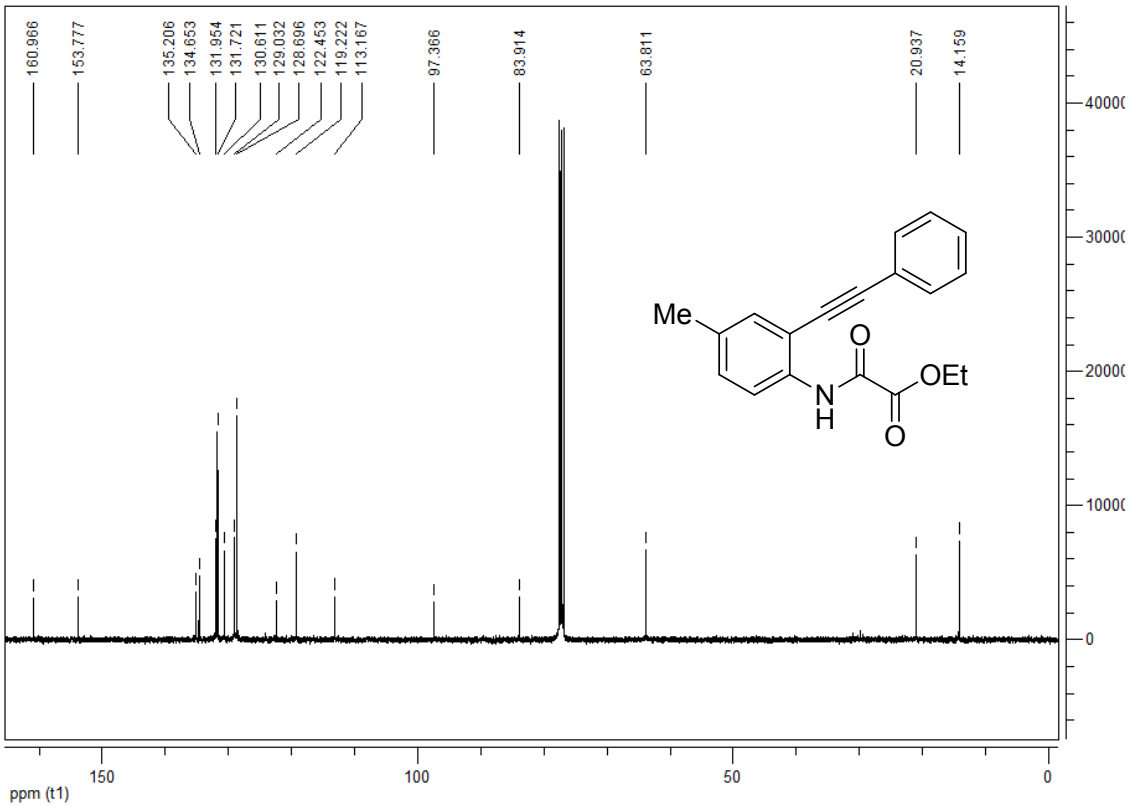
4.98
1.21
2.21
3.31
3.57
10.0
5.0
0.0
ppm (t1)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129.032
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122.453
119.222
113.167
97.366
83.914
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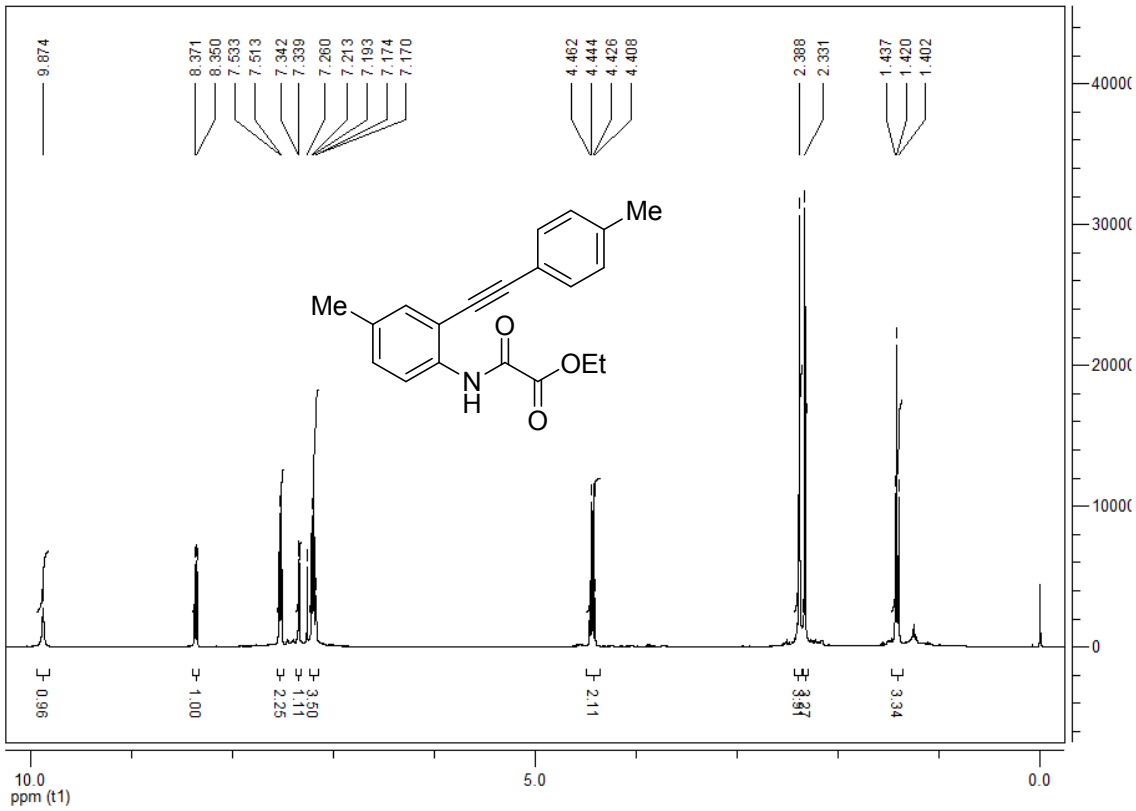
20.937
14.159
Me
O
N
H
OEt
O
150
100
50
0
ppm (t1)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7.342
7.339
7.260
7.213
7.193
7.174
7.170
4.462
4.444
4.426
4.408
2.388
2.331
1.437
1.420
1.402
Me
Me
O
OEt
N
H
O
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2.11
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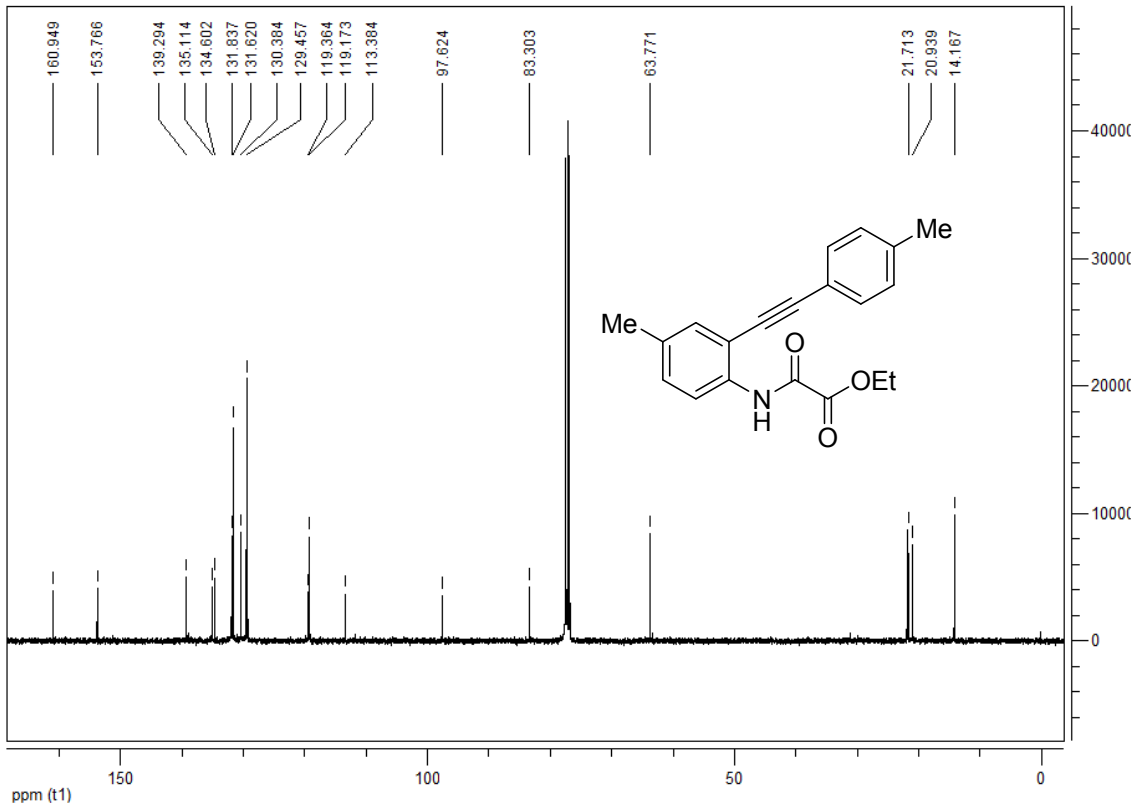
ppm (t1)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135.114
134.602
131.837
131.620
130.384
129.457
119.364
119.173
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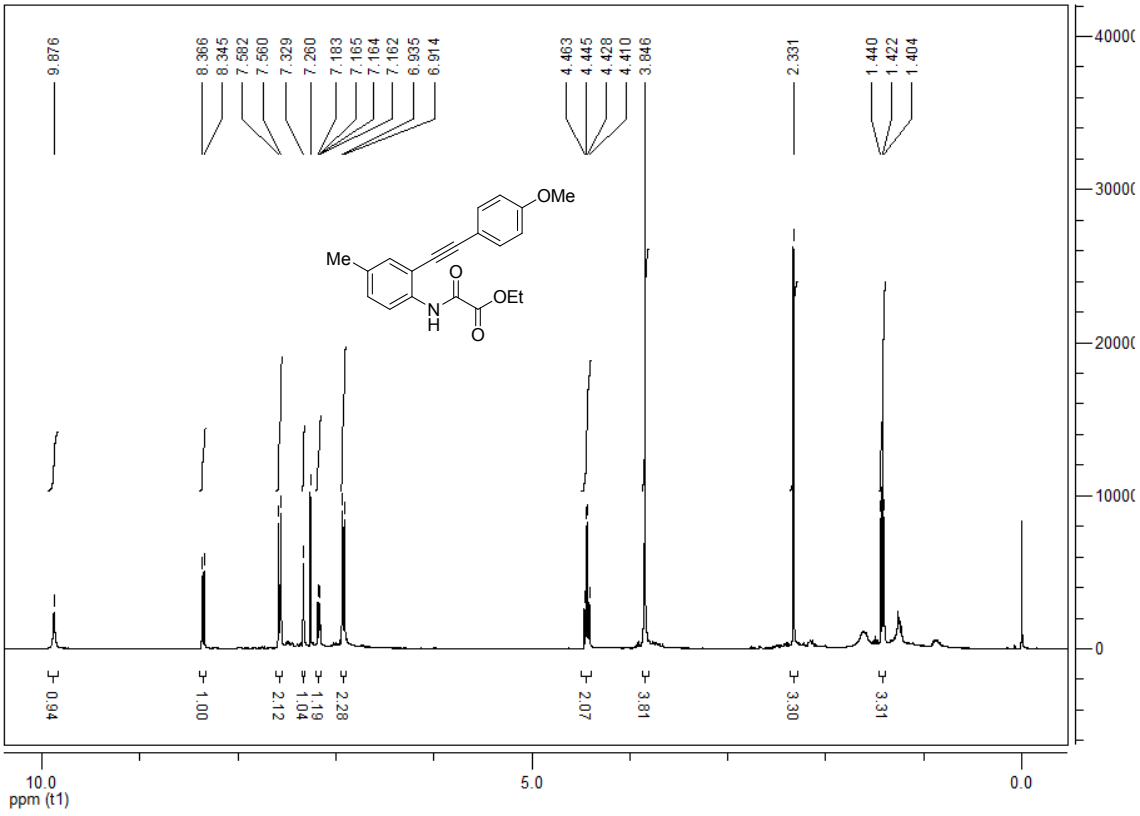
97.624
83.303
63.771
21.713
20.939
14.167
Me
Me
O
OEt
N
H
O
150
100
50
0
ppm (t1)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7.329
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7.183
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7.164
7.162
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4.463
4.445
4.428
4.410
3.846
2.331
1.440
1.422
1.404
OMe
Me
O
OEt
N
H
O
0.94
1.00
2.12
1.04
1.19
2.28
2.07
3.81
3.30
3.31
10.0
ppm (t1)
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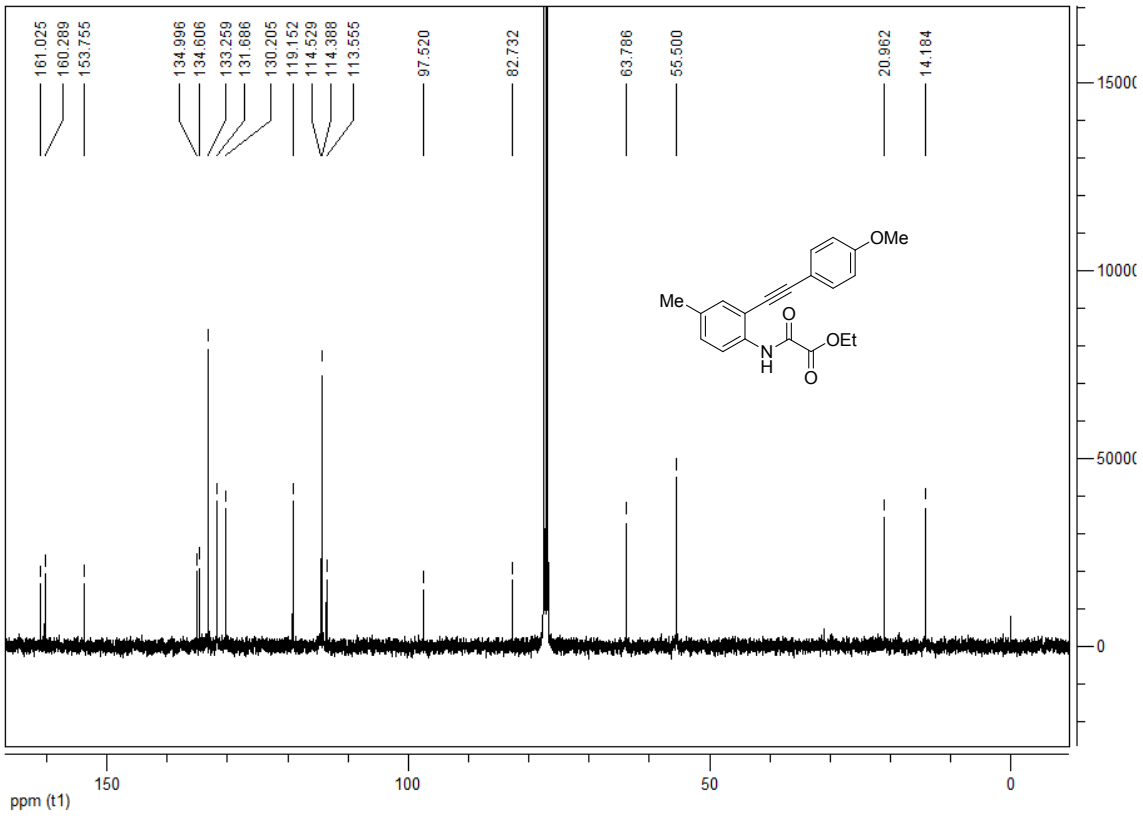
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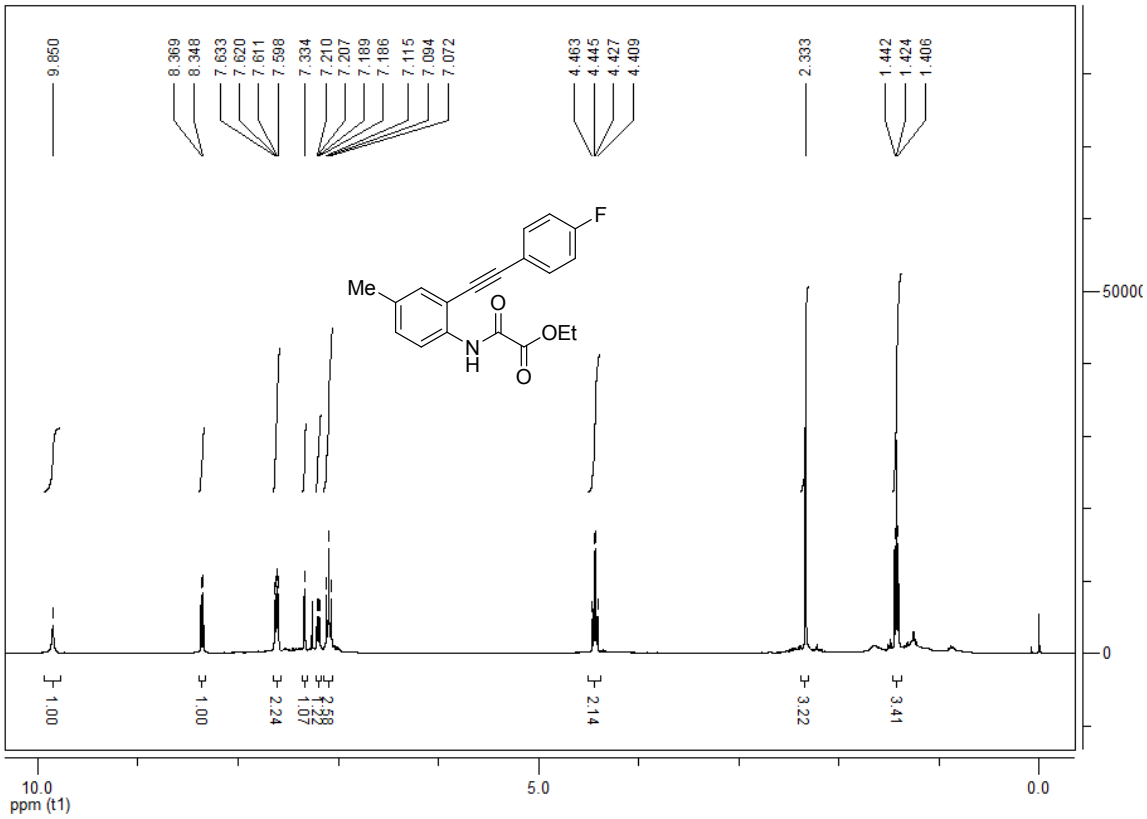
134.606
133.259
131.686
130.205
119.152
114.529
114.388
113.555
97.520
82.732
63.786
55.500
20.962
14.184
OMe
Me
O
OEt
N
H
O
150
100
50
0
ppm (t1)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8.369
8.348
7.633
7.620
7.611
7.598
7.334
7.210
7.207
7.189
7.186
7.115
7.094
7.072
4.463
4.445
4.427
4.409
2.333
1.442
1.424
1.406
F
Me
O
OEt
N
H
O
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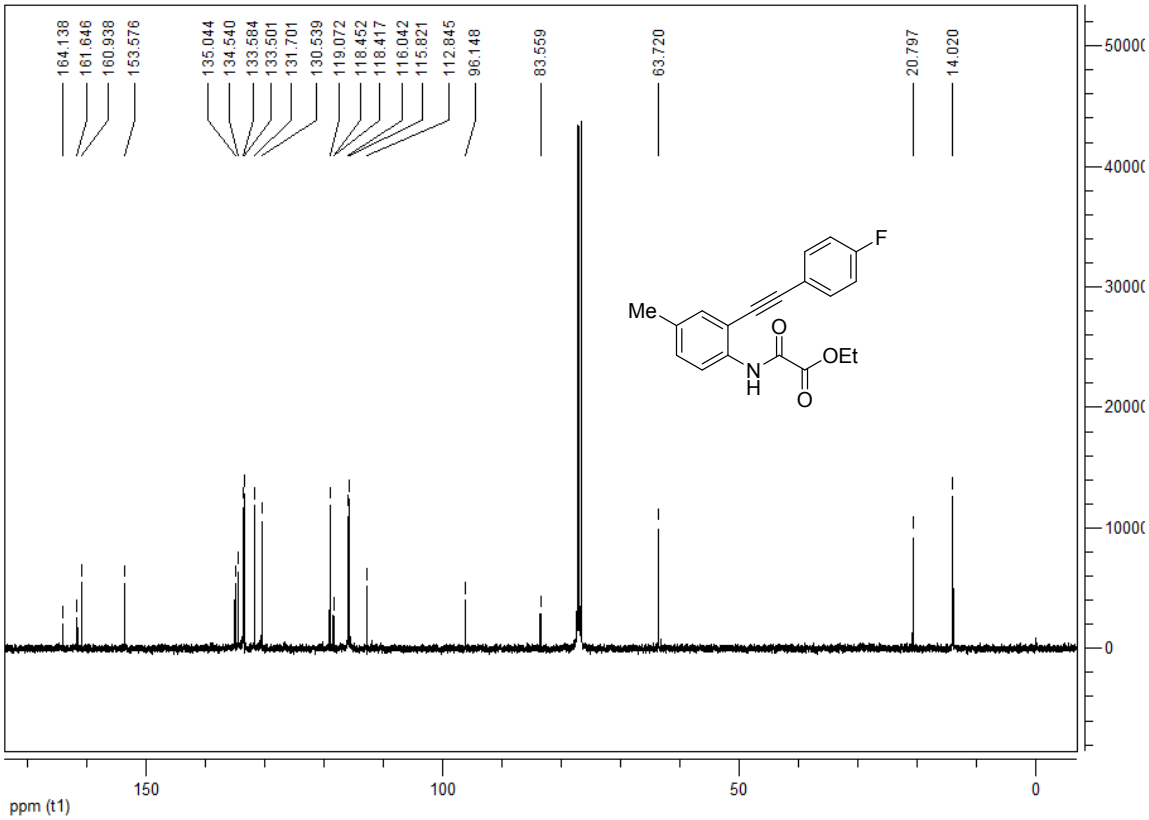
1.00
2.24
1.07
2.14
3.22
3.41
10.0
ppm (t1)
5.0
0.0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160.938
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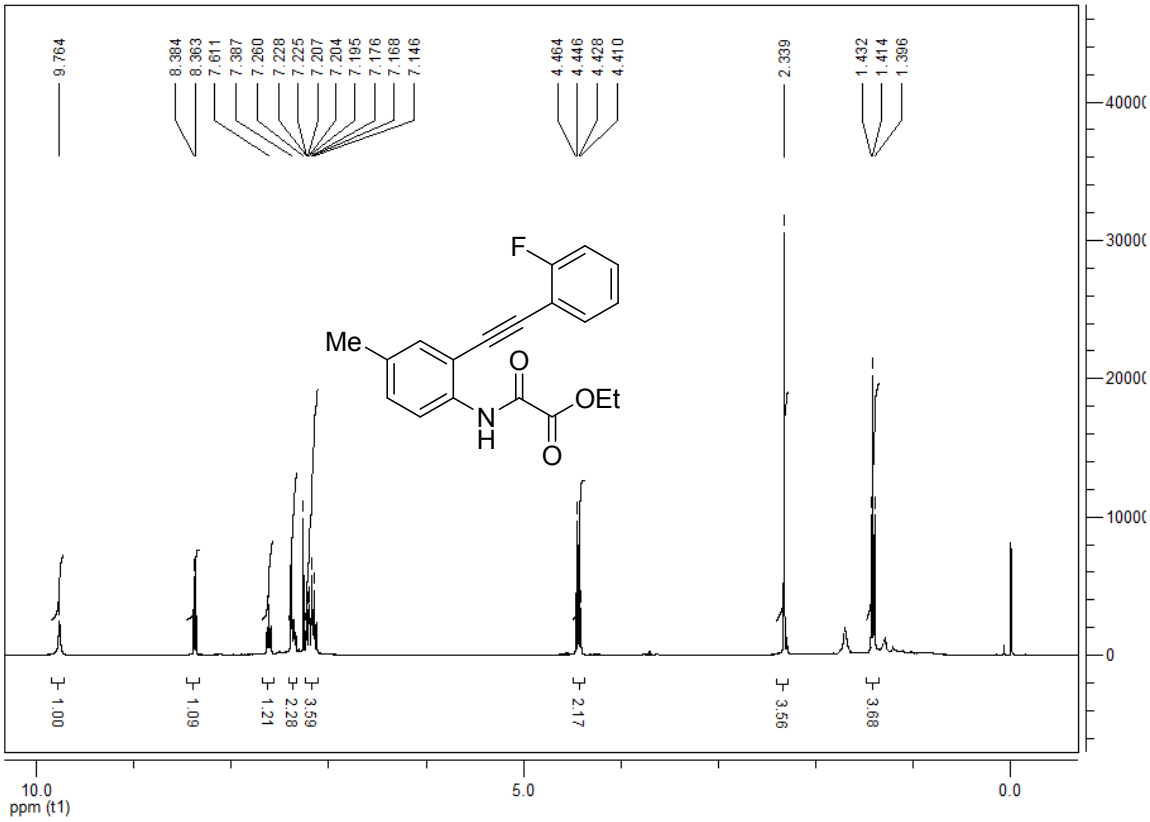
135.044
134.540
133.584
133.501
131.701
130.539
119.072
118.452
118.417
116.042
115.821
112.845
96.148
83.559
63.720
20.797
14.020
F
Me
O
OEt
N
H
O
150
100
50
0
ppm (t1)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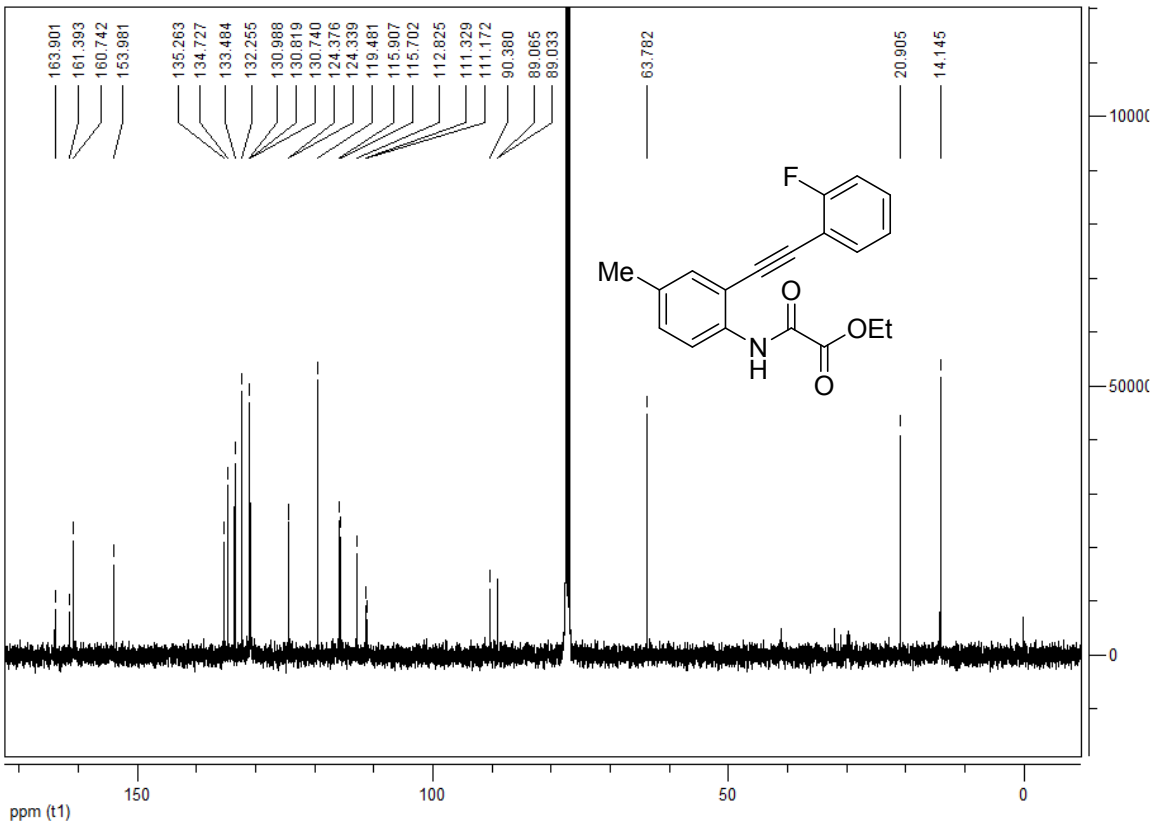
8.384
8.363
7.611
7.387
7.260
7.228
7.225
7.207
7.204
7.195
7.176
7.168
7.146
4.464
4.446
4.428
4.410
2.339
1.432
1.414
1.396
F
Me
O
N
H
OEt
O
1.00
1.09
1.21
2.28
3.59
2.17
3.56
3.68
10.0
5.0
0.0
ppm (t1)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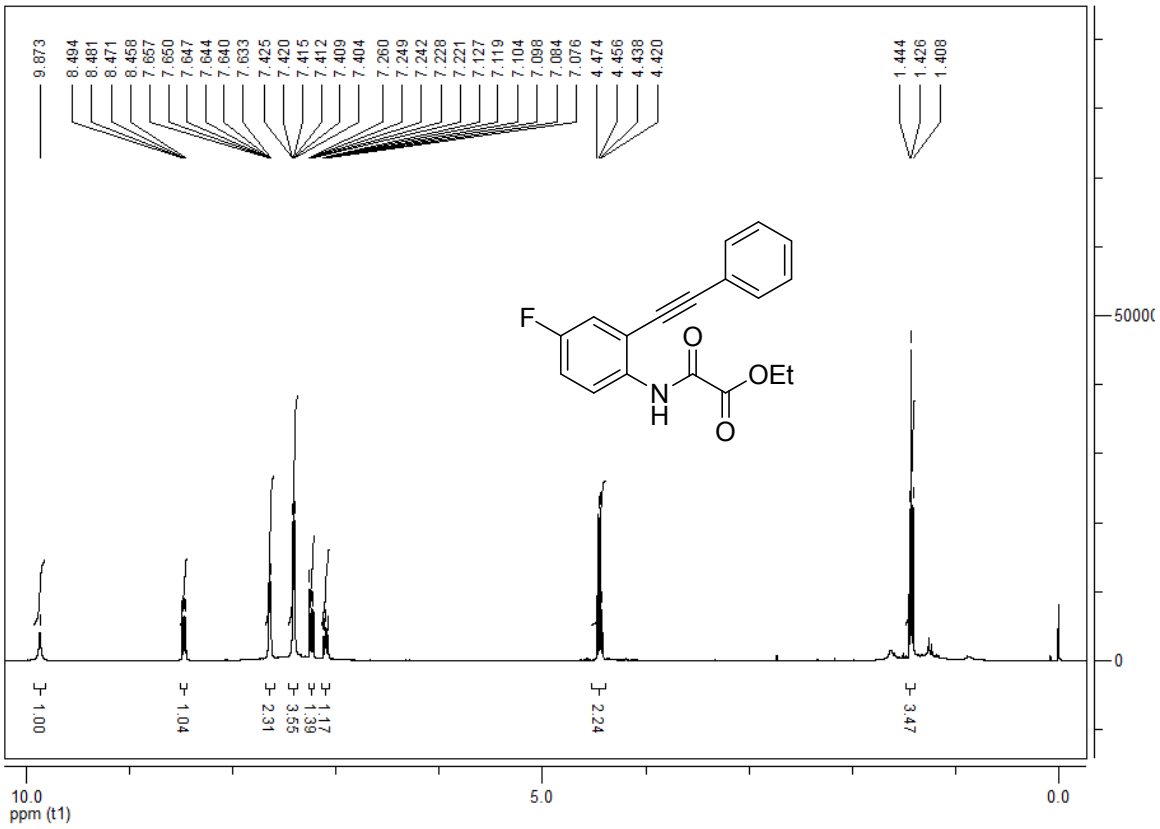
153.981
135.263
134.727
133.484
132.255
130.988
130.819
130.740
124.376
124.339
119.481
115.907
115.702
112.825
111.329
111.172
90.380
89.065
89.033
63.782
20.905
14.145
F
Me
O
N
H
OEt
O
150
100
50
0
ppm (t1)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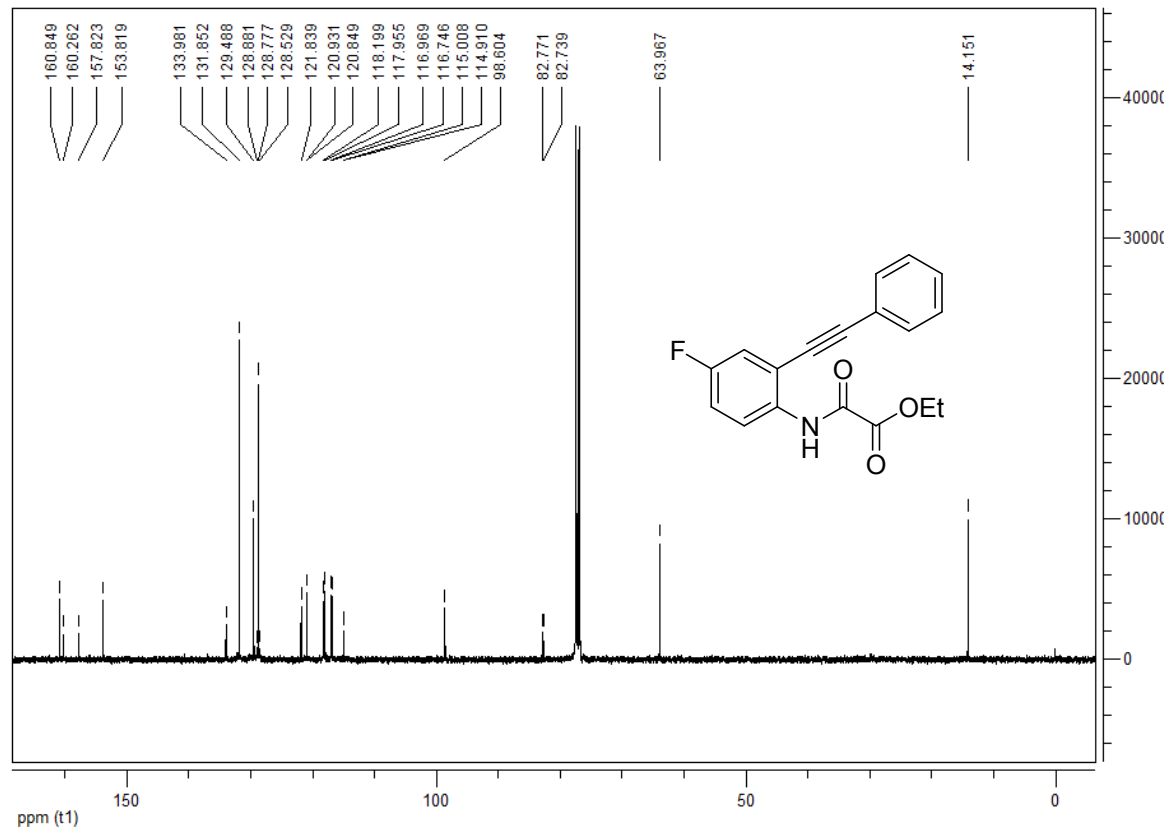
8.471
8.458
7.657
7.650
7.647
7.644
7.640
7.633
7.425
7.420
7.415
7.412
7.409
7.404
7.260
7.249
7.242
7.228
7.221
7.127
7.119
7.104
7.098
7.084
7.076
4.474
4.456
4.438
4.420
1.444
1.426
1.408
F
O
N
H
OEt
O
1.00
1.04
2.31
3.55
1.39
1.17
2.24
3.47
50000
0
10.0
5.0
0.0
ppm (t1)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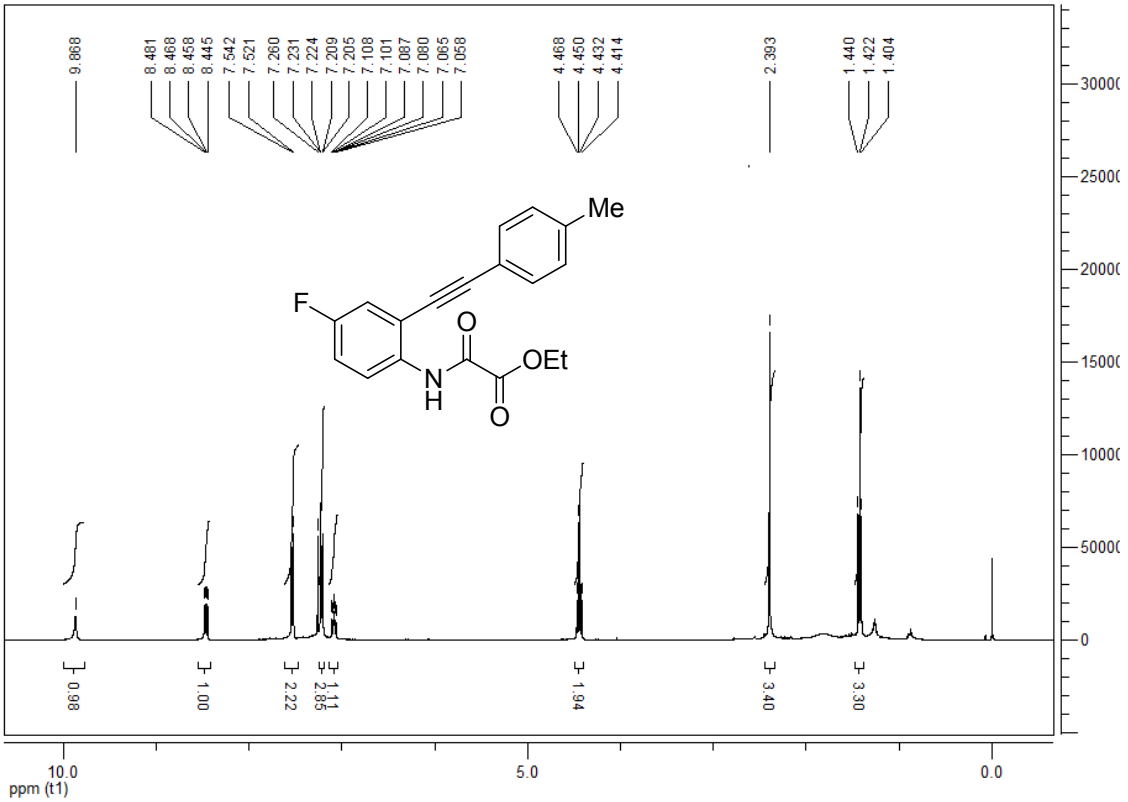
157.823
153.819
133.981
131.852
129.488
128.881
128.777
128.529
121.839
120.931
120.849
118.199
117.955
116.969
116.746
115.008
114.910
98.604
82.771
82.739
63.967
14.151
F
O
N
H
OEt
O
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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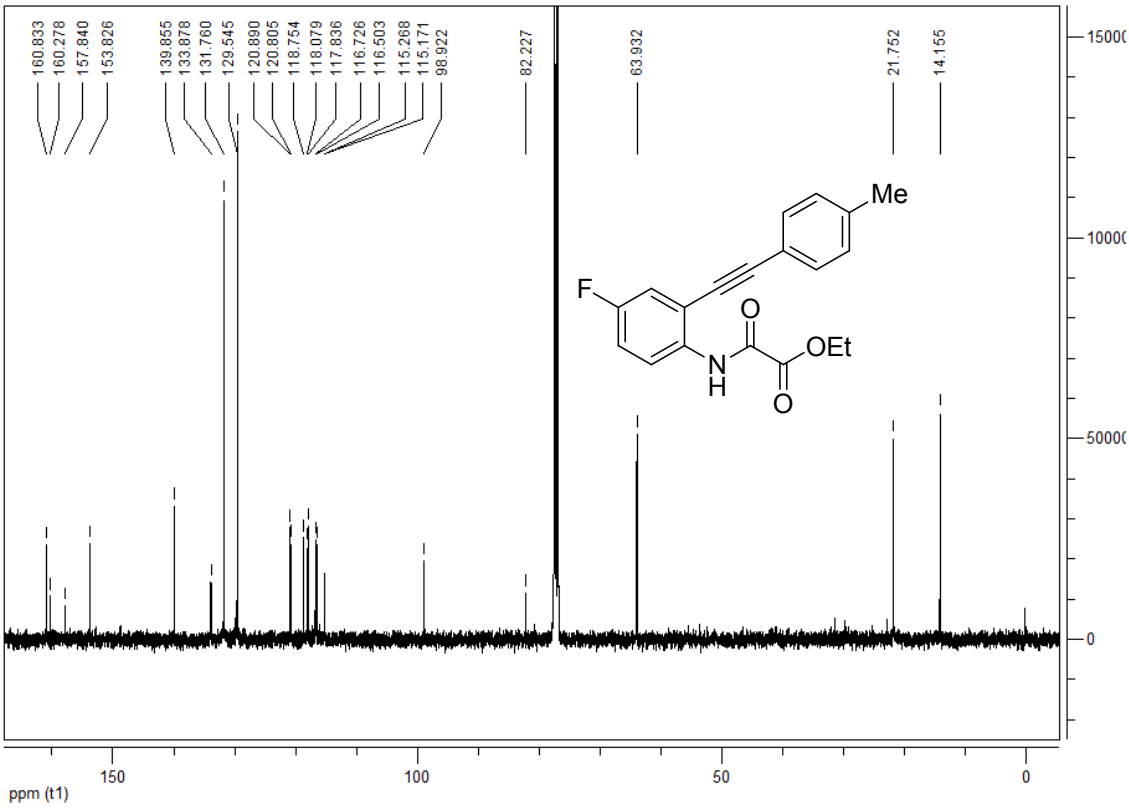
8.468
8.458
8.445
7.542
7.521
7.260
7.231
7.224
7.209
7.205
7.108
7.101
7.087
7.080
7.065
7.058
4.468
4.450
4.432
4.414
2.393
1.440
1.422
1.404
Me
F
O
OEt
N
H
O
0.98
1.00
2.22
2.85
1.11
1.94
3.40
3.30
10.0
5.0
0.0
ppm (t1)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129.545
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118.079
117.836
116.726
116.503
115.268
115.171
98.922
82.227
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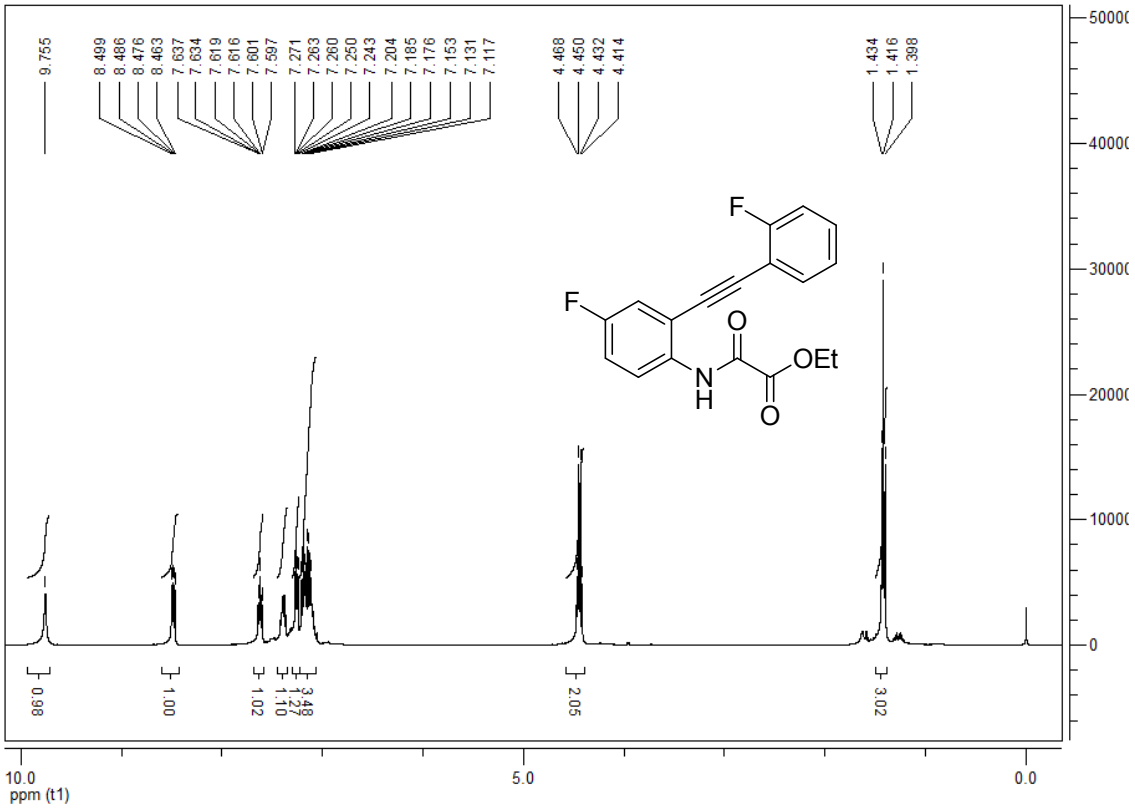
21.752
14.155
Me
F
O
OEt
N
H
O
150
100
50
0
ppm (t1)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8.476
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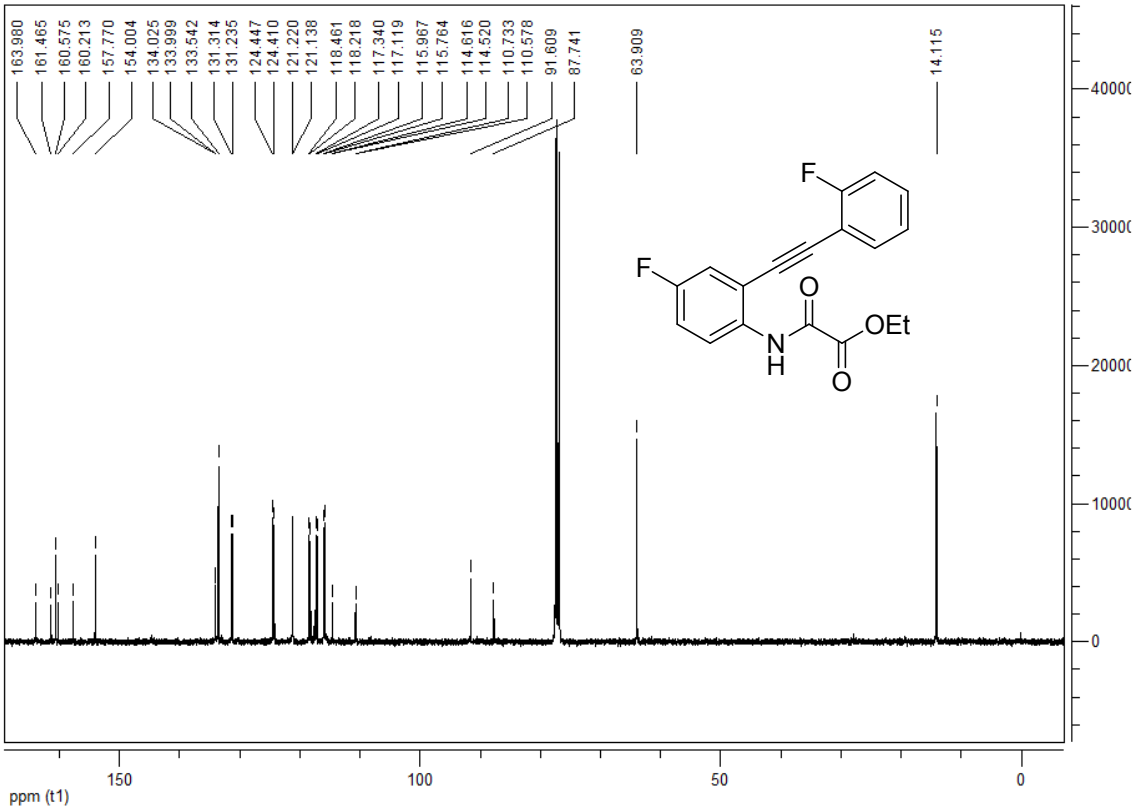
7.634
7.619
7.616
7.601
7.597
7.271
7.263
7.260
7.250
7.243
7.204
7.185
7.176
7.153
7.131
7.117
4.468
4.450
4.432
4.414
1.434
1.416
1.398
F
F
O
N
H
OEt
O
0.98
1.00
2.01
1.10
1.27
3.48
2.05
3.02
10.0
5.0
0.0
ppm (t1)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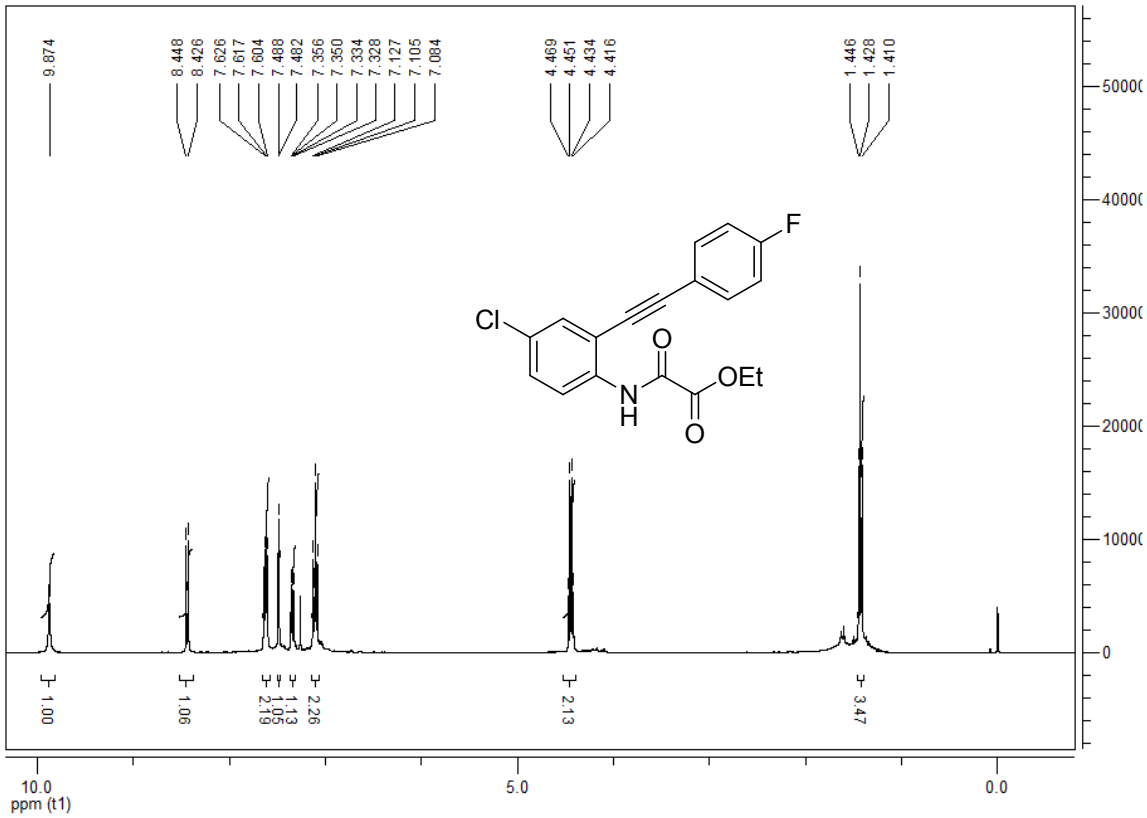
160.213
157.770
154.004
134.025
133.999
133.542
131.314
131.235
124.447
124.410
121.220
121.138
118.461
118.218
117.340
117.119
115.967
115.764
114.616
114.520
110.733
110.578
91.609
87.741
63.909
14.115
F
F
O
N
H
OEt
O
150
100
50
0
ppm (t1)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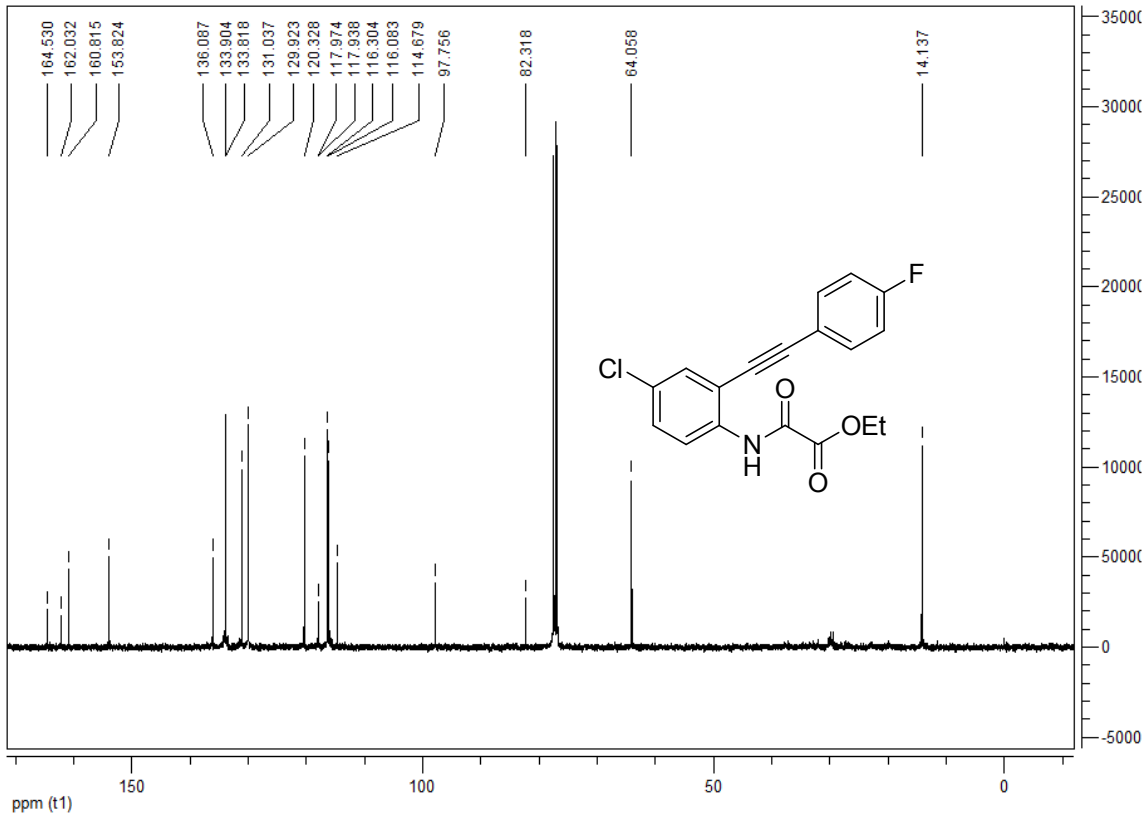
7.488
7.482
7.356
7.350
7.334
7.328
7.127
7.105
7.084
4.469
4.451
4.434
4.416
1.446
1.428
1.410
F
Cl
O
OEt
N
H
O
1.00
1.06
2.19
1.05
1.13
2.26
2.13
3.47
10.0
ppm (t1)
5.0
0.0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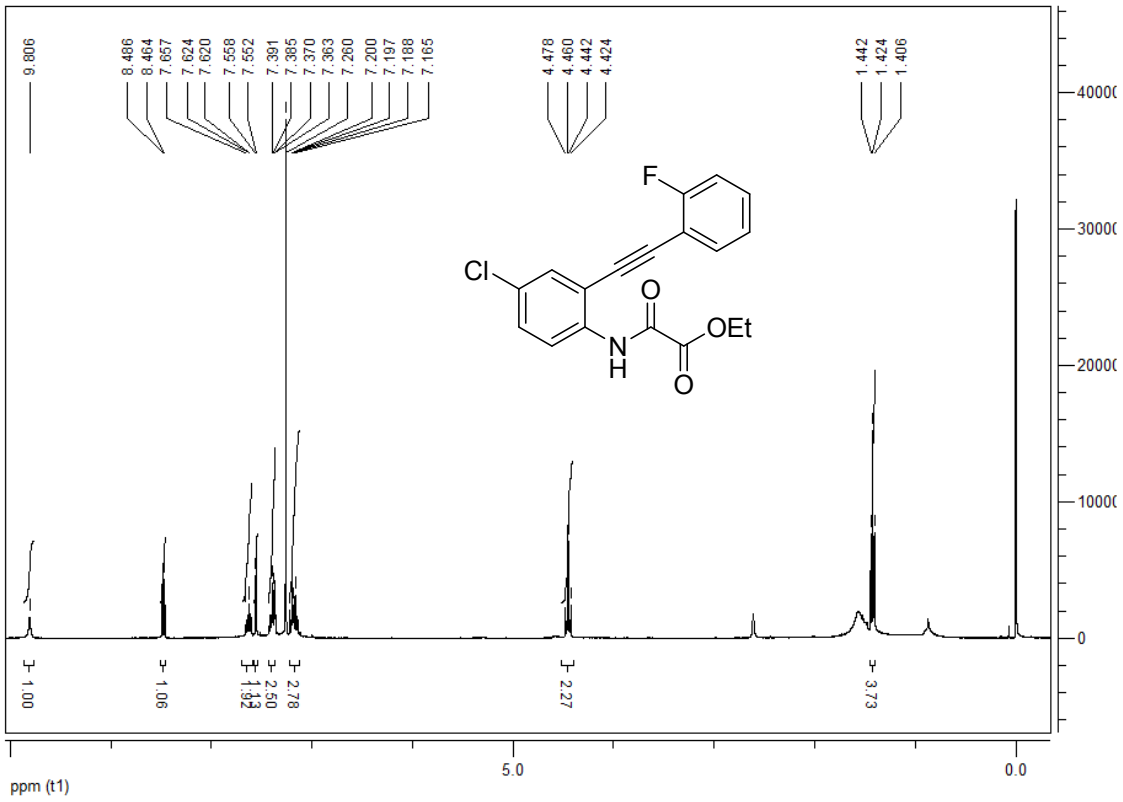
160.815
153.824
136.087
133.904
133.818
131.037
129.923
120.328
117.974
117.938
116.304
116.083
114.679
97.756
82.318
64.058
14.137
F
Cl
O
OEt
N
H
O
150
100
50
0
ppm (t1)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7.620
7.558
7.552
7.391
7.385
7.370
7.363
7.260
7.200
7.197
7.188
7.165
4.478
4.460
4.442
4.424
1.442
1.424
1.406
F
Cl
O
OEt
N
H
O
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1.06
1.92
1.13
2.50
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3.73
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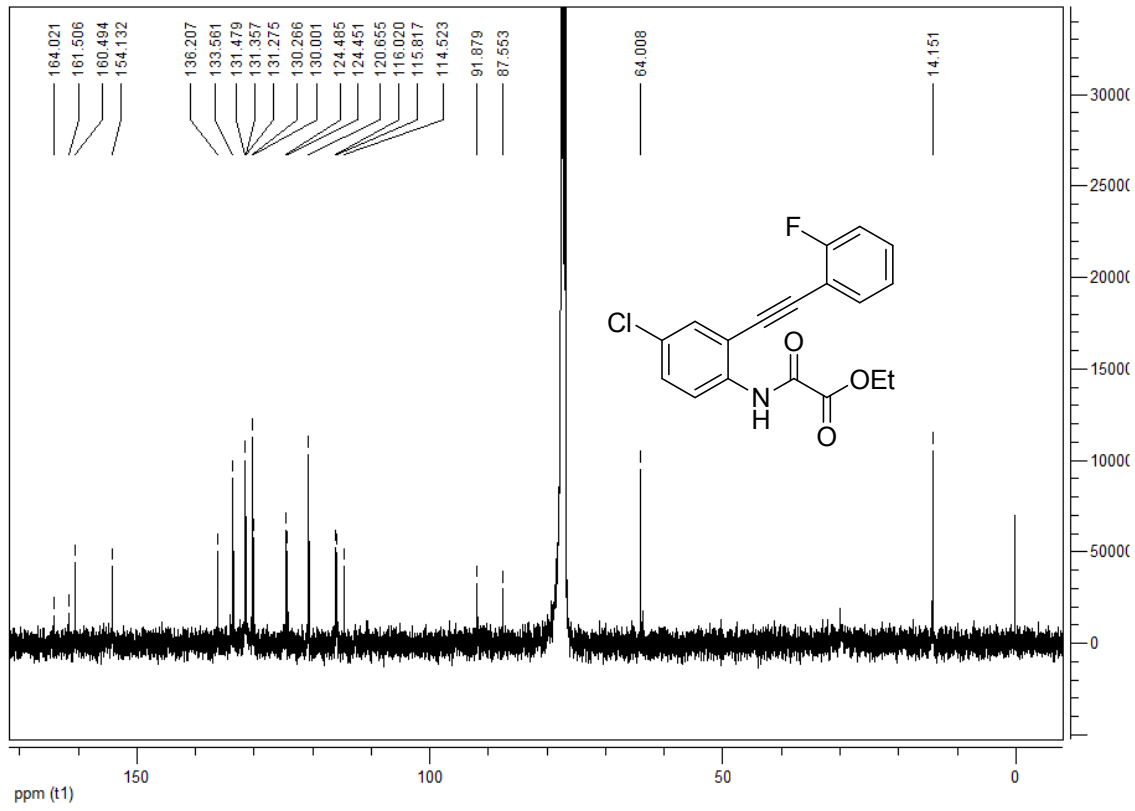
ppm (t1)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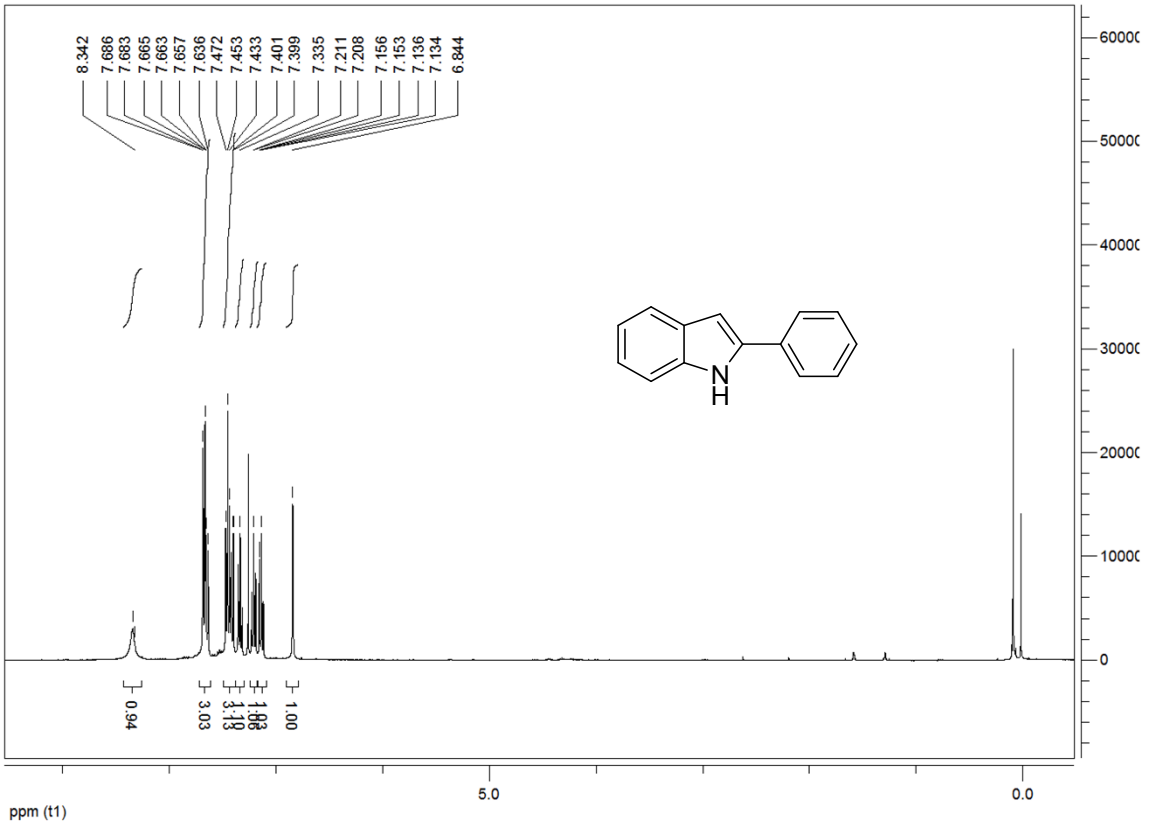
131.479
131.357
131.275
130.266
130.001
124.485
124.451
120.655
116.020
115.817
114.523
91.879
87.553
64.008
14.151
F
Cl
O
OEt
N
H
O
150
100
50
0
ppm (t1)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7.433
7.401
7.399
7.335
7.211
7.208
7.156
7.153
7.136
7.134
6.844
0.94
3.03
1.13
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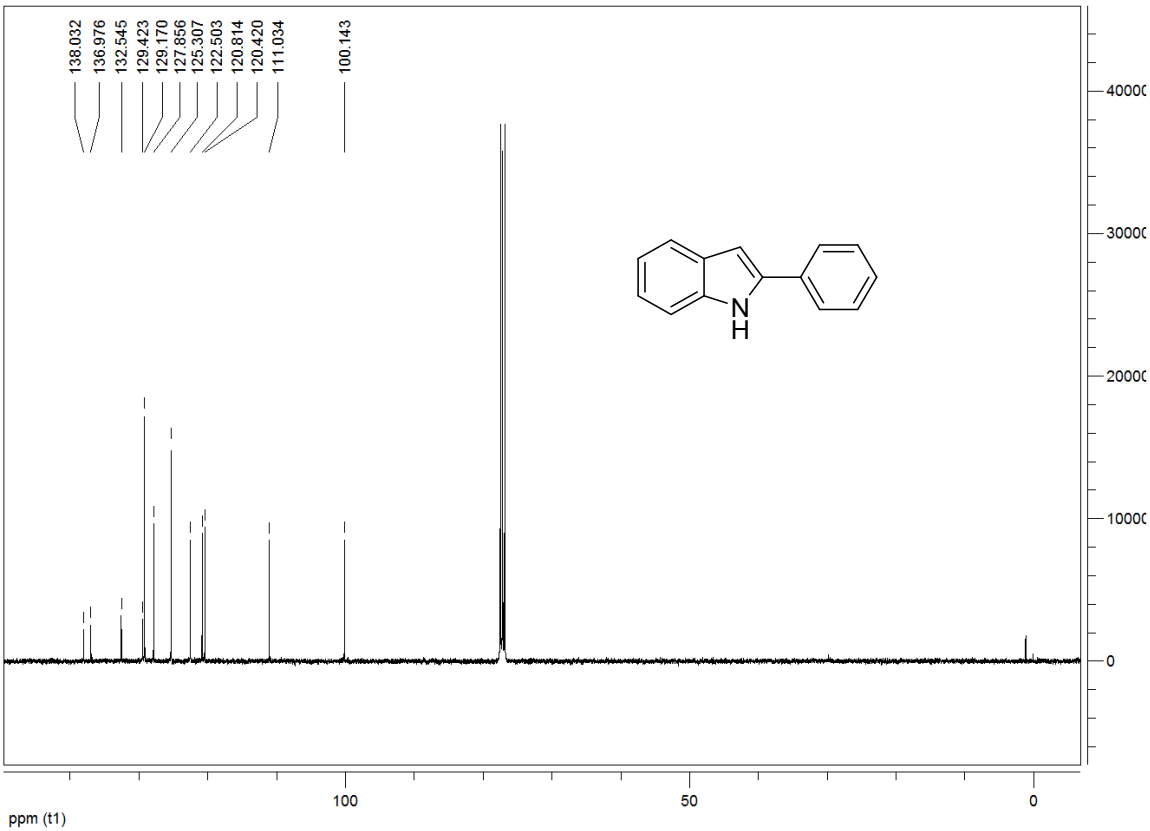
N
H
60000
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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122.503
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20000
10000
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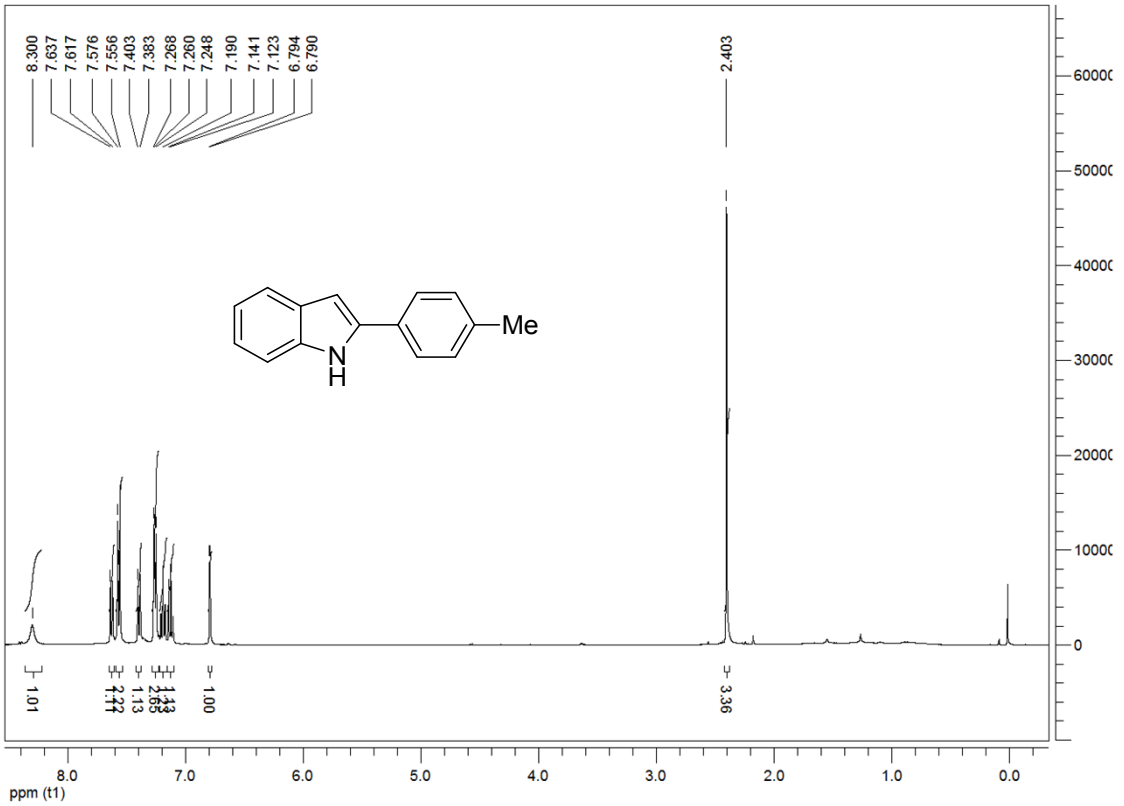
50
0
ppm (t1)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7.556
7.403
7.383
7.268
7.260
7.248
7.190
7.141
7.123
6.794
6.790
2.403
Me
N
H
1.01
1.13
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7.0
6.0
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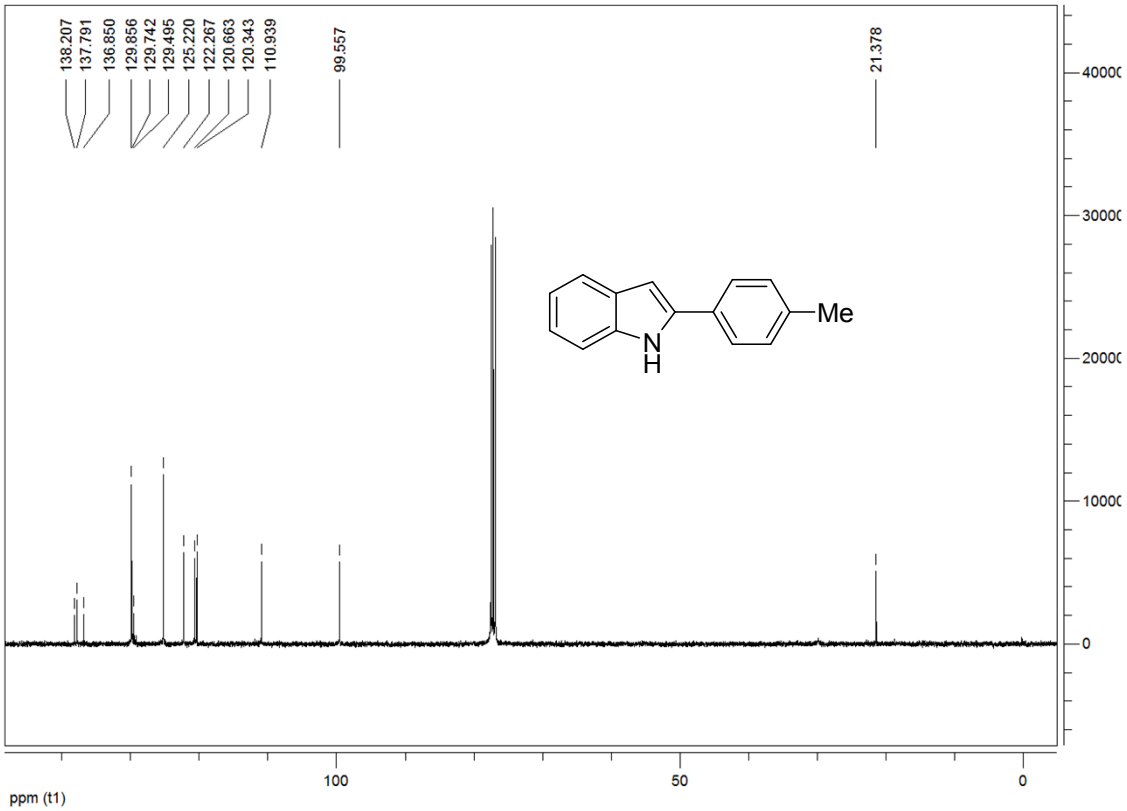
2.0
1.0
0.0
ppm (t1)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120.343
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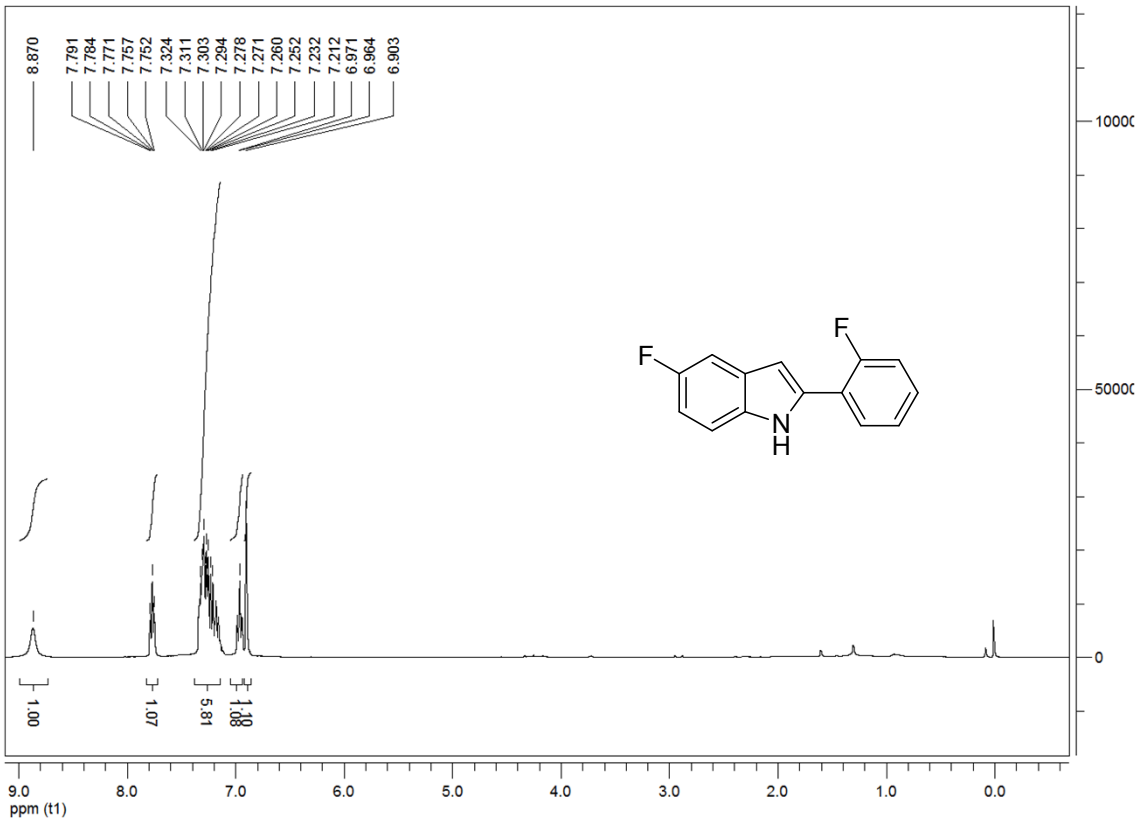
99.557
21.378
Me
N
H
100
50
0
ppm (t1)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7.311
7.303
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7.278
7.271
7.260
7.252
7.232
7.212
6.971
6.964
6.903
1.00
1.07
5.81
1.08
1.10
F
F
N
H
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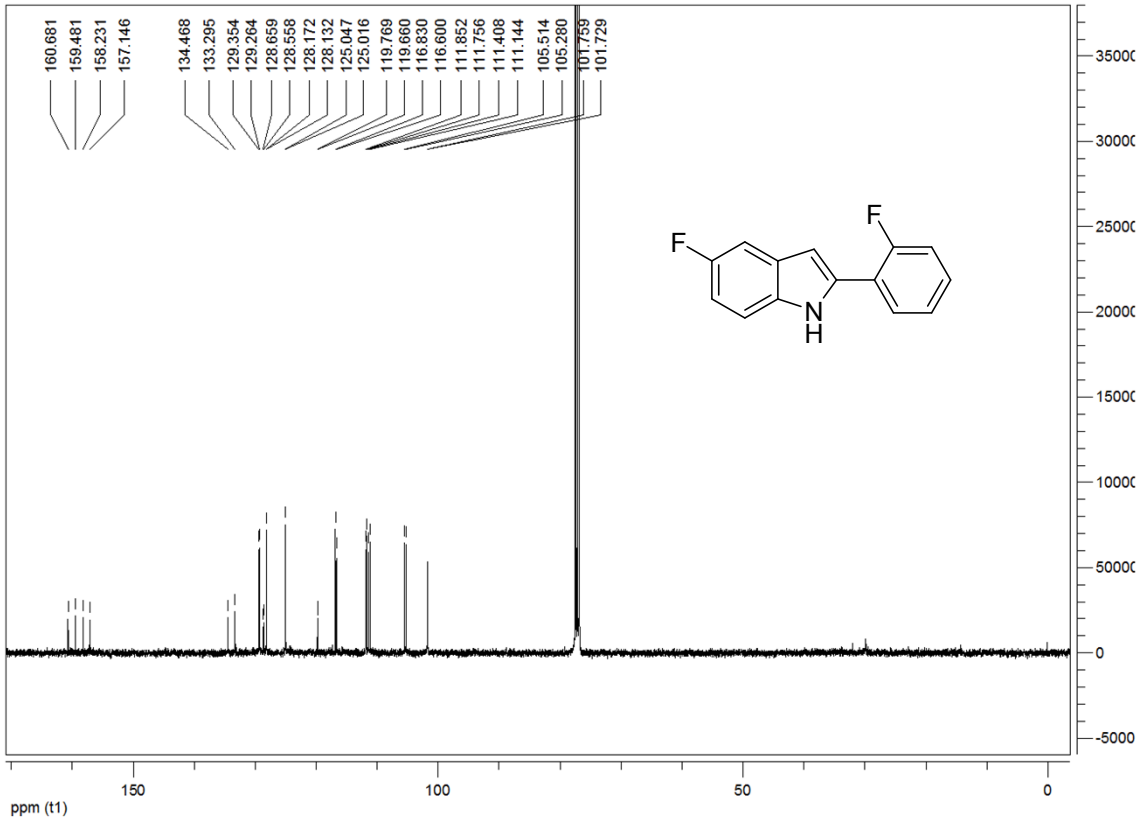
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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158.231
157.146
134.468
133.295
129.354
129.264
128.659
128.558
128.172
128.132
125.047
125.016
119.769
119.660
116.830
116.600
111.852
111.756
111.408
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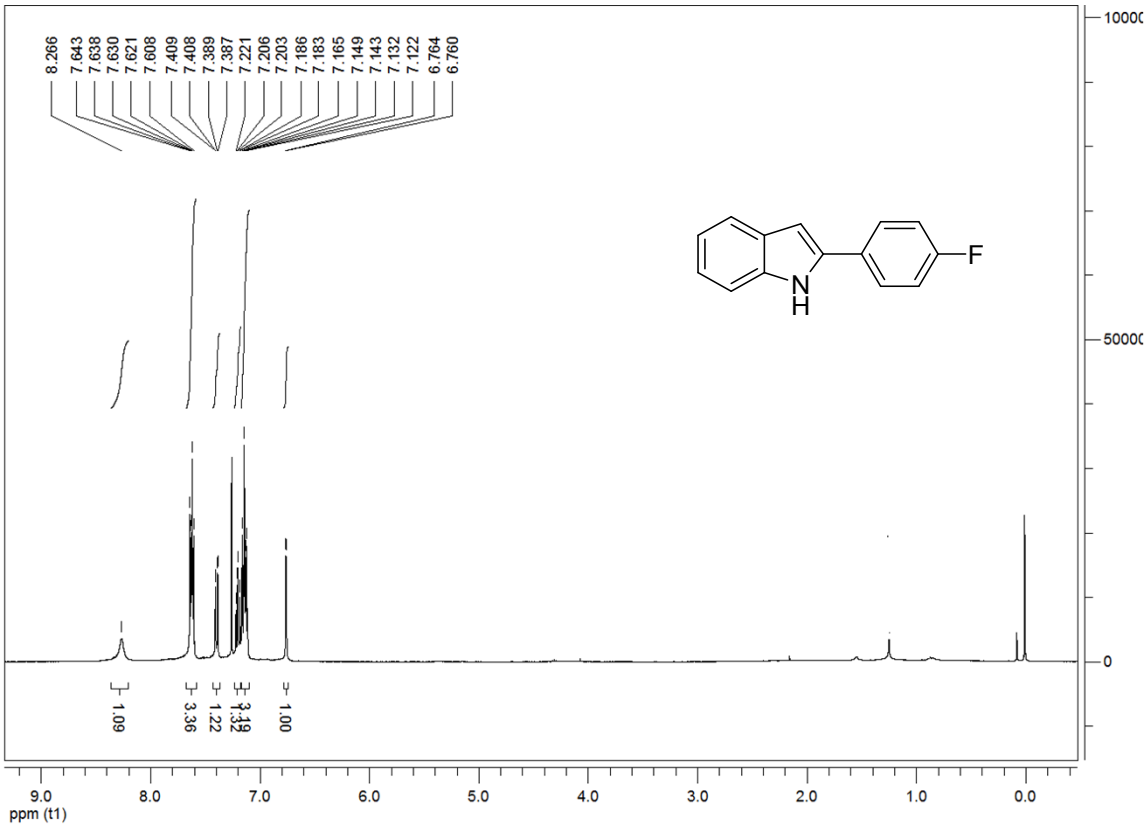
105.280
101.759
101.729
F
F
N
H
150
100
50
0
ppm (t1)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7.630
7.621
7.608
7.409
7.408
7.389
7.387
7.221
7.206
7.203
7.186
7.183
7.165
7.149
7.143
7.132
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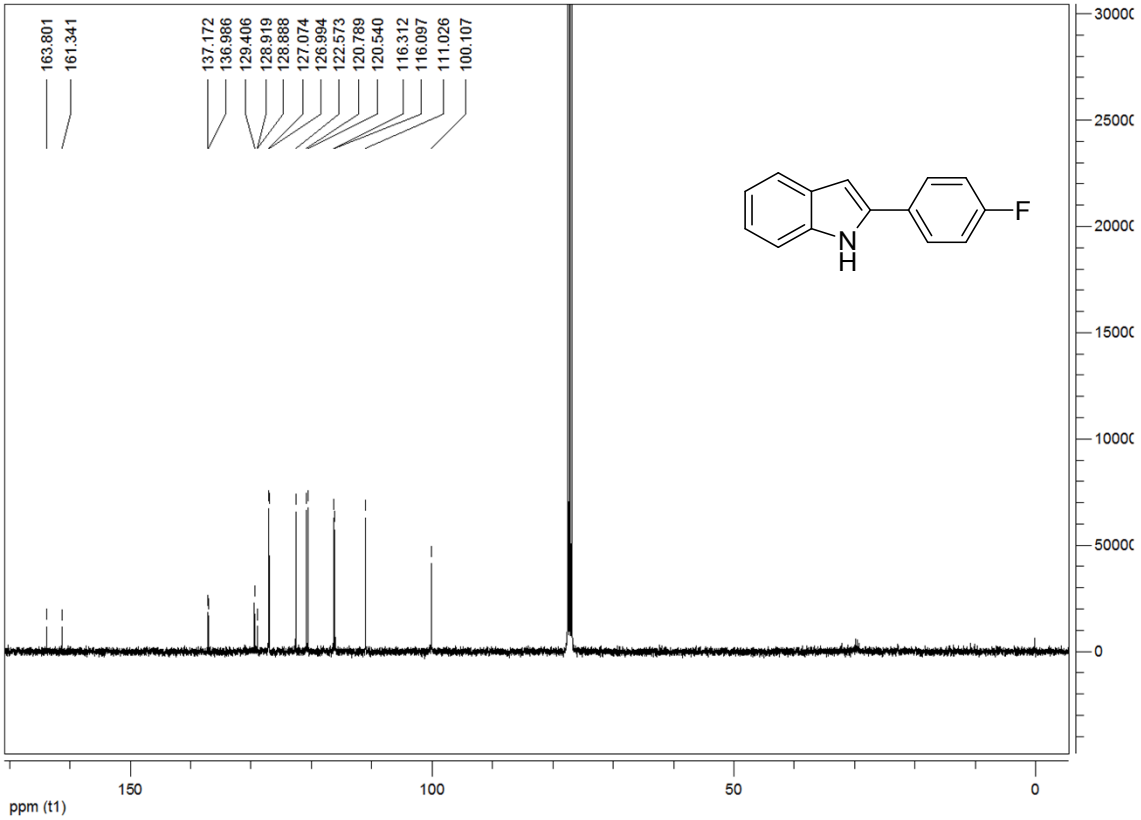
1.22
3.19
3.19
1.00
F
N
H
ppm (t1)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116.312
116.097
111.026
100.107
F
N
H
ppm (t1)