Rh(III)- or Ir(III)-Catalyzed Ynone Synthesis from Aldehydes via Chelation-Assisted C-H Bond Activation

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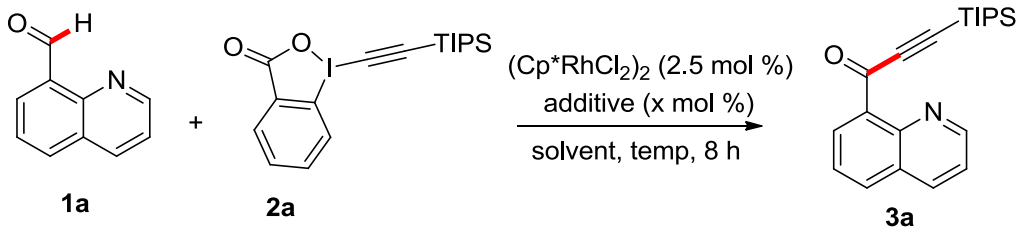
General methods:

^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (125, 100 MHz) spectra were determined with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm from internal TMS (δ). All coupling constants (J values) were reported in hertz (Hz). High-resolution mass spectra were recorded using the EI method with a double focusing magnetic mass analyzer. Reactions were monitored by thin-layer chromatography or LC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh).

Materials:

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. $[Cp^*RhCl_2]_2$,[S1] $[IrCp^*Cl_2]_2$,[S2] N-Sulfonyl 2-aminobenzaldehyde,[S3] Ethynyl benziodoxolones[S4] were prepared according to the previously reported synthetic methods.

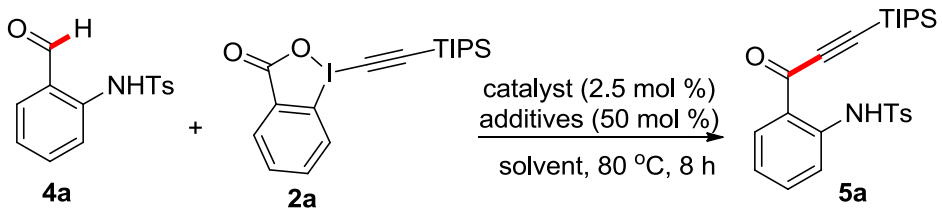
Table S1. Optimization of the Rh-catalyzed ynone synthesis.[a]



entry	additive (x mol %)	solvent	*T* (^{o}C)	yield (%)
1	$AgSbF_6$ (10 mol %)	DCE	80	50
2	AgOTf (10 mol %)	DCE	80	34
3	$AgBF_4$ (10 mol %)	DCE	80	<10
4	CsOAc (20 mol %)	DCE	80	0
5	$Cu(OAc)_2$ (20 mol %)	DCE	80	0
6	$Zn(OTf)_2$ (10 mol %)	DCE	80	86
7	$Zn(OTf)_2$ (10 mol %)	MeOH	80	<10
8	$Zn(OTf)_2$ (10 mol %)	THF	80	30
9	$Zn(OTf)_2$ (10 mol %)	CH_3CN	80	<10
10	$Zn(OTf)_2$ (10 mol %)	DCE	60	86
11[b]	$Zn(OTf)_2$ (10 mol %)	DCE	60	84
12[c]	$Zn(OTf)_2$ (10 mol %)	DCE	60	0

[a] **1a** (0.2 mmol), **2a** (0.22 mmol), $(Cp^*RhCl_2)_2$ (2.5 mol %), additive (x mol %), and solvent (2 mL) at 80 ^{o}C for 8 h. Yield of isolated product. [b] H_2O (1 mmol, 5 equiv) was added and the reaction mixture was heated under air at 60 ℃ for 8 h. [c] No $(Cp^*RhCl_2)_2$ was used.

Table S2. Optimization of the ynone synthesis from **4a**.[a]

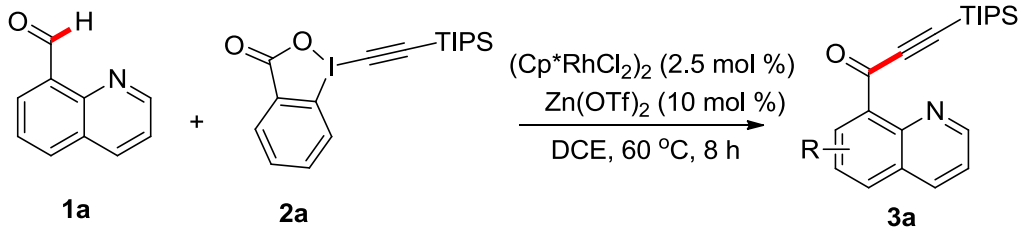


entry	catalyst (2.5 mol %)	additives	solvent	yield (%)
1	$(Cp^*RhCl_2)_2/Zn(OTf)_2$	-	DCE	0
2	$(Cp^*RhCl_2)_2/AgSbF_6$	-	DCE	0
3	$(Cp^*IrCl_2)_2/AgNTf_2$	-	DCE	14
4	$(Cp^*IrCl_2)_2/Zn(OTf)_2$	-	DCE	<5
5	$(Cp^*IrCl_2)_2/AgNTf_2$	NaOAc (50 mol %)	DCE	35
6	$(Cp^*IrCl_2)_2/AgNTf_2$	NaOAc (50 mol %)	THF	20
7	$(Cp^*IrCl_2)_2/AgNTf_2$	NaOAc (50 mol %)	dioxane	60
8	$(Cp^*IrCl_2)_2/AgNTf_2$	NaOAc (50 mol %)	MeOH	<5
9	$(Cp^*IrCl_2)_2/AgNTf_2$	NaOAc (50 mol %)	CH_3CN	<10
10	$(Cp^*IrCl_2)_2/AgNTf_2$	NaOAc (50 mol %)	DCE/AcOH	85

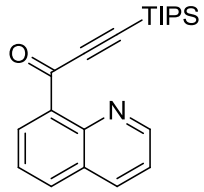
[a] **4a** (0.2 mmol), **2a** (0.24 mmol), Ir/Ag = 1:4, and solvent (2 mL) at 80 °C for 8 h. Yield of isolated product.

Experimental Procedures and Characterizations:

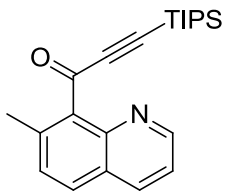
a) General procedure for the synthesis of **3** (taking **3a** as an example):



$(RhCp^*Cl_2)_2$ (2.5 mol %), $Zn(OTf)_2$ (10 mol %), 8-quinolinecarbaldehydes **1a** (0.2 mmol), alkyne **2a** (0.22 mmol, 1.1 equiv) and DCE (2 mL, 0.1 M) were added to a test tube. The reaction mixture was stirred at 60 °C for 8 h. On completion, a solution of NaOH (0.5 M aqueous solution) was added. After additional stirring at room temperature for 30 min, CH_2Cl_2 was added, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: PE:EtOAc = 10: 1) gave the title compound **3a**.

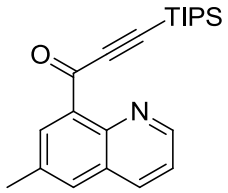


Compound **3a**: 86%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (dd, J = 4.2, 1.8 Hz, 1H), 8.32 (dd, J = 7.2, 1.4 Hz, 1H), 8.20 (dd, J = 8.3, 1.8 Hz, 1H), 8.00 (dd, J = 8.2, 1.4 Hz, 1H), 7.66 – 7.56 (m, 1H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 1.17 – 1.08 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 151.7, 145.8, 136.8, 136.3, 132.9, 132.5, 128.6, 125.8, 121.9, 105.8, 98.2, 18.7, 11.3; HRMS (EI) Calcd for $C_{21}H_{27}NOSi$ $[M]^+$ 337.1862, found 337.1858.

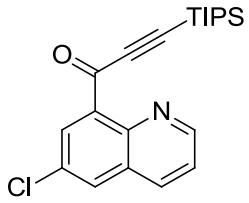


Compound **3b**: 70%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.81 (m, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.38

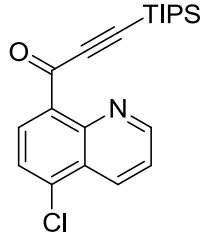
– 7.34 (m, 1H), 2.57 (s, 3H), 1.07 – 0.94 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.6, 150.6, 146.3, 138.2, 136.5, 135.7, 129.7, 129.0, 126.4, 121.0, 106.2, 99.4, 19.6, 18.6, 11.2; HRMS (EI) Calcd for $C_{22}H_{29}NOSi$ $[M]^+$ 351.2018, found 351.2015.



Compound **3c**: 67%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 4.0 Hz, 1H), 8.20 (s, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.76 (s, 1H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 2.57 (s, 3H), 1.13 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 150.9, 144.5, 136.4, 135.7, 135.6, 135.1, 131.9, 128.7, 121.9, 105.8, 98.1, 21.5, 18.7, 11.3; HRMS (EI) Calcd for $C_{22}H_{29}NOSi$ $[M]^+$ 351.2018, found 351.2014.

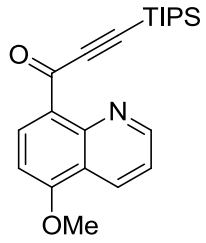


Compound **3d**: 64%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (dd, J = 4.1, 1.6 Hz, 1H), 8.23 (d, J = 2.3 Hz, 1H), 8.13 (dd, J = 8.3, 1.5 Hz, 1H), 7.97 (d, J = 2.3 Hz, 1H), 7.49 (dd, J = 8.3, 4.2 Hz, 1H), 1.12 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 151.7, 144.3, 138.4, 135.4, 132.9, 131.8, 131.1, 129.5, 122.7, 105.4, 99.8, 18.7, 11.3; HRMS (EI) Calcd for $C_{21}H_{26}ClNOSi$ $[M]^+$ 371.1472, found 371.1468.



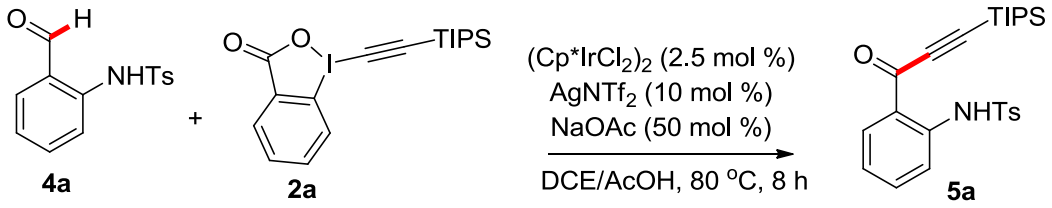
Compound **3e**: 60%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (dd, J = 4.1, 1.5 Hz, 1H), 8.64 (dd, J = 8.6, 1.5 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.59 (dd, J = 8.6, 4.2 Hz, 1H), 1.12 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 152.1, 146.4, 136.5, 136.0, 133.1, 132.0, 126.6, 126.1, 122.6, 105.7,

98.9, 18.7, 11.3; HRMS (EI) Calcd for $C_{21}H_{26}ClNOSi$ $[M]^+$ 371.1472, found 371.1466.

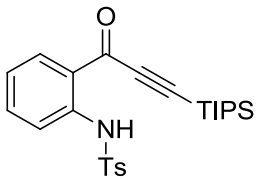


Compound **3f**: 74%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 2.6 Hz, 1H), 8.60 (dd, J = 8.5, 1.3 Hz, 1H), 8.48 (d, J = 8.3 Hz, 1H), 7.44 (dd, J = 8.5, 4.2 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 4.08 (s, 3H), 1.14 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 159.5, 152.1, 147.1, 136.0, 131.0, 128.8, 121.0, 120.8, 105.8, 103.4, 96.3, 56.3, 18.7, 11.3; HRMS (EI) Calcd for $C_{22}H_{29}NO_2Si$ $[M]^+$ 367.1968, found 367.1965.

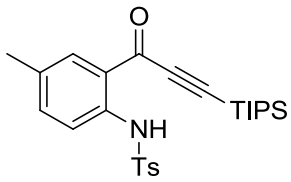
b) General procedure for the synthesis of **5** (taking **5a** as an example):



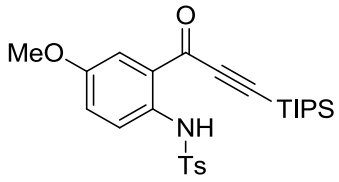
$(IrCp^*Cl_2)_2$ (2.5 mol %), $AgNTf_2$ (10 mol %), NaOAc (50 mol %), *N*-sulfonyl-2-aminobenzaldehyde **4a** (0.2 mmol), alkyne **2a** (0.24 mmol, 1.2 equiv) and DCE-AcOH (2 mL, 0.1 M, ratio = 3:1) were added to a test tube. The reaction mixture was stirred at 80 ^{o}C for 8 h. On completion, the resulting mixture was diluted by adding water and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: PE:EtOAc = 8: 1) gave the title compound **5a**.



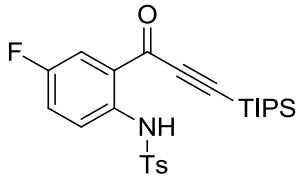
Compound **5a**: 85%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.24 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.69 (dd, J = 8.4, 0.7 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 – 7.06 (m, 1H), 2.36 (s, 3H), 1.21 – 1.09 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.1, 144.2, 141.1, 136.6, 135.8, 134.9, 129.9, 127.4, 122.7, 122.3, 118.3, 102.5, 100.9, 21.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{25}H_{33}NO_3SSi$ $[M]^+$ 455.1950, found 455.1944.



Compound **5b**: 82%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.08 (d, J = 1.7 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.5 Hz, 1H), 7.30 (dd, J = 8.5, 2.0 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H), 2.29 (s, 3H), 1.21 – 1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 144.0, 138.6, 136.7, 136.5, 135.3, 132.4, 129.8, 127.4, 122.5, 118.7, 102.5, 100.7, 21.6, 20.6, 18.6, 11.2; HRMS (EI) Calcd for $C_{26}H_{35}NO_3SSi$ $[M]^+$ 469.2107, found 469.2105.

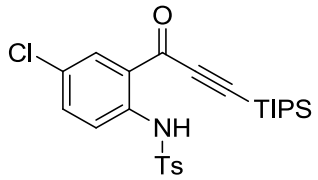


Compound **5c**: 92%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.72 – 7.63 (m, 4H), 7.19 (d, J = 8.1 Hz, 2H), 7.08 (dd, J = 9.1, 3.0 Hz, 1H), 3.77 (s, 3H), 2.34 (s, 3H), 1.22 – 1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 155.2, 143.9, 136.4, 134.2, 129.7, 127.3, 123.9, 123.1, 121.5, 117.4, 102.5, 100.6, 55.6, 21.6, 18.6, 11.1; HRMS (EI) Calcd for $C_{26}H_{35}NO_4SSi$ $[M]^+$ 485.2056, found 485.2053.

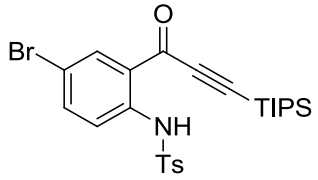


Compound **5d**: 94%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.90 (dd, J = 8.9, 3.0 Hz, 1H), 7.75 – 7.67 (m, 3H), 7.26 – 7.19 (m, 3H), 2.36 (s, 3H), 1.23 – 1.06 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.8, 157.7 (d, J = 243.7 Hz),

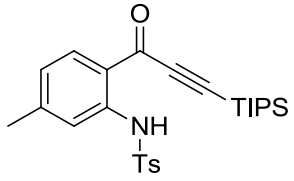
144.3, 137.1, 136.3, 129.9, 127.4, 123.7 (d, *J* = 5.0 Hz), 123.1 (d, *J* = 22.5 Hz), 121.1 (d, *J* = 6.25 Hz), 120.3 (d, *J* = 23.7 Hz), 102.0, 21.7, 18.6, 11.2; HRMS (EI) Calcd for $C_{25}H_{32}FNO_3SSi$ $[M]^+$ 473.1856, found 473.1852.



Compound **5e**: 83%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 8.25 (d, *J* = 2.5 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.37 (s, 3H), 1.17 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 144.5, 139.5, 136.3, 135.6, 134.4, 129.9, 128.0, 127.4, 123.4, 119.9, 102.4, 101.9, 21.7, 18.6, 11.2; HRMS (EI) Calcd for $C_{25}H_{32}ClNO_3SSi$ $[M]^+$ 489.1561, found 489.1559.

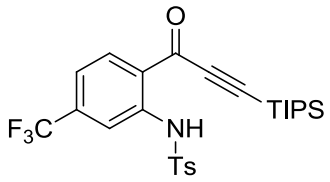


Compound **5f**: 82%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 8.41 (d, *J* = 2.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.58 (dt, *J* = 8.9, 5.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 2.37 (s, 3H), 1.23 – 1.10 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.8, 144.5, 139.9, 138.4, 137.4, 136.2, 129.9, 127.4, 123.7, 120.1, 115.1, 102.5, 101.9, 21.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{25}H_{32}BrNO_3SSi$ $[M]^+$ 533.1056, found 533.1052.

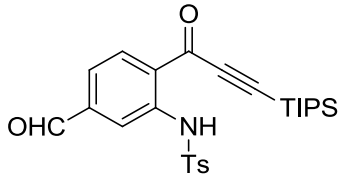


Compound **5g**: 84%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.50 (s, 1H), 7.26 – 7.19 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 1.15 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 147.7, 144.1, 141.2, 136.6, 134.9, 129.8, 127.4, 123.8, 120.3,

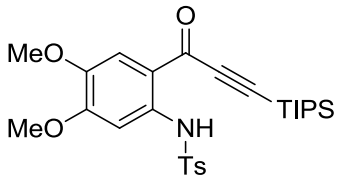
118.6, 102.6, 100.2, 22.4, 21.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{26}H_{35}NO_3SSi$ $[M]^+$ 469.2107, found 469.2103.



Compound **5h**: 75%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.37 (d, J = 8.3 Hz, 1H), 7.99 (s, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H), 1.30 – 1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 144.76, 141.41, 136.8 (q, J = 33.0 Hz), 135.9, 135.4, 130.0, 127.5, 123.9, 123.0 (d, J = 271 Hz), 118.9 (q, J = 4.0 Hz), 115.1 (q, J = 4.0 Hz), 102.9, 102.1, 21.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{26}H_{32}F_3NO_3SSi$ $[M]^+$ 523.1824, found 523.1819.

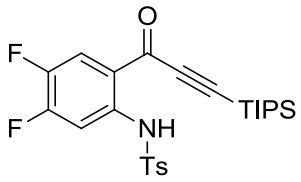


Compound **5i**: 83%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (s, 1H), 10.02 (s, 1H), 8.41 (d, J = 8.1 Hz, 1H), 8.17 (s, 1H), 7.81 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 7.7 Hz, 2H), 2.37 (s, 3H), 1.14 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 179.5, 144.7, 141.7, 140.5, 136.2, 135.5, 130.1, 127.5, 125.4, 121.8, 119.9, 103.0, 102.4, 21.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{26}H_{33}NO_4SSi$ $[M]^+$ 483.1900, found 483.1897.

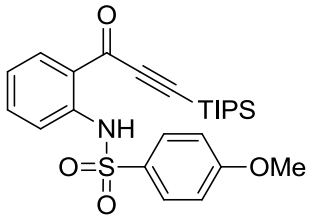


Compound **5j**: 83%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.63 (s, 1H), 7.29 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 3.93 (s, 3H), 3.81 (s, 3H), 2.35 (s, 3H), 1.19 – 1.07 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 155.4, 144.5, 144.2, 137.5, 136.4, 129.8, 127.4, 115.6, 115.2, 102.8, 101.9,

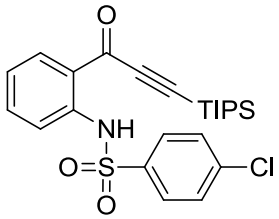
99.5, 56.5, 56.0, 21.7, 18.7, 18.4, 11.1; HRMS (EI) Calcd for $C_{27}H_{37}NO_5SSi$ $[M]^+$ 515.2162, found 515.2157.



Compound **5k**: 83%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (s, 1H), 8.05 (dd, *J* = 10.5, 8.6 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 12.1, 6.8 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 1.23 – 1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 156.1 (d, *J* = 16.2 Hz), 153.5 (d, *J* = 21.3 Hz), 146.5 (d, *J* = 16.3 Hz), 144.7, 144.1 (d, *J* = 16.3 Hz), 138.8 (d, *J* = 13.7 Hz), 135.9, 130.1, 127.4, 122.8 (d, *J* = 23.7), 118.7, 107.8 (d, *J* = 28.7 Hz), 101.9 (d, *J* = 72.5 Hz), 21.7, 18.6, 11.1; HRMS (EI) Calcd for $C_{25}H_{31}F_2NO_3SSi$ $[M]^+$ 491.1762, found 491.1758.

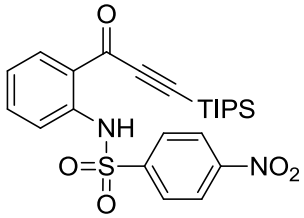


Compound **5l**: 84%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (s, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 1.15 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 163.3, 141.2, 135.8, 134.9, 131.0, 129.6, 122.6, 122.3, 118.3, 114.4, 102.5, 100.9, 55.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{25}H_{33}NO_4SSi$ $[M]^+$ 471.1900, found 471.1898.

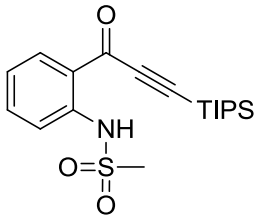


Compound **5m**: 76%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.71 – 7.65 (m, 1H), 7.56 – 7.46 (m, 1H), 7.46 – 7.35 (m, 2H), 7.19 – 7.10 (m, 1H), 1.19 – 1.08 (m, 21H); ^{13}C NMR

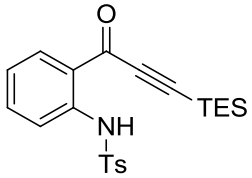
(100 MHz, $CDCl_3$) δ 180.1, 140.6, 139.9, 137.9, 135.9, 135.1, 129.6, 128.9, 123.3, 122.6, 118.6, 102.4, 101.5, 18.7, 11.2; HRMS (EI) Calcd for $C_{24}H_{30}ClNO_3SSi$ $[M]^+$ 475.1404, found 475.1401.



Compound **5n**: 65%, amorphous solid, ^1H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.27 (t, J = 8.2 Hz, 3H), 8.04 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 1.15 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 150.4, 145.2, 139.9, 136.1, 135.2, 128.7, 124.5, 123.9, 122.9, 118.9, 102.2, 18.7, 11.2; HRMS (EI) Calcd for $C_{24}H_{30}N_2O_5SSi$ $[M]^+$ 486.1645, found 486.1641.

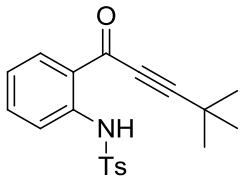


Compound **5o**: 75%, amorphous solid, ^1H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.38 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 3.08 (s, 3H), 1.18 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 141.4, 136.3, 135.3, 122.8, 122.1, 117.6, 102.5, 101.3, 40.4, 18.7, 11.2; HRMS (EI) Calcd for $C_{19}H_{29}NO_3SSi$ $[M]^+$ 379.1637, found 379.1632.

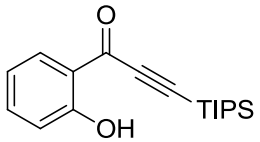


Compound **5p**: 60%, amorphous solid, ^1H NMR (400 MHz, $CDCl_3$) δ 11.17 (s, 1H), 8.22 (dd, J = 8.0, 1.5 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.52 – 7.44 (m, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 – 7.05 (m, 1H), 2.36 (s, 3H), 1.05 (t, J = 7.9 Hz, 9H), 0.74 (q, J = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.1, 144.2,

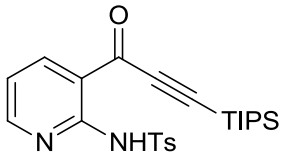
141.1, 136.6, 135.9, 135.1, 129.9, 127.4, 122.7, 122.2, 118.3, 101.6, 21.7, 7.51, 3.97; HRMS (EI) Calcd for $C_{22}H_{27}NO_3SSi$ $[M]^+$ 413.1481, found 413.1478.



Compound **5q**: 55%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.13 (dd, J = 8.0, 1.5 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.9 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.23 (d, J = 8.1 Hz, 2H), 7.07 (dd, J = 11.2, 4.0 Hz, 1H), 2.37 (d, J = 10.9 Hz, 3H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.1, 144.1, 140.9, 136.7, 135.6, 134.9, 129.8, 127.4, 122.6, 118.3, 106.3, 30.2, 28.3, 21.7; HRMS (EI) Calcd for $C_{20}H_{21}NO_3S$ $[M]^+$ 355.1242, found 355.1238.

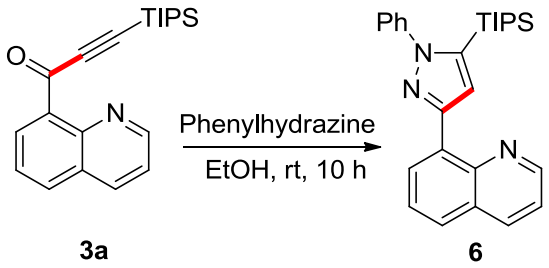


Compound **5r**: 55%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.08 (dd, J = 7.9, 1.4 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.03 – 6.92 (m, 2H), 1.23 – 1.10 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 163.1, 137.3, 133.2, 120.8, 119.6, 118.2, 101.7, 101.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{18}H_{26}O_2Si$ $[M]^+$ 302.1702, found 302.1698.



Compound **5s**: 76%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 8.55 – 8.43 (m, 1H), 8.41 (dd, J = 4.8, 1.9 Hz, 1H), 8.04 (d, J = 8.2 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.02 (dd, J = 7.8, 4.9 Hz, 1H), 2.39 (s, 3H), 1.18 – 1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 153.7, 151.9, 144.2, 142.8, 137.1, 129.3, 128.8, 117.5, 116.4, 102.4, 101.8, 21.7, 18.7, 11.2; HRMS (EI) Calcd for $C_{24}H_{32}N_2O_3SSi$ $[M]^+$ 456.1903, found 456.1900.

c) Procedure for the synthesis of pyrazole **6**:

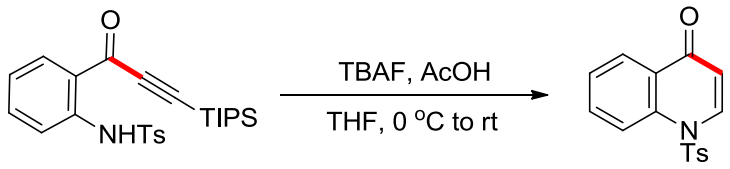


3a **6**

To a flask equipped with a magnetic stirring bar under argon were added ynone **3a** (1 mmol, 1.00 equiv.) and EtOH (30 mL). Phenylhydrazine (1.2 mmol, 1.20 equiv) was added dropwise via microsyringe. The reaction mixture was stirring at room temperature. After 10 hours, the mixture was passed through a Celite pad and the filtrate was washed with brine. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel column (eluent: petroleum ether/ethyl acetate = 20:1) to afford the pyrazole product **6**.

Compound **6**: 84%, amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.94 (dd, J = 4.1, 1.8 Hz, 1H), 8.16 (dd, J = 8.3, 1.8 Hz, 1H), 8.09 (dd, J = 7.2, 1.5 Hz, 1H), 7.82 (dd, J = 8.2, 1.4 Hz, 1H), 7.59 (dd, J = 8.1, 7.3 Hz, 1H), 7.41 (dd, J = 8.3, 4.1 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.20 (dd, J = 8.6, 1.1 Hz, 2H), 6.93 (tt, J = 7.5, 1.1 Hz, 1H), 1.20 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 146.1, 143.8, 136.1, 135.0, 129.5, 129.2, 128.6, 128.5, 126.4, 125.3, 121.3, 121.1, 113.6, 106.9, 98.6, 18.9, 11.4; HRMS (EI) Calcd for $C_{27}H_{33}N_3Si$ $[M]^+$ 427.2444, found 427.2441.

d) Procedure for the synthesis of 1-tosylquinolin-4(1H)-one **6a**:



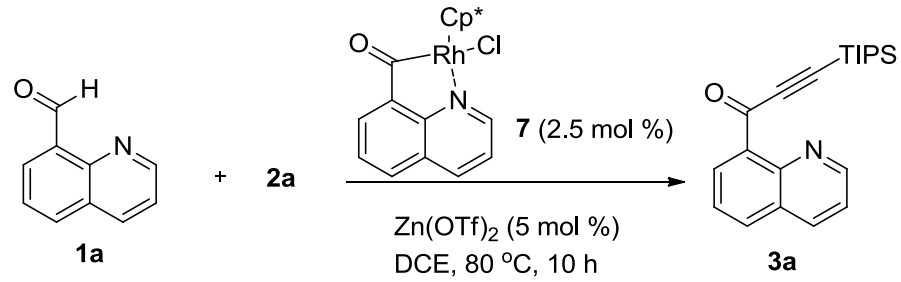
5a **6a**, 78%

To a solution of ynone **5a** (0.1 mmol) in THF (1 mL) was added HOAc (0.3 mmol) and TBAF (0.2 mmol) at 0 °C. After addition, the solution was warmed up to room temperature and stirred for another 1h and quenched with water, extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$. The volatile

compounds were removed in vacuo and the residue was subjected to column chromatography on silica gel to afford **6a** in 78% yield.

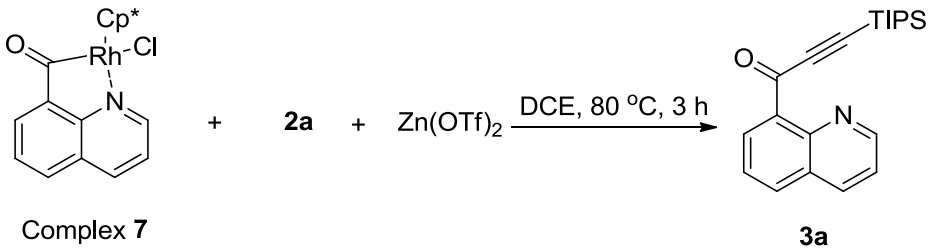
Compound **6a**: amorphous solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.5 Hz, 1H), 8.32 (dd, J = 8.0, 1.6 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.57 (ddd, J = 8.8, 7.1, 1.8 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.31 (d, J = 8.1 Hz, 2H), 6.38 (d, J = 8.5 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 146.5, 137.9, 137.0, 133.9, 132.8, 130.5, 127.6, 127.3, 126.6, 125.8, 118.4, 112.6, 21.8; HRMS (EI) Calcd for $C_{16}H_{13}NO_3S$ $[M]^+$ 299.0616, found 299.0612.

e) Mechanic Studies: Procedure for the alkynylation catalyzed by Rh(III) complex.



8-quinolinecarbaldehydes **1a** (0.2 mmol), alkyne **2a** (0.22 mmol, 1.1 equiv), Complex **7** (2.5 mol%), $Zn(OTf)_2$ (5 mol%) and DCE (2 mL) were charged into a test tube. The reaction mixture was stirred at 80 ^{o}C for 8 h. On completion, a solution of NaOH (0.5 M aqueous solution) was added. After additional stirring at room temperature for 30 min, CH_2Cl_2 was added, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: PE:EtOAc = 10: 1) gave the title compound **3a**, yield: 76%.

f) Mechanic Studies: The reaction of stoichiometric amounts of complex 7 with alkene **2a**



Complex **7** (0.1 mmol), alkyne **2a** (0.1 mmol, 1 equiv), $Zn(OTf)_2$ (0.1 mmol, 1 equiv) and DCE (1 mL) were charged into a test tube. The reaction mixture was stirred at 80 ^oC for 3 h. On completion, a solution of NaOH (0.5 M aqueous solution) was added. After additional stirring at room temperature for 30 min, CH_2Cl_2 was added, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: PE:EtOAc = 10: 1) gave the title compound **3a**, yield: 66%.

Reference:

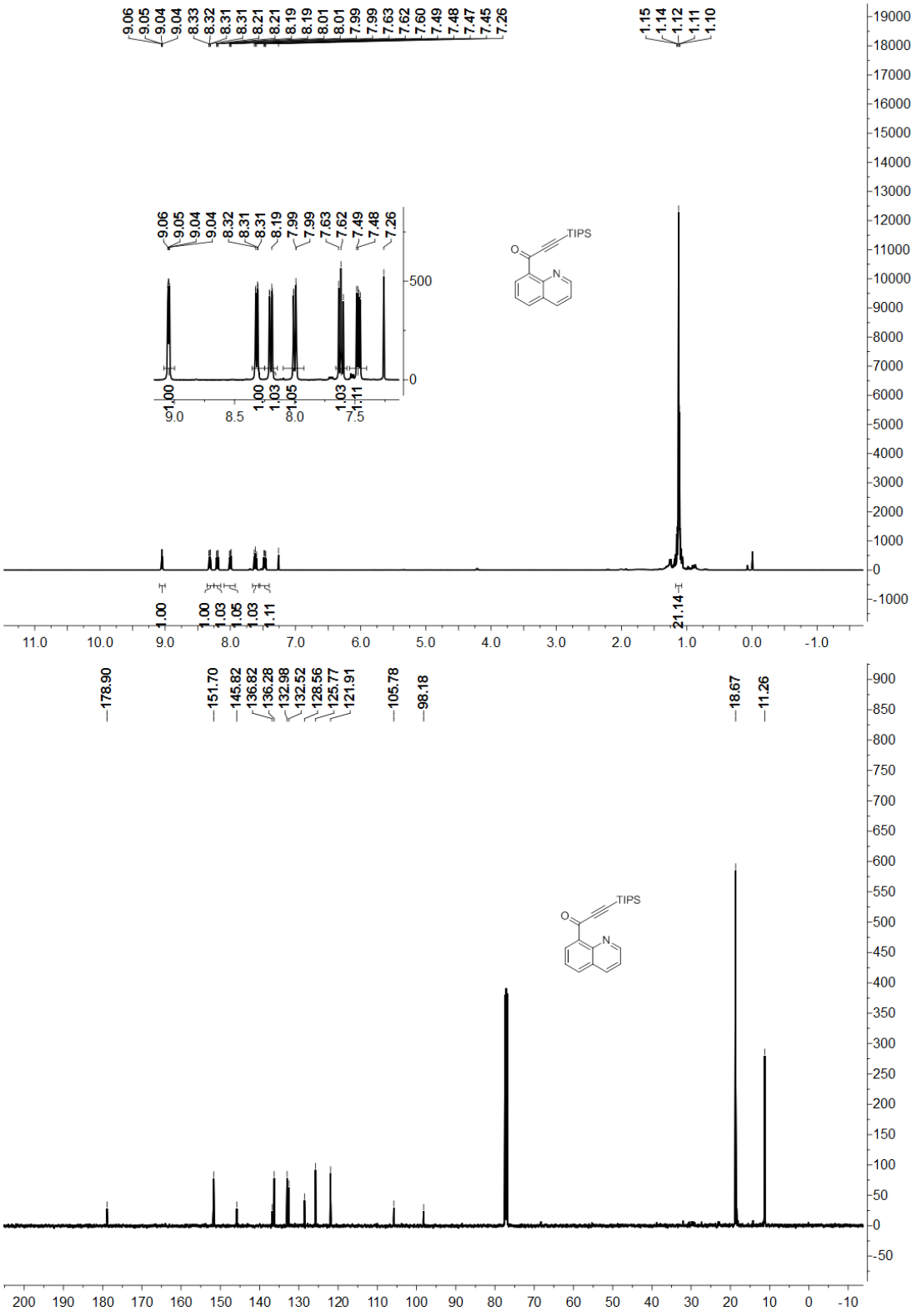
S1: K. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi*, *Org. Lett.* **2004**, *6*, 2785.

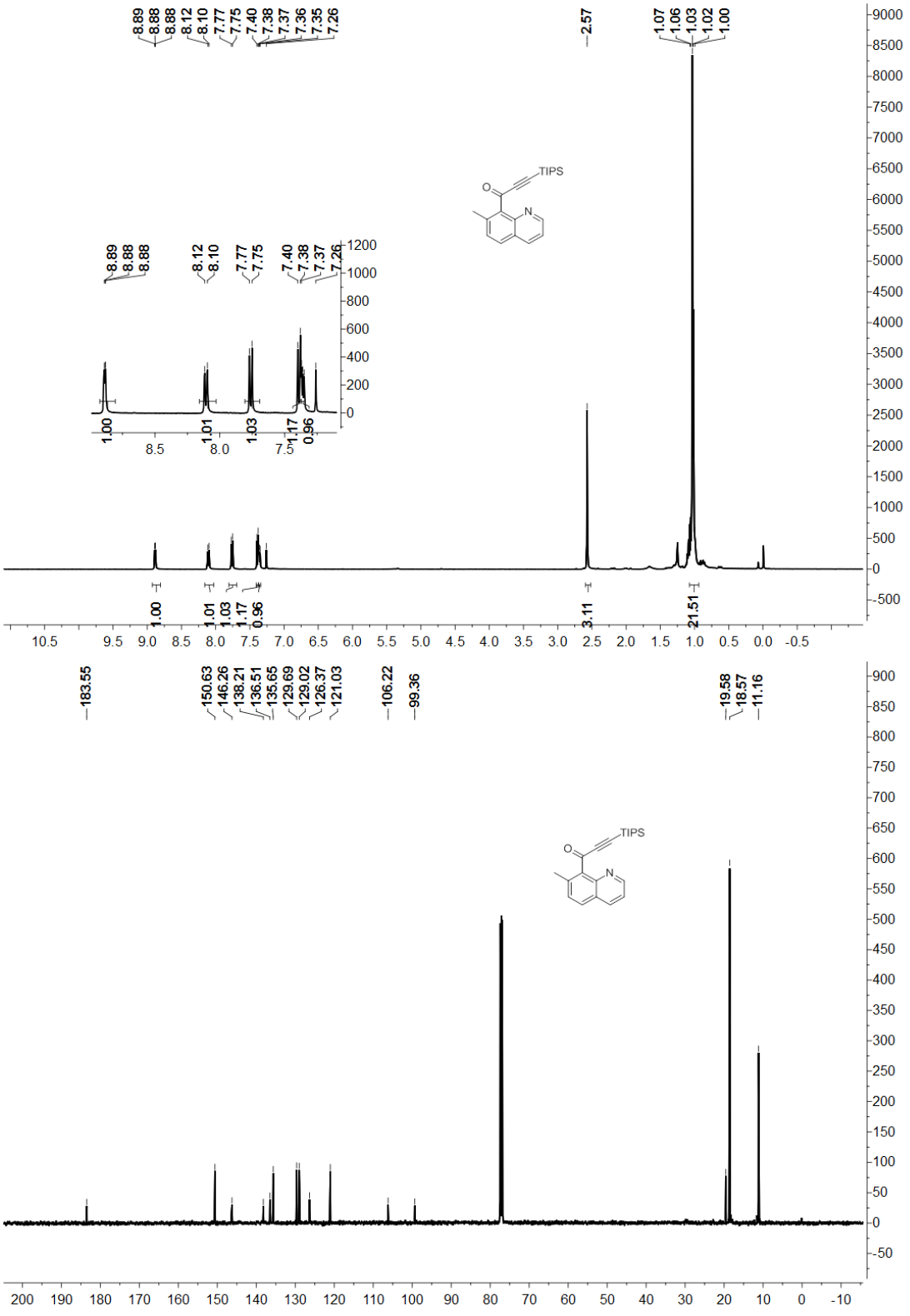
S2: R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, S. T. Michel, *Inorg. Chem.*, **1990**, 29, 2023.

S3: (a) Tao Zhang, Zisong Qi, Xueyun Zhang, Lamei Wu, and Xingwei Li*, *Chemistry-A European Journal*, **2014**, *20*, 3283; (b) Alexey Kuznetsov, Anton Makarov, Aleksandr E. Rubtsov, Alexander V. Butin,* and Vladimir Gevorgyan*, *J. Org. Chem*. **2013**, *78*, 12144.

S4: J. P. Brand, C. Chevalley, R. Scopelliti and J. Waser*, *Chemistry-A European Journal*, **2012**, *18*, 5655.

^{1}H and ^{13}C NMR Spectra of Compounds

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2.57
1.07
1.06
1.03
1.02
1.00
TIPS
O
N
1.00
1.01
1.03
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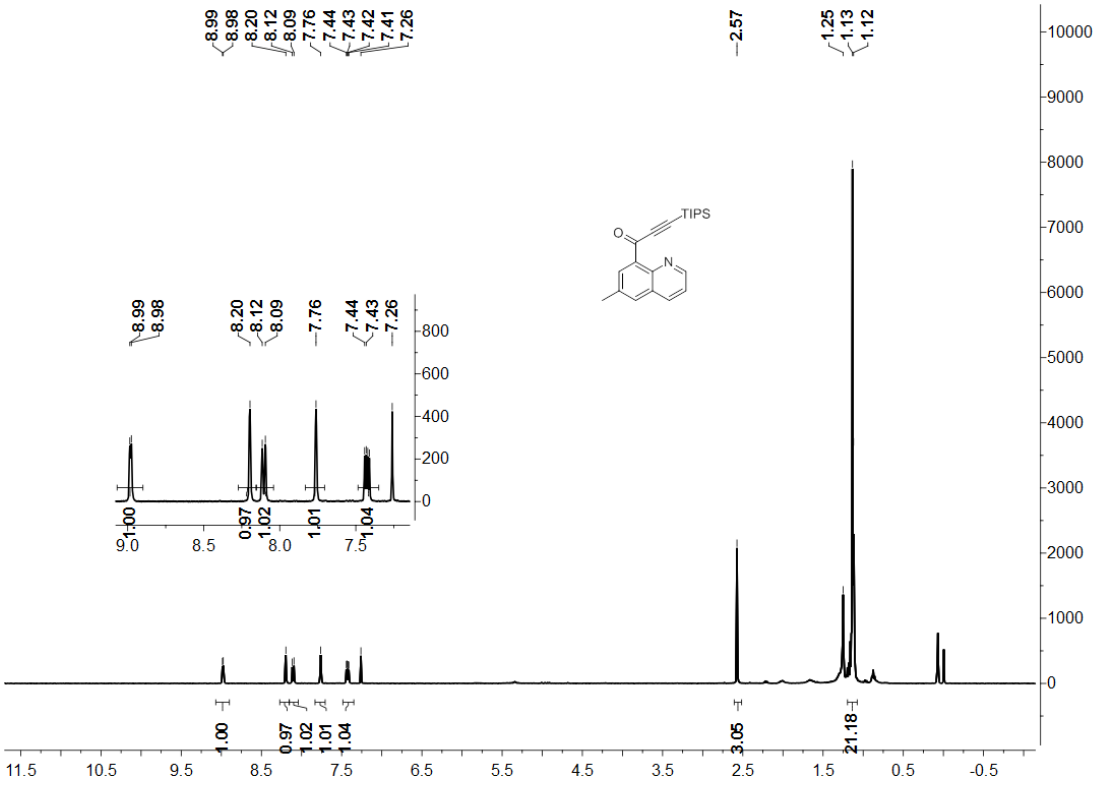
11.16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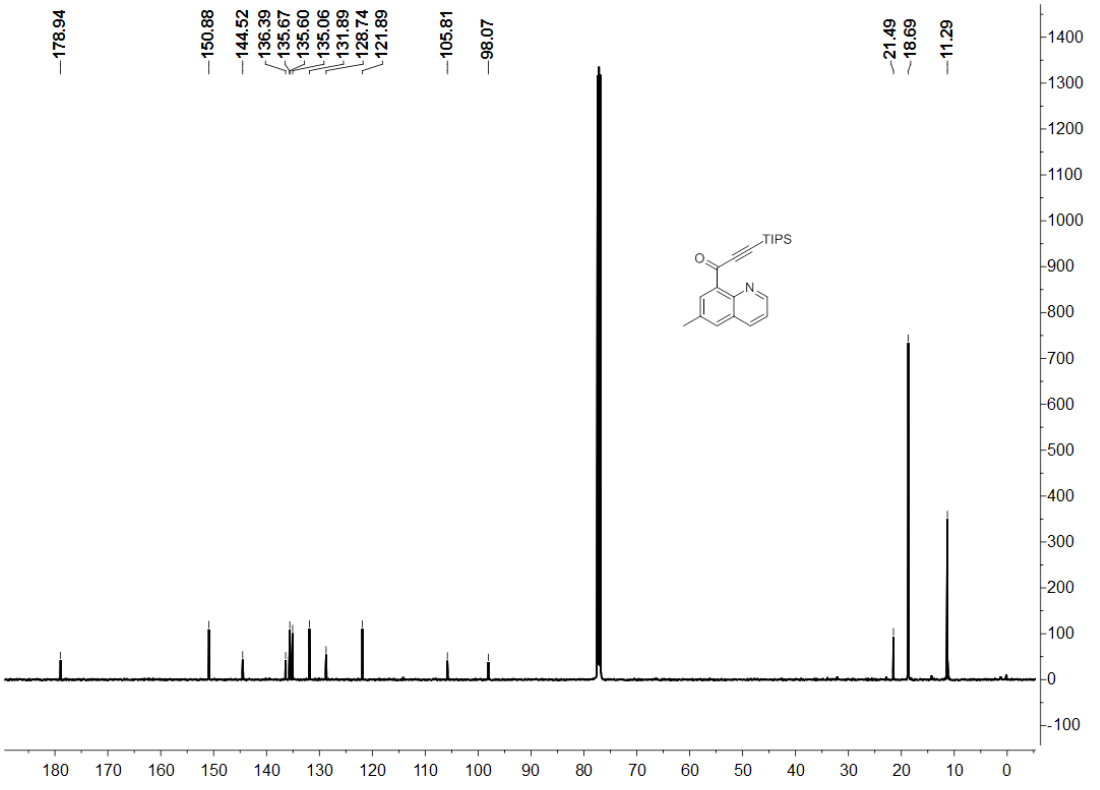
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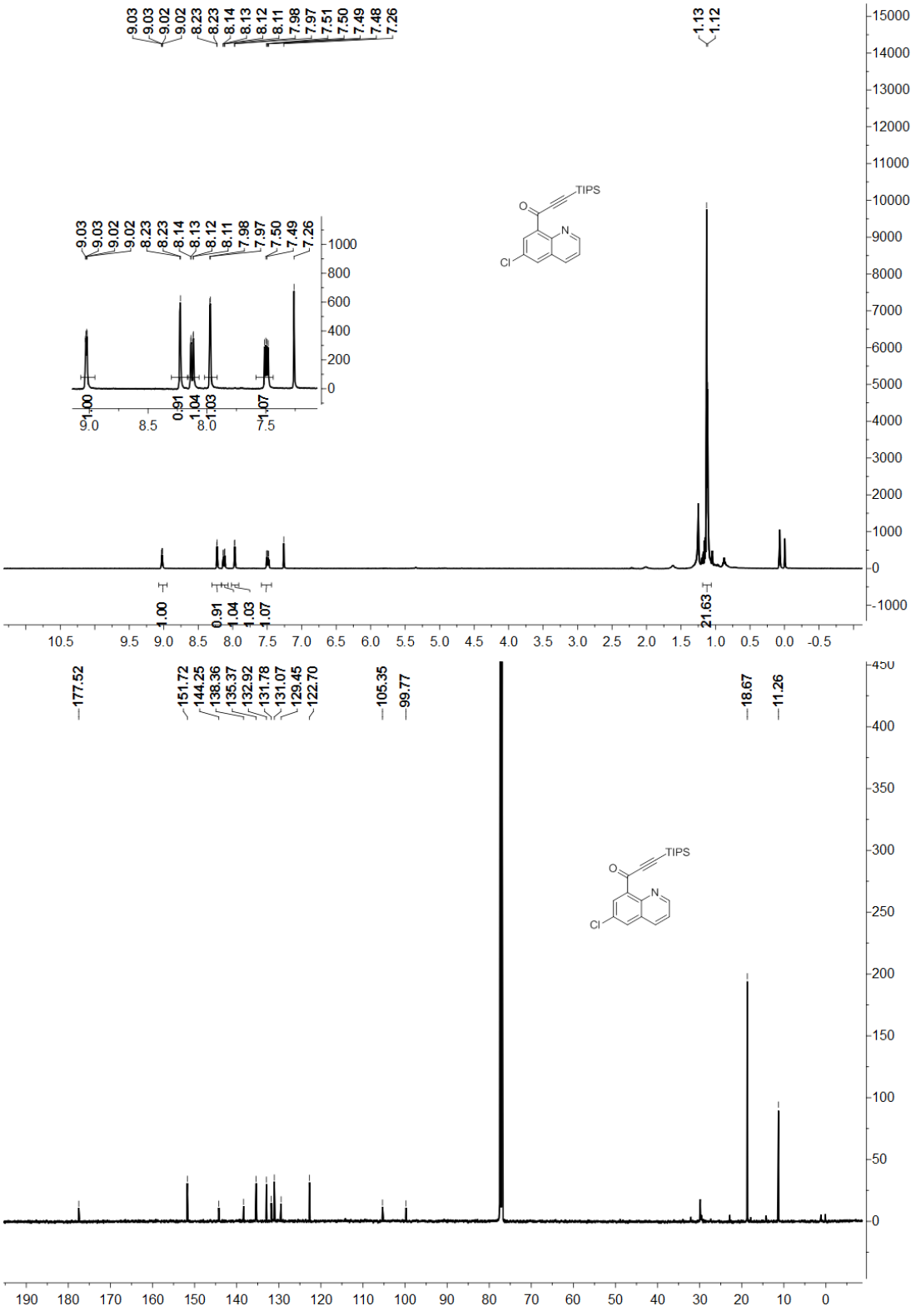
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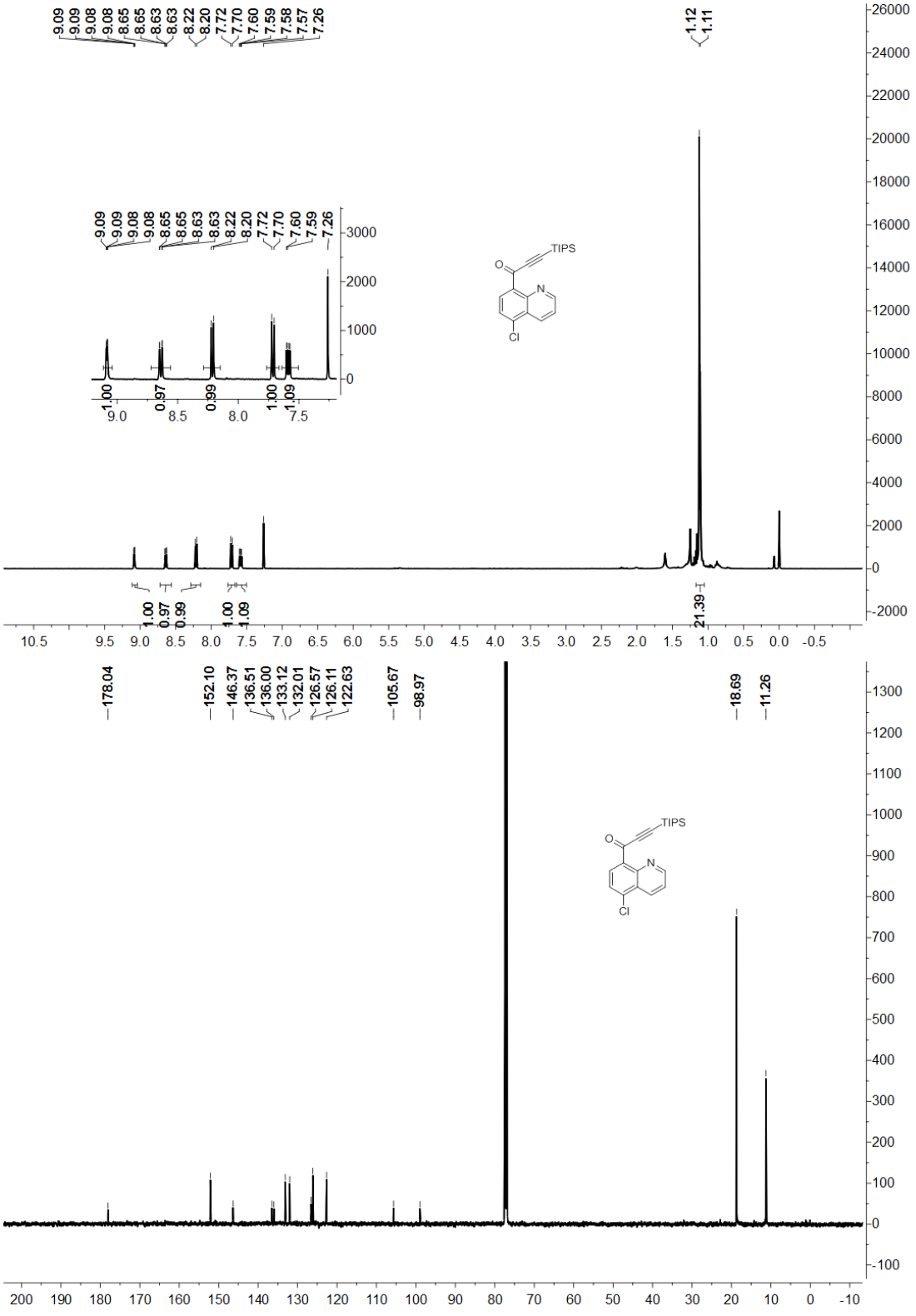
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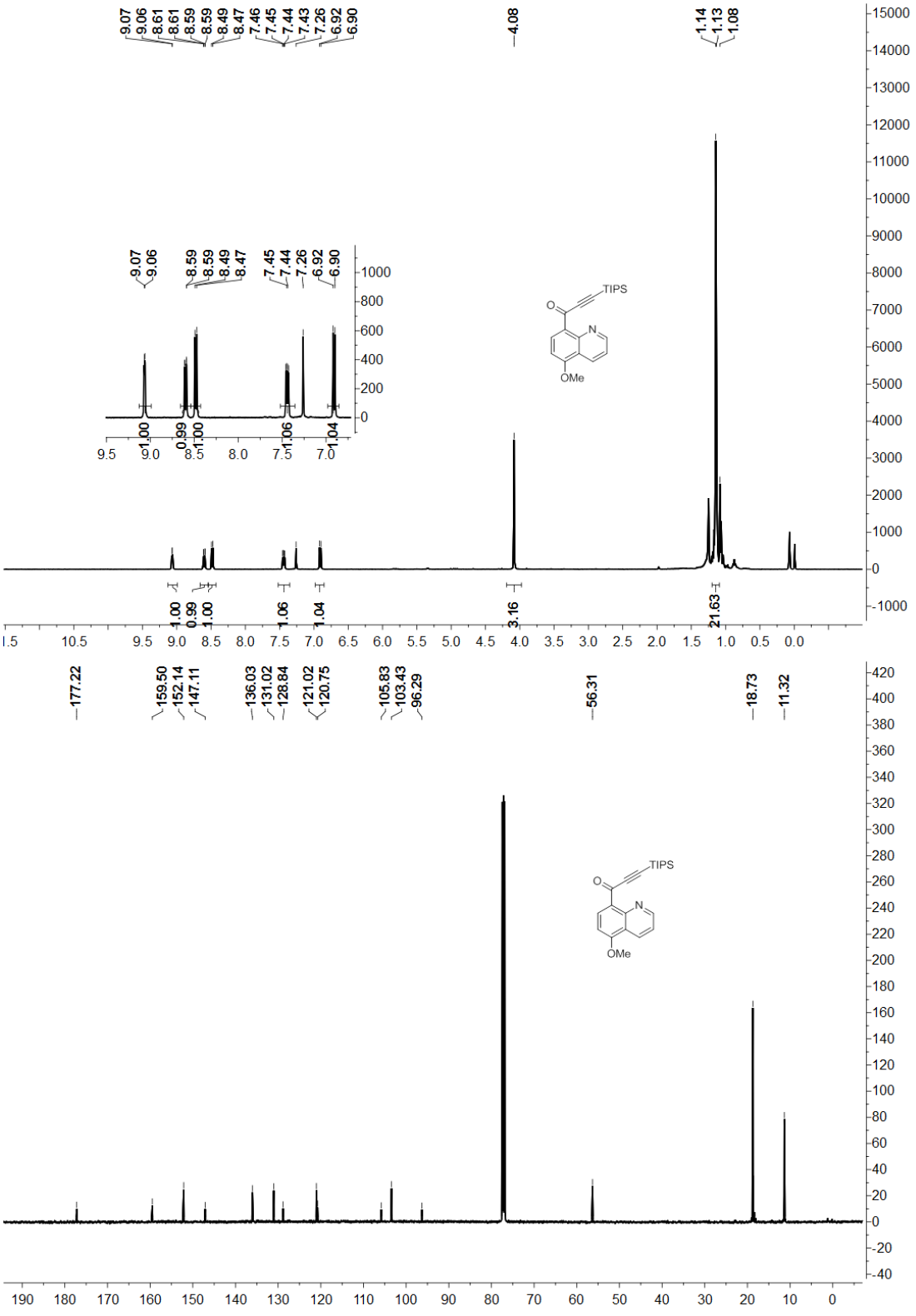
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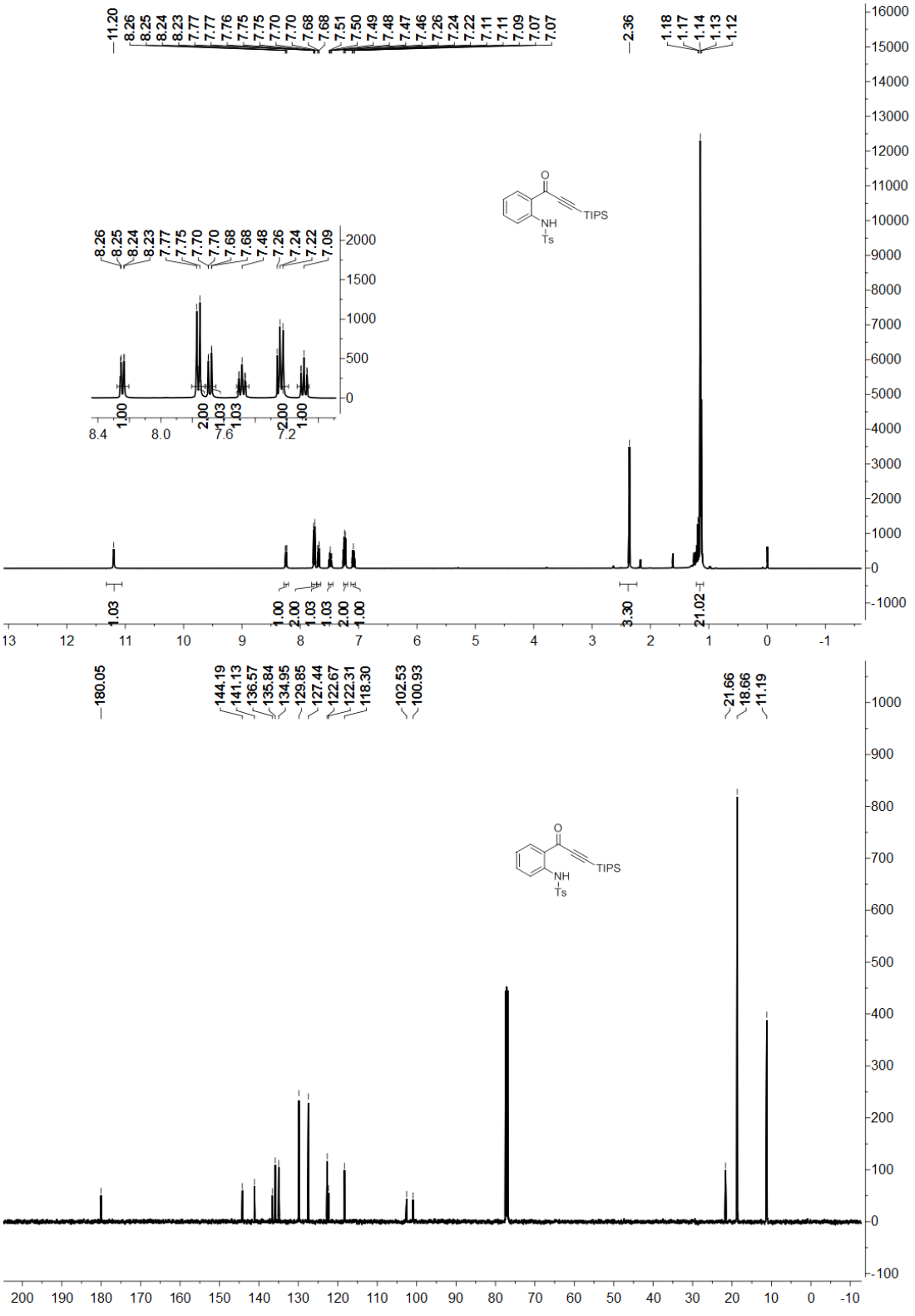
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1.14
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1.12
TIPS
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Ts
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2.00
1.03
1.03
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1.00
3.30
21.02
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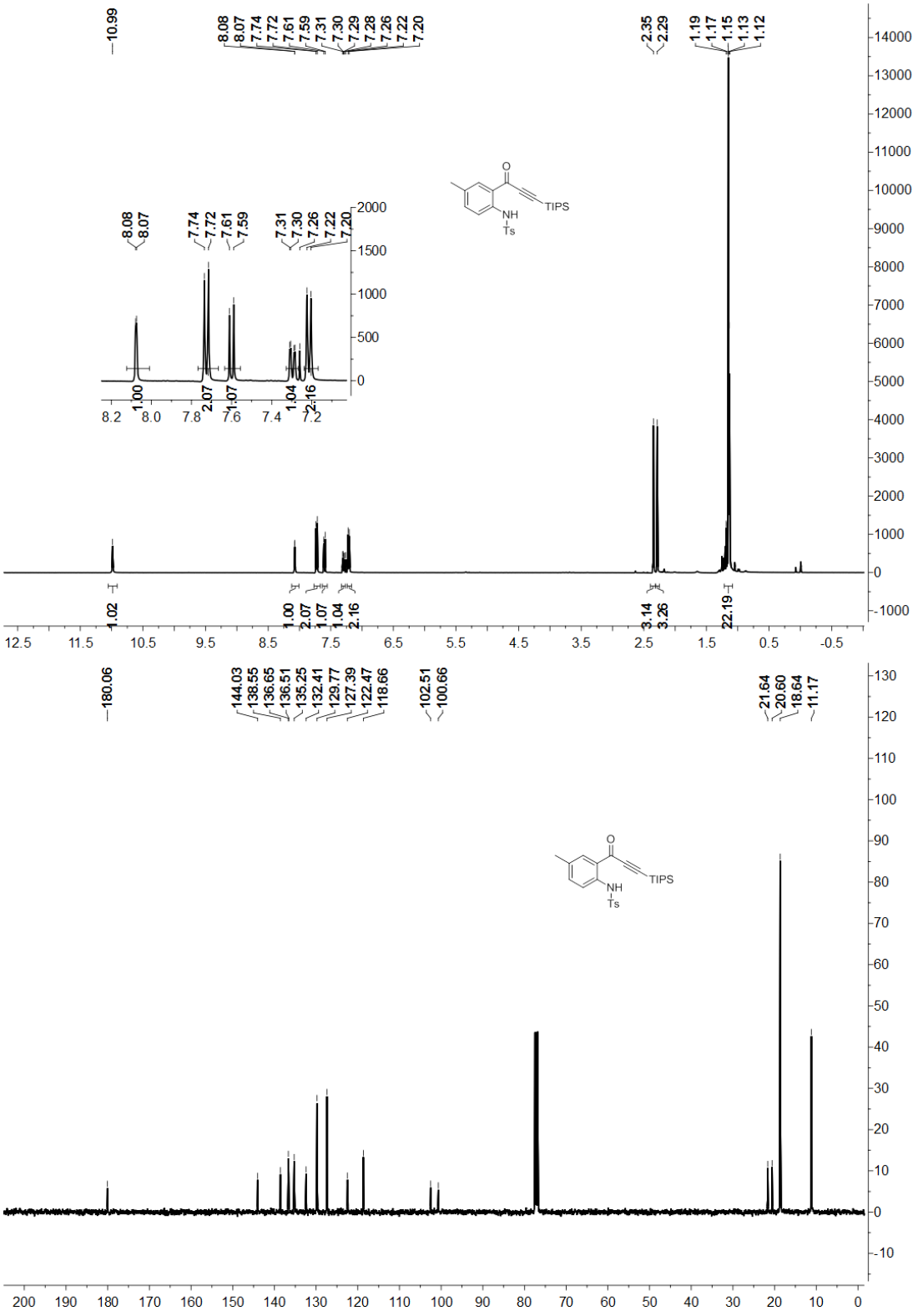
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2.29
1.19
1.17
1.15
1.13
1.12
O
TIPS
NH
Ts
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1.00
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1.07
1.04
2.16
3.14
3.26
22.19
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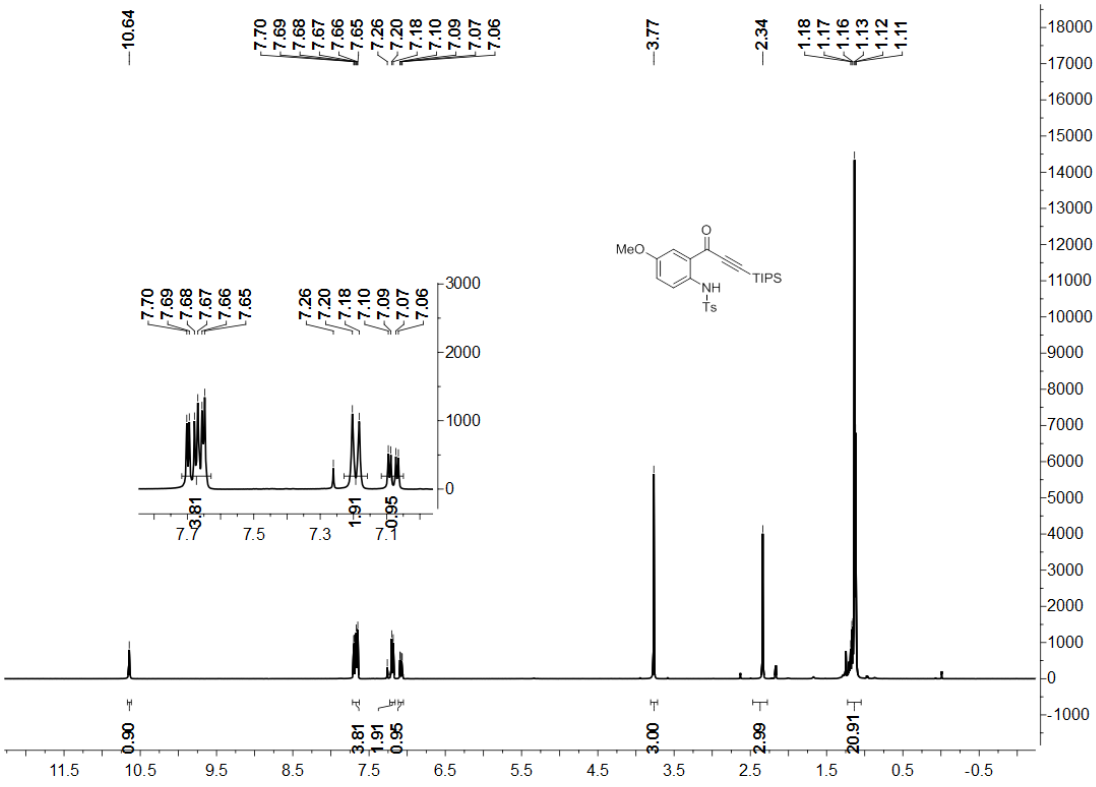
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7.06
3.77
2.34
1.18
1.17
1.16
1.13
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Ts
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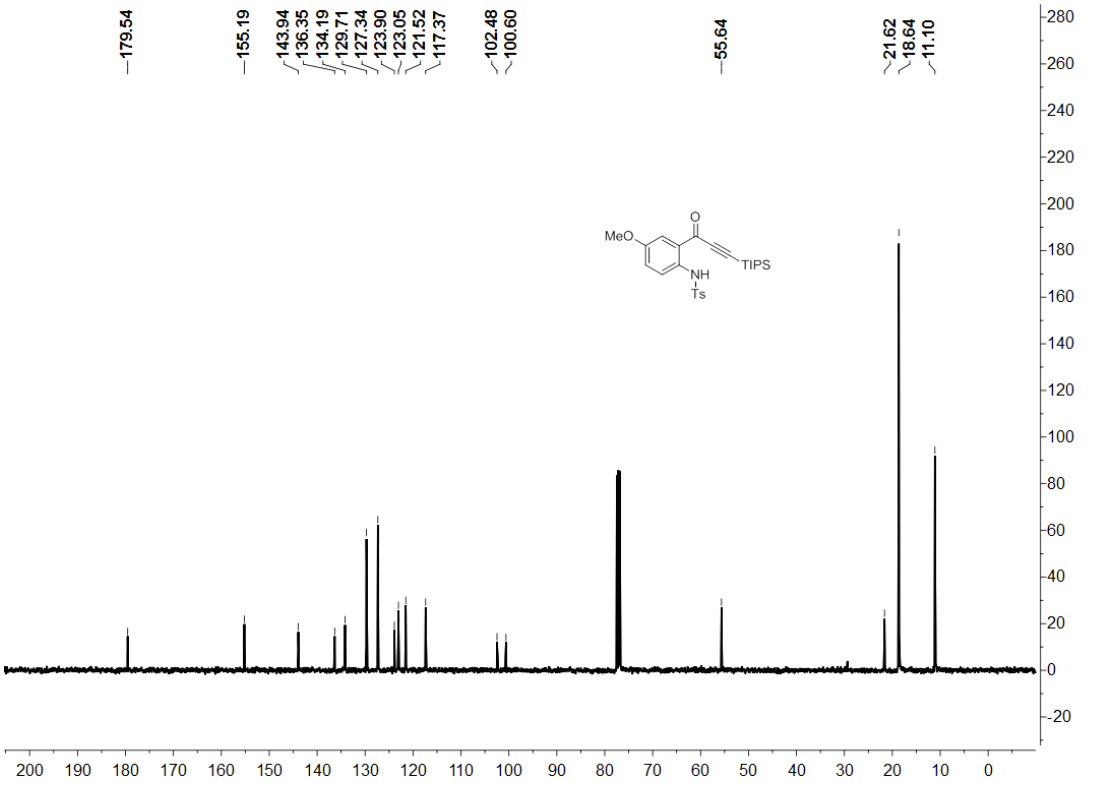
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O
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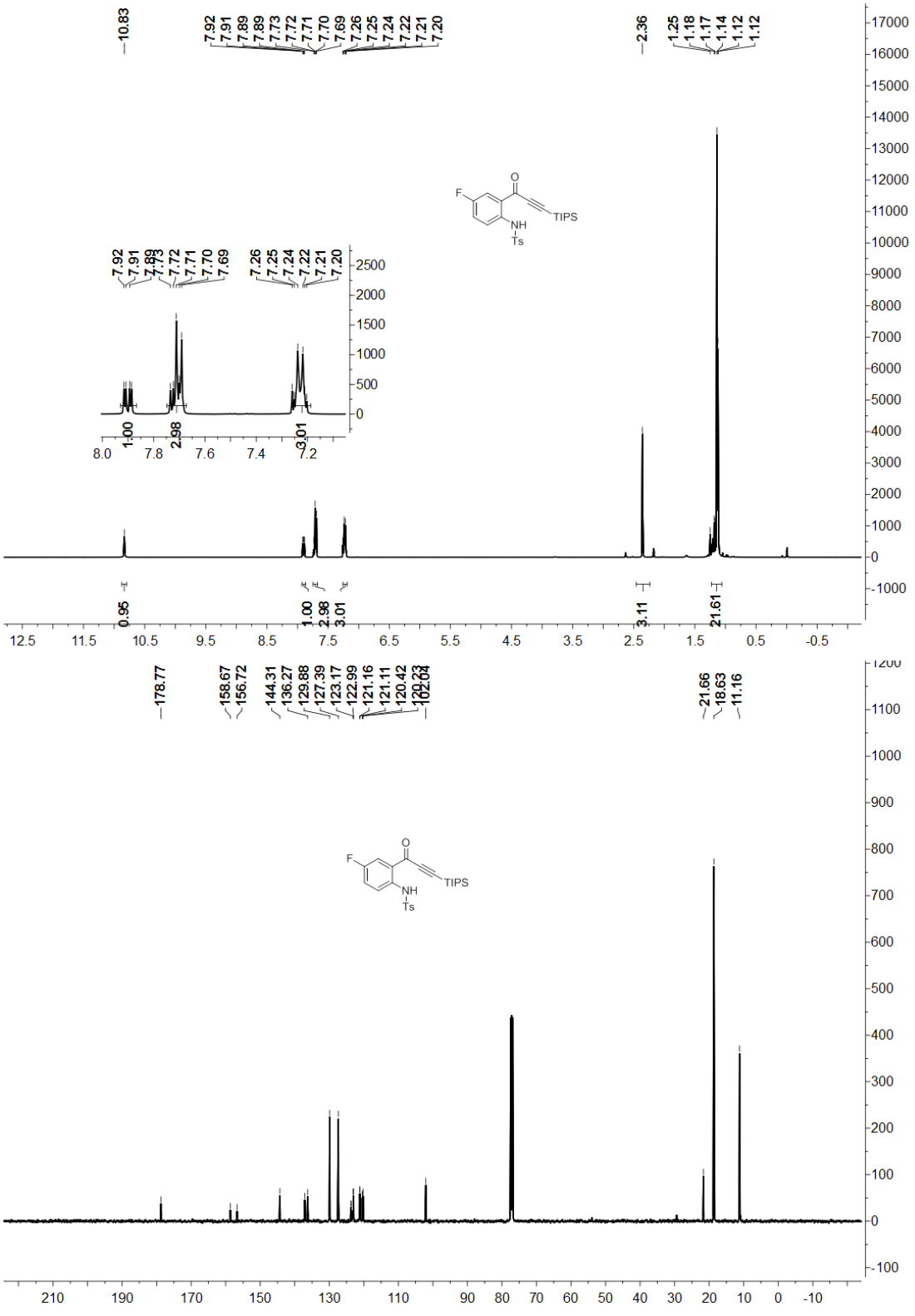
NH
Ts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7.21
7.20
2.36
1.25
1.18
1.17
1.14
1.12
1.12
F
O
TIPS
NH
Ts
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1.00
2.98
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3.11
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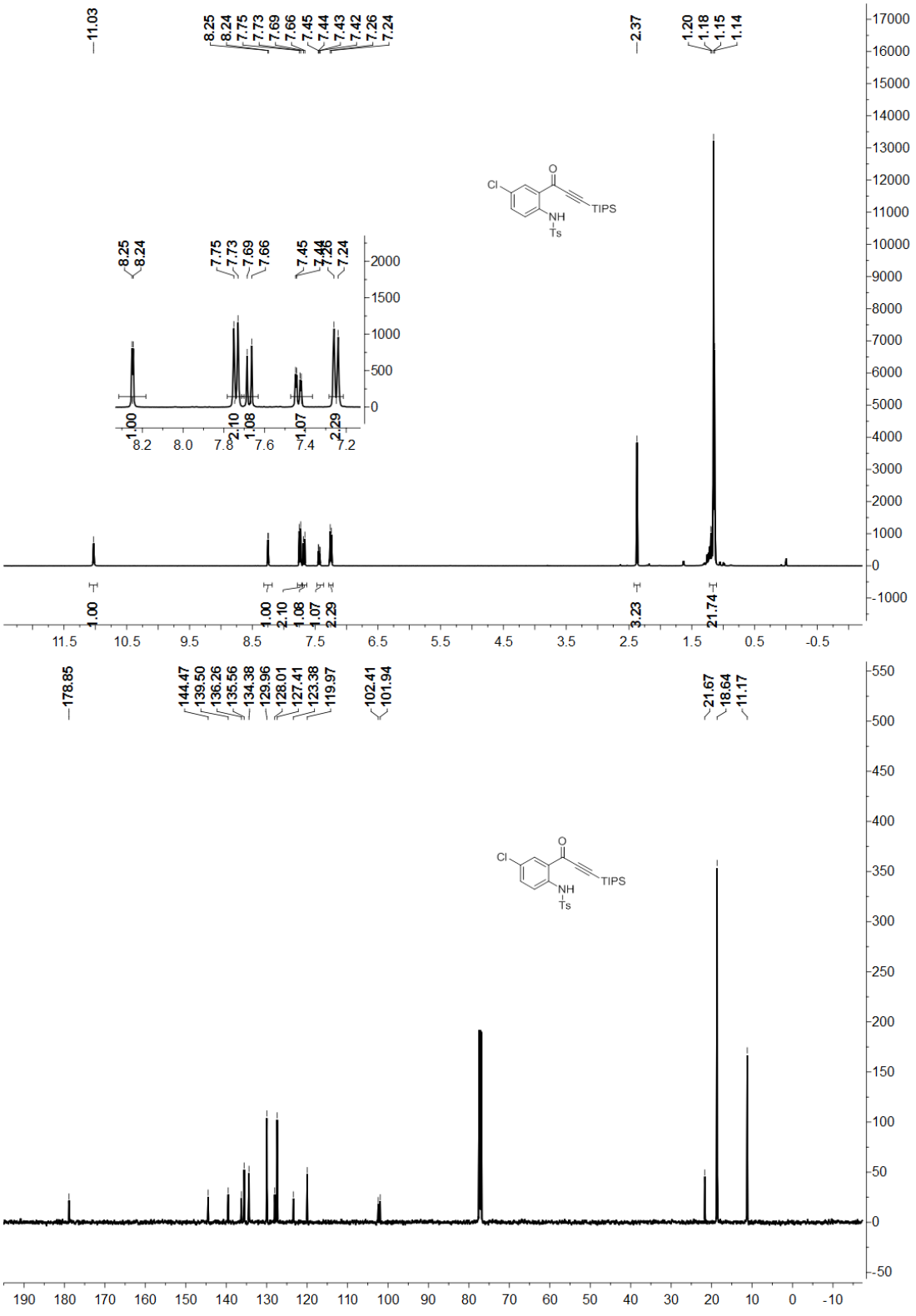
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2.37
1.20
1.18
1.15
1.14
Cl
O
TIPS
NH
Ts
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2.10
1.08
1.07
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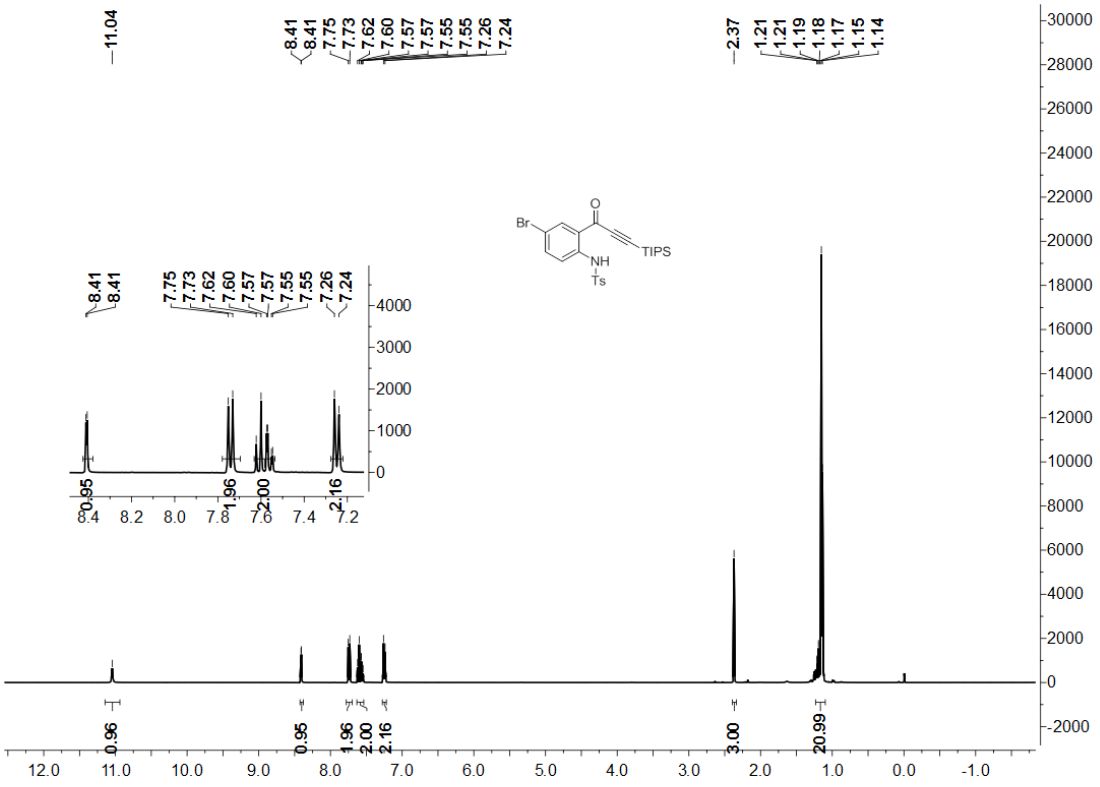
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2.37
1.21
1.21
1.19
1.18
1.17
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Ts
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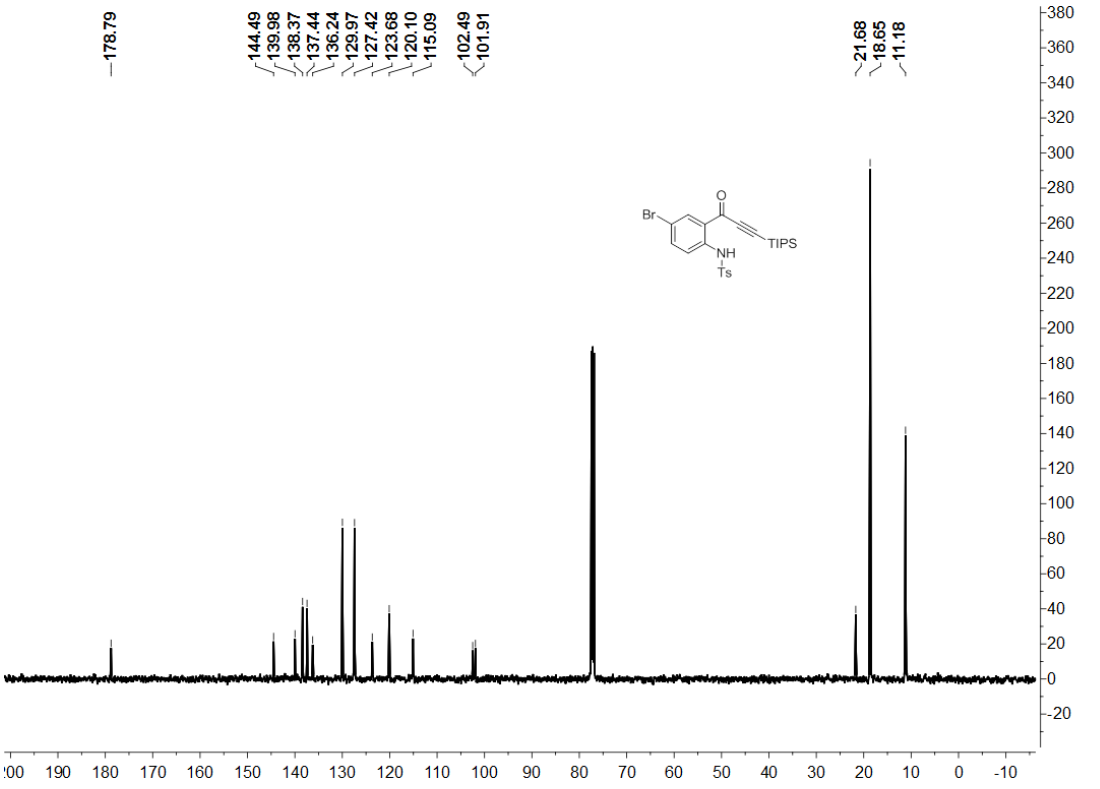
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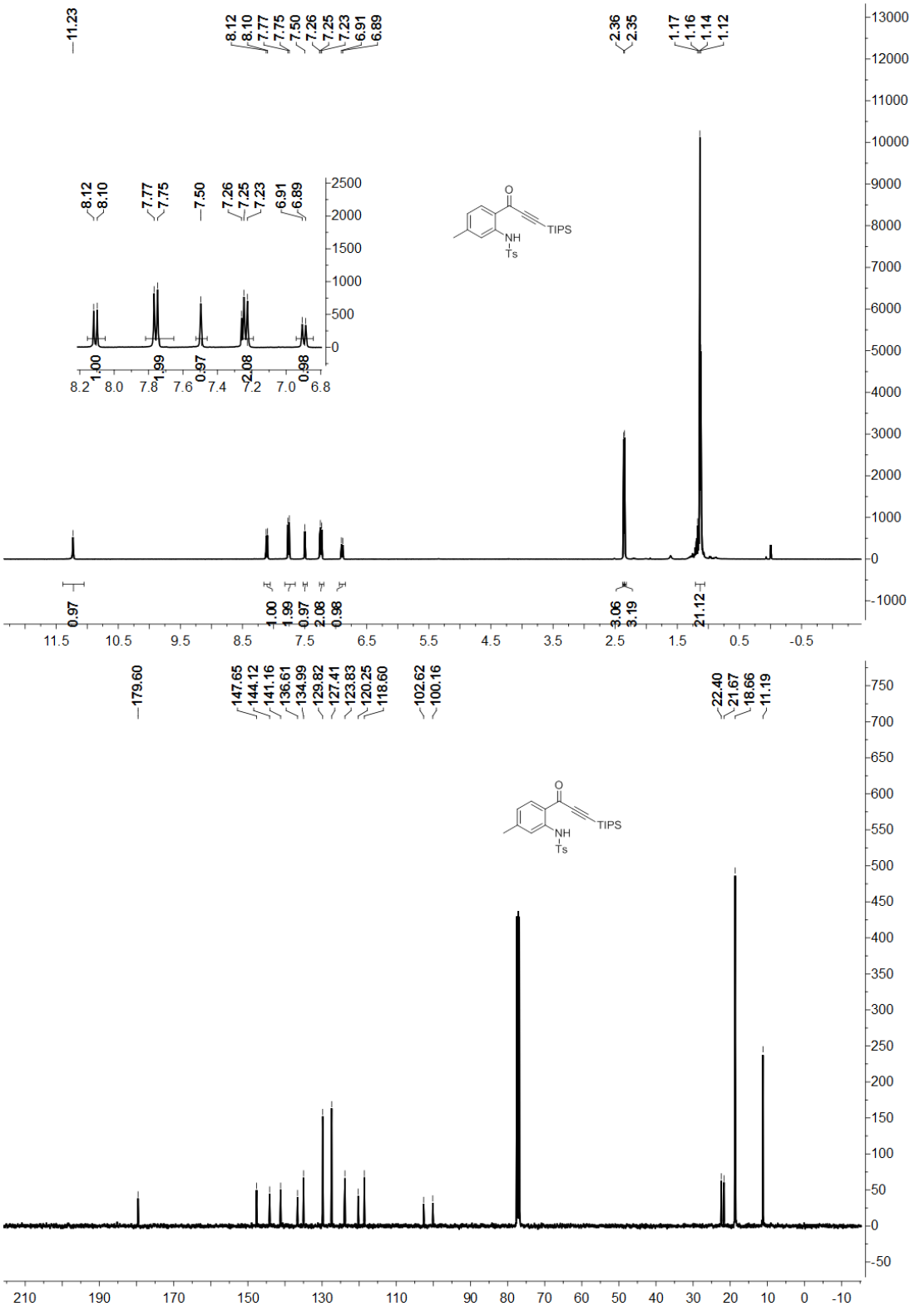
Br
O
TIPS
NH
Ts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6.91
6.89
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2.35
1.17
1.16
1.14
1.12
TIPS
NH
Ts
0.97
1.00
1.99
0.97
2.08
0.98
3.06
3.19
21.12
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144.12
141.16
136.61
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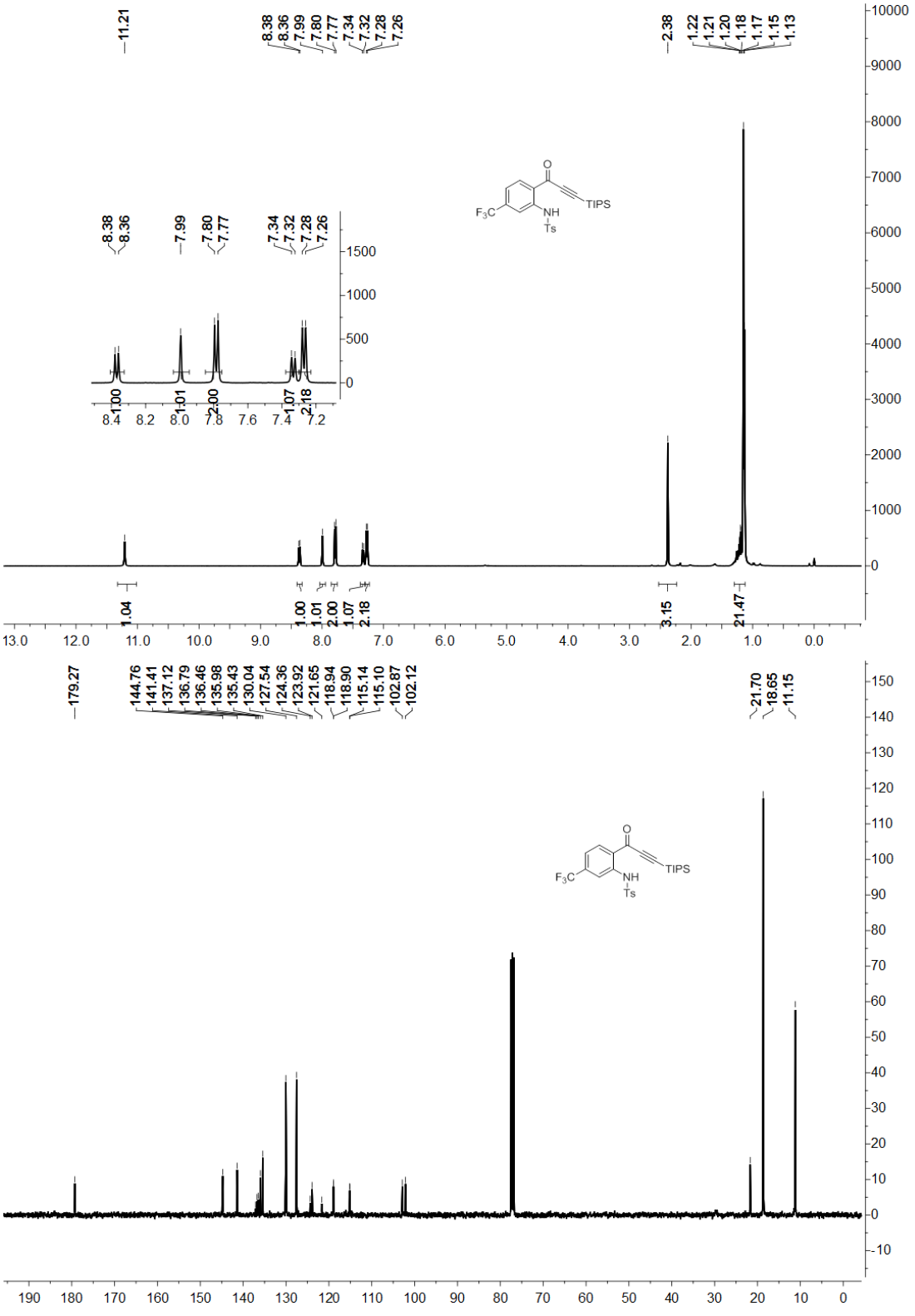
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7.26
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1.21
1.20
1.18
1.17
1.15
1.13
TIPS
NH
Ts
1.04
1.00
1.01
2.00
1.07
2.18
3.15
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127.54
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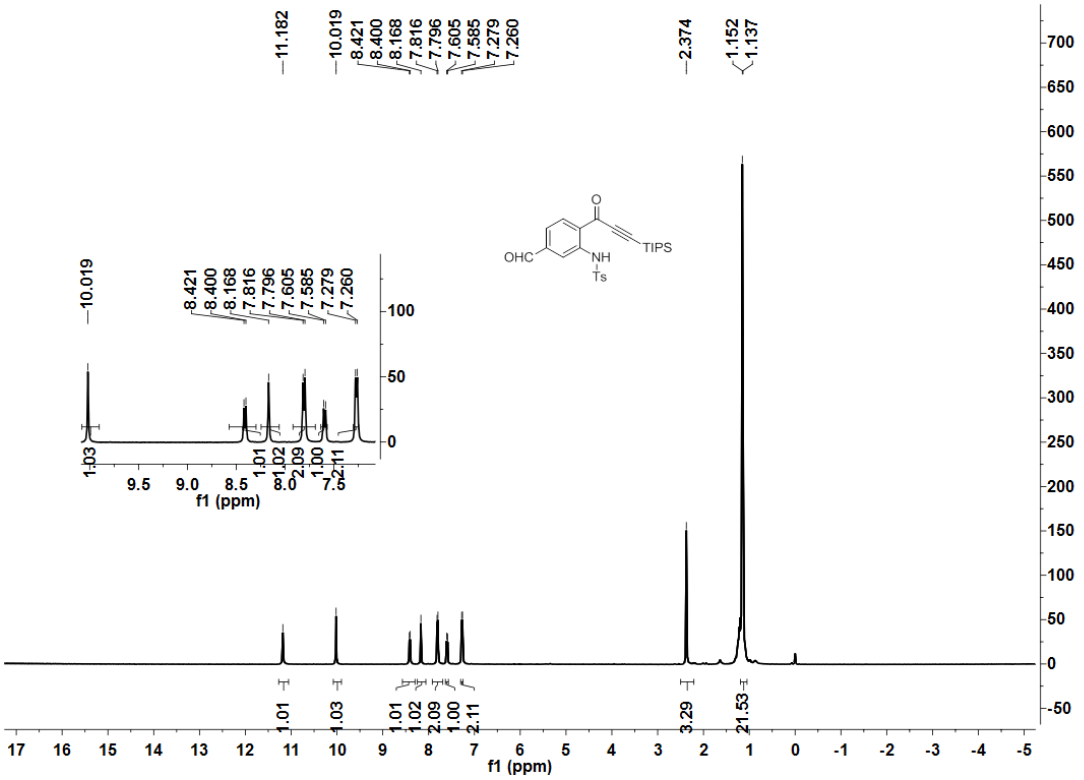
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7.260
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1.152
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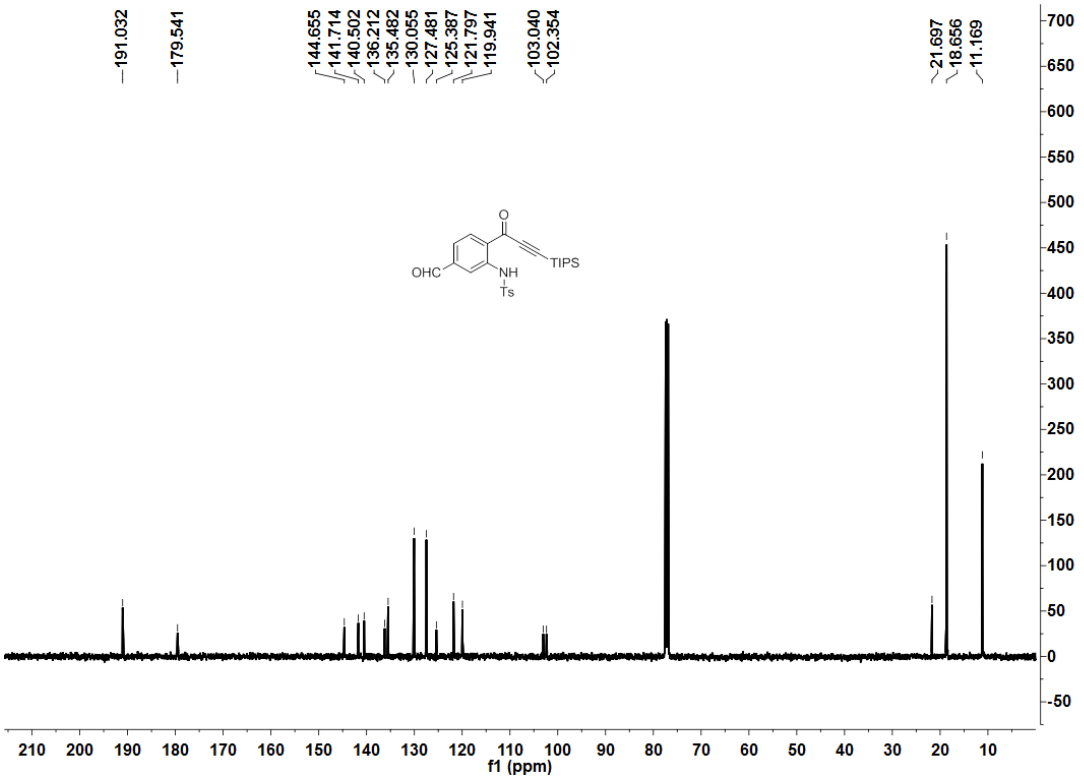
OHC
NH
Ts
TIPS
O
f1 (ppm)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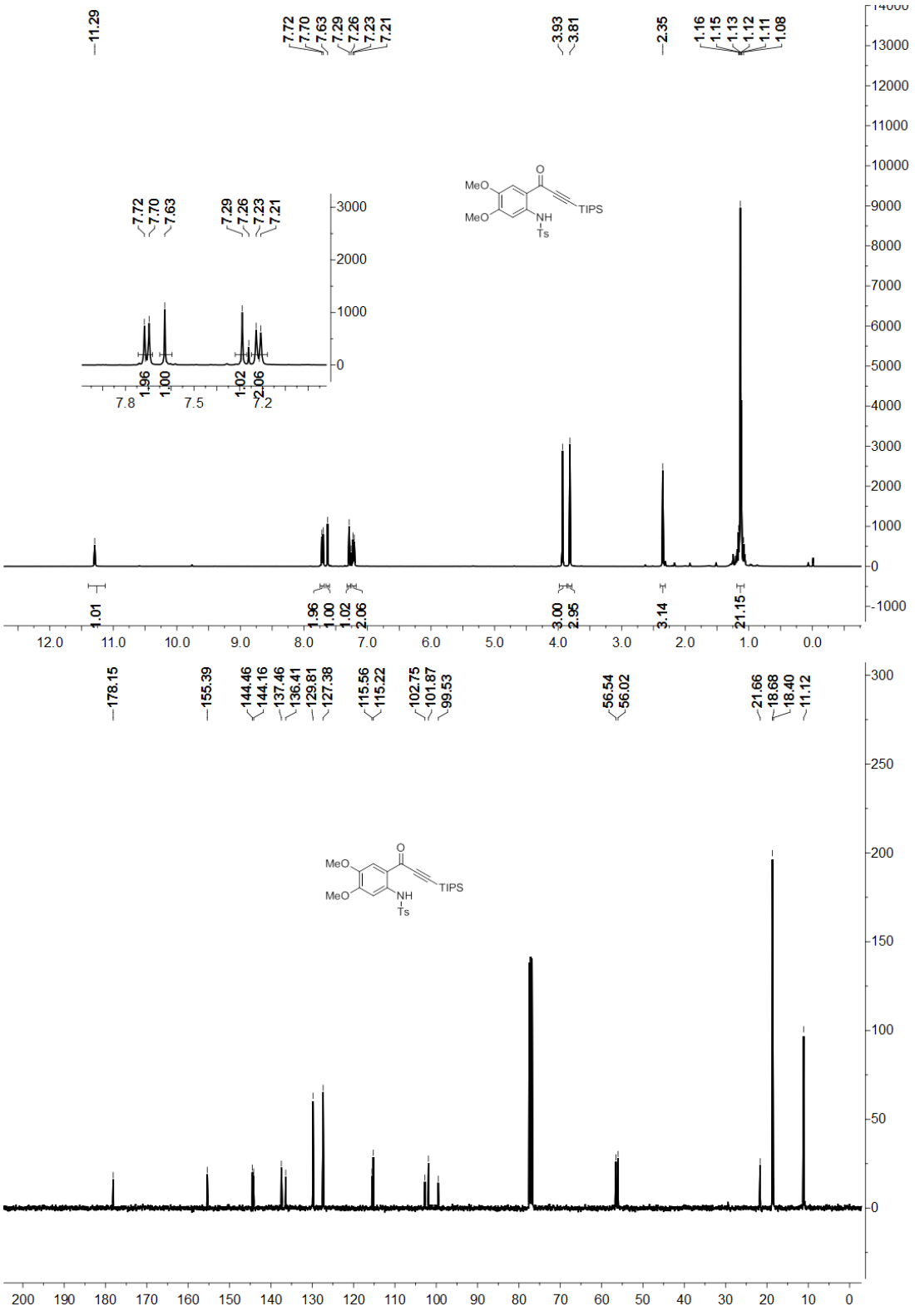
OHC
NH
Ts
TIPS
O
f1 (ppm)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1.13
1.12
1.11
1.08
MeO
MeO
NH
Ts
TIPS
1.01
1.96
1.00
1.02
2.06
3.00
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144.46
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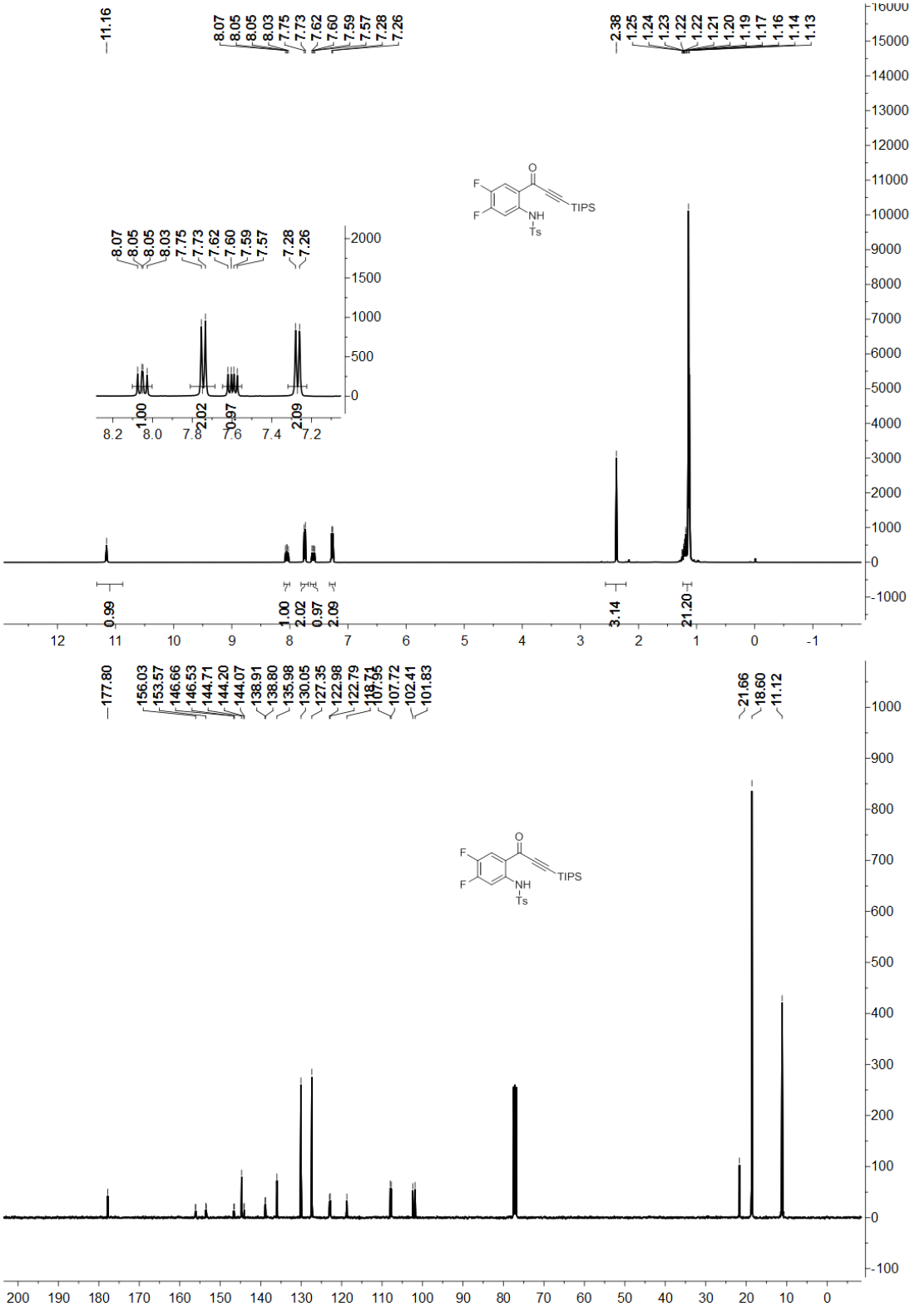
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7.59
7.57
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7.26
2.38
1.25
1.24
1.23
1.22
1.22
1.21
1.20
1.19
1.17
1.16
1.14
1.13
F
F
O
NH
Ts
TIPS
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1.00
2.02
0.97
2.09
3.14
21.20
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153.57
146.66
146.53
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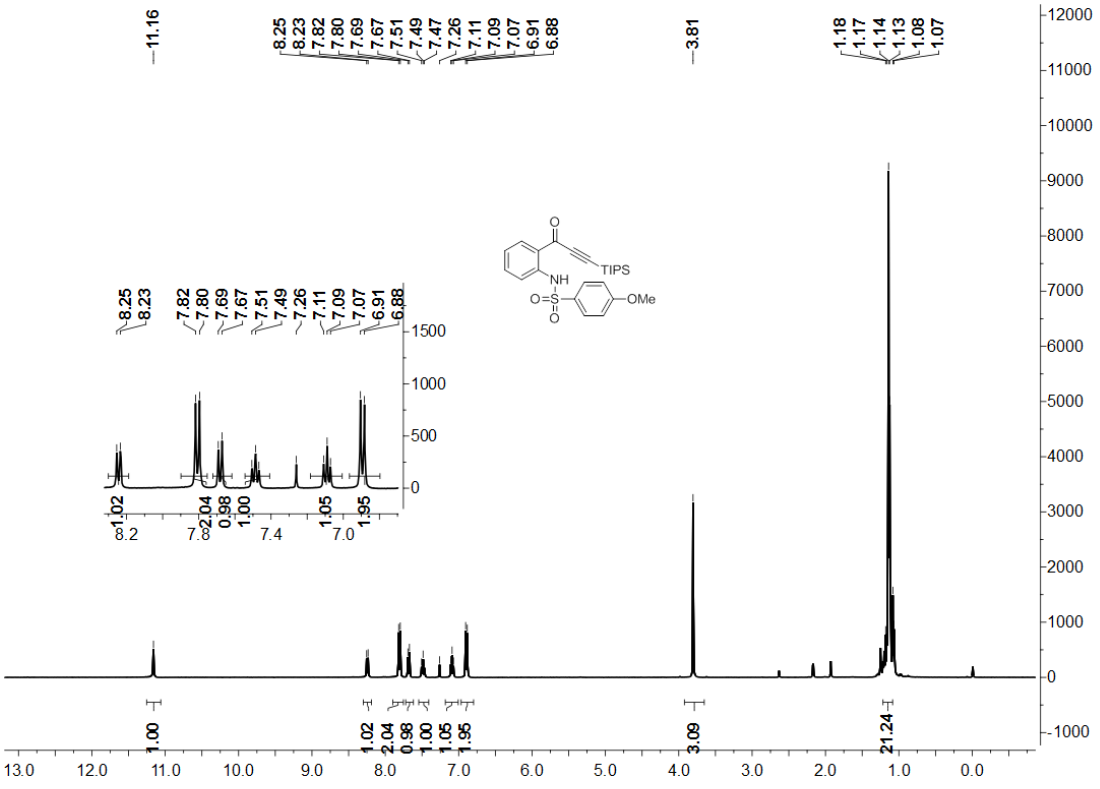
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1.14
1.13
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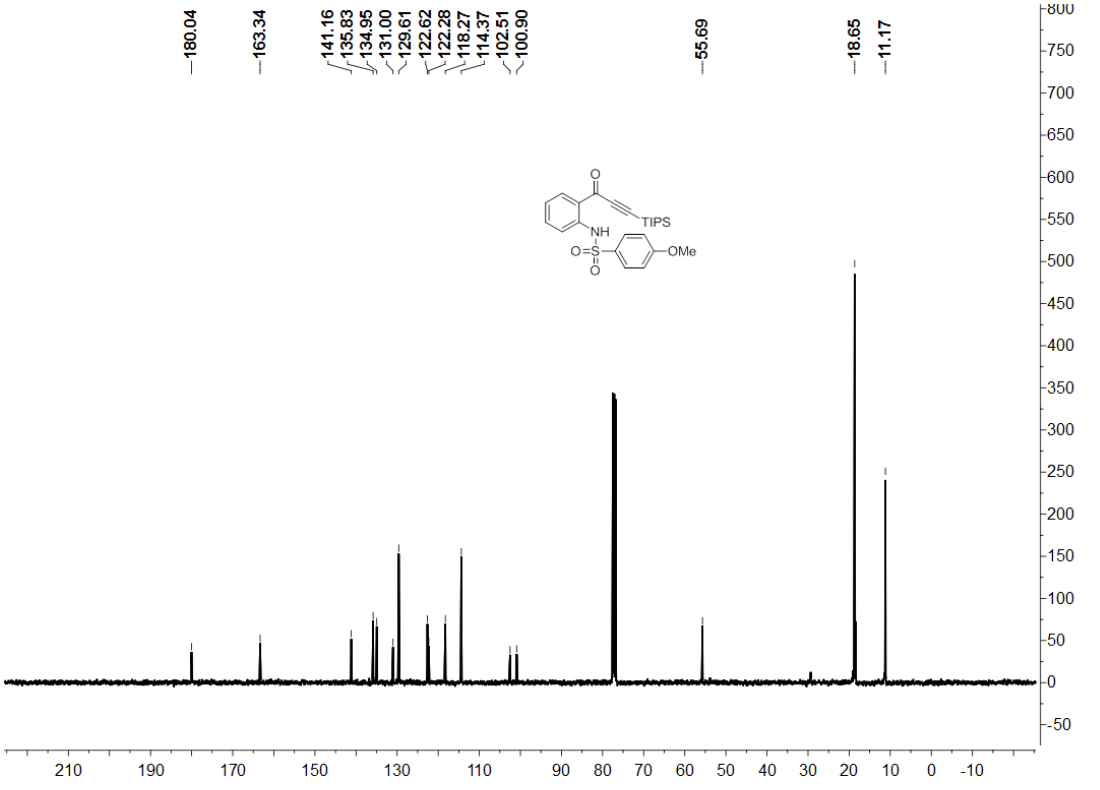
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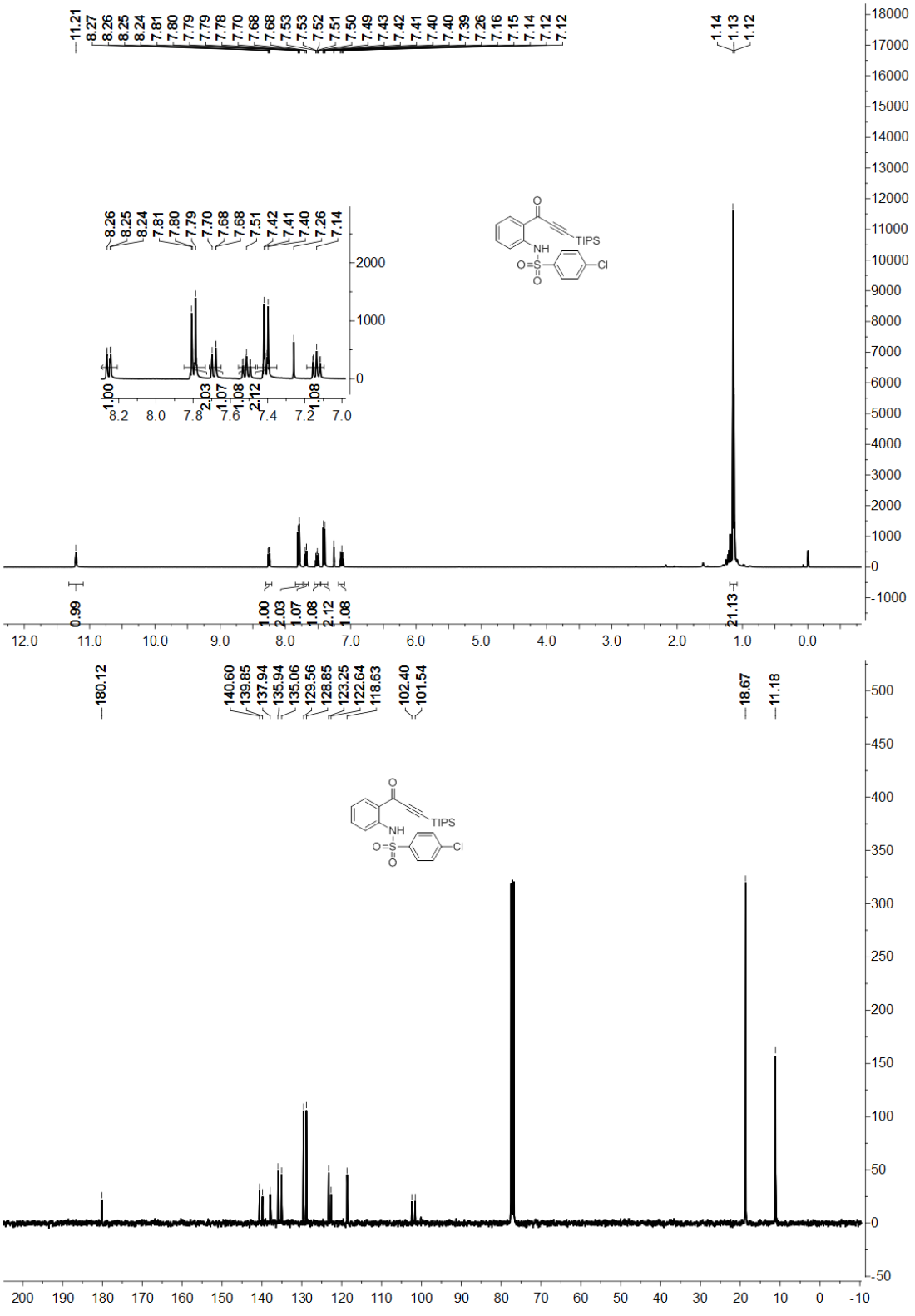
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1.12
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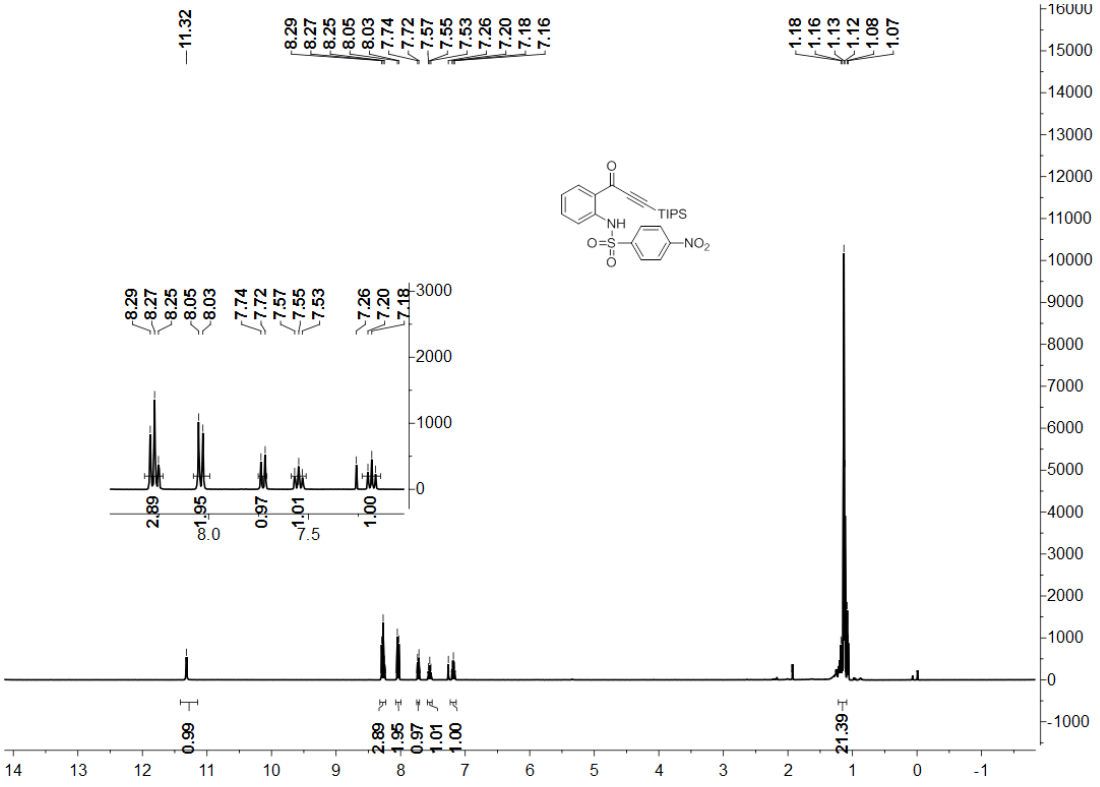
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7.18
7.16
1.18
1.16
1.13
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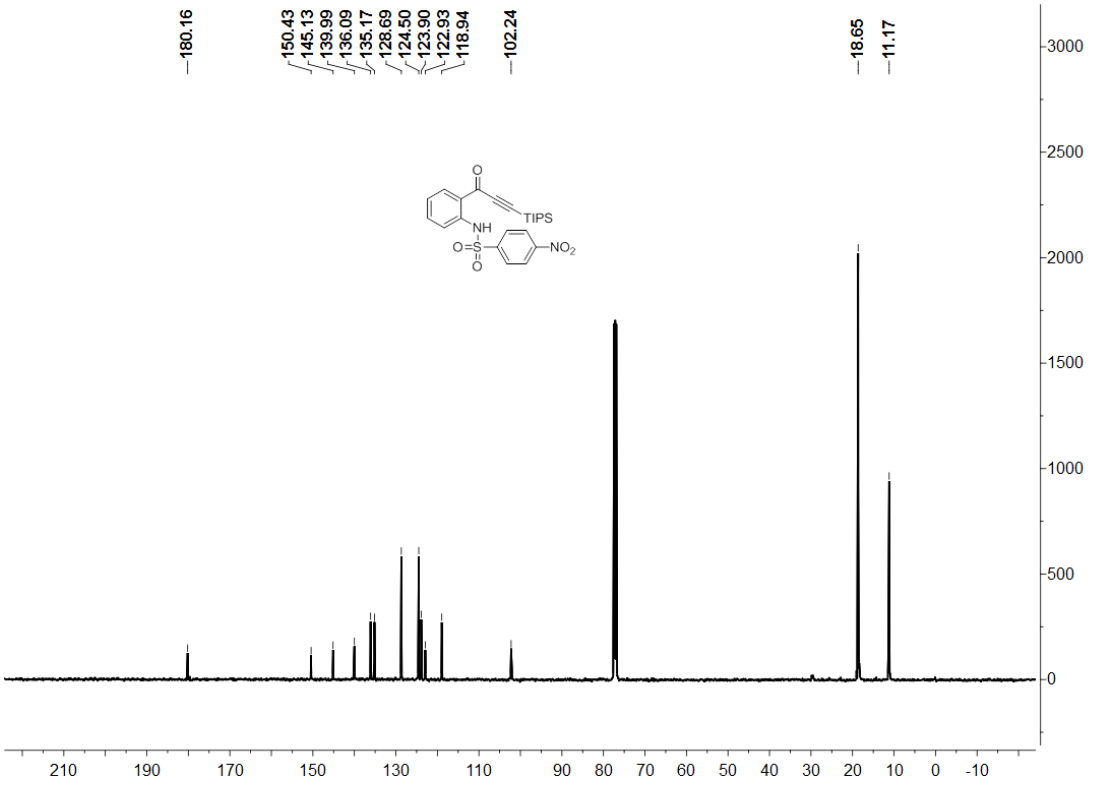
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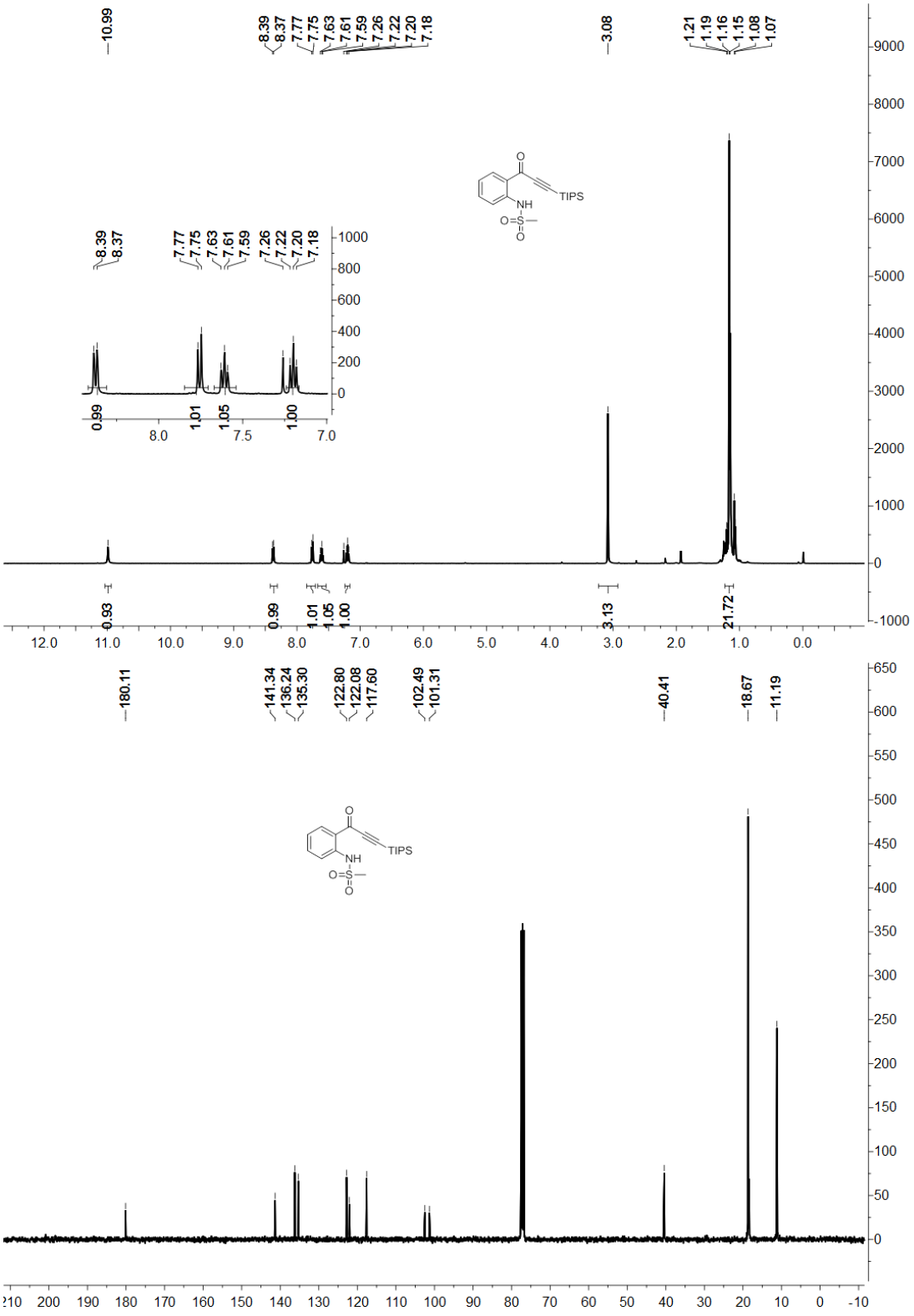
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1.19
1.16
1.15
1.08
1.07
TIPS
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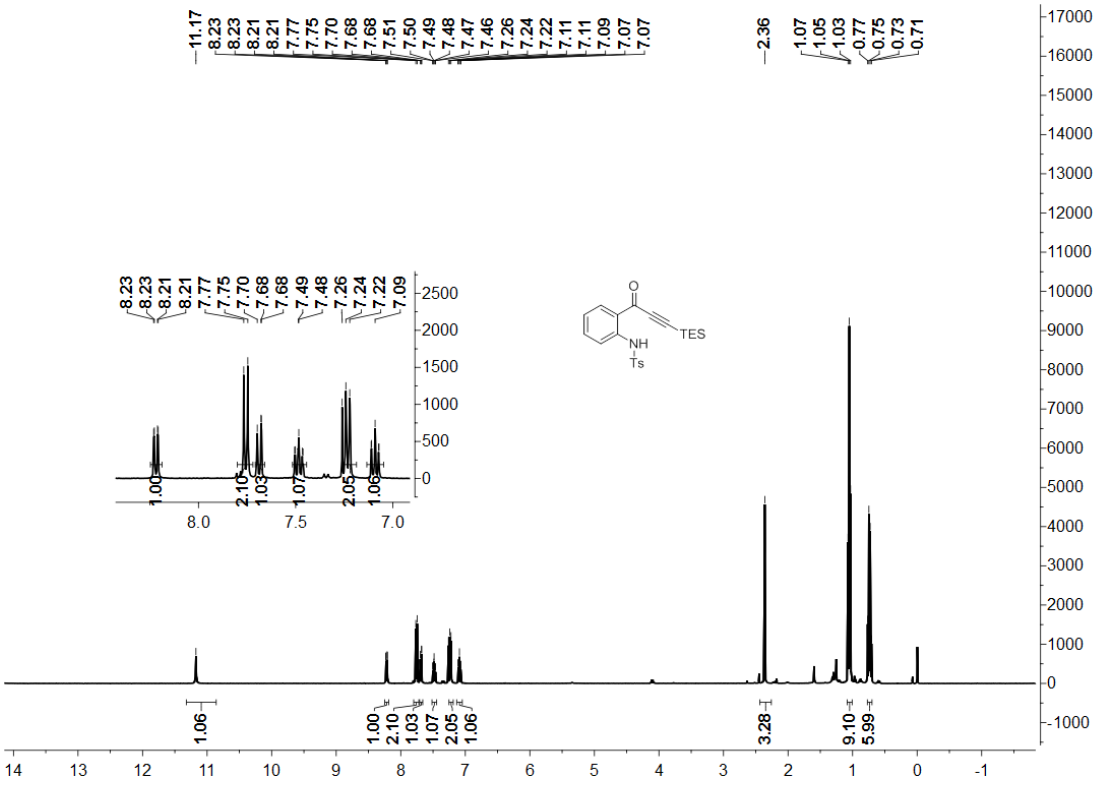
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7.22
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7.07
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2.36
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1.05
1.03
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0.75
0.73
0.71
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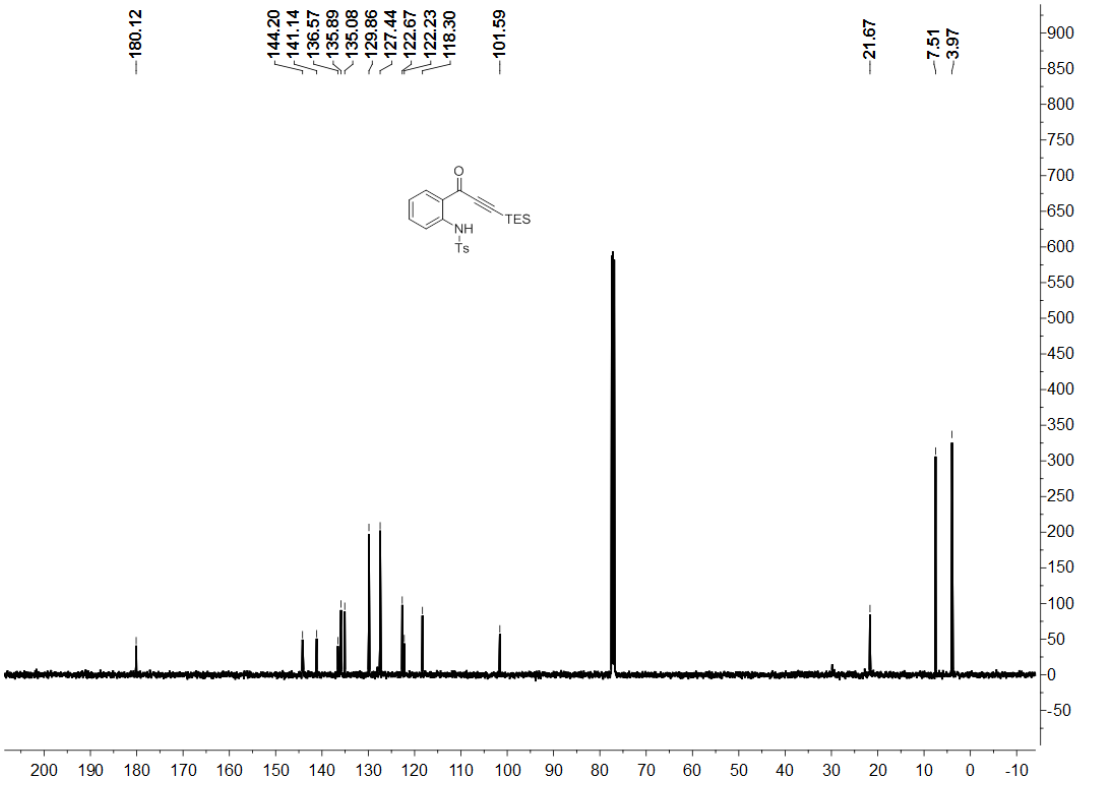
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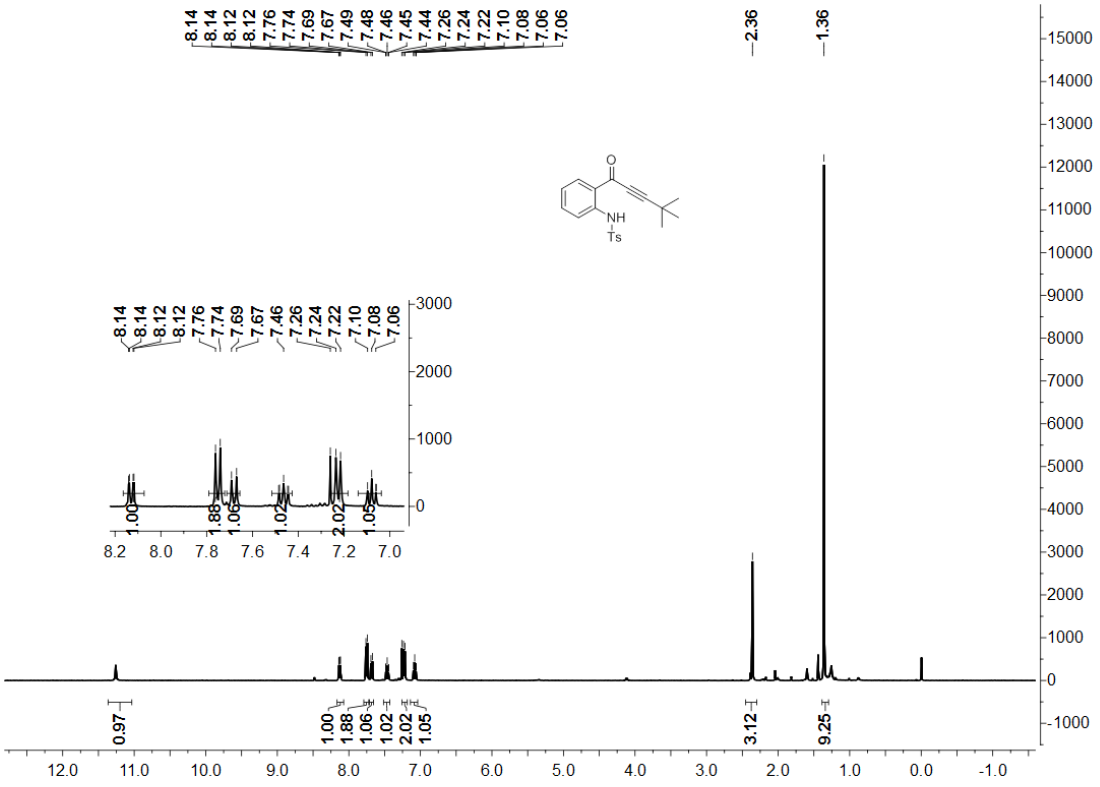
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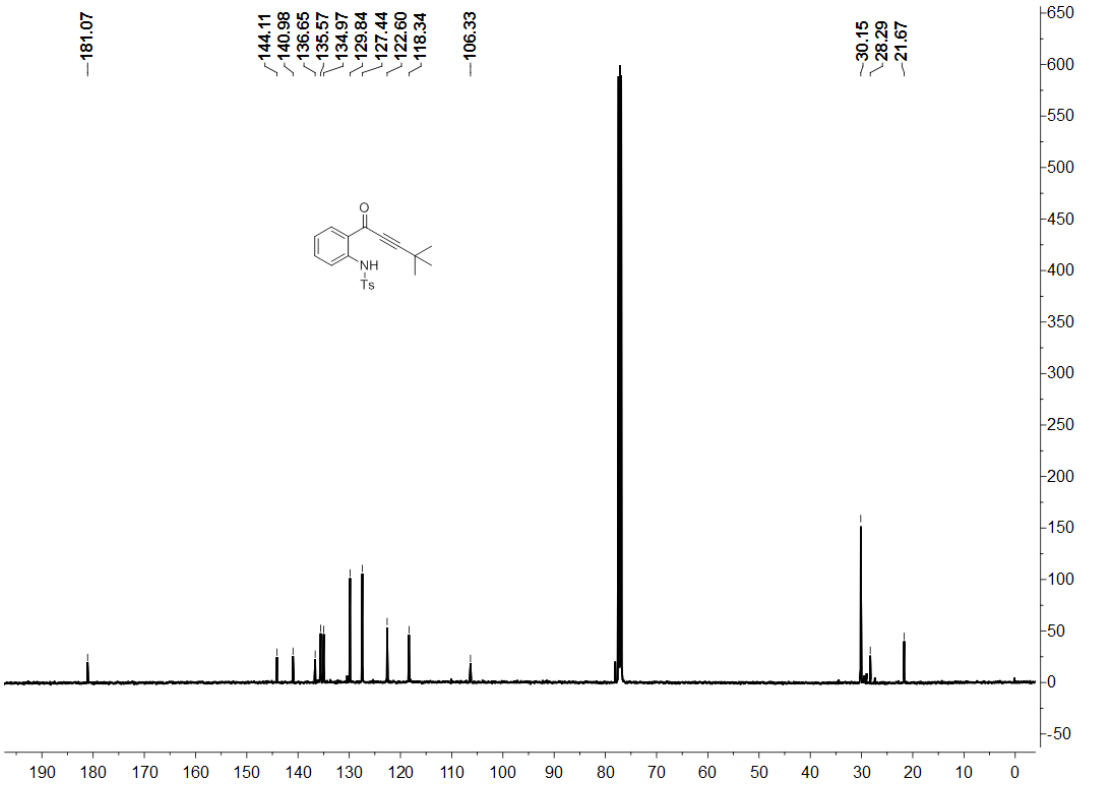
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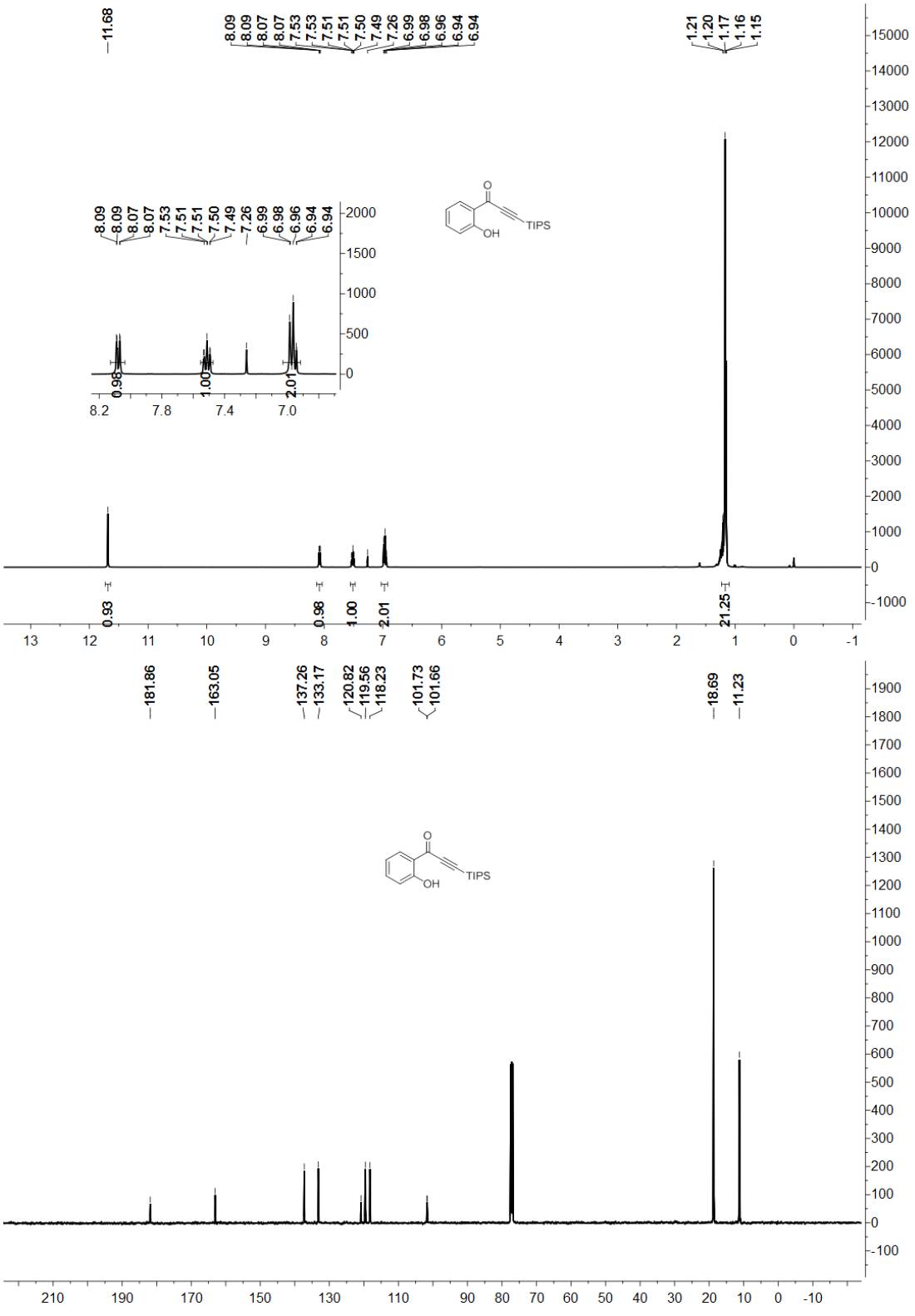
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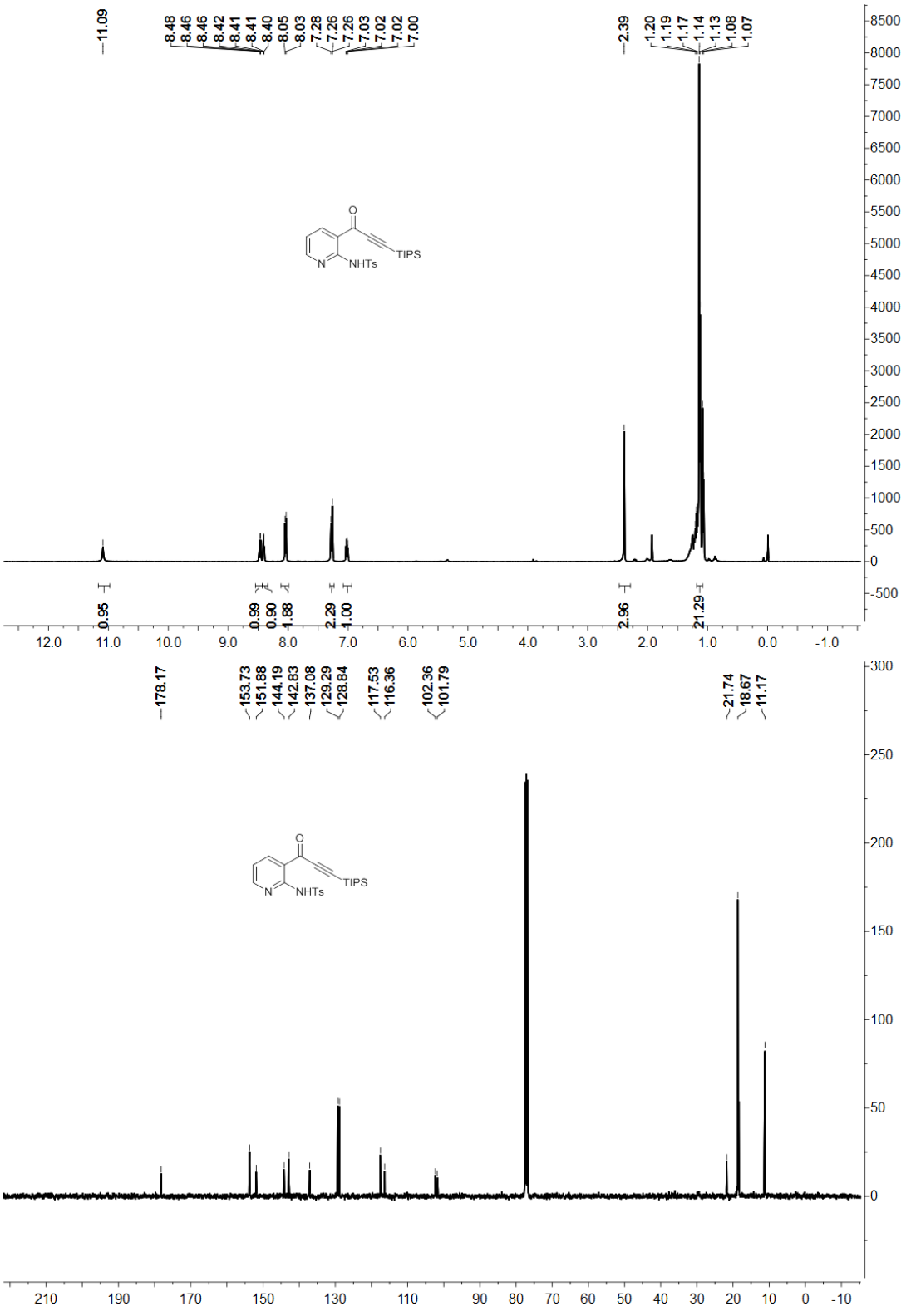
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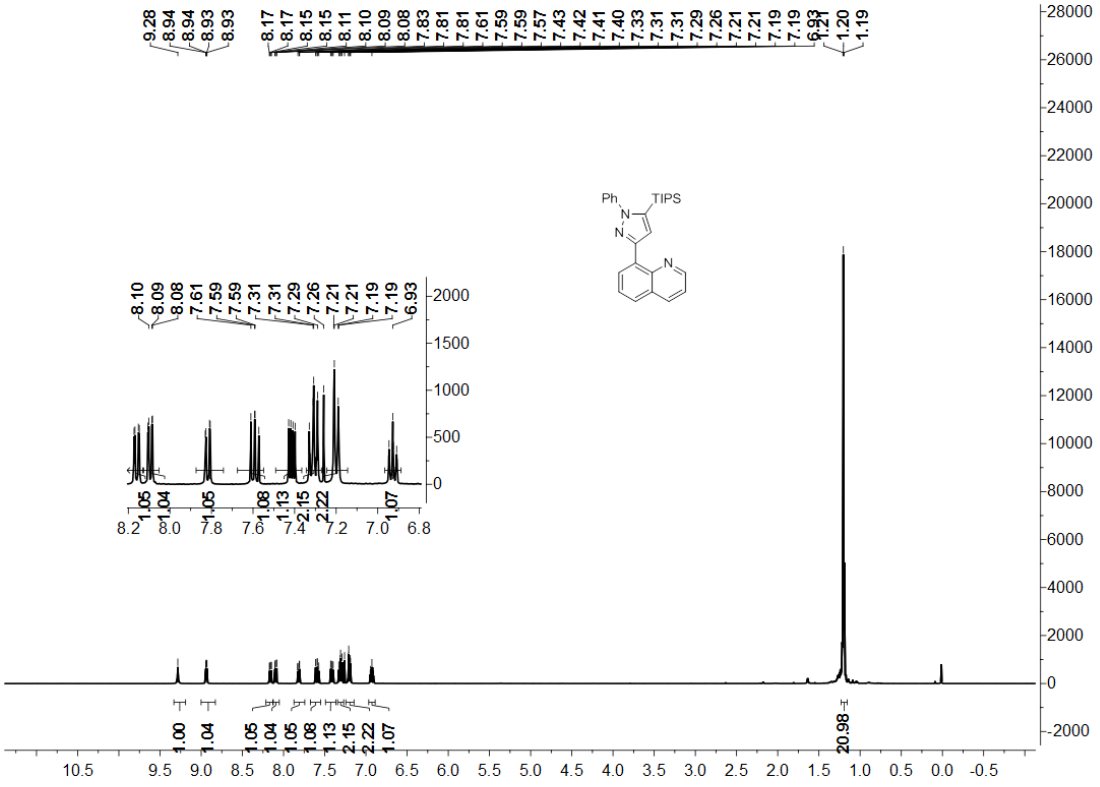
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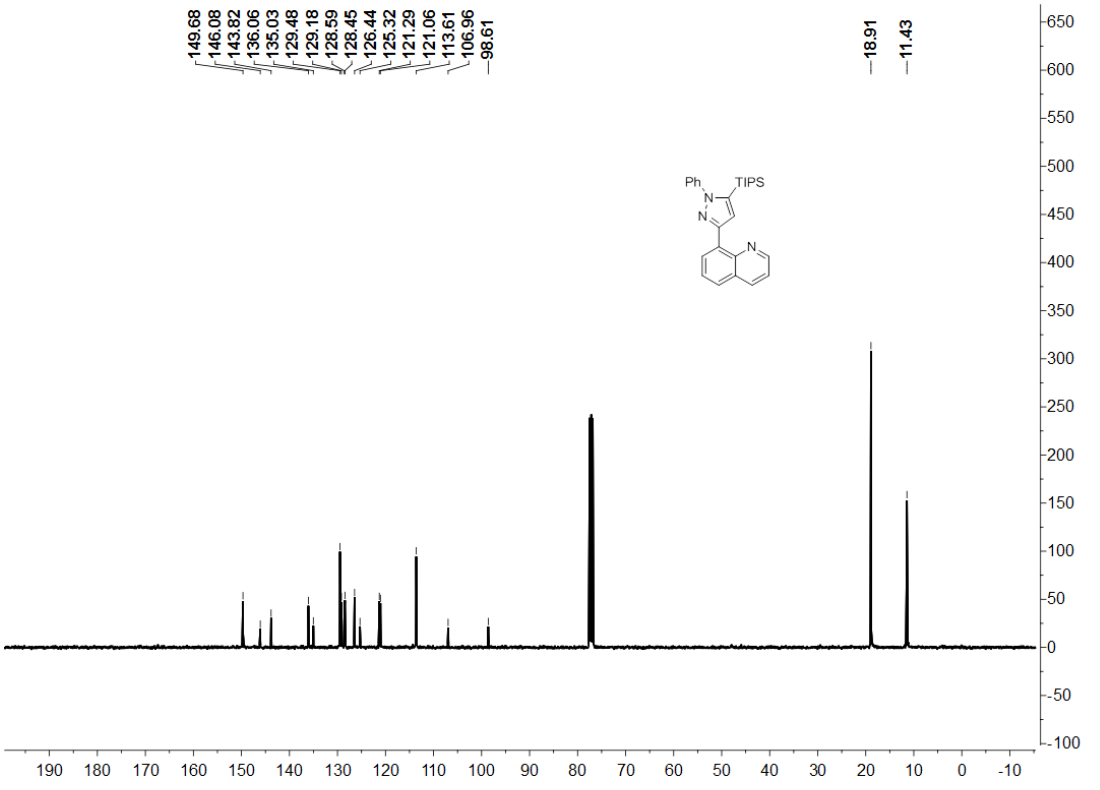
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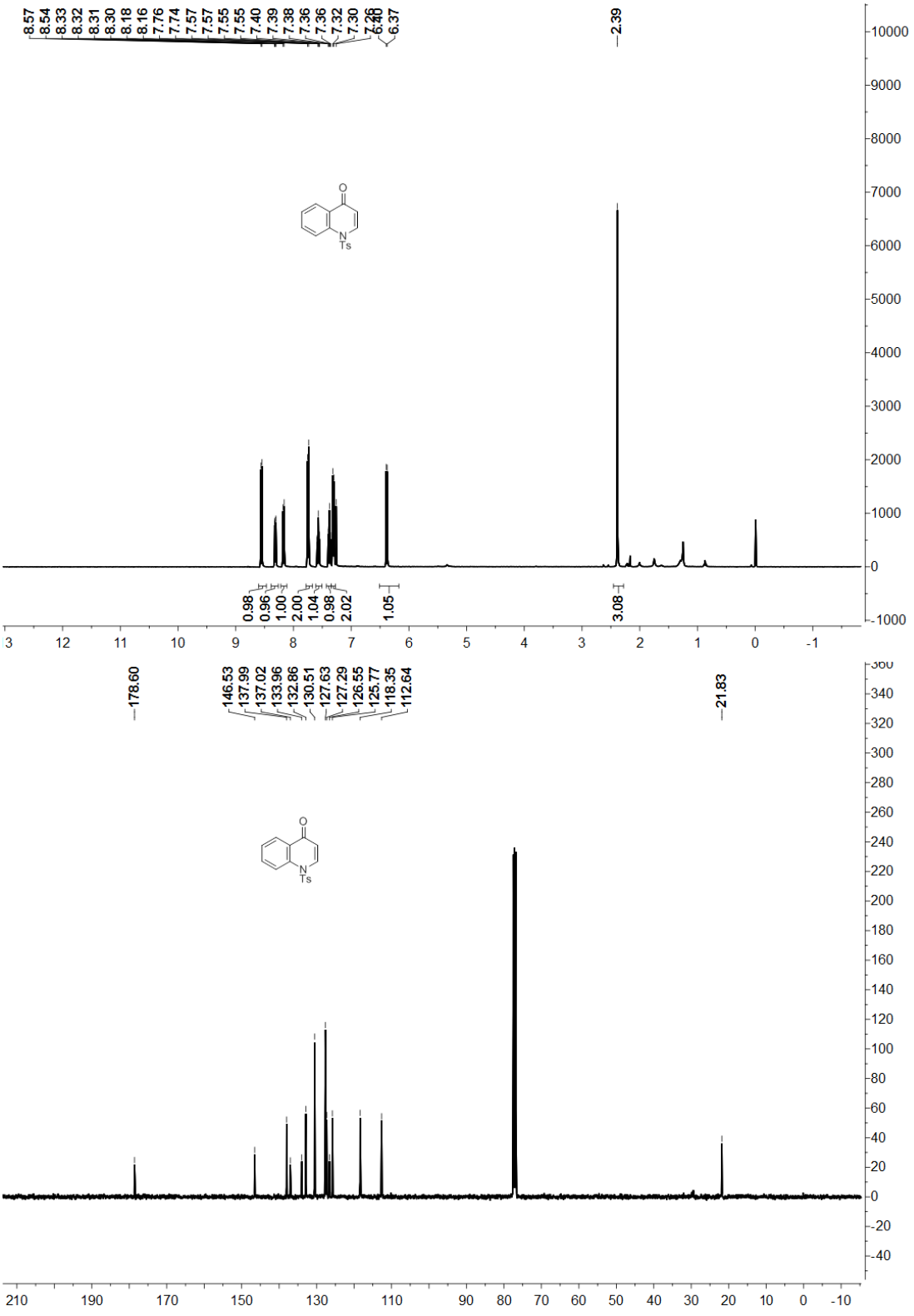
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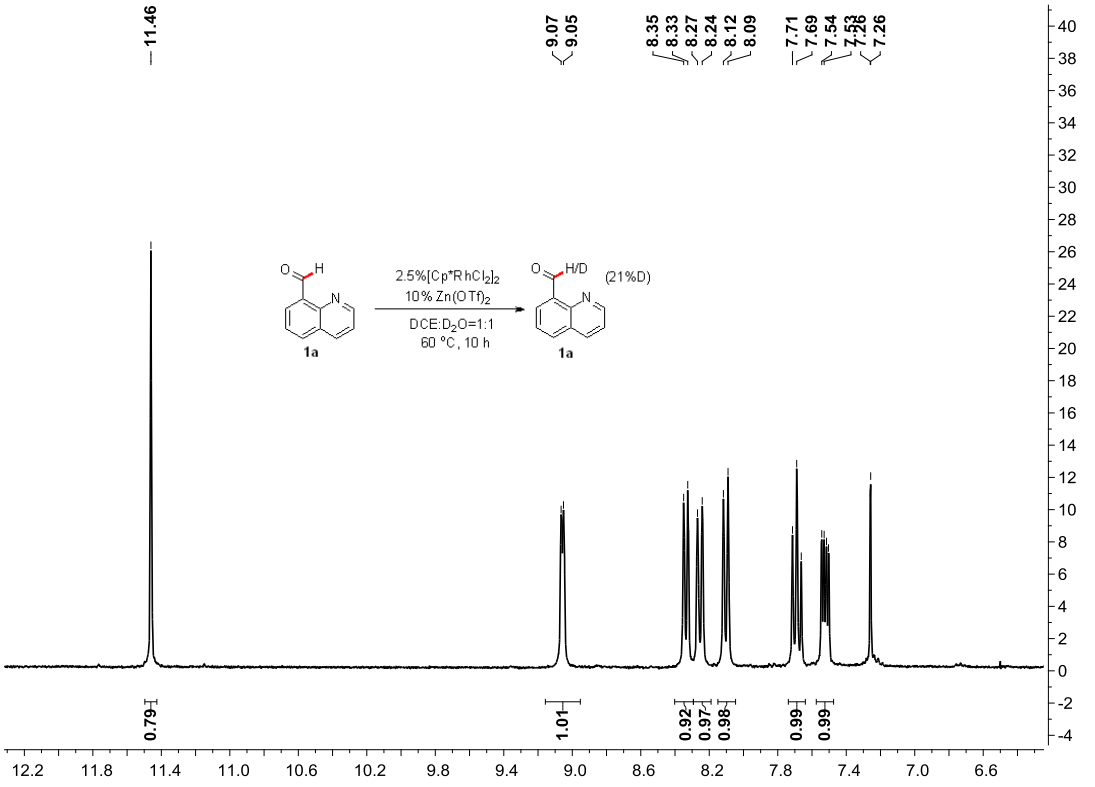
Ts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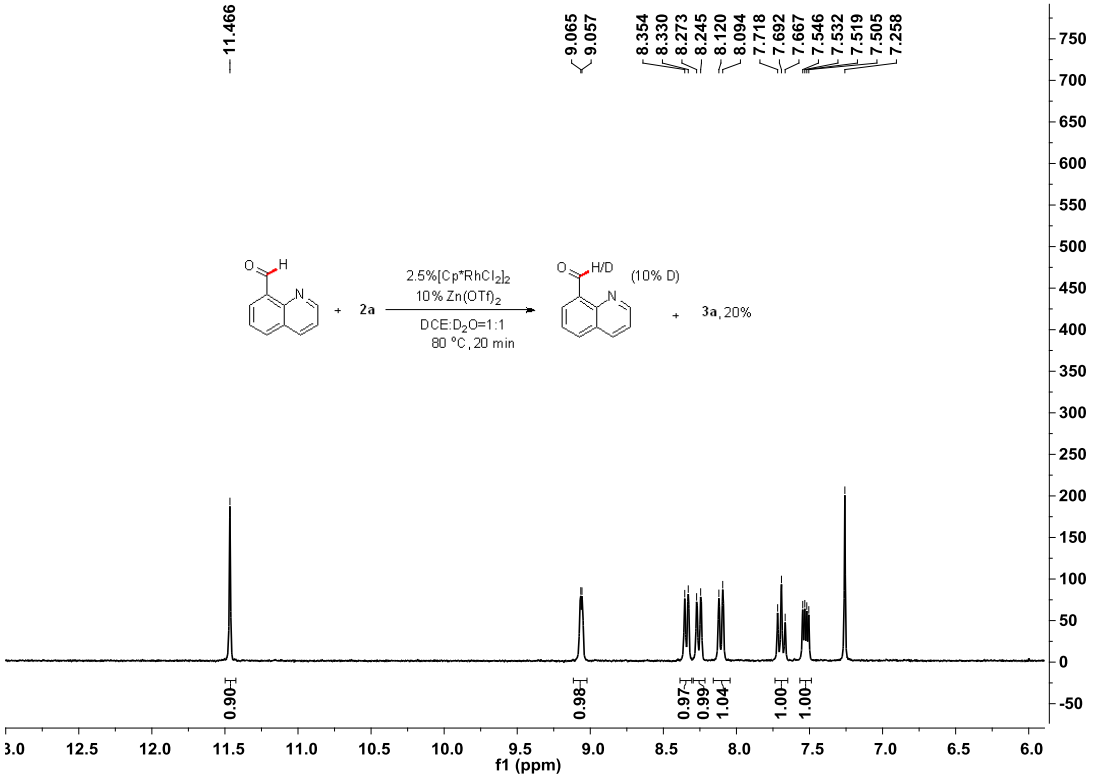
8.12
8.09
7.71
7.69
7.54
7.53
7.26
2.5%[Cp*RhCl2]2
10% Zn(OTf)2
DCE:D2O=1:1
60 °C, 10 h
1a
H/D
(21%D)
1a
0.79
1.01
0.92
0.97
0.98
0.99
0.99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9.057
8.354
8.330
8.273
8.245
8.120
8.094
7.718
7.692
7.667
7.546
7.532
7.519
7.505
7.258
2.5%[Cp*RhCl2]2
10% Zn(OTf)2
DCE:D2O=1:1
80 °C, 20 min
2a
H/D
(10% D)
3a, 20%
0.90
0.98
0.97
0.99
1.04
1.00
1.00
f1 (ppm)