Palladium-Catalyzed Oxalyl Amide Assisted Direct *ortho*-Alkynylation of Arylalkylamines Derivatives at δ and ε Positions

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Supporting information

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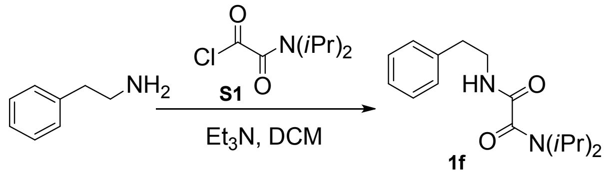
1. Reagents: Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 300–400 mesh silica gel.

2. Instruments: NMR spectra were recorded on Varian Inova–400 MHz, Inova–300 MHz, Bruker DRX–400 or Bruker DRX–500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br = broad singlet, m = multiplet. HRMS analyses were carried out using a Bruker micrOTOF–Q instrument or a TOF–MS instrument.

3. Preparation of Oxalamide Substrates



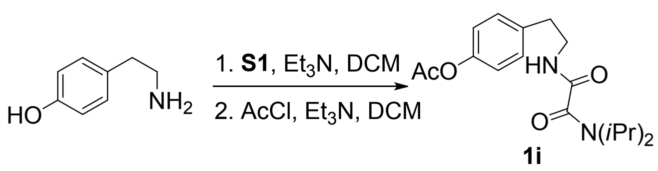
3.1 Preparation of N, N–Diisopropyloxamoyl Chloride S1[1]

A solution of Diisopropylamine (7.01 mL, 50 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was added dropwise to a solution of oxalyl chloride (6.44 ml, 75 mmol, 1.5 equiv) in CH_2Cl_2 (100 mL) at 0 °C, after stirring for 5 min, triethylamine (7.30 mL, 52.5 mmol, 1.05 equiv) was added dropwise. The solution was warmed to room temperature and stirred for 6 hours. The excess of oxalyl chloride and the solvent were removed under reduce pressure and CH_2Cl_2 (30 mL) was added and evaporated. This operation was performed twice to give **1f** as a pale yellow solid. The crude product was used in the next step without any purification.

3.2 General procedures for the preparation of oxalamide substrates 1a-1r (except 1i, 1k, 1l, 1q), 4a-4h, 4j[2]

A solution of amine (20 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) was added dropwise to a solution of N,N–Diisopropyloxamoyl chloride **S1** (25 mmol, 1.25 equiv) in CH_2Cl_2 (50 mL) at 0 °C, after stirring for 5 min, triethylamine (2.92 ml, 21 mmol, 1.05 equiv) was added dropwise and then the mixture was stirred for 6 hours at room temperature before quenched by water (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel afforded corresponding amide substrates as white solid or colourless liquid with >90% yield

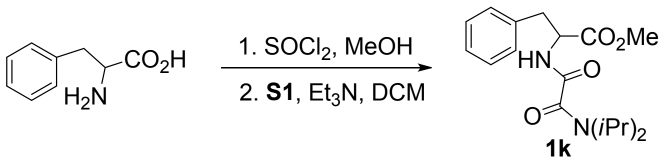
3.3 Preparation of 1i[3]



The first step using 4–(2–aminoethyl)phenol (2.74 g, 20 mmol, 1.0 equiv) as starting material followed the general oxalamide coupling procedure, affording a white solid. The solid was dissolved in DCM

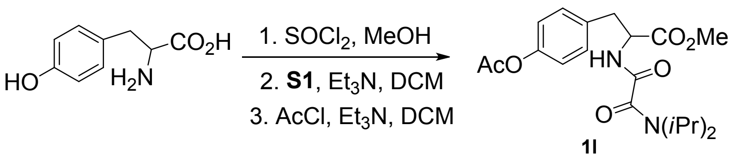
(30 mL) and treated with AcCl (1.56 mL, 22 mmol, 1.1 equiv) and Et_3N (5.56 mL, 40 mmol, 2.0 equiv) at room temperature overnight. Water was added and the mixture was extracted with DCM. The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the product **1i** 4.21 g, 63%.

3.4 Preparation of 1k[4]



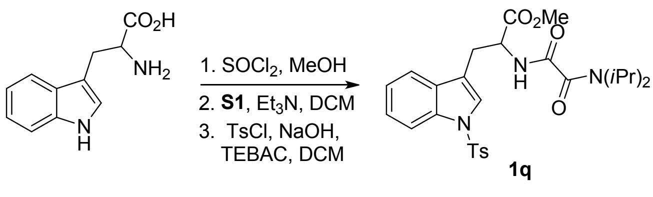
To a solution of homophenylalanine (3.30g, 20 mmol, 1.0 equiv) in MeOH (30 mL), at 0 °C, was added $SOCl_2$ (4.35 mL, 60 mmol, 3.0 equiv) dropwise. The resulting mixture was allowed to stir from 0 °C to room temperature overnight. The solvent was removed under reduced pressure to afford a white solid, which was used directly for next step. The second step followed the general oxalamide coupling procedure, to give the product **1k** 5.21 g, 78%.

3.5 Preparation of 1l



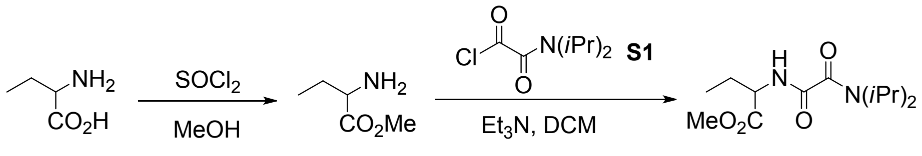
To a solution of homophenylalanine (3.30g, 20 mmol, 1.0 equiv) in MeOH (30 mL), at 0 °C, was added $SOCl_2$ (4.35 mL, 60 mmol, 3.0 equiv) dropwise. The resulting mixture was allowed to stir from 0 °C to room temperature overnight. The solvent was removed under reduced pressure to afford a white solid, which was used directly for next step. The second step followed the procedure of **1i** to give the product **1l** 5.65 g, 72%.

3.6 Preparation of 1q [5]



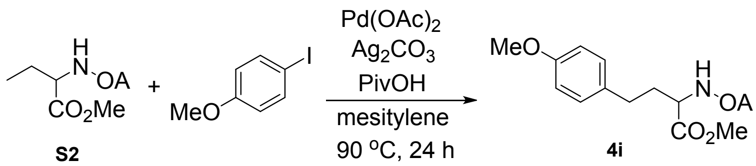
To a solution of tryptophan (2 g, 10 mmol, 1.0 equiv) in MeOH (20 mL), at 0 °C, was added $SOCl_2$ (2.1 mL, 30 mmol, 3.0 equiv) dropwise. The resulting mixture was allowed to stir from 0 °C to room temperature overnight. The solvent was removed under reduced pressure to afford a white solid, which was used directly for next step. The second step followed the procedure of **1a**. Then TsCl (15 mmol, 1.5 equiv), NaOH (0.8 g, 20 mmol, 2.0 equiv), TEBAC (3.4 g, 15 mmol, 1.5 equiv) were added, the resulting mixture was allowed to stir at room temperature overnight. Water was added and the mixture was extracted with DCM. The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the product **1q** 3.90 g, 74%.

3.7 Preparation of 1q

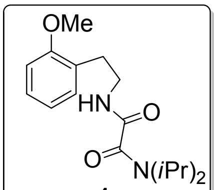


S2

$SOCl_2$ (4.35 mL, 60 mmol, 3.0 equiv) was added dropwise to a solution of amino acid (20 mmol, 1.0 equiv) in MeOH (30 mL) at 0 °C. The resulting mixture was allowed to stir from 0 °C to rt overnight. The solvent was removed under reduced pressure to give white solid, which was used directly for next step. A solution of white solid (20 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) was added dropwise to a solution of N,N–Diisopropyloxamoyl chloride **S1** (25 mmol, 1.25 equiv) in CH_2Cl_2 (50 mL) at 0 °C, after stirring for 5 min, triethylamine (2.92 mL, 21 mmol, 1.05 equiv) was added dropwise and then the mixture was stirred for 6 hours at room temperature before quenched by water (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel afforded corresponding amide substrates as white solid or colourless oil with >70% yield.

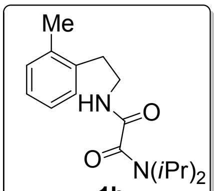


A mixture of **S2** (545 mg, 2 mmol), ArI (3 mmol, 1.5 equiv), $Pd(OAc)_2$ (22 mg, 5 mol %), Ag_2CO_3 (552 mg, 1.0 equiv), PivOH (61 mg, 0.3 equiv) and 6 mL mesitylene in a 25 mL glass vial was heated at 90 °C with vigorous stirring for 24 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuoand purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:20 to 1:2) to give product **4i** 643mg, 85%.



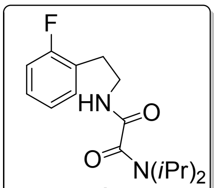
1a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.6 Hz, 1H), 7.14–7.13 (m , 2H), 6.90–6.84 (m, 2H), 4.62–4.59 (m, 1H), 3.82 (s, 3H), 3.53–3.43 (m, 3H), 2.86 (t, J = 6.7 Hz, 2H), 1.39 (d, J = 6.7 Hz, 6H), 1.18 (d, J = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41, 157.56, 130.64, 128.00, 127.12, 120.69, 110.36, 55.30, 49.64, 46.45, 39.65, 30.13, 20.92, 20.11. This compound was known. [5]



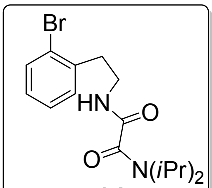
1b

[1]H NMR (400 MHz, $CDCl_3$) δ 7.15–7.14 (m, 5H), 4.68–4.62 (m, 1H), 3.53–3.48 (m, 3H), 2.88–2.84 (m, 2H), 2.34 (s, 3H), 1.41 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.7 Hz, 6H); [13]C NMR (101 MHz, $CDCl_3$) δ 163.41, 163.28, 136.77, 136.46, 130.55, 129.36, 126.78, 126.24, 49.75, 46.58, 39.47, 32.98, 20.96, 20.15, 19.45. This compound was known. [5]



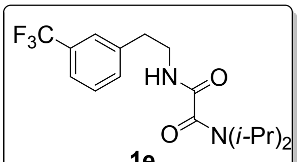
1c

[1]H NMR (400 MHz, $CDCl_3$) δ 7.20–7.18 (m, 2H), 7.10–7.06 (m, 1H), 7.05–7.00 (m, 1H), 6.93 (br s, 1H), 4.67–4.60 (m, 1H), 3.58–3.53 (m, 2H), 3.51–3.46 (m, 1H), 2.90 (t, J = 7.1 Hz, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.22 (t, J = 11.6 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 163.49, 163.27, 161.40 (d, J_{C-F} = 244 Hz), 131.18 (d, J_{C-F} = 5.0 Hz), 128.47 (d, J_{C-F} = 8.0 Hz), 125.63 (d, J_{C-F} = 16.0 Hz), 124.30 (d, J_{C-F} = 4.0 Hz), 115.48 (d, J_{C-F} = 22.0 Hz), 49.76, 46.55, 39.38, 29.02 (d, J_{C-F} = 2.0 Hz), 20.93, 20.15. This compound was known. [5]



1d

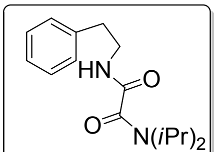
[1]H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.9 Hz, 1H), 7.29 (br s, 1H), 7.26–7.20 (m, 2H), 7.07–7.03 (m, 1H), 4.55–4.52 (m, 1H), 3.57–3.52 (m, 2H), 3.49–3.42 (m, 1H), 2.98 (t, J = 7.2 Hz, 2H), 1.37 (d, J = 6.8 Hz, 6H), 1.17 (d, J = 6.7 Hz, 6H); [13]C NMR (101 MHz, $CDCl_3$) δ 163.49, 163.40, 138.04, 132.95, 130.97, 128.32, 127.65, 124.63, 49.73, 46.44, 38.96, 35.65, 20.87, 20.09. This compound was known. [5]



1e

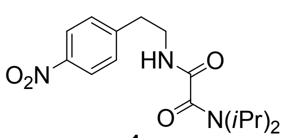
[1]H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.43 (t, J = 6.7 Hz, 2H), 7.17 (br s, 1H), 4.63–4.57 (m, 1H), 3.60–3.55 (m, 2H), 3.53–3.46 (m, 1H), 2.93 (t, J = 7.2 Hz, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H); [13]C NMR (101 MHz, $CDCl_3$) δ 163.58, 163.42, 139.68, 132.32, 130.98 (q, J_{C-F} =

32 Hz), 129.14, 125.60 (q, J_{C-F} = 4 Hz), 124.22 (q, J_{C-F} = 270 Hz), 123.55 (q, J_{C-F} = 4 Hz), 49.89, 46.58, 40.24, 35.33, 20.86, 20.12. This compound was known. [5]



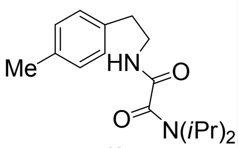
1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 2H), 7.23–7.20 (m, 3H), 7.11 (br s, 1H), 4.60–4.53 (m, 1H), 3.58–3.53 (m, 2H), 3.52–3.45 (m, 1H), 2.86 (t, J = 7.2 Hz, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.45, 163.41, 138.68, 128.85, 128.70, 126.62, 49.78, 46.52, 40.53, 35.55, 20.92, 20.16. This compound was known.[5]



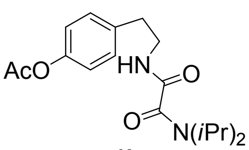
1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.16 (m, 2H), 7.40–7.38 (m, 2H), 7.14 (br s, 1H), 4.63–4.57 (m, 1H), 3.61–3.55 (m, 2H), 3.53–3.46 (m, 1H), 2.97 (t, J = 7.1 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.52, 163.16, 146.94, 146.53, 129.80, 123.92, 49.87, 46.64, 39.96, 35.47, 20.91, 20.13. This compound was known. [5]



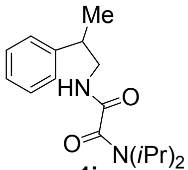
1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.6 Hz, 4H), 6.95 (br s, 1H), 4.65–4.58 (m, 1H), 3.55–3.45 (m, 3H), 2.81 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.40 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 163.26, 136.18, 135.53, 129.44, 128.74, 49.75, 46.58, 40.68, 35.14, 21.14, 20.96, 20.18. This compound was known. [5]



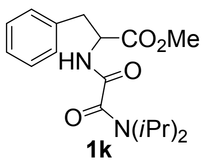
1i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 3H), 6.99 (d, J = 8.4 Hz, 2H), 4.52–4.47 (m, 1H), 3.54–3.49 (m, 2H), 3.48–3.43 (m, 1H), 2.82 (t, J = 7.2 Hz, 2H), 2.26 (s, 3H), 1.38 (d, J = 6.8 Hz, 6H), 1.17 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58, 163.54, 163.52, 149.34, 136.26, 129.77, 121.69, 49.82, 46.42, 40.38, 34.88, 21.17, 20.85, 20.11. This compound was known. [5]



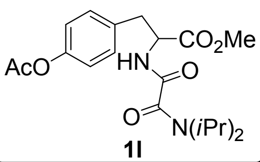
1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.23–7.19 (m, 3H), 6.94 (br s, 1H), 4.42–4.37 (m, 1H), 3.54–3.39 (m, 3H), 3.03–2.94 (m, 1H), 1.38–1.35 (m, 6H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.16–1.12 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.54, 143.93, 128.72, 127.28, 126.77, 49.83, 46.40, 45.86, 39.78, 20.88, 20.16, 20.14, 19.45. This compound was known. [5]



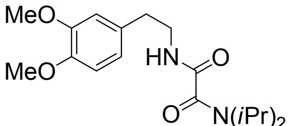
1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.16 (m, 6H), 4.87–4.84 (m, 1H), 4.39–4.34 (m, 1H), 3.72 (s, 3H), 3.49–3.46 (m, 1H), 3.22–3.07 (m, 2H), 1.42–1.40 (m, 6H), 1.18–1.16 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.32, 162.95, 135.74, 129.34, 128.69, 127.21, 53.24, 52.52, 49.81, 46.50, 38.03, 20.90, 20.81, 20.10. This compound was known. [5]



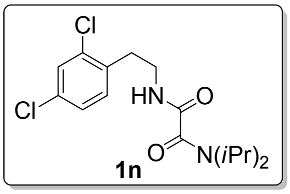
1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.5 Hz, 3H), 7.11 (br s, 1H), 7.04 – 7.00 (m, 2H), 4.86 – 4.81 (m, 1H), 4.47 – 4.41 (m, 1H), 3.71 (s, 3H), 3.53 – 3.45 (m, 1H), 3.17 (dd, *J* = 14.0, 5.8 Hz, 1H), 3.08 (dd, *J* = 14.0, 6.7 Hz, 1H), 2.27 (s, 4H), 1.41 (dd, *J* = 6.8, 2.7 Hz, 7H), 1.18 (d, *J* = 6.6 Hz, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.17, 169.47, 162.94, 162.53, 149.95, 133.37, 130.41, 121.86, 53.25, 52.60, 49.83, 46.63, 37.55, 21.25, 20.94, 20.90, 20.17; HRMS (ESI-TOF) m/z [M–H^{+}] Calcd for $C_{20}H_{27}N_2O_6$: 391.1869; Found: 391.1865.

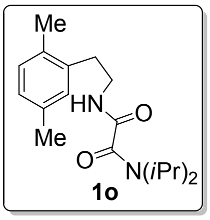


1m

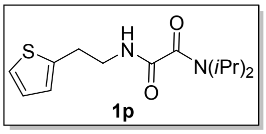
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (br s, 1H), 6.81–6.78 (m, 1H), 6.74 (dd, *J* = 5.9, 1.8 Hz, 2H), 4.61–4.54 (m, 1H), 3.85 (d, *J* = 9.5 Hz, 6H), 3.54–3.44 (m, 3H), 2.78 (t, *J* = 7.1 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 6H), 1.18 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41, 163.29, 149.09, 147.80, 131.16, 120.77, 112.02, 111.45, 56.00, 55.94, 49.76, 46.54, 40.60, 35.16, 20.91, 20.14. This compound was known. [4]



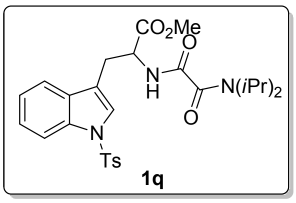
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (br s, 1H), 7.28 (s, 1H), 7.22–7.17 (m, 2H), 4.57–4.52 (m, 1H), 3.57–3.52 (m, 2H), 3.51–3.46 (m, 1H), 2.97 (t, J = 7.1 Hz, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.52, 163.26, 134.99, 134.92, 133.12, 131.82, 129.45, 127.29, 49.81, 46.55, 38.71, 32.76, 20.90, 20.12. This compound was known. [5]



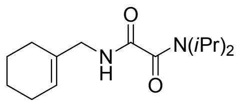
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (br s, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.00–6.90 (m, 2H), 4.64 (m, 1H), 3.60–3.35 (m, 3H), 2.92–2.71 (m, 2H), 2.29 (d, J = 4.9 Hz, 6H), 1.41 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.55, 163.46, 136.54, 135.46, 133.16, 130.30, 130.05, 127.30, 53.51, 49.73, 46.40, 39.48, 32.85, 20.89, 20.82, 20.05, 18.83. This compound was known. [5]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (br s, 1H), 7.13 (d, J = 4.9 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.85 (s, 1H), 4.59 – 4.52 (m, 1H), 3.55 (dd, J = 13.1, 6.6 Hz, 2H), 3.51 – 3.44 (m, 1H), 3.06 (t, J = 6.8 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 163.42, 140.98, 127.09, 125.47, 123.95, 49.81, 46.47, 40.69, 29.63, 20.88, 20.13; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{14}H_{22}N_2O_2SNa$: 305.1300; found: 305.1299.

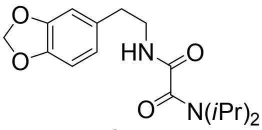


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.7 Hz, 1H), 7.43 (s, 1H), 7.33–7.27 (m, 2H), 7.25–7.19 (m, 3H), 4.87 (m, J = 8.0, 6.1 Hz, 1H), 4.56 (m, J = 13.3, 6.7 Hz, 1H), 3.62 (s, 3H), 3.50 (m, J = 13.6, 6.8 Hz, 1H), 3.24 (t, J = 6.4 Hz, 2H), 2.33 (s, 3H), 1.42 (dd, J = 6.8, 3.1 Hz, 6H), 1.19 (t, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.19, 162.95, 162.27, 145.01, 135.23, 135.16, 130.67, 130.02, 127.01, 125.04, 124.71, 123.39, 119.45, 116.85, 113.83, 52.68, 52.27, 49.84, 46.73, 27.73, 21.71, 20.94, 20.92, 20.17; HRMS (ESI-TOF) m/z $[M+Na^+]$ Calcd for $C_{27}H_{33}N_3O_6S$: 550.1988; Found: 550.1997.



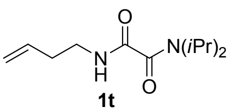
1r

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (br s, 1H), 5.48 (s, 1H), 4.70 (m, 1H), 3.50 (m, 1H), 3.35 (m, 2H), 2.16 (t, J = 6.8 Hz, 2H), 1.97 (m, 4H), 1.65-1.58 (m, 2H), 1.57-1.50 (m, 2H), 1.41 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.32, 163.27, 134.38, 123.73, 49.77, 46.60, 37.52, 37.36, 28.10, 25.36, 22.94, 22.44, 21.01, 20.22; HRMS (ESI-TOF) m/z [M+Na^+] Calcd for $C_{15}H_{26}N_2NaO_2$: 289.1892; Found: 289.1901.



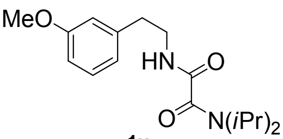
1s

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (br s, 1H), 6.73 (d, J = 7.9 Hz, 1H), 6.69 (d, J = 1.4 Hz, 1H), 6.65 (dd, J = 7.9, 1.6 Hz, 1H), 5.91 (s, 2H), 4.62–4.55 (m, 1H), 3.51–3.44(m, 3H), 2.76 (t, J = 7.1 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41, 163.33, 147.87, 146.30, 132.39, 121.77, 109.18, 108.46, 100.99, 49.79, 46.54, 40.73, 35.24, 20.92, 20.15. This compound was known. [4]



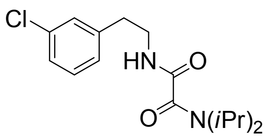
1t

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (br s, 1H), 5.82 – 5.71 (m, 1H), 5.15 – 5.06 (m, 2H), 4.72 – 4.67 (m, 1H), 3.51 – 3.46 (m, 1H), 3.35 (dd, J = 12.9, 6.7 Hz, 2H), 2.33 – 2.26 (m, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 134.99, 117.39, 49.76, 46.53, 38.46, 33.48, 20.92, 20.16; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{12}H_{22}N_2O_2Na$: 249.1579; found: 249.1580.



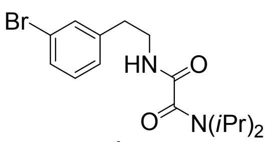
1u

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.18 (m, 1H), 7.10 (br s, 1H), 6.80 (d, J = 7.7 Hz, 1H), 6.77–6.75 (m, 2H), 4.58–4.52 (m, 1H), 3.78 (s, 3H), 3.56–3.51 (m, 2H), 3.49–3.44 (m, 1H), 2.82 (t, J = 7.2 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.46, 159.87, 140.22, 129.68, 121.15, 114.36, 112.18, 55.25, 49.80, 46.50, 40.39, 35.57, 20.90, 20.14. This compound was known. [5]



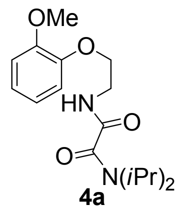
1v

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.6 Hz, 1H), 7.21–7.17 (m, 3H), 7.10 (d, J = 7.0 Hz, 1H), 4.53–4.46 (m, 1H), 3.56–3.50 (m, 2H), 3.49–3.44 (m, 1H), 2.83 (t, J = 7.2 Hz, 2H), 1.38 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.55, 163.45, 140.75, 134.40, 129.94, 128.99, 127.07, 126.83, 49.90, 46.54, 40.21, 35.16, 20.91, 20.15. This compound was known. [5]



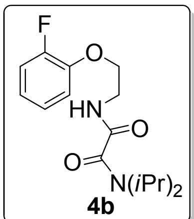
1w

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (br s, 1H), 7.38 (s, 1H), 7.35–7.34 (m, 1H), 7.16 (d, J = 4.6 Hz, 2H), 4.46–4.41 (m, 1H), 3.57–3.52 (m, 2H), 3.50–3.44 (m, 1H), 2.84 (t, J = 7.2 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.65, 163.61, 141.08, 131.85, 130.15, 129.66, 127.49, 122.58, 49.93, 46.40, 40.11, 35.03, 20.85, 20.11. This compound was known. [5]



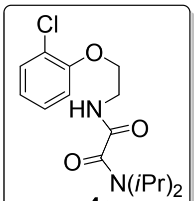
4a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (br s, 1H), 6.98–6.87 (m, 4H), 4.67–4.61 (m, 1H), 4.13–4.10 (m, 2H), 3.86 (s, 3H), 3.70–3.66 (m, 2H), 3.53–3.46 (m, 1H), 1.42 (d, J = 6.6 Hz, 6H), 1.21 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.72, 171.32, 162.95, 135.74, 129.34, 128.69, 127.21, 53.24, 52.52, 49.81, 46.50, 38.03, 20.90, 20.81, 20.10. This compound was known. [5]



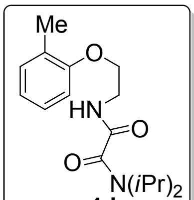
4b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (br s, 1H), 7.11 – 7.01 (m, 2H), 7.09–7.02 (m, 2H), 4.68–4.64 (m, 1H), 4.14 (t, J = 5.2 Hz, 2H), 3.74–3.70 (m, 2H), 3.54–3.47 (m, 1H), 1.41 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.66, 162.91, 152.92 (d, $J_{C-F=}$ 244 Hz), 146.65 (d, $J_{C-F=}$ 10 Hz), 124.50 (d, $J_{C-F=}$ 4 Hz), 121.98 (d, $J_{C-F=}$ 7 Hz), 116.49 (d, $J_{C-F=}$ 18 Hz), 115.56, 68.04, 49.85, 46.67, 38.89, 20.95, 20.16. This compound was known. [5]



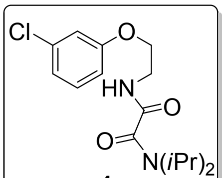
4c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.30 (br s, 1H), 7.22–7.18 (m, 1H), 6.93–6.89 (m, 2H), 4.69–4.66 (m, 1H), 4.13 (t, *J* = 5.2 Hz, 2H), 3.77–3.73 (m, 2H), 3.52–3.49 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63, 162.87, 154.07, 130.51, 127.92, 123.35, 122.22, 114.04, 67.80, 49.81, 46.69, 38.81, 20.98, 20.17. This compound was known. [5]



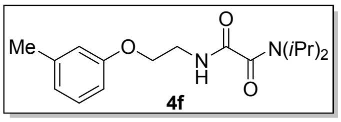
4d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (br s, 1H), 7.14 (t, *J* = 6.7 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.78–4.74 (m, 1H), 4.07 (t, *J* = 5.2 Hz, 2H), 3.74–3.70 (m, 2H), 3.53–3.49 (m, 1H), 2.23 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 162.78, 156.58, 130.90, 126.93, 120.98, 111.08, 66.39, 49.73, 46.71, 39.07, 20.97, 20.15, 16.37. This compound was known. [5]



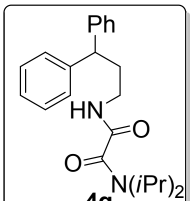
4e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (br s, 1H), 7.17 (t, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.86 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.69–4.62 (m, 1H), 4.03 (t, *J* = 5.2 Hz, 2H), 3.69–3.65 (m, 2H), 3.52–3.45 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.51, 162.94, 159.17, 134.94, 130.36, 121.37, 115.01, 112.95, 66.47, 49.81, 46.62, 38.72, 20.90, 20.11. This compound was known. [5]



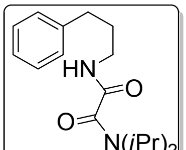
4f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (br s, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 4.71 – 4.67 (m, 1H), 4.04 (t, *J* = 5.2 Hz, 2H), 3.68 (dd, *J* = 10.9, 5.5 Hz, 2H), 3.53 – 3.46 (m, 1H), 2.31 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 162.99, 158.46, 139.61, 129.30, 122.03, 115.43, 111.38, 66.10, 49.74, 46.59, 38.90, 21.56, 20.90, 20.12; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{17}H_{25}N_2O_3Na$: 329.1841; found: 329.1838.



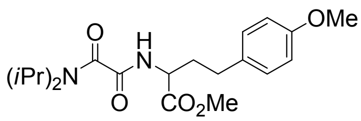
4g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 8H), 7.18 (t, *J* = 6.9 Hz, 2H), 6.96 (br s, 1H), 4.80–4.74 (m, 1H), 3.99 (t, *J* = 7.9 Hz, 1H), 3.54–3.48 (m, 1H), 3.26–3.21 (m, 2H), 2.36–2.30 (m, 2H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.28, 163.16, 144.06, 128.70, 127.83, 126.51, 49.71, 48.89, 46.61, 38.22, 34.83, 20.97, 20.17. This compound was known. [5]



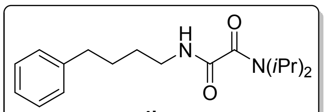
4h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.22–7.19 (m, 3H), 7.12 (br s, 1H), 4.79–4.73 (m, 1H), 3.55–3.50 (m, 1H), 3.36–3.31 (m, 2H), 2.71–2.67 (m, 2H), 1.94–1.87 (m, 2H), 1.44 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.36, 163.26, 141.32, 128.57, 128.49, 126.13, 49.77, 46.67, 39.03, 33.28, 30.92, 20.98, 20.19. This compound was known. [5]



4i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.68–4.62 (m, 1H), 4.59–4.54 (m, 1H), 3.74 (d, *J* = 20.0 Hz, 6H), 3.55–3.48(m, 1H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.23–2.14 (m, 1H), 2.07–1.98 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 6H), 1.23 (dd, *J* = 6.4, 4.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.02, 163.15, 162.61, 158.15, 132.48, 129.47, 114.01, 55.34, 52.56, 51.98, 49.79, 46.68, 34.01, 30.82, 20.97, 20.94, 20.22, 20.14; HRMS (ESI-TOF) m/z [M+H$^+$] Calcd for $C_{20}H_{31}N_2O_5$: 379.2233; Found: 379.2230.

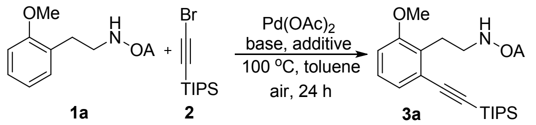


4j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.17 (dd, *J* = 10.4, 4.5 Hz, 3H), 4.68 (br s, 1H), 3.53 – 3.46 (m, 1H), 3.29 (dd, *J* = 13.1, 6.8 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.62 – 1.54 (m, 2H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 142.11, 128.47, 128.39, 125.87, 49.75, 46.54, 39.18, 35.51, 28.87, 28.73, 20.91, 20.15; HRMS (ESI-TOF) m/z [M+H$^+$] Calcd for $C_{18}H_{29}N_2O_2$: 305.2229; Found: 305.2231.

4. Optimization of Reaction Conditions[a]

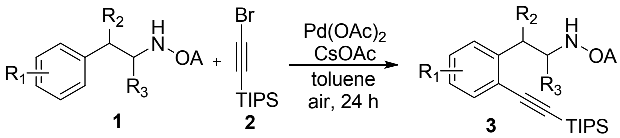
Table 1S Optimization of Reaction Conditions



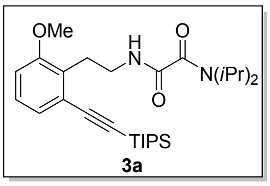
entry	$Pd(OAc)_2$ (mol %)	base	additive (equiv)	Yield (%)
1	5	–	AgOAc (2), PivOH (0.3)	67
2	5	LiOAc	–	4
3	5	NaOAc	–	31
4	5	KOAc	–	62
5	5	CsOAc	–	93(**85**[b])
6	5	Na_2CO_3	–	22
7	5	K_2CO_3	–	36
8	5	$KHCO_3$	–	56
9	5	Na_2CO_3	PivOH (0.3)	47
10	5	K_2CO_3	PivOH (0.3)	36
11	5	CsOAc	PivOH (0.3)	51
12	–	CsOAc	–	NR

[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.12 mmol), $Pd(OAc)_2$ (5 mol %), base (2 equiv), toluene (0.5 mL), 100 °C, air, 24 h. Yield was based on LC using acetophenone as the internal standard. [b]Isolated yield at 0.2 mmol scale.

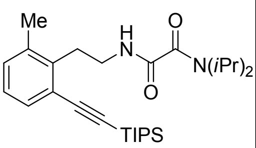
5. *ortho*-Alkynylation of *β*-Arylethamine Derivatives



A mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (1.1 mg, 0.05 equiv), CsOAc (76.8 mg, 2 equiv), toluene (0.5 mL) in a 15 mL glass vial (sealed with PTFE cap) was heated at 80 °C for 24 hours. The reaction mixture was cooled to rt, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the alkynylation product.

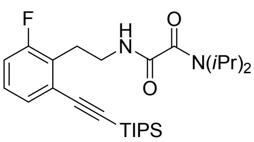


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (br s, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.10 – 7.07 (m, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.64 – 4.57 (m, 1H), 3.83 (s, 3H), 3.53 (dd, *J* = 12.2, 6.2 Hz, 2H), 3.48 – 3.42 (m, 1H), 3.15 (t, *J* = 6.6 Hz, 2H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.7 Hz, 6H), 1.12 (s, 18H), 1.10 – 1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.26, 163.14, 157.56, 129.75, 127.42, 125.30, 124.75, 110.88, 105.09, 94.78, 55.63, 49.45, 46.43, 39.60, 27.41, 20.92, 20.08, 18.77, 11.39; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_3SiNa$: 509.3175; found: 509.3177.



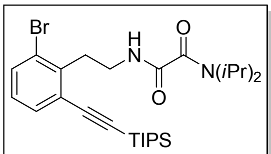
3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.1 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.92 (br s, 1H), 4.68 – 4.62 (m, 1H), 3.55 (dd, J = 14.4, 6.6 Hz, 2H), 3.52 – 3.45 (m, 1H), 3.14 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H), 1.41 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H), 1.13 (s, 18H), 1.12 – 1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 163.02, 138.99, 137.16, 131.04, 130.94, 126.39, 123.81, 106.03, 94.24, 49.59, 46.59, 38.97, 31.20, 20.99, 20.14, 19.93, 18.83, 11.46; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_2SiNa$: 493.3226; found: 493.3217.



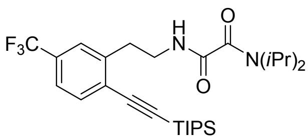
3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.1 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.01 (t, J = 8.6 Hz, 1H), 6.90 (br s, 1H), 4.64 – 4.57 (m, 1H), 3.63 – 3.58 (m, 2H), 3.51 – 3.44 (m, 1H), 3.13 (t, J = 6.3 Hz, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H), 1.13 (d, J = 2.8 Hz, 18H), 1.10 (dd, J = 9.8, 4.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 163.08, 161.30 (d, $J_{C-F=}$ 244 Hz), 128.86, 128.06 (d, $J_{C-F=}$ 17 Hz), 127.86 (d, $J_{C-F=}$ 9 Hz), 125.61 (d, $J_{C-F=}$ 5 Hz), 115.85 (d, $J_{C-F=}$ 23 Hz), 103.87 (d, $J_{C-F=}$ 4 Hz), 96.13, 49.60, 46.49, 38.88, 27.23, 20.90, 20.11, 18.75, 11.35; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.66; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}FN_2O_2SiNa$: 497.2976; found: 497.2972.



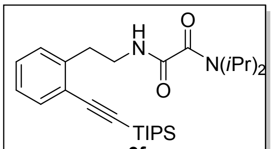
3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 7.4, 3.4 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.97 (br s, 1H), 4.70 – 4.64 (m, 1H), 3.62 (dd, J = 13.4, 6.9 Hz, 2H), 3.50 – 3.44 (m, 1H), 3.29 (dd, J = 9.1, 5.1 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H), 1.16 – 1.11 (m, 18H), 1.08 (dd, J = 11.0, 3.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.09, 162.86, 140.18, 133.28, 132.42, 127.83, 125.53, 125.18, 104.48, 96.30, 49.50, 46.59, 38.58, 34.36, 20.97, 20.13, 18.78, 11.37; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}BrN_2O_2SiNa$: 557.2175; found: 557.2161.



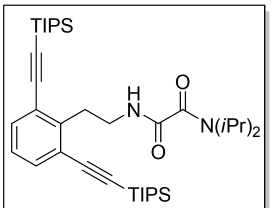
3e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.11 (br s, 1H), 4.67 – 4.60 (m, 1H), 3.64 – 3.59 (m, 2H), 3.51 – 3.44 (m, 1H), 3.11 (dd, J = 8.9, 5.1 Hz, 2H), 1.38 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H), 1.13 (t, J = 3.7 Hz, 18H), 1.09 (dd, J = 11.0, 3.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.37, 162.93, 141.69, 133.44, 130.26 (q, $J_{C-F=}$ 32 Hz), 127.60, 126.19 (d, $J_{C-F=}$ 3 Hz), 123.91 (q, $J_{C-F=}$ 271 Hz), 123.41 (d, $J_{C-F=}$ 3 Hz), 103.74, 98.22, 49.70, 46.61, 39.28, 34.30, 20.86, 20.06, 18.74, 11.34; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{43}F_3N_2O_2SiNa$: 547.2944; found: 547.2948.



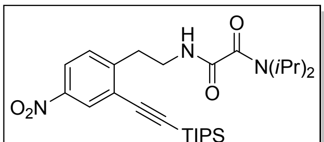
3f$_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.3 Hz, 1H), 7.26 (dd, J = 7.6, 6.0 Hz, 1H), 7.22 (d, J = 6.1 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.82 (br s, 1H), 4.63 – 4.57 (m, 1H), 3.64 – 3.59 (m, 2H), 3.52 – 3.45 (m, 1H), 3.06 (t, J = 6.9 Hz, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H), 1.13 (s, 18H), 1.07 (dd, J = 13.0, 7.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 163.21, 140.81, 133.22, 129.54, 128.80, 126.65, 123.32, 105.21, 95.04, 49.76, 46.58, 39.56, 34.40, 20.98, 20.16, 18.83, 11.43; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{44}N_2O_2SiNa$: 479.3070; found: 479.3063.



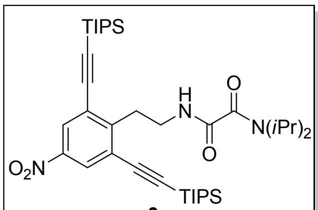
3f$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 2H), 7.12 (t, J = 7.7 Hz, 1H), 6.88 (br s, 1H), 4.61 – 4.53 (m, 1H), 3.65 (dd, J = 12.8, 7.1 Hz, 2H), 3.48 – 3.42 (m, 1H), 3.34 (dd, J = 9.3, 5.0 Hz, 2H), 1.38 (d, J = 6.8 Hz, 6H), 1.16 (s, 6H), 1.12 (d, J = 2.5 Hz, 36H), 1.11 – 1.06 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.94, 162.86, 142.74, 133.17, 126.45, 124.09, 104.77, 95.48, 49.45, 46.52, 39.30, 32.61, 20.99, 20.17, 18.83, 11.43; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{38}H_{64}N_2O_2SiNa$: 659.4404; found: 659.4410.



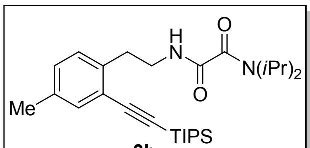
3g$_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 2.4 Hz, 1H), 8.08 (dd, J = 8.4, 2.4 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.02 (br s, 1H), 4.63 – 4.56 (m, 1H), 3.65 – 3.60 (m, 2H), 3.52 – 3.45 (m, 1H), 3.15 (dd, J = 8.7, 4.8 Hz, 2H), 1.38 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H), 1.16 – 1.12 (m, 18H), 1.12 – 1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 162.82, 148.16, 146.67, 130.53, 127.81, 124.86, 123.23, 102.62, 98.61, 49.71, 46.65, 38.97, 34.53, 20.94, 20.12, 18.77, 11.33; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}N_3O_4SiNa$: 524.2921; found: 524.2914.



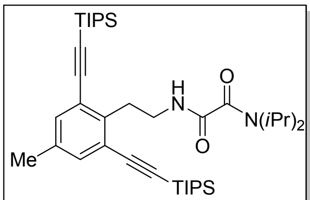
3g$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 6.95 (br s, 1H), 4.62 – 4.55 (m, 1H), 3.67 (dd, J = 13.1, 6.9 Hz, 2H), 3.47 (dd, J = 13.6, 6.8 Hz, 1H), 3.43 – 3.38 (m, 2H), 1.38 (d, J = 6.8 Hz, 6H), 1.16 (s, 6H), 1.15 – 1.12 (m, 36H), 1.12 – 1.06 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.82, 162.36, 149.62, 146.24, 127.10, 125.70, 102.46, 99.04, 49.43, 46.68, 38.65, 33.23, 20.96, 20.13, 18.81, 11.35; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{38}H_{63}N_3O_4Si_2Na$: 704.4255; found: 704.4239.



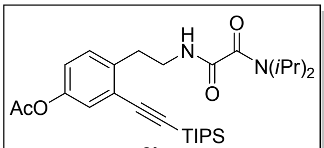
3h$_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.11 (d, J = 7.8 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.80 (br s, 1H), 4.63 – 4.56 (m, 1H), 3.61 – 3.56 (m, 2H), 3.51 – 3.44 (m, 1H), 3.01 (t, J = 6.9 Hz, 2H), 2.28 (s, 3H), 1.39 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.7 Hz, 6H), 1.13 (s, 18H), 1.07 (dd, J = 10.2, 5.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 163.20, 137.78, 136.25, 133.62, 129.69, 129.44, 123.07, 105.46, 94.48, 49.70, 46.55, 39.66, 33.92, 20.96, 20.85, 20.16, 18.82, 11.44; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_2SiNa$: 493.3226; found: 493.3226.



3h$_{di}$

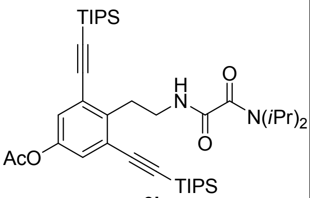
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 6.87 (br s, 1H), 4.60 – 4.54 (m, 1H), 3.63 (dd, J = 12.7, 7.0 Hz, 2H), 3.49 – 3.42 (m, 1H), 3.30 (dd, J = 9.2, 5.0 Hz, 2H), 2.27 (s, 3H), 1.39 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.7 Hz, 6H), 1.13 (d, J = 1.9 Hz, 36H), 1.11 – 1.06 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.95, 162.89, 139.85, 136.16, 133.84, 123.88, 105.01, 94.92, 49.46, 46.53, 39.42, 32.13, 20.99, 20.64, 20.18, 18.84, 11.44; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{39}H_{66}N_2O_2Si_2Na$: 673.4561; found: 673.4559.



3i$_{mono}$

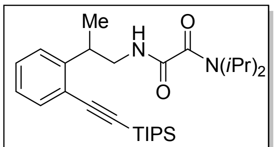
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 2.5 Hz, 1H), 6.99 (dd, J = 8.3, 2.5 Hz, 1H), 6.82 (br s, 1H), 4.63 – 4.57 (m, 1H), 3.61` – 3.56 (m, 2H), 3.51 – 3.44 (m, 1H), 3.03 (dd, J =

8.7, 5.0 Hz, 2H), 2.27 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H), 1.15 – 1.11 (m, 18H), 1.11 – 1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.46, 163.46, 163.11, 149.07, 138.51, 130.53, 125.93, 124.51, 122.23, 104.18, 96.13, 49.73, 46.56, 39.47, 33.90, 21.16, 20.96, 20.16, 18.79, 11.38; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{29}H_{46}N_2O_4SiNa$: 537.3125; found: 537.3133.



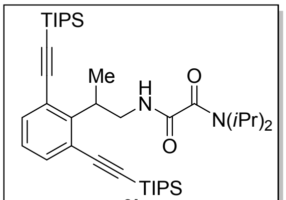
3i$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 1.6 Hz, 2H), 6.87 (br s, 1H), 4.65 – 4.54 (m, 1H), 3.63 (dd, *J* = 13.0, 7.0 Hz, 2H), 3.49 – 3.42 (m, 1H), 3.30 (dd, *J* = 9.3, 5.1 Hz, 2H), 2.27 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.7 Hz, 6H), 1.11 (d, *J* = 3.0 Hz, 36H), 1.07 (dd, *J* = 10.9, 3.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.22, 162.93, 162.80, 148.56, 140.54, 126.23, 125.25, 103.88, 96.57, 49.50, 46.54, 39.18, 32.28, 21.12, 20.96, 20.17, 18.82, 11.39; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{42}H_{68}N_2O_6Si_2Na$: 775.4514; found: 775.4530.



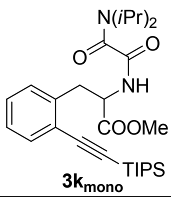
3j$_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.25 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.15 (td, *J* = 7.6, 1.6 Hz, 1H), 6.60 (br s, 1H), 4.41 – 4.35 (m, 1H), 3.72 – 3.59 (m, 2H), 3.57 – 3.50 (m, 1H), 3.47 – 3.40 (m, 1H), 1.37 (dd, *J* = 6.8, 1.7 Hz, 6H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.13 (d, *J* = 2.7 Hz, 6H), 1.12 (d, *J* = 2.0 Hz, 18H), 1.08 (d, *J* = 9.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 163.41, 145.49, 133.46, 128.97, 126.40, 125.84, 123.26, 105.25, 95.45, 49.75, 46.43, 44.30, 37.35, 20.92, 20.86, 20.18, 20.13, 18.80, 18.64, 11.45; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_2SiNa$: 493.3226; found: 493.3221.



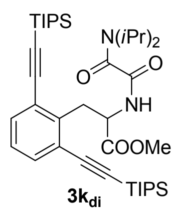
3j$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.60 (br s, 1H), 4.57 – 4.50 (m, 1H), 4.21 – 4.13 (m, 1H), 4.08 – 3.99 (m, 1H), 3.85 – 3.78 (m, 1H), 3.46 – 3.40 (m, 1H), 1.50 (dd, *J* = 7.1, 2.7 Hz, 3H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.15 (s, 6H), 1.12 (d, *J* = 2.9 Hz, 36H), 1.09 – 0.99 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.28, 162.94, 146.54, 126.28, 49.65, 46.44, 42.92, 38.37, 20.96, 20.25, 20.16, 18.82, 17.03, 11.50; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{39}H_{66}N_2O_2Si_2Na$: 673.4561; found: 673.4562.



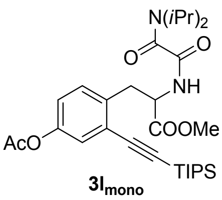
$3k_{mono}$

^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 2.6 Hz, 1H), 7.26 (br s, 1H), 7.24 – 7.20 (m, 1H), 7.18 (dd, *J* = 7.7, 3.6 Hz, 1H), 1.41 – 1.37 (m, 6H), 1.14 (d, *J* = 2.7 Hz, 18H), 1.12 (s, 6H), 1.11 – 1.08 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.48, 162.88, 162.47, 138.26, 133.18, 129.58, 128.68, 126.98, 123.85, 105.01, 95.55, 52.96, 52.51, 49.58, 46.51, 36.74, 20.98, 20.81, 20.17, 20.06, 18.80, 18.79, 11.41; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{29}H_{46}N_2O_4SiNa$: 537.3125; found: 537.3130.



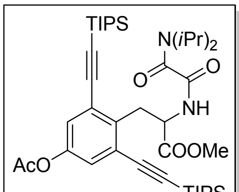
$3k_{di}$

^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 6.2 Hz, 1H), 5.13 – 5.06 (m, 1H), 3.98 – 3.92 (m, 1H), 3.74 (d, *J* = 2.5 Hz, 3H), 3.67 – 3.62 (m, 1H), 3.51 – 3.44 (m, 1H), 3.42 – 3.35 (m, 1H), 1.35 (dd, *J* = 6.8, 2.5 Hz, 6H), 1.14 (t, *J* = 3.6 Hz, 36H), 1.11 (d, *J* = 5.3 Hz, 3H), 1.07 (d, *J* = 6.1 Hz, 6H), 1.03 (d, *J* = 14.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.39, 163.23, 162.85, 140.31, 133.16, 126.79, 124.60, 104.54, 96.38, 52.43, 52.08, 49.51, 46.30, 35.31, 21.07, 20.79, 20.21, 20.02, 18.84, 18.83, 11.41; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{40}H_{66}N_2O_4Si_2Na$: 717.4459; found: 717.4469.



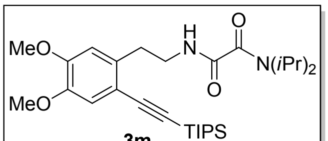
$3l_{mono}$

^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 7.16 (br s, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 4.82 – 4.72 (m, 1H), 4.26 – 4.19 (m, 1H), 3.64 (s, 3H), 3.43 – 3.29 (m, 2H), 3.18 – 3.08 (m, 1H), 2.20 (s, 3H), 1.32 (dd, *J* = 6.8, 2.9 Hz, 6H), 1.08 (d, *J* = 6.2 Hz, 6H), 1.06 (d, *J* = 3.1 Hz, 18H), 1.01 (d, *J* = 8.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.35, 169.24, 162.90, 162.42, 149.34, 135.97, 130.58, 125.84, 125.01, 122.19, 103.97, 96.65, 52.85, 52.54, 49.66, 46.52, 36.23, 21.14, 20.89, 20.76, 20.17, 20.04, 18.76, 11.35; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{31}H_{48}N_2O_6SiNa$: 595.3179; found: 595.3187.



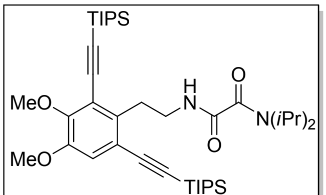
3l$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 1.9 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.12 – 5.05 (m, 1H), 4.03 – 3.97 (m, 1H), 3.74 (d, *J* = 2.5 Hz, 3H), 3.63 – 3.57 (m, 1H), 3.47 – 3.37 (m, 2H), 2.27 (s, 3H), 1.38 – 1.33 (m, 6H), 1.18 – 1.15 (m, 3H), 1.15 – 1.12 (m, 36H), 1.11 (d, *J* = 4.3 Hz, 3H), 1.10 – 1.07 (m, 6H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.30, 169.05, 163.20, 162.77, 148.88, 138.11, 126.22, 125.75, 103.68, 97.44, 52.48, 51.97, 49.64, 46.32, 35.03, 21.13, 20.94, 20.71, 20.23, 20.00, 18.83, 18.82, 11.38; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{42}H_{68}N_2O_6Si_2Na$: 775.4514; found: 775.4530.



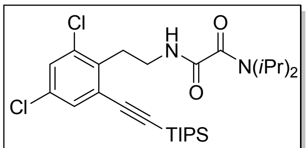
3m$_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.82 (br s, 1H), 6.74 (s, 1H), 4.68 – 4.61 (m, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.59 – 3.54 (m, 2H), 3.51 – 3.44 (m, 1H), 3.00 (t, *J* = 6.8 Hz, 2H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.19 (d, *J* = 6.7 Hz, 6H), 1.13 (s, 18H), 1.12 – 1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 163.04, 149.64, 147.39, 134.46, 115.26, 114.93, 112.61, 105.41, 93.03, 56.14, 56.11, 49.65, 46.59, 39.72, 34.12, 20.98, 20.15, 18.86, 11.49; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{29}H_{48}N_2O_4SiNa$: 539.3281; found: 539.3272.



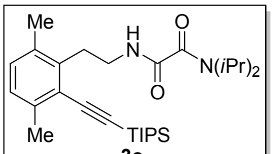
3m$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.90 (br s, 1H), 4.68 – 4.61 (m, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.60 (dd, *J* = 12.7, 7.0 Hz, 2H), 3.49 – 3.43 (m, 1H), 3.25 (dd, *J* = 9.4, 4.9 Hz, 2H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.7 Hz, 6H), 1.14 (s, 18H), 1.12 (d, *J* = 2.4 Hz, 18H), 1.10 – 0.99 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.92, 162.79, 151.97, 151.12, 136.48, 119.24, 119.20, 116.67, 104.80, 100.40, 100.36, 94.27, 61.07, 56.22, 49.47, 46.56, 39.44, 32.08, 31.08, 21.02, 20.19, 18.87, 18.83, 11.47; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{40}H_{68}N_2O_4Si_2Na$: 719.4615; found: 719.4611.



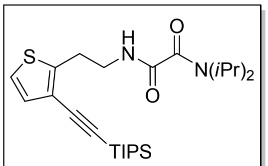
3n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.0 Hz, 1H), 7.31 (br s, 1H), 7.04 (s, 1H), 4.64 – 4.57 (m, 1H), 3.60 – 3.55 (m, 2H), 3.49 – 3.42 (m, 1H), 3.20 (dd, *J* = 8.9, 5.0 Hz, 2H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.7 Hz, 6H), 1.10 (d, *J* = 3.7 Hz, 18H), 1.09 – 1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.30, 162.99, 139.01, 139.00, 134.11, 130.37, 127.63, 123.68, 104.51, 99.08, 49.58, 46.60, 39.00, 31.44, 21.34, 20.99, 20.14, 19.67, 18.85, 11.46; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{42}Cl_2N_2O_2SiNa$: 547.2290; found: 547.2280.



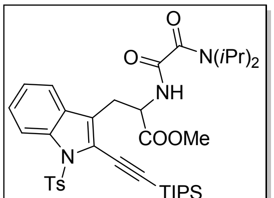
3o

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.98 (m, 2H), 6.92 (br s, 1H), 4.75 – 4.66 (m, 1H), 3.58 – 3.52 (m, 2H), 3.48 (dd, *J* = 13.6, 6.8 Hz, 1H), 3.18 – 3.12 (m, 2H), 2.42 (s, 3H), 2.34 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H), 1.14 (d, *J* = 1.8 Hz, 18H), 1.13 – 1.07 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.04, 162.70, 137.17, 135.47, 132.49, 131.26, 129.53, 126.55, 102.97, 97.76, 49.44, 46.49, 38.23, 31.30, 20.81, 20.00, 18.65, 11.22; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{29}H_{48}N_2O_2SiNa$: 507.3383; found: 507.3375.



3p

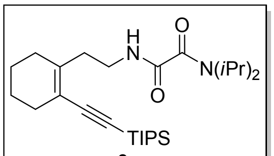
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 5.2 Hz, 1H), 7.01 (d, *J* = 5.2 Hz, 1H), 6.94 (br s, 1H), 4.70 – 4.63 (m, 1H), 3.63 – 3.58 (m, 2H), 3.53 – 3.46 (m, 1H), 3.17 (t, *J* = 6.8 Hz, 2H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.7 Hz, 6H), 1.11 (s, 18H), 1.08 – 1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 162.94, 144.90, 130.29, 122.83, 121.16, 100.89, 93.79, 49.73, 46.67, 39.94, 28.97, 21.01, 20.19, 18.83, 11.41; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{25}H_{42}N_2O_2SSiNa$: 485.2634; found: 485.2643.



3q

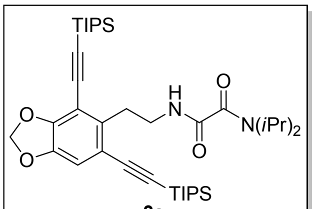
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.35 (br s, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.79 – 4.73 (m, 1H), 4.44 – 4.37 (m, 1H), 3.49 (s, 3H), 3.45 (dd, *J* = 13.3, 6.5 Hz, 1H), 3.26 (d, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.41 (s, 6H), 1.20 (d, *J* = 4.9 Hz, 18H), 1.15 (s, 3H), 1.11 (d, *J* = 5.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =171.21, 162.77, 162.06, 144.91, 135.95, 129.85, 128.78, 127.14, 126.57, 125.86, 124.10, 119.96, 119.67, 114.81, 104.29, 95.32, 52.58, 52.09, 49.61, 46.65, 28.80, 21.71, 20.92,

20.18, 20.13, 18.81, 11.54; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{36}H_{51}N_3O_4SSiNa$: 672.3267; found: 672.3271.



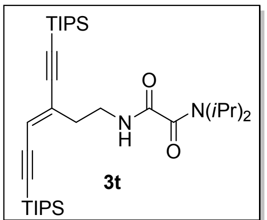
3r

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (br s, 1H), 4.67 – 4.60 (m, 1H), 3.48 (dd, *J* = 13.6, 6.8 Hz, 1H), 3.41 (dd, *J* = 13.2, 6.9 Hz, 2H), 2.54 (t, *J* = 7.0 Hz, 2H), 2.16 (s, 2H), 2.10 (s, 2H), 1.61 – 1.54 (m, 4H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H), 1.05 (s, 18H), 1.04 – 0.93 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =163.44, 163.25, 142.79, 117.81, 107.45, 92.48, 49.74, 46.53, 37.77, 35.80, 30.18, 29.35, 22.50, 22.35, 21.00, 20.17, 18.81, 11.41; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{48}N_2O_2SiNa$: 483.3383; found: 483.3379.



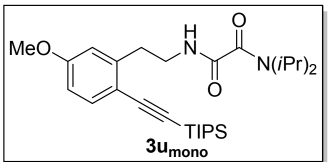
3s

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (br s, 1H), 6.86 (s, 1H), 6.02 (s, 2H), 4.68 – 4.60 (m, 1H), 3.60 (d, *J* = 5.7 Hz, 2H), 3.50 – 3.43 (m, 1H), 3.25 (s, 2H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.17 (d, *J* = 6.7 Hz, 6H), 1.12 (d, *J* = 3.0 Hz, 18H), 1.11 (d, *J* = 1.8 Hz, 18H), 1.08 (dd, *J* = 6.3, 4.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.94, 162.82, 150.37, 145.98, 137.35, 116.63, 112.25, 105.92, 105.03, 102.10, 100.30, 98.23, 93.53, 49.49, 46.56, 39.48, 32.06, 21.01, 20.19, 18.85, 18.82, 11.46, 11.39; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{39}H_{64}N_2O_4Si_2Na$: 703.4302; found: 703.4312.



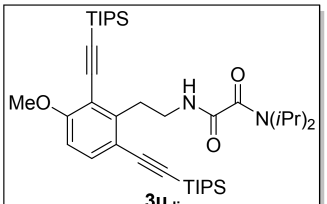
3t

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (br s, 1H), 6.00 (s, 1H), 4.78 – 4.71 (m, 1H), 3.55 (dd, *J* = 12.8, 6.5 Hz, 2H), 3.48 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.68 (t, *J* = 6.7 Hz, 2H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H), 1.06 (d, *J* = 1.2 Hz, 36H), 1.05 – 0.99 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.06, 162.81, 133.13, 118.62, 106.61, 102.92, 102.79, 97.36, 49.57, 46.61, 37.75, 33.25, 20.97, 20.16, 18.73, 11.32, 11.30; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{34}H_{62}N_2O_2Si_2Na$: 609.4248; found: 609.4248.



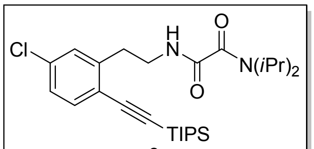
$3u_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, 1H), 6.88 (br s, 1H), 6.75 (d, J = 2.3 Hz, 1H), 6.69 (dd, J = 8.5, 2.3 Hz, 1H), 4.63 – 4.56 (m, 1H), 3.78 (s, 3H), 3.62 – 3.54 (m, 2H), 3.50 – 3.43 (m, 1H), 3.02 (t, J = 6.8 Hz, 2H), 1.38 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H), 1.12 (d, J = 7.6 Hz, 18H), 1.09 – 1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 163.14, 159.81, 142.60, 134.43, 115.43, 114.79, 112.59, 105.31, 92.98, 55.37, 49.66, 46.49, 39.44, 34.56, 20.90, 20.11, 18.78, 11.43; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_3SiNa$: 509.3175; found: 509.3168.



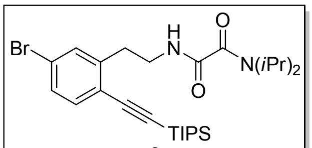
3u$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.6 Hz, 1H), 6.86 (br s, 1H), 6.69 (d, J = 8.7 Hz, 1H), 4.64 – 4.54 (m, 1H), 3.84 (s, 3H), 3.64 (dd, J = 12.7, 7.1 Hz, 2H), 3.49 – 3.42 (m, 1H), 3.32 (dd, J = 9.3, 5.1 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.15 (d, J = 6.7 Hz, 6H), 1.13 (d, J = 1.7 Hz, 18H), 1.12 (s, 18H), 1.10 – 0.94 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.98, 162.93, 161.36, 144.70, 134.03, 116.13, 113.61, 109.07, 104.96, 100.50, 100.45, 93.28, 56.08, 49.49, 46.51, 39.31, 32.71, 21.00, 20.20, 18.87, 18.84, 11.49; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{39}H_{66}N_2O_3Si_2Na$: 689.4510; found: 689.4503.



3v

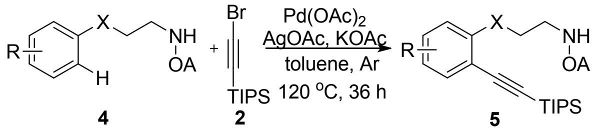
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 8.2, 3.2 Hz, 1H), 7.20 (d, J = 1.9 Hz, 1H), 7.14 (dd, J = 8.2, 2.0 Hz, 1H), 6.98 (br s, 1H), 4.64 – 4.57 (m, 1H), 3.62 – 3.57 (m, 2H), 3.51 – 3.44 (m, 1H), 3.02 (t, J = 6.9 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H), 1.11 (d, J = 2.2 Hz, 18H), 1.10 – 1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 163.11, 142.69, 134.37, 134.20, 129.52, 126.83, 121.81, 104.05, 96.20, 49.75, 46.52, 39.27, 34.17, 20.92, 20.12, 18.75, 11.34; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}ClN_2O_2SiNa$: 513.2680; found: 513.2669.



3w

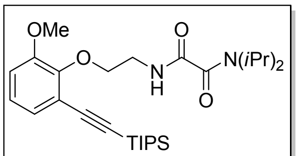
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 1.4 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 1.7 Hz, 1H), 6.96 (br s, 1H), 4.66 – 4.59 (m, 1H), 3.61 – 3.56 (m, 2H), 3.52 – 3.45 (m, 1H), 3.02 (dd, J = 8.8, 5.2 Hz, 2H), 1.39 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H), 1.11 (d, J = 2.5 Hz, 18H), 1.07 (dd, J = 9.4, 5.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.40, 163.02, 142.86, 134.39, 132.42, 129.80, 122.69, 122.29, 104.11, 96.50, 49.74, 46.58, 39.33, 34.17, 20.98, 20.15, 18.77, 11.36; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{43}BrN_2O_2SiNa$: 557.2175; found: 557.2158.

6. *ortho*-Alkynylation of *γ*-Arylpropamine Derivatives



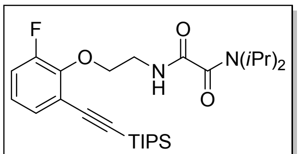
4 2 5

A mixture of **4** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2 equiv), $Pd(OAc)_2$ (1.1 mg, 0.05 equiv), AgOAc (66.8 mg, 2 equiv), KOAc (58.9 mg, 2 equiv), toluene (1 mL) in a 25 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 120 °C for 36 hours. The reaction mixture was cooled to rt, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the alkynylation product.



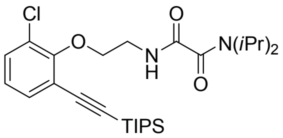
5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.03 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.64 – 4.57 (m, 1H), 4.27 – 4.22 (m, 2H), 3.89 (s, 3H), 3.60 – 3.55 (m, 2H), 3.51 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.7 Hz, 6H), 1.12 (d, *J* = 1.6 Hz, 18H), 1.08 (dd, *J* = 8.0, 5.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.77, 163.42, 152.58, 149.19, 125.74, 124.39, 118.72, 112.74, 102.59, 95.90, 72.08, 56.05, 49.75, 46.43, 39.60, 20.98, 20.16, 18.76, 11.41; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_4SiNa$: 525.3125; found: 525.3124.



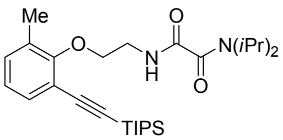
5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (br s, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 13.8, 5.0 Hz, 1H), 6.97 – 6.92 (m, 1H), 4.68 – 4.62 (m, 1H), 4.29 (t, *J* = 5.0 Hz, 2H), 3.65 (dd, *J* = 10.7, 5.4 Hz, 2H), 3.54 – 3.47 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.7 Hz, 6H), 1.12 (d, *J* = 2.3 Hz, 18H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.65, 162.95, 155.41 (d, $J_{C-F=}$ 245 Hz), 147.65 (d, $J_{C-F=}$ 12 Hz), 129.50 (d, $J_{C-F=}$ 3 Hz), 123.97 (d, $J_{C-F=}$ 8 Hz), 119.36, 117.29 (d, $J_{C-F=}$ 19 Hz), 101.68 (d, $J_{C-F=}$ 4 Hz), 97.02, 72.48 (d, $J_{C-F=}$ 3 Hz), 49.77, 46.59, 39.55, 20.94, 20.15, 18.76, 11.38; ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.58; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}FN_2O_3SiNa$: 513.2925; found: 513.2927.



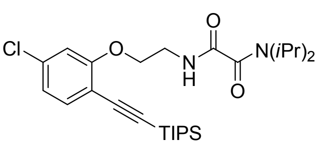
5c

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.40 (br s, 1H), 7.36 – 7.31 (m, 2H), 6.98 (t, J = 7.9 Hz, 1H), 4.72 – 4.65 (m, 1H), 4.31 (t, J = 5.1 Hz, 2H), 3.68 (dd, J = 10.5, 5.5 Hz, 2H), 3.54 – 3.47 (m, 1H), 1.43 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.7 Hz, 6H), 1.12 (d, J = 2.7 Hz, 18H), 1.11 – 1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =163.59, 162.91, 155.69, 133.02, 130.72, 128.07, 124.69, 119.35, 101.94, 97.38, 72.06, 49.73, 46.61, 39.63, 21.01, 20.16, 18.78, 11.40; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}ClN_2O_3SiNa$: 529.2629; found: 529.2625.



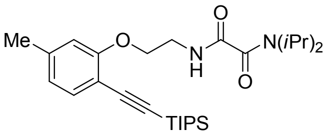
5d

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.35 (br s, 1H), 7.29 (dd, J = 7.6, 1.3 Hz, 1H), 7.12 (dd, J = 7.5, 0.8 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 4.79 – 4.72 (m, 1H), 4.24 (t, J = 5.2 Hz, 2H), 3.68 (dd, J = 10.9, 5.5 Hz, 2H), 3.55 – 3.48 (m, 1H), 2.26 (s, 3H), 1.43 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 6.7 Hz, 6H), 1.12 (s, 18H), 1.11 – 1.05 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =163.45, 162.77, 158.04, 132.44, 131.71, 131.25, 123.74, 116.92, 103.68, 95.37, 71.00, 49.68, 46.68, 39.88, 21.00, 20.15, 18.81, 16.41, 11.46; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{43}N_2O_3SiNa$: 509.3175; found: 509.3176.



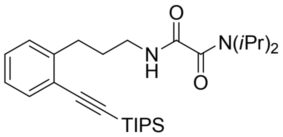
5e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.2 Hz, 1H), 7.21 (br s, 1H), 6.89 (dd, J = 8.2, 1.9 Hz, 1H), 6.81 (d, J = 1.8 Hz, 1H), 4.73 – 4.67 (m, 1H), 4.10 (t, J = 5.2 Hz, 2H), 3.72 (dd, J = 11.0, 5.5 Hz, 2H), 3.54 – 3.47 (m, 1H), 1.41 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.7 Hz, 6H), 1.13 (s, 18H), 1.09 (dd, J = 9.3, 3.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.57, 162.44, 159.99, 135.20, 134.59, 121.25, 112.70, 111.96, 101.84, 96.36, 67.44, 49.71, 46.73, 38.86, 21.00, 20.14, 18.84, 11.41; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{27}H_{43}ClN_2O_3SiNa$: 529.2629; found: 529.2619.



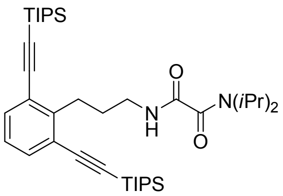
5f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.7 Hz, 1H), 7.18 (br s, 1H), 6.74 – 6.69 (m, 1H), 6.63 (s, 1H), 4.69 – 4.62 (m, 1H), 4.11 (t, J = 5.2 Hz, 2H), 3.72 (dd, J = 10.9, 5.5 Hz, 2H), 3.53 – 3.46 (m, 1H), 2.32 (s, 3H), 1.41 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.7 Hz, 6H), 1.13 (s, 18H), 1.09 (dd, J = 7.1, 4.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.67, 162.68, 159.44, 140.41, 133.80, 121.82, 113.05, 110.39, 103.23, 94.19, 67.15, 49.73, 46.64, 39.04, 21.97, 20.97, 20.13, 18.86, 11.46; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_3SiNa$: 509.3175; found: 509.3172.



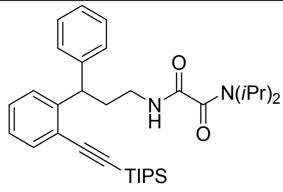
5g$_{mono}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.18 (d, J = 6.6 Hz, 1H), 7.14 (dd, J = 11.7, 4.4 Hz, 1H), 6.97 (br s, 1H), 4.81 – 4.70 (m, 1H), 3.54 – 3.47 (m, 1H), 3.31 (d, J = 6.8 Hz, 2H), 2.91 – 2.81 (m, 2H), 1.92 (s, 2H), 1.42 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.8 Hz, 6H), 1.13 (s, 18H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.24, 163.14, 143.55, 133.19, 128.96, 128.68, 126.12, 123.01, 105.51, 94.54, 49.74, 46.70, 39.19, 32.32, 30.02, 21.00, 20.19, 18.83, 11.45; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{46}N_2O_2SiNa$: 493.3226; found:493.3227.



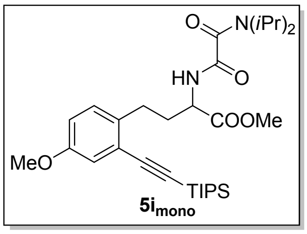
5g$_{di}$

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.7 Hz, 1H), 7.09 (t, J = 7.7 Hz, 1H), 6.76 (br s, 1H), 4.79 – 4.72 (m, 1H), 3.53 – 3.46 (m, 1H), 3.35 (dd, J = 15.3, 6.0 Hz, 1H), 3.18 – 3.08 (m, 1H), 1.98 – 1.88 (m, 1H), 1.41 (d, J = 6.8 Hz, 3H), 1.21 (d, J = 6.7 Hz, 3H), 1.13 (d, J = 2.4 Hz, 18H), 1.09 (d, J = 2.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.90, 145.75, 133.29, 125.97, 123.60, 105.08, 94.97, 49.59, 46.64, 39.60, 31.12, 29.70, 21.01, 20.21, 18.84, 11.44; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{39}H_{66}N_2O_2Si_2Na$: 673.4561; found:673.4563.

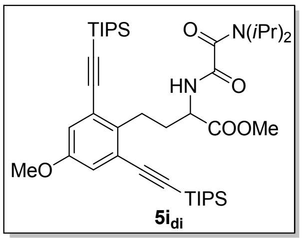


5h

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.47 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.4 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H), 7.25 (s, 1H), 7.23 (d, J = 6.5 Hz, 1H), 7.16 (dd, J = 11.0, 3.6 Hz, 1H), 7.14 – 7.10 (m, 1H), 6.97 (br s, 1H), 4.80 – 4.68 (m, 2H), 3.52 – 3.45 (m, 1H), 3.33 – 3.17 (m, 2H), 2.41 – 2.29 (m, 2H), 1.40 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.6 Hz, 6H), 1.16 (s, 18H), 1.11 (d, J = 10.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =163.09, 162.89, 146.05, 143.47, 133.54, 129.03, 128.60, 127.92, 126.77, 126.50, 126.22, 123.17, 105.87, 95.38, 49.57, 46.66, 46.14, 38.60, 34.94, 20.98, 20.14, 18.87, 11.49; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{34}H_{50}N_2O_2SiNa$: 569.3539; found:569.3532.



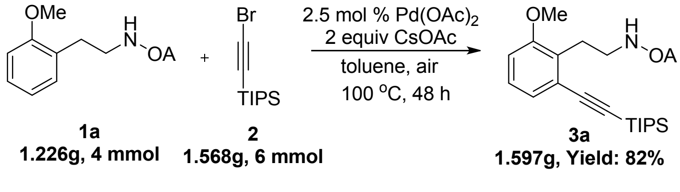
^{1}H NMR (400 MHz, $CDCl_3$) δ =7.22 (d, J = 8.2 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 2.7 Hz, 1H), 6.80 (dd, J = 8.5, 2.8 Hz, 1H), 4.72 – 4.66 (m, 1H), 4.54 – 4.48 (m, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.55 – 3.48 (m, 1H), 2.88 – 2.79 (m, 2H), 2.35 – 2.27 (m, 1H), 2.06 – 1.97 (m, 1H), 1.44 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 6.6 Hz, 6H), 1.13 (d, J = 1.5 Hz, 18H), 1.08 (dd, J = 9.4, 5.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =172.12, 163.17, 162.45, 157.82, 134.88, 130.26, 123.80, 117.99, 115.11, 105.30, 94.67, 55.50, 52.47, 52.00, 49.73, 46.73, 32.81, 30.18, 21.00, 20.98, 20.22, 20.16, 18.83, 11.43; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{31}H_{50}N_2O_5SiNa$: 581.3387; found:581.3381.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.1 Hz, 1H), 6.96 (d, J = 1.8 Hz, 2H), 4.75 – 4.68 (m, 1H), 4.63 – 4.56 (m, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.54 – 3.47 (m, 1H), 3.17 – 3.02 (m, 2H), 2.18 – 2.10 (m, 1H), 2.06 – 1.99 (m, 1H), 1.42 (dd, J = 6.8, 4.3 Hz, 6H), 1.22 (dd, J = 8.1, 6.8 Hz, 6H), 1.16 – 1.13 (m, 36H), 1.13 – 1.07 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.95, 163.23, 162.18, 157.21, 137.32, 124.40, 119.14, 104.88, 95.02, 55.65, 53.11, 52.35, 49.57, 46.69, 32.34, 29.73, 21.05, 21.02, 20.22, 20.18, 18.89, 11.42; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{42}H_{70}N_2O_5Si_2Na$: 761.4721; found: 761.4721.

7. Gram Scale Reaction

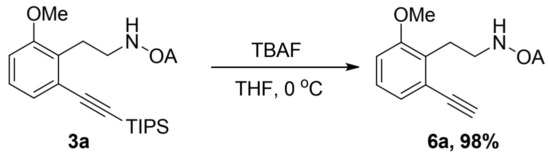
Scheme 1S Gram Scale Reaction.



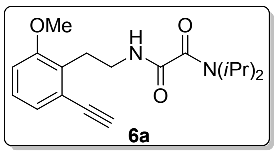
A mixture of **1a** (1.226 g, 4 mmol, 1.0 equiv), **2** (1.568 g, 6 mmol, 1.5 equiv), $Pd(OAc)_2$ (11 mg, 0.025 equiv), CsOAc (1.536 g, 2 equiv) and toluene (10 mL) in a 50 mL glass vial (sealed with PTFE cap) was heated at 100 °C for 48 hours. The reaction mixture was cooled to rt, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give **3a** as yellow solid in 82% yield.

8. Removal of the TIPS[6]

Scheme 2S Removal of the TIPS.



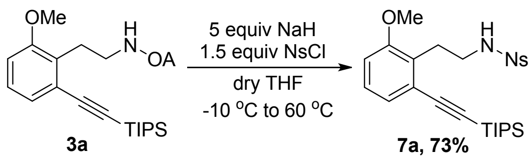
3a (0.146 g, 0.3 mmol) was dissolved in dry THF (10 mL). After cooling to 0 °C TBAF (400 µL, 0.4 mmol, 1M solution in THF) were added and the reaction mixture stirred for 1h. Then some drops of water and CH_2Cl_2 (20 mL) were added. The organic layer was washed three times with water and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography on silica gel afforded **6a** as pale yellow solid in 98% yield.



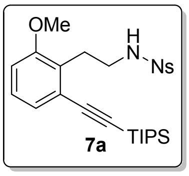
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (br s, 1H), 7.10 – 7.05 (m, 1H), 7.04 – 7.00 (m, 1H), 4.52 – 4.46 (m, 1H), 3.77 (s, 3H), 3.48 (dd, *J* = 12.5, 6.7 Hz, 2H), 3.44 – 3.37 (m, 1H), 3.22 (s, 1H), 3.07 (t, *J* = 6.8 Hz, 2H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.10 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 163.31, 157.43, 129.90, 127.35, 124.93, 123.24, 111.10, 81.88, 81.02, 55.45, 49.41, 46.20, 39.06, 27.39, 20.74, 19.94; HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{27}N_2O_3$: 331.2022; found: 331.2017.

9. Removal of the Directing Group[7]

Scheme 3S Removal of the Directing Group.



A mixture of **3a** (0.146 g, 0.3 mmol, 1.0 equiv) in THF (2 mL) was stirred for 10 min at -10 °C, NaH (60 %) (0.06 g, 2.5 mmol, 5.0 equiv) was slowly added, and then stirred for another 1 hour. NsCl (0.1 g, 7.5 mmol, 1.5 equiv) was added slowly for thirty minutes. The mixture was stirred over night at room temperature and heated at 60 °C for another 12 hours. The reaction mixture was cooled to rt, quenched with water (20 mL), extracted with CH_2Cl_2 (10 mL × 2). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel afforded **7a** as pale yellow solid in 73% yield.

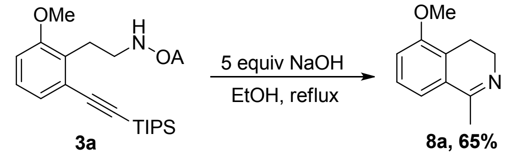


7a

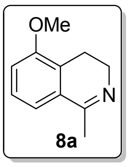
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.02 (br s, 1H), 3.79 (s, 3H), 3.41 – 3.30 (m, 2H), 3.07 – 2.98 (m, 2H), 1.14 (d, *J* = 2.6 Hz, 18H), 1.06 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.22, 145.43, 128.32, 127.93, 127.87, 125.60, 124.83, 124.03, 111.02, 104.84, 95.92, 55.90, 43.30, 27.32, 18.83, 11.42; HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{26}H_{37}N_2O_5SSi$: 517.2192; found: 517.2187.

10. Synthesis of 3,4-Dihydroisoquinoline 8a

Scheme 4S Synthesis of 3,4-Dihydroisoquinoline **8a**.



A mixture of **3a** (0.146 g, 0.3 mmol, 1.0 equiv) and NaOH (0.06 g, 1.5 mmol, 5.0 equiv) in EtOH (2 mL) was stirred at 80 °C for 12 hours. The reaction mixture was cooled to rt, then some drops of water and CH_2Cl_2 (20 mL) were added. The organic layer was washed three times with water and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography on silica gel afforded **8a** as pale yellow solid in 65% yield.

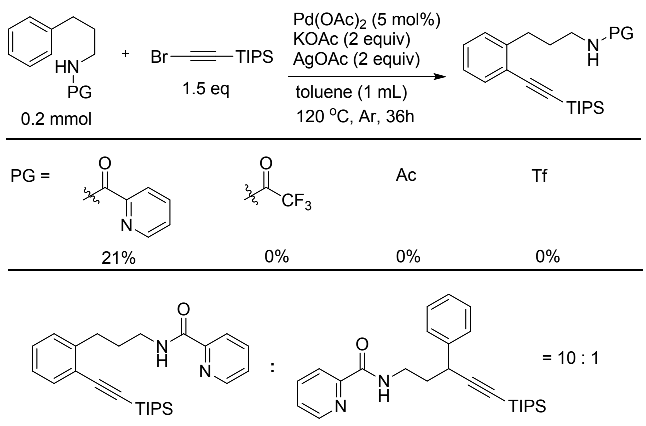


8a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 3.76 – 3.71 (m, 2H), 2.85 – 2.80 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.08, 128.91, 127.89, 125.89, 119.18, 114.92, 55.89, 44.29, 29.84, 22.22, 18.71; HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{11}H_{14}NO$: 176.1075; found: 176.1070.

11. Optimization of Protecting Group

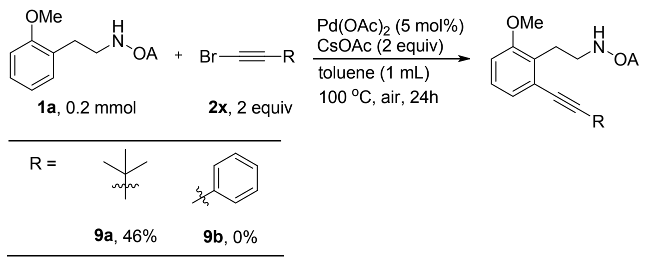
Table 2S Optimization of Protecting Group



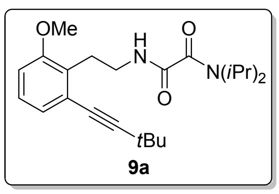
A variety of protecting group for γ-Arylpropamine had been tested: However none could give synthetic acceptable yield. It worth to note that the picolinamide assisted alkynylation gave a mixture of γ and ε-alkynylated products analyzed by proton NMR.

12. Alkynylation of different substituted bromoalkyne

Table 3S Alkynylation of different substituted bromoalkyne



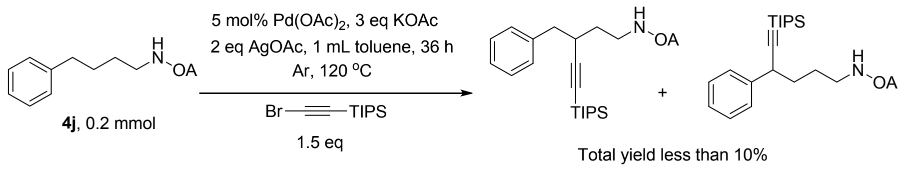
We had tested the alkyl and aryl alkynyl bromide under standard condition. The alkyl alkynyl bromide (**2a**) gave the desired products in 46% isolated yield. Unfortunately, the aryl alkynyl bromide (**2b**) failed to give any alkynylated product, only starting material recovered.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 (d, J = 7.9 Hz, 1H), 7.08 (br s, 1H), 6.99 (dd, J = 7.7, 0.8 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 4.58 – 4.51 (m, 1H), 3.82 (s, 3H), 3.55 – 3.50 (m, 2H), 3.45 (dd, J = 13.6, 6.8 Hz, 1H), 1.40 (d, J = 6.8 Hz, 6H), 1.32 (s, 9H), 1.14 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.47, 163.41, 157.52, 129.20, 127.31, 125.27, 124.52, 110.05, 102.79, 55.60, 49.55, 46.43, 39.62, 31.11, 28.28, 27.24, 20.95, 20.17; HRMS (ESI-TOF) m/z [M+H]$^+$ Calcd for $C_{23}H_{35}N_2O_3$: 387.2648; found: 387.2645.

13. Alkynylation of δ-Arylbutamine Derivatives

Scheme 5S Alkynylation of δ-Arylbutamine Derivatives.



We had tested the delta-amide (**4j**) under standard condition. However it failed to give any delta-position alkynylated product. In fact a mixture of γ and δ-alkynylated product was observed which was analyzed by proton NMR.

14. References

[1] T.-S. Mei, X. Wang and J.-Q. Yu, *J. Am. Chem. Soc.,* 2009, **131**, 10806.
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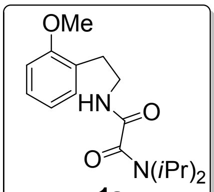
15. NMR spectra



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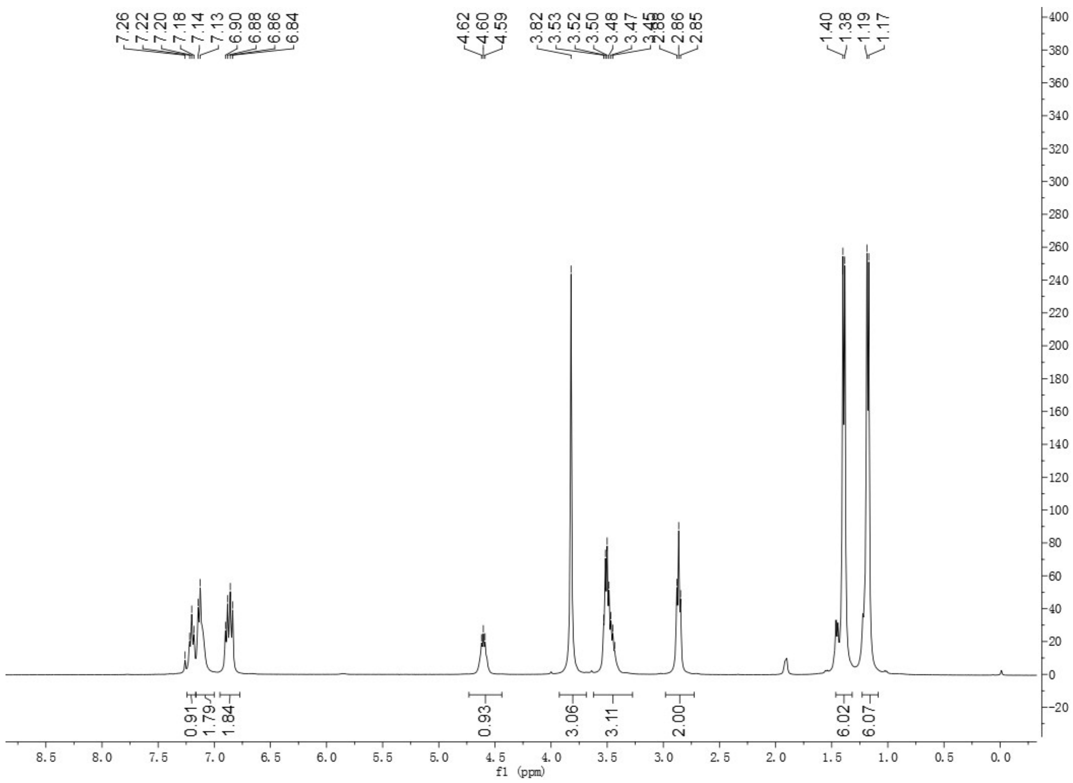

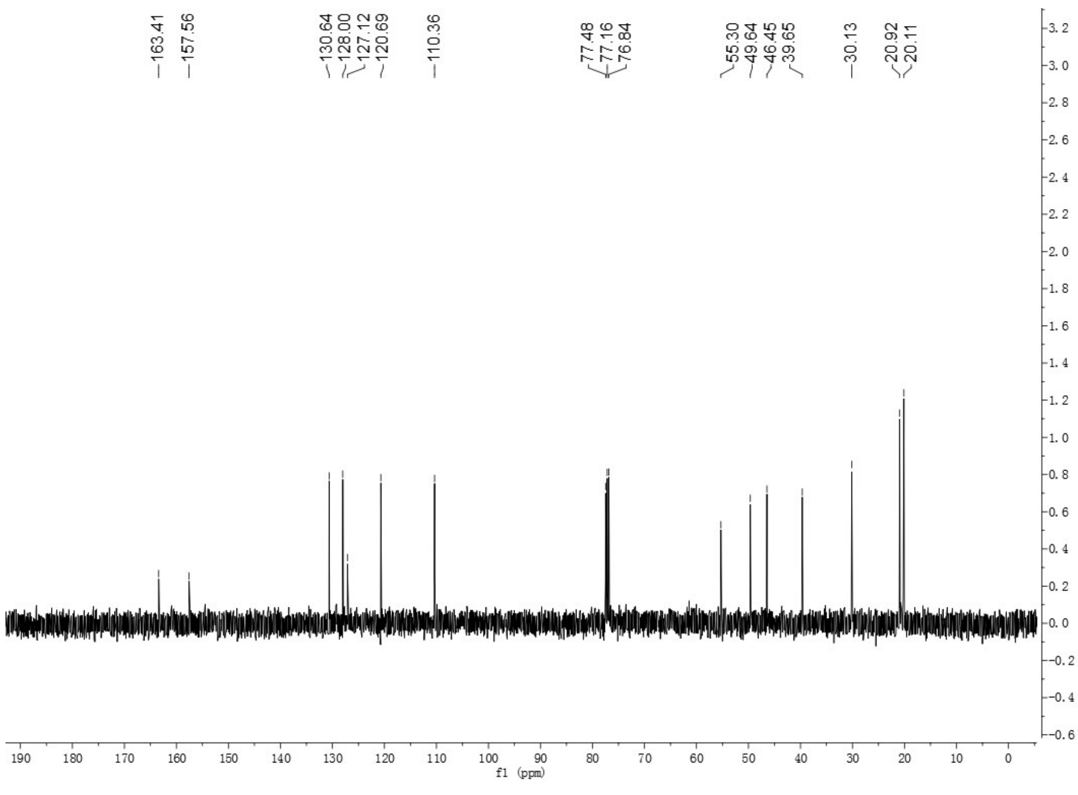

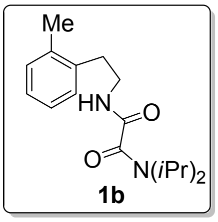
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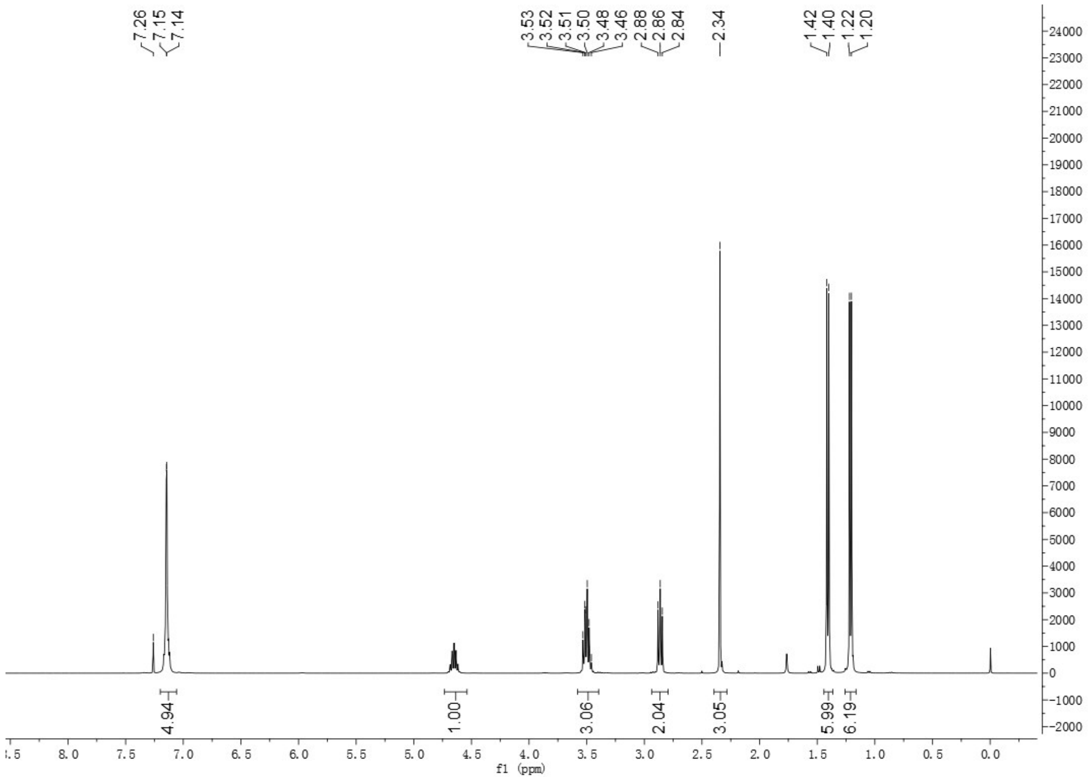
HN
O
O
N(iPr)2

1b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7.15
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2.88
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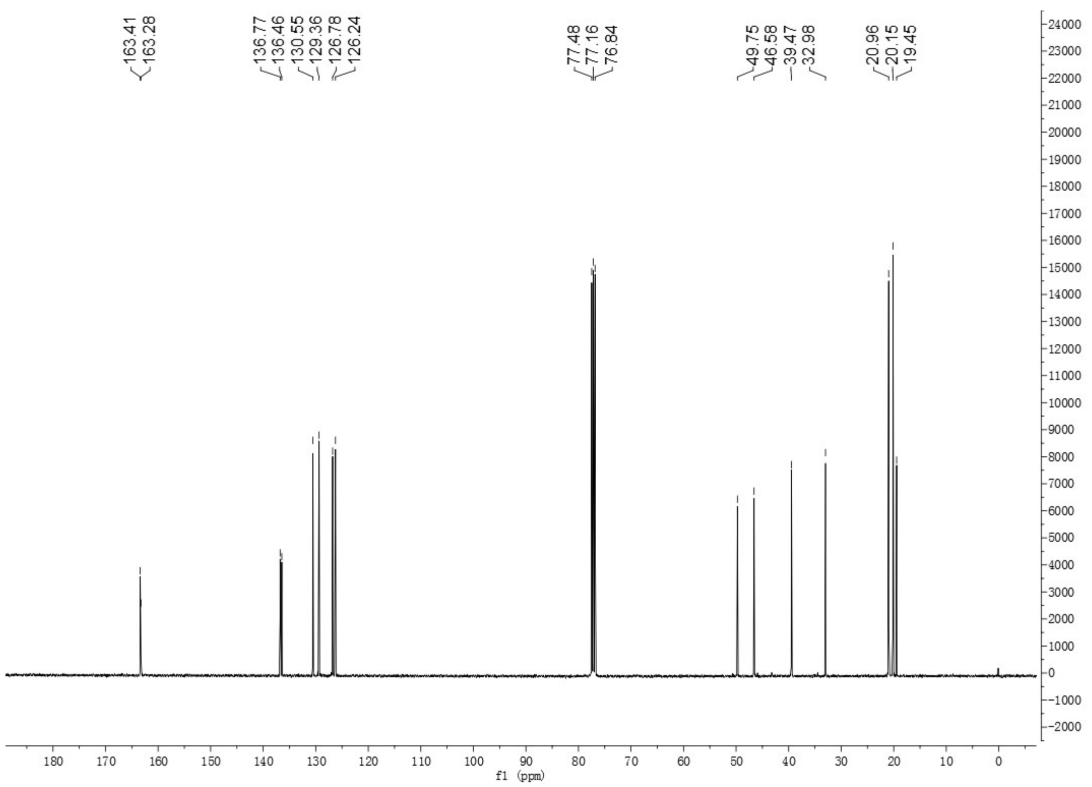
2.34
1.42
1.40
1.22
1.20
4.94
1.00
3.06
2.04
3.05
5.99
6.19
f1 (ppm)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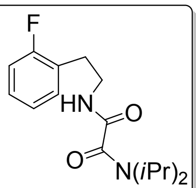
f1 (ppm)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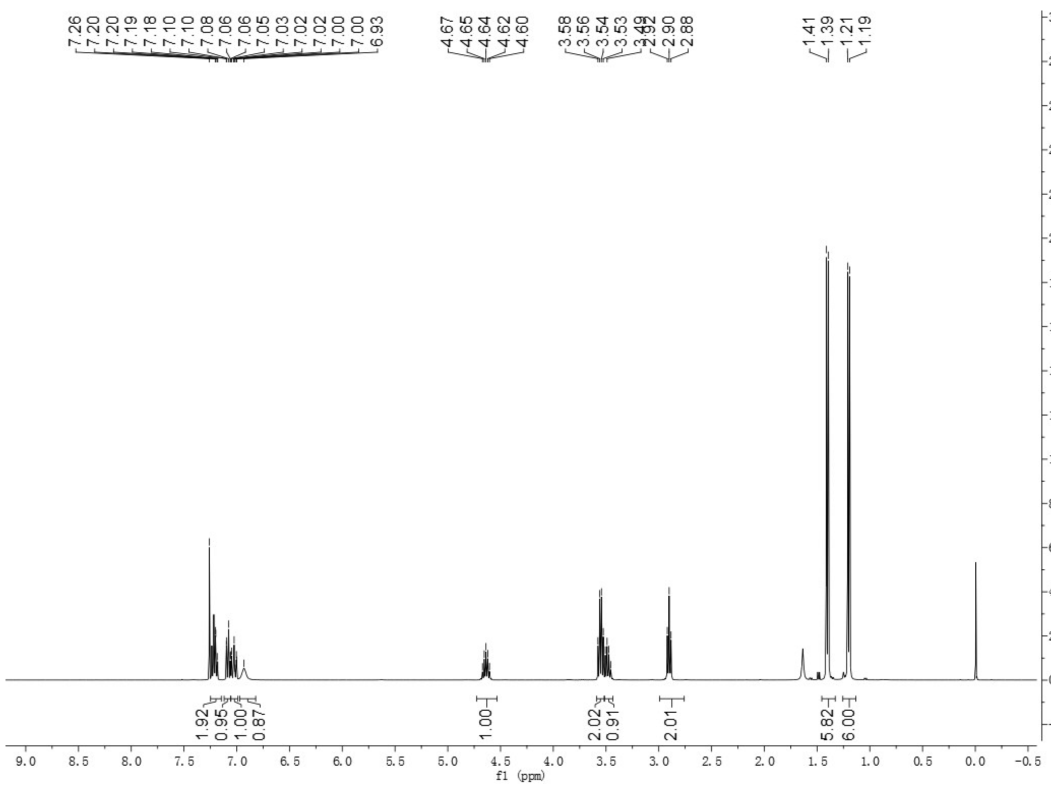
HN
O
O
N(iPr)2

1c



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7.02
7.00
7.00
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4.65
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3.54
3.53
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2.90
2.88
1.41
1.39
1.21
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1.00
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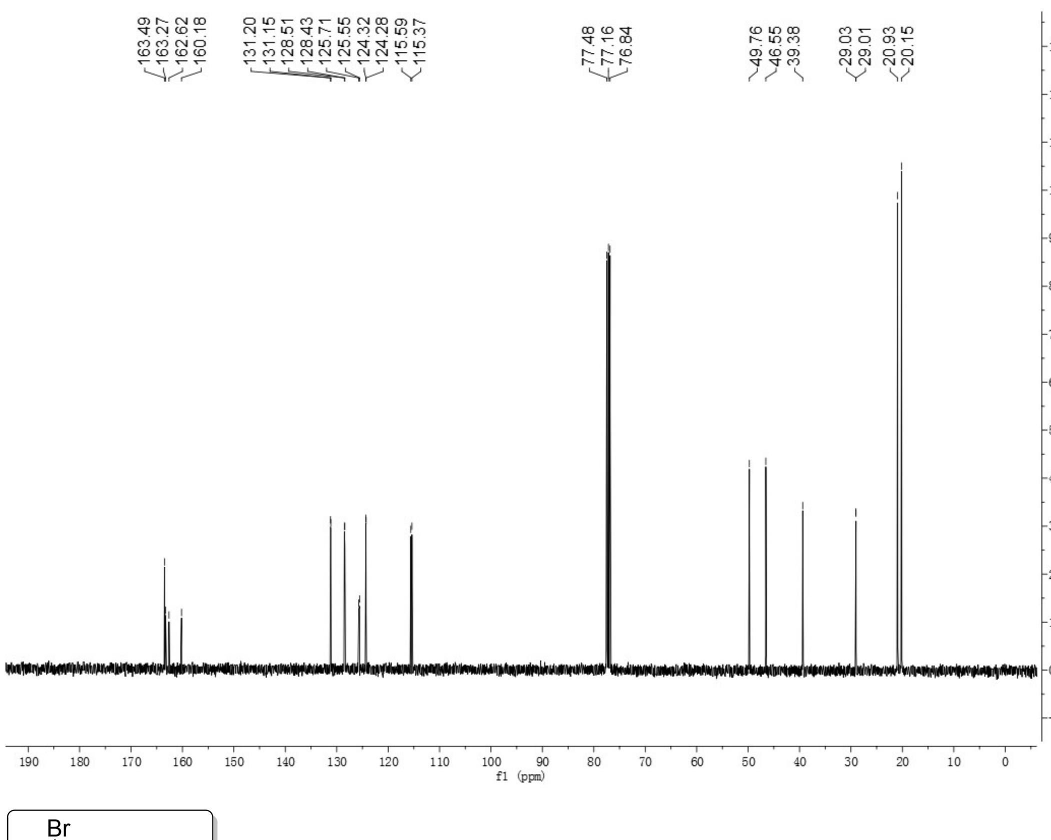
f1 (ppm)



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46.55
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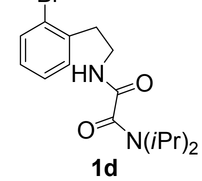
20.15
f1 (ppm)



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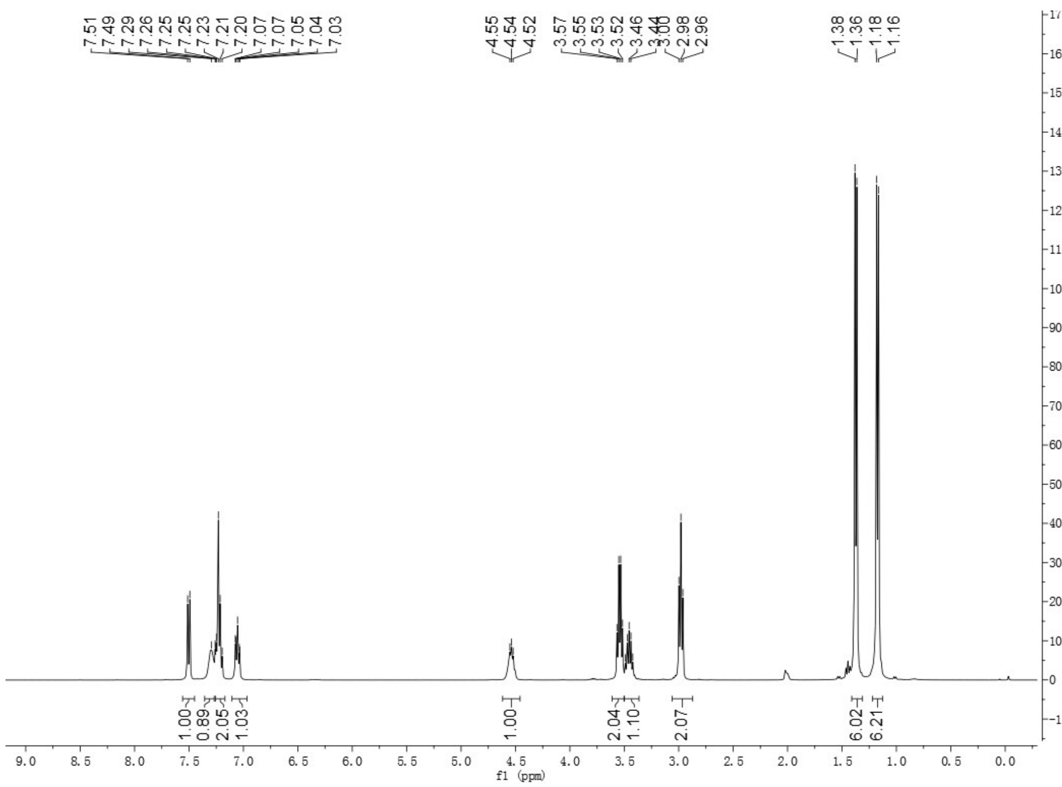
HN
O
O
N(iPr)2

1d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1.00 0.89 2.05 1.03
1.00
2.04 1.10
2.07
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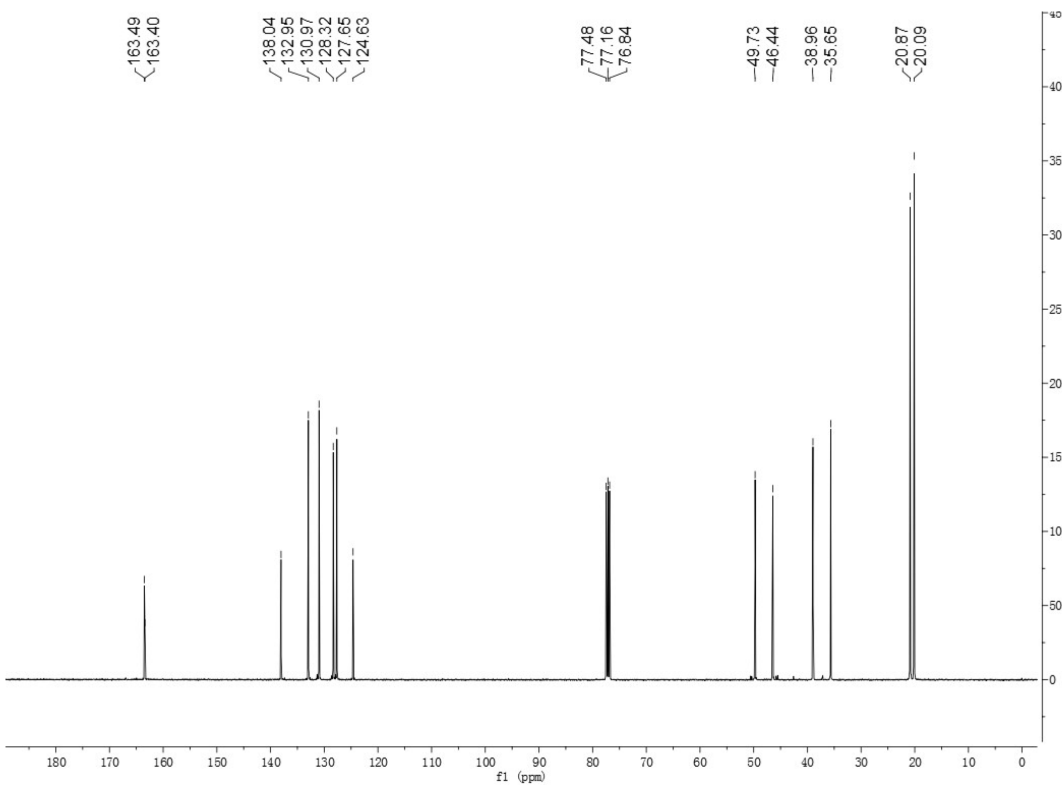
f1 (ppm)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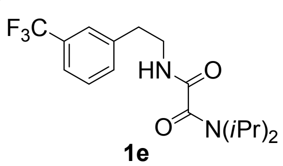
f1 (ppm)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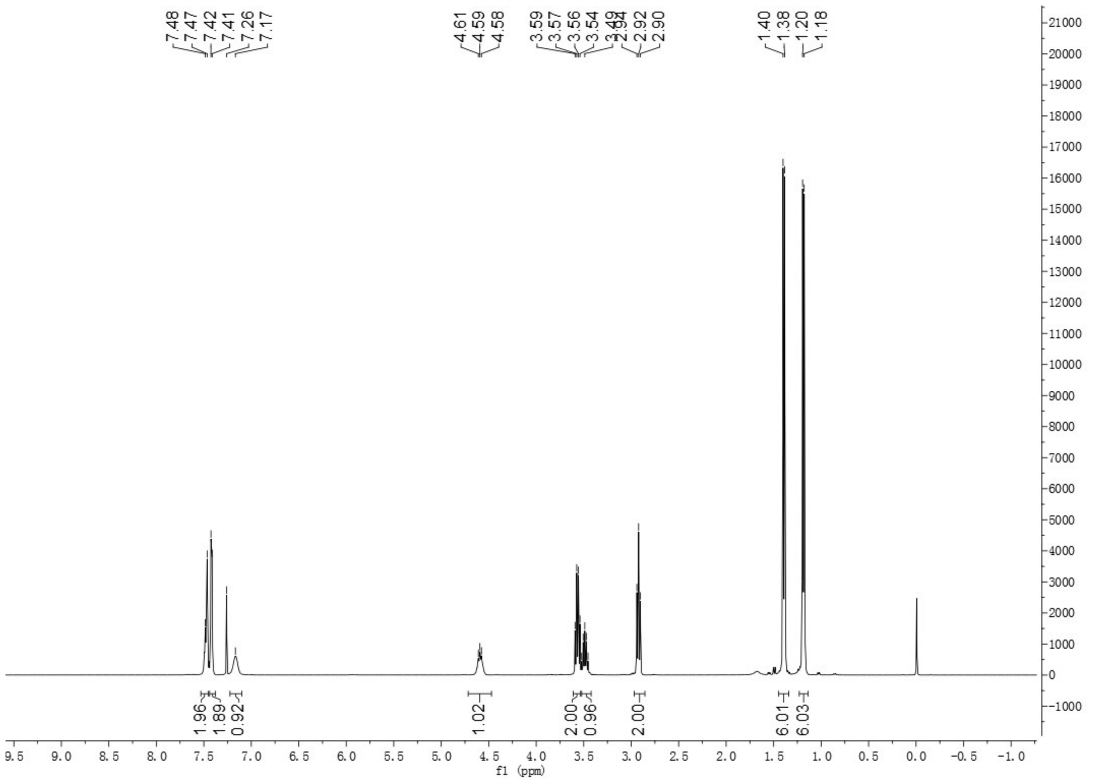
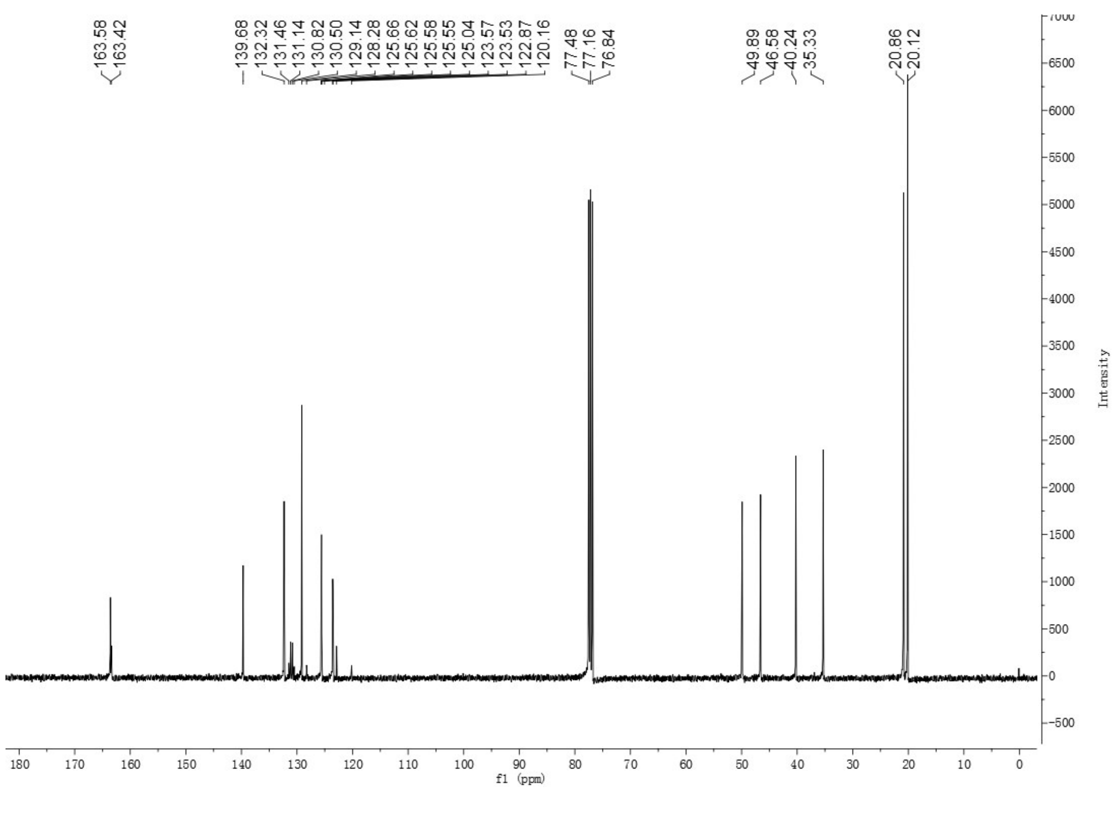
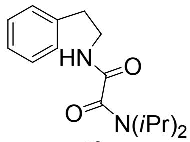
O
N(iPr)2

1e







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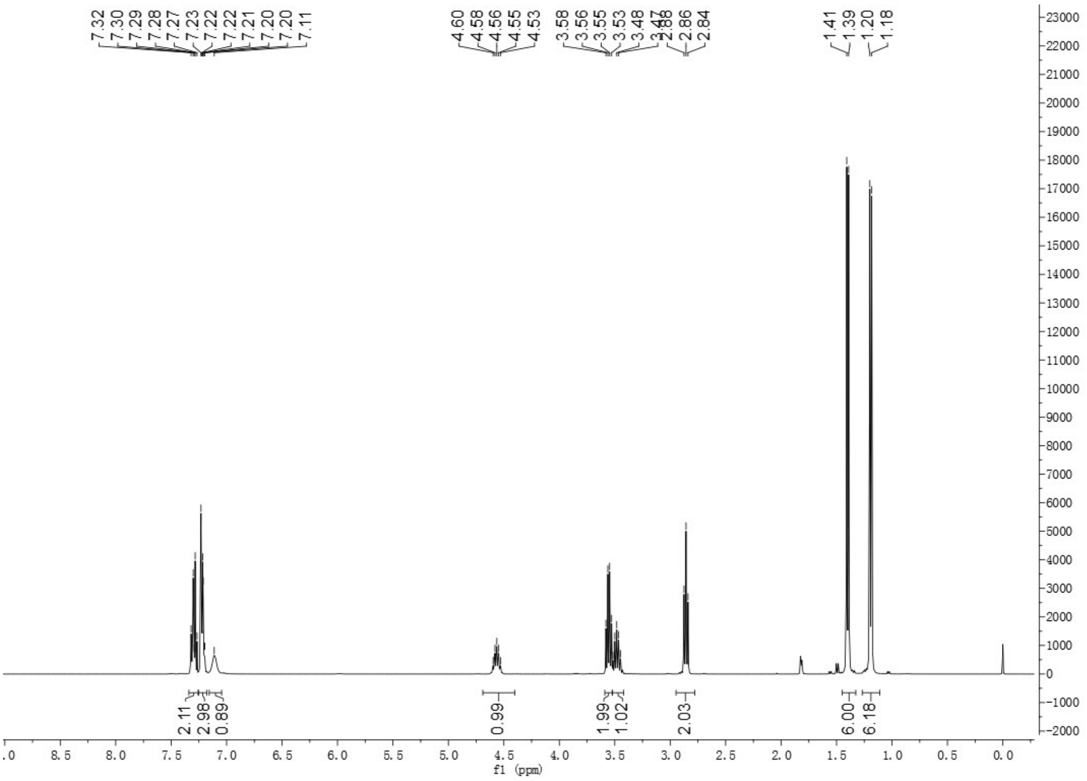

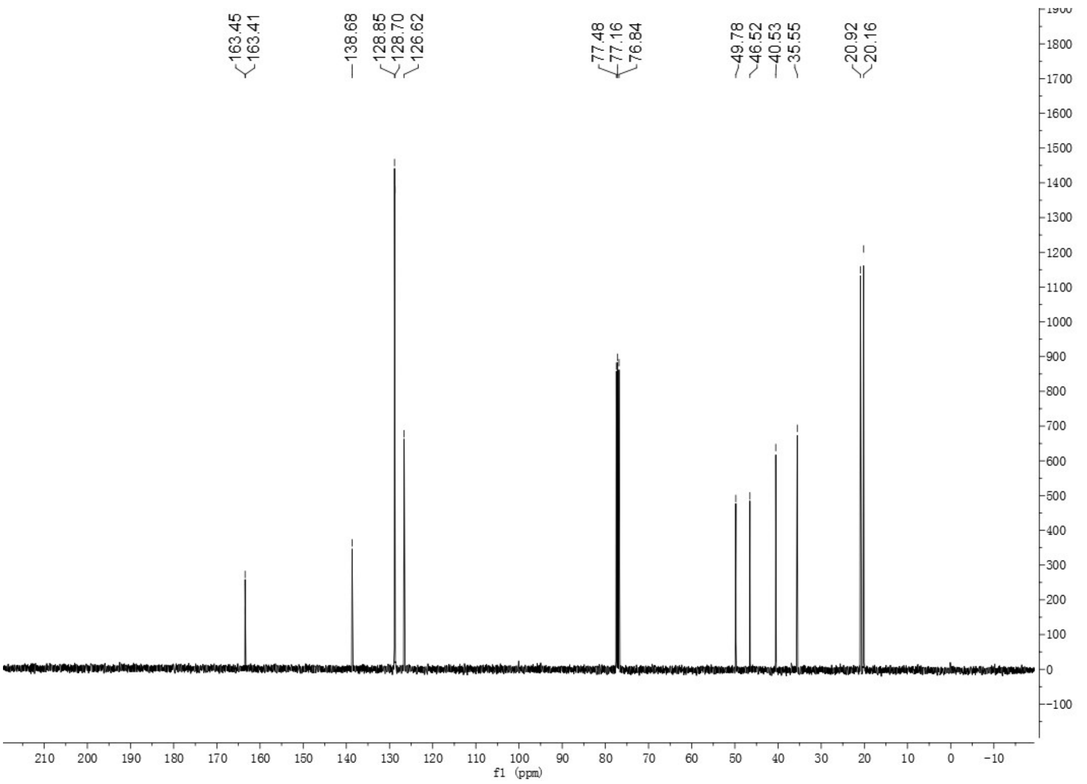

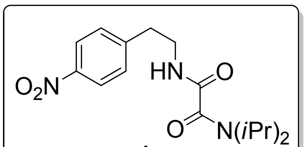
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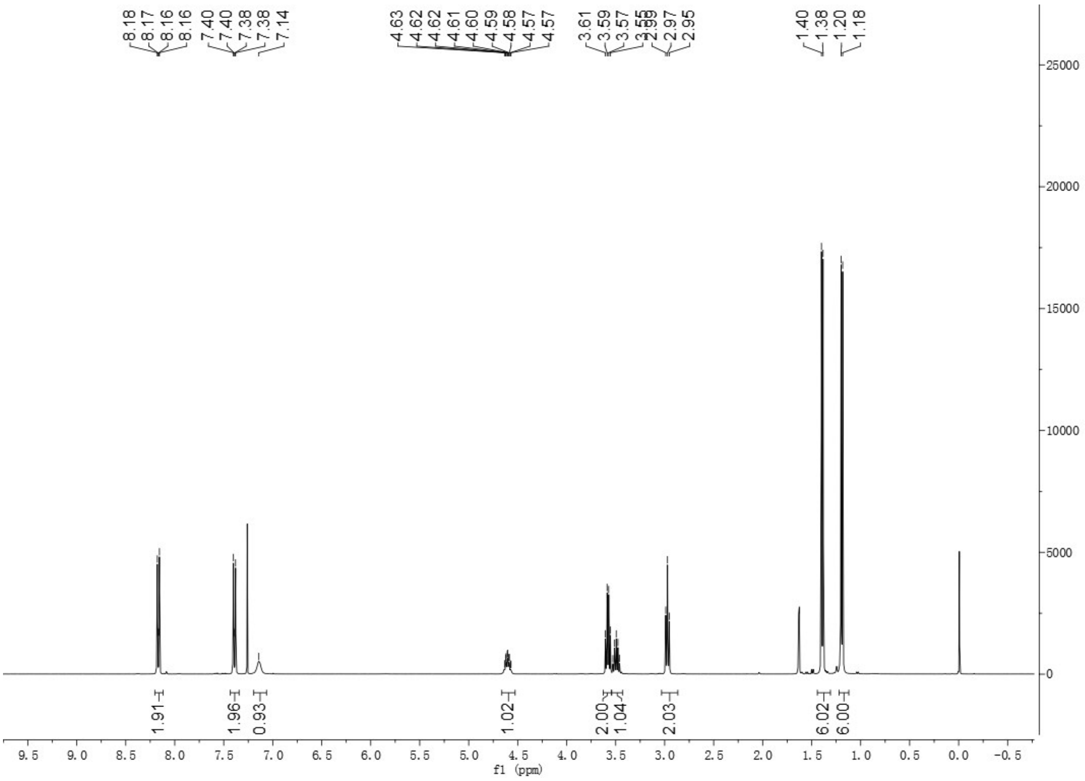
O
O
N(iPr)2

1g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7.40
7.38
7.38
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4.58
4.57
4.57
3.61
3.59
3.57
3.55
2.99
2.97
2.95
1.40
1.38
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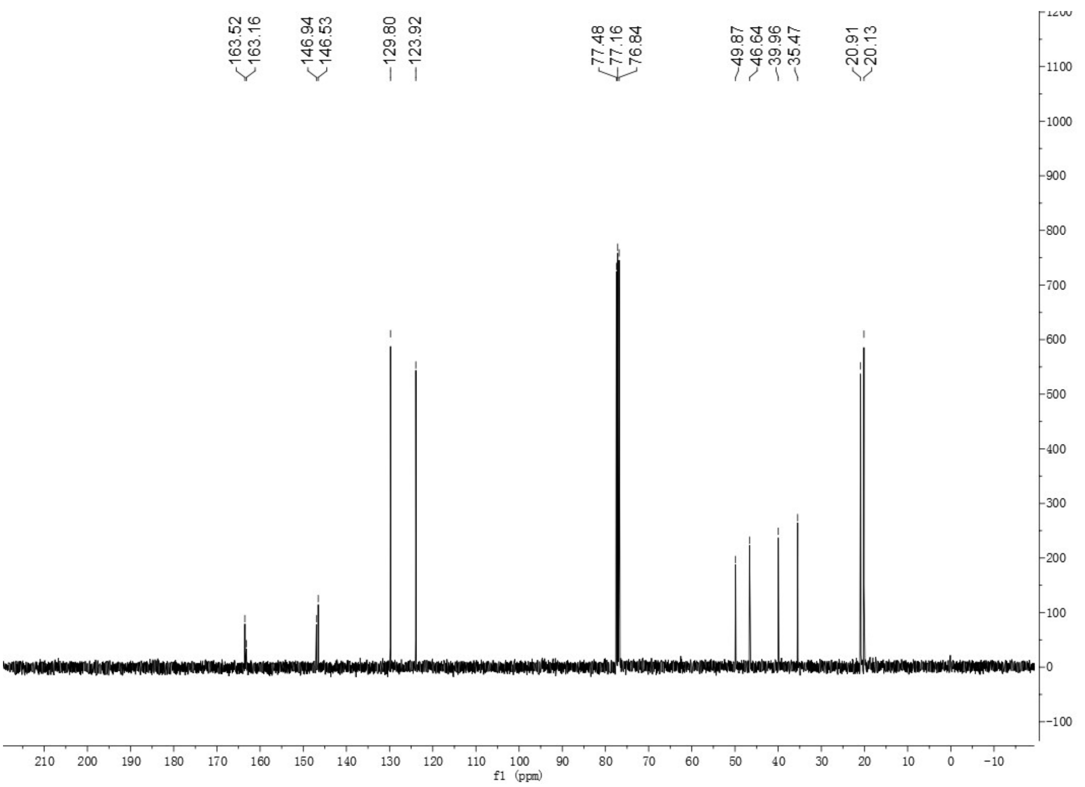
1.04
2.03
6.02
6.00
f1 (ppm)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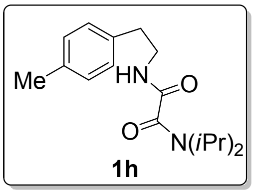
f1 (ppm)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O
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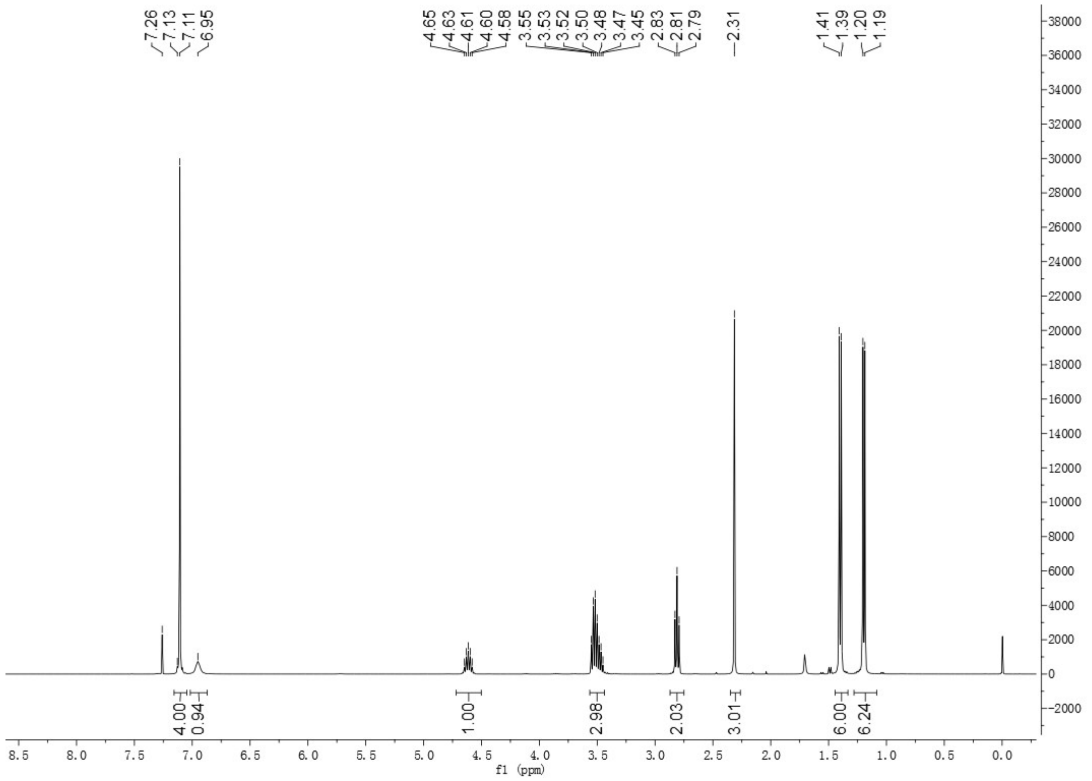
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3.50
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3.47
3.45
2.83
2.81
2.79
2.31
1.41
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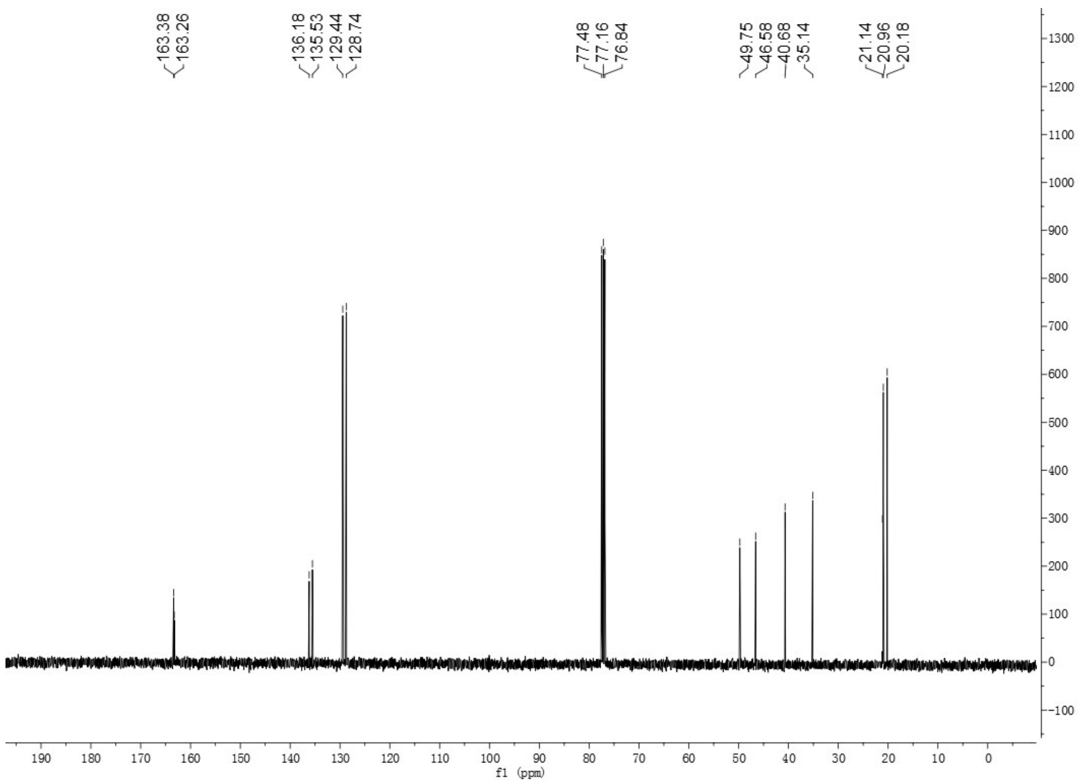
1.00
2.98
2.03
3.01
6.00
6.24
f1 (ppm)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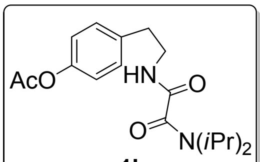
f1 (ppm)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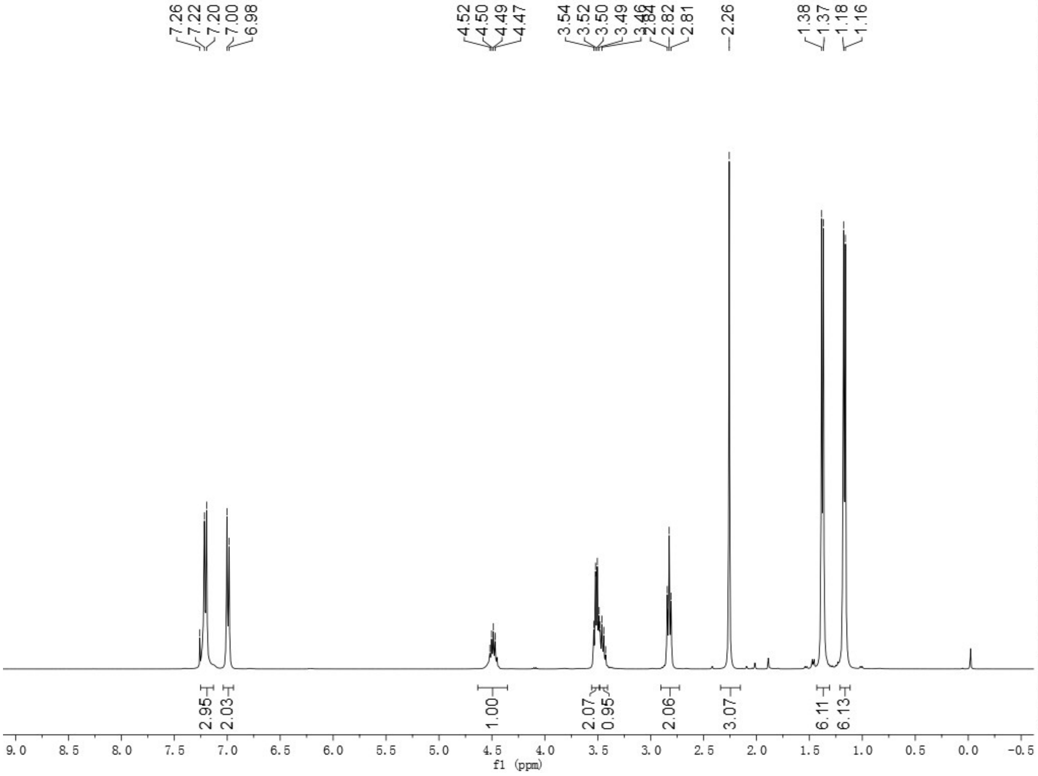
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1.37
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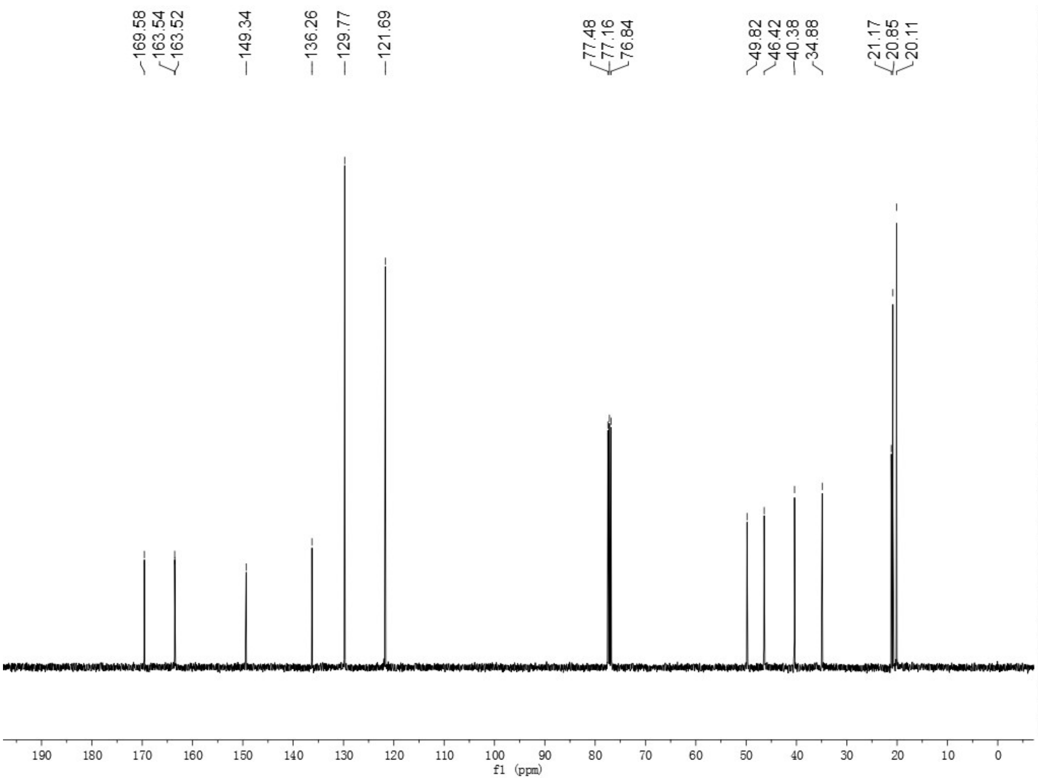
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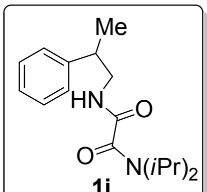
20.11
f1 (ppm)



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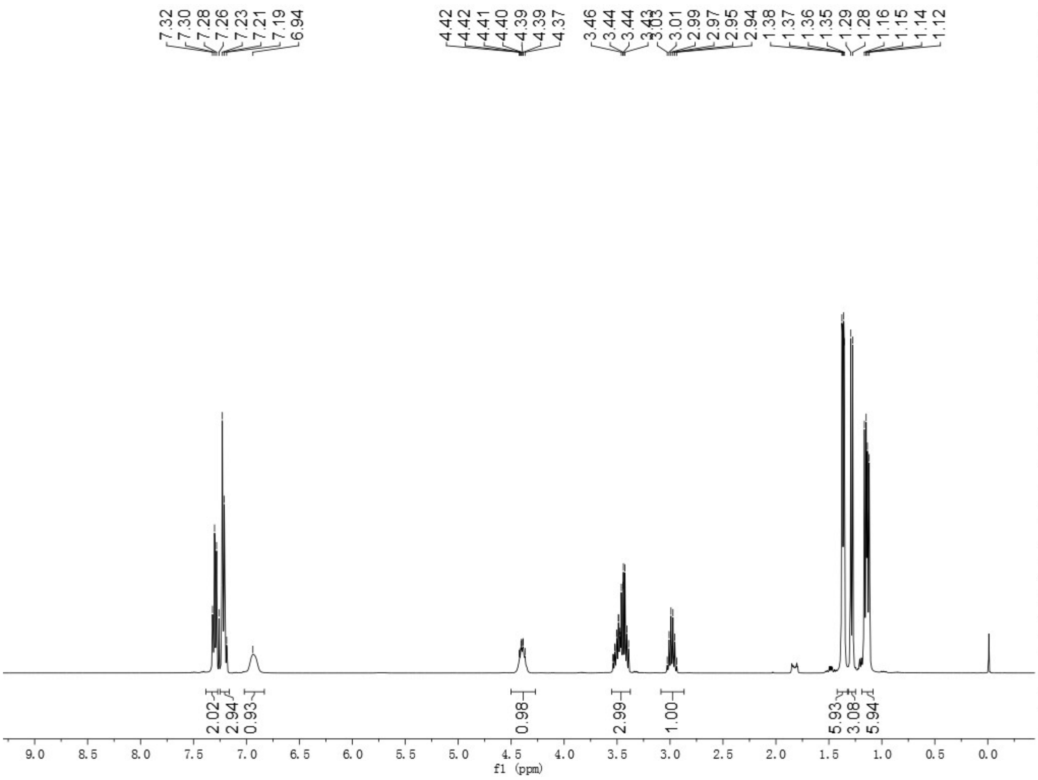

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1.38
1.37
1.36
1.35
1.29
1.28
1.16
1.15
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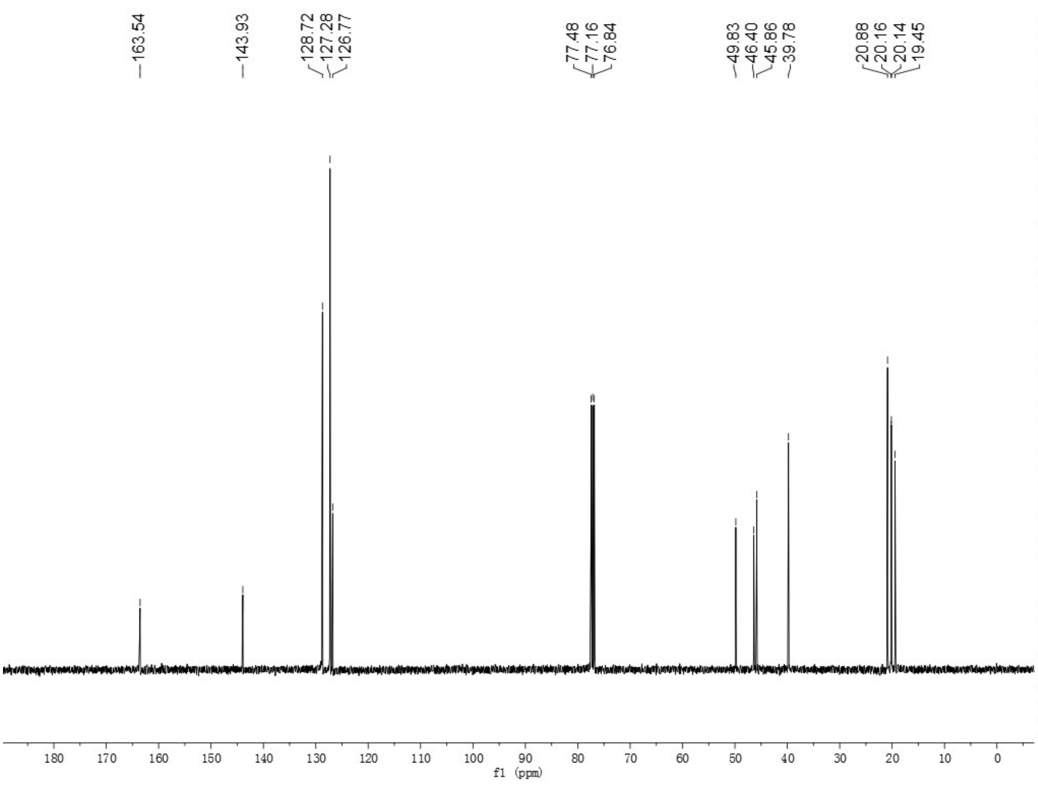

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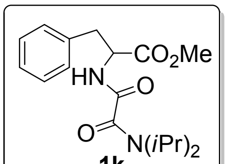

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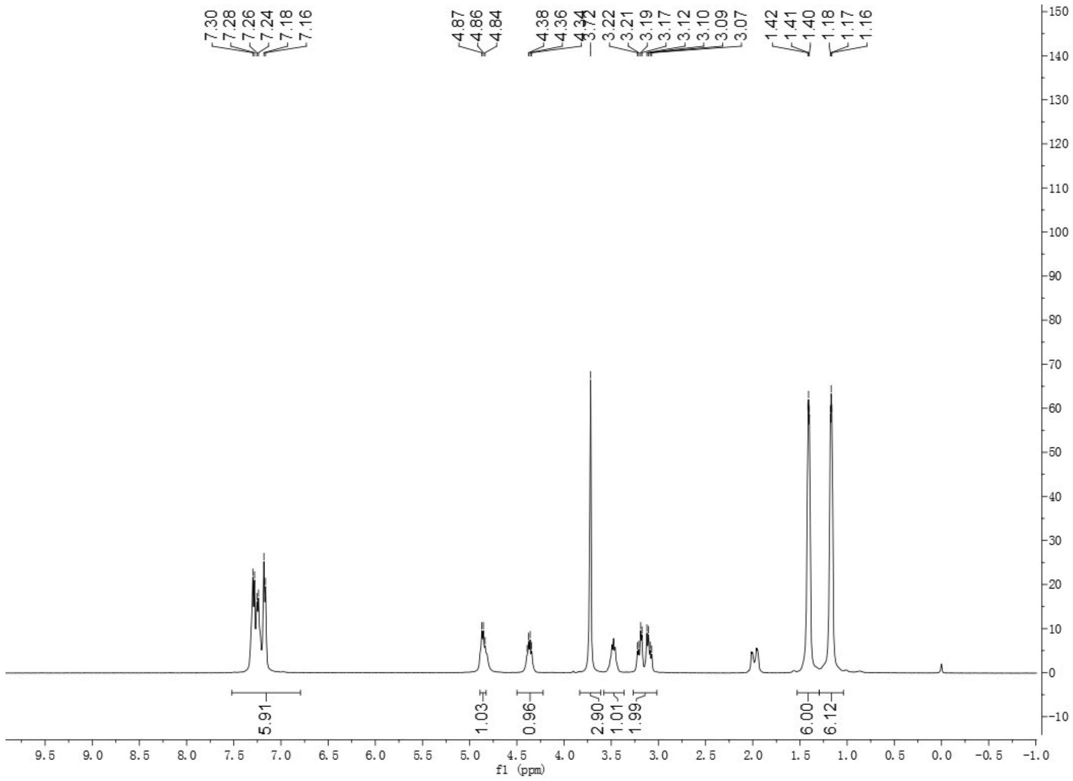

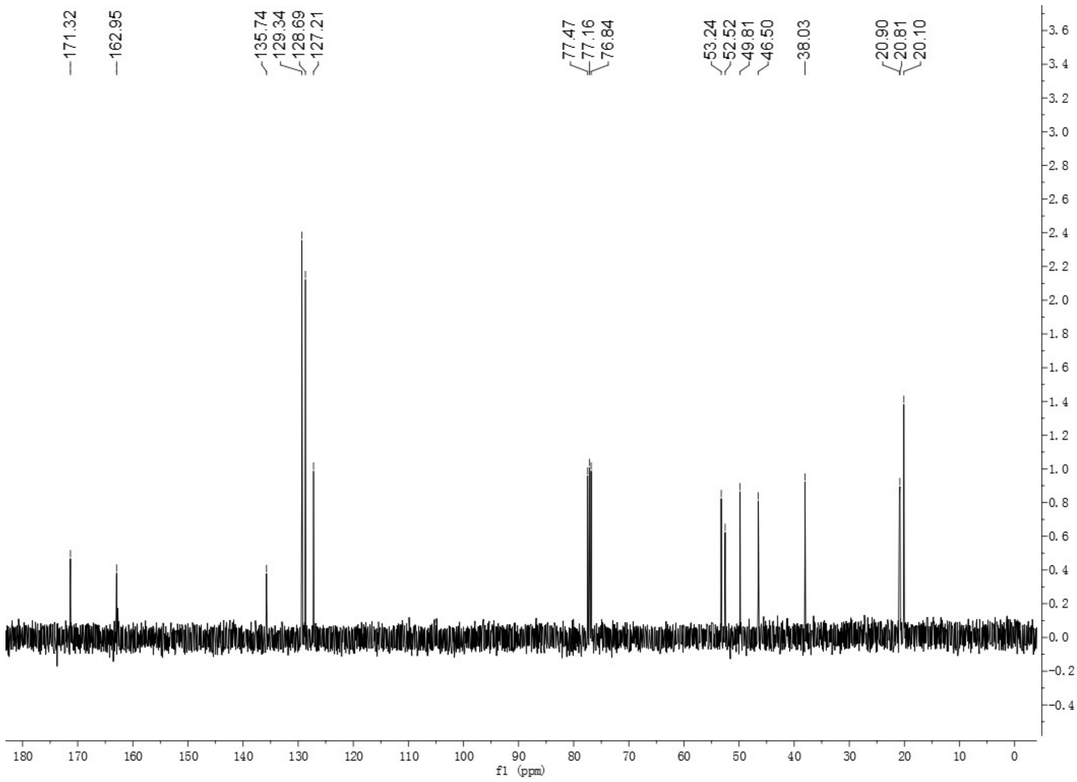

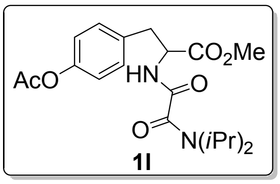
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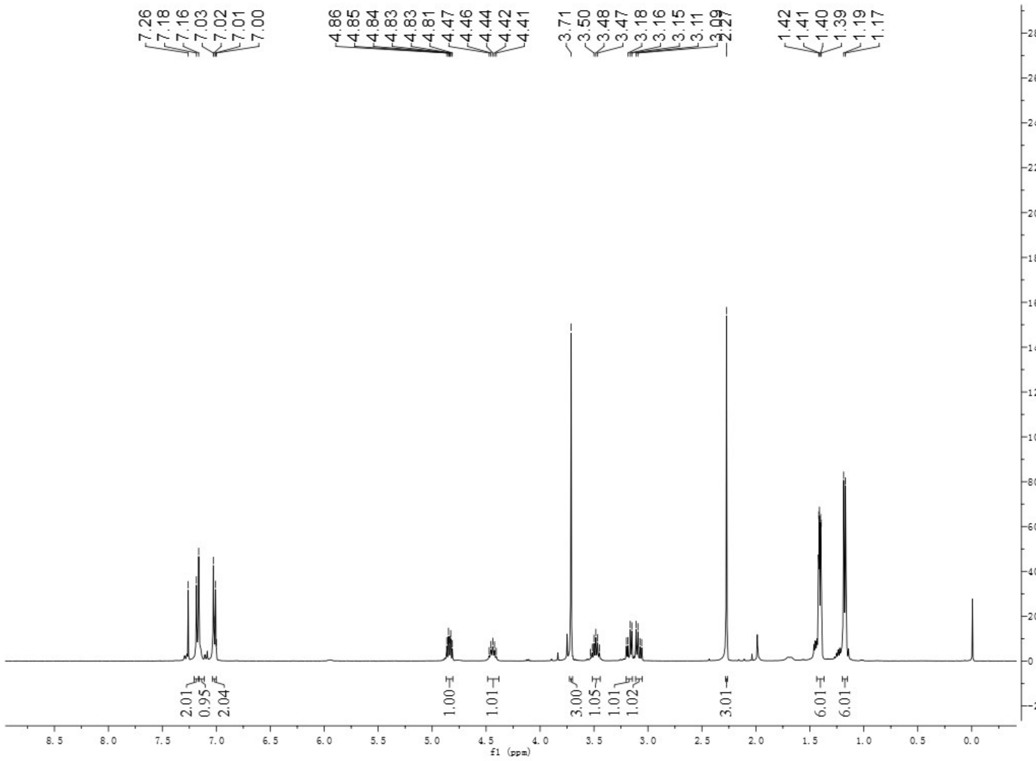
O
N(iPr)2

1l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4.83
4.83
4.81
4.47
4.46
4.44
4.42
4.41
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3.50
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3.47
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3.15
3.11
3.09
2.27
1.42
1.41
1.40
1.39
1.19
1.17
2.01
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1.05
1.01
1.02
3.01
6.01
6.01
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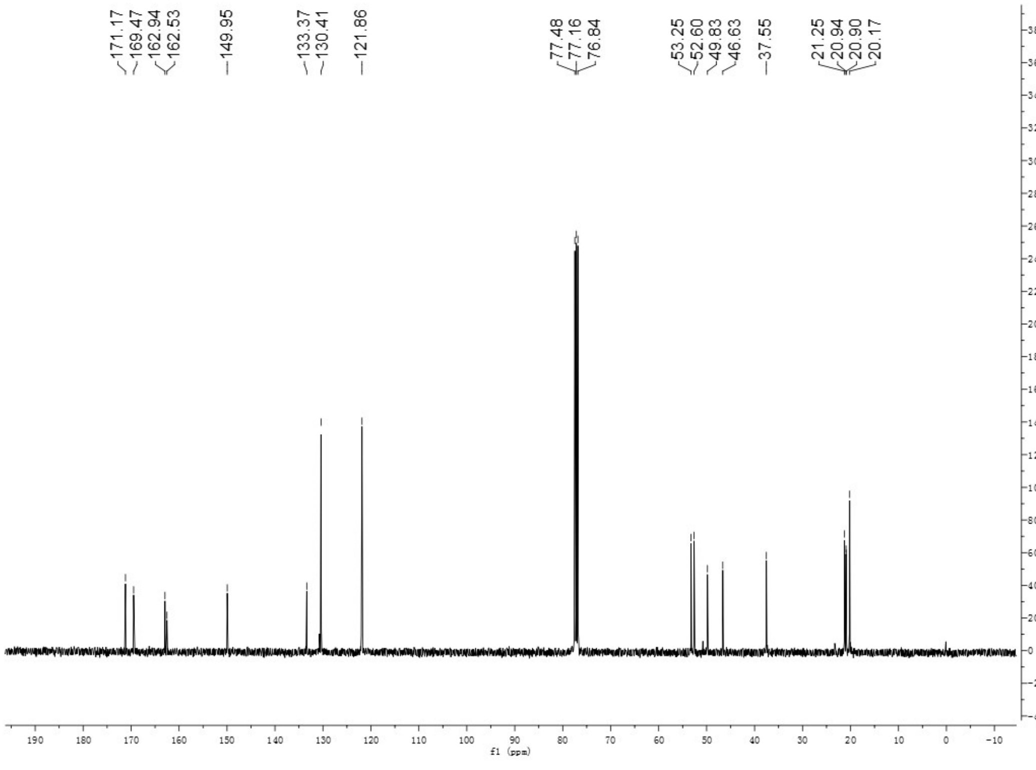
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37.55
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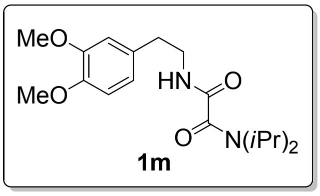
20.90
20.17
f1 (ppm)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O
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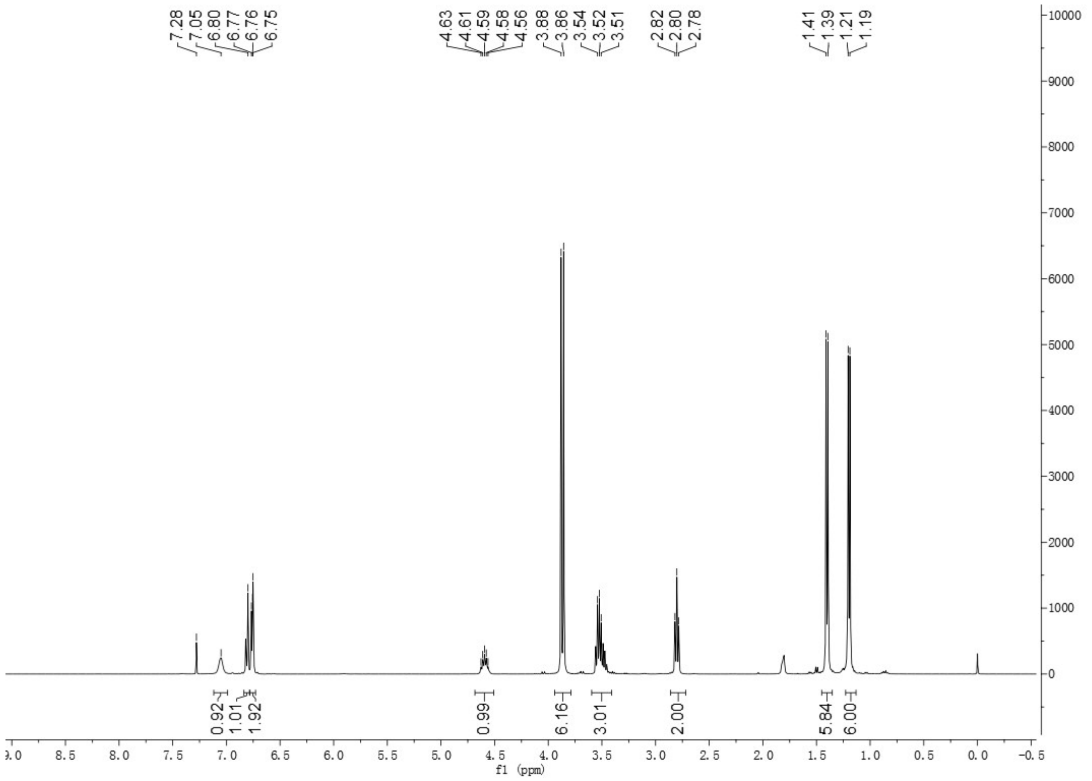
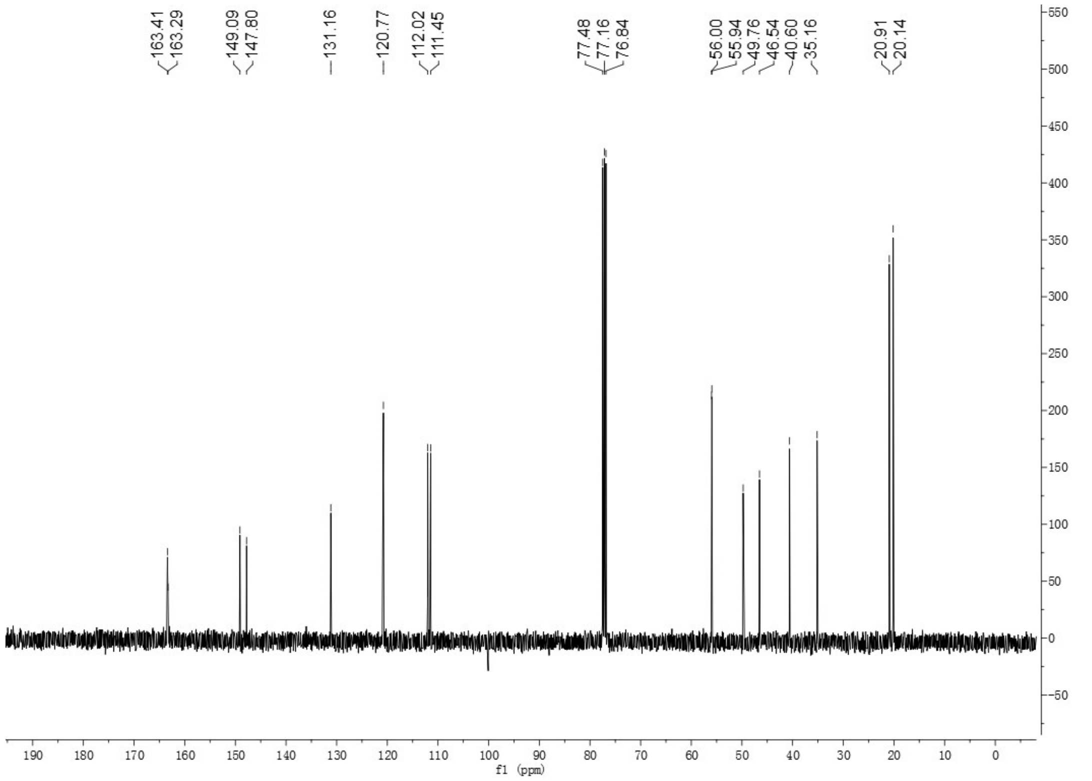
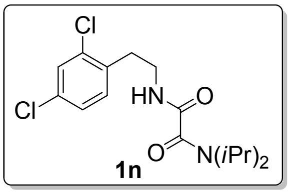
1m



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Cl
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O
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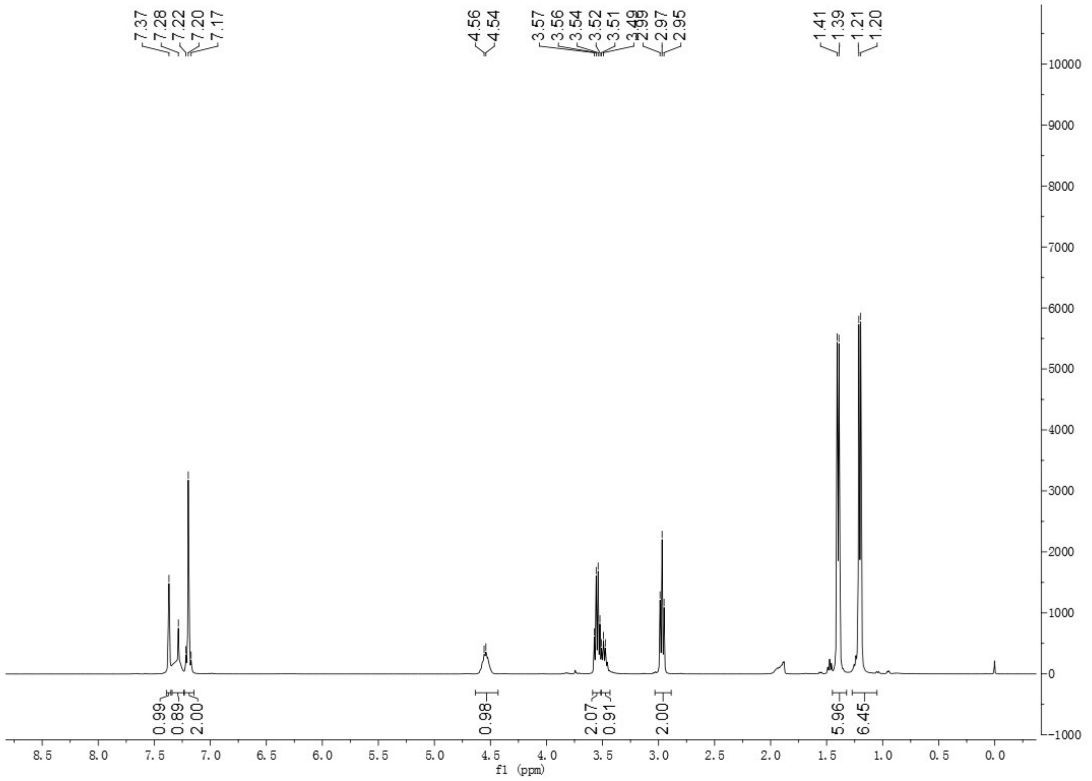
1n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3.49
2.99
2.97
2.95
1.41
1.39
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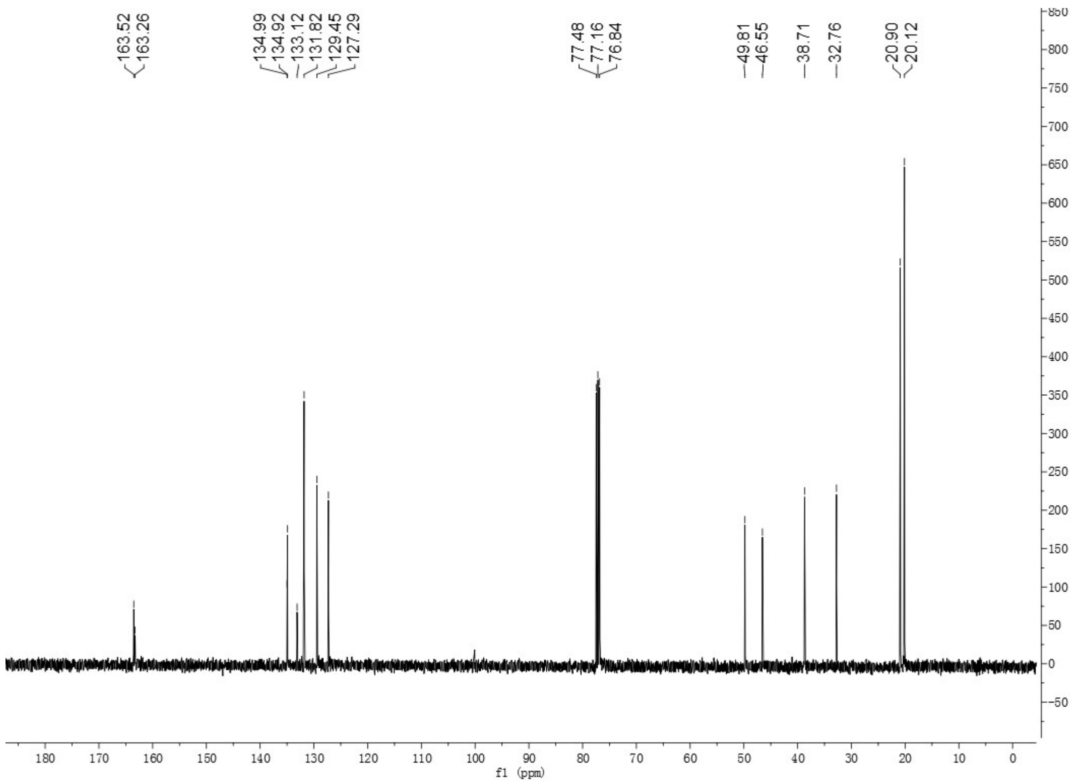
2.00
5.96
6.45
f1 (ppm)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46.55
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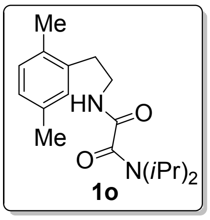
32.76
20.90
20.12
f1 (ppm)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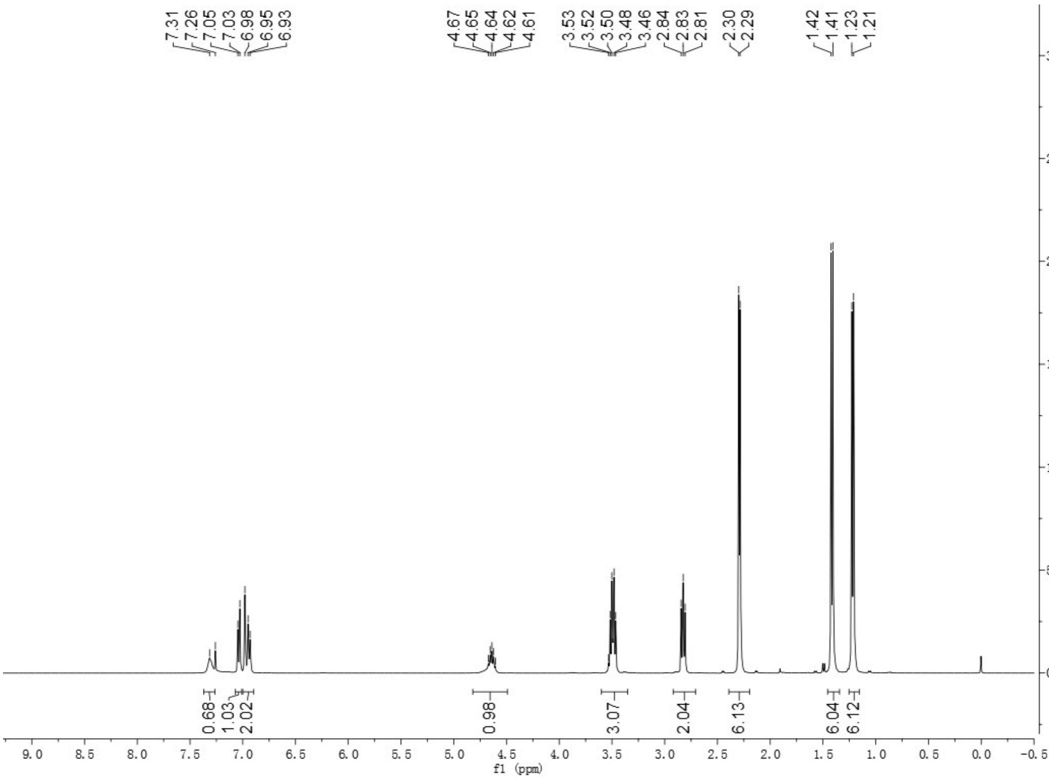
O
Me
O
N(iPr)2
1o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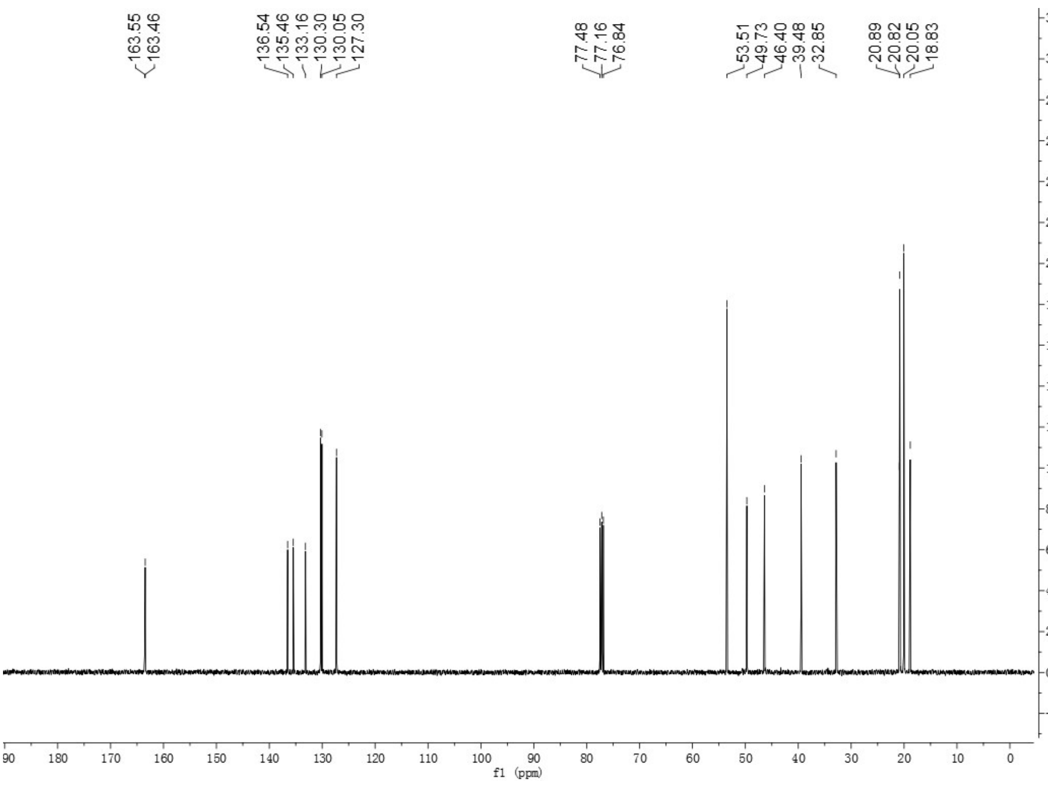
2.30 2.29
1.42 1.41 1.23 1.21
0.68 1.03 2.02 0.98 3.07 2.04 6.13 6.04 6.12
f1 (ppm)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53.51 49.73 46.40 39.48 32.85
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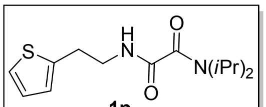
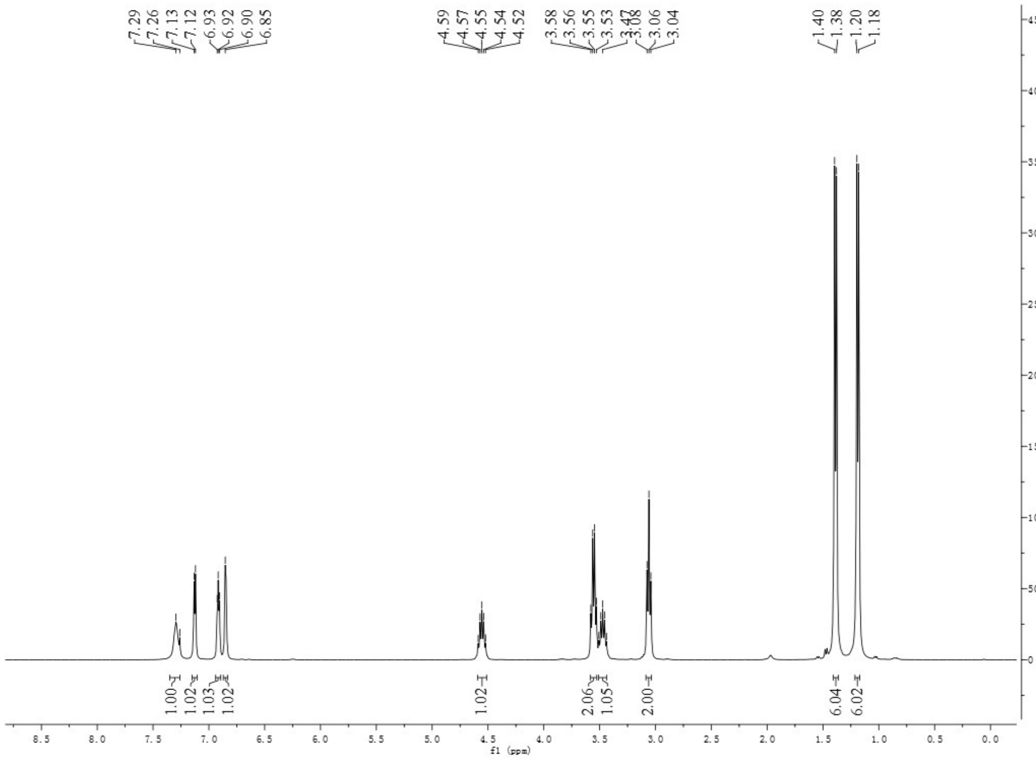
f1 (ppm)


S
H
N
O
O
N(iPr)2

1p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7.26
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6.90
6.85
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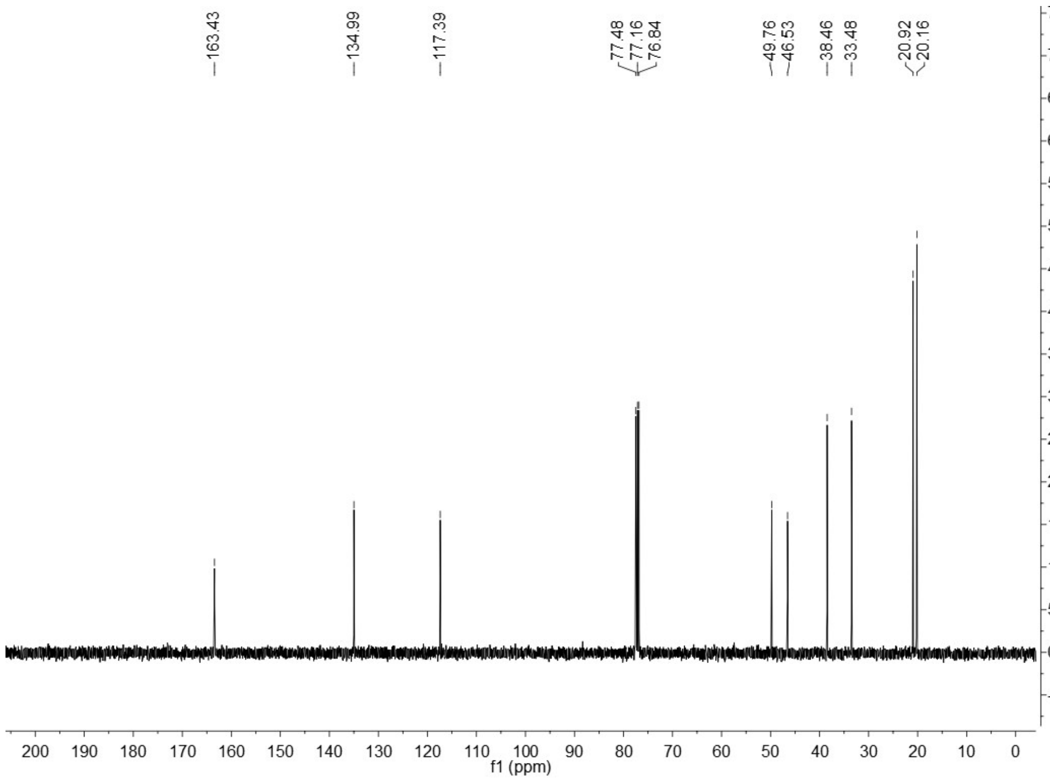
4.57
4.55
4.54
4.52
3.58
3.56
3.55
3.53
3.47
3.08
3.06
3.04
1.40
1.38
1.20
1.18
1.00
1.02
1.03
1.02
1.02
2.06
1.05
2.00
6.04
6.02
f1 (ppm)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46.53
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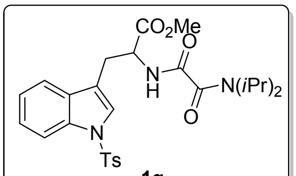
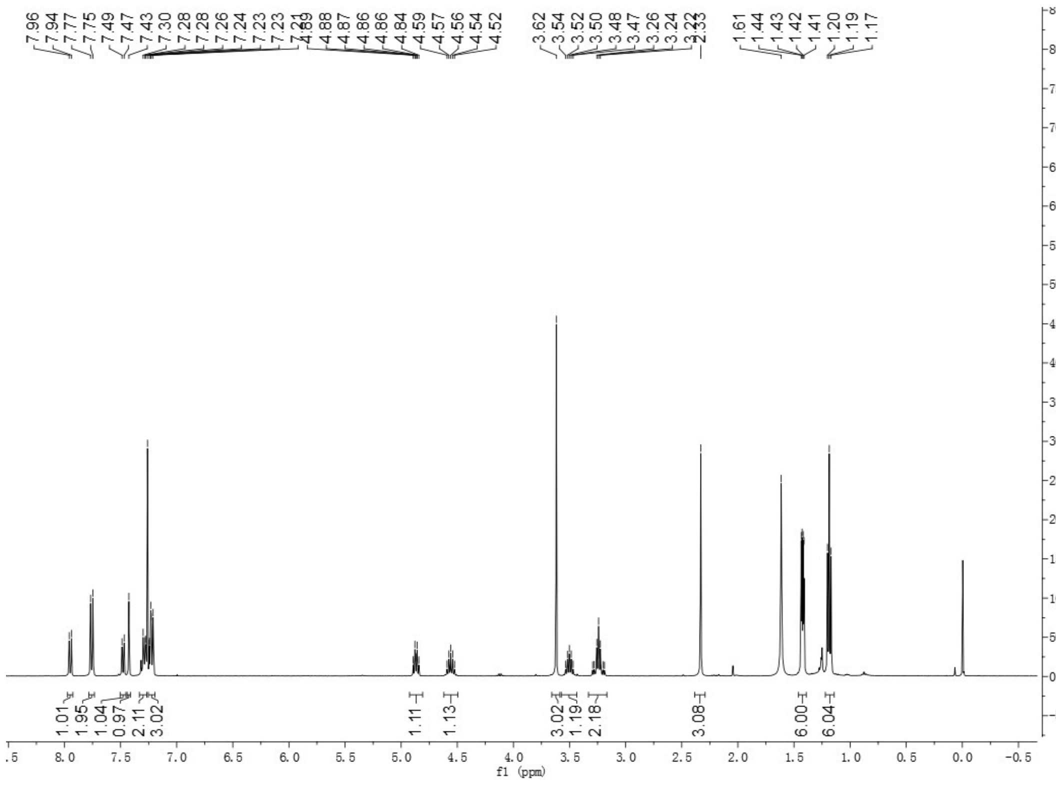
20.16
f1 (ppm)


CO2Me
O
N
H
N(iPr)2
O
N
Ts

1q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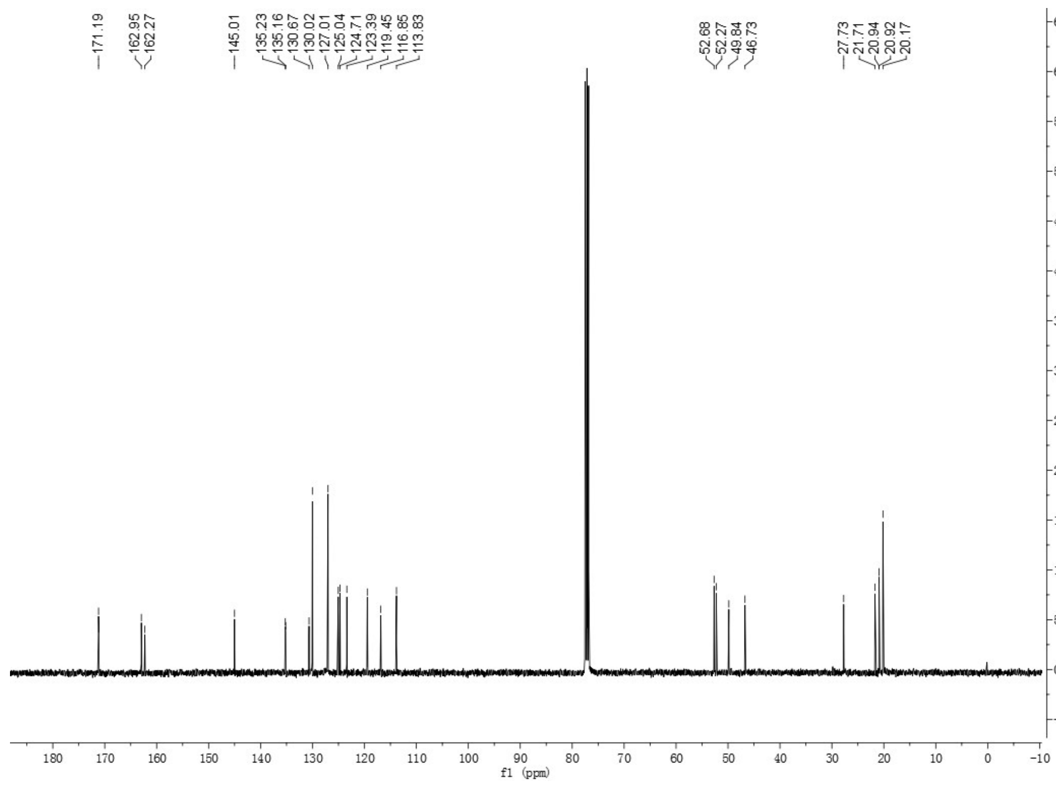
1.01 1.95 1.04 0.97 2.11 3.02 1.11 1.13 3.02 1.19 2.18 3.08 6.00 6.04
f1 (ppm)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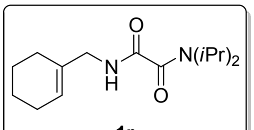
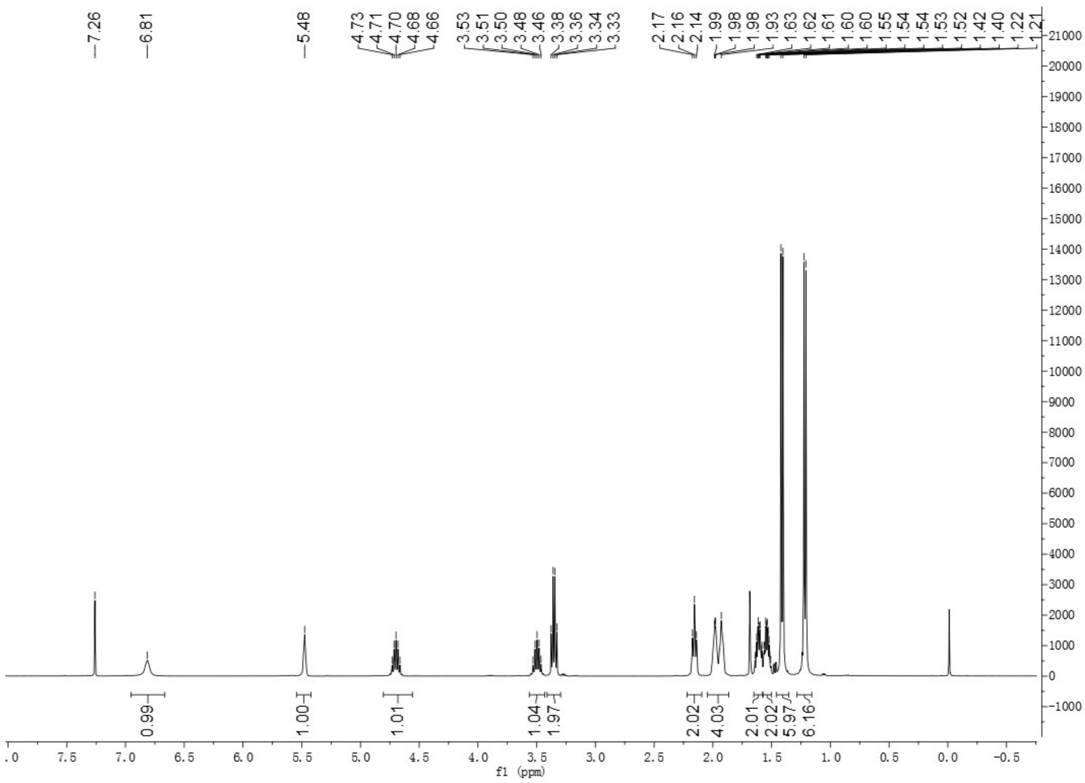
f1 (ppm)


O
N(iPr)2
N
H
O

1r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3.46
3.38
3.36
3.34
3.33
2.17
2.16
2.14
1.99
1.98
1.98
1.93
1.63
1.62
1.61
1.60
1.60
1.55
1.54
1.54
1.53
1.52
1.42
1.40
1.22
1.21
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1.00
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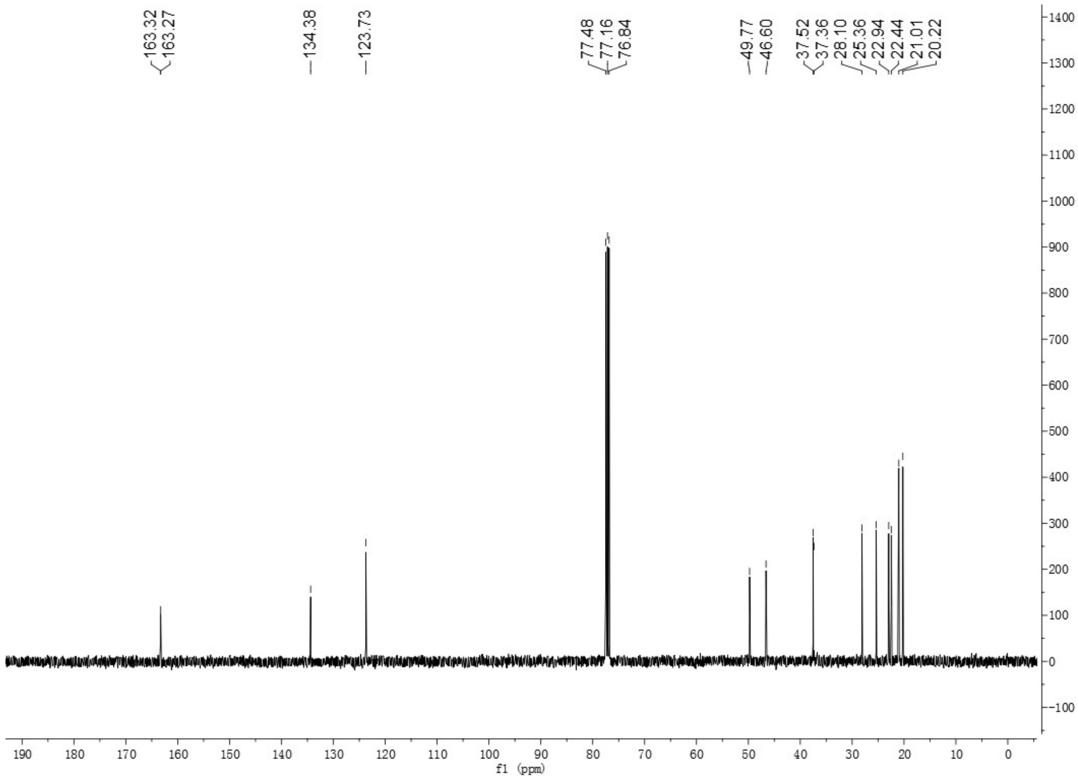
1.04
1.97
2.02
4.03
2.01
2.02
5.97
6.16
f1 (ppm)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123.73
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77.16
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49.77
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37.52
37.36
28.10
25.36
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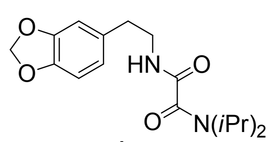
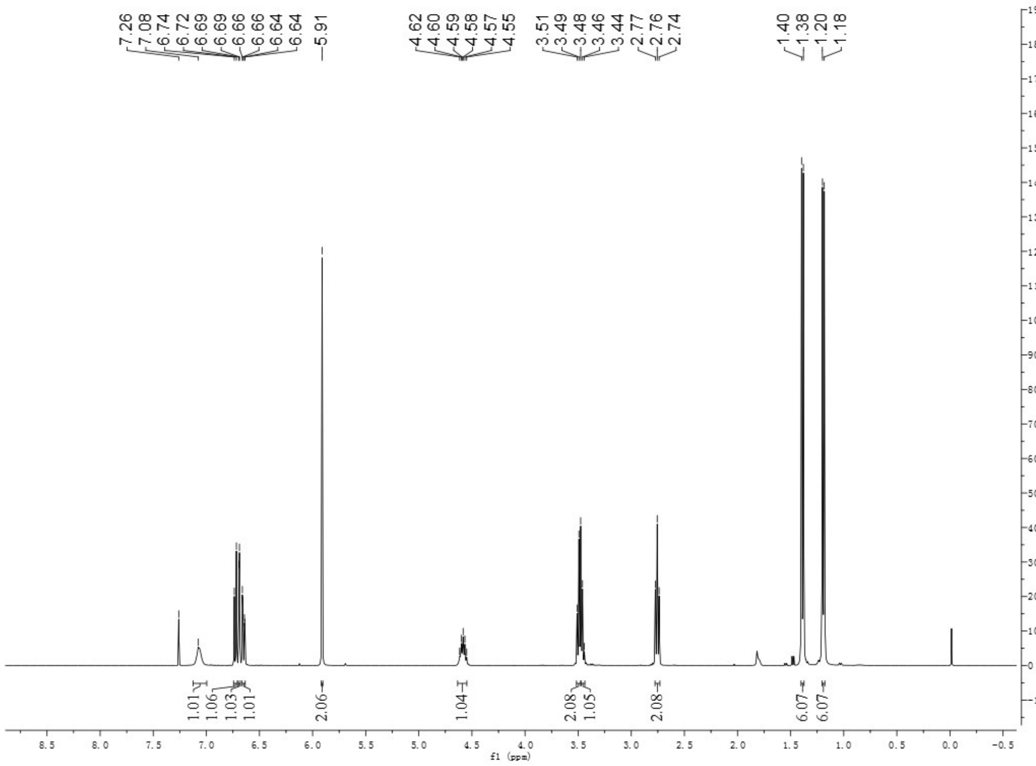
22.44
21.01
20.22
f1 (ppm)


HN
O
O
N(iPr)2

1s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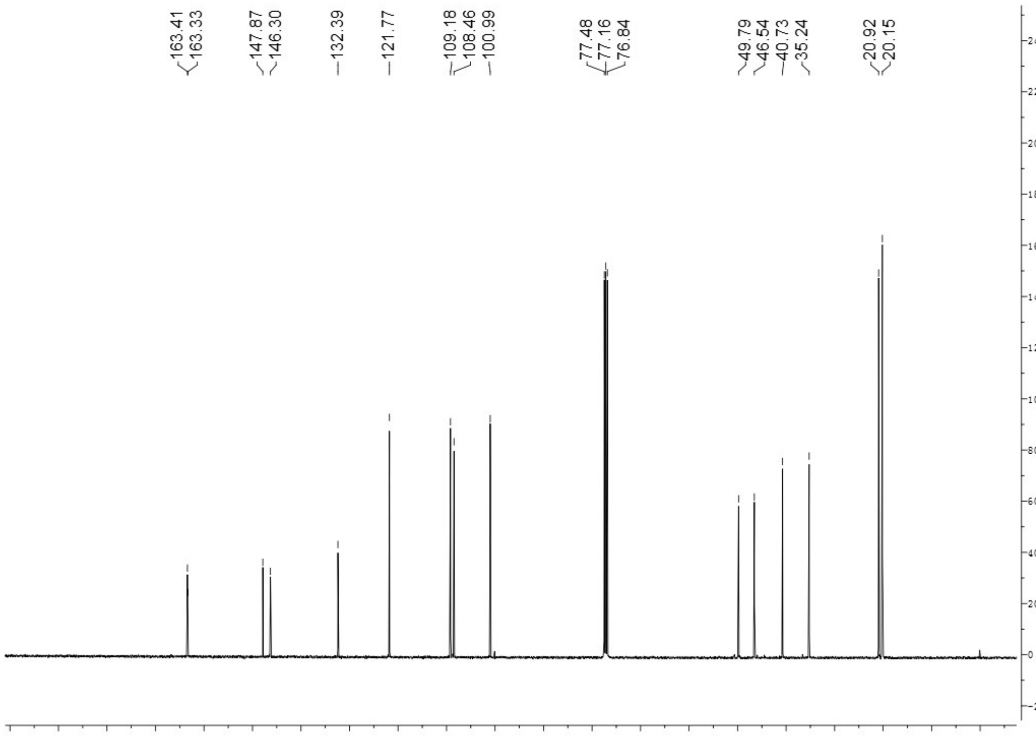
1.01 1.06 1.03 1.01 2.06 1.04 2.08 1.05 2.08 6.07 6.07
f1 (ppm)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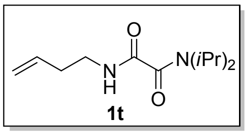
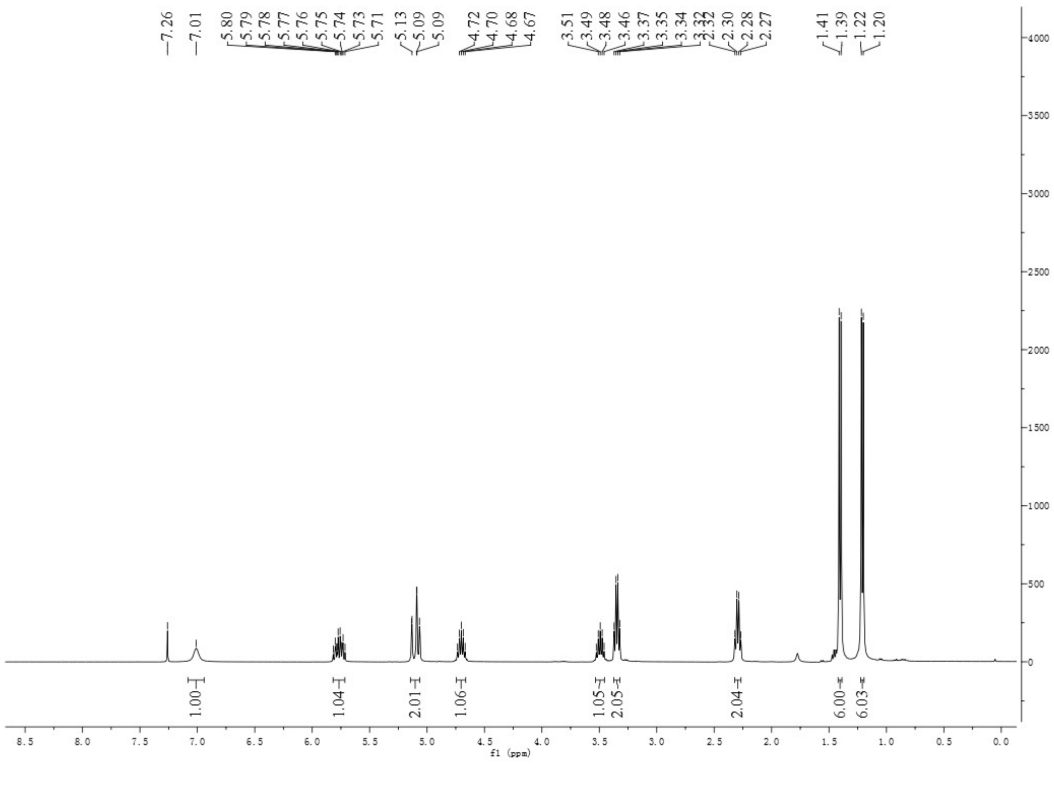
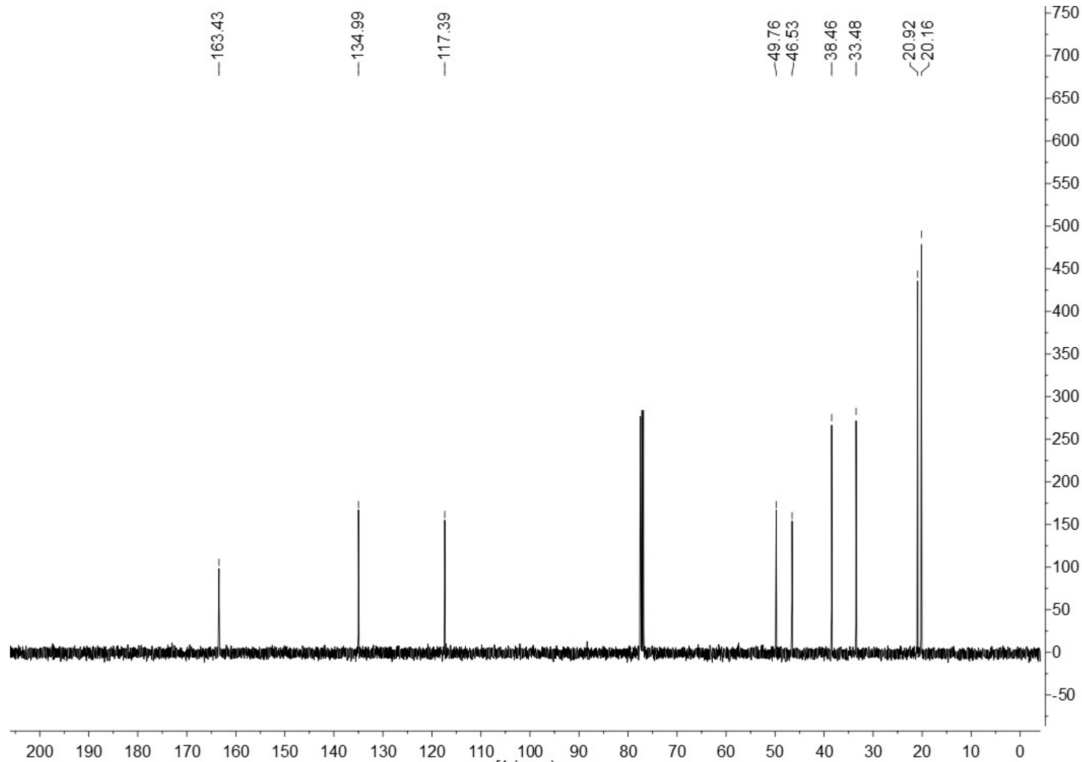
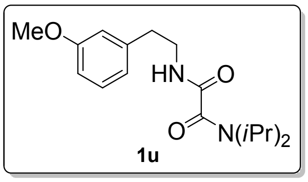
f1 (ppm)

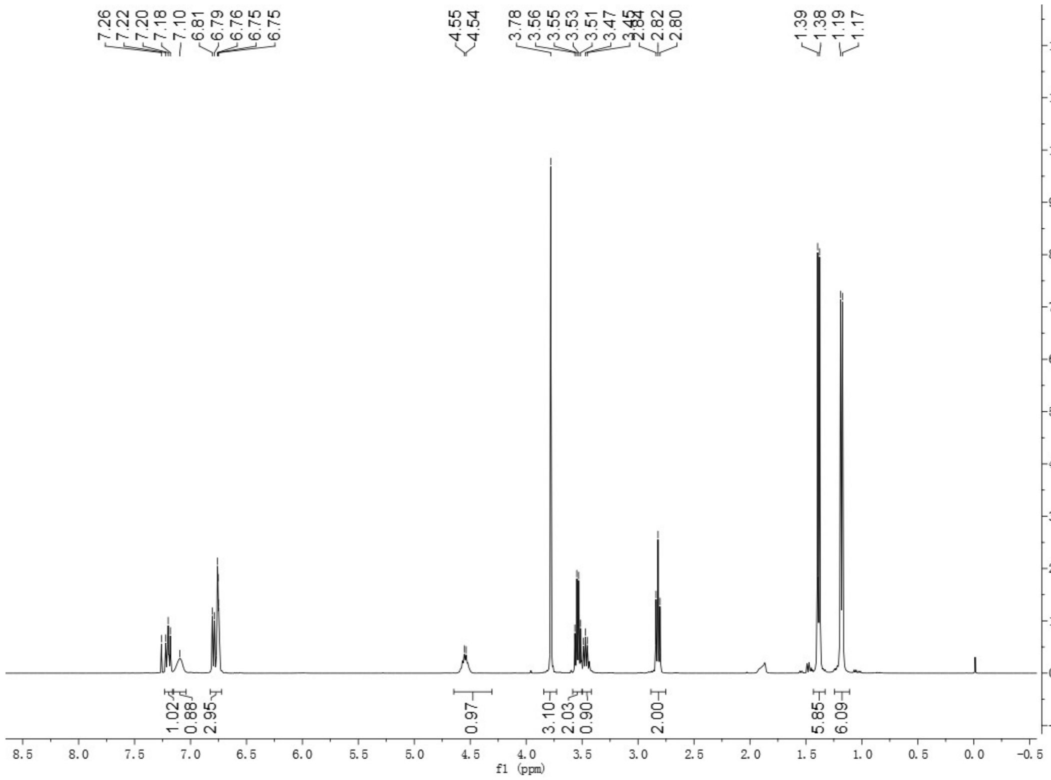

N(iPr)2
1t






MeO
HN
O
O
N(iPr)2

1u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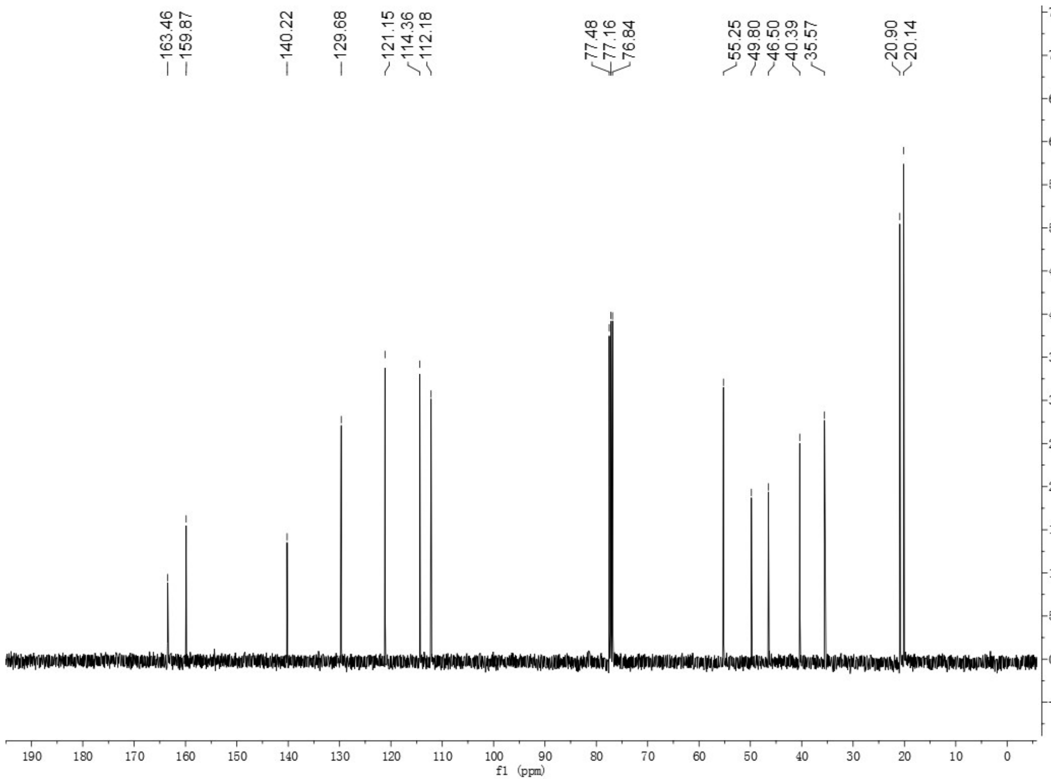
4.55 4.54
3.78 3.56 3.55 3.53 3.51 3.47 3.45 2.84 2.82 2.80
1.39 1.38 1.19 1.17
1.02 0.88 2.95 0.97 3.10 2.03 0.90 2.00 5.85 6.09
f1 (ppm)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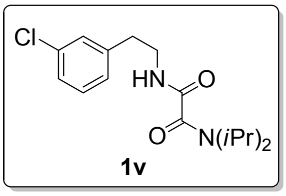
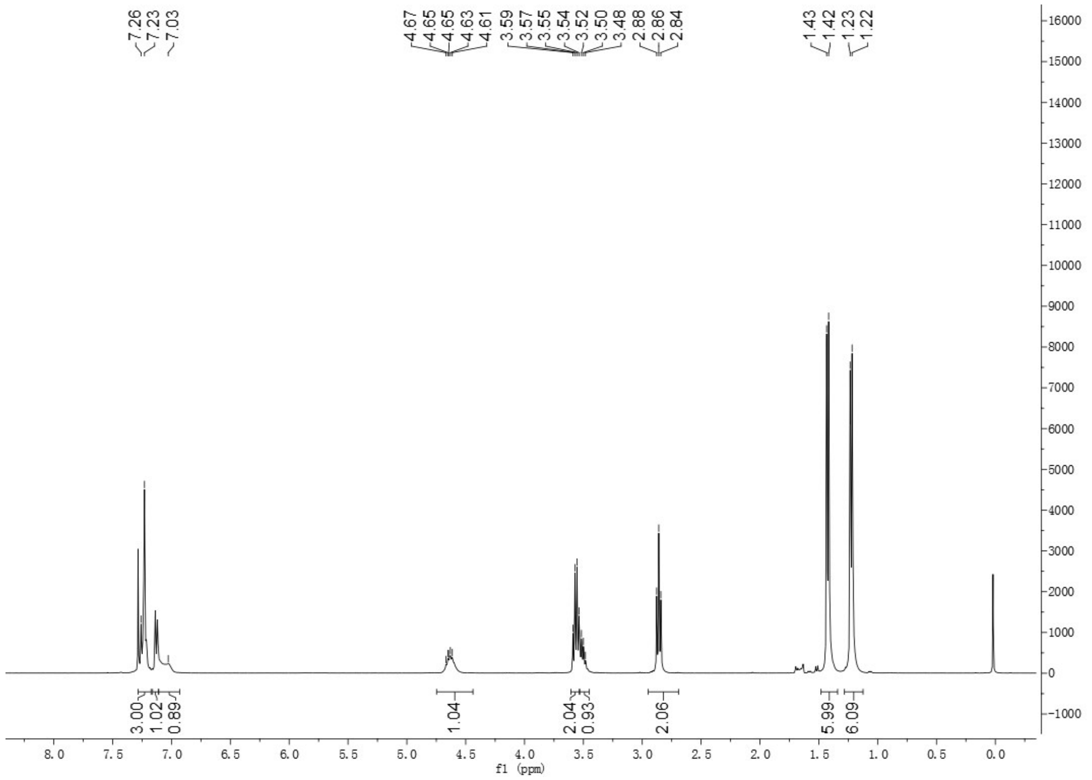
77.48 77.16 76.84
55.25 49.80 46.50 40.39 35.57 20.90 20.14
f1 (ppm)


Cl
HN
O
O
N(iPr)2
1v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7.23
7.03
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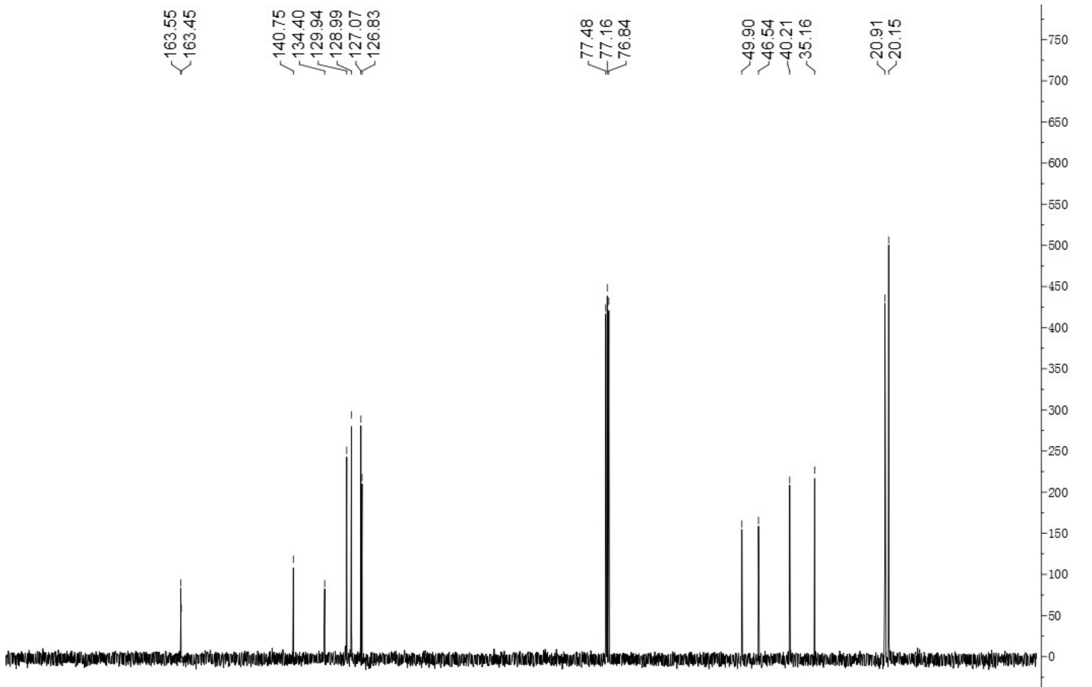
4.65
4.65
4.63
4.61
3.59
3.57
3.55
3.54
3.52
3.50
3.48
2.88
2.86
2.84
1.43
1.42
1.23
1.22
3.00
1.02
0.89
1.04
2.04
0.93
2.06
5.99
6.09
f1 (ppm)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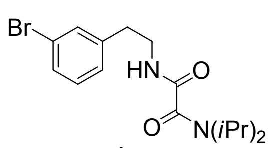
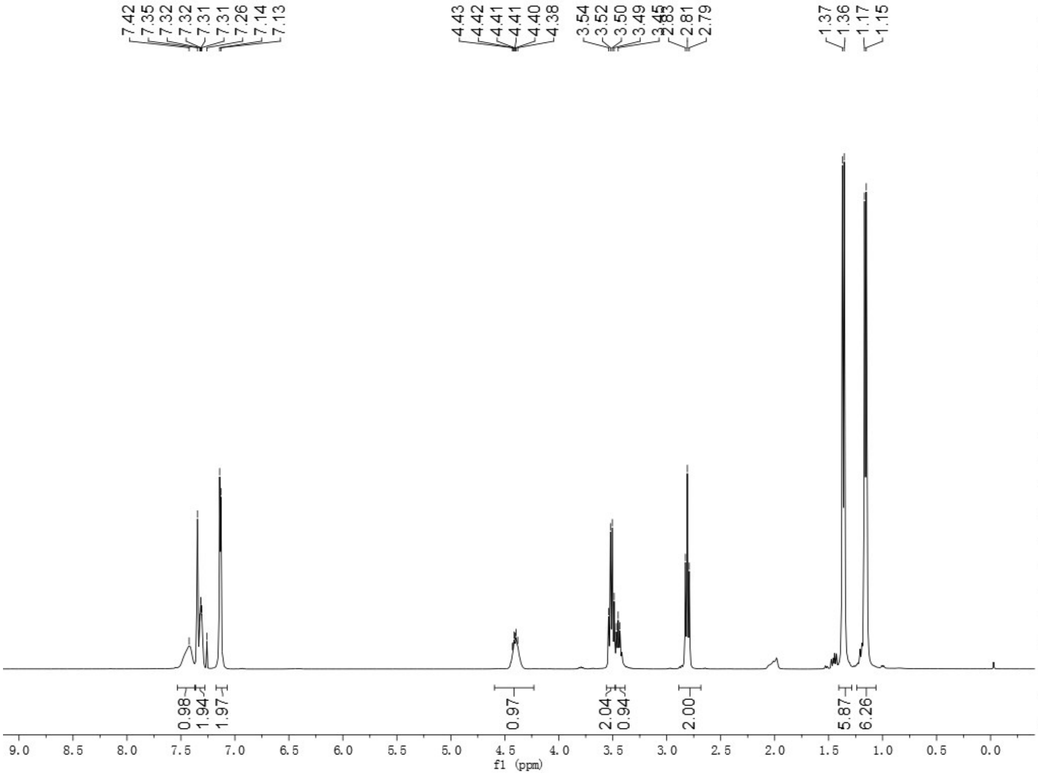
163.45
140.75
134.40
129.94
128.99
127.07
126.83
77.48
77.16
76.84
49.90
46.54
40.21
35.16
20.91
20.15
f1 (ppm)


Br
HN
O
O
N(iPr)2

1w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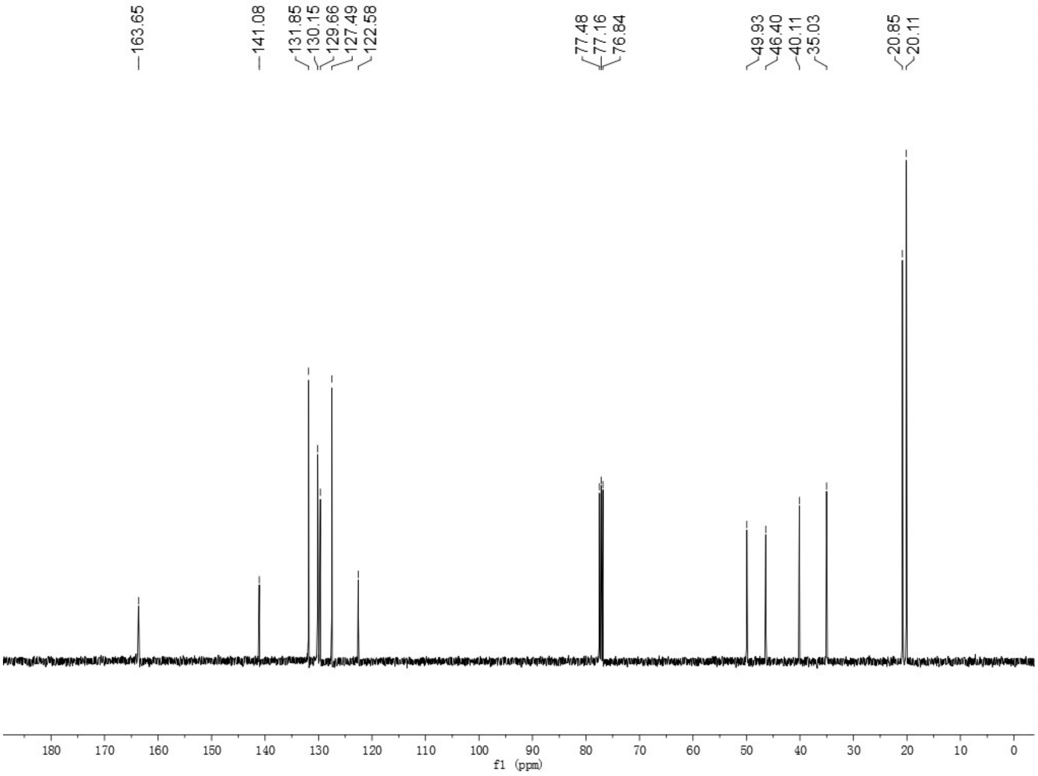
4.43 4.42 4.41 4.41 4.40 4.38
3.54 3.52 3.50 3.49 3.45 2.83 2.81 2.79
1.37 1.36 1.17 1.15
0.98 1.94 1.97 0.97 2.04 0.94 2.00 5.87 6.26
f1 (ppm)


163.65
141.08
131.85 130.15 129.66 127.49 122.58
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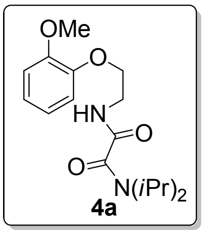
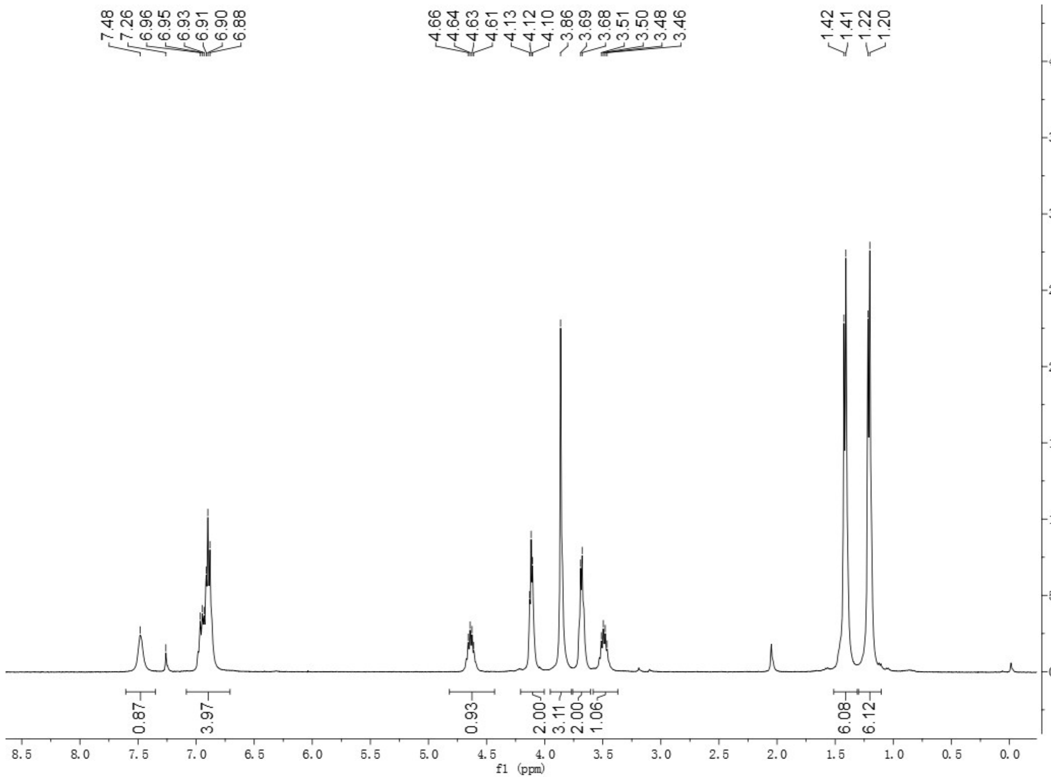
49.93 46.40 40.11 35.03
20.85 20.11
f1 (ppm)

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7.26
6.96
6.95
6.93
6.91
6.90
6.88
4.66
4.64
4.63
4.61
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4.12
4.10
3.86
3.69
3.68
3.51
3.50
3.48
3.46
1.42
1.41
1.22
1.20
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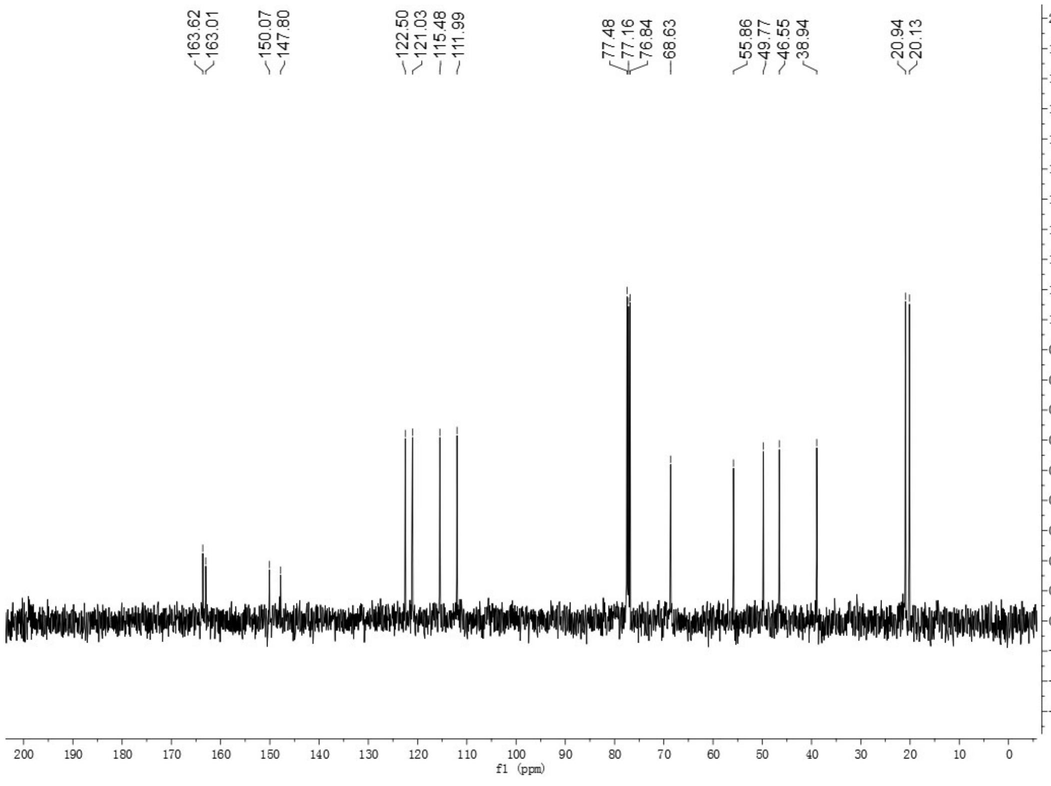
3.97
0.93
2.00
3.11
2.00
1.06
6.08
6.12
f1 (ppm)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147.80
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77.48
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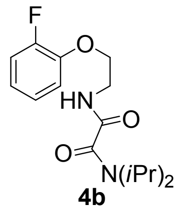
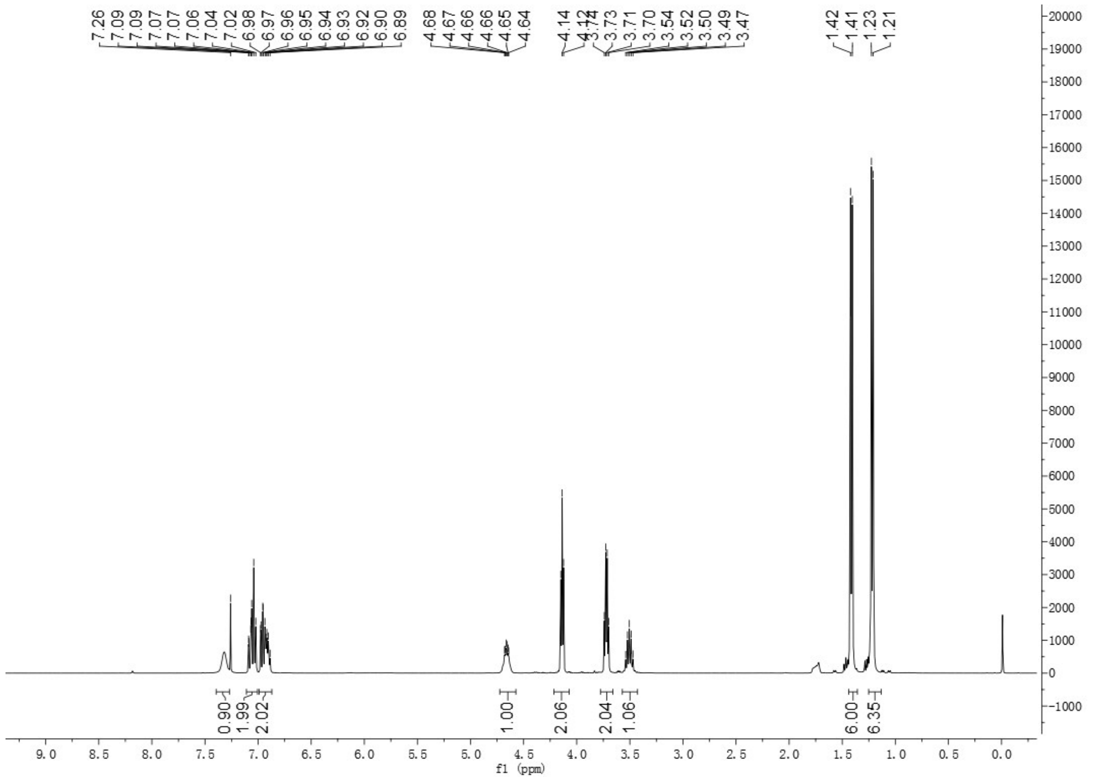
76.84
68.63
55.86
49.77
46.55
38.94
20.94
20.13
f1 (ppm)


F
O
HN
O
O
N(iPr)2

4b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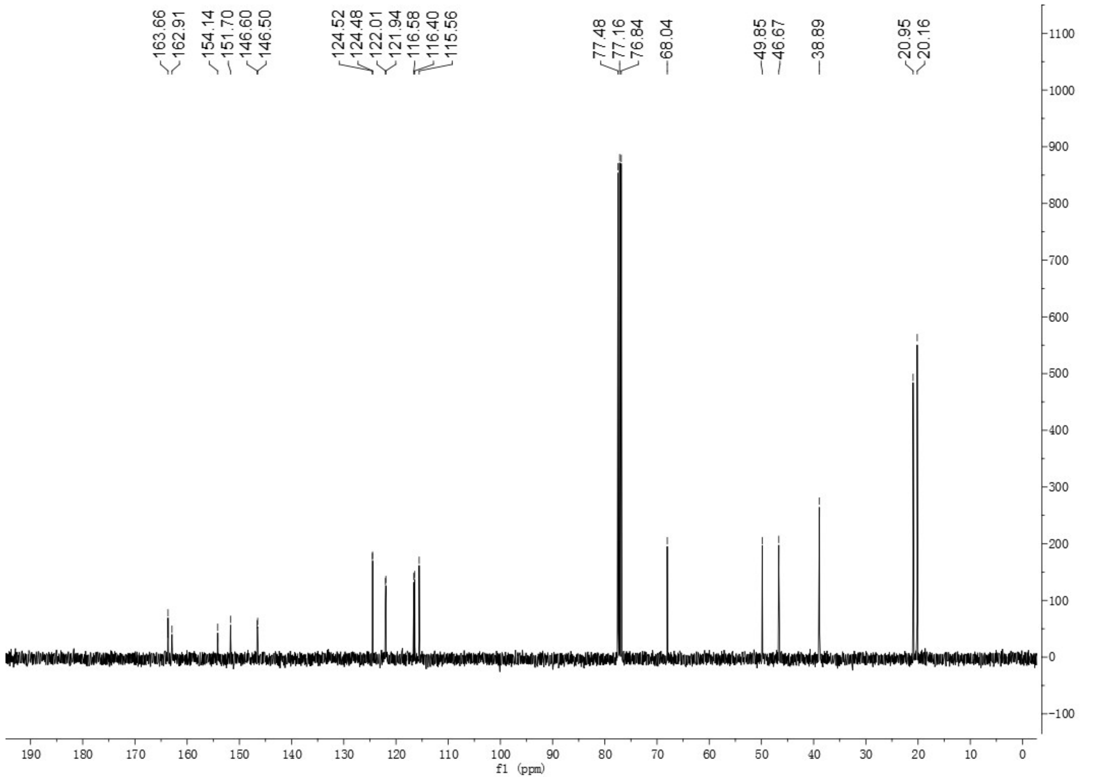
4.68 4.67 4.66 4.66 4.65 4.64
4.14 4.12 3.74 3.73 3.71 3.70 3.54 3.52 3.50 3.49 3.47
1.42 1.41 1.23 1.21
0.90 1.99 2.02 1.00 2.06 2.04 1.06 6.00 6.35
f1 (ppm)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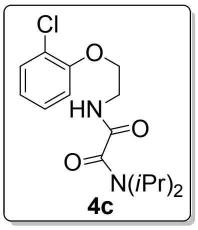
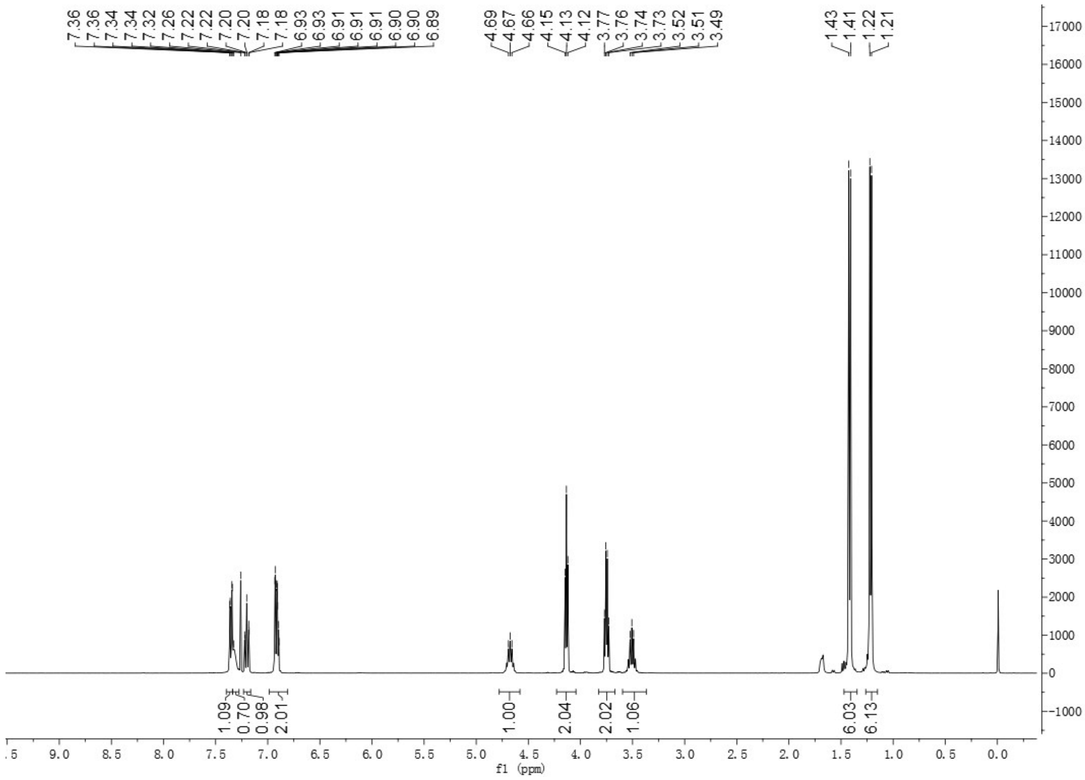
124.52 124.48 122.01 121.94 116.58 116.40 115.56
77.48 77.16 76.84 68.04
49.85 46.67 38.89
20.95 20.16
f1 (ppm)


Cl
O
HN
O
O
N(iPr)2
4c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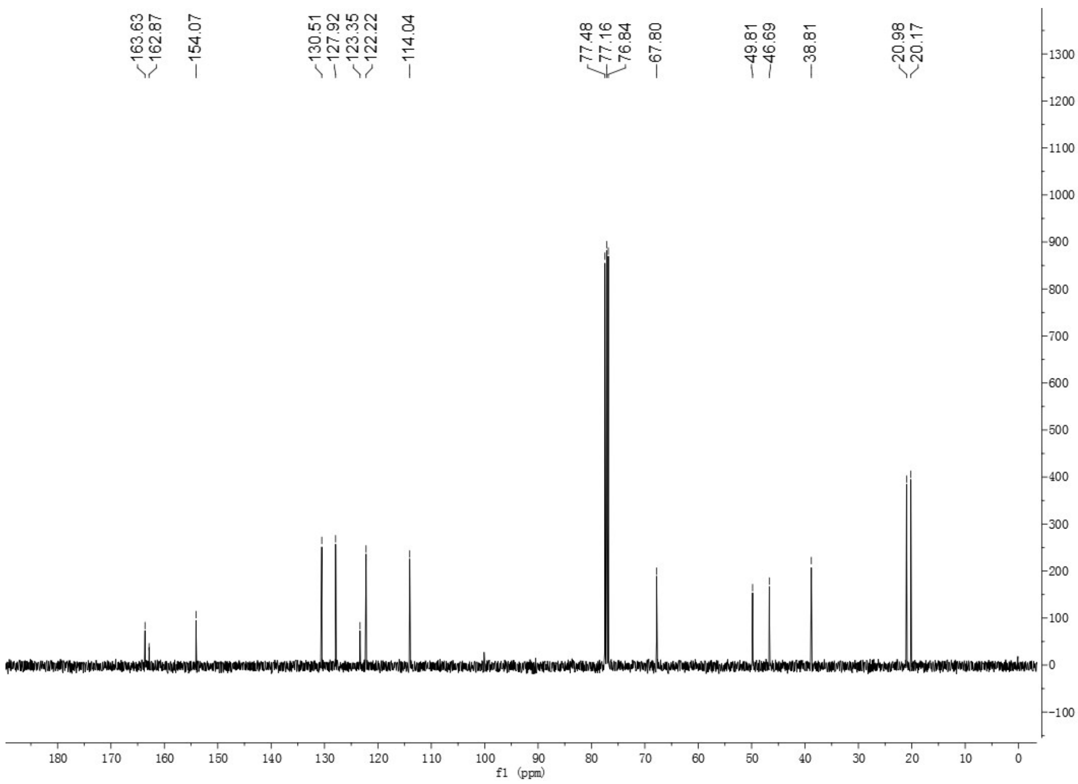
4.69 4.67 4.66 4.15 4.13 4.12 3.77 3.76 3.74 3.73 3.52 3.51 3.49
1.43 1.41 1.22 1.21
1.09 0.70 0.98 2.01 1.00 2.04 2.02 1.06 6.03 6.13
f1 (ppm)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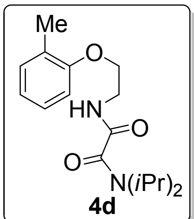
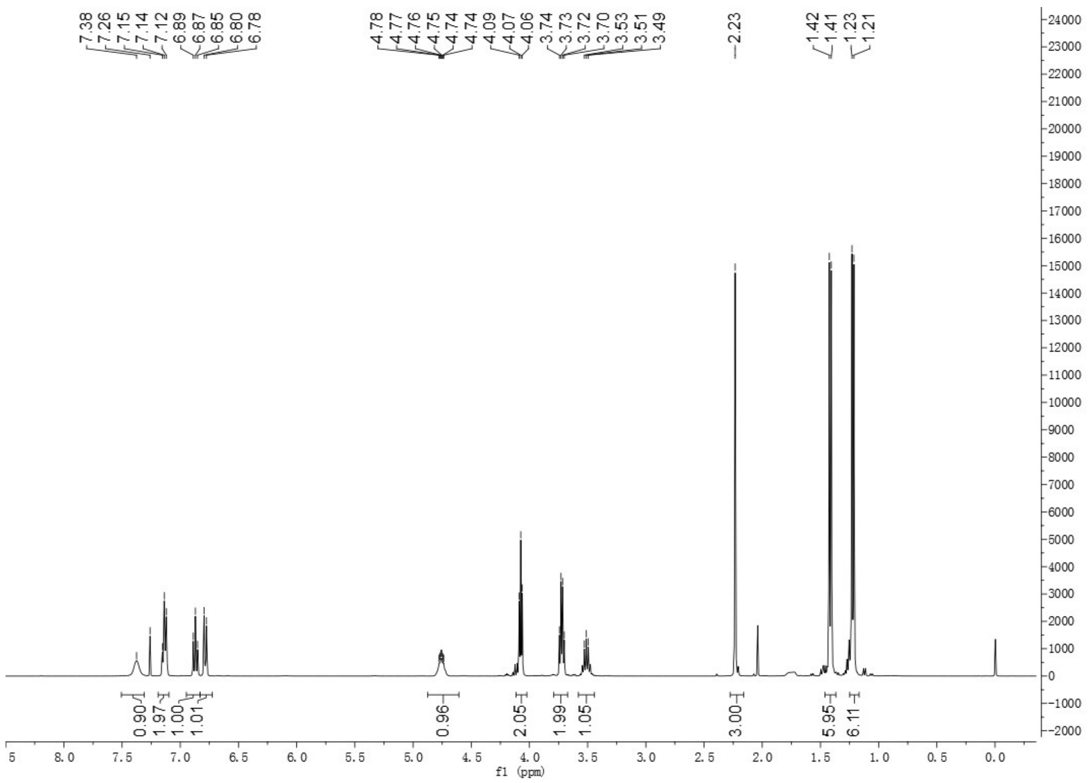
77.48 77.16 76.84 67.80
49.81 46.69 38.81
20.98 20.17
f1 (ppm)


Me
O
HN
O
O
N(iPr)2

4d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3.74
3.73
3.72
3.70
3.53
3.51
3.49
2.23
1.42
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1.23
1.21
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1.01
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2.05
1.99
1.05
3.00
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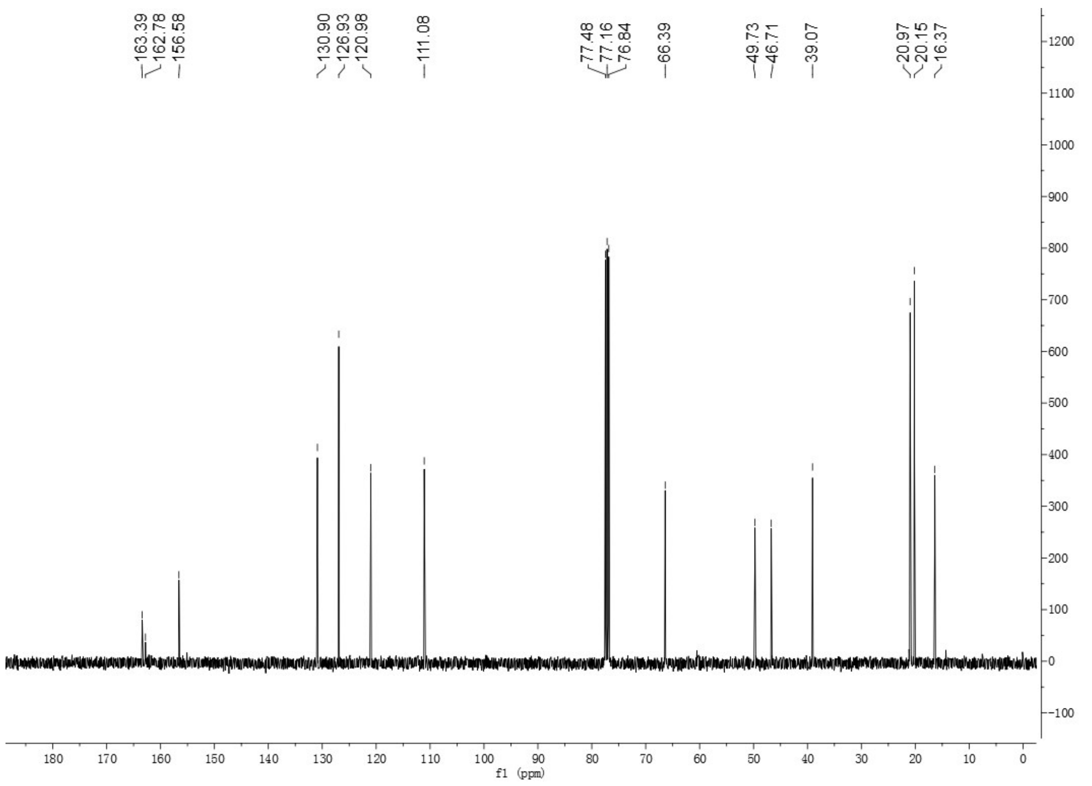
6.11
f1 (ppm)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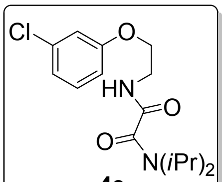
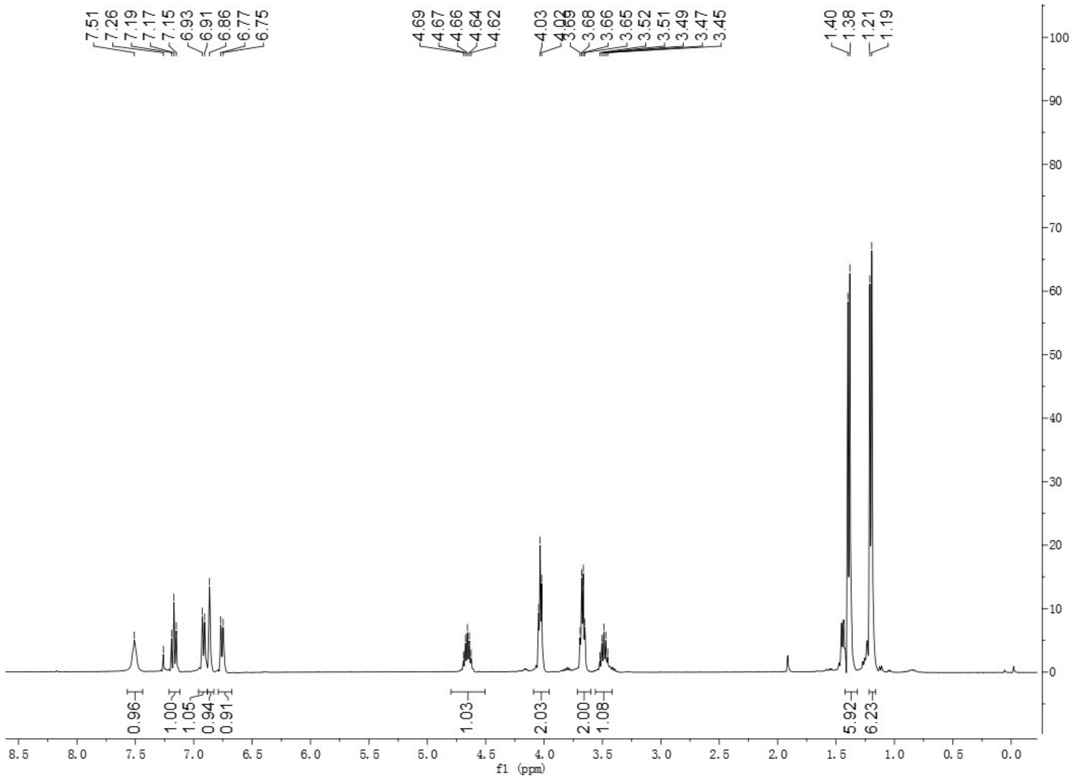
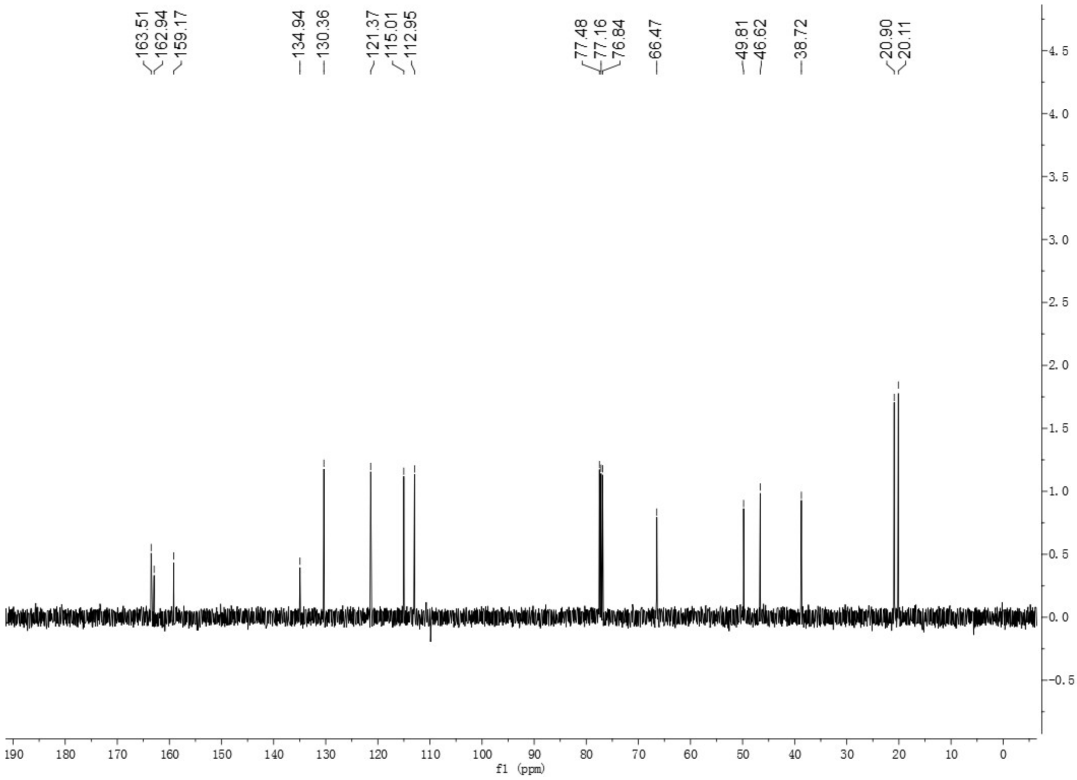
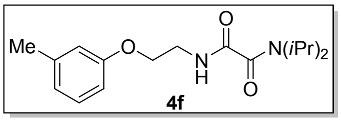
76.84
66.39
49.73
46.71
39.07
20.97
20.15
16.37
f1 (ppm)



4e







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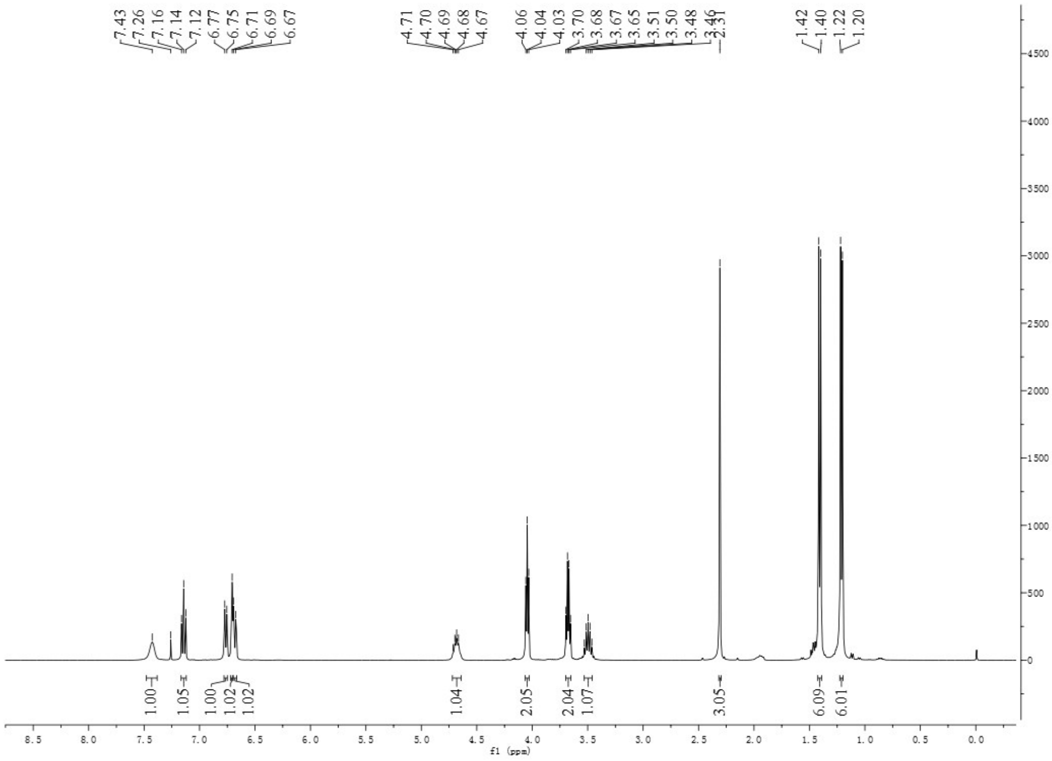
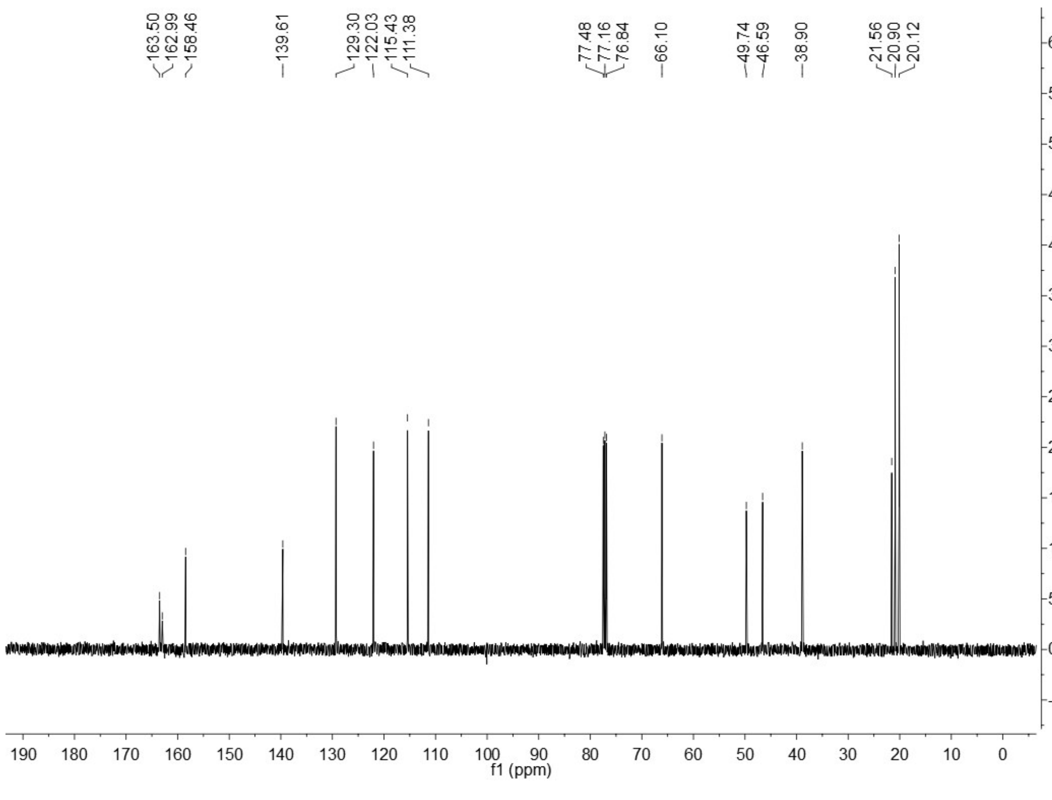
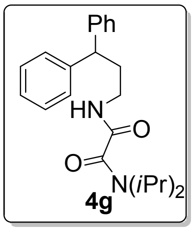
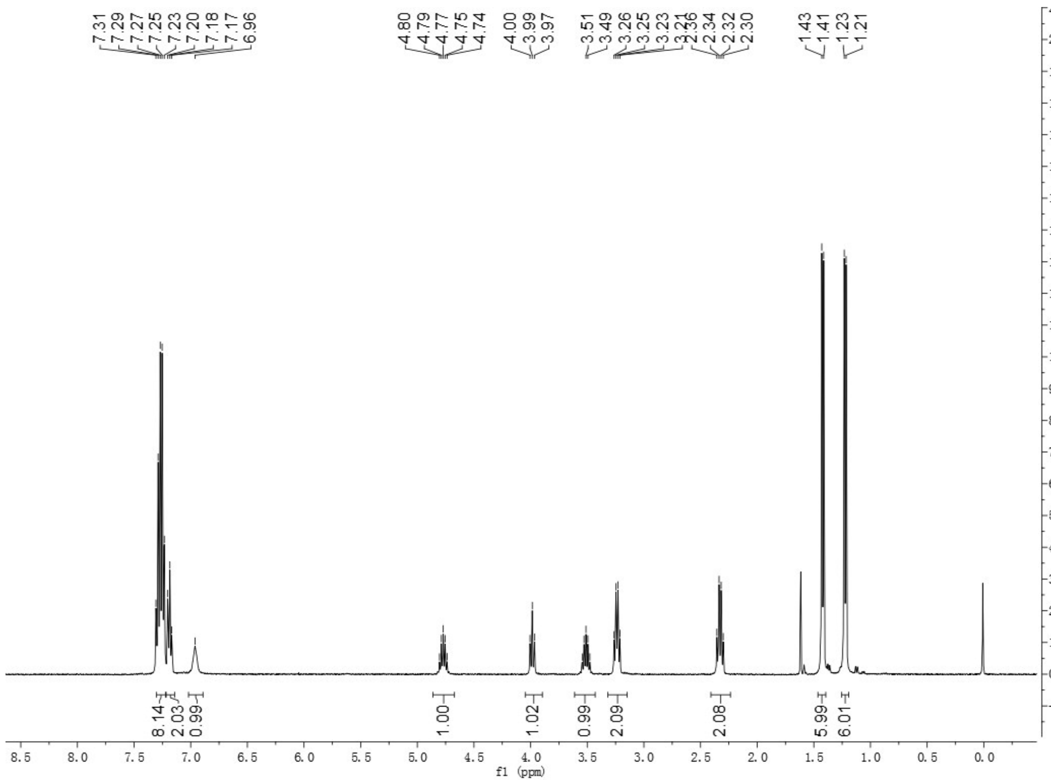





Ph
HN
O
O
N(*i*Pr)2
4g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7.29
7.27
7.25
7.23
7.20
7.18
7.17
6.96
4.80
4.79
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4.75
4.74
4.00
3.99
3.97
3.51
3.49
3.26
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3.23
3.21
2.36
2.34
2.32
2.30
1.43
1.41
1.23
1.21
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0.99
1.00
1.02
0.99
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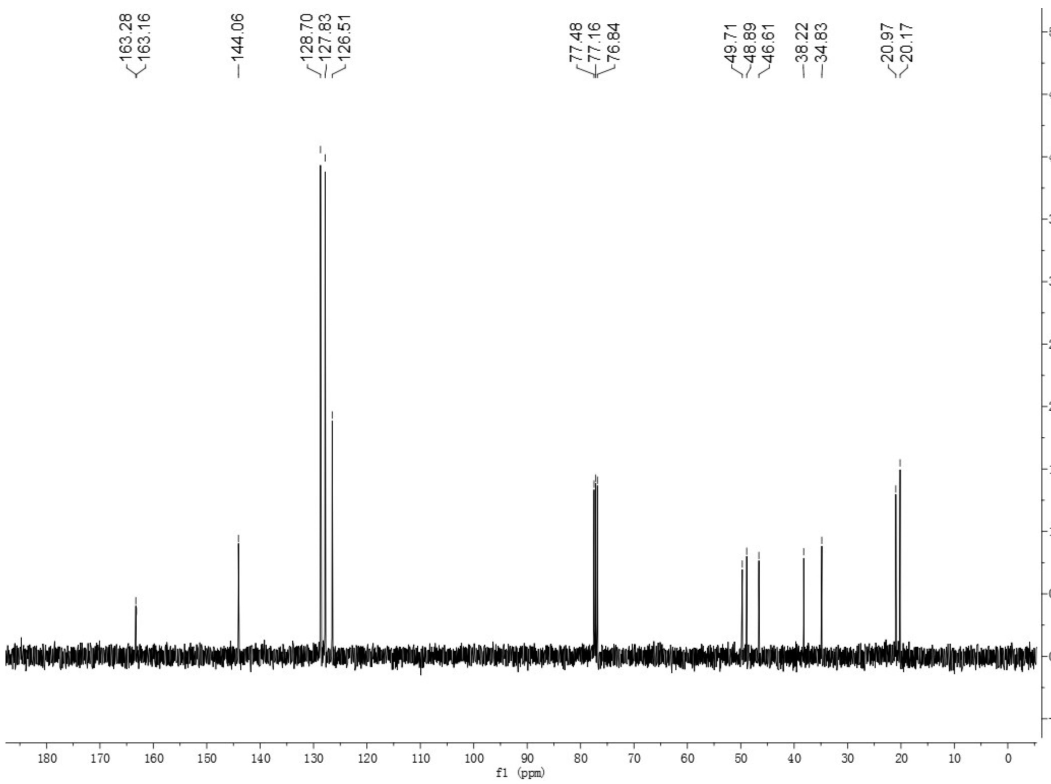
2.08
5.99
6.01
f1 (ppm)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48.89
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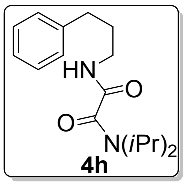
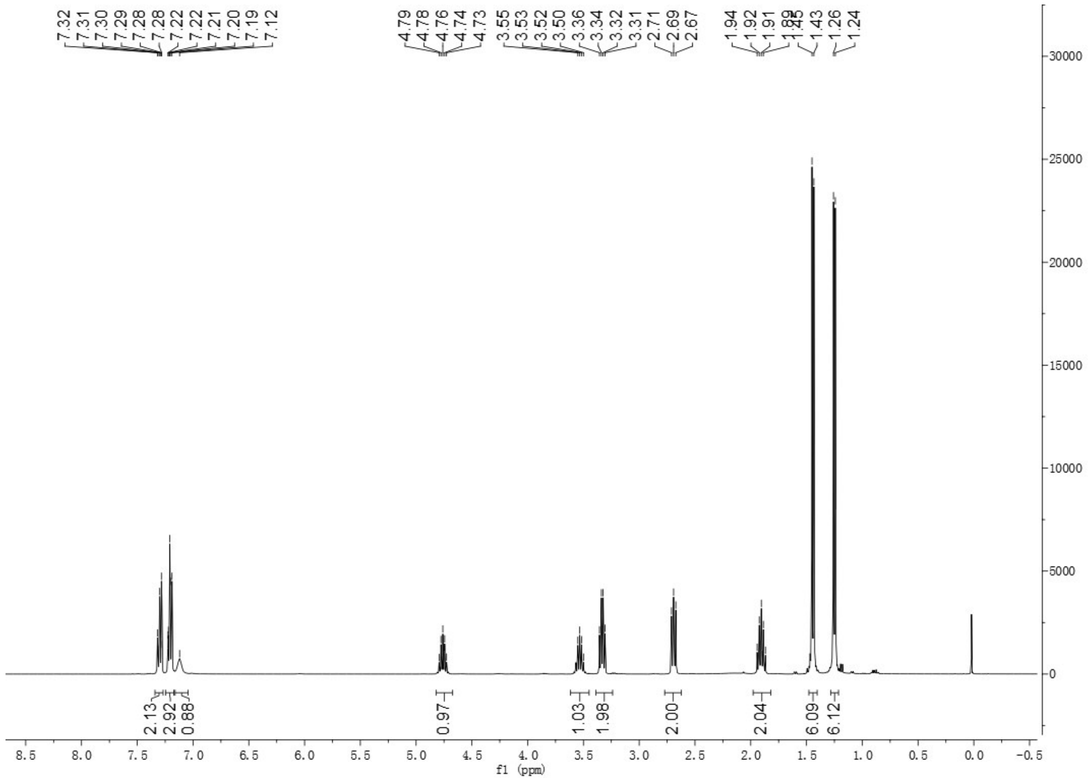
34.83
20.97
20.17
f1 (ppm)


HN
O
O
N(iPr)2

4h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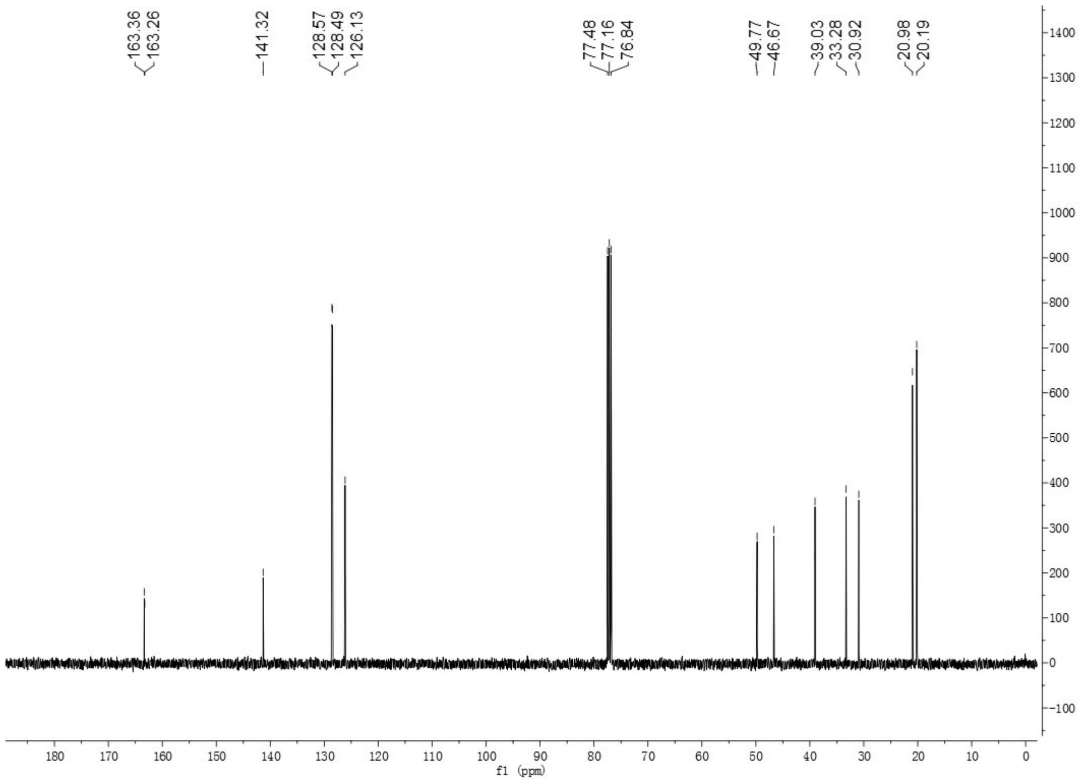
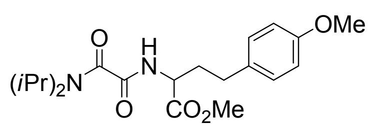
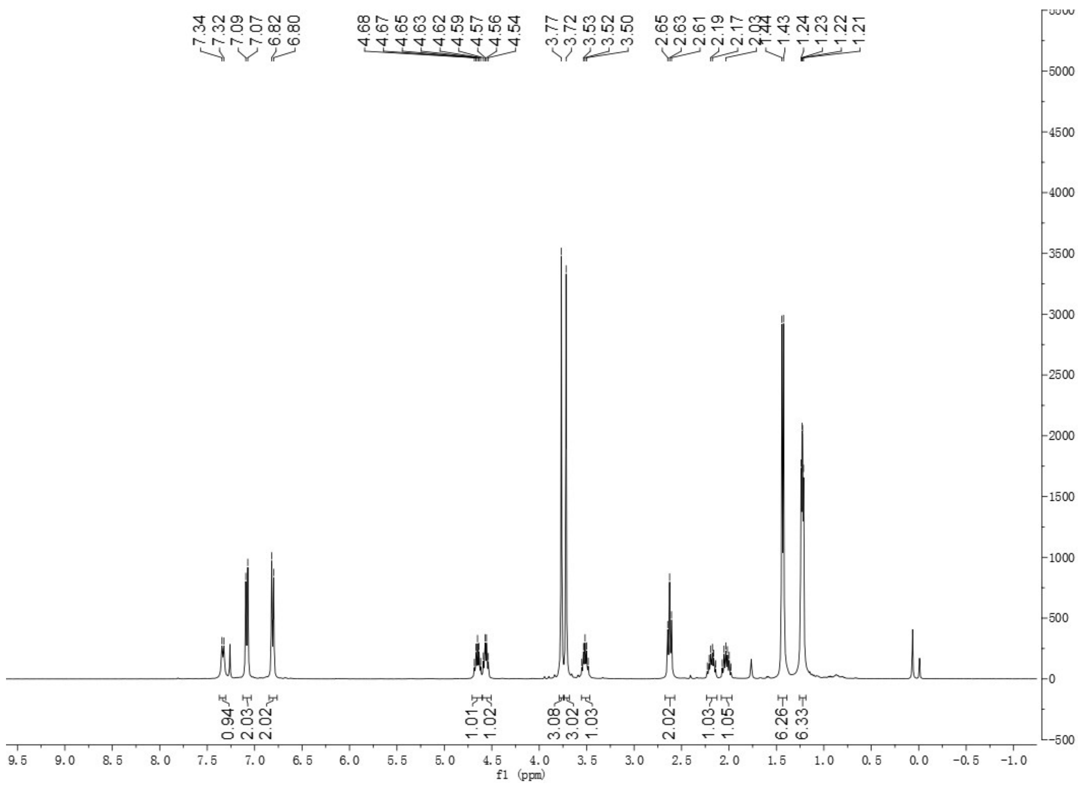
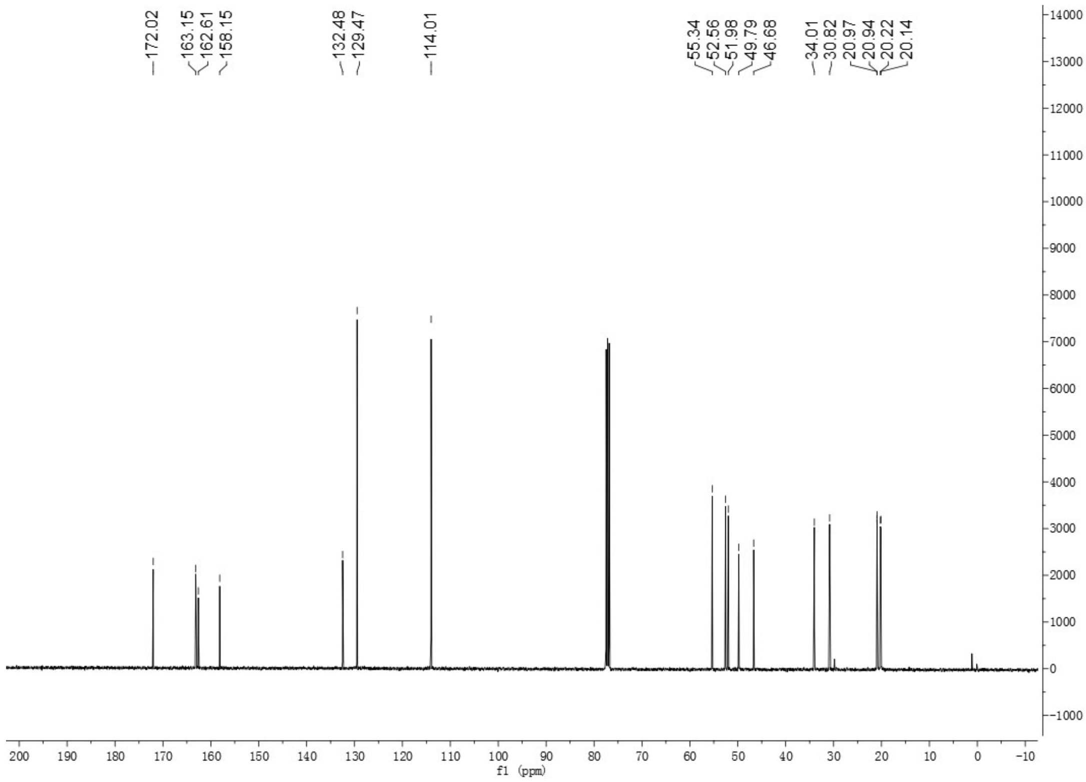
7.20
7.19
7.12
4.79
4.78
4.76
4.74
4.74
4.73
3.55
3.53
3.52
3.50
3.36
3.34
3.32
3.31
2.71
2.69
2.67
1.94
1.92
1.91
1.89
1.45
1.43
1.26
1.24
2.13
2.92
0.88
0.97
1.03
1.98
2.00
2.04
6.09
6.12
f1 (ppm)

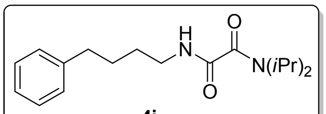

163.36
163.26
141.32
128.57
128.49
126.13
77.48
77.16
76.84
49.77
46.67
39.03
33.28
30.92
20.98
20.19
f1 (ppm)



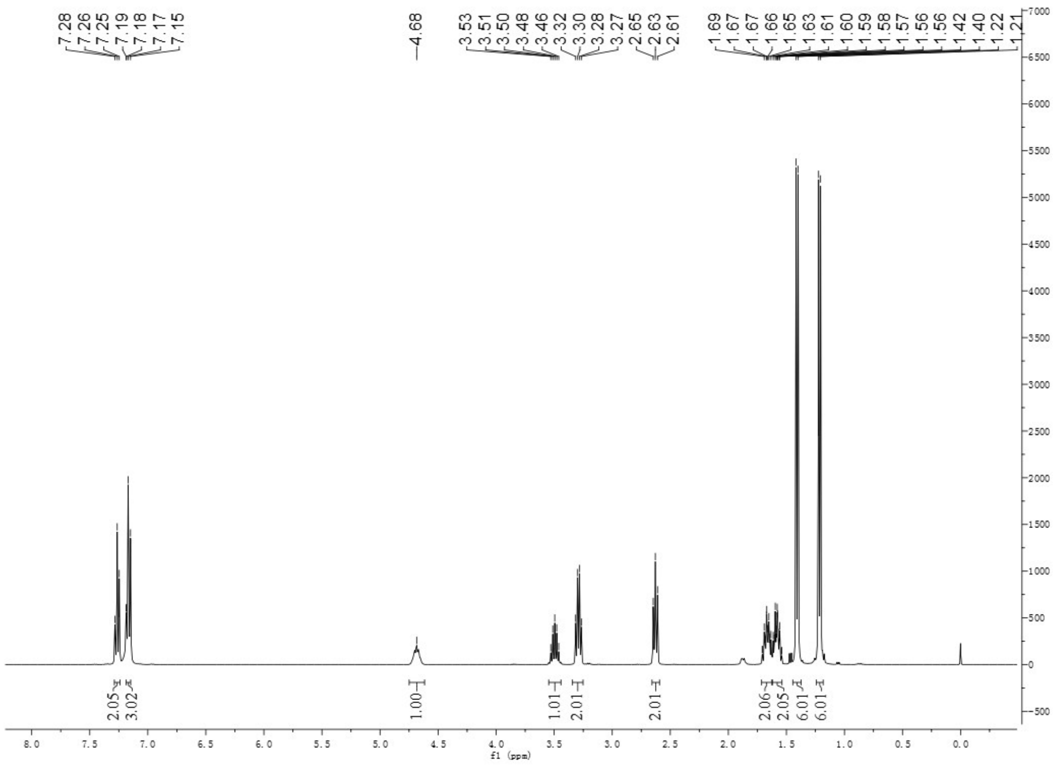
4i

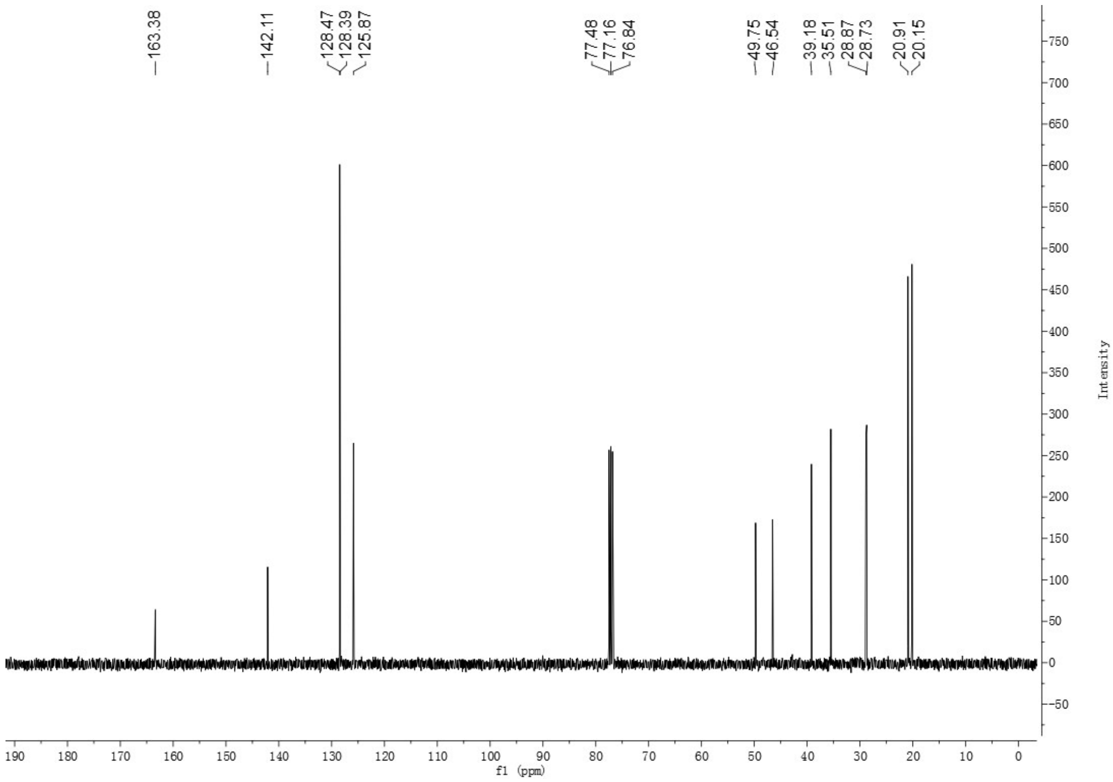


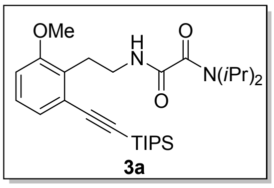




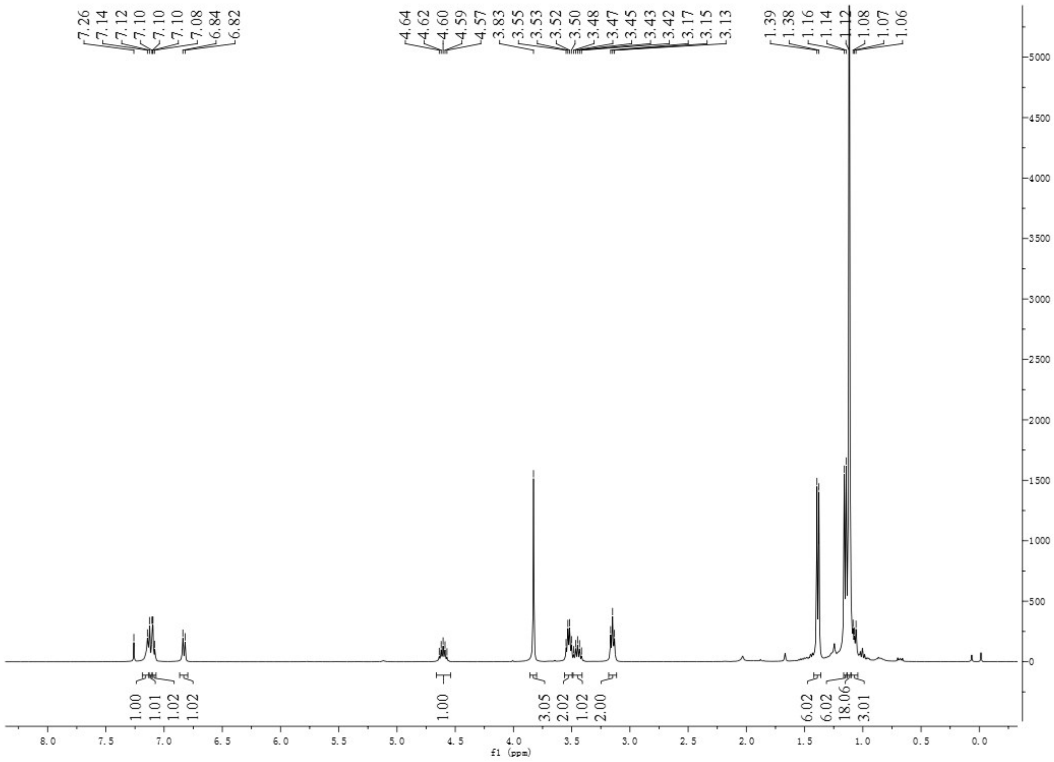
4j

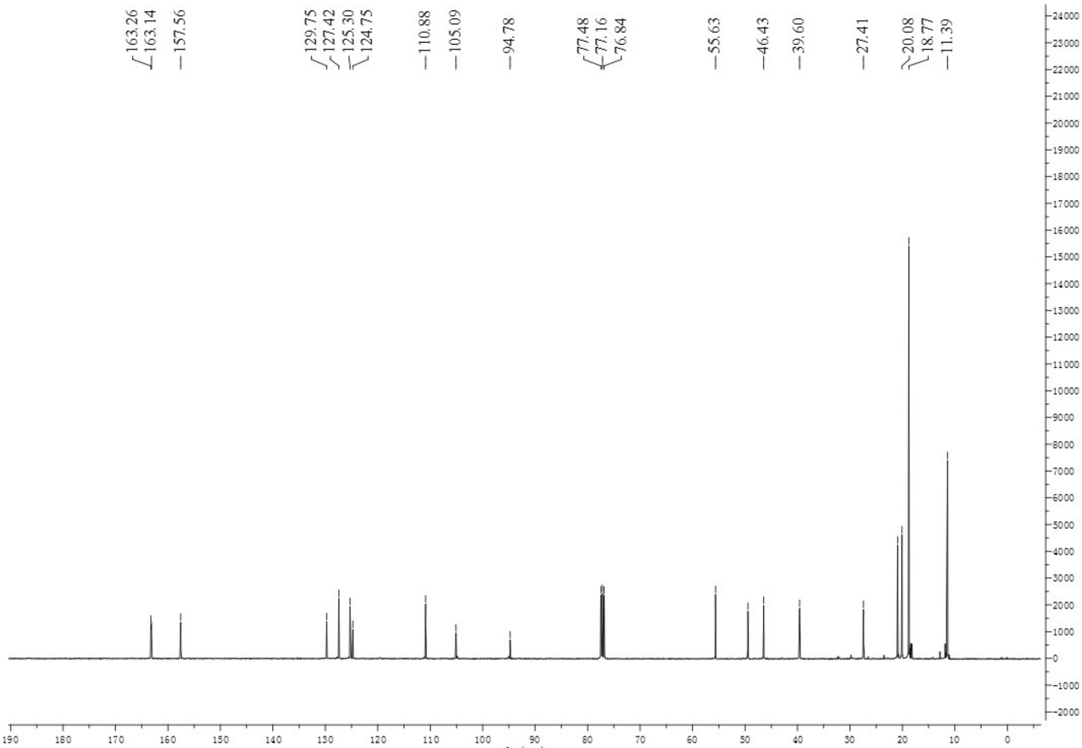


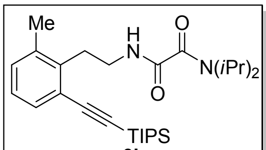




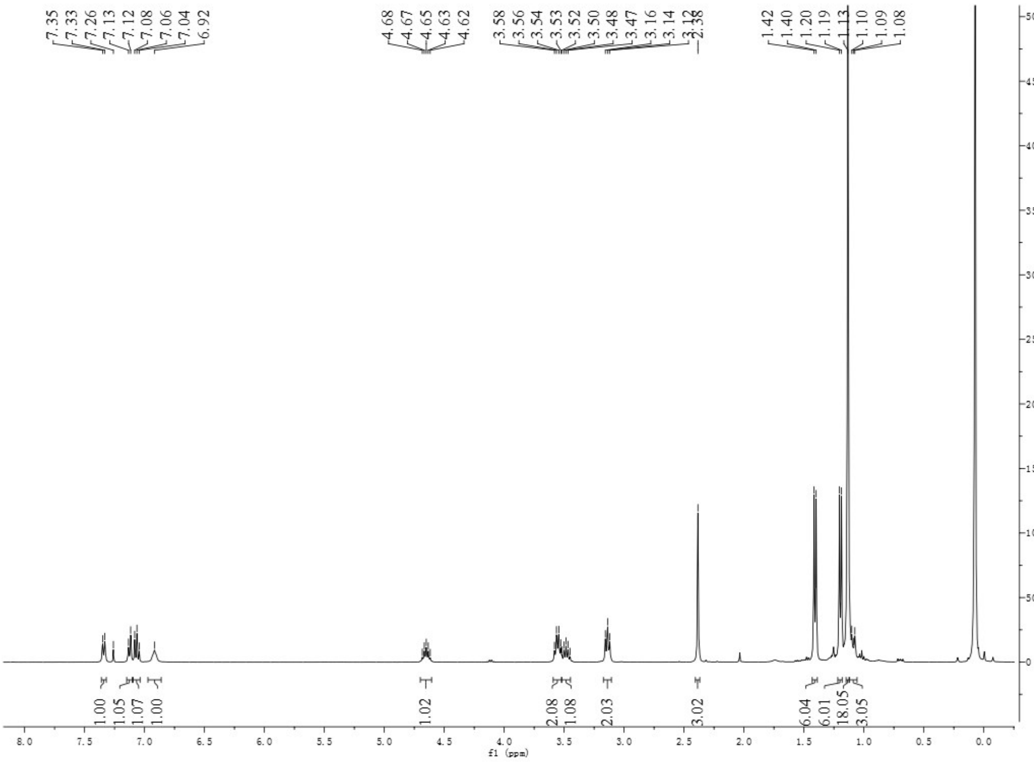
3a






Me
H
N
O
O
N(iPr)2
TIPS

3b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7.33
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7.13
7.12
7.08
7.06
7.04
6.92
4.68
4.67
4.65
4.63
4.62
3.58
3.56
3.54
3.53
3.52
3.50
3.48
3.47
3.16
3.14
3.12
2.38
1.42
1.40
1.20
1.19
1.13
1.10
1.09
1.08
1.00
1.05
1.07
1.00
1.02
2.08
1.08
2.03
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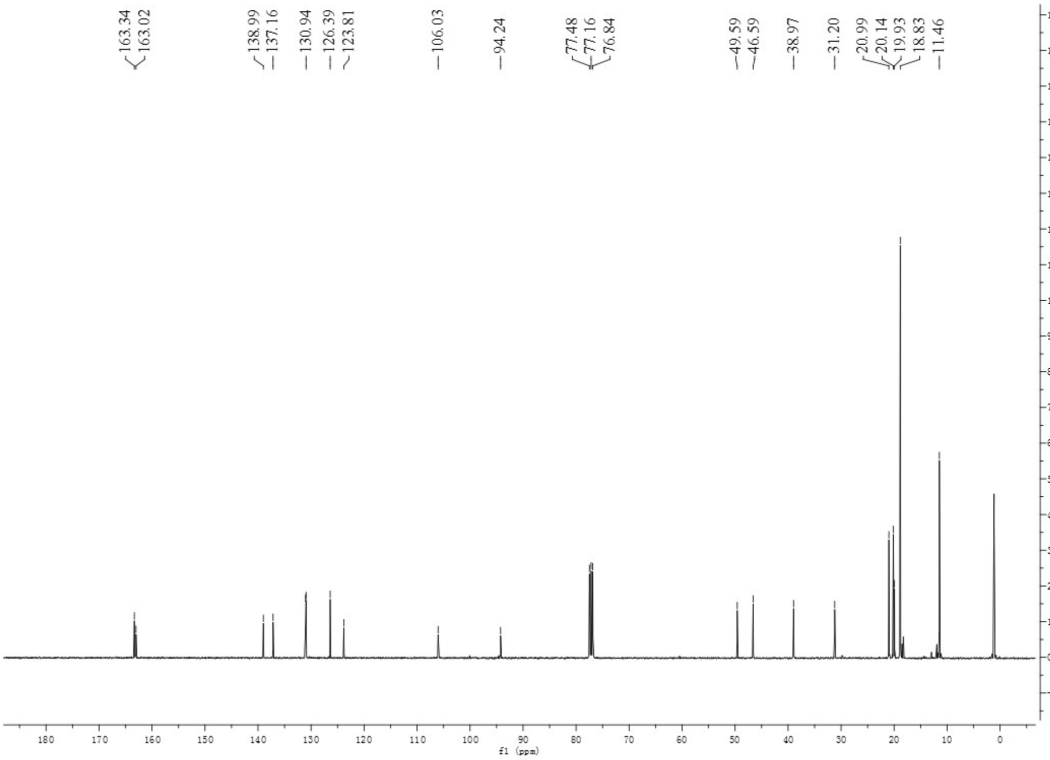
18.05
3.05
f1 (ppm)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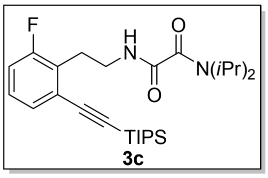
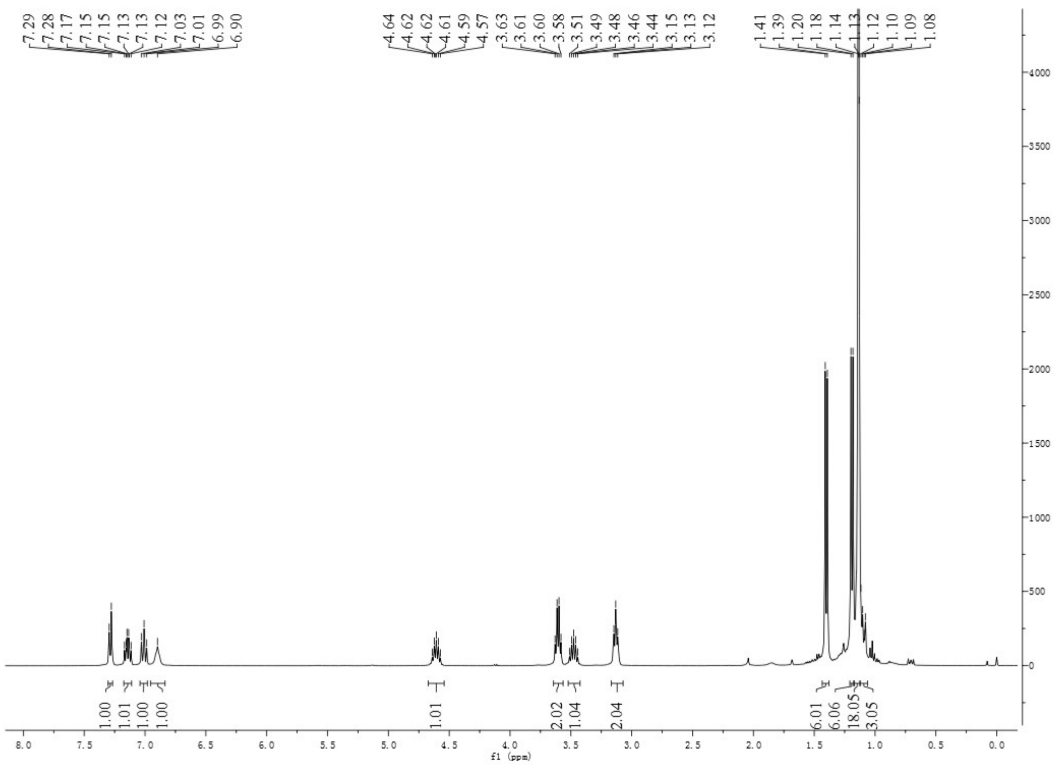
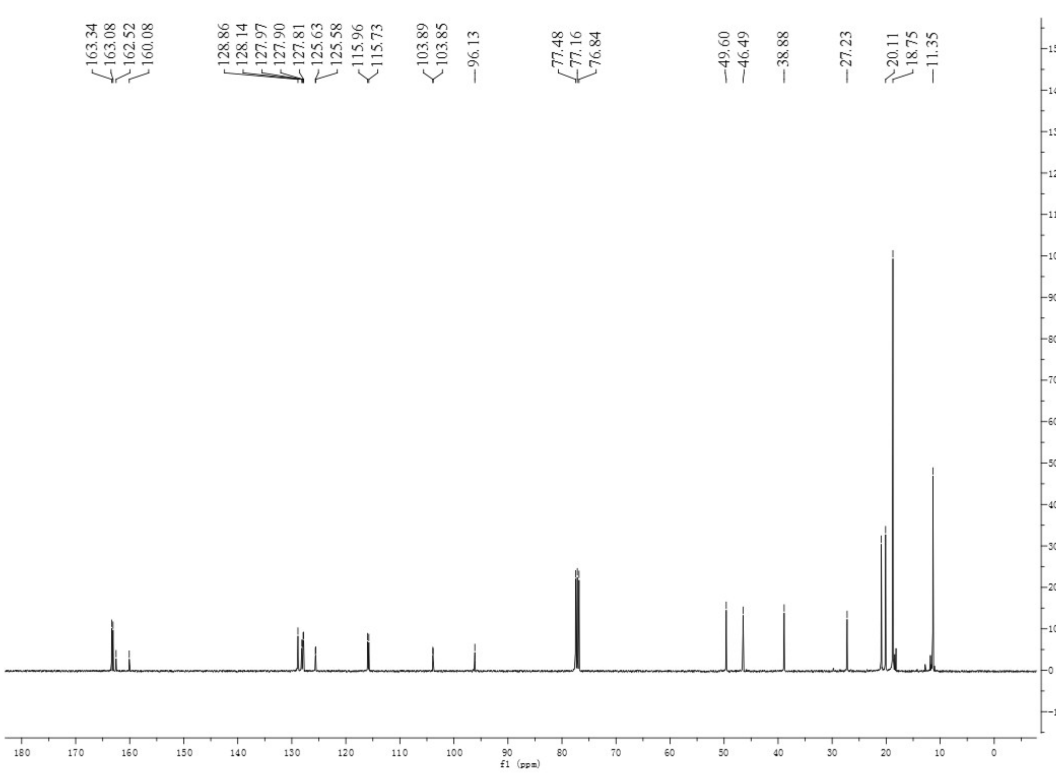
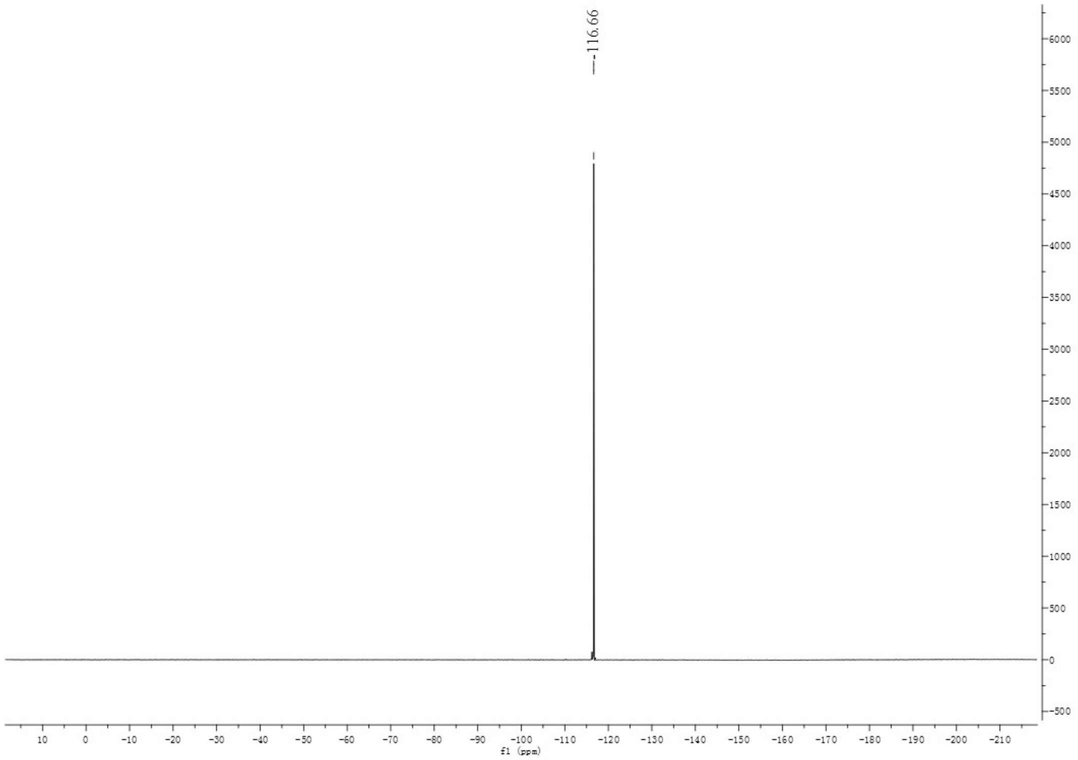
163.02
138.99
137.16
130.94
126.39
123.81
106.03
94.24
77.48
77.16
76.84
49.59
46.59
38.97
31.20
20.99
20.14
19.93
18.83
11.46
f1 (ppm)



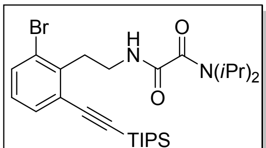
3c





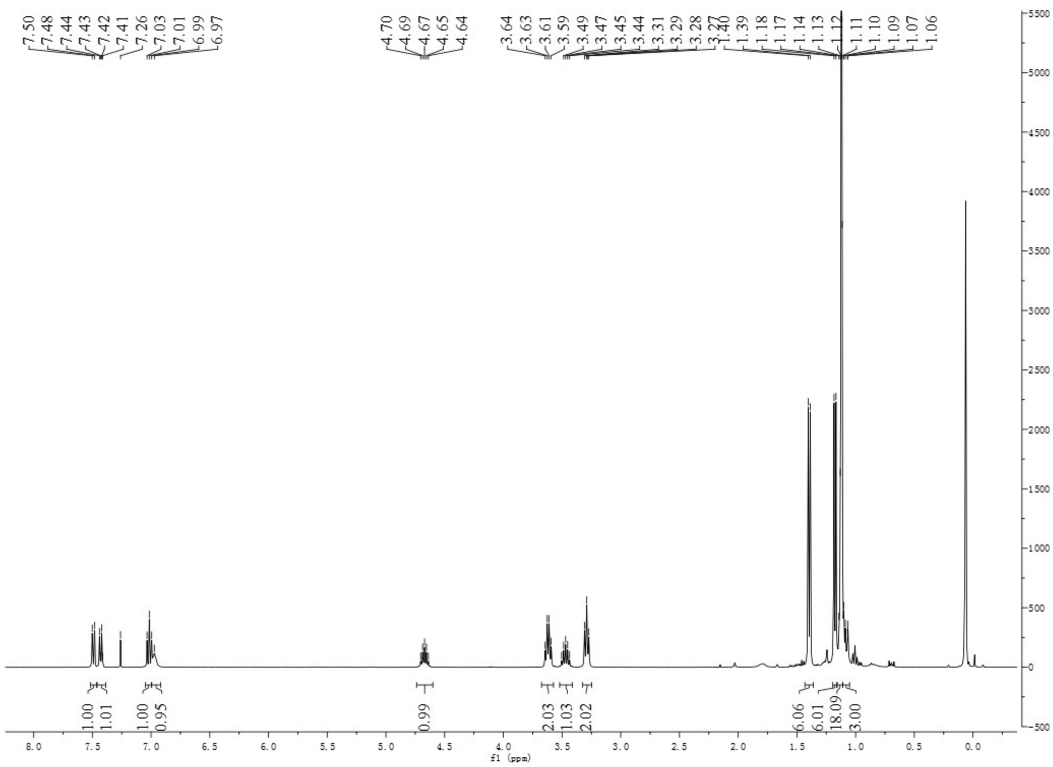


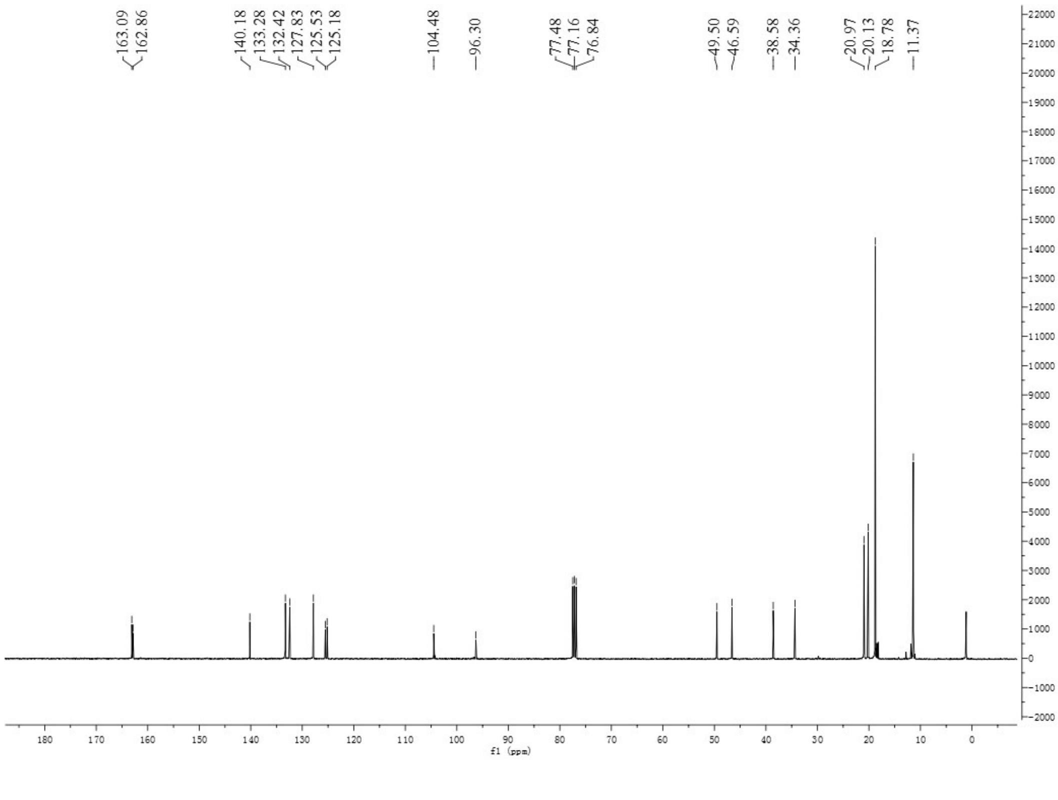
-116.66
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

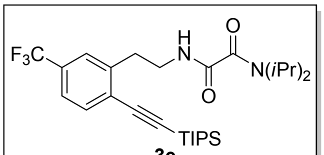


Br
H
N
O
O
N(iPr)2
TIPS

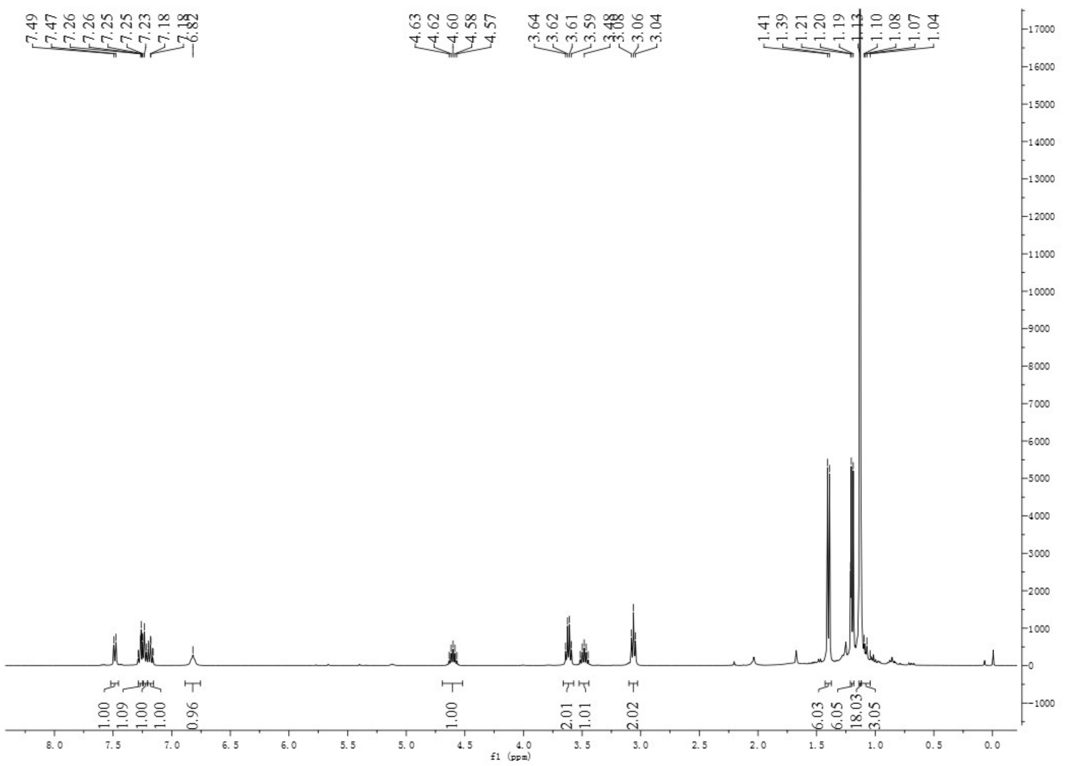
3d

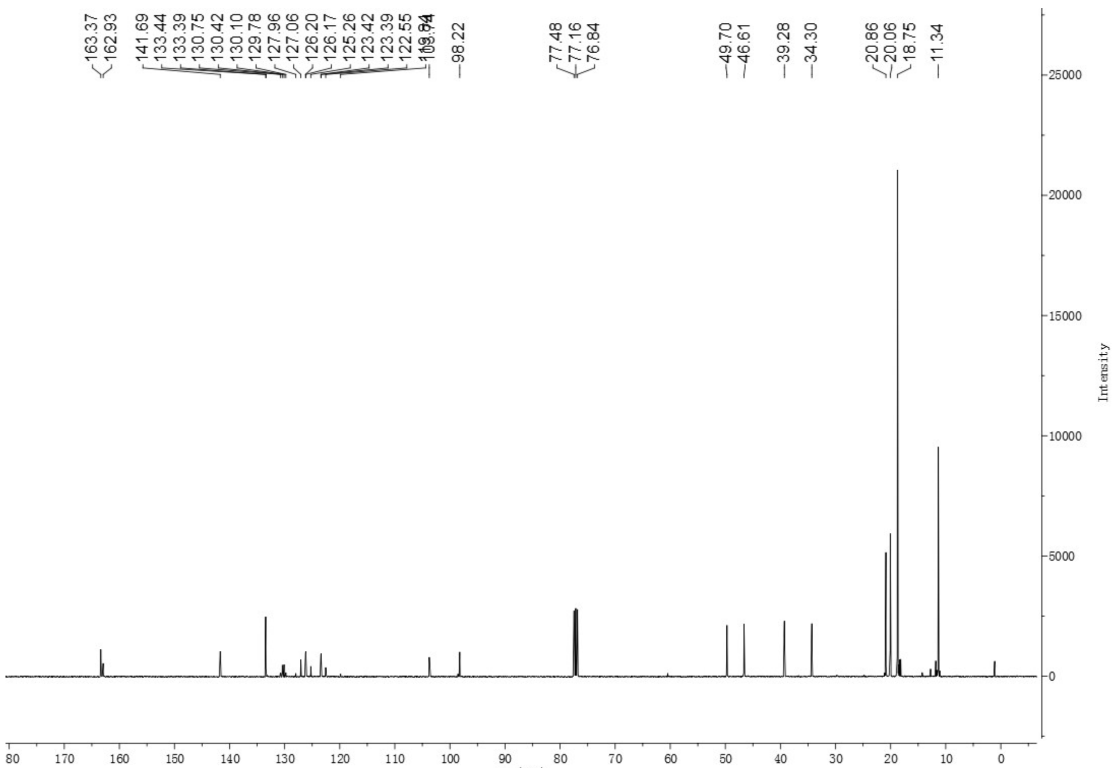

7.50
7.48
7.44
7.43
7.42
7.41
7.26
7.03
7.01
6.99
6.97
4.70
4.69
4.67
4.65
4.64
3.64
3.63
3.61
3.59
3.49
3.47
3.45
3.44
3.31
3.29
3.28
3.27
1.40
1.39
1.18
1.17
1.14
1.13
1.12
1.11
1.10
1.09
1.07
1.06
1.00
1.01
1.00
0.95
0.99
2.03
1.03
2.02
6.06
6.01
18.09
3.00
f1 (ppm)

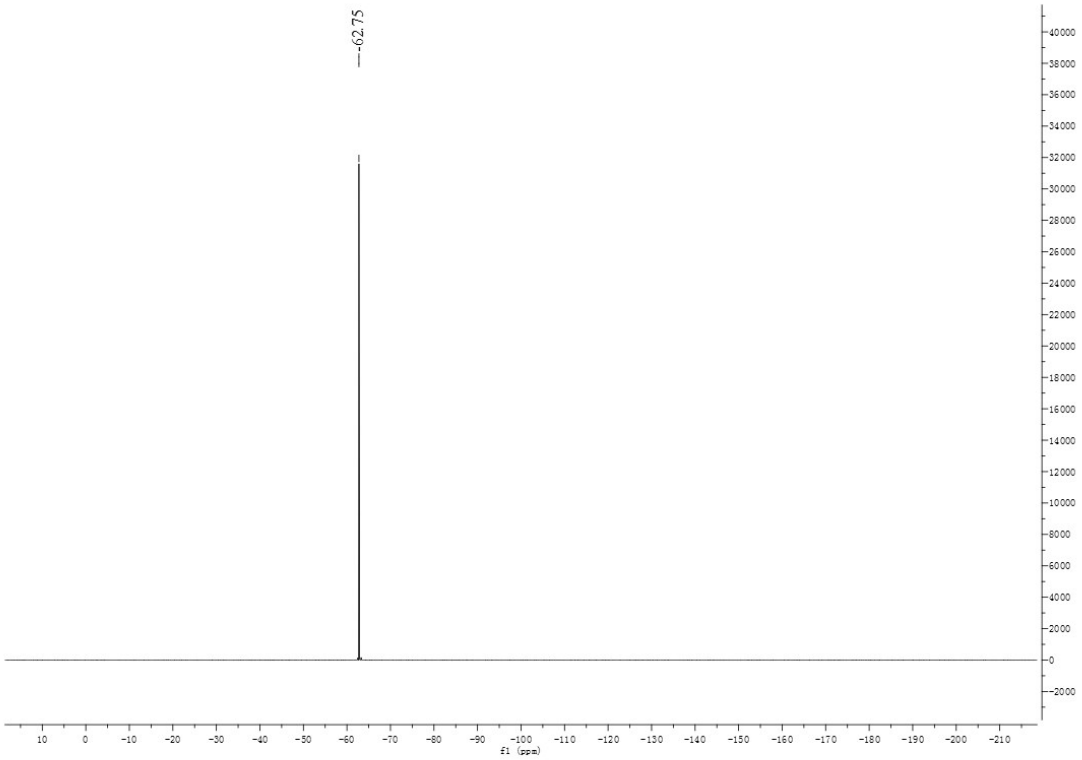

163.09
162.86
140.18
133.28
132.42
127.83
125.53
125.18
104.48
96.30
77.48
77.16
76.84
49.50
46.59
38.58
34.36
20.97
20.13
18.78
11.37
f1 (ppm)



3e







-62.75
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-100
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-120
-130
-140
-150
-160
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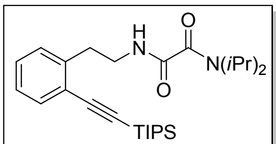
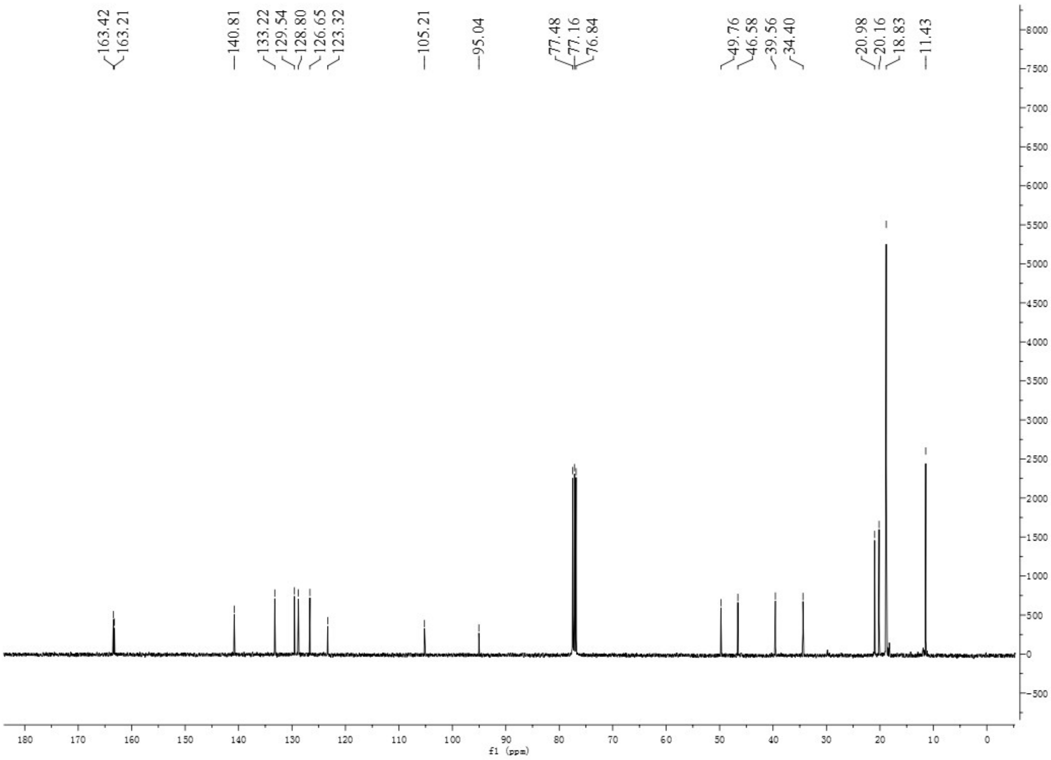
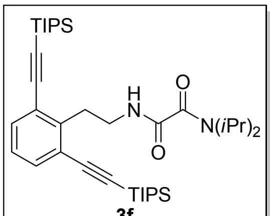
-200
-210
f1 (ppm)



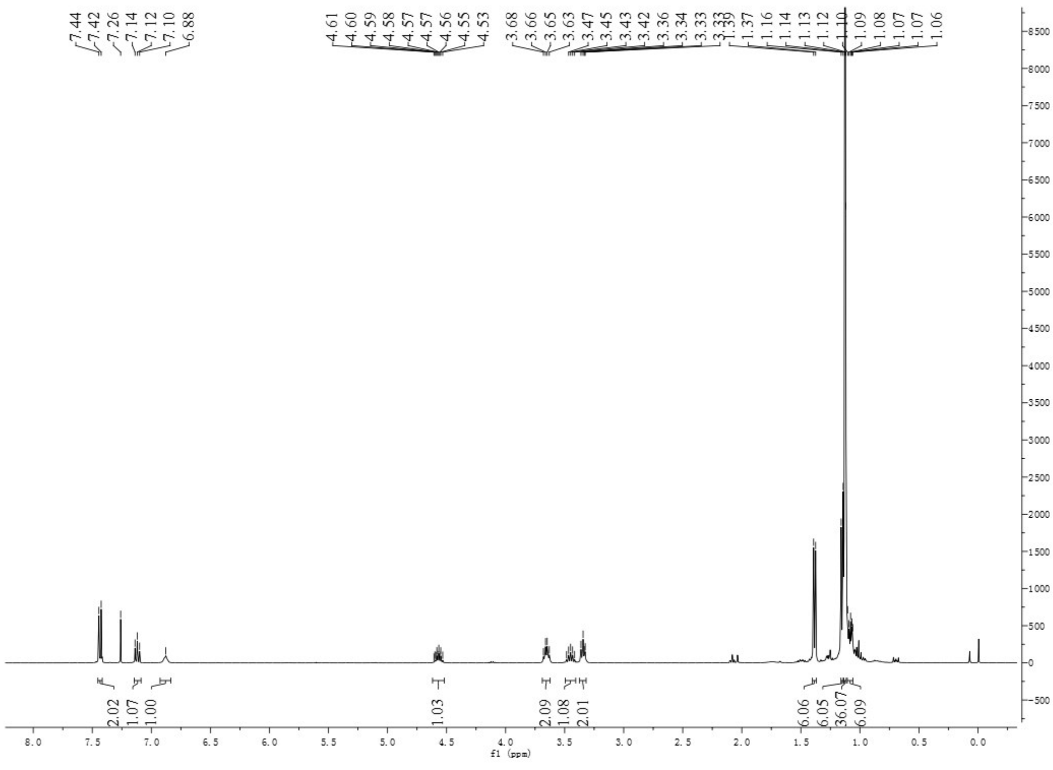
H
N
O
O
N(iPr)2
TIPS

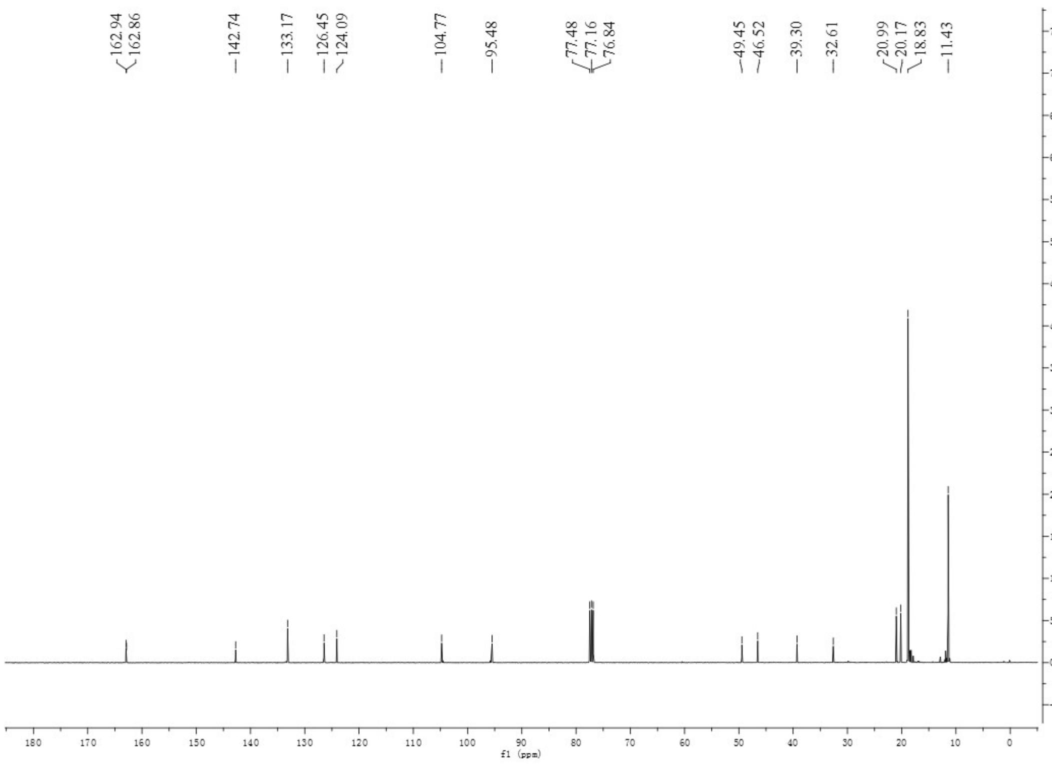
3f$_{mono}$

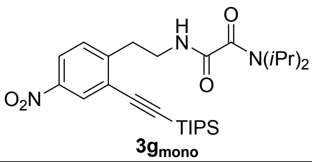

163.42
163.21
140.81
133.22
129.54
128.80
126.65
123.32
105.21
95.04
77.48
77.16
76.84
49.76
46.58
39.56
34.40
20.98
20.16
18.83
11.43
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500



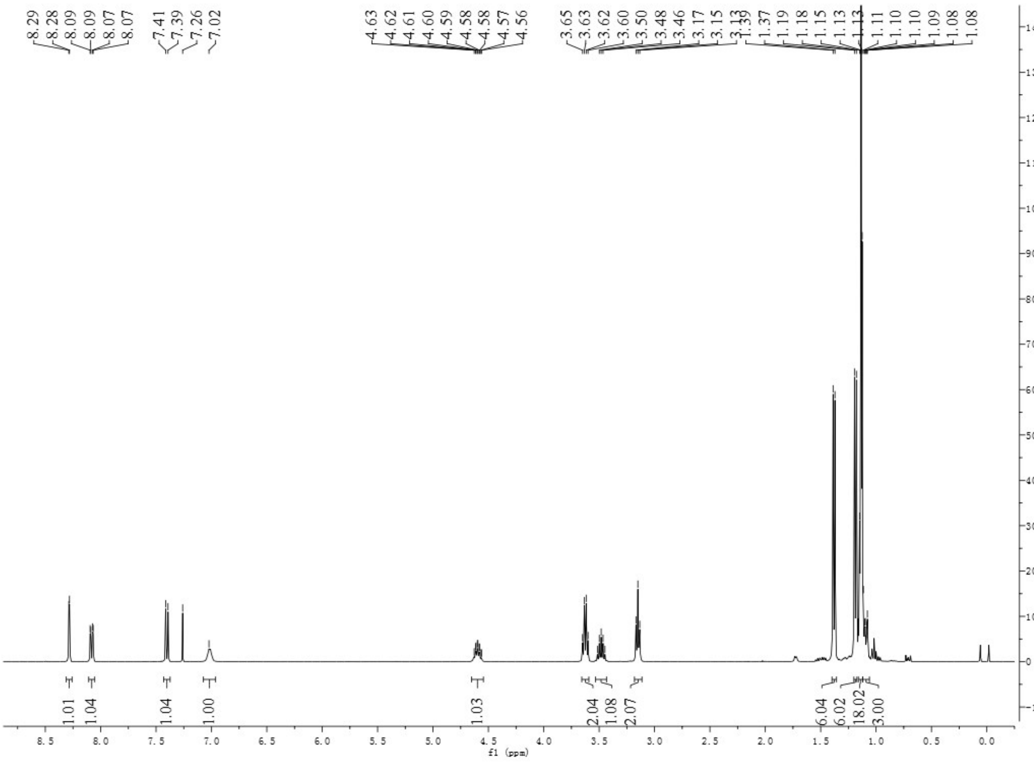
3f$_{di}$

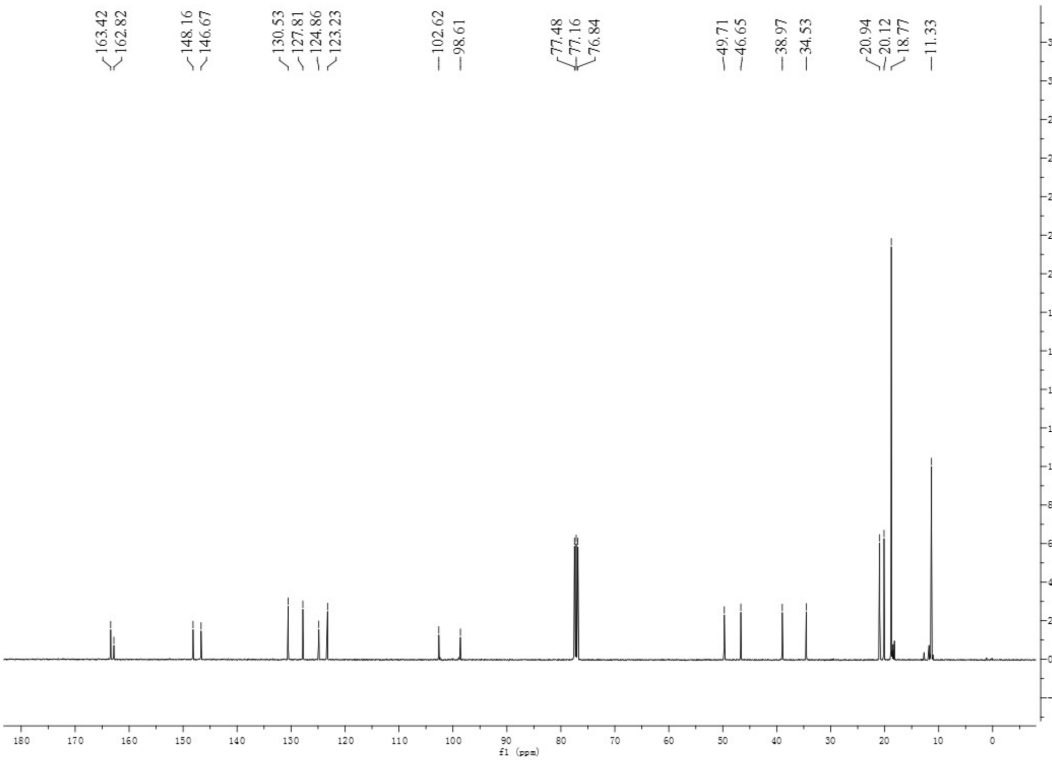


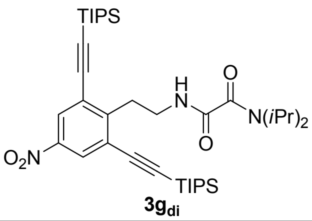



H
O
N(iPr)2
O
O2N
TIPS

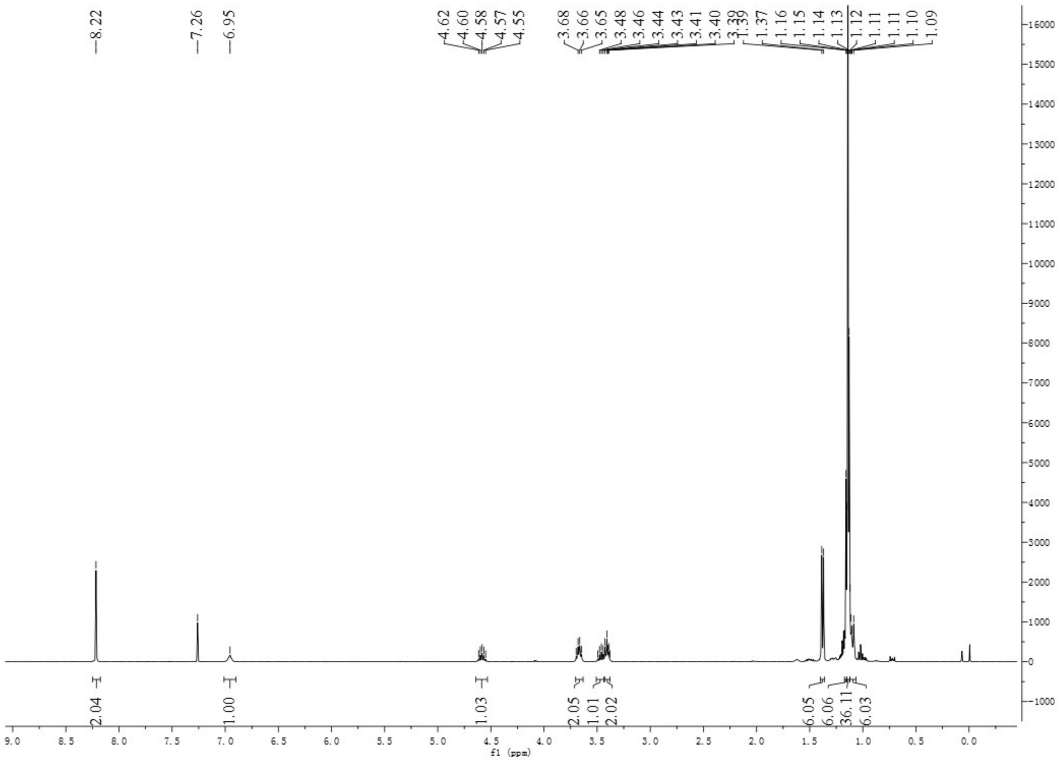
$3g_{mono}$

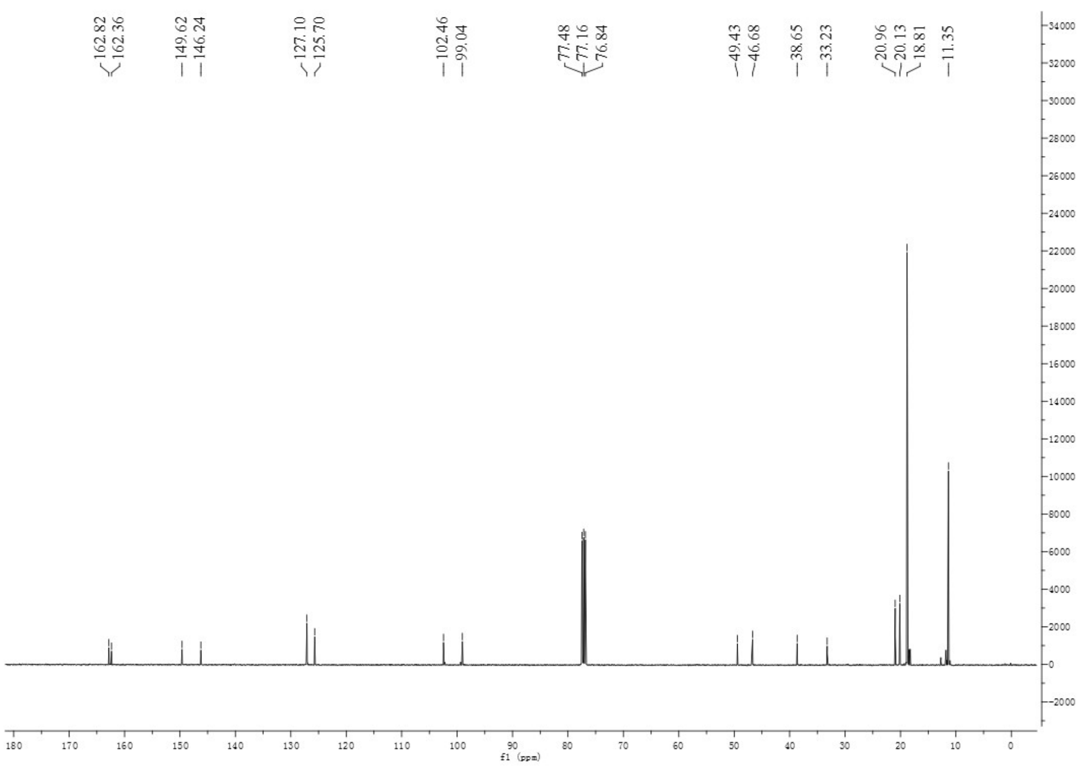

8.29 8.28 8.09 8.09 8.07 8.07 7.41 7.39 7.26 7.02
4.63 4.62 4.61 4.60 4.59 4.58 4.58 4.57 4.56
3.65 3.63 3.62 3.60 3.50 3.48 3.46 3.17 3.15 3.13 1.39 1.37 1.19 1.18 1.15 1.13 1.13 1.11 1.10 1.10 1.09 1.08 1.08
1.01 1.04 1.04 1.00 1.03 2.04 1.08 2.07 6.04 6.02 18.02 3.00
f1 (ppm)


163.42 162.82 148.16 146.67 130.53 127.81 124.86 123.23 102.62 98.61 77.48 77.16 76.84 49.71 46.65 38.97 34.53 20.94 20.12 18.77 11.33
f1 (ppm)



3g$_{di}$

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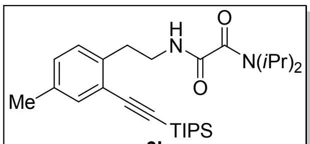
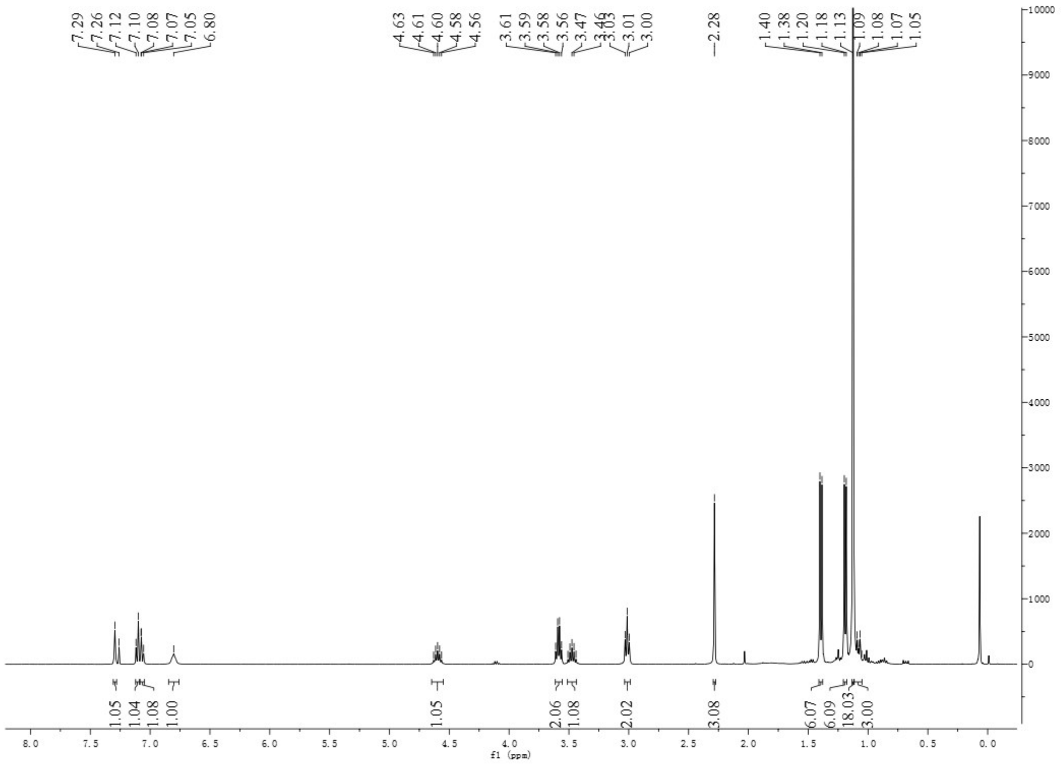
149.62
146.24
127.10
125.70
102.46
99.04
77.48
77.16
76.84
49.43
46.68
38.65
33.23
20.96
20.13
18.81
11.35
f1 (ppm)


H
N
O
O
N(iPr)2
Me
TIPS

$3h_{mono}$


7.29
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7.07
7.05
6.80
4.63
4.61
4.60
4.58
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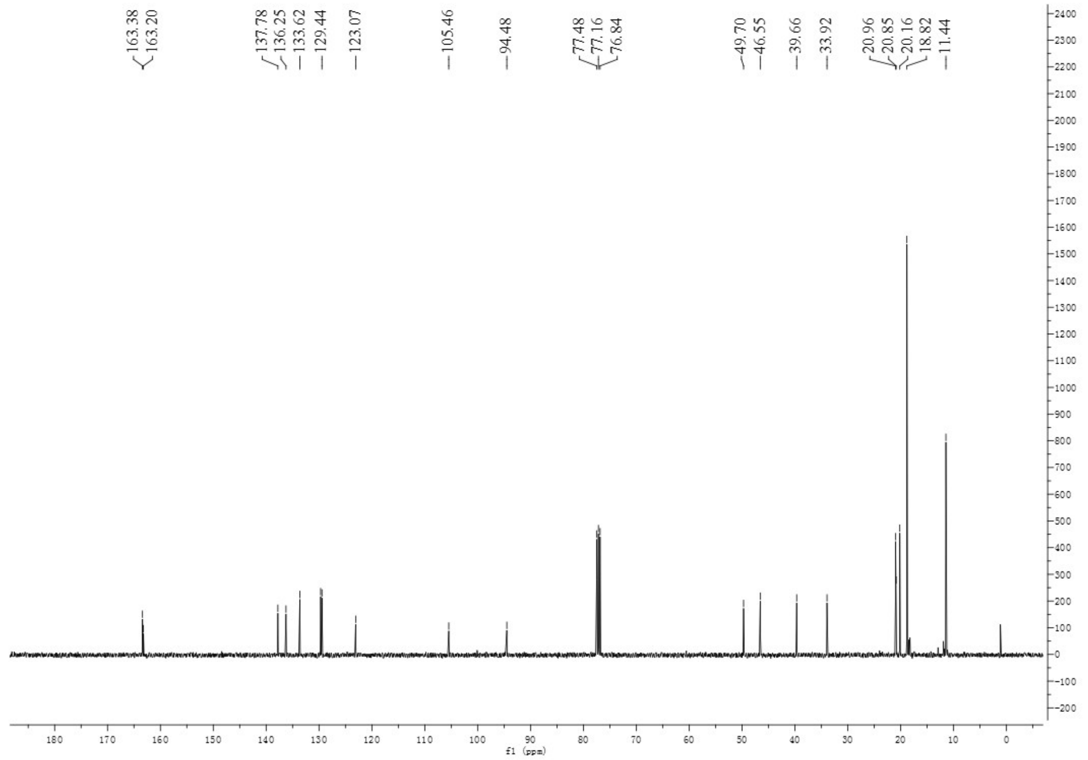
3.61
3.59
3.58
3.56
3.47
3.46
3.03
3.01
3.00
2.28
1.40
1.38
1.20
1.18
1.13
1.09
1.08
1.07
1.05
1.05
1.04
1.08
1.00
1.05
2.06
1.08
2.02
3.08
6.07
6.09
18.03
3.00
f1 (ppm)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105.46
94.48
77.48
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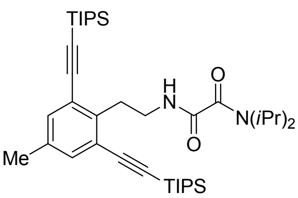
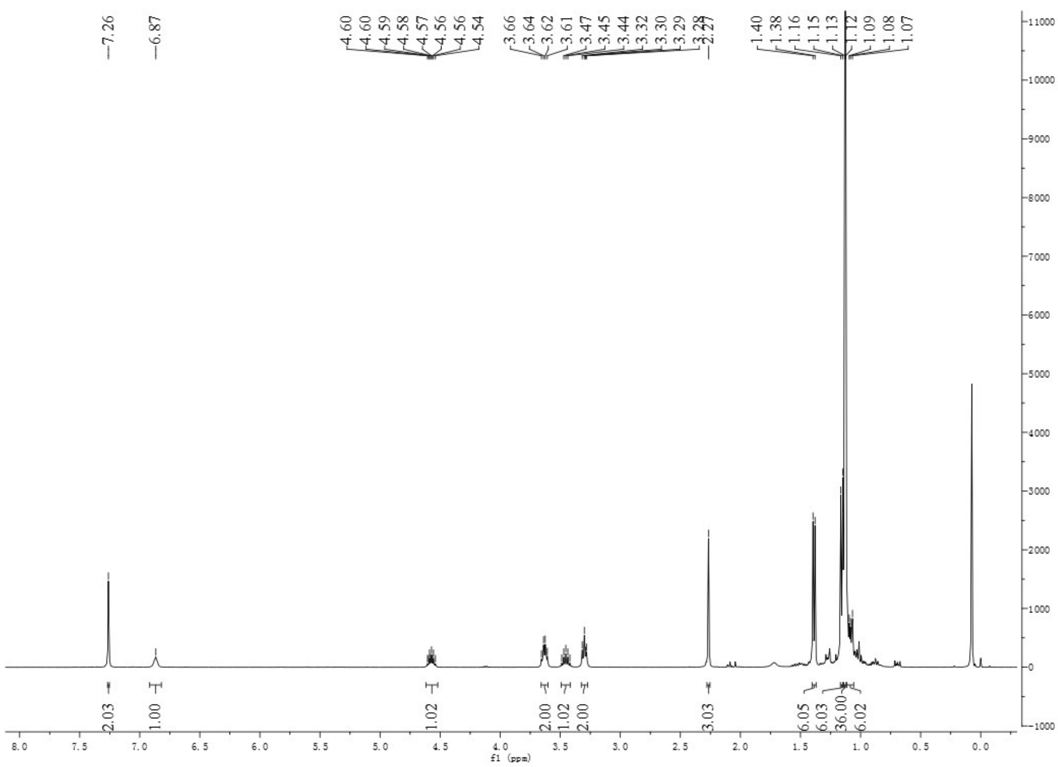
46.55
39.66
33.92
20.96
20.85
20.16
18.82
11.44
f1 (ppm)


TIPS
H
N
O
O
N(iPr)2
Me
TIPS

$\mathbf{3h_{di}}$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4.56
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3.62
3.61
3.47
3.45
3.44
3.32
3.30
3.29
3.28
2.27
1.40
1.38
1.16
1.15
1.13
1.12
1.09
1.08
1.07
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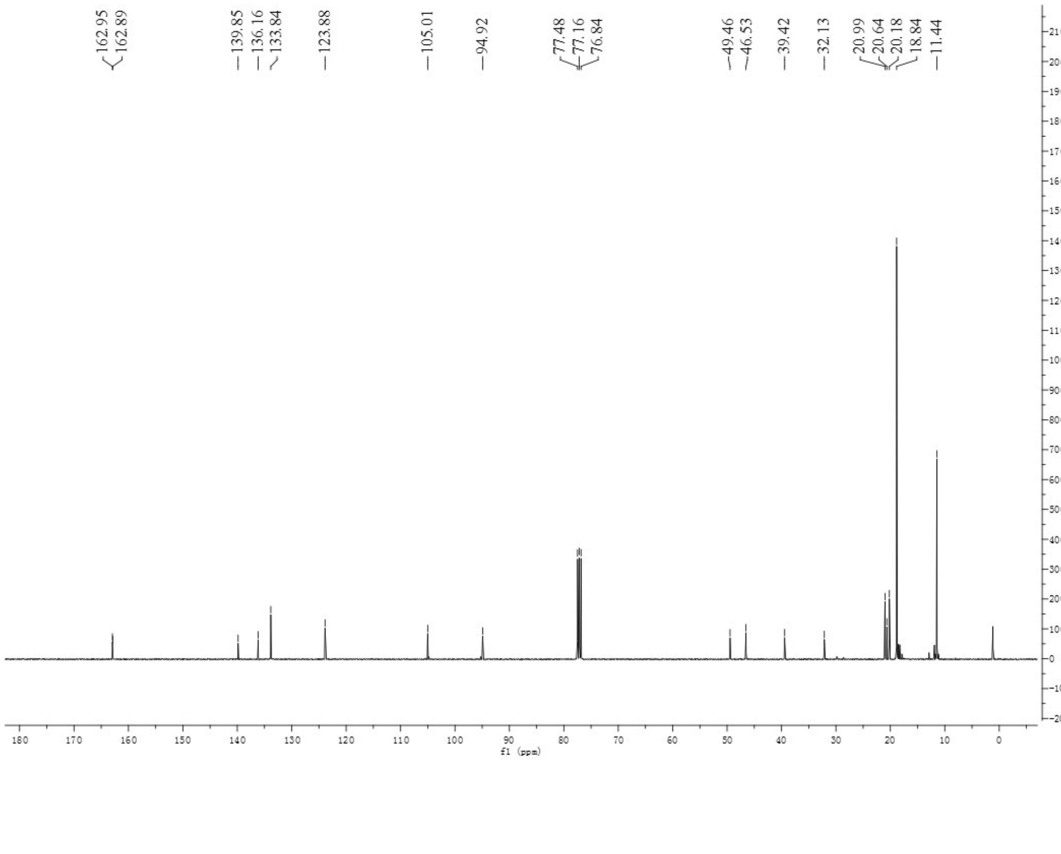
36.00
6.02
f1 (ppm)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105.01
94.92
77.48
77.16
76.84
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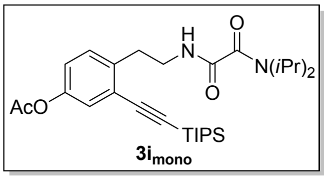
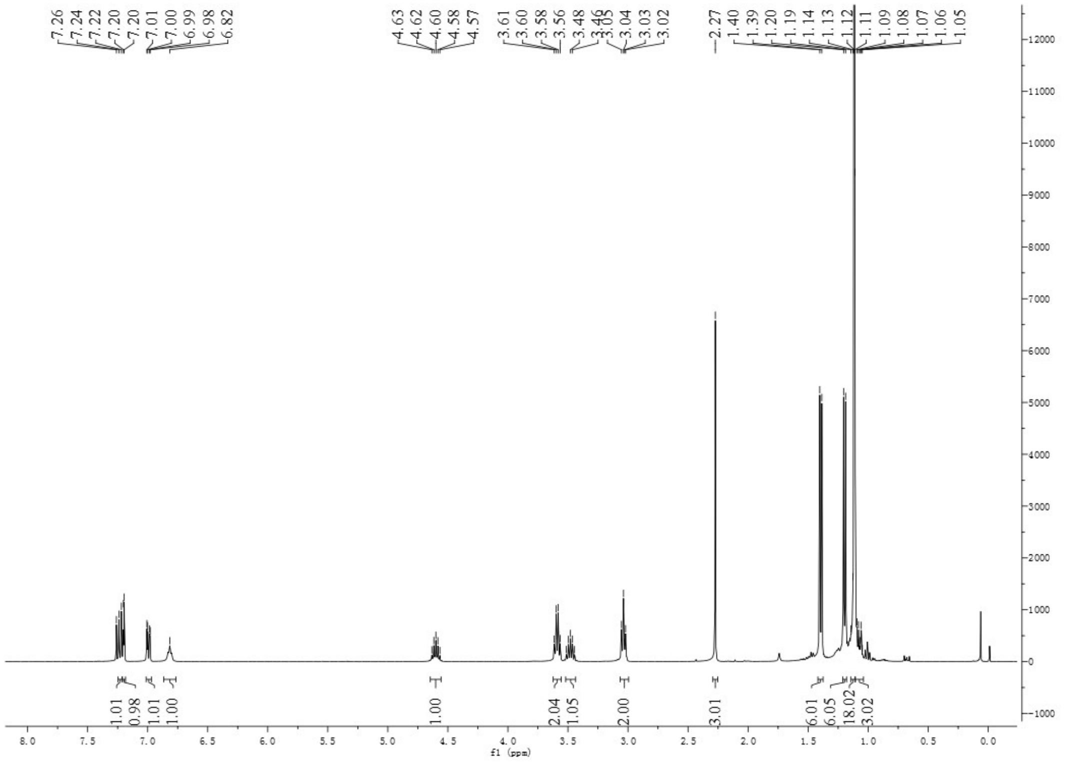
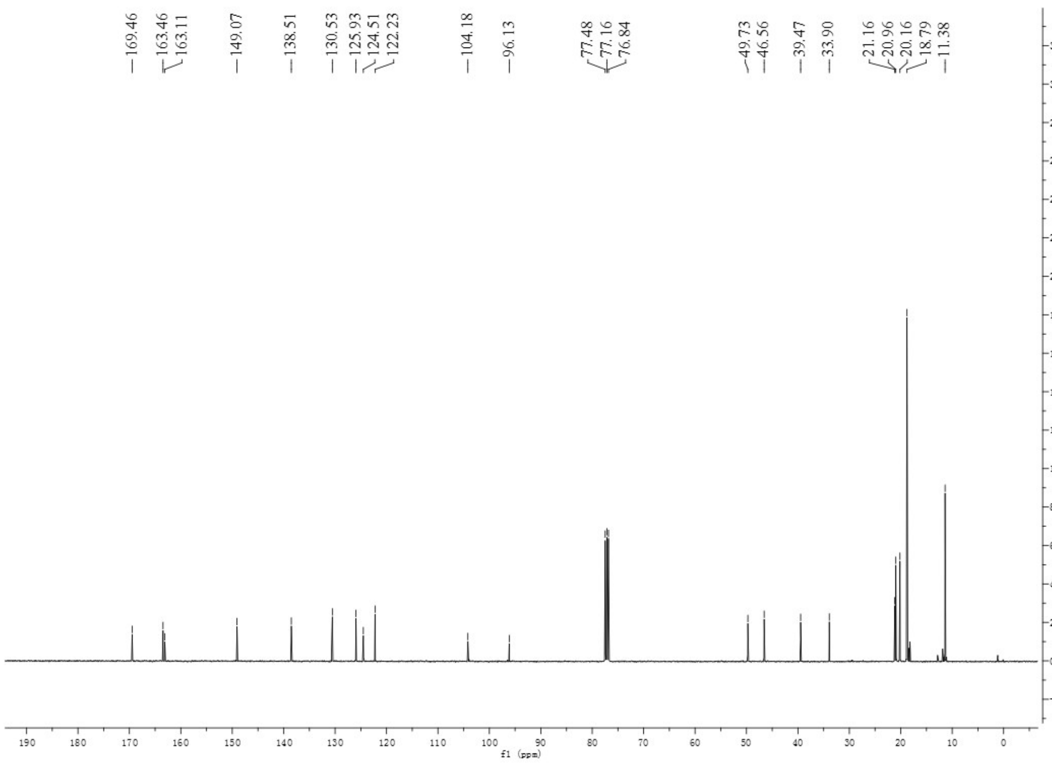
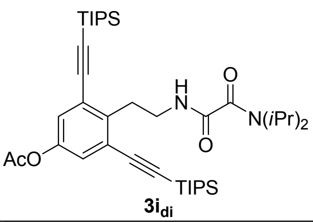
46.53
39.42
32.13
20.99
20.64
20.18
18.84
11.44
f1 (ppm)



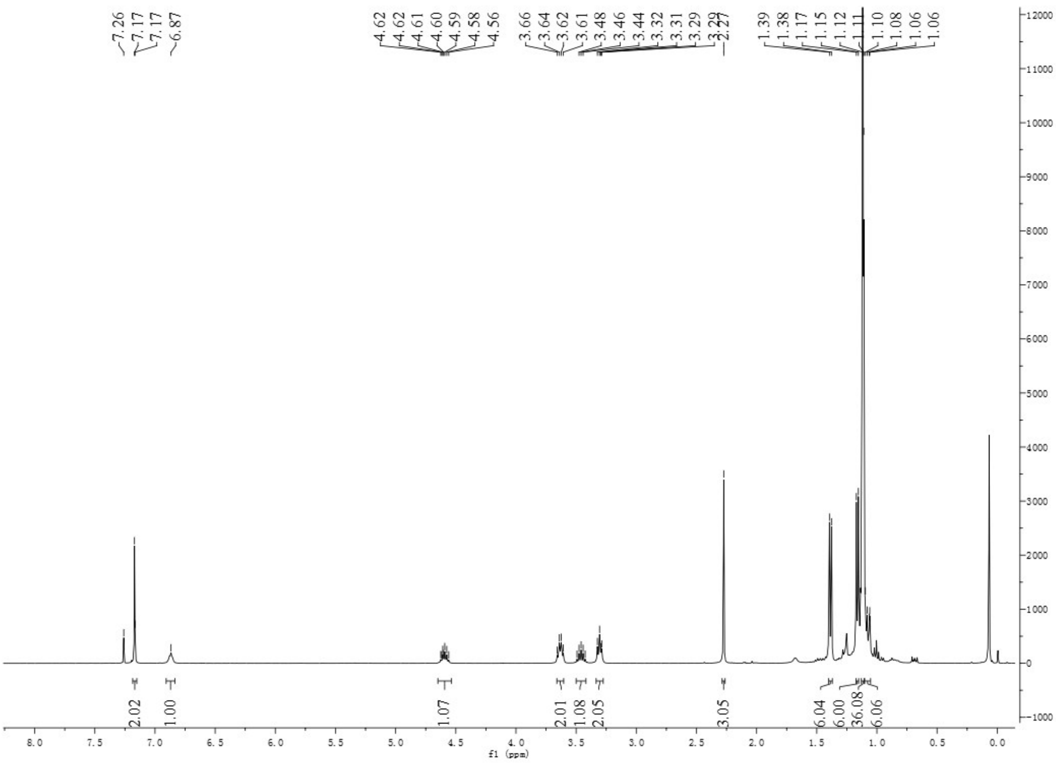
3i_mono

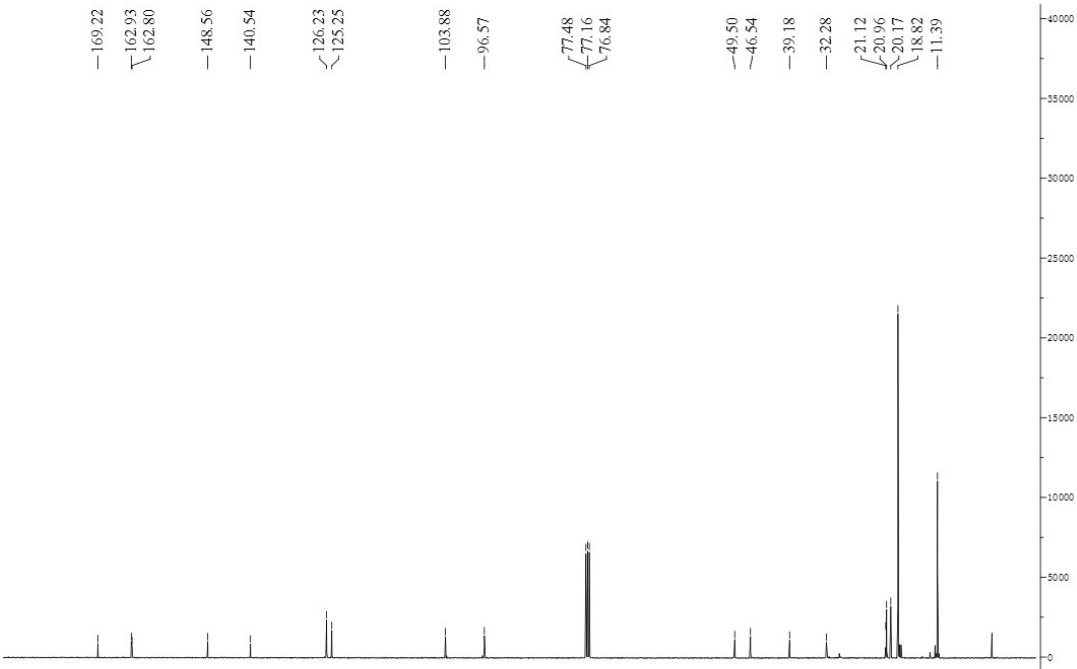


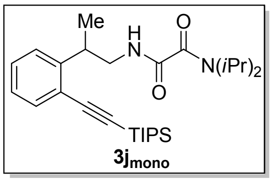


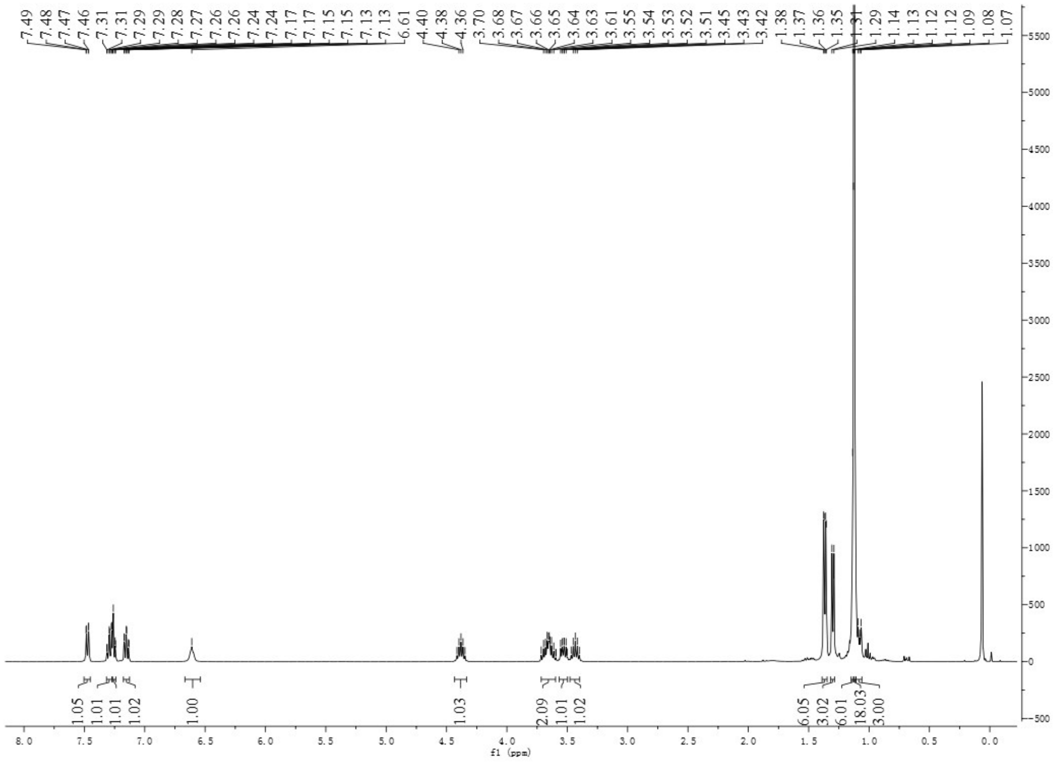


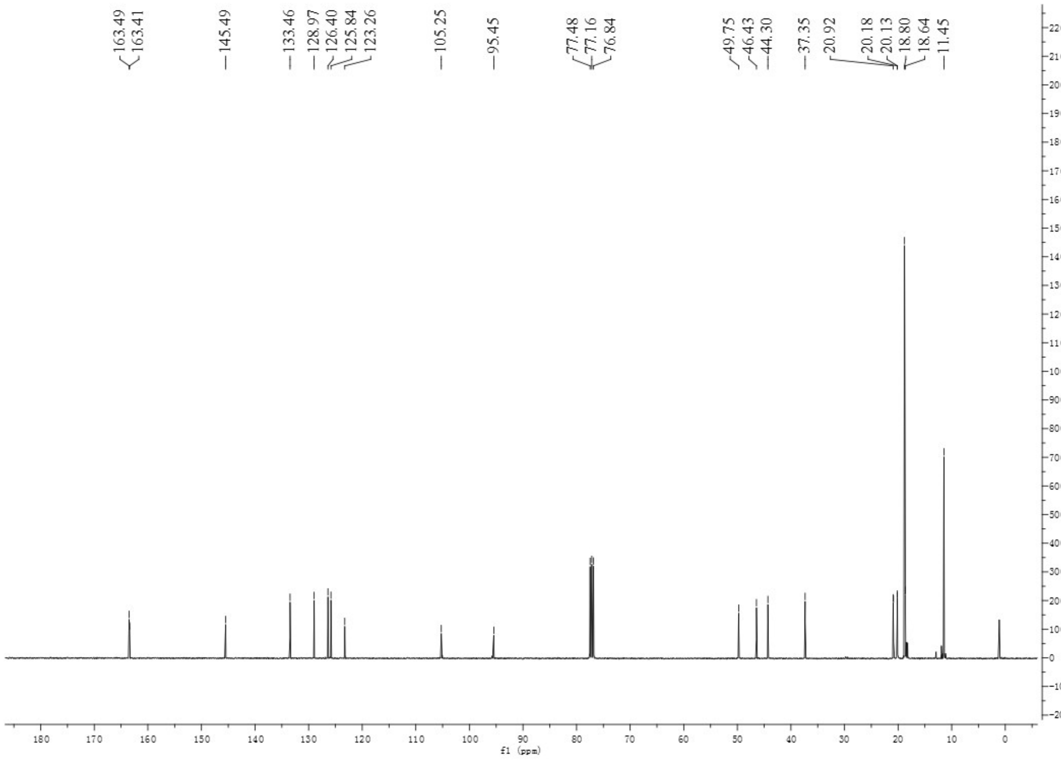
3i$_{di}$

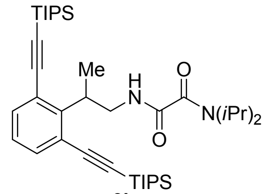




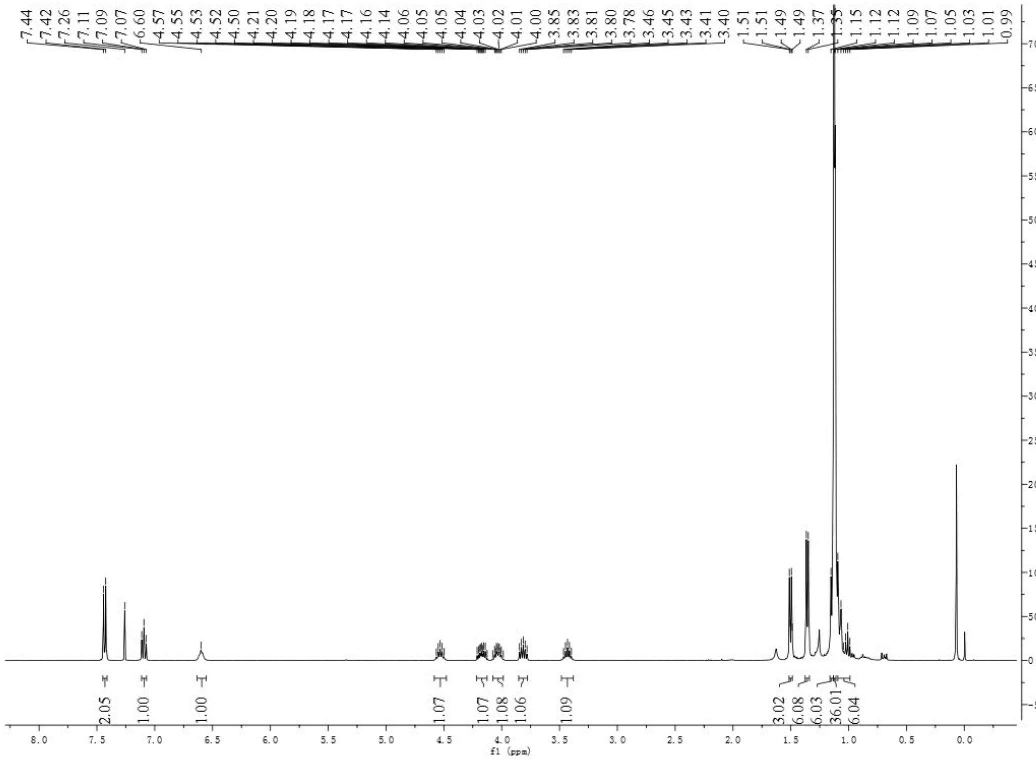

Me
H
N
O
O
N(iPr)2
TIPS
3j_mono

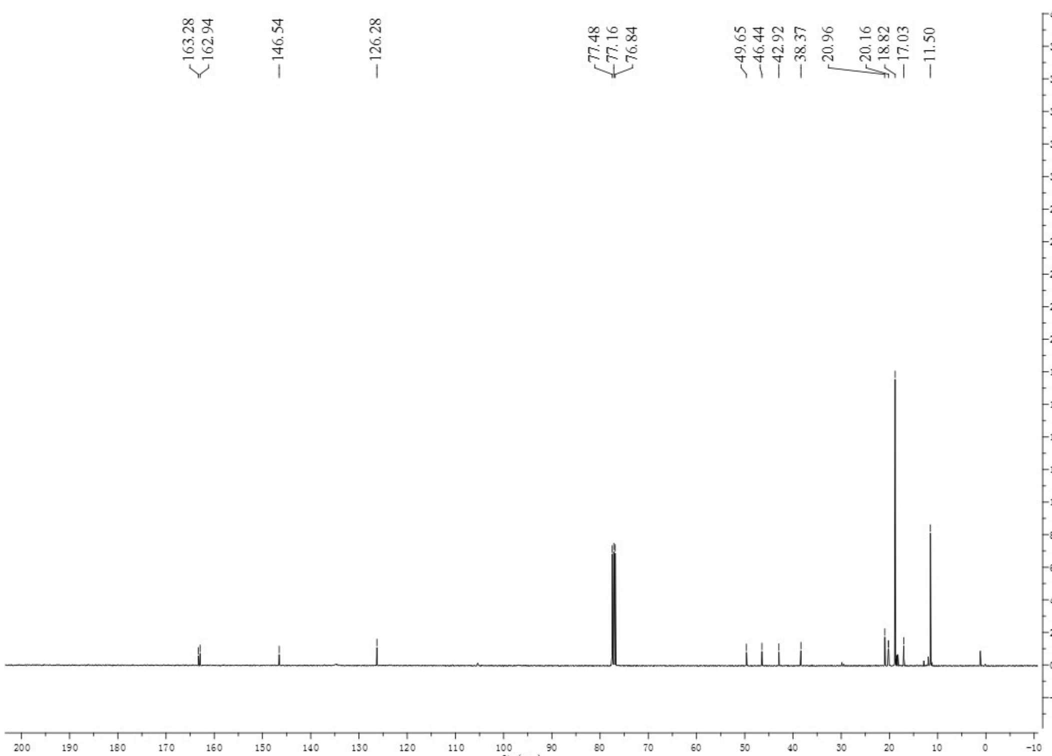

7.49 7.48 7.47 7.46 7.31 7.31 7.29 7.29 7.28 7.27 7.26 7.26 7.24 7.24 7.17 7.17 7.15 7.15 7.13 7.13 6.61 4.40 4.38 4.36 3.70 3.68 3.67 3.66 3.65 3.64 3.63 3.61 3.55 3.54 3.53 3.52 3.51 3.45 3.43 3.42 1.38 1.37 1.36 1.35 1.31 1.29 1.14 1.13 1.12 1.12 1.09 1.08 1.07
1.05 1.01 1.01 1.02 1.00 1.03 2.09 1.01 1.02 6.05 3.02 6.01 18.03 3.00
f1 (ppm)

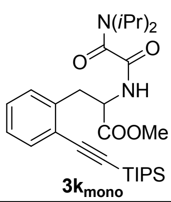

163.49 163.41 145.49 133.46 128.97 126.40 125.84 123.26 105.25 95.45 77.48 77.16 76.84 49.75 46.43 44.30 37.35 20.92 20.18 20.13 18.80 18.64 11.45
f1 (ppm)


TIPS
Me
H
N
O
O
N(iPr)2
TIPS

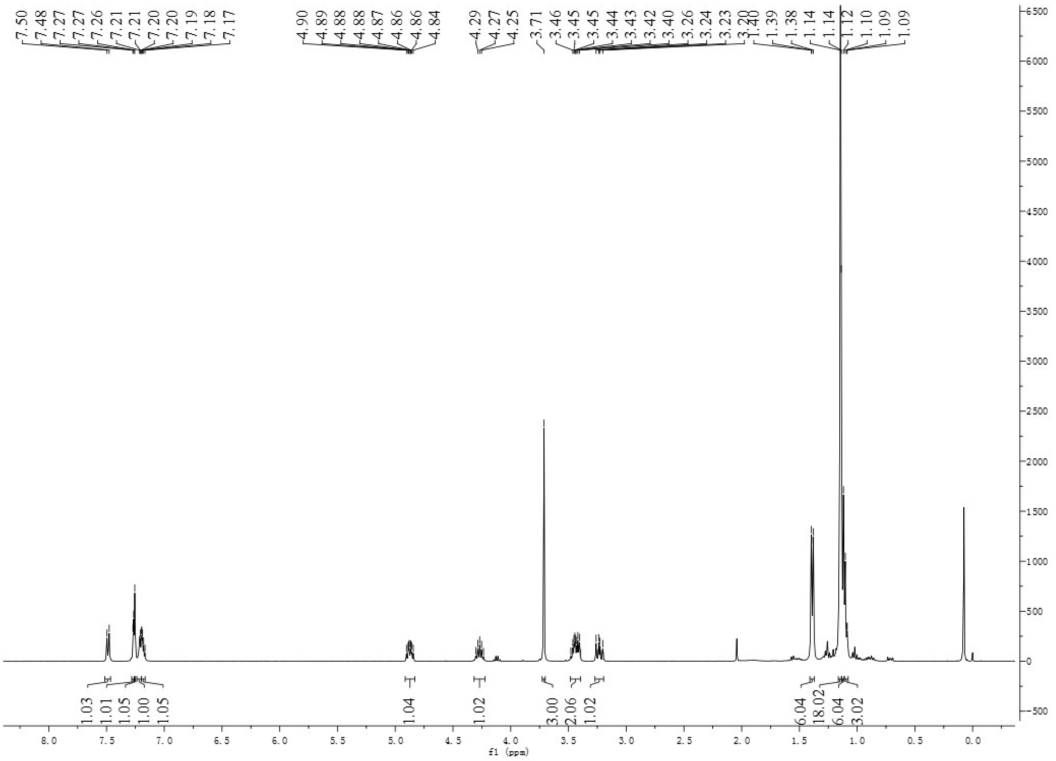
3j$_{di}$

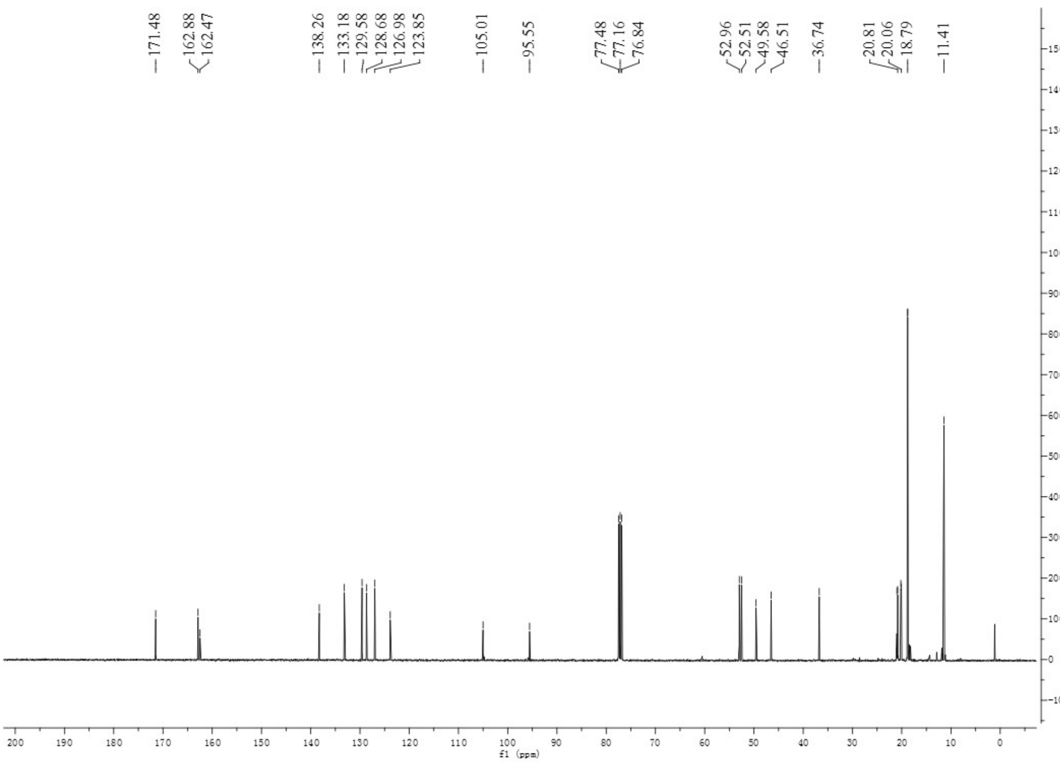

7.44 7.42 7.26 7.11 7.09 7.07 6.60 4.57 4.55 4.53 4.52 4.50 4.21 4.20 4.19 4.18 4.17 4.17 4.16 4.14 4.06 4.05 4.05 4.04 4.03 4.02 4.01 4.00 3.85 3.83 3.81 3.80 3.78 3.46 3.45 3.43 3.41 3.40 1.51 1.51 1.49 1.49 1.37 1.35 1.15 1.12 1.12 1.09 1.07 1.05 1.03 1.01 0.99
2.05 1.00 1.00 1.07 1.07 1.08 1.06 1.09 3.02 6.08 6.03 36.01 6.04
f1 (ppm)

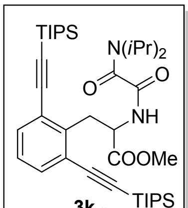

163.28 162.94 146.54 126.28 77.48 77.16 76.84 49.65 46.44 42.92 38.37 20.96 20.16 18.82 17.03 11.50
f1 (ppm)


N(iPr)2
O
O
NH
COOMe
TIPS

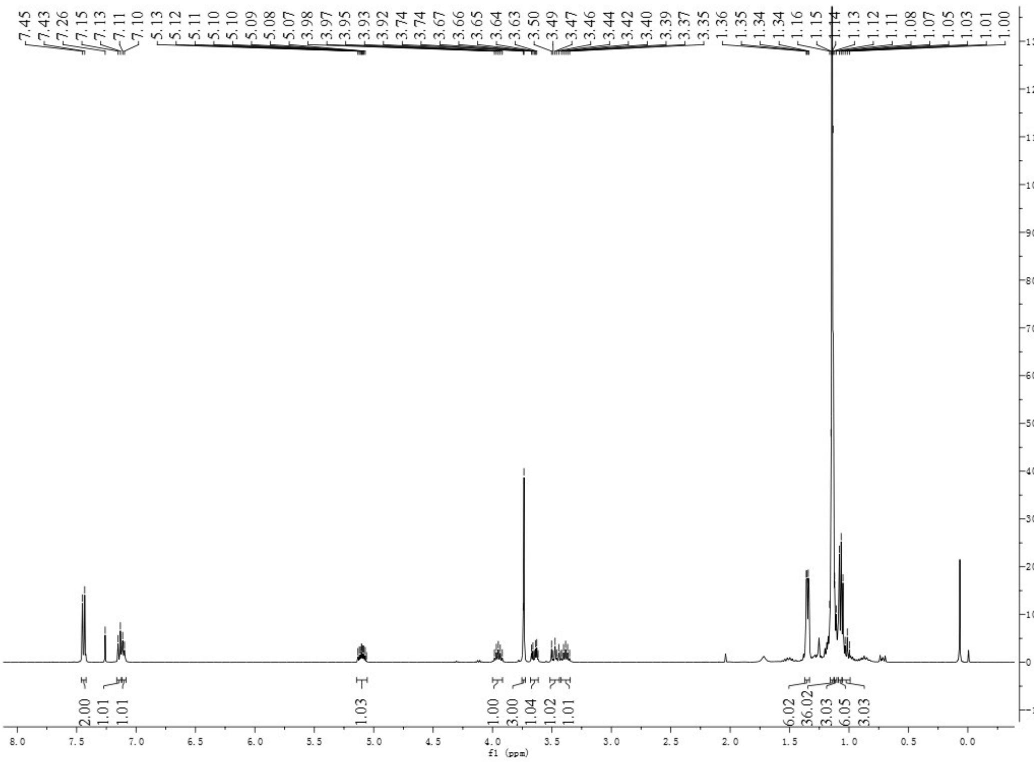
3k$_{mono}$

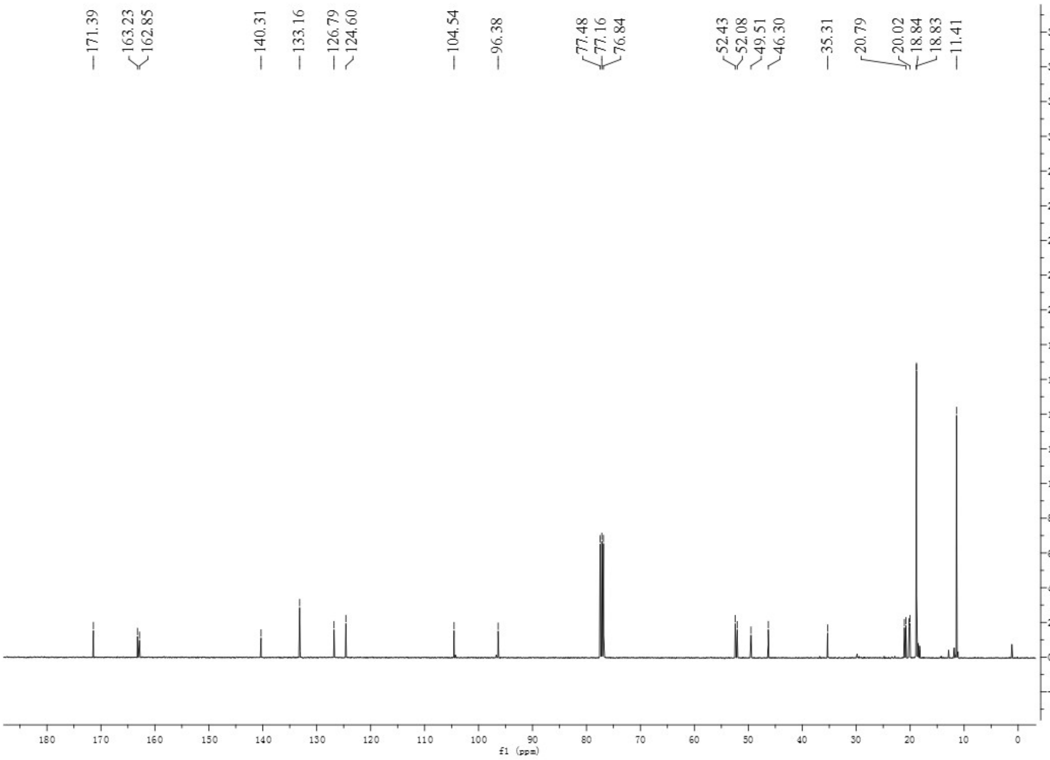

7.50 7.48 7.27 7.27 7.26 7.21 7.21 7.20 7.20 7.19 7.18 7.17
4.90 4.89 4.88 4.88 4.87 4.86 4.86 4.84
4.29 4.27 4.25
3.71
3.46 3.45 3.45 3.44 3.43 3.42 3.40 3.26 3.24 3.23 3.20
1.40 1.39 1.38 1.14 1.12 1.10 1.09 1.09
1.03 1.01 1.05 1.00 1.05 1.04 1.02 3.00 2.06 1.02 6.04 18.02 6.04 3.02
f1 (ppm)

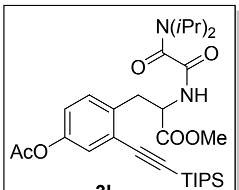

171.48
162.88 162.47
138.26 133.18 129.58 128.68 126.98 123.85
105.01
95.55
77.48 77.16 76.84
52.96 52.51 49.58 46.51
36.74
20.81 20.06 18.79
11.41
f1 (ppm)



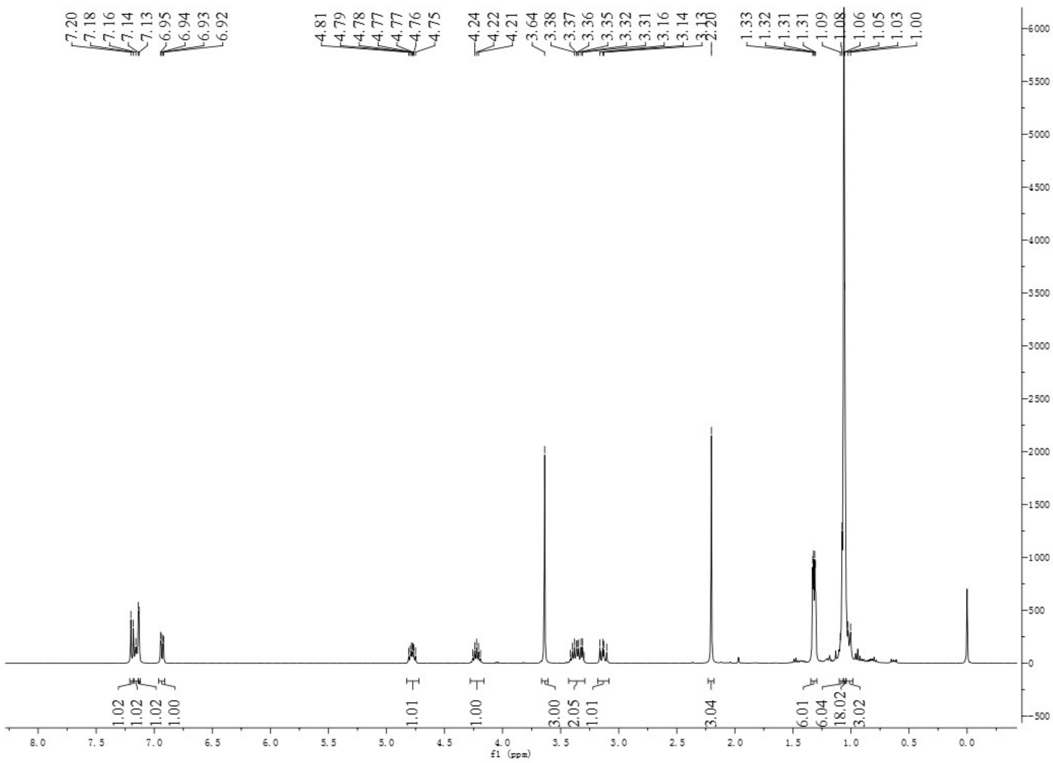
3k$_{di}$

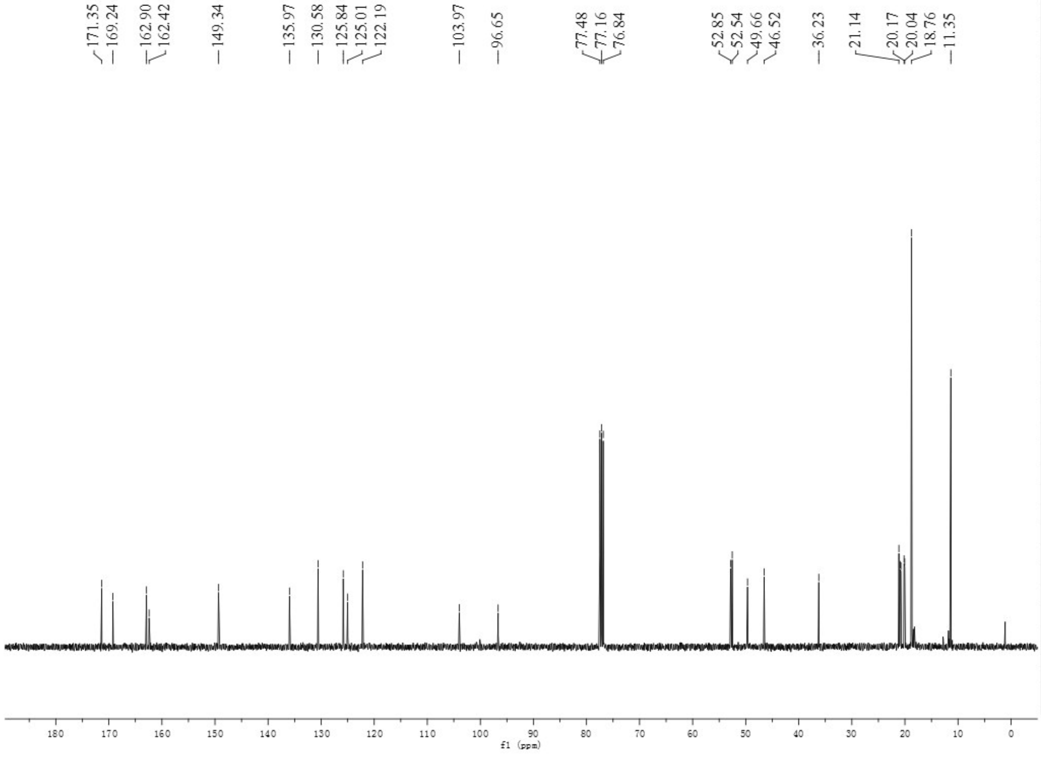


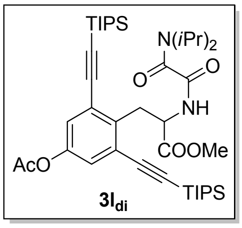


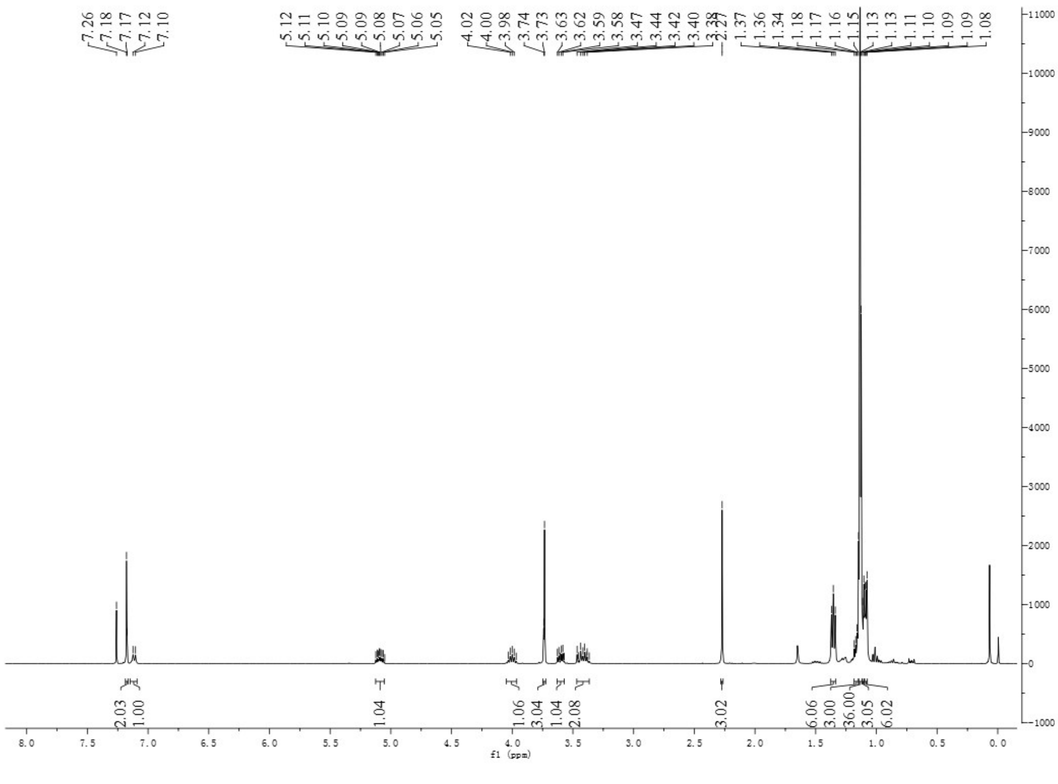


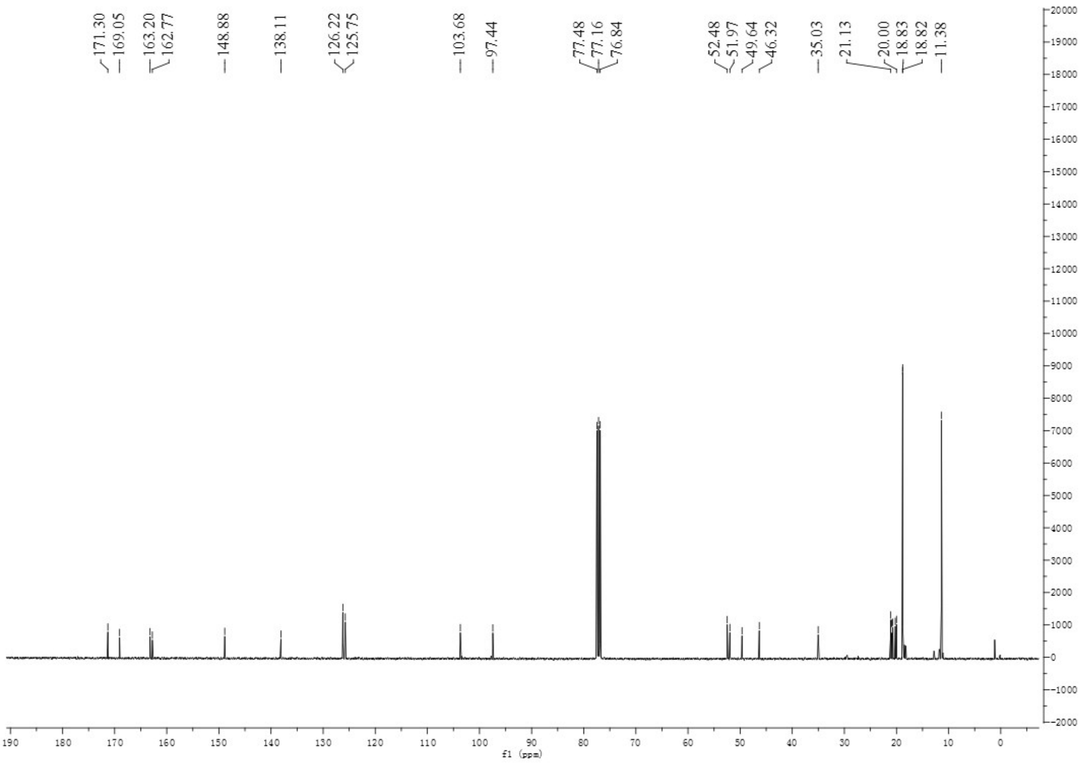
3l$_{mono}$

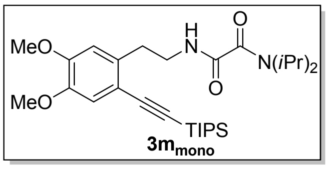




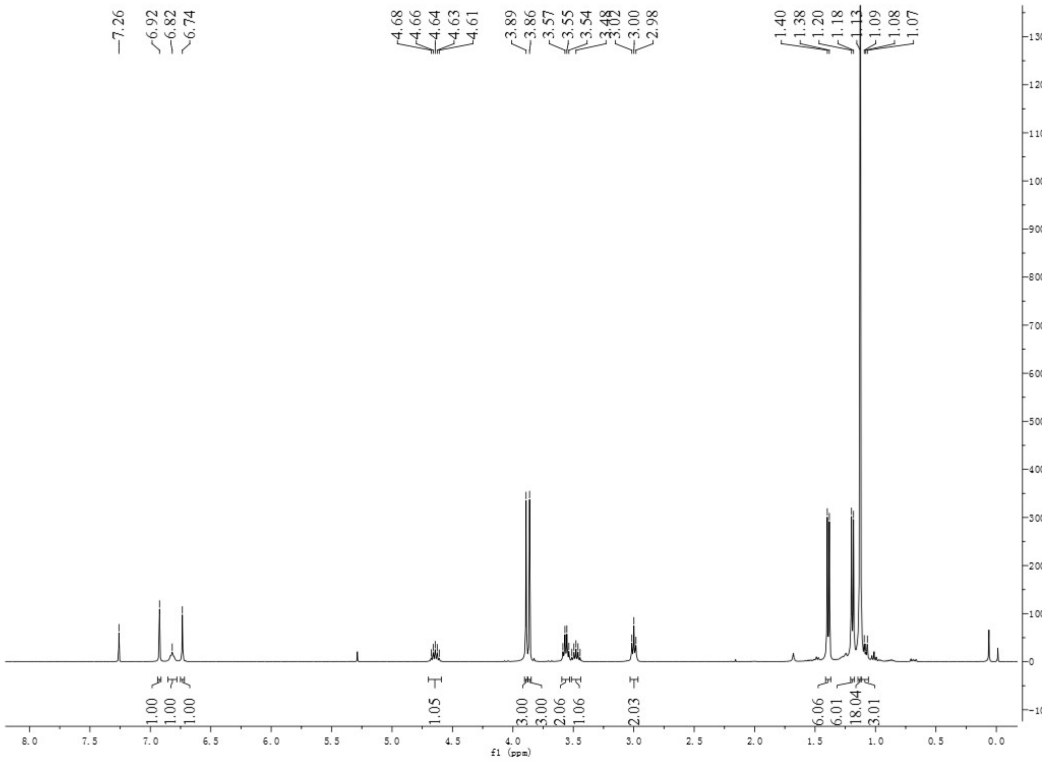

TIPS
N(iPr)2
O
O
NH
COOMe
AcO
TIPS
3l_di

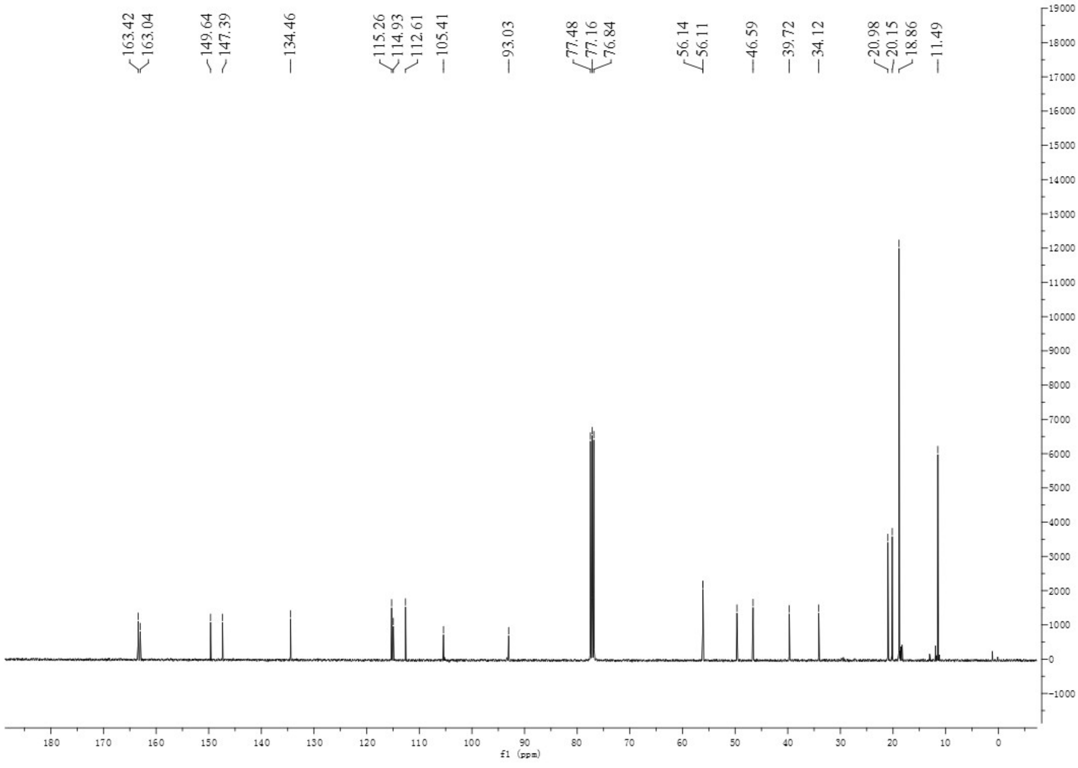

7.26
7.18
7.17
7.12
7.10
5.12
5.11
5.10
5.09
5.09
5.08
5.07
5.06
5.05
4.02
4.00
3.98
3.74
3.73
3.63
3.62
3.59
3.58
3.47
3.44
3.42
3.40
1.37
1.36
1.34
1.18
1.17
1.16
1.15
1.13
1.13
1.11
1.10
1.09
1.09
1.08
2.03
1.00
1.04
1.06
3.04
1.04
2.08
3.02
6.06
3.00
36.00
3.05
6.02
f1 (ppm)

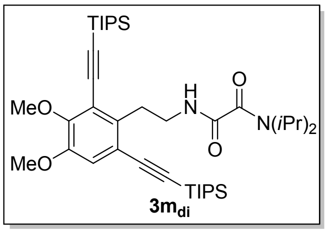

171.30
169.05
163.20
162.77
148.88
138.11
126.22
125.75
103.68
97.44
77.48
77.16
76.84
52.48
51.97
49.64
46.32
35.03
21.13
20.00
18.83
18.82
11.38
f1 (ppm)


MeO
MeO
H
N
O
O
N(iPr)2
TIPS

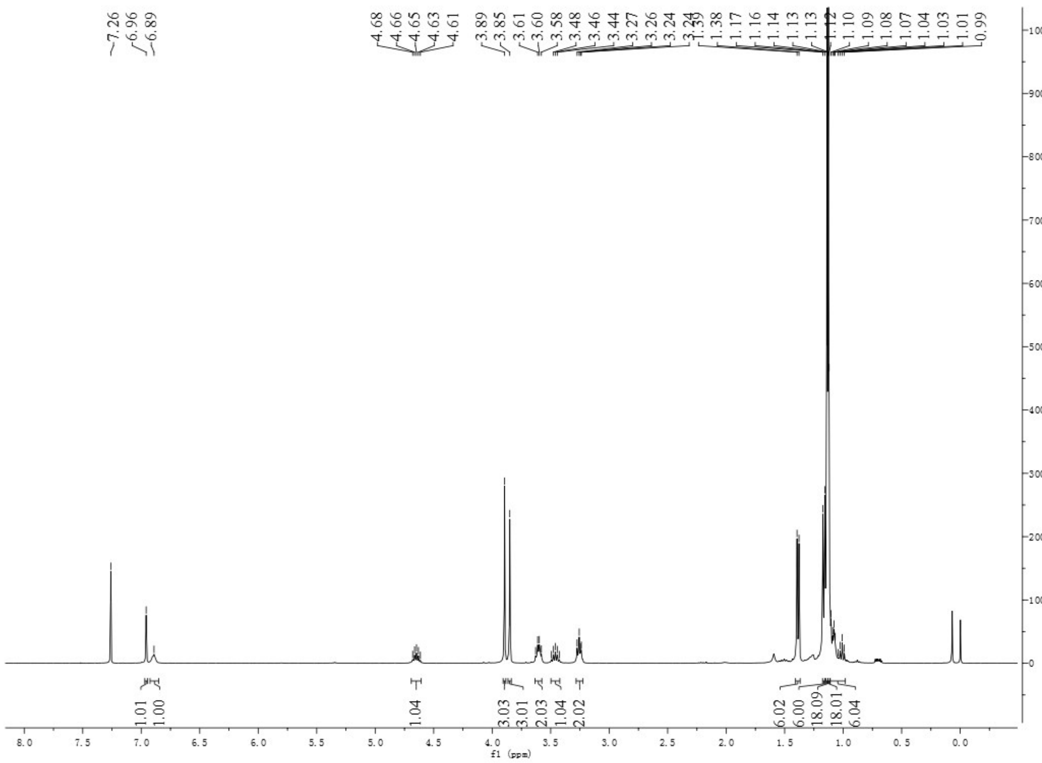
3m$_{mono}$

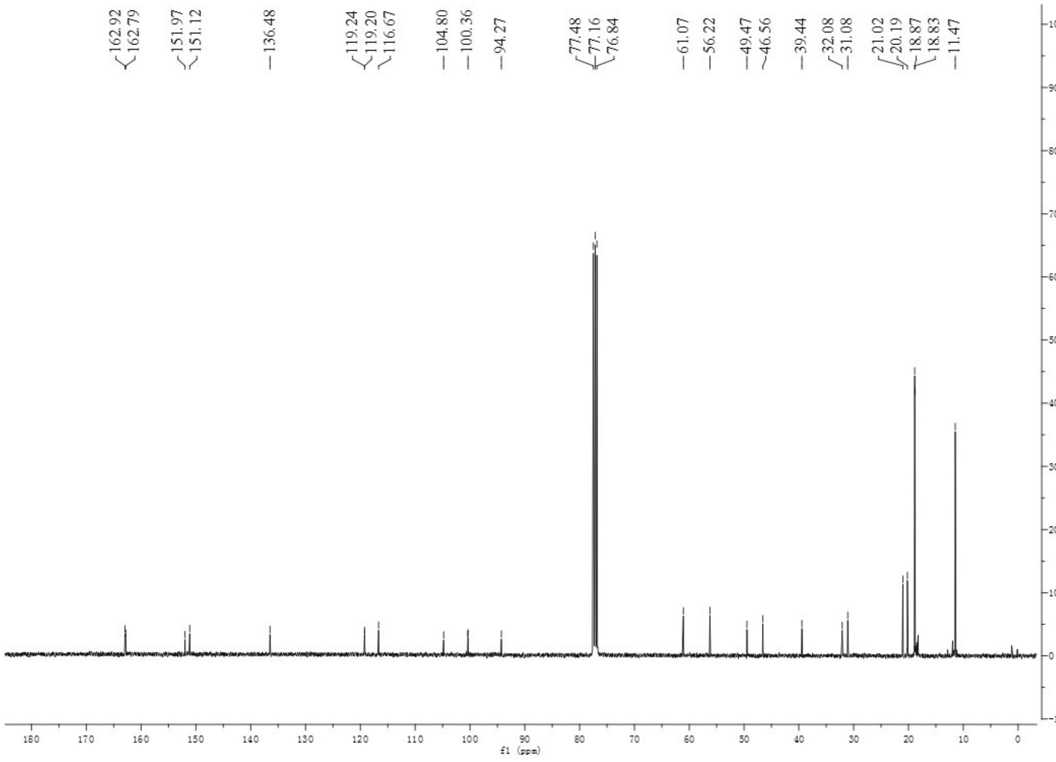

7.26
6.92
6.82
6.74
4.68
4.66
4.64
4.63
4.61
3.89
3.86
3.57
3.55
3.54
3.48
3.02
3.00
2.98
1.40
1.38
1.20
1.18
1.13
1.09
1.08
1.07
1.00
1.00
1.00
1.05
3.00
3.00
2.06
1.06
2.03
6.06
6.01
18.04
3.01
f1 (ppm)

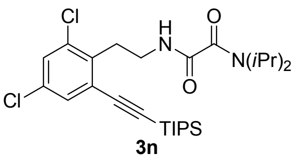

163.42
163.04
149.64
147.39
134.46
115.26
114.93
112.61
105.41
93.03
77.48
77.16
76.84
56.14
56.11
46.59
39.72
34.12
20.98
20.15
18.86
11.49
f1 (ppm)


TIPS
MeO
MeO
H
N
O
O
N(iPr)2
TIPS

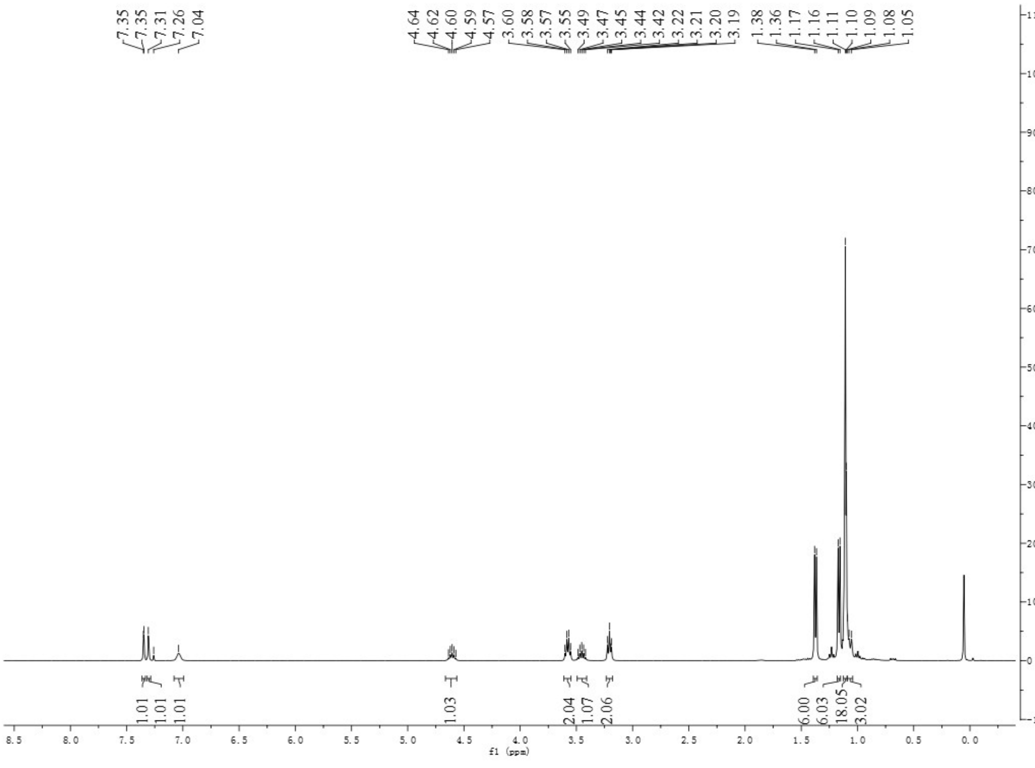
3m_di

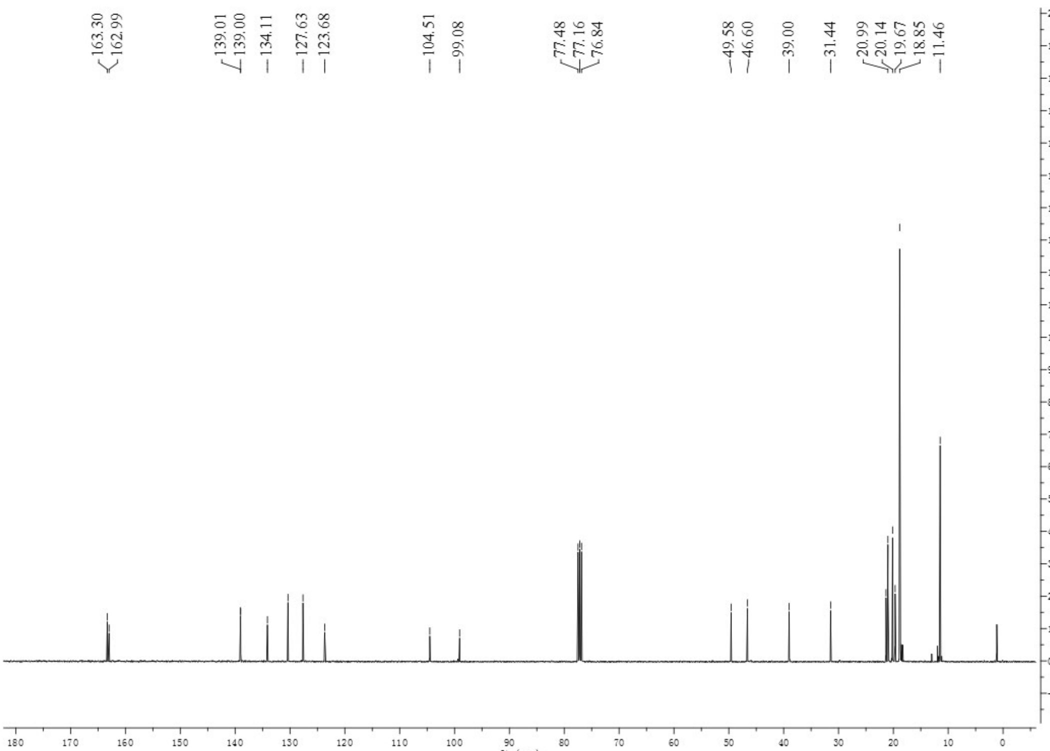

7.26
6.96
6.89
4.68
4.66
4.65
4.63
4.61
3.89
3.85
3.61
3.60
3.58
3.48
3.46
3.44
3.27
3.26
3.24
3.24
1.39
1.38
1.17
1.16
1.14
1.13
1.13
1.12
1.10
1.09
1.08
1.07
1.04
1.03
1.01
0.99
1.01
1.00
1.04
3.03
3.01
2.03
1.04
2.02
6.02
6.00
18.09
18.01
6.04
f1 (ppm)


162.92
162.79
151.97
151.12
136.48
119.24
119.20
116.67
104.80
100.36
94.27
77.48
77.16
76.84
61.07
56.22
49.47
46.56
39.44
32.08
31.08
21.02
20.19
18.87
18.83
11.47
f1 (ppm)


Cl
H
N
O
N(iPr)2
O
Cl
TIPS

3n


7.35
7.35
7.31
7.26
7.04
4.64
4.62
4.60
4.59
4.57
3.60
3.58
3.57
3.55
3.49
3.47
3.45
3.44
3.42
3.22
3.21
3.20
3.19
1.38
1.36
1.17
1.16
1.11
1.10
1.09
1.08
1.05
1.01
1.01
1.01
1.01
1.03
2.04
1.07
2.06
6.00
6.03
18.05
3.02
f1 (ppm)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162.99
139.01
139.00
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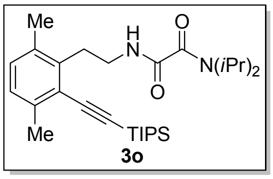
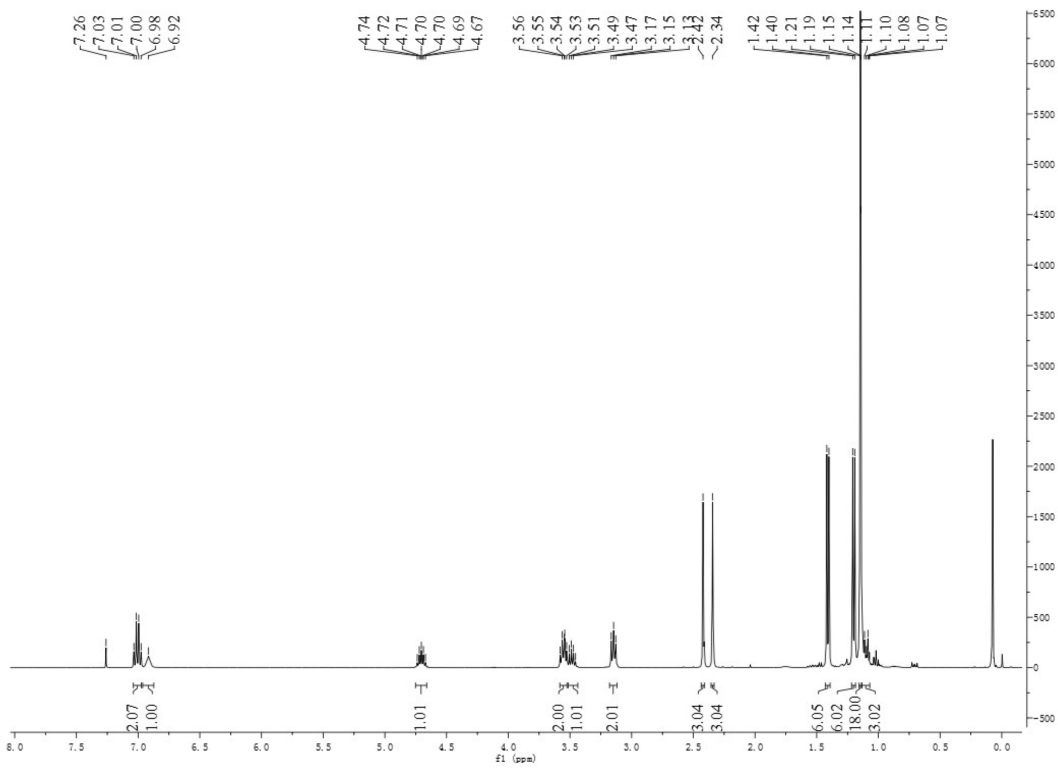
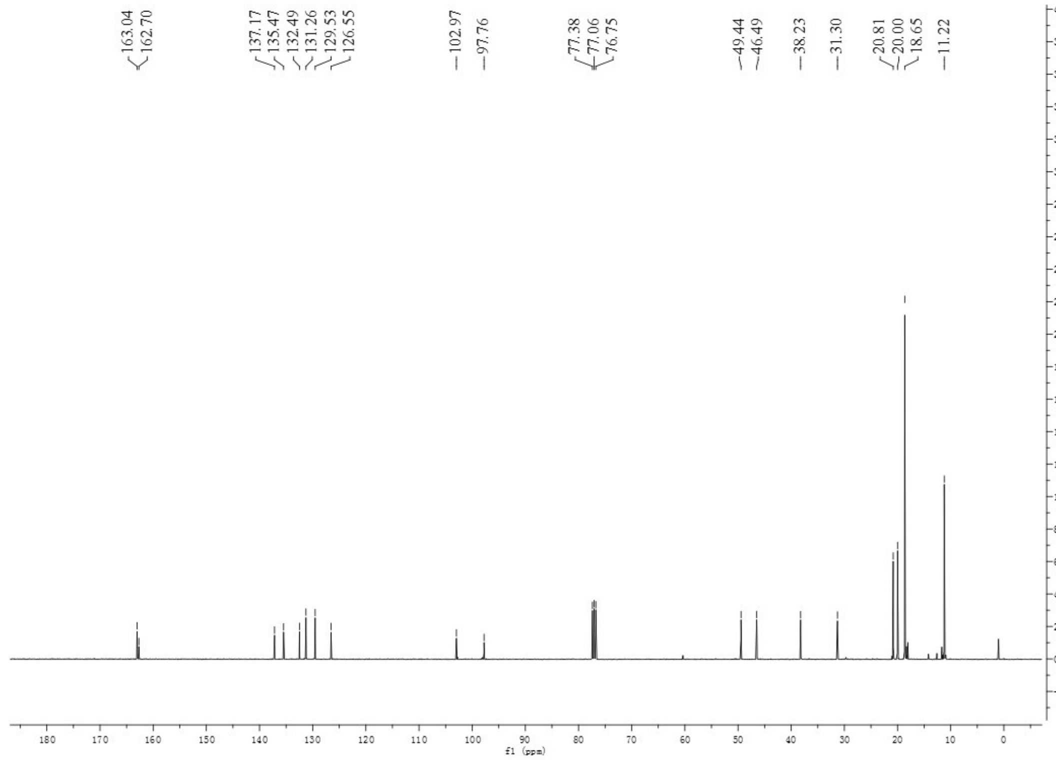
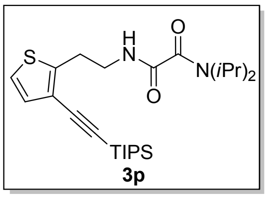
127.63
123.68
104.51
99.08
77.48
77.16
76.84
49.58
46.60
39.00
31.44
20.99
20.14
19.67
18.85
11.46
f1 (ppm)



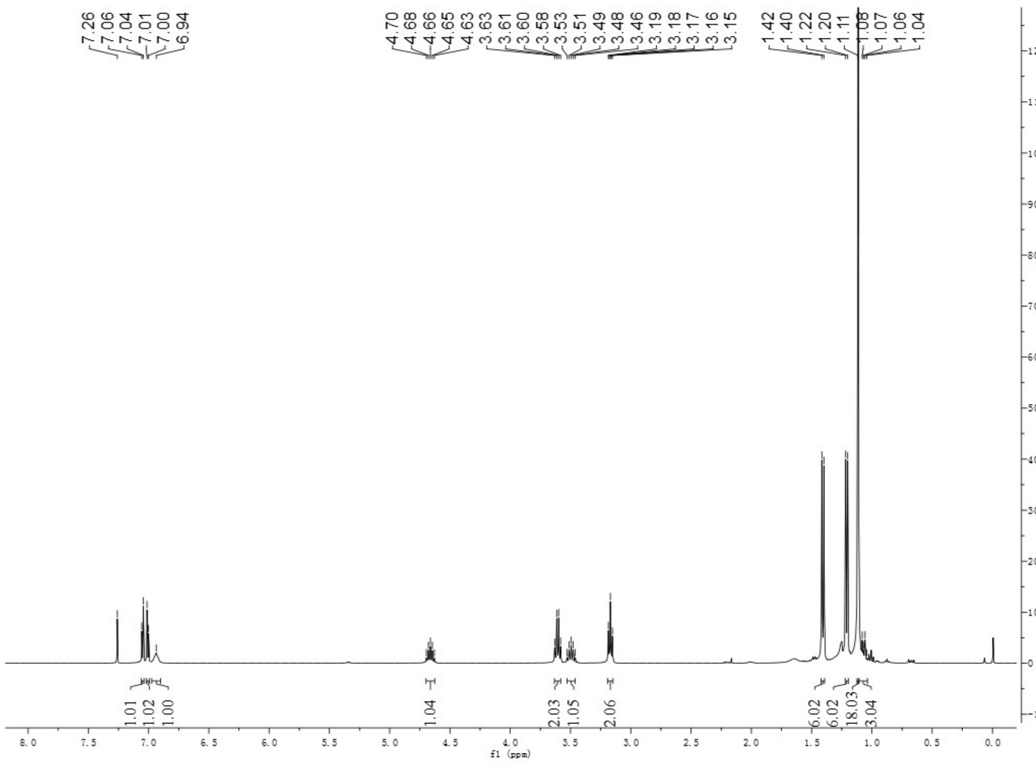
3o

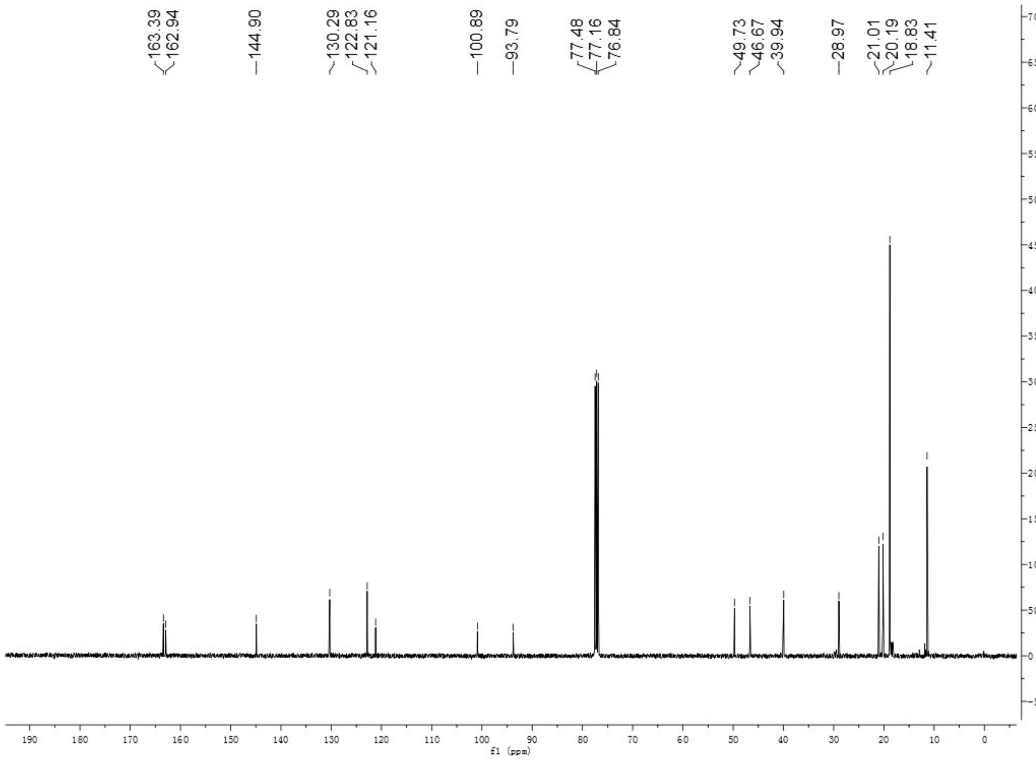


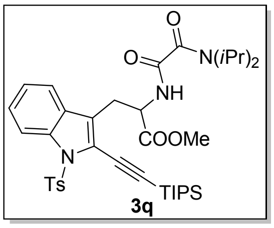


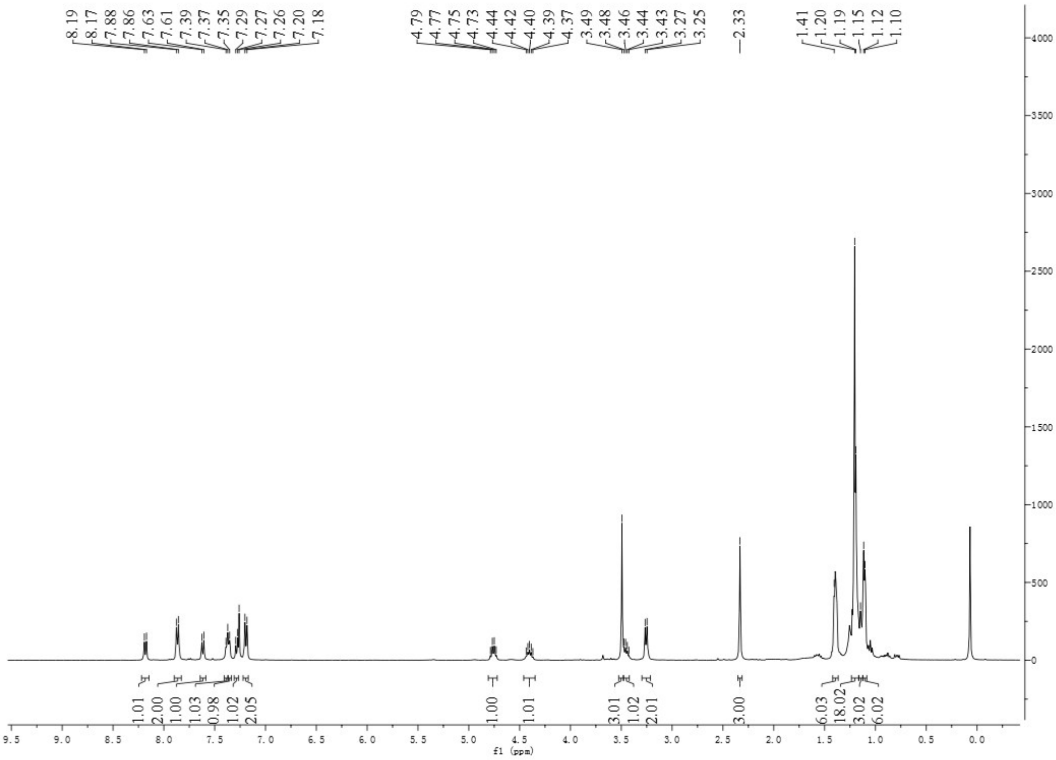


3p






O
O
N(iPr)2
NH
COOMe
N
Ts
TIPS
3q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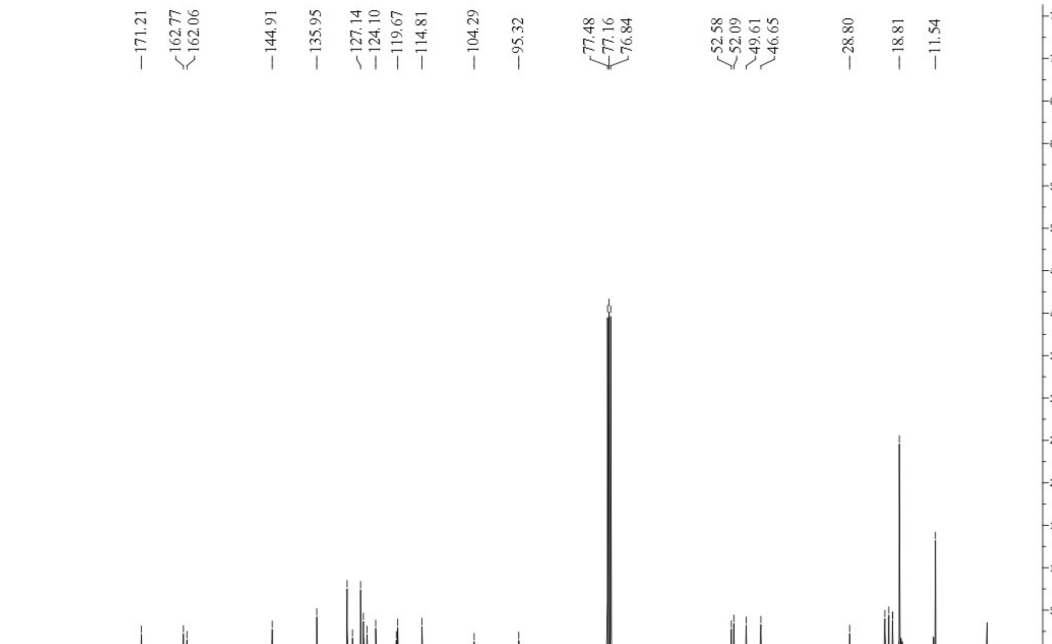
4.79 4.77 4.75 4.73 4.44 4.42 4.40 4.39 4.37
3.49 3.48 3.46 3.44 3.43 3.27 3.25
2.33
1.41 1.20 1.19 1.15 1.12 1.10
1.01 2.00 1.00 1.03 0.98 1.02 2.05 1.00 1.01 3.01 1.02 2.01 3.00 6.03 18.02 3.02 6.02
f1 (ppm)


171.21
162.77 162.06
144.91
135.95
127.14 124.10 119.67 114.81
104.29
95.32
77.48 77.16 76.84
52.58 52.09 49.61 46.65
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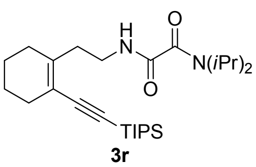
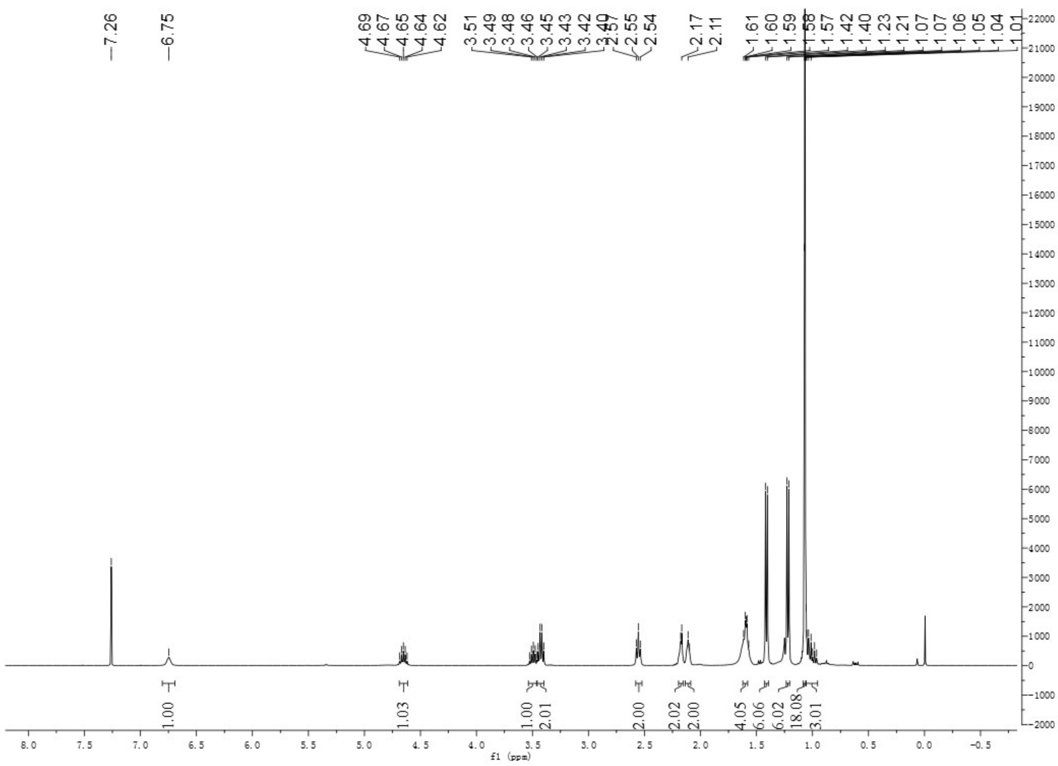
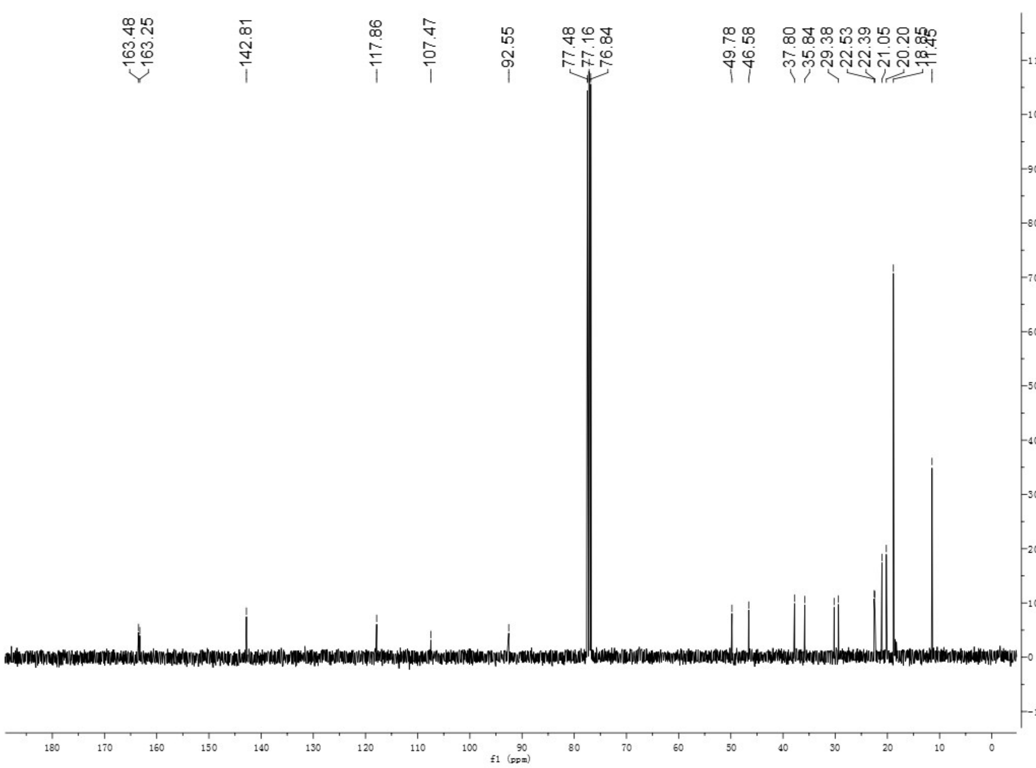
18.81
11.54
f1 (ppm)


H
N
O
O
N(iPr)2
TIPS

3r


7.26
6.75
4.69
4.67
4.65
4.64
4.62
3.51
3.49
3.48
3.46
3.45
3.43
3.42
3.40
2.57
2.55
2.54
2.17
2.11
1.61
1.60
1.59
1.58
1.57
1.42
1.40
1.23
1.21
1.07
1.07
1.06
1.05
1.04
1.01
1.00
1.03
1.00
2.01
2.00
2.02
2.00
4.05
6.06
6.02
18.08
3.01
f1 (ppm)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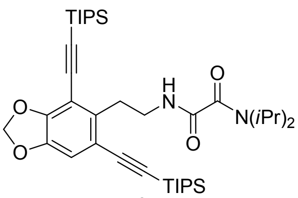
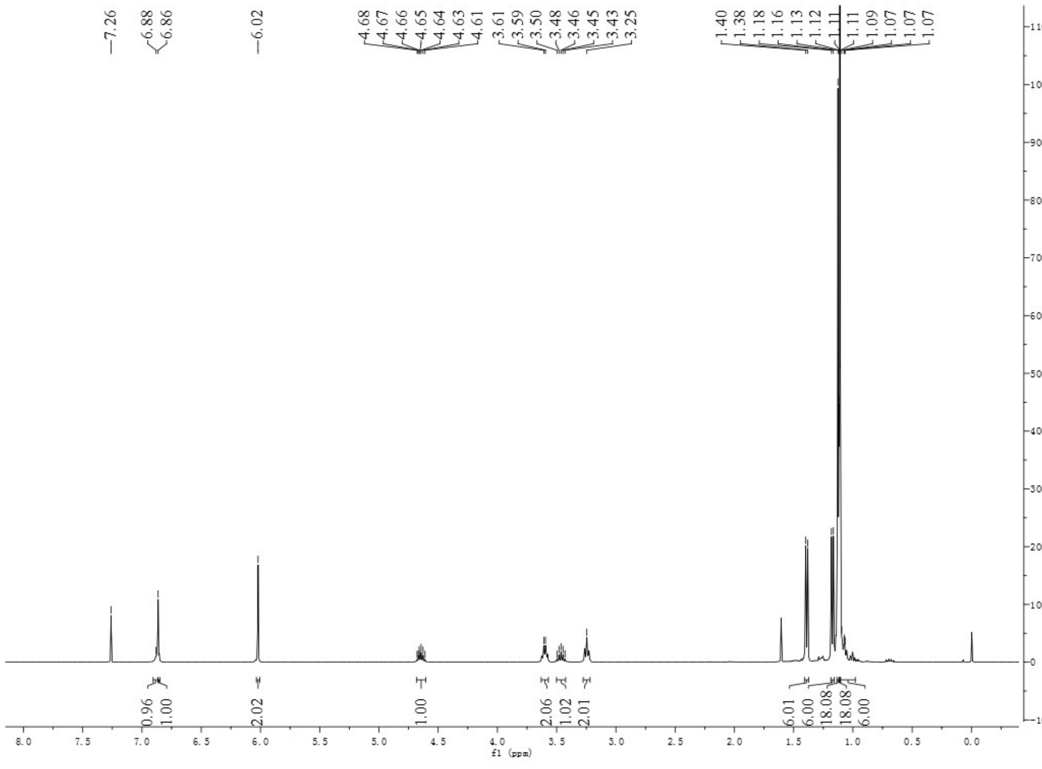
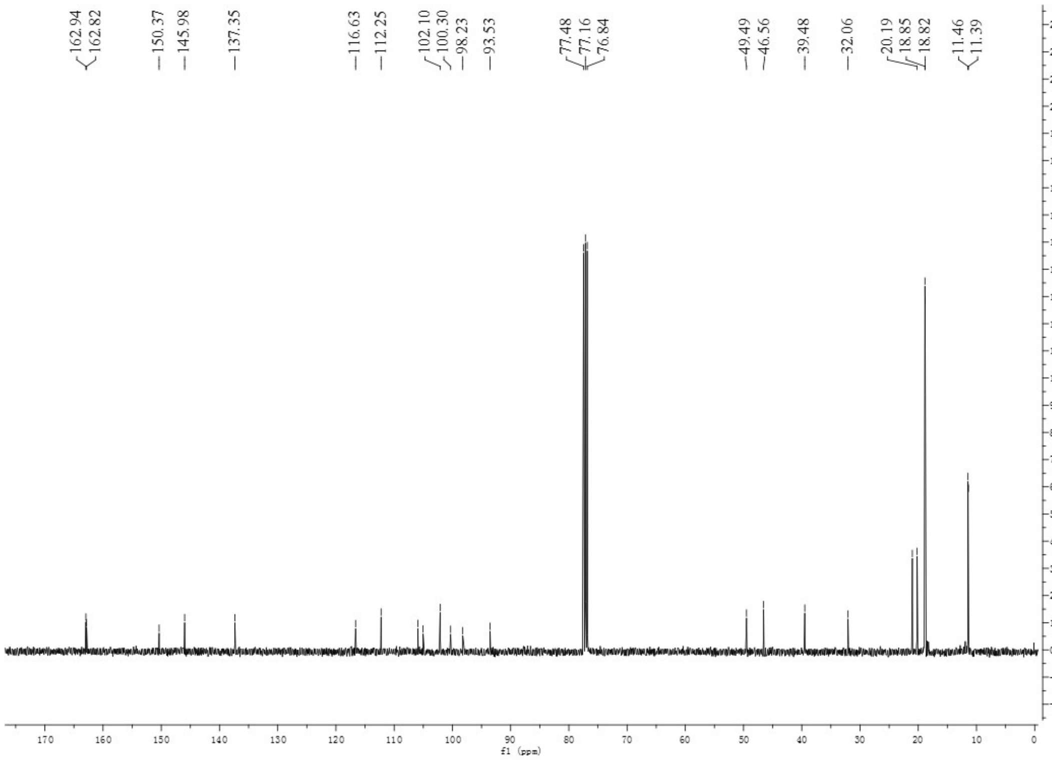
142.81
117.86
107.47
92.55
77.48
77.16
76.84
49.78
46.58
37.80
35.84
29.38
22.53
22.39
21.05
20.20
18.85
11.45
f1 (ppm)


TIPS
H
O
N(iPr)2
O
O
O
TIPS

3s


7.26
6.88
6.86
6.02
4.68
4.67
4.66
4.65
4.64
4.63
4.61
3.61
3.59
3.50
3.48
3.46
3.45
3.43
3.25
1.40
1.38
1.18
1.16
1.13
1.12
1.11
1.11
1.09
1.07
1.07
1.07
0.96
1.00
2.02
1.00
2.06
1.02
2.01
6.01
6.00
18.08
18.08
6.00
f1 (ppm)


162.94
162.82
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137.35
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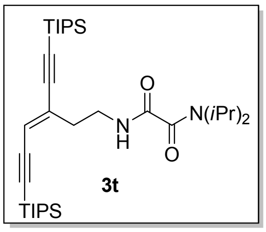
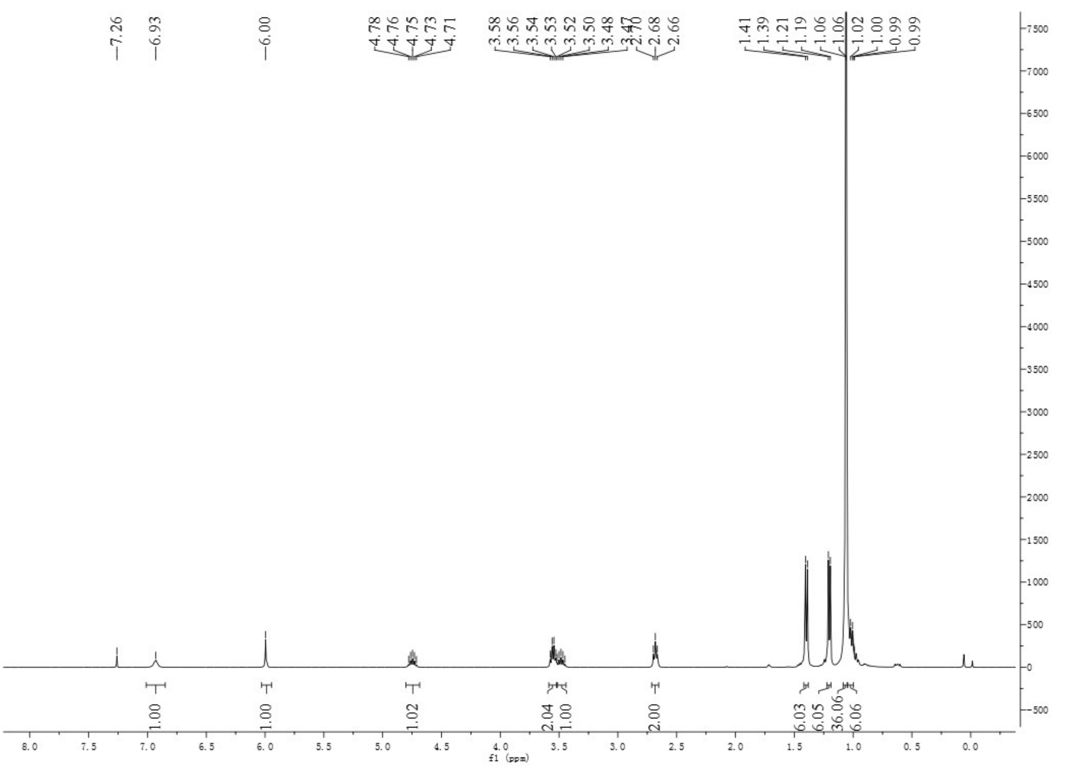
112.25
102.10
100.30
98.23
93.53
77.48
77.16
76.84
49.49
46.56
39.48
32.06
20.19
18.85
18.82
11.46
11.39
f1 (ppm)


TIPS
O
N(iPr)2
H
O
3t
TIPS


7.26
6.93
6.00
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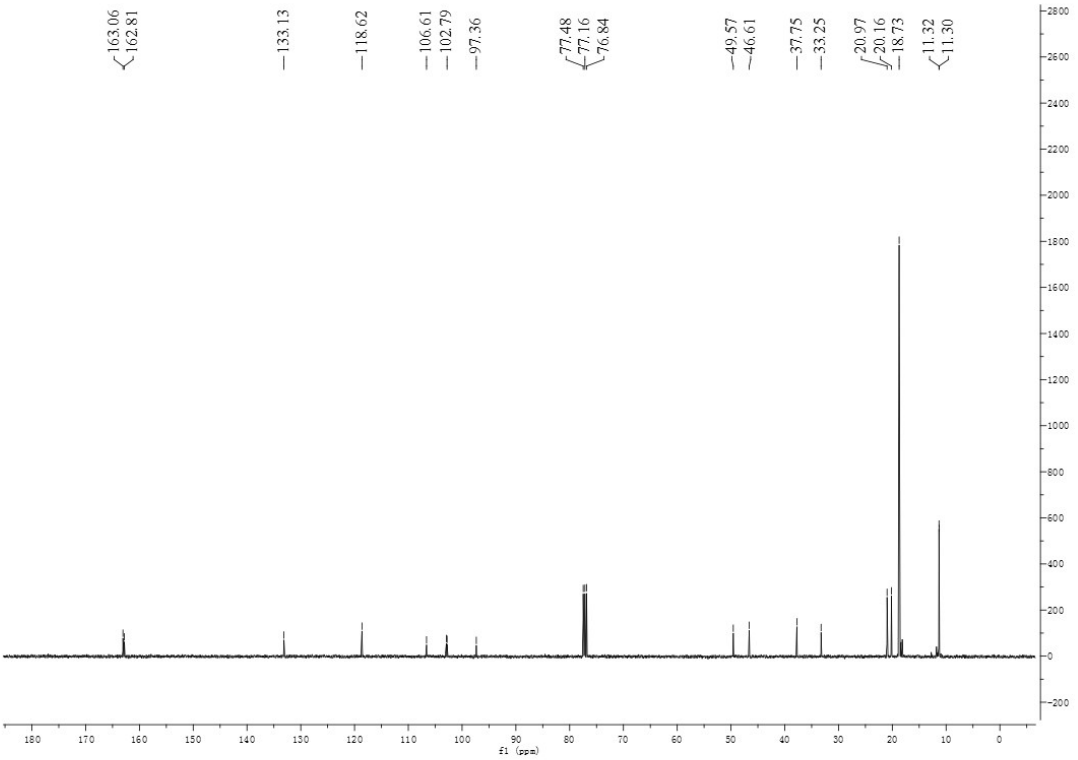
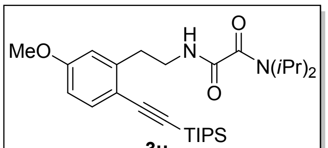
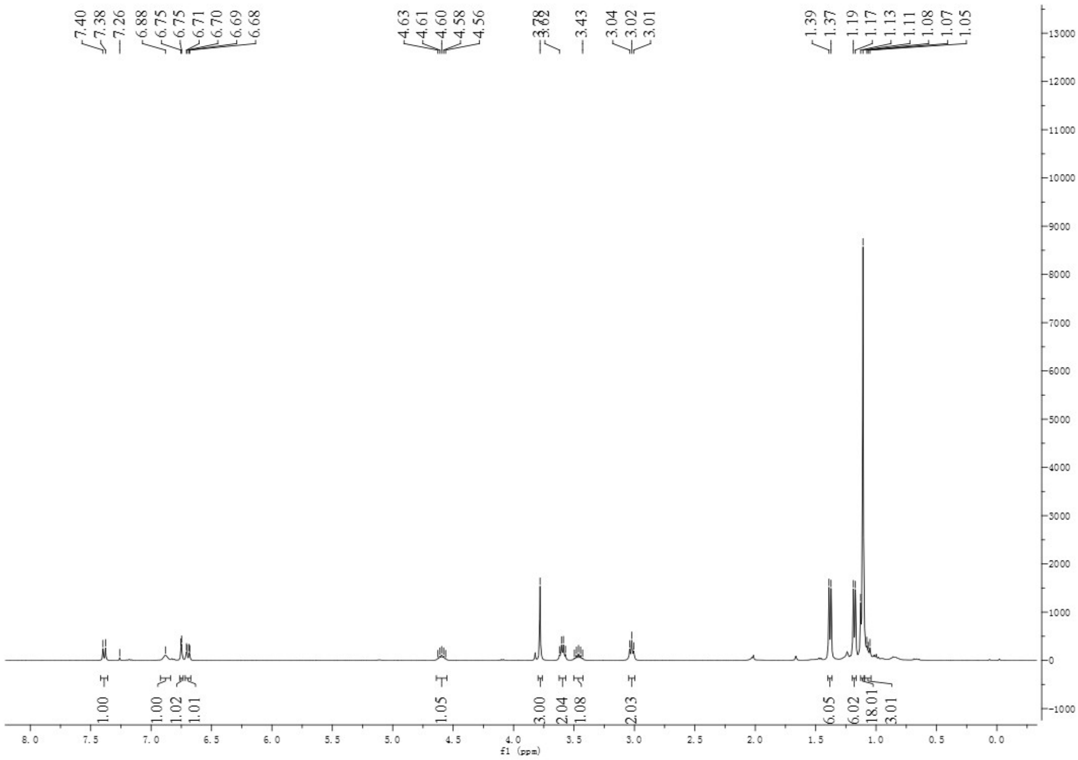
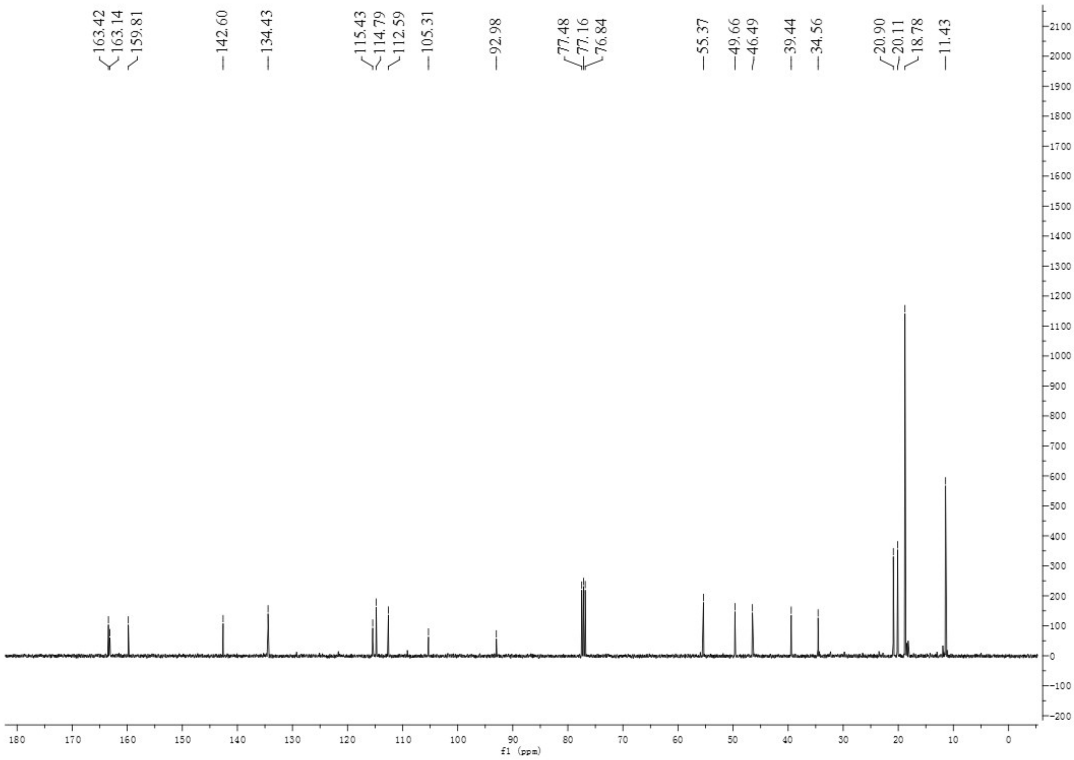
4.75
4.73
4.71
3.58
3.56
3.54
3.53
3.52
3.50
3.48
3.47
2.70
2.68
2.66
1.41
1.39
1.21
1.19
1.06
1.06
1.02
1.00
0.99
0.99
1.00
1.00
1.02
2.04
1.00
2.00
6.03
6.05
36.06
6.06
f1 (ppm)

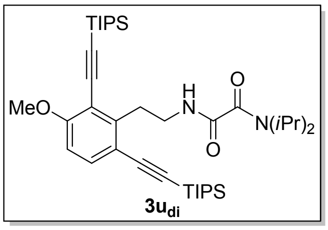

163.06
162.81
133.13
118.62
106.61
102.79
97.36
77.48
77.16
76.84
49.57
46.61
37.75
33.25
20.97
20.16
18.73
11.32
11.30
f1 (ppm)

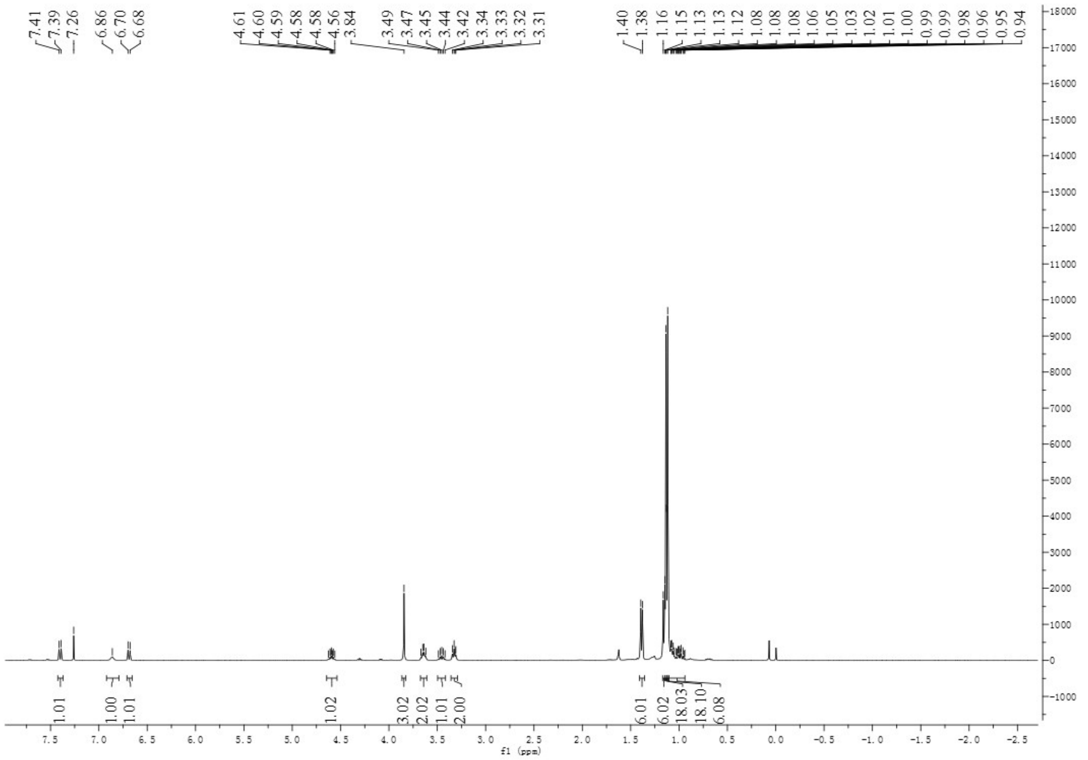


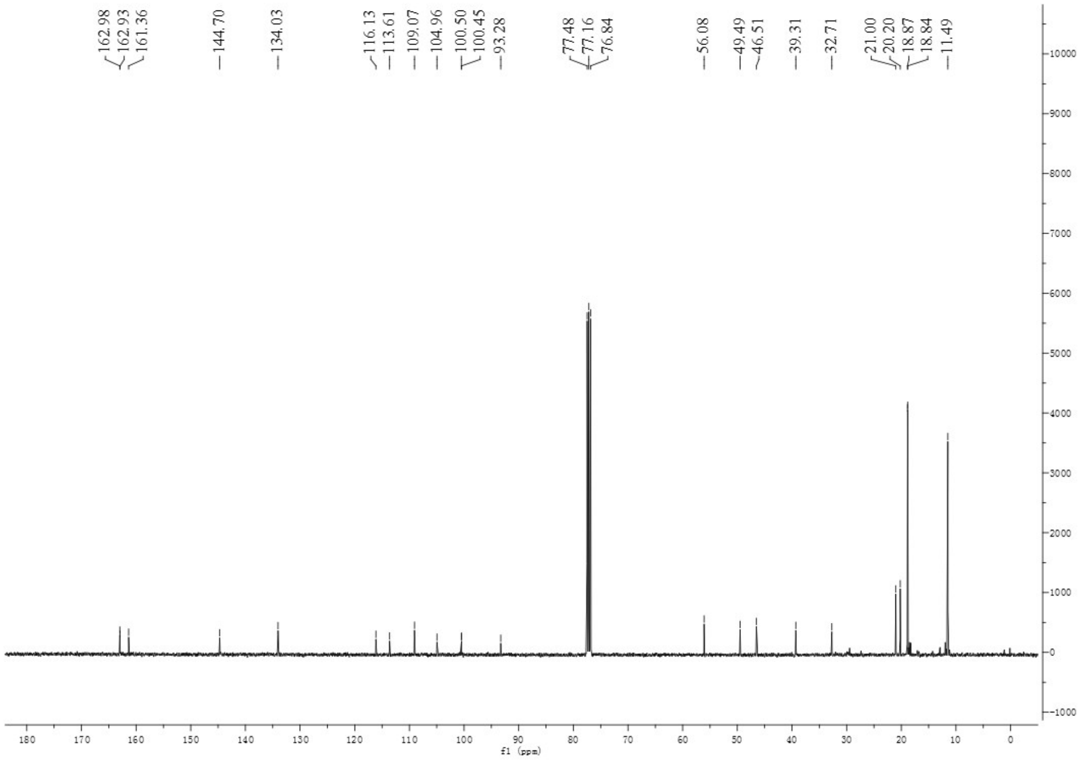
$\mathbf{3u_{mono}}$






TIPS
MeO
H
N
O
N(iPr)2
O
TIPS
3udi


7.41
7.39
7.26
6.86
6.70
6.68
4.61
4.60
4.59
4.58
4.58
4.56
3.84
3.49
3.47
3.45
3.44
3.42
3.34
3.33
3.32
3.31
1.40
1.38
1.16
1.15
1.13
1.13
1.12
1.08
1.08
1.06
1.05
1.03
1.02
1.01
1.00
0.99
0.99
0.98
0.96
0.95
0.94
1.01
1.00
1.01
1.02
3.02
2.02
1.01
2.00
6.01
6.02
18.03
18.10
6.08
f1 (ppm)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162.93
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144.70
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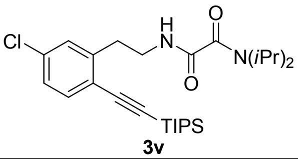
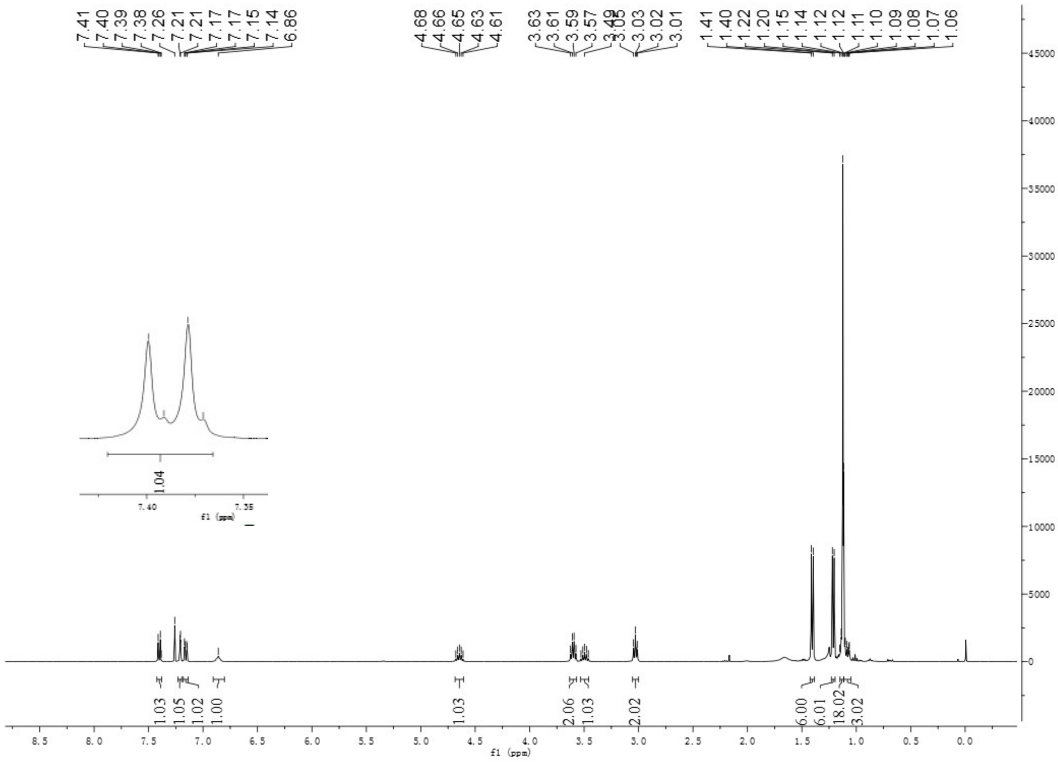
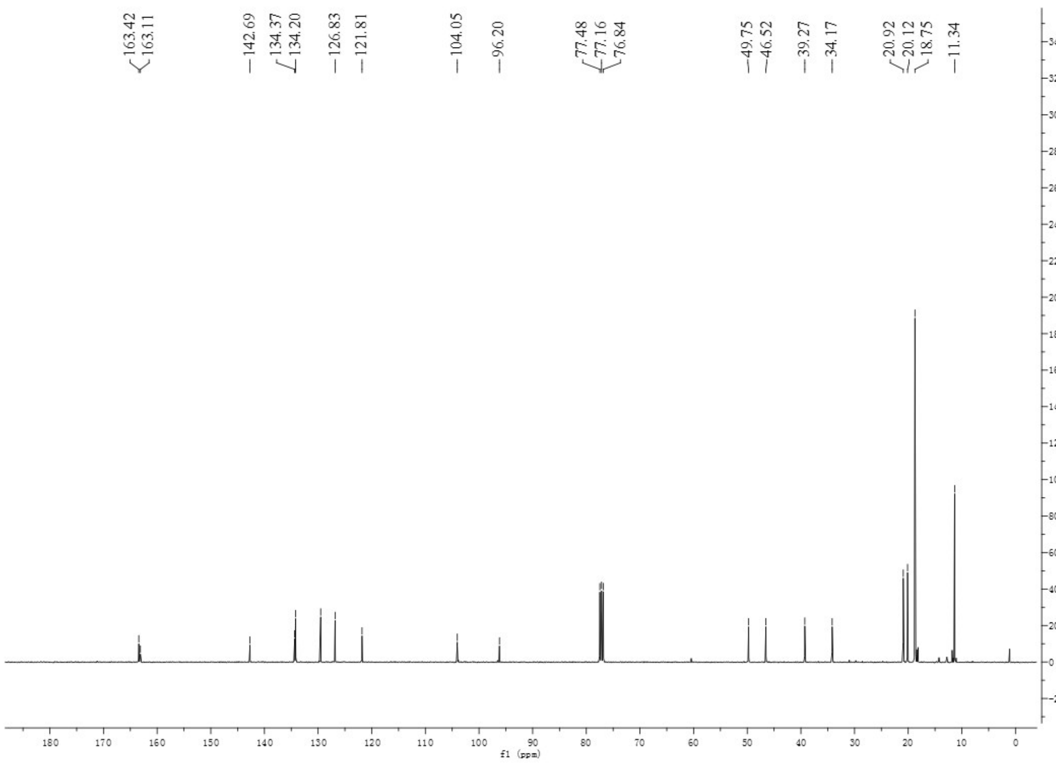
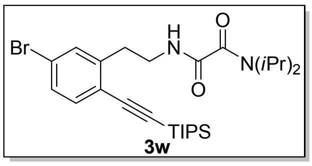
116.13
113.61
109.07
104.96
100.50
100.45
93.28
77.48
77.16
76.84
56.08
49.49
46.51
39.31
32.71
21.00
20.20
18.87
18.84
11.49
f1 (ppm)


Cl
H
N
O
N(iPr)2
TIPS

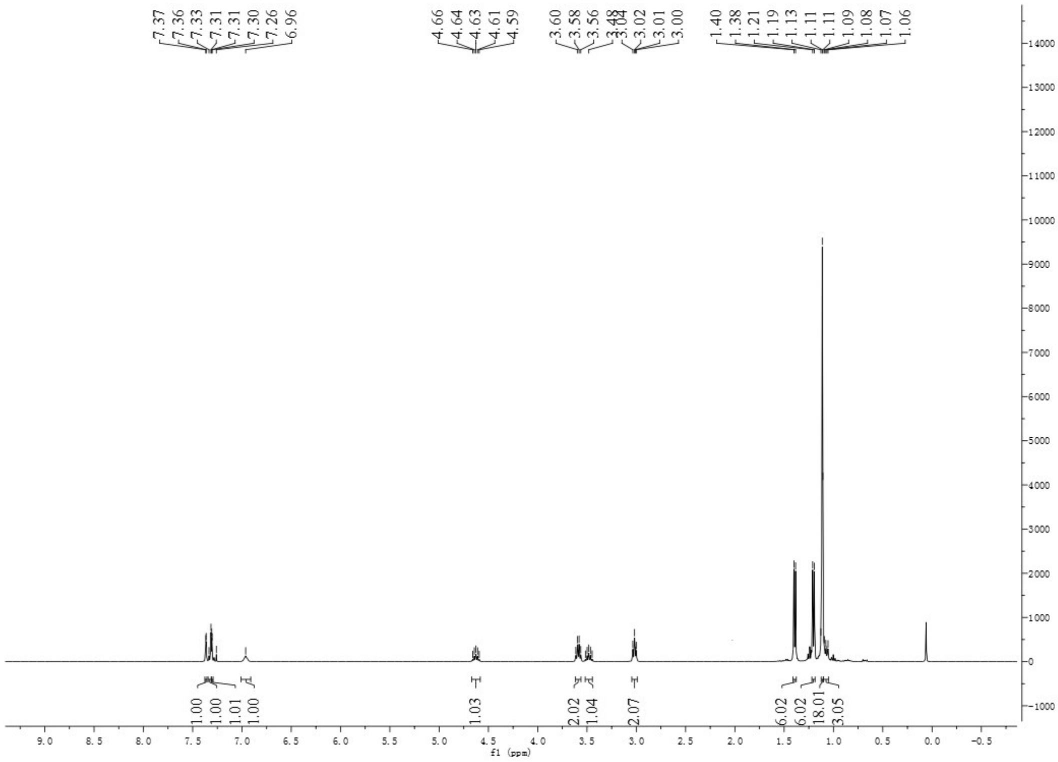
3v

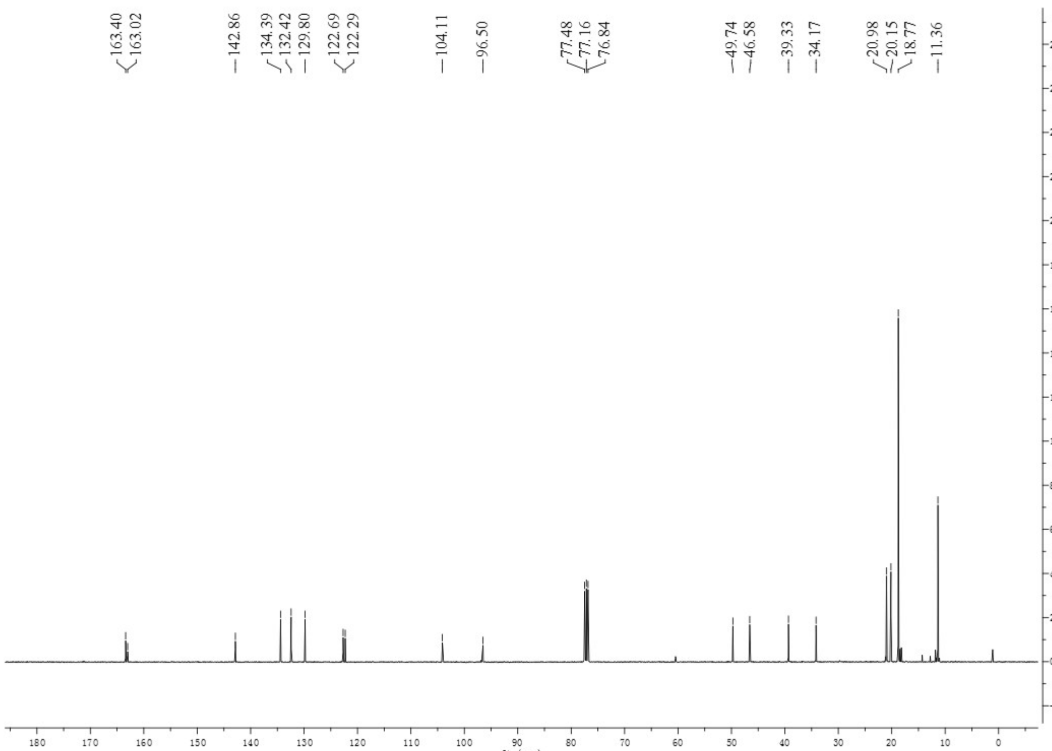

7.41 7.40 7.39 7.38 7.26 7.21 7.21 7.17 7.15 7.14 6.86
4.68 4.66 4.65 4.63 4.61
3.63 3.61 3.59 3.57 3.49 3.05 3.03 3.02 3.01
1.41 1.40 1.22 1.20 1.15 1.14 1.12 1.12 1.11 1.10 1.09 1.08 1.07 1.06
1.04
1.03 1.05 1.02 1.00 1.03 2.06 1.03 2.02 6.00 6.01 18.02 3.02
f1 (ppm)

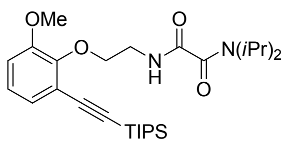

163.42 163.11 142.69 134.37 134.20 126.83 121.81 104.05 96.20 77.48 77.16 76.84 49.75 46.52 39.27 34.17 20.92 20.12 18.75 11.34
f1 (ppm)



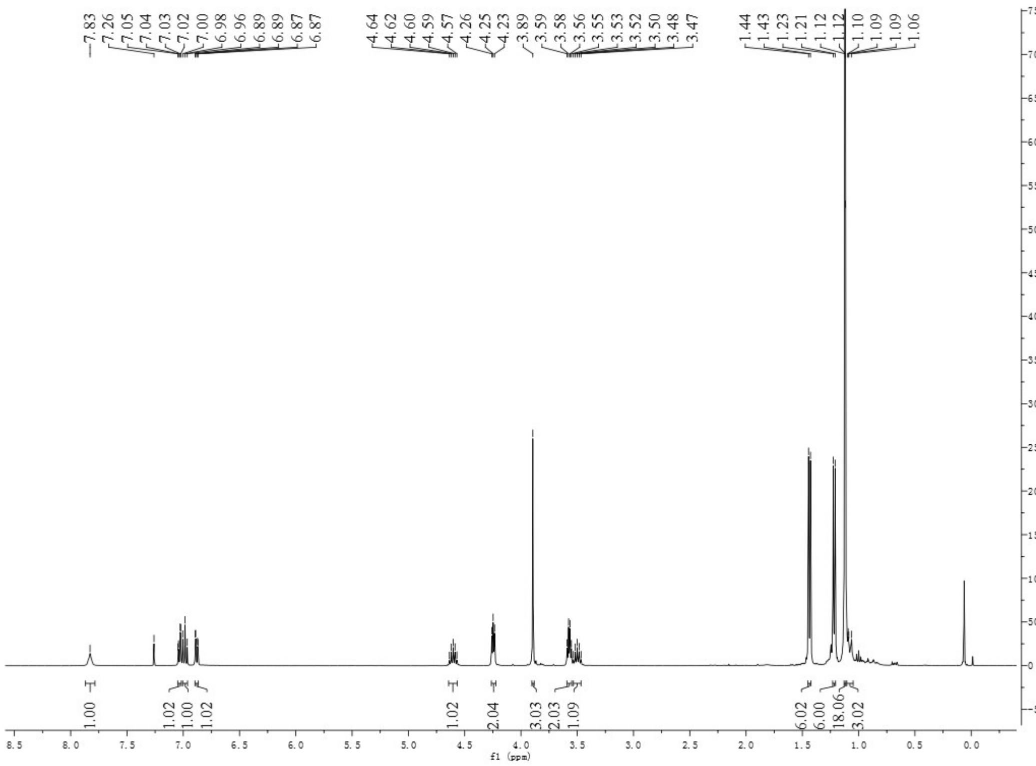
3w






OMe
O
O
N
H
N(iPr)2
O
TIPS

5a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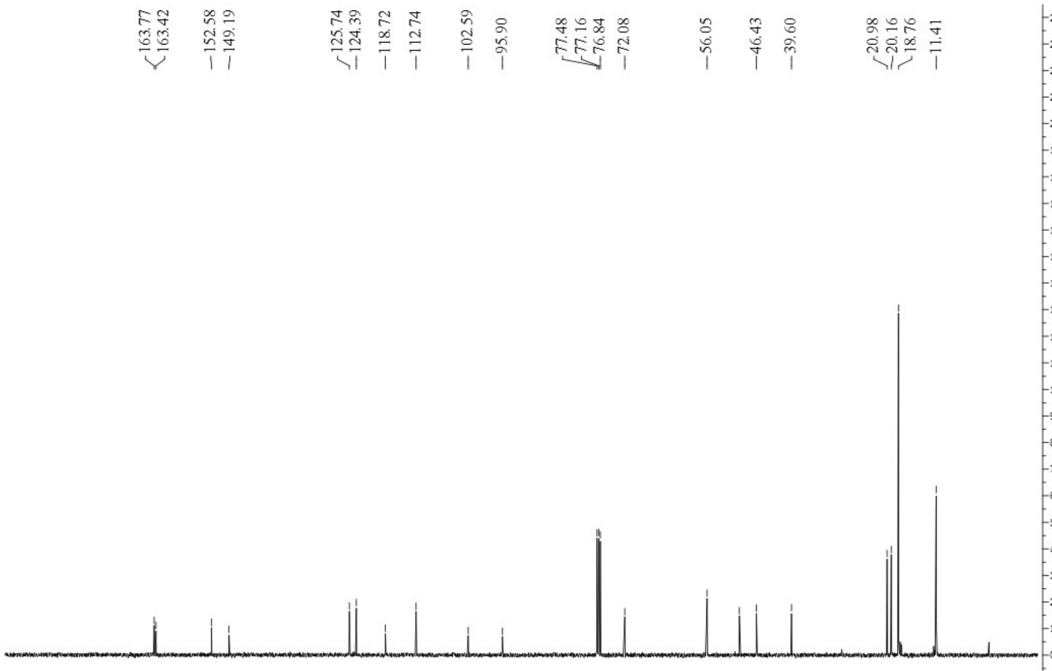
7.26
7.05
7.04
7.03
7.02
7.00
6.98
6.96
6.89
6.89
6.89
6.87
4.64
4.62
4.60
4.59
4.57
4.26
4.25
4.23
3.89
3.59
3.58
3.56
3.55
3.53
3.52
3.50
3.48
3.47
1.44
1.43
1.23
1.21
1.12
1.12
1.10
1.09
1.09
1.06
1.00
1.02
1.00
1.02
1.02
2.04
3.03
2.03
1.09
6.02
6.00
18.06
3.02
f1 (ppm)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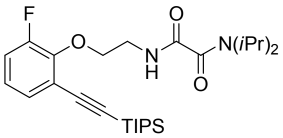
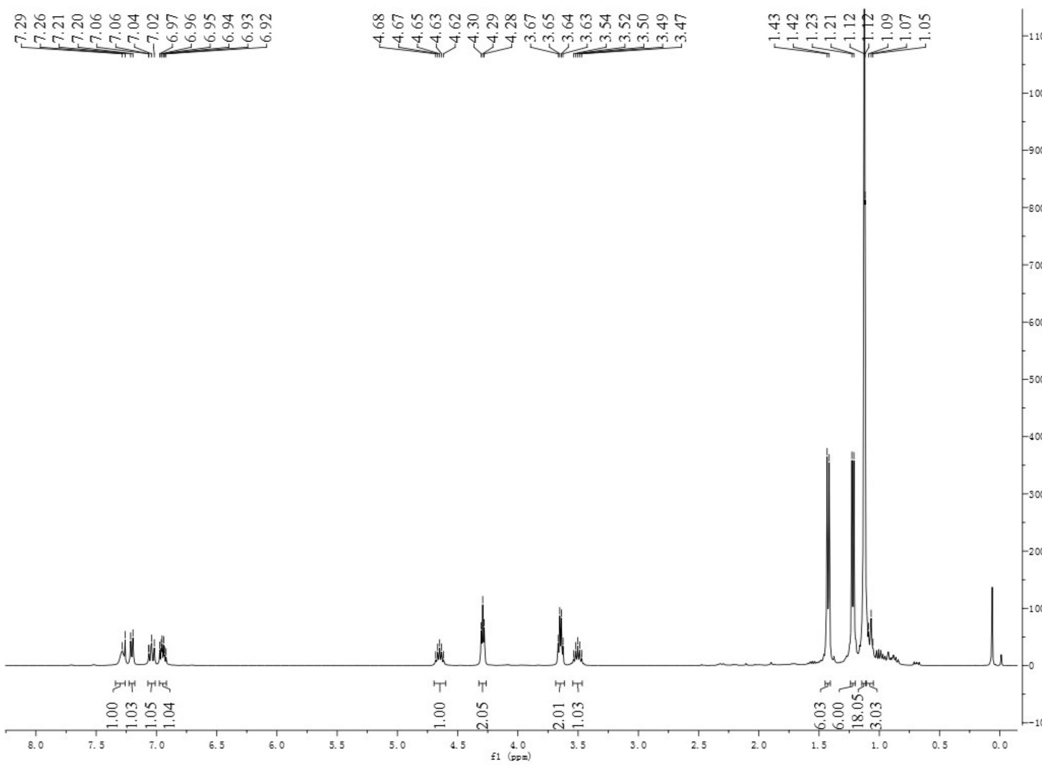
163.42
152.58
149.19
125.74
124.39
118.72
112.74
102.59
95.90
77.48
77.16
76.84
72.08
56.05
46.43
39.60
20.98
20.16
18.76
11.41
f1 (ppm)


F
O
N
H
O
O
N(iPr)2
TIPS

5b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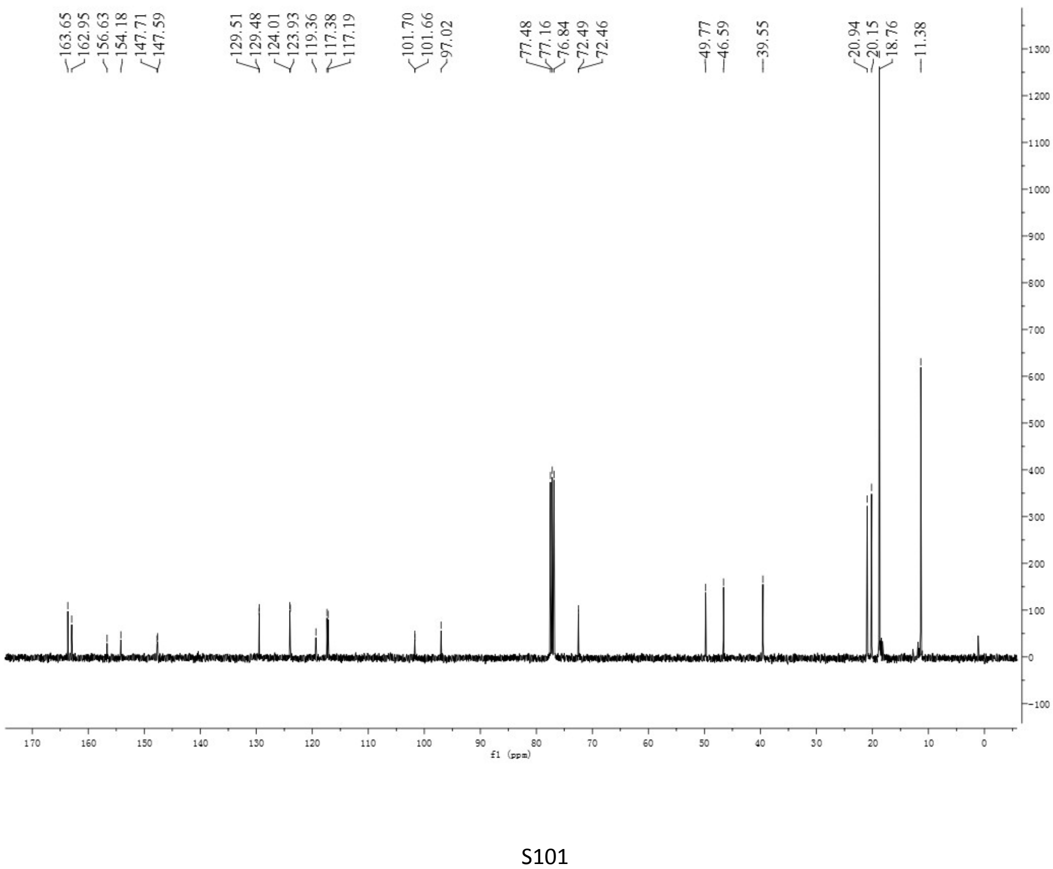
7.26
7.21
7.20
7.06
7.06
7.04
7.02
6.97
6.96
6.95
6.94
6.93
6.92
4.68
4.67
4.65
4.63
4.62
4.30
4.29
4.28
3.67
3.65
3.64
3.63
3.54
3.52
3.50
3.49
3.47
1.43
1.42
1.23
1.21
1.12
1.12
1.09
1.07
1.05
1.00
1.03
1.05
1.04
1.00
2.05
2.01
1.03
6.03
6.00
18.05
3.03
f1 (ppm)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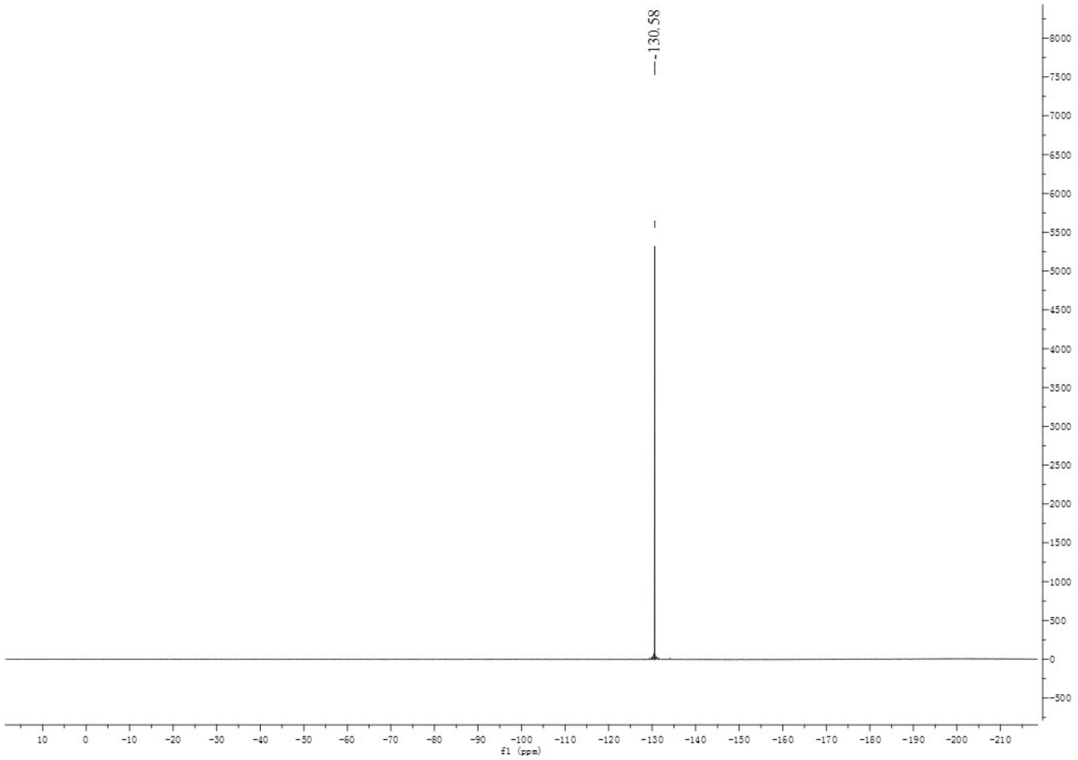
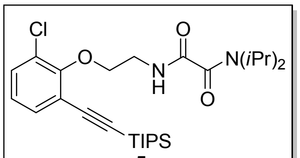
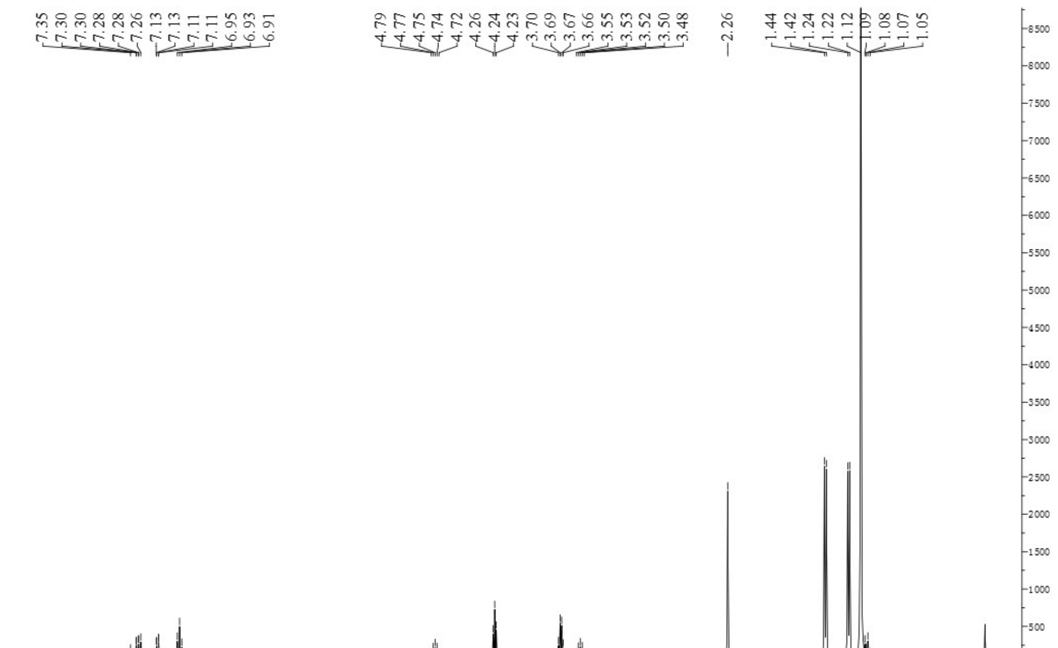
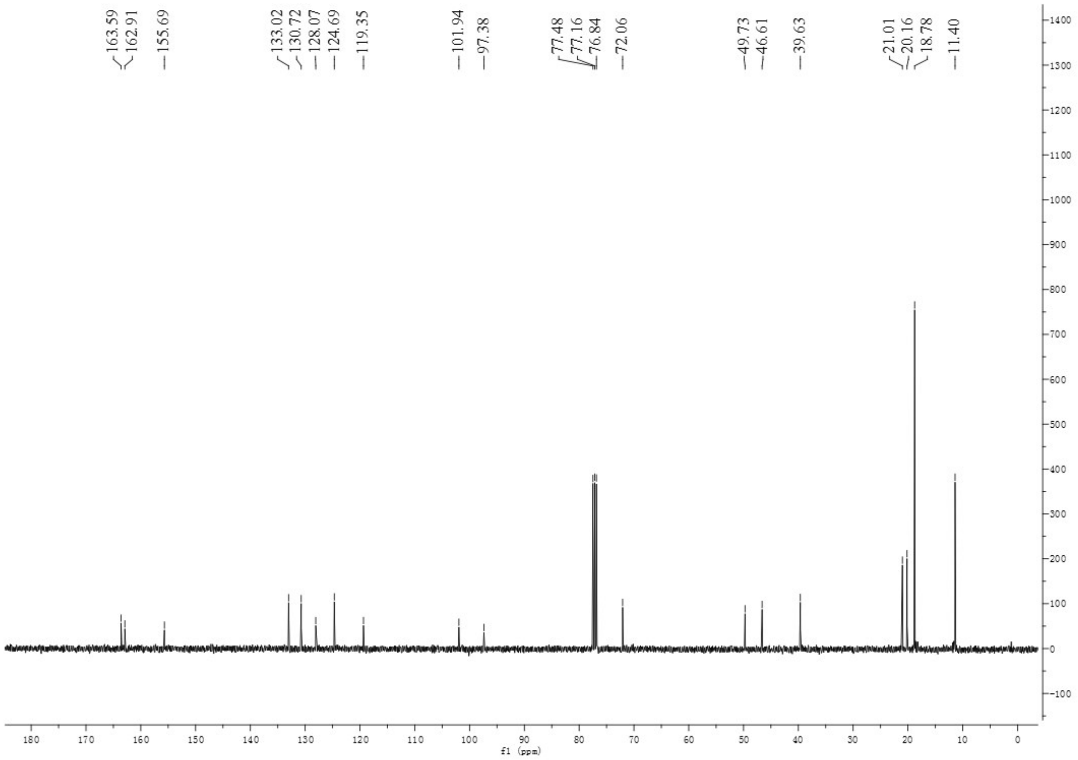
154.18
147.71
147.59
129.51
129.48
124.01
123.93
119.36
117.38
117.19
101.70
101.66
97.02
77.48
77.16
76.84
72.49
72.46
49.77
46.59
39.55
20.94
20.15
18.76
11.38
f1 (ppm)

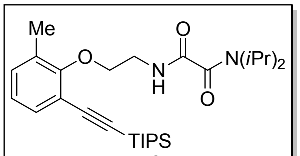


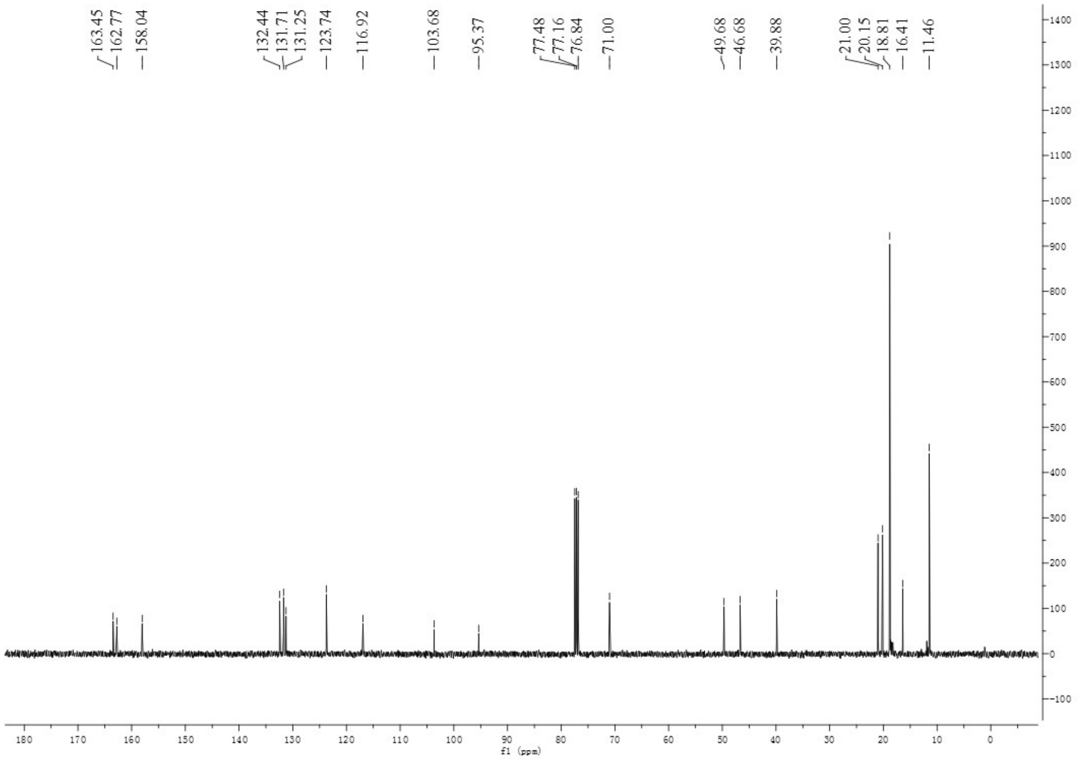


5c




163.59
162.91
155.69
133.02
130.72
128.07
124.69
119.35
101.94
97.38
77.48
77.16
76.84
72.06
49.73
46.61
39.63
21.01
20.16
18.78
11.40
f1 (ppm)


Me
O
N
H
O
N(iPr)2
O
TIPS
5d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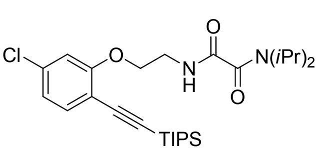
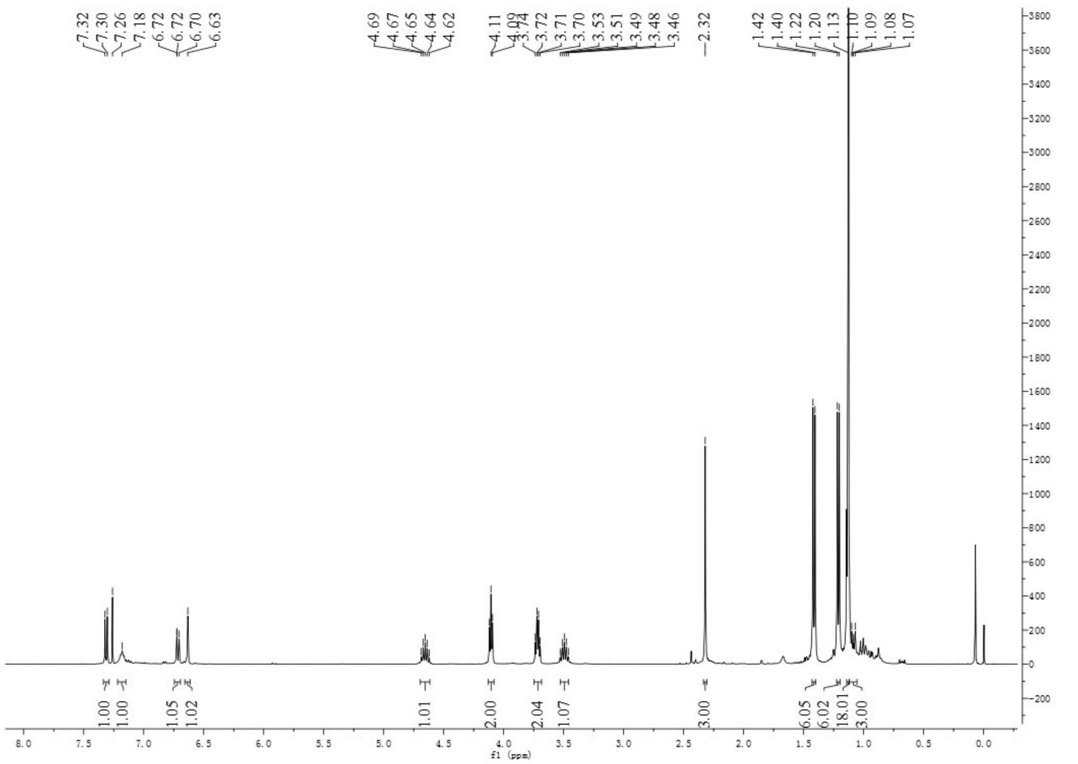
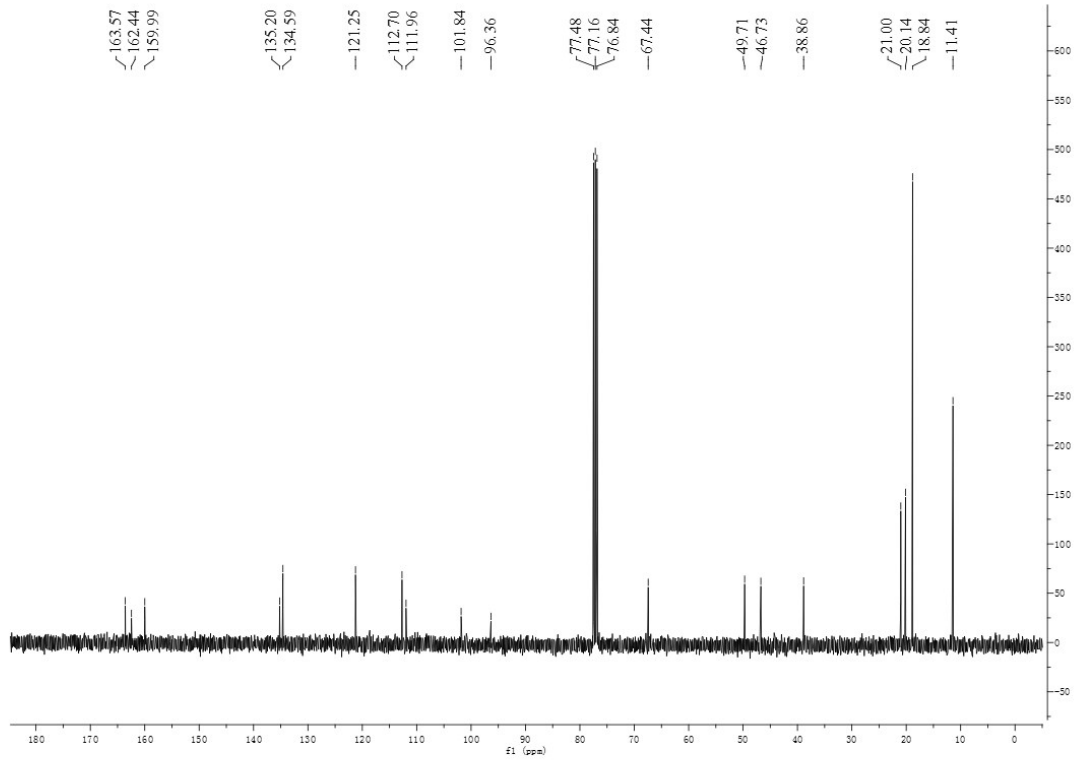
162.77
158.04
132.44
131.71
131.25
123.74
116.92
103.68
95.37
77.48
77.16
76.84
71.00
49.68
46.68
39.88
21.00
20.15
18.81
16.41
11.46
f1 (ppm)


Cl
O
N
H
O
O
N(*i*Pr)$_2$
TIPS
5e


7.32
7.30
7.26
7.18
6.72
6.72
6.70
6.63
4.69
4.67
4.65
4.64
4.62
4.11
4.09
3.74
3.72
3.71
3.70
3.53
3.51
3.49
3.48
3.46
2.32
1.42
1.40
1.22
1.20
1.13
1.10
1.09
1.08
1.07
1.00
1.00
1.05
1.02
1.01
2.00
2.04
1.07
3.00
6.05
6.02
18.01
3.00
f1 (ppm)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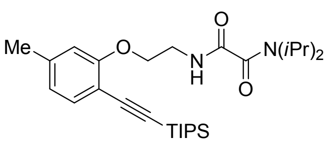
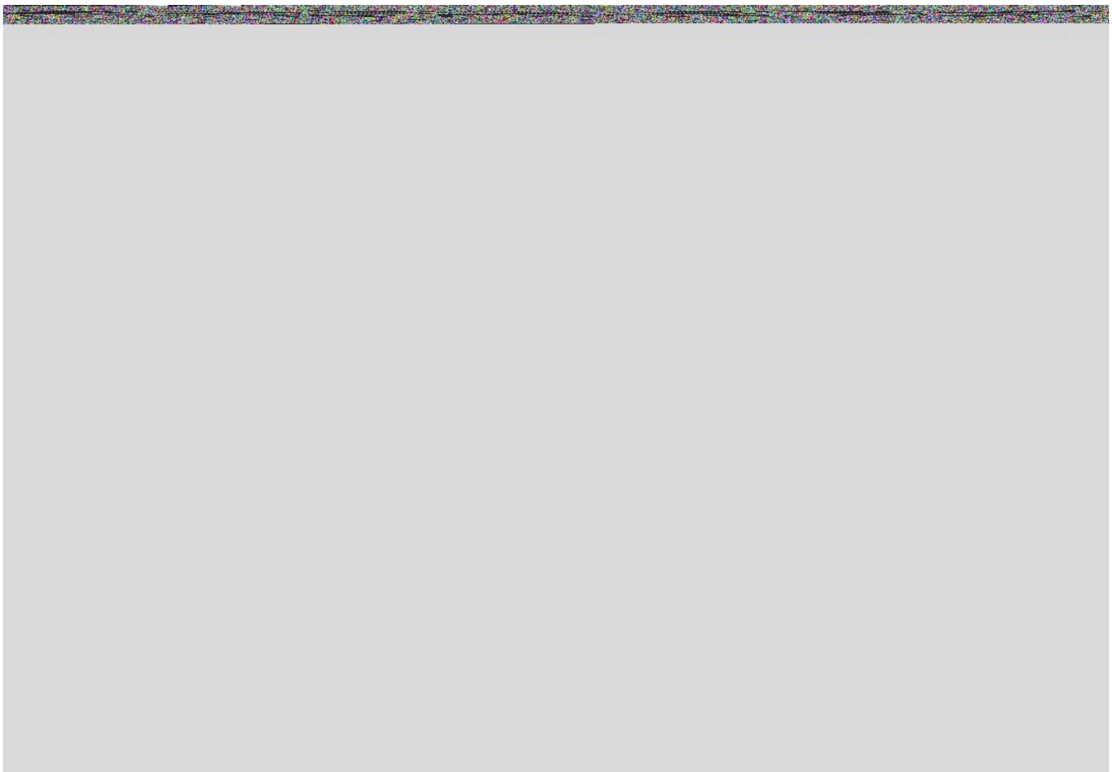
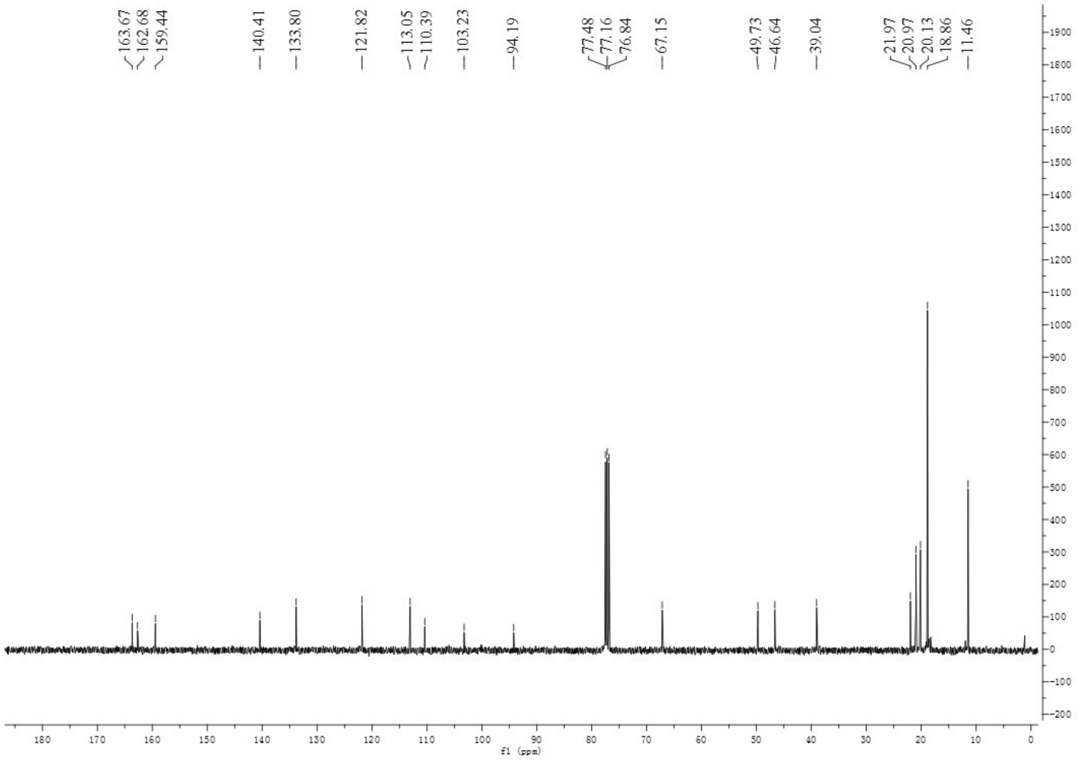
121.25
112.70
111.96
101.84
96.36
77.48
77.16
76.84
67.44
49.71
46.73
38.86
21.00
20.14
18.84
11.41
f1 (ppm)


Me
O
N
H
O
O
N(iPr)2
TIPS

5f

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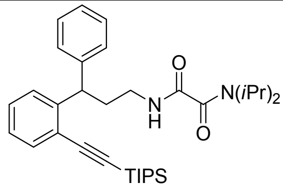
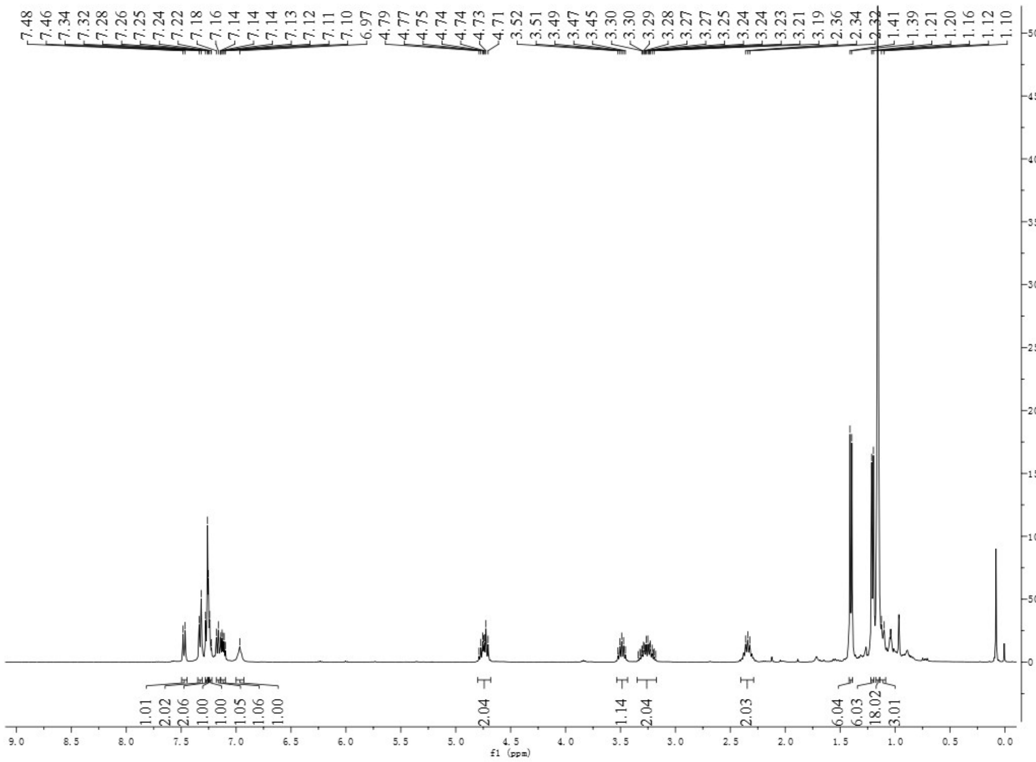
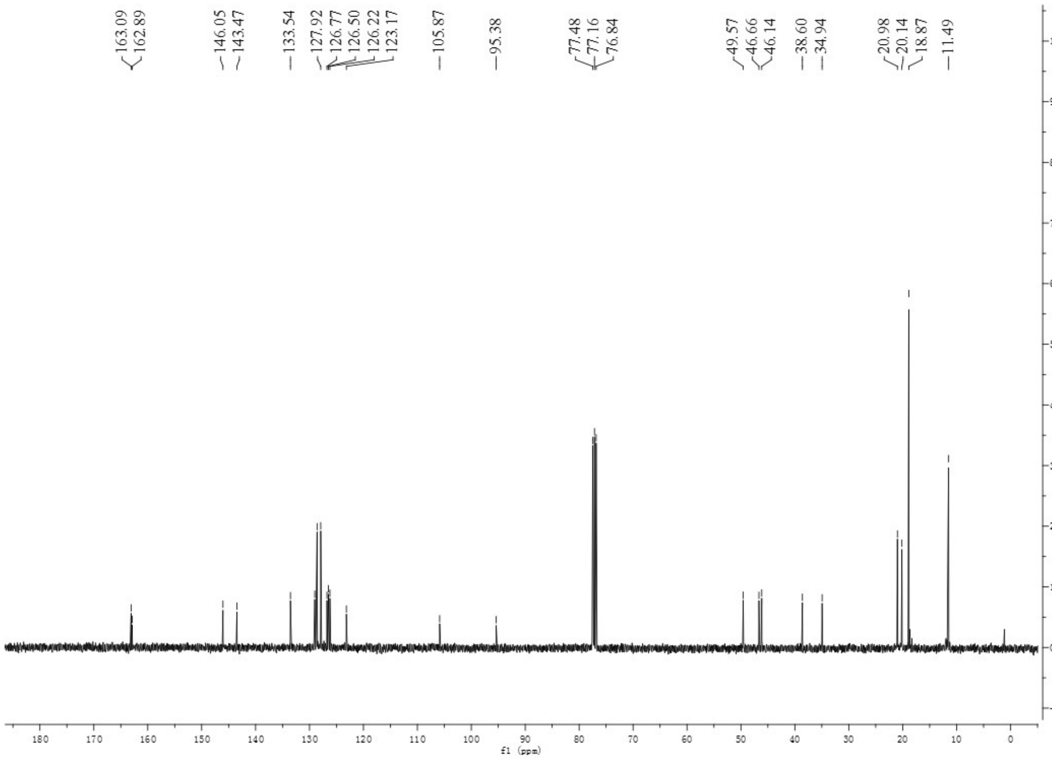
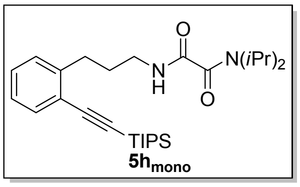
113.05
110.39
103.23
94.19
77.48
77.16
76.84
67.15
49.73
46.64
39.04
21.97
20.97
20.13
18.86
11.46
f1 (ppm)

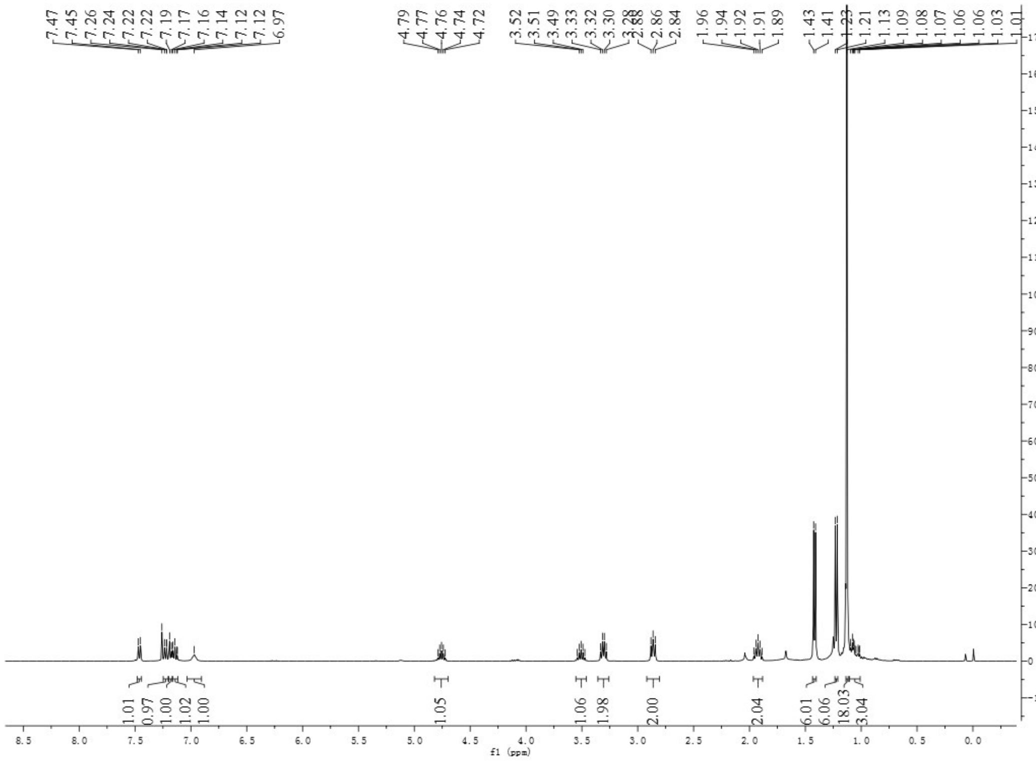

O
N(iPr)2
N
H
O
TIPS
5g

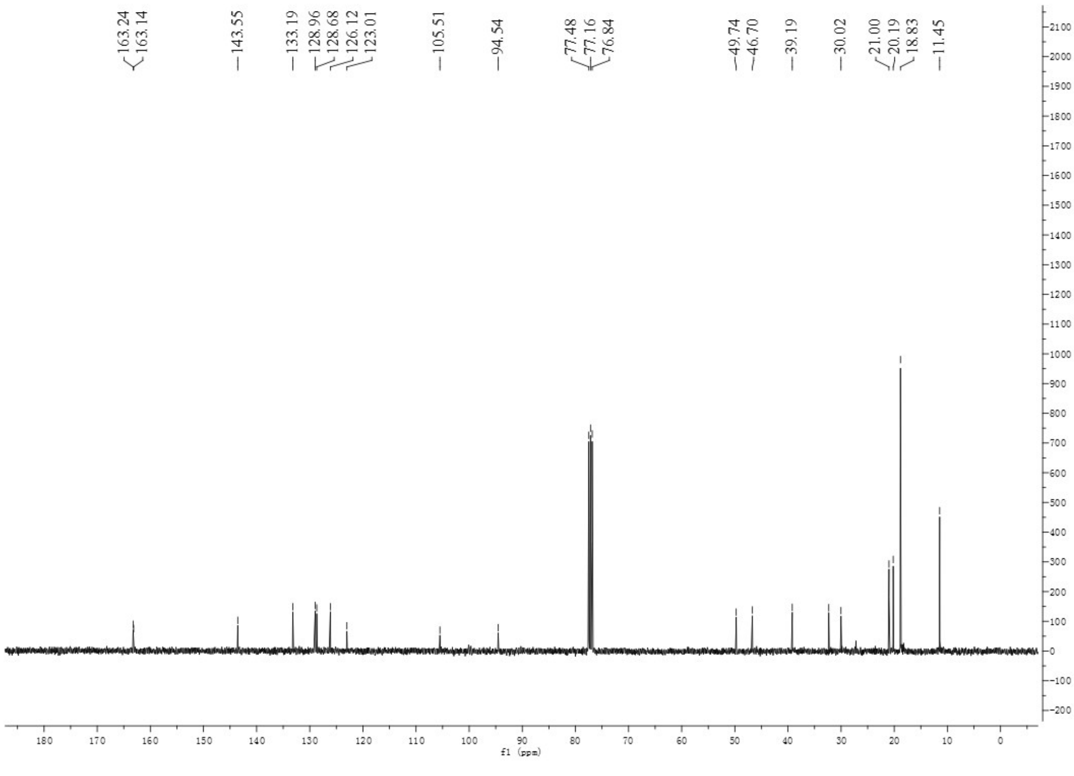

7.48 7.46 7.34 7.32 7.28 7.26 7.25 7.24 7.22 7.18 7.16 7.14 7.14 7.13 7.12 7.11 7.10 6.97 4.79 4.77 4.75 4.74 4.74 4.73 4.71 3.52 3.51 3.49 3.47 3.45 3.30 3.30 3.29 3.28 3.27 3.27 3.25 3.24 3.24 3.23 3.21 3.19 2.36 2.34 2.32 1.41 1.39 1.21 1.20 1.16 1.12 1.10
1.01 2.02 2.06 1.00 1.00 1.05 1.06 1.00 2.04 1.14 2.04 2.03 6.04 6.03 18.02 3.01
f1 (ppm)

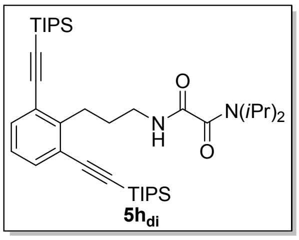

163.09 162.89 146.05 143.47 133.54 127.92 126.77 126.50 126.22 123.17 105.87 95.38 77.48 77.16 76.84 49.57 46.66 46.14 38.60 34.94 20.98 20.14 18.87 11.49
f1 (ppm)

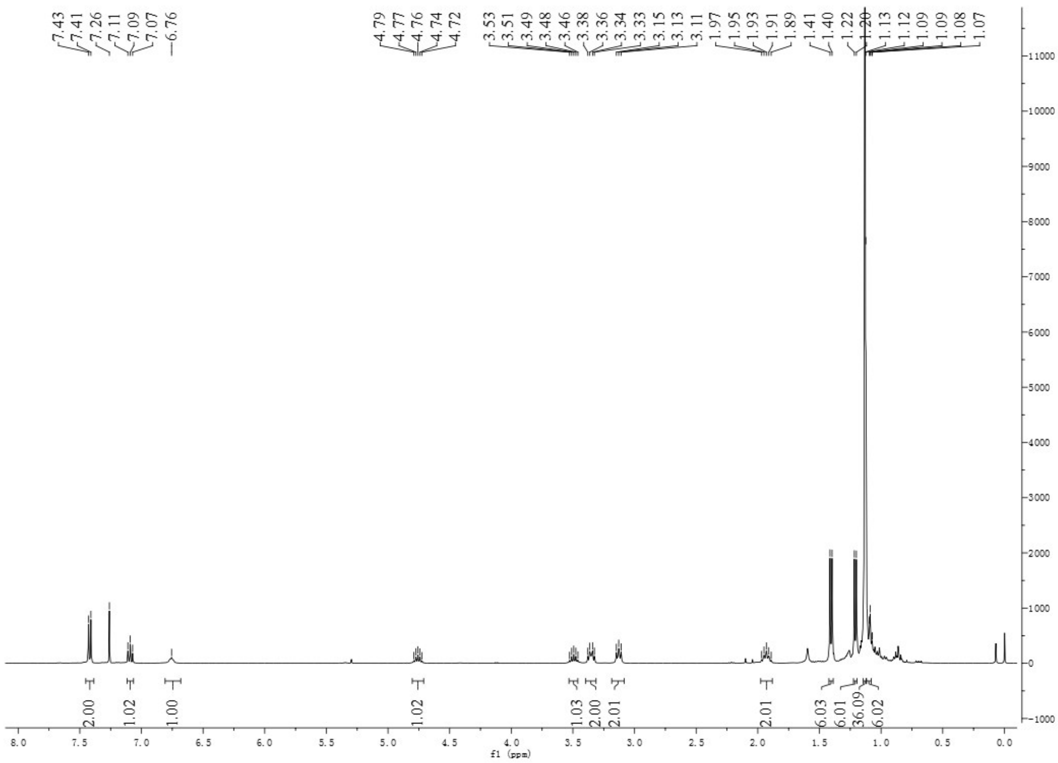


5h$_{mono}$






TIPS
O
N(iPr)2
N
H
O
TIPS
5hdi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7.26
7.11
7.09
7.07
6.76
4.79
4.77
4.76
4.74
4.72
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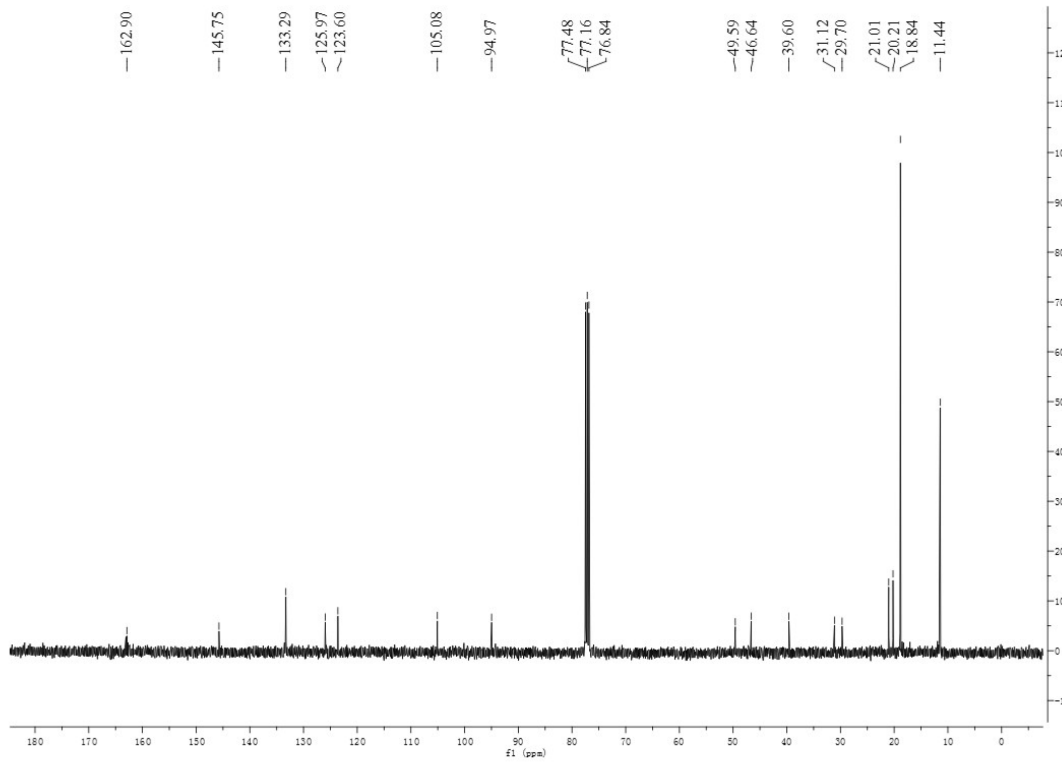
3.51
3.49
3.48
3.46
3.38
3.36
3.34
3.33
3.15
3.13
3.11
1.97
1.95
1.93
1.91
1.89
1.41
1.40
1.22
1.20
1.13
1.12
1.09
1.09
1.08
1.07
2.00
1.02
1.00
1.02
1.03
2.00
2.01
2.01
6.03
6.01
36.09
6.02
f1 (ppm)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123.60
105.08
94.97
77.48
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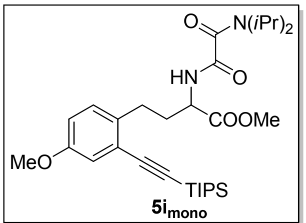
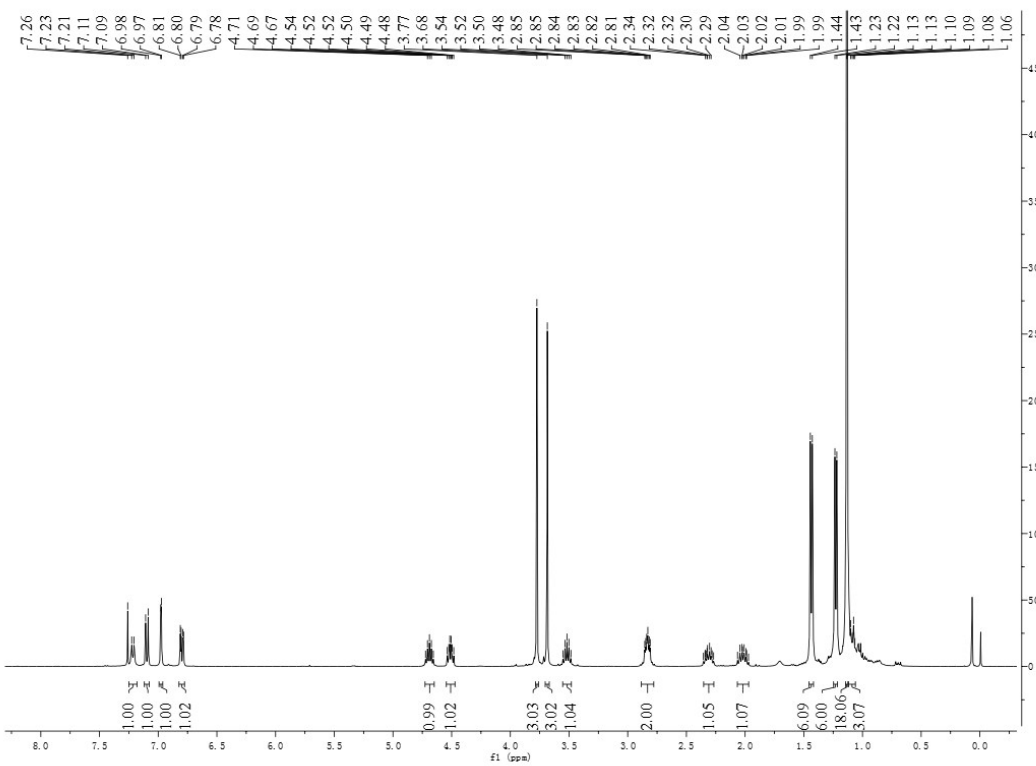
76.84
49.59
46.64
39.60
31.12
29.70
21.01
20.21
18.84
11.44
f1 (ppm)


O
N(iPr)2
HN
O
COOMe
MeO
TIPS

5i$_{mono}$


7.26
7.23
7.21
7.11
7.09
6.98
6.97
6.81
6.80
6.79
6.78
4.71
4.69
4.67
4.54
4.52
4.52
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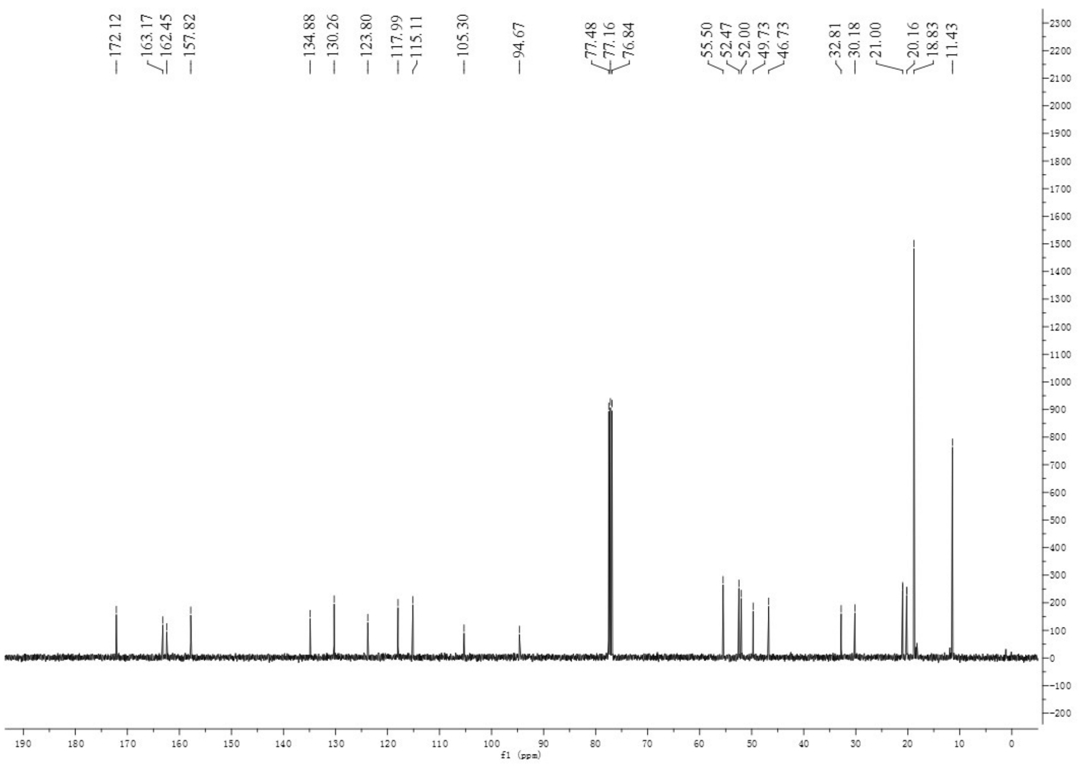
3.52
3.50
3.48
2.85
2.84
2.83
2.82
2.81
2.34
2.32
2.32
2.30
2.29
2.04
2.03
2.02
2.01
1.99
1.99
1.44
1.43
1.23
1.22
1.13
1.13
1.10
1.09
1.08
1.06
1.00
1.00
1.00
1.02
0.99
1.02
3.03
3.02
1.04
2.00
1.05
1.07
6.09
6.00
18.06
3.07
f1 (ppm)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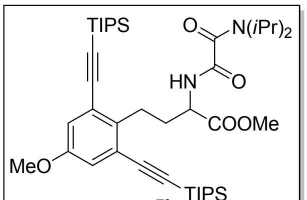
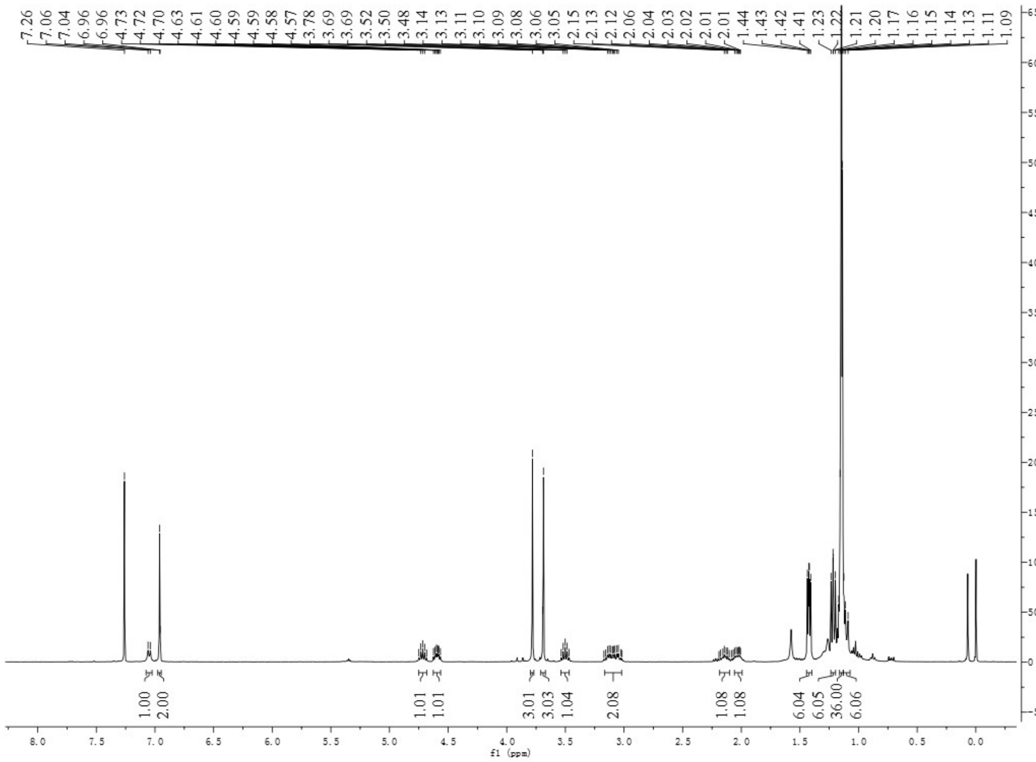
130.26
123.80
117.99
115.11
105.30
94.67
77.48
77.16
76.84
55.50
52.47
52.00
49.73
46.73
32.81
30.18
21.00
20.16
18.83
11.43
f1 (ppm)


TIPS
N(iPr)2
HN
COOMe
MeO
TIPS

5i$_{di}$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6.96
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4.70
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4.59
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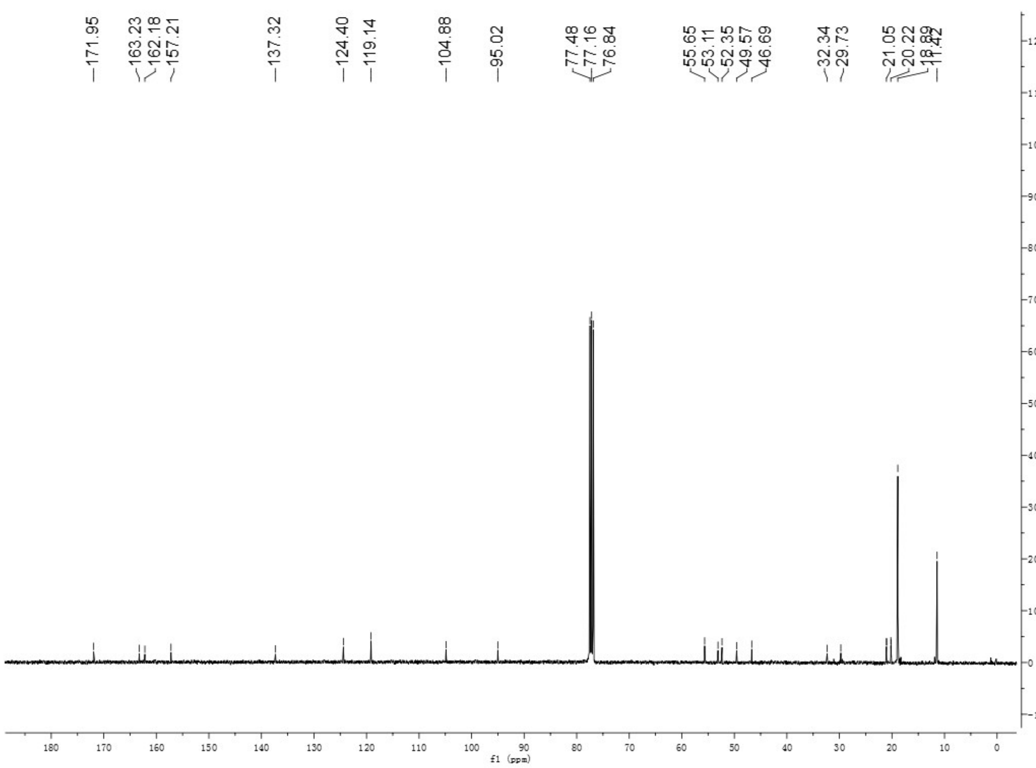
4.58
4.57
3.78
3.69
3.69
3.52
3.50
3.48
3.14
3.13
3.11
3.10
3.09
3.08
3.06
3.05
2.15
2.13
2.13
2.12
2.06
2.04
2.03
2.02
2.01
2.01
1.44
1.43
1.42
1.41
1.23
1.22
1.21
1.20
1.17
1.16
1.15
1.14
1.13
1.11
1.09
1.00
2.00
1.01
1.01
3.01
3.03
1.04
2.08
1.08
1.08
6.04
6.05
36.00
6.06
f1 (ppm)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104.88
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77.16
76.84
55.65
53.11
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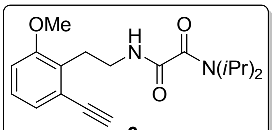
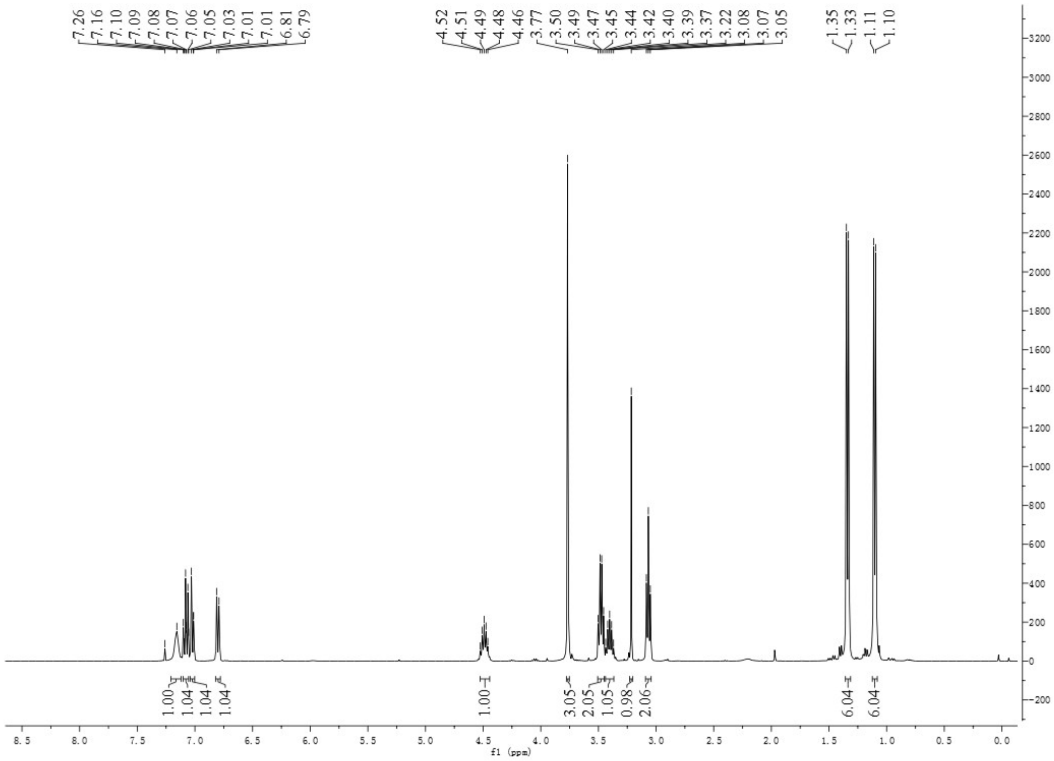
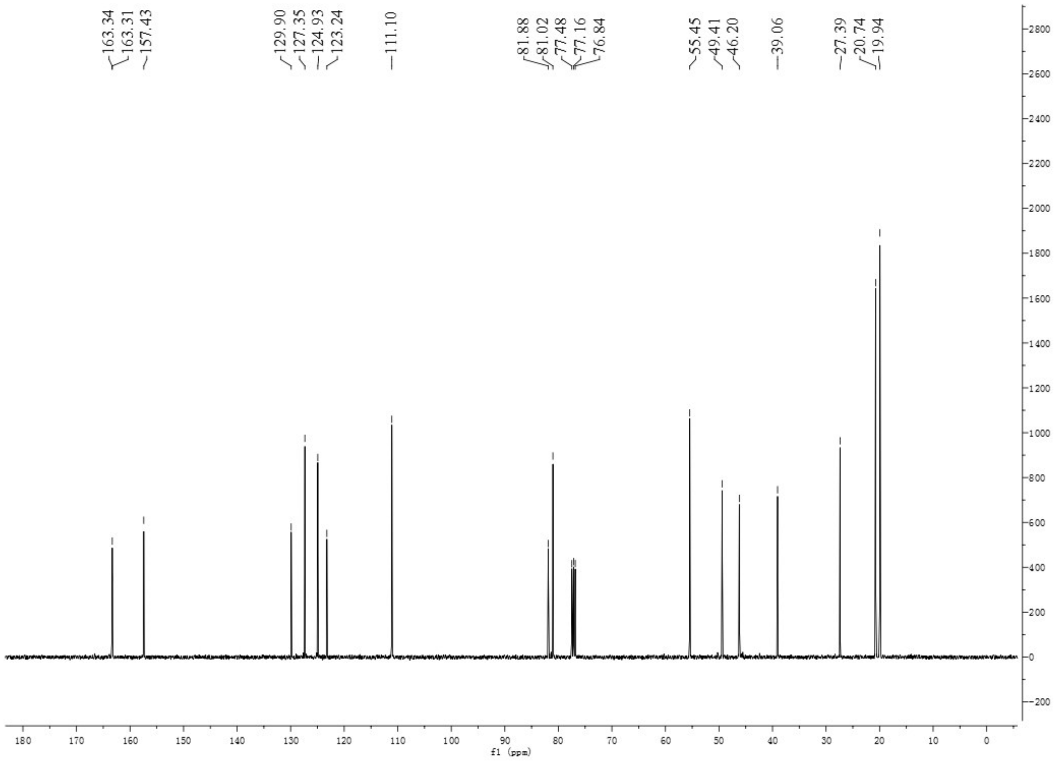
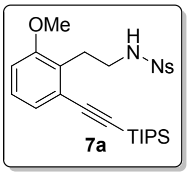
49.57
46.69
32.34
29.73
21.05
20.22
18.89
11.42
f1 (ppm)

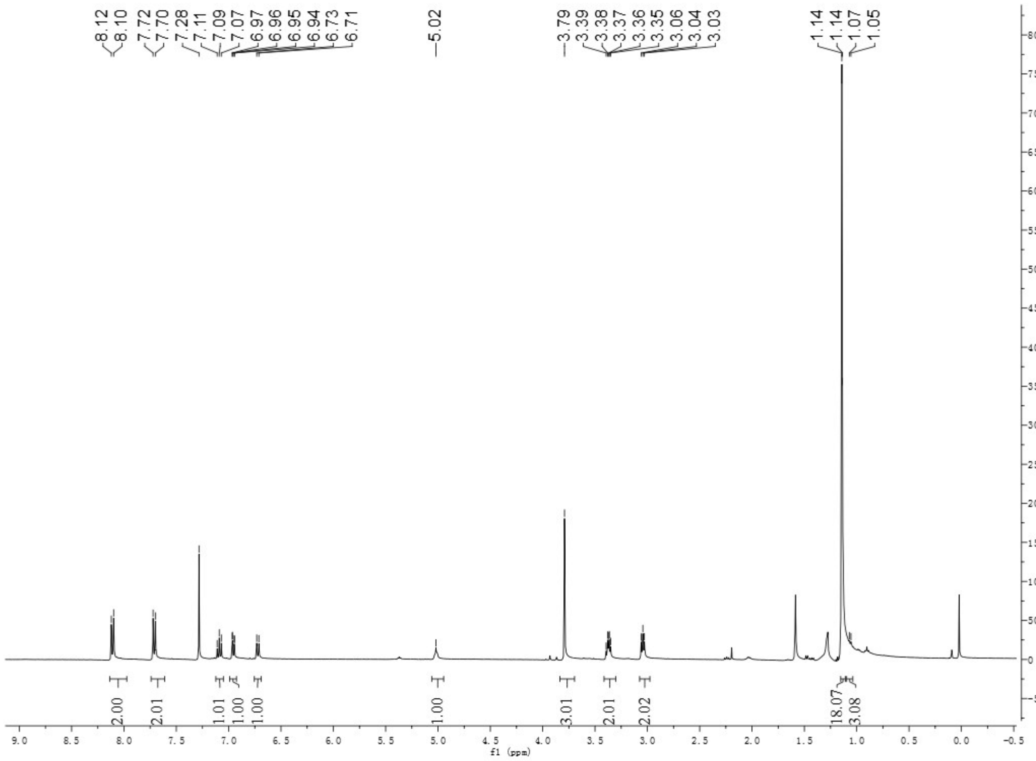


6a






OMe
H
N
Ns
TIPS
7a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8.10
7.72
7.70
7.28
7.11
7.09
7.07
6.97
6.96
6.95
6.94
6.73
6.71
5.02
3.79
3.39
3.38
3.37
3.36
3.35
3.06
3.04
3.03
1.14
1.14
1.07
1.05
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2.01
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1.00
1.00
1.00
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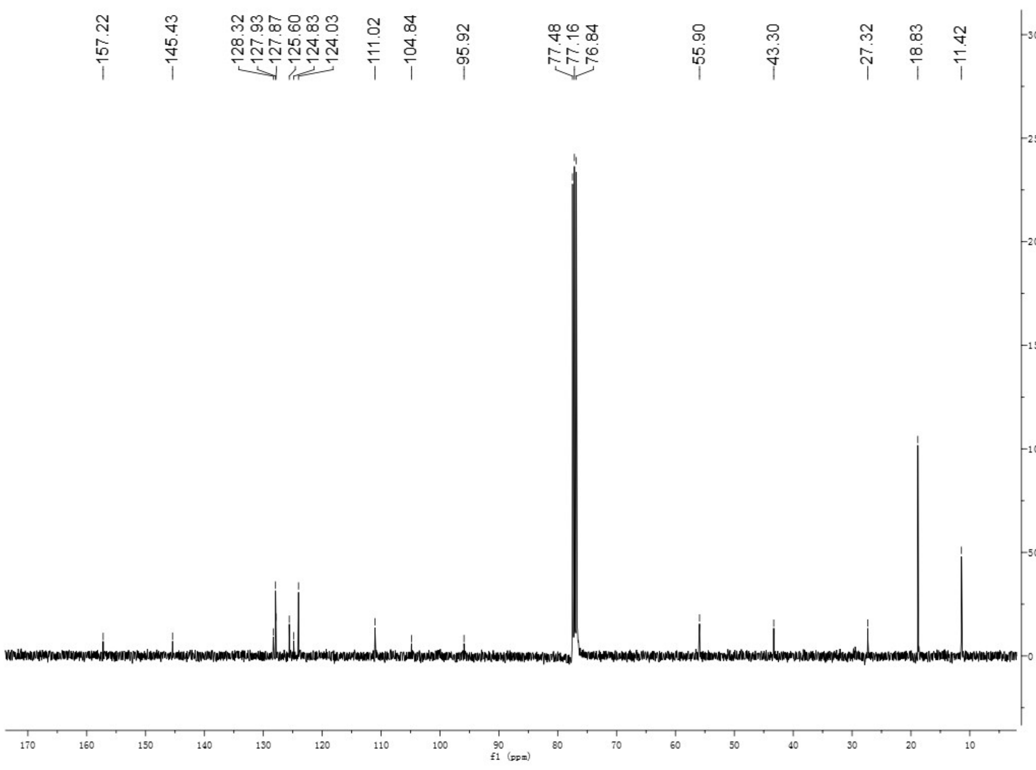
2.01
2.02
18.07
3.08
f1 (ppm)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124.03
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27.32
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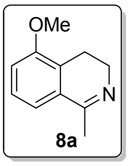
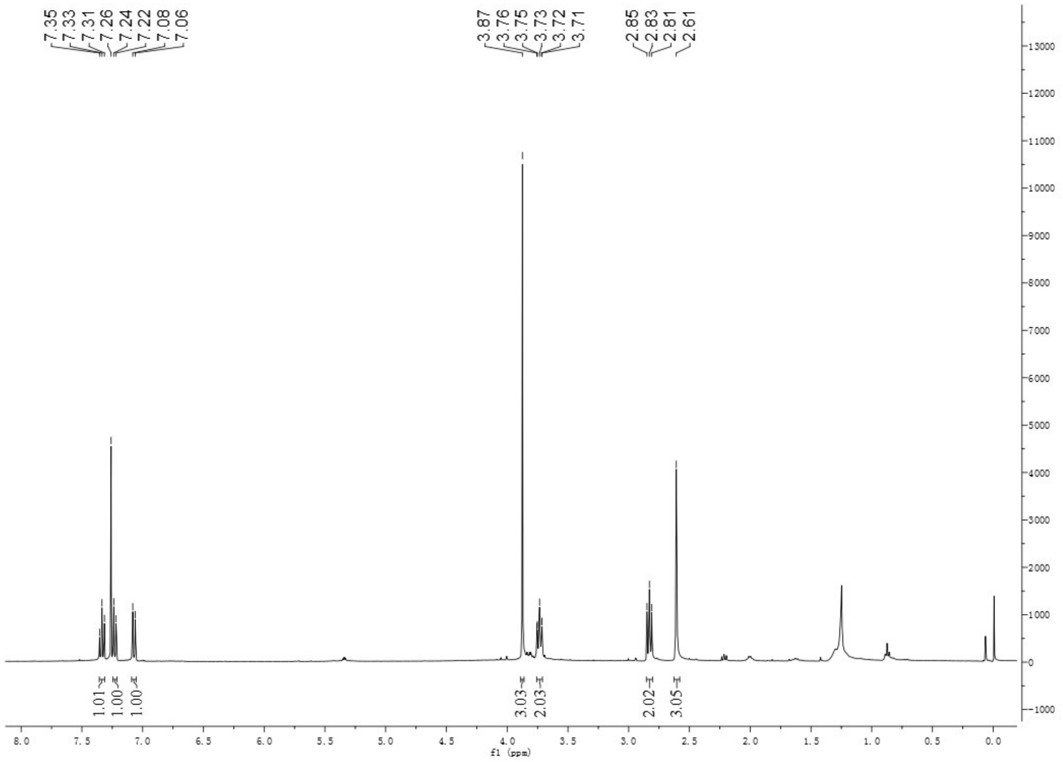
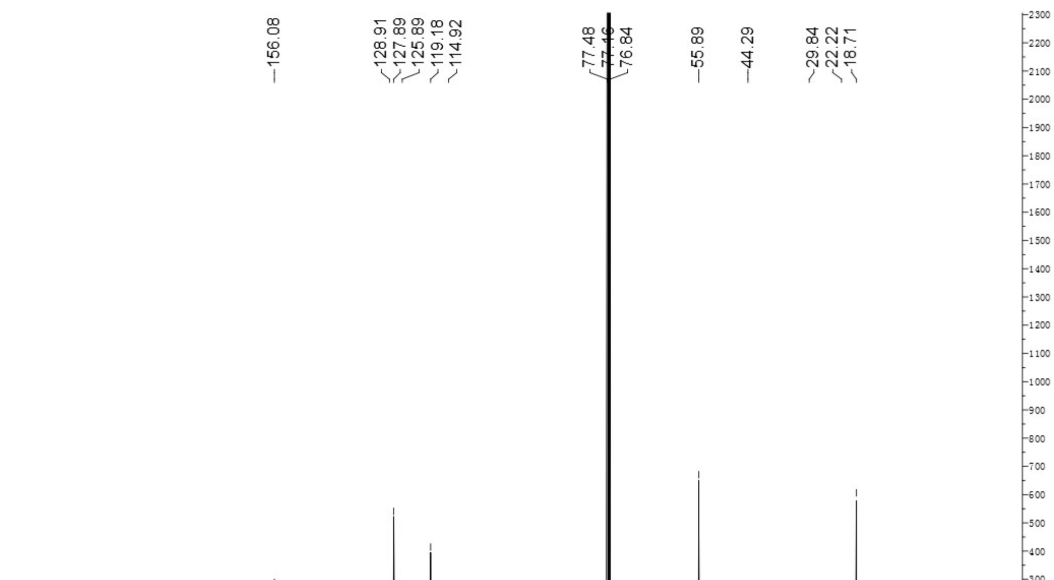
11.42
f1 (ppm)


OMe
N
8a


7.35
7.33
7.31
7.26
7.24
7.22
7.08
7.06
3.87
3.76
3.75
3.73
3.72
3.71
2.85
2.83
2.81
2.61
1.01
1.00
1.00
3.03
2.03
2.02
3.05
f1 (ppm)


156.08
128.91
127.89
125.89
119.18
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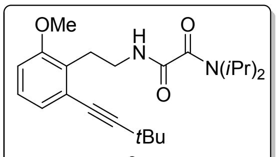
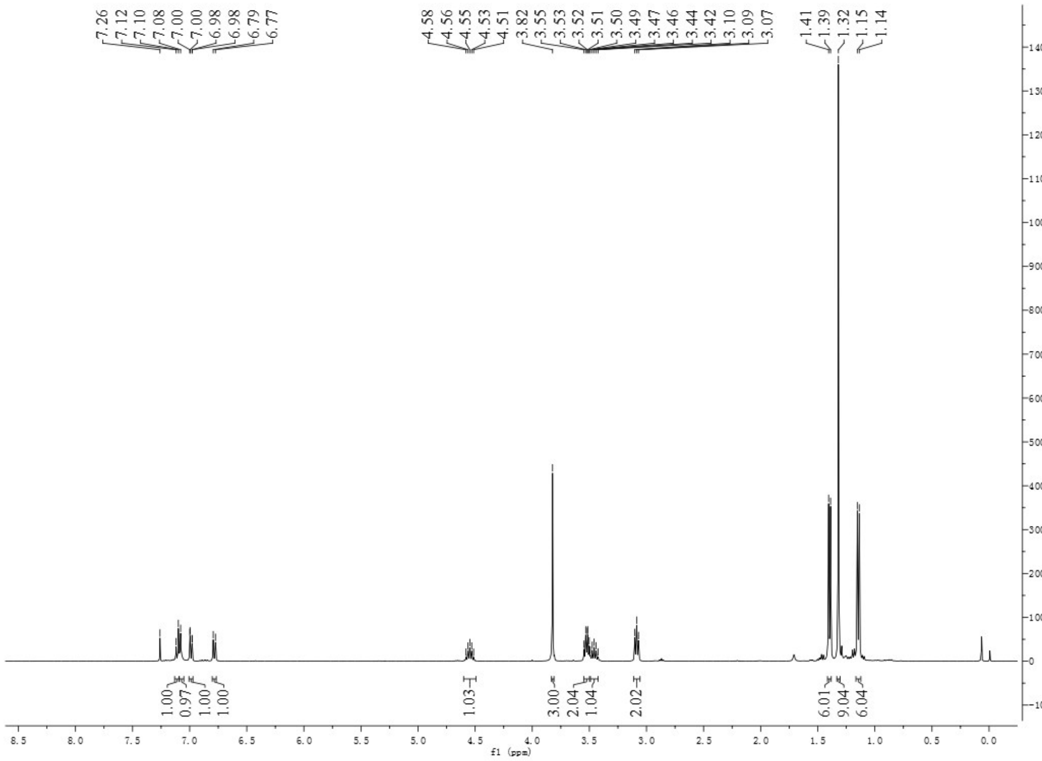
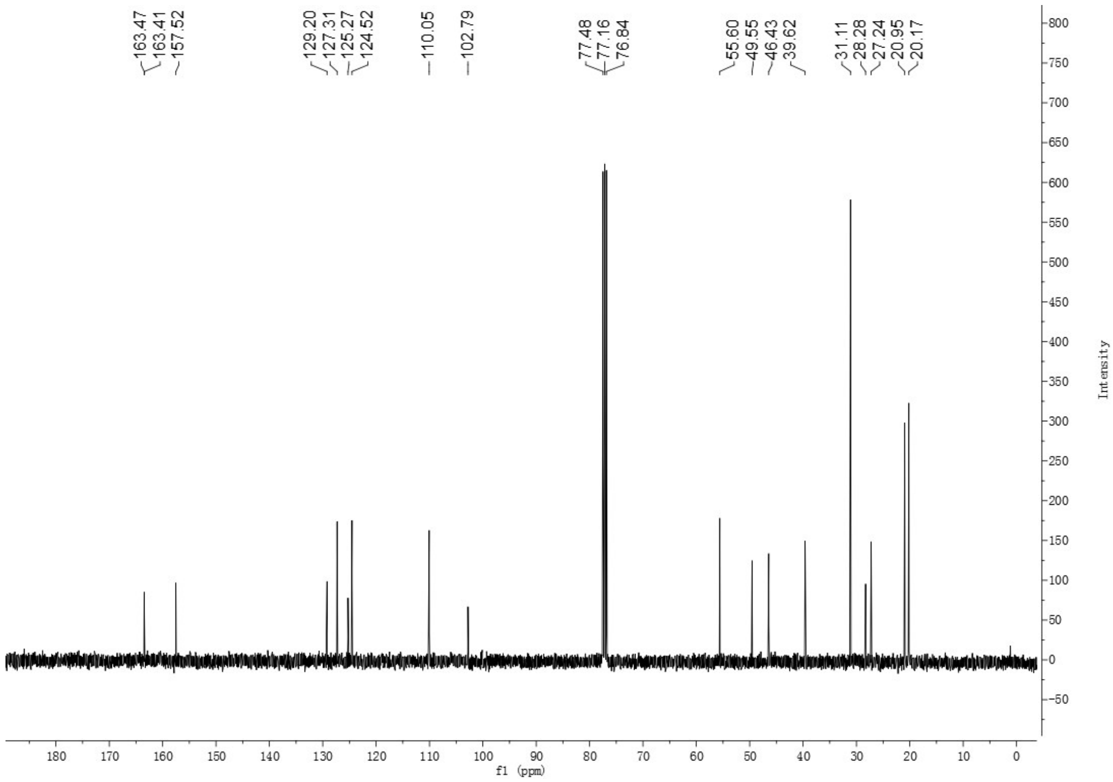
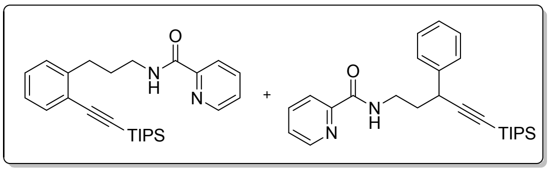
77.48
77.16
76.84
55.89
44.29
29.84
22.22
18.71
f1 (ppm)



9a







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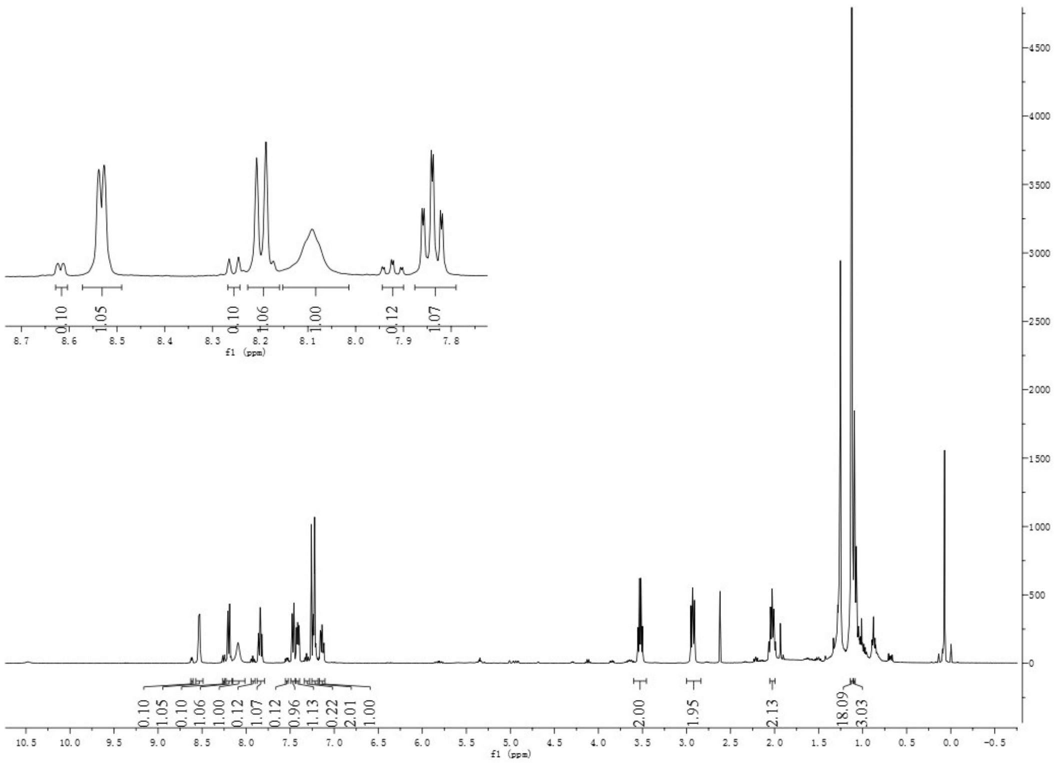

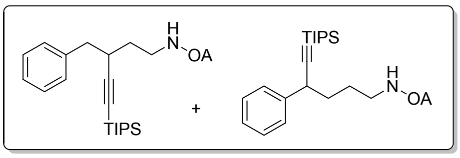

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