Electronic Supplementary Information

Rhodium(III)-Catalyzed C-H Alkynylation of Azomethine Imines at Mild Conditions

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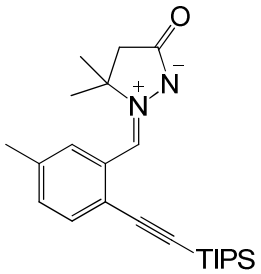
Content

I. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All syntheses were conducted under ambient atmosphere unless otherwise stated. NMR Spectra were obtained on a Bruker 400 MHz or 500 MHz NMR spectrometer in the deuterated solvents indicated. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. HRMS data were obtained on a Thermo Scientific LTQ Orbirap Discovery (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using methanol (MeOH)/ethyl acetate (EA). azomethine imine[1] and ethynyl benziodoxolones[2] were prepared according to the literature.

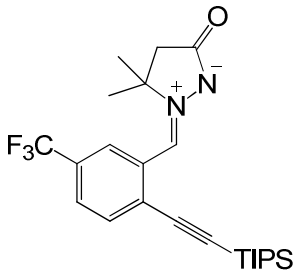
II. General procedures for the synthesis of alkyne compounds 3

Azomethine imine derivative **1a** (1.0 equiv, 0.2 mmol), alkyne **2a** (1.1 equiv, 0.22 mmol), $[Cp^*RhCl_2]_2$ (0.006 mol, 3 mol%), $Zn(OTf)_2$ (0.024 mmol, 12 mol%), and dichloroethane (2 mL) were charged into a pressure tube under argon. The reaction mixture was stirred at 30 °C for 16 h. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using MeOH / EA to afford the alkynylation product **3**.



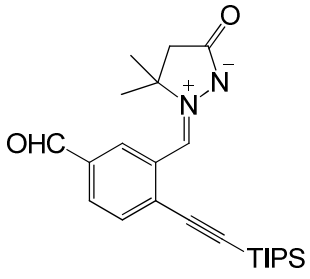
3aa, White solid, 75 mg, 95% yield, mp: 139 – 140 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.81 (s, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.19 (dd, J = 7.9, 0.8 Hz, 1H), 2.73 (s, 2H), 2.40 (s, 3H), 1.69 (s, 6H), 1.17 – 1.09 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 139.7, 133.2, 132.0, 131.4, 129.9, 127.9, 122.2, 104.0, 97.6, 74.2, 44.3, 29.0, 21.8, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{24}H_{37}N_2OSi$: 397.2675, found 397.2687.



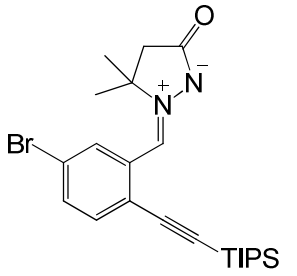
3ba, Yellow solid, 68 mg, 76% yield, mp: 142 – 143 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.83 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.2 Hz, 1H), 2.77 (s, 2H), 1.74 (s, 6H), 1.21 – 1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 133.6, 131.0 (*J* = 32.8 Hz), 130.9, 127.8 (*J* = 3.9Hz), 127.7 (*J* = 1.1 Hz), 127.0 (*J* = 3.7 Hz), 125.2, 123.4 (*J* = 271.4 Hz), 102.6, 101.8, 74.9, 44.1, 29.0, 18.7, 11.2. HRMS: $[M + H]^+$ calculated for $C_{24}H_{34}F_3N_2OSi$: 451.2392, found 451.2388.



3ca, Yellow solid, 38 mg, 46% yield, mp: 179 – 180 ℃

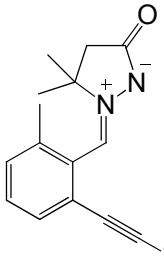
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.82 (d, *J* = 1.4 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 2.79 (s, 2H), 1.75 (s, 6H), 1.21 – 1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 182.0, 136.2, 134.6, 133.9, 131.1, 129.7, 128.5, 125.5, 103.4, 103.1, 74.9, 44.1, 29.1, 18.7, 11.2. HRMS: $[M + H]^+$ calculated for $C_{24}H_{35}N_2O_2Si$: 411.2468, found 411.2462. IR (KBr) cm^{-1}: 3070, 2941, 2864, 2149, 1705, 1671, 1575, 1463, 1413, 1306, 1158, 1108, 1091, 1020, 994, 881, 837, 788, 669.



3da, Yellow solid, 64.5mg, 70% yield, mp: 164 – 165 ℃

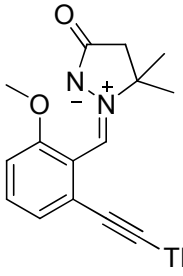
1H NMR (400 MHz, CDCl3) δ 9.48 (d, J = 1.2 Hz, 1H), 7.74 (s, 1H), 7.50 (dd, J = 8.2, 1.4 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 2.74 (s, 2H), 1.70 (s, 6H), 1.19 – 1.10 (m, 21H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 134.2, 134.1, 133.3, 131.6, 125.6, 123.5, 123.4, 102.9, 100.0, 74.7, 44.1, 29.0, 18.7, 11.2. HRMS: $[M + H]^+$ calculated for $C_{23}H_{34}BrN_2OSi$: 461.1624, found 461.1631.



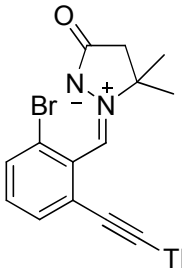
3ea, White solid, 56.4 mg, 71% yield, mp: 179 – 180 ℃

1H NMR (400 MHz, CDCl3) δ 7.56 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 2.77 (s, 2H), 2.32 (s, 3H), 1.77 (s, 6H), 1.12 (s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 138.7, 131.1, 130.7, 130.4, 130.3, 130.0, 122.9, 104.6, 97.0, 73.4, 45.1, 29.1, 20.6, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{24}H_{37}N_2OSi$: 397.2675, found 397.2677.



3fa, Yellow solid, 60.3 mg, 73% yield, mp: 201 – 203 ℃

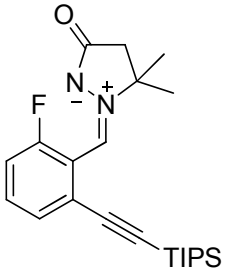
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.73 (s, 2H), 1.71 (s, 6H), 1.10 (s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 157.4, 131.4, 127.1, 125.4, 124.1, 120.7, 112.4, 104.1, 97.0, 72.9, 56.2, 45.3, 29.1, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{24}H_{37}N_2O_2Si$: 413.2624, found 413.2627.



3ga, Yellow solid, 80.2 mg, 87% yield, mp: 209 – 210 ℃

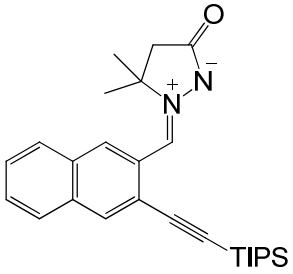
1H NMR (400 MHz, CDCl3) δ 7.55 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.48 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.24 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 2.73 (s, 2H), 1.77 (s, 6H), 1.09 (s,

21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 133.0, 132.5, 132.3, 130.6, 126.9, 125.2, 123.1, 103.3, 98.0, 73.6, 45.1, 28.9, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{23}H_{34}BrN_2OSi$: 461.1624, found 461.1618.



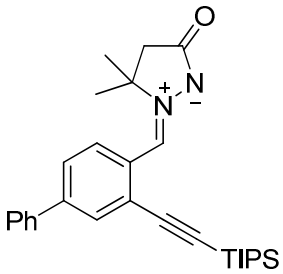
3ha, White solid, 62.9 mg, 79% yield, mp: 180 – 181 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.13 – 7.09 (m, 1H), 2.78 (s, 2H), 1.76 (s, 6H), 1.13 (s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 159.5 (*J* = 256.7Hz), 131.9 (*J* = 9.7Hz), 128.9 (*J* = 3.1Hz), 124.5 (*J* = 4.8Hz), 123.4, 119.9 (*J* = 15.4Hz), 117.0 (*J* = 21.3Hz), 103.0, 98.6, 73.8, 45.1, 29.1, 18.7, 11.2. HRMS: $[M + H]^+$ calculated for $C_{23}H_{34}FN_2OSi$: 401.2424, found 401.2418.



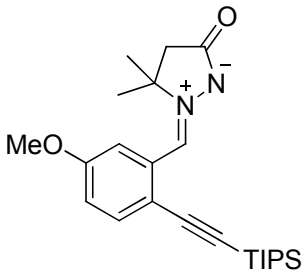
3ia, Yellow solid, 69.2 mg, 80% yield, mp: 162 – 163 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.08 – 7.99 (m, 3H), 7.79 - 7.73 (m, 1H), 7.59 – 7.52 (m, 2H), 2.80 (s, 2H), 1.76 (s, 6H), 1.23 – 1.14 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 133.6, 133.5, 133.1, 132.7, 130.3, 129.0, 127.8, 127.5, 127.2, 125.8, 120.7, 104.3, 97.3, 74.3, 44.4, 29.1, 18.8, 11.4. HRMS: $[M + H]^+$ calculated for $C_{27}H_{37}N_2OSi$: 433.2675, found 433.2658. IR (KBr) cm^{-1}: 3055, 2938, 2864, 2146, 1673, 1571, 1463, 1303, 1110, 1085, 884, 740, 674, 598.



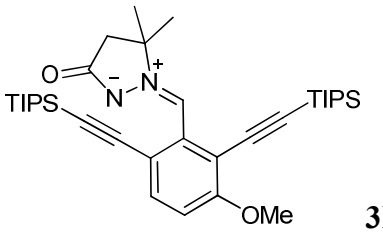
3ja, Yellow solid, 39.7 mg, 39% yield

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (d, *J* = 8.5 Hz, 1H), 7.89 (s, 1H), 7.76 (d, *J* = 1.9 Hz, 1H), 7.67 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 2.88 (s, 2H), 1.71 (s, 6H), 1.20 – 1.14 (m, 21H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.7, 144.1, 138.9, 132.1, 131.6, 129.0, 128.8, 128.7, 128.6, 127.8, 127.2, 125.6, 103.8, 98.7, 74.5, 44.4, 29.0, 18.8, 11.3. HRMS: $[M + H]^+$ calculated for $C_{29}H_{39}N_2OSi$: 459.2832, found 459.2852.



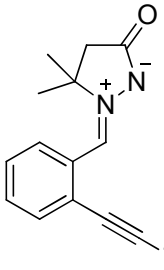
3ka, Yellow solid, 30 mg, 33% yield, mp: 109 – 110 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 2.6 Hz, 1H), 7.85 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.6 Hz, 1H), 3.90 (s, 3H), 2.78 (s, 2H), 1.71 (s, 6H), 1.15 – 1.12 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 134.4, 131.4, 128.3, 118.9, 117.5, 114.8, 103.9, 96.7, 74.5, 55.9, 44.3, 29.0, 18.8, 11.3. HRMS: $[M + H]^+$ calculated for $C_{24}H_{37}N_2O_2Si$: 413.2624, found 413.2629.



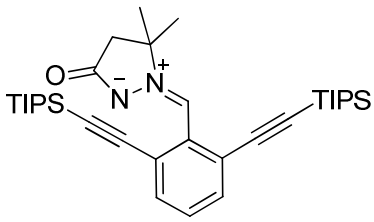
3kaa, Yellow solid, 50.4 mg, 38% yield, mp: 218 – 220 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 1H), 7.34 (s, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 3.85 (s, 3H), 2.71 (s, 2H), 1.75 (s, 6H), 1.10 (d, *J* = 6.6 Hz, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 161.4, 135.0, 134.3, 127.2, 115.5, 113.0, 111.9, 104.0, 102.3, 99.7, 94.9, 73.2, 56.1, 45.2, 29.1, 18.7, 18.6, 11.3, 11.3. HRMS: $[M + H]^+$ calculated for $C_{35}H_{57}N_2O_2Si_2$: 593.3959, found 593.3953. IR (KBr) cm^{-1}: 3028, 2943, 2865, 2142, 1672, 1586, 1464, 1295, 1100, 1076, 997, 882, 822, 738, 676, 620.



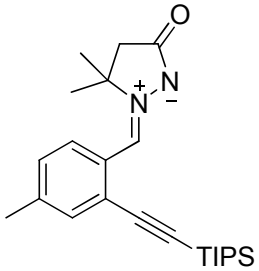
3la, White solid, 28.2 mg, 34% yield, mp: 103 – 104 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.1 Hz, 1H), 7.86 (s, 1H), 7.59 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.46 (td, *J* = 7.9, 1.3 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 2.78 (s, 2H), 1.72 (s, 6H), 1.17 (d, *J* = 3.1 Hz, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 133.3, 131.4, 131.1, 130.1, 129.1, 127.8, 124.9, 103.8, 98.6, 74.4, 44.3, 29.0, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{23}H_{35}N_2OSi$: 383.2519, found 383.2518.



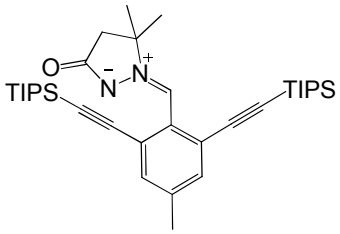
3laa, White solid, 35.7 mg, 29%, yield, mp: 185 – 187 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.38 (s, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 2.72 (s, 2H), 1.76 (s, 6H), 1.11 (s, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 133.7, 132.7, 129.4, 127.0, 123.7, 104.0, 97.6, 73.2, 45.2, 29.1, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{34}H_{55}N_2OSi_2$: 563.3853, found 563.3855.



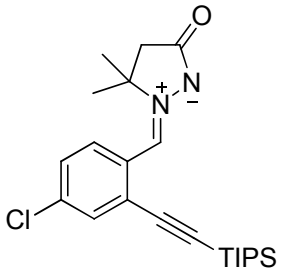
3ma, Yellow solid, 27.9 mg, 32% yield, mp: 157 – 158 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 2.7 Hz, 1H), 7.85 (s, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.90 (s, 3H), 2.79 (s, 2H), 1.71 (s, 6H), 1.15 - 1.12 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 134.4, 131.4, 128.4, 118.9, 117.6, 114.8, 103.9, 96.8, 74.5, 55.9, 44.3, 29.0, 18.8, 11.3. HRMS: $[M + H]^+$ calculated for $C_{24}H_{37}N_2OSi$: 397.2675, found 397.2679.



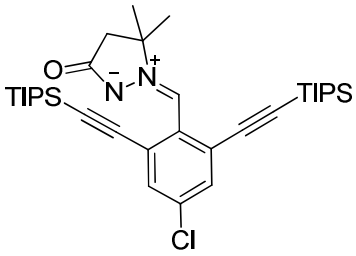
3maa, White solid, 45.7 mg, 36% yield, mp: 205 – 206 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.31 (s, 2H), 2.73 (s, 2H), 2.32 (s, 3H), 1.75 (s, 6H), 1.11 (s, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 139.8, 134.4, 130.0, 127.6, 123.5, 104.2, 97.0, 73.1, 45.2, 29.1, 20.9, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{35}H_{57}N_2OSi_2$: 577.4009, found 577.4010.



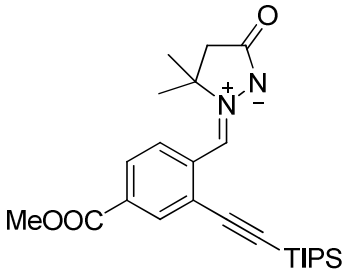
3na, Yellow solid, 37.9 mg, 41% yield, mp: 162 – 164 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (d, J = 8.9 Hz, 1H), 7.76 (s, 1H), 7.55 (d, J = 2.2 Hz, 1H), 7.41 (dd, J = 8.8, 2.0 Hz, 1H), 2.75 (s, 2H), 1.72 (s, 6H), 1.19 – 1.14 (m, 21H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 136.9, 132.9, 132.6, 129.4, 128.7, 126.2, 126.1, 102.4, 100.2, 74.6, 44.2, 29.1, 18.8, 11.3. HRMS: $[M + H]^+$ calculated for $C_{23}H_{34}ClN_2OSi$: 417.2129, found 417.2125.



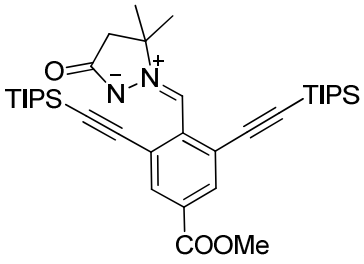
3naa, Yellow solid, 38.9 mg, 29% yield, mp: 165 – 166 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.30 (s, 1H), 2.72 (s, 2H), 1.74 (s, 6H), 1.09 (s, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 135.3, 133.4, 131.2, 126.0, 125.1, 102.6, 99.4, 73.5, 45.1, 29.1, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{34}H_{54}ClN_2OSi_2$: 597.3463, found 597.3465.



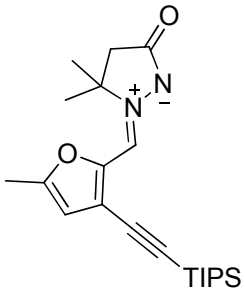
3oa, Yellow solid, 44.7 mg, 46% yield, mp: 166 – 167 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 1.7 Hz, 1H), 8.05 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.85 (s, 1H), 3.96 (s, 3H), 2.78 (s, 2H), 1.75 (s, 6H), 1.20 – 1.15 (m, 21H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.2, 165.6, 134.1, 133.6, 131.6, 131.1, 129.7, 125.8, 124.8, 103.0, 99.7, 75.1, 52.5, 44.1, 29.1 18.8, 11.3. HRMS: $[M + H]^+$ calculated for $C_{25}H_{37}N_2O_3Si$: 441.2573, found 441.2576. IR (KBr) cm^{-1}: 3071, 2942, 2866, 2150, 1731, 1685, 1571, 1464, 1434, 1288, 1262, 1212, 1106, 996, 920, 883, 862, 833, 790, 761, 681, 666, 641.



3oaa, Yellow solid, 37.2 mg, 27% yield, mp: 164 – 165 ℃

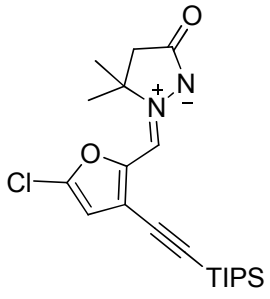
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.40 (s, 1H), 3.95 (s, 3H), 2.75 (s, 2H), 1.78 (s, 6H), 1.12 (s, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 165.2, 136.3, 134.3, 131.25, 126.0, 124.2, 103.1, 99.0, 73.7, 52.6, 45.0, 29.0, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{36}H_{57}N_2O_3Si_2$: 621.3908, found 621.3947.



3pa, Yellow solid, 68.9 mg, 89% yield, mp: 174 – 175 ℃

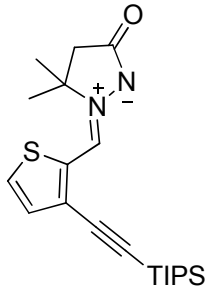
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.20 (s, 1H), 2.72 (s, 2H), 2.40 (s, 3H), 1.63 (s, 6H), 1.12 – 1.10 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 158.8, 147.3,

118.2, 115.1, 111.4, 100.9, 96.6, 72.9, 44.6, 28.8, 18.7, 14.3, 11.2. HRMS: $[M + H]^+$ calculated for $C_{22}H_{35}N_2O_2Si$: 387.2468, found 387.2470. IR (KBr) cm^{-1}: 3079, 2941, 2865, 2144, 1659, 1595, 1497, 1417, 1290, 1101, 993, 882, 735, 671, 647.



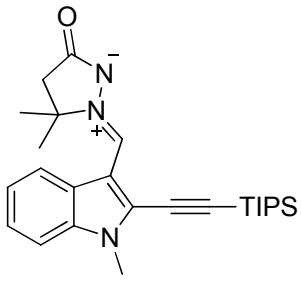
3qa, Gray solid, 65.9 mg, 81% yield, mp: 150 – 152 ℃

^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.36 (s, 1H), 2.79 (s, 2H), 1.64 (s, 6H), 1.14 – 1.09 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 147.7, 142.8, 117.9, 114.1, 111.4, 102.7, 95.0, 73.8, 44.3, 28.8, 18.6, 11.1. HRMS: $[M + H]^+$ calculated for $C_{21}H_{32}ClN_2O_2Si$: 407.1922, found 407.1924.



3ra, Yellow solid, 58.3 mg, 75% yield, mp: 98 – 100 ℃

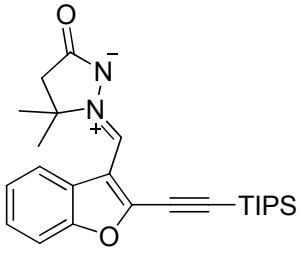
^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 5.4 Hz, 1H), 7.41 (s, 1H), 7.27 (d, J = 3.5 Hz, 1H), 2.78 (s, 2H), 1.68 (s, 6H), 1.17 -1.05 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 129.5, 129.1, 126.4, 123.7, 104.3, 97.0, 73.0, 44.8, 28.9, 18.7, 11.2. HRMS: $[M + H]^+$ calculated for $C_{21}H_{33}N_2OSSi$: 389.2083, found 389.2088.



3sa, Yellow solid, 80.9 mg, 93% yield, mp: 192 – 193 ℃

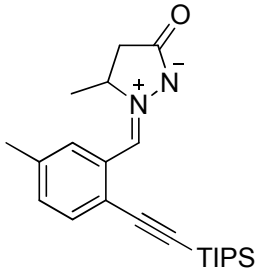
^1H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.35 – 7.22 (m, 3H), 3.87 (s, 3H), 2.84 (s, 2H), 1.68 (s, 6H), 1.26 – 1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 138.3, 129.3, 128.0, 127.7, 125.4, 123.5, 122.7, 113.1, 109.2,

107.2, 94.9, 71.6, 45.8, 31.6, 28.9, 18.7, 11.2. HRMS: $[M + H]^+$ calculated for $C_{26}H_{38}N_3OSi$: 436.2784, found 436.2786. IR (KBr) cm^{-1}: 3071, 2941, 2864, 2359, 2152, 1659, 1610, 1463, 1305, 1137, 1083, 1017, 881, 794, 749, 729, 681, 675, 652.



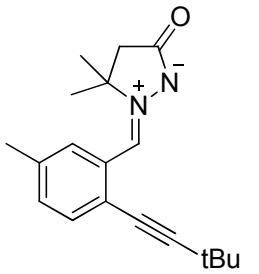
3ta, Yellow solid, 39.8 mg, 47% yield, mp: 146 – 147 ℃

^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.31 (s, 1H), 2.85 (s, 2H), 1.72 (s, 6H), 1.23 – 1.13 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 155.3, 143.2, 128.1, 127.5, 124.5, 123.6, 122.7, 119.2, 110.9, 107.8, 94.2, 77.4, 77.0, 76.7, 73.2, 45.2, 29.0, 18.7, 11.1. HRMS: $[M + H]^+$ calculated for $C_{25}H_{35}N_2O_2Si$: 423.2468, found 423.2468.



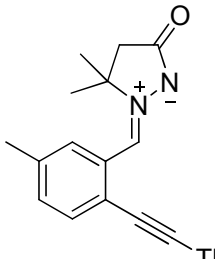
3ua, White solid, 31.4 mg, 41% yield, mp: 162 – 164 ℃

^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.85 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 4.71 – 4.61 (m, 1H), 3.08 – 3.01 (m, 1H), 2.51 – 2.46 (m, 1H), 2.42 (s, 3H), 1.68 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 3.1 Hz, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 139.7, 132.9, 132.1, 131.6, 130.0, 129.8, 122.1, 103.9, 97.8, 66.8, 37.3, 22.6, 21.8, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{23}H_{35}N_2OSi$: 383.2519, found 383.2513.



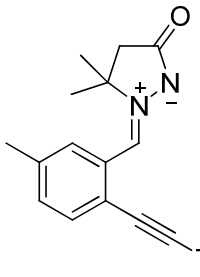
3ab, Yellow solid, 68.9 mg, 90% yield, mp: 125 – 126 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.73 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 2.74 (s, 2H), 2.32 (s, 3H), 1.66 (s, 6H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 138.5, 132.2, 132.0, 131.3, 129.4, 129.2, 123.0, 105.3, 76.3, 74.1, 44.2, 31.0, 29.2, 28.3, 21.6. HRMS: $[M + H]^+$ calculated for $C_{19}H_{25}N_2O$: 297.1967, found 297.1960.



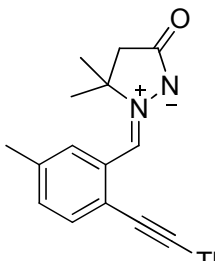
3ac, Yellow solid, 55.7 mg, 89% yield, mp: 196 - 197℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.78 (s, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.18 (dd, *J* = 7.9, 1.0 Hz, 1H), 2.76 (s, 2H), 2.39 (s, 3H), 1.70 (s, 6H), 0.27 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.3, 140.0, 132.5, 132.3, 131.6, 130.2, 128.5, 122.1, 102.2, 101.5, 74.5, 44.3, 29.4, 21.9, 0.1. HRMS: $[M + H]^+$ calculated for $C_{18}H_{25}N_2OSi$: 313.1736, found 313.1736.



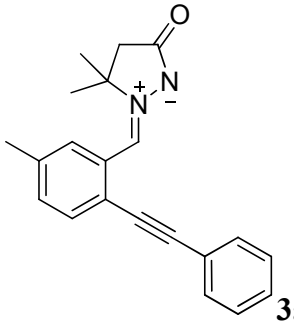
3ad, Yellow solid, 64.6 mg, 91% yield, mp: 139 – 140 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.83 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.21 (dd, *J* = 7.9, 1.0 Hz, 1H), 2.78 (s, 2H), 2.42 (s, 3H), 1.72 (s, 6H), 1.07 (t, *J* = 7.9 Hz, 9H), 0.72 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.3, 139.9, 133.0, 132.3, 131.6, 130.2, 128.5, 122.3, 103.3, 99.0, 74.4, 44.4, 29.3, 23.0, 7.8, 4.6. HRMS: $[M + H]^+$ calculated for $C_{21}H_{31}N_2OSi$: 355.2206, found 355.2205.



3ae, Yellow solid, 92.9 mg, 97% yield, mp: 161 – 162 ℃

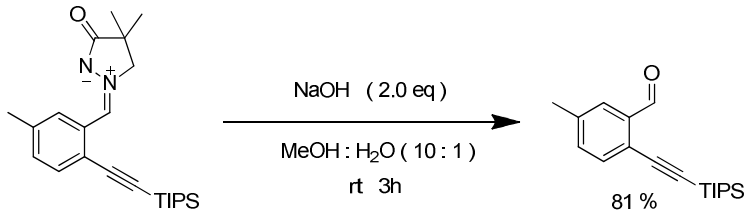
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.83 – 7.80 (m, 5H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.37 (m, 6H), 7.26 (d, *J* = 7.8 Hz, 1H), 2.75 (s, 2H), 2.43 (s, 3H), 1.46 (s, 6H), 1.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.6, 140.4, 135.6, 133.0, 132.9, 132.2, 131.8, 130.4, 129.9, 128.5, 128.0, 121.7, 105.9, 97.0, 74.5, 44.2, 28.8, 27.3, 21.9, 18.7. HRMS: $[M + H]^+$ calculated for $C_{31}H_{35}N_2OSi$: 479.2519, found 479.2516. IR (KBr) cm^{-1}: 3069, 2930, 2856, 2146, 1662, 1570, 1471, 1428, 1287, 1157, 1093, 1031, 920, 821, 700, 611.



3af, Yellow solid, 50.6 mg, 80% yield, mp: 101 – 103 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.85 (s, 1H), 7.56 – 7.48 (m, 3H), 7.45 – 7.37 (m, 3H), 7.24 (d, *J* = 7.9 Hz, 1H), 2.82 (s, 2H), 2.42 (s, 3H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 132.4, 132.2, 131.5, 131.4, 129.6, 129.0, 128.8, 128.7, 122.4, 122.2, 95.9, 86.2, 74.4, 44.1, 29.2, 21.7. HRMS: $[M + H]^+$ calculated for $C_{21}H_{21}N_2O$: 317.1654, found 317.1658.

III. Derivatization



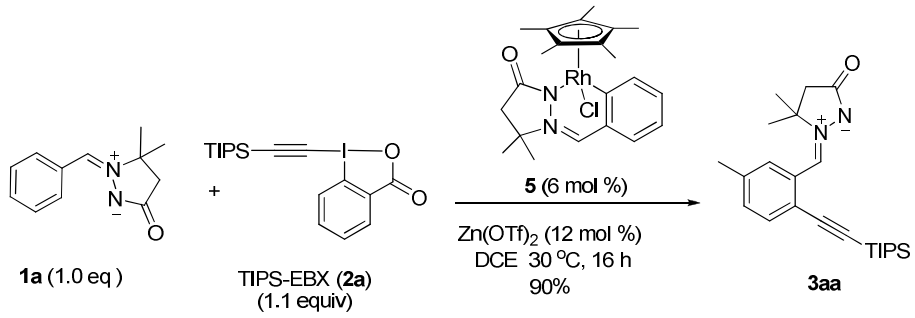
3aa **4**

3aa (79.4 mg, 0.2 mmol) and NaOH (16 mg, 0.4 mmol) were stirred in MeOH/H_2O (10: 1, 2.2 ml) at room temperature for 3h, After the removal of the solvents, the residue was absorbed to small amounts of silica. The purification was performed by

flash column chromatography on silica gel to afford compound **4** (48.6 mg, 0.16 mmol, 81%).

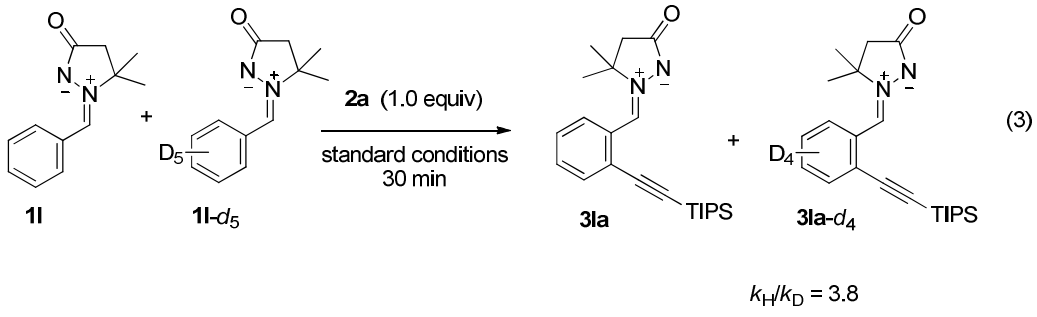
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.72 (s, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.34 (dd, J = 7.9, 1.2 Hz, 1H), 2.39 (s, 3H), 1.14 (d, J = 2.9 Hz, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 139.1, 136.1, 134.6, 133.8, 127.1, 124.4, 102.2, 98.1, 21.3, 18.7, 11.3. HRMS: $[M + H]^+$ calculated for $C_{19}H_{29}OSi$: 301.1988, found 301.1986.

IV. Mechanistic Studies



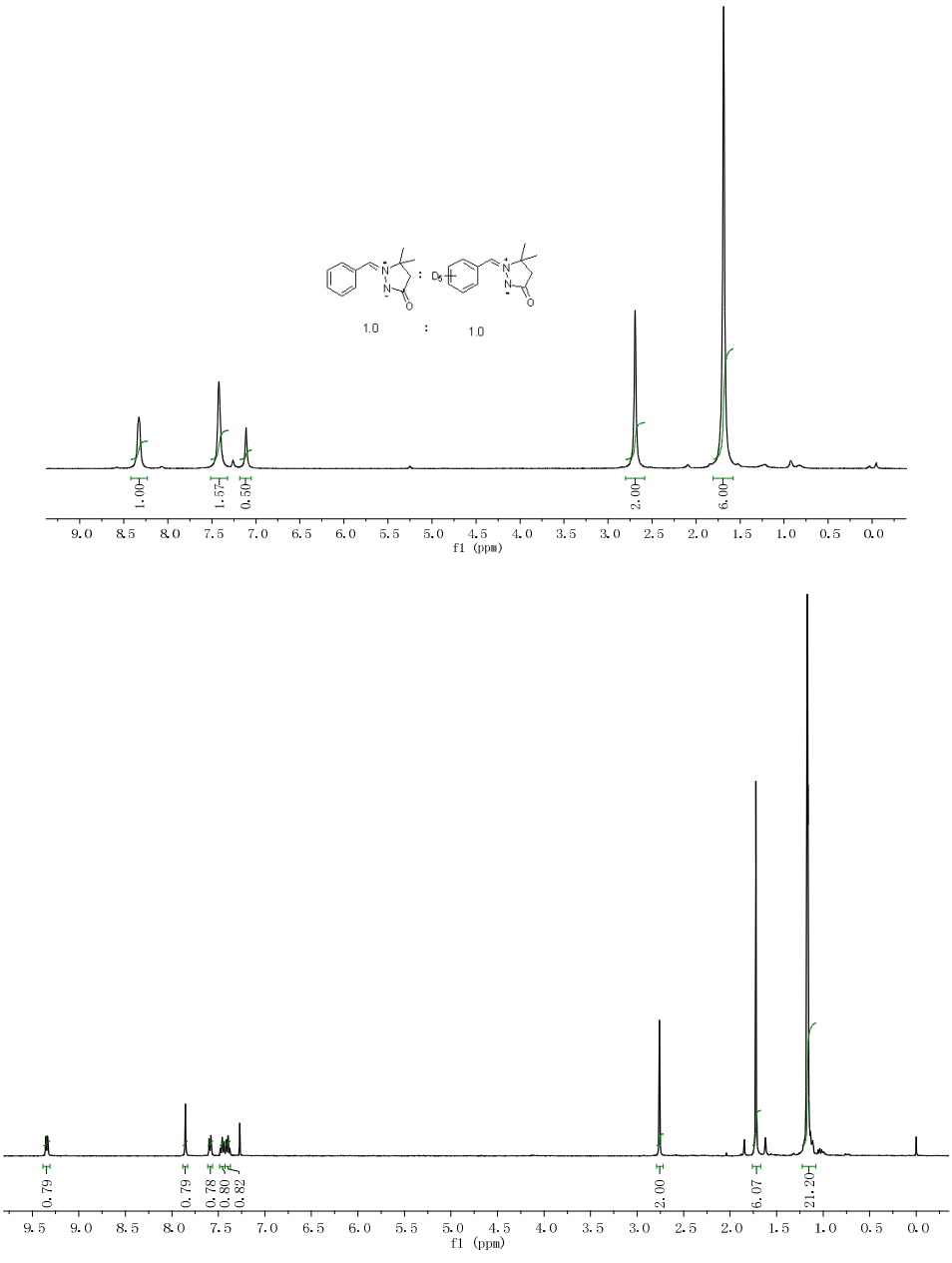
Procedures for the reaction: **1a** (1.0 equiv, 0.2 mmol), alkyne **2a** (1.1 equiv, 0.22 mmol), complex **5** (0.012 mol, 6 mol%), $Zn(OTf)_2$ (0.024 mmol, 12 mol%), and DCE (2 mL) were charged into a pressure tube under argon. The reaction mixture was stirred at 30 °C for 16 h. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using MeOH/EA to afford the alkynylation product **3aa**.

KIE Studies



Procedures for the reaction: **2a** (0.2 mmol), azomethine imine (**1a**/**1a**-d_5 = 1/1, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), $Zn(OTf)_2$ (12 mol %), and DCE (2 mL) were charged

into a pressure tube under argon. The reaction mixture was stirred at 30 °C for 30 min. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using MeOH / EA to afford the mixed product. KIE value (k_H/k_D = 3.8) was determined on the basis of ^{1}H NMR analysis.

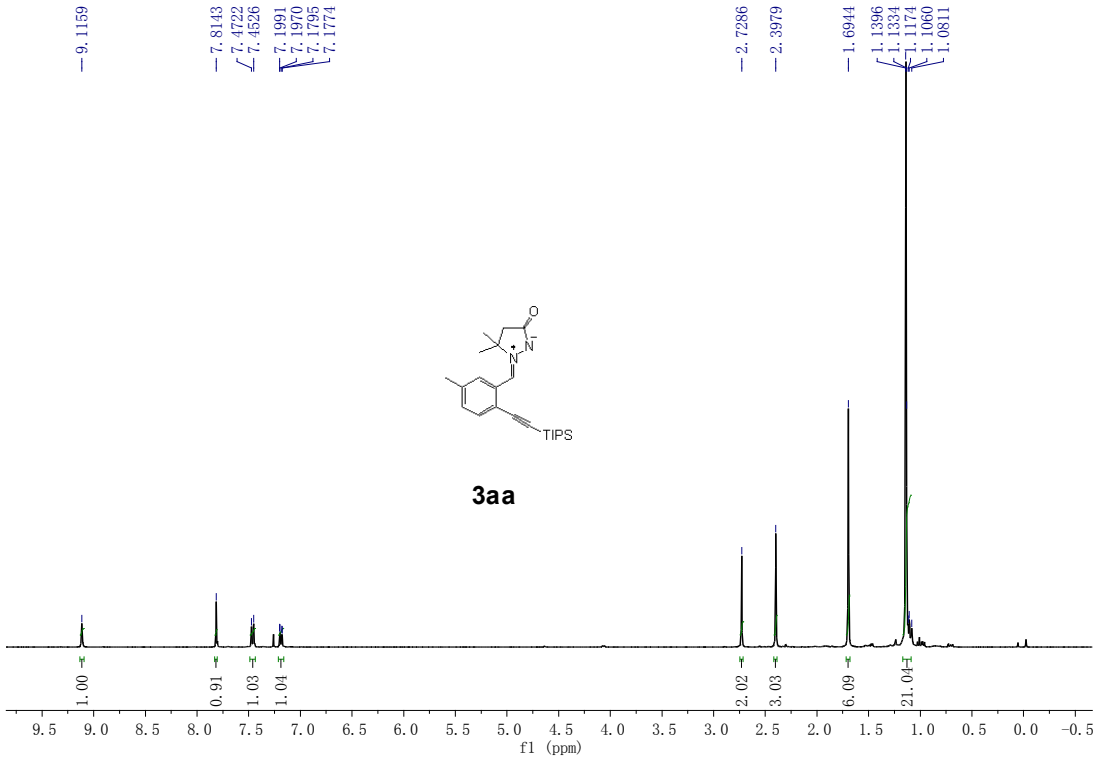


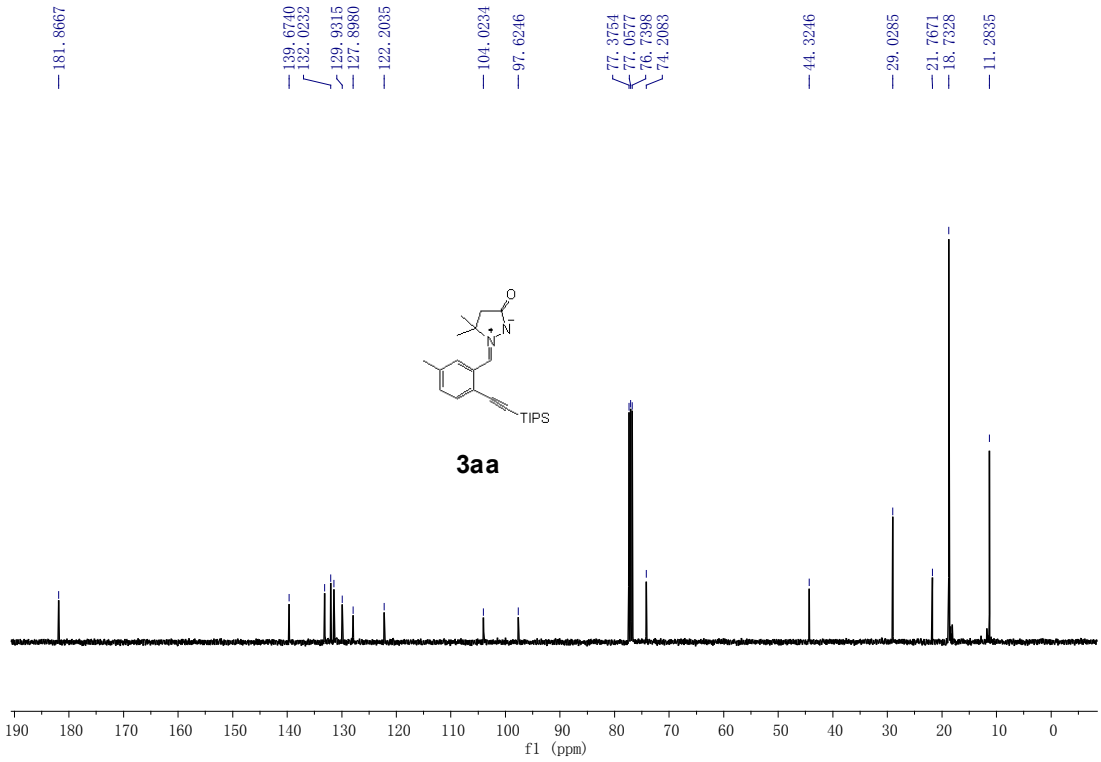
V. References

[1] Perry, S. T.; Slater, S. C.; Toske, S. G.; White, J. D. *J. Org. Chem.* **1990**, *55*, 6037.

[2] Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem.Eur. J.* **2012**, *18*, 5655

VI. NMR Spectra

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77.3754
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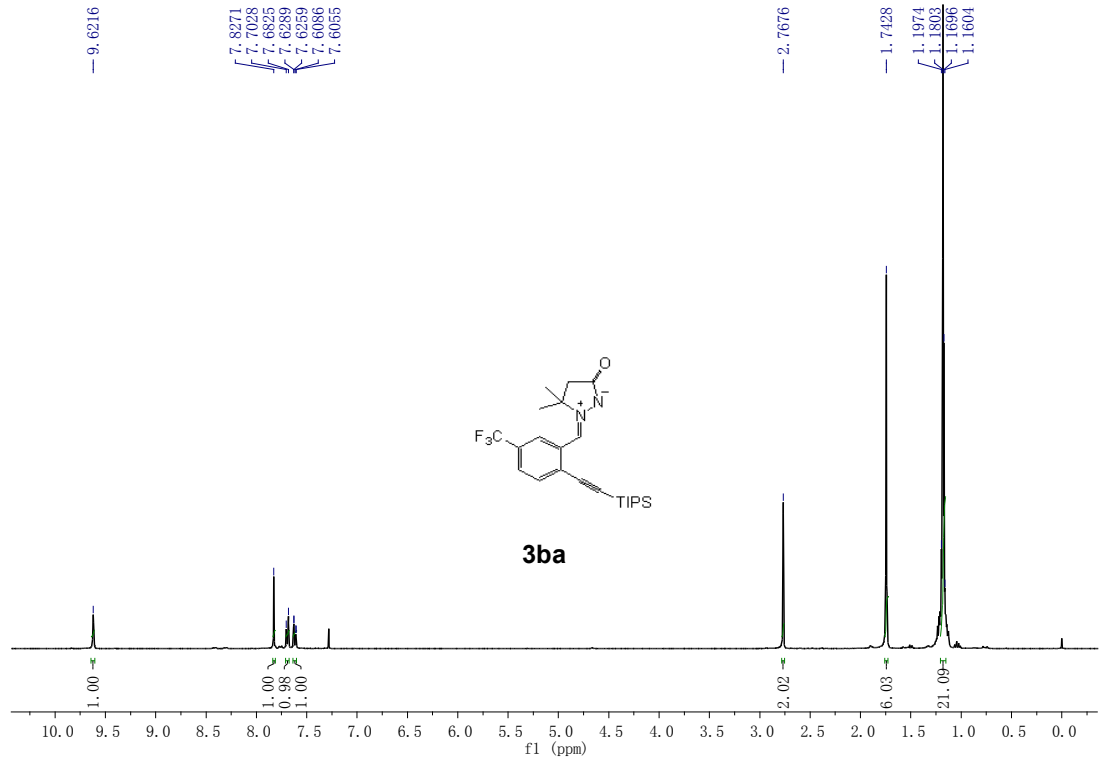
TIPS
3aa
f1 (ppm)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2.7676
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1.1974
1.1803
1.1696
1.1604
F3C
TIPS
3ba
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1.00
0.98
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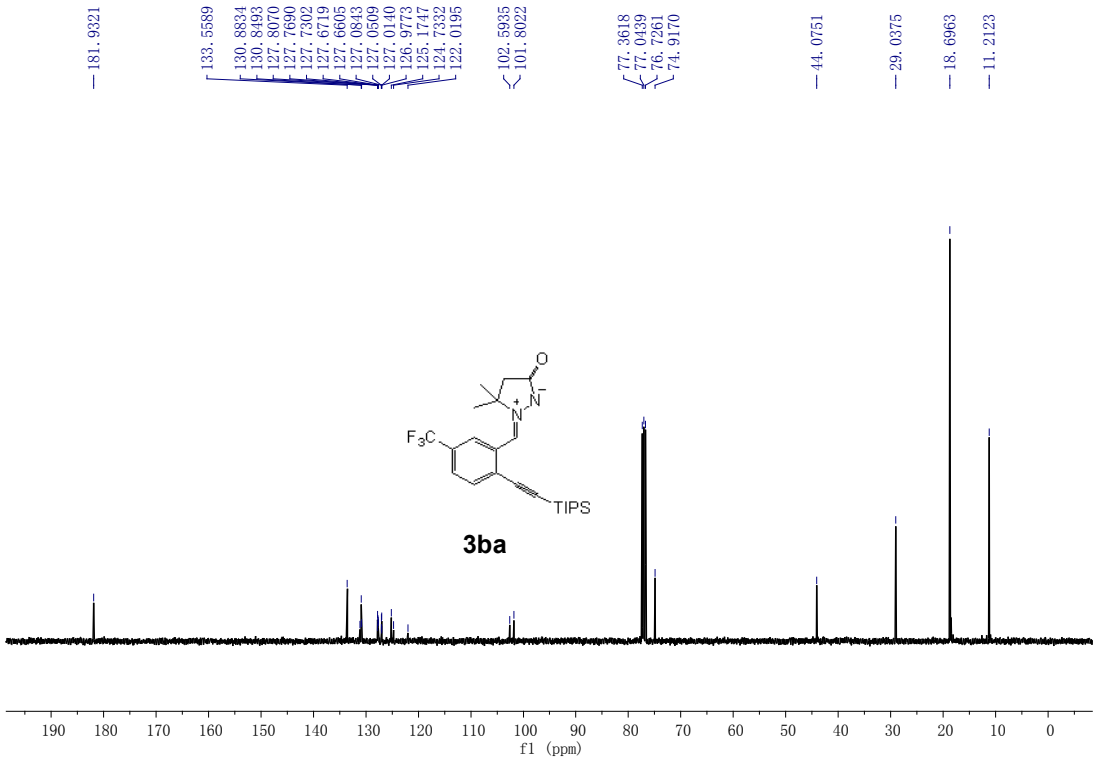
2.02
6.03
21.09
f1 (ppm)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130.8493
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127.6605
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127.0509
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122.0195
102.5935
101.8022
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77.0439
76.7261
74.9170
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29.0375
18.6963
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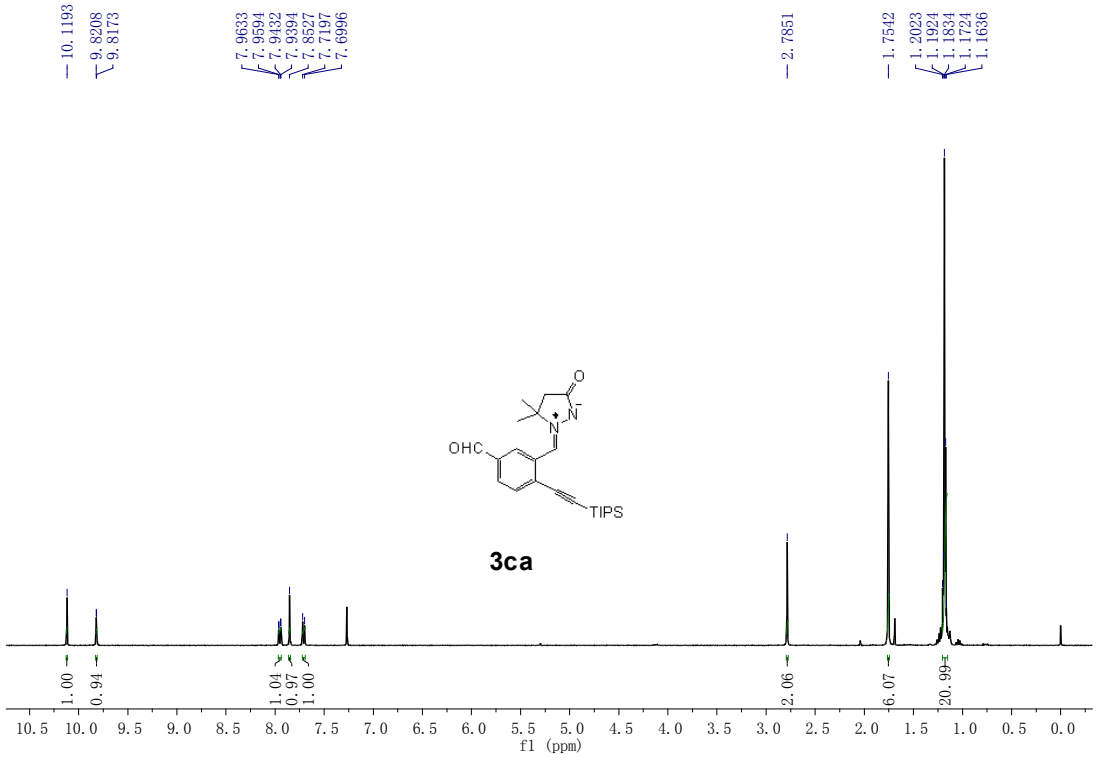
N
N
F3C
TIPS
3ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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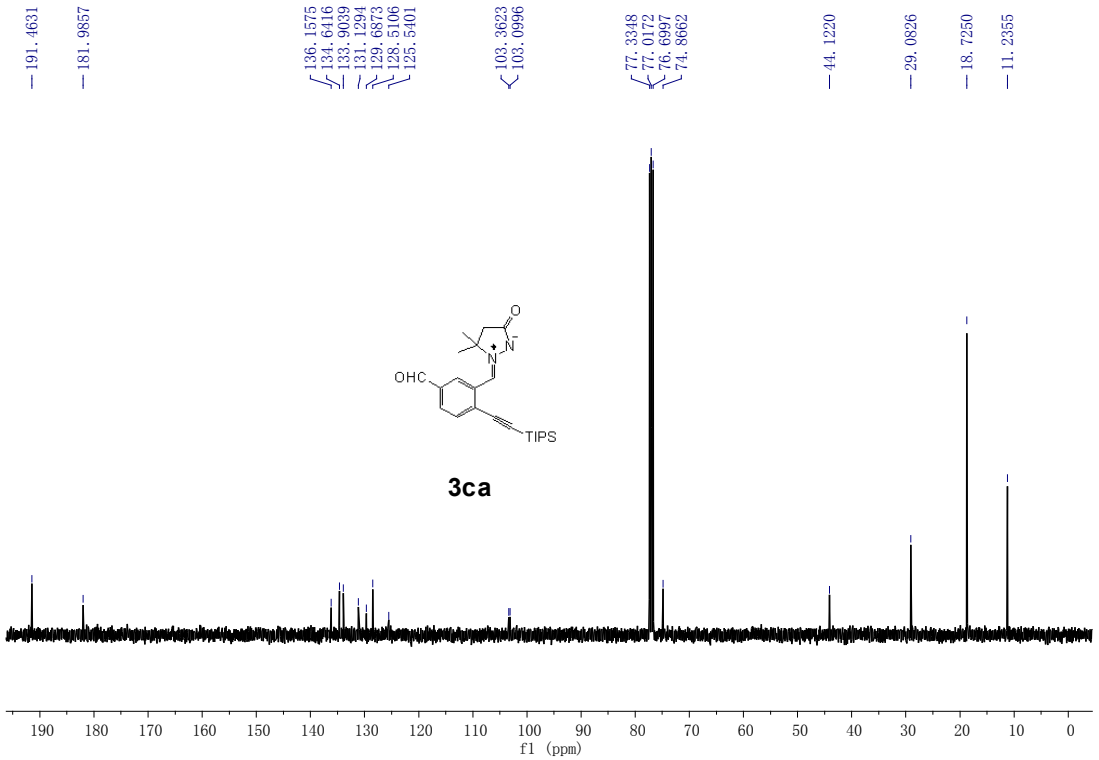
1.7542
1.2023
1.1924
1.1834
1.1724
1.1636
O
N
N
OHC
TIPS
3ca
1.00
0.94
1.04
0.97
1.00
2.06
6.07
20.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.6873
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125.5401
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77.3348
77.0172
76.6997
74.8662
44.1220
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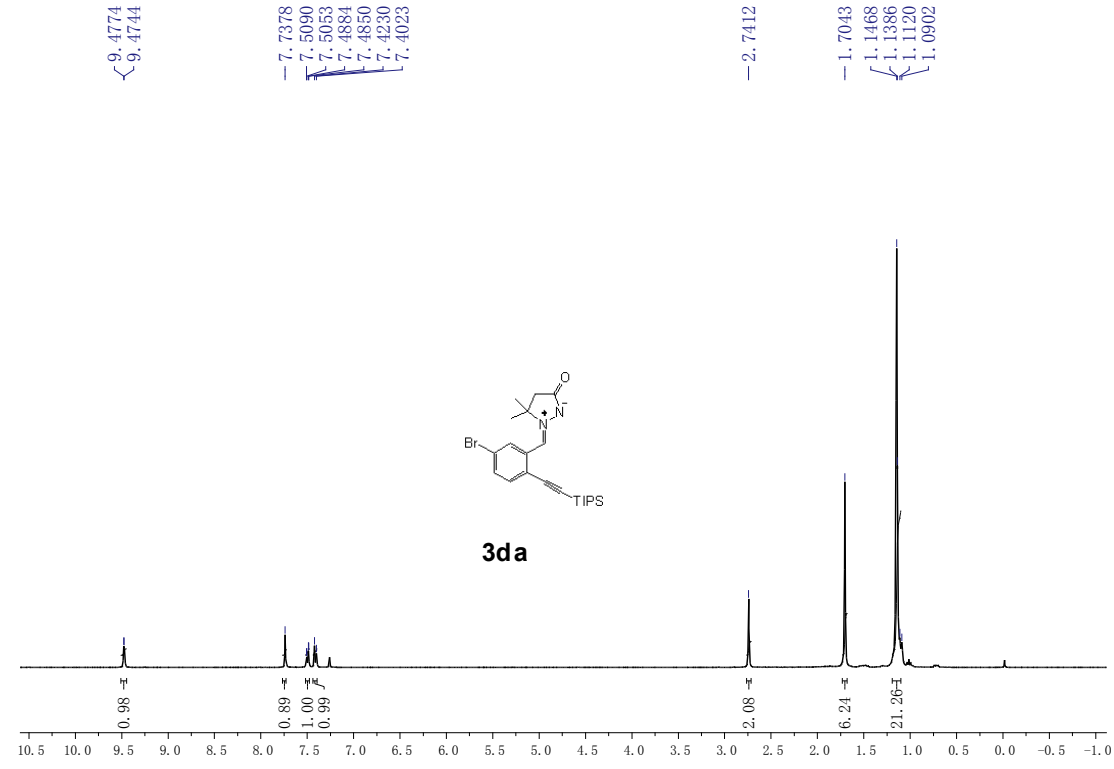
11.2355
OHC
TIPS
3ca
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5053
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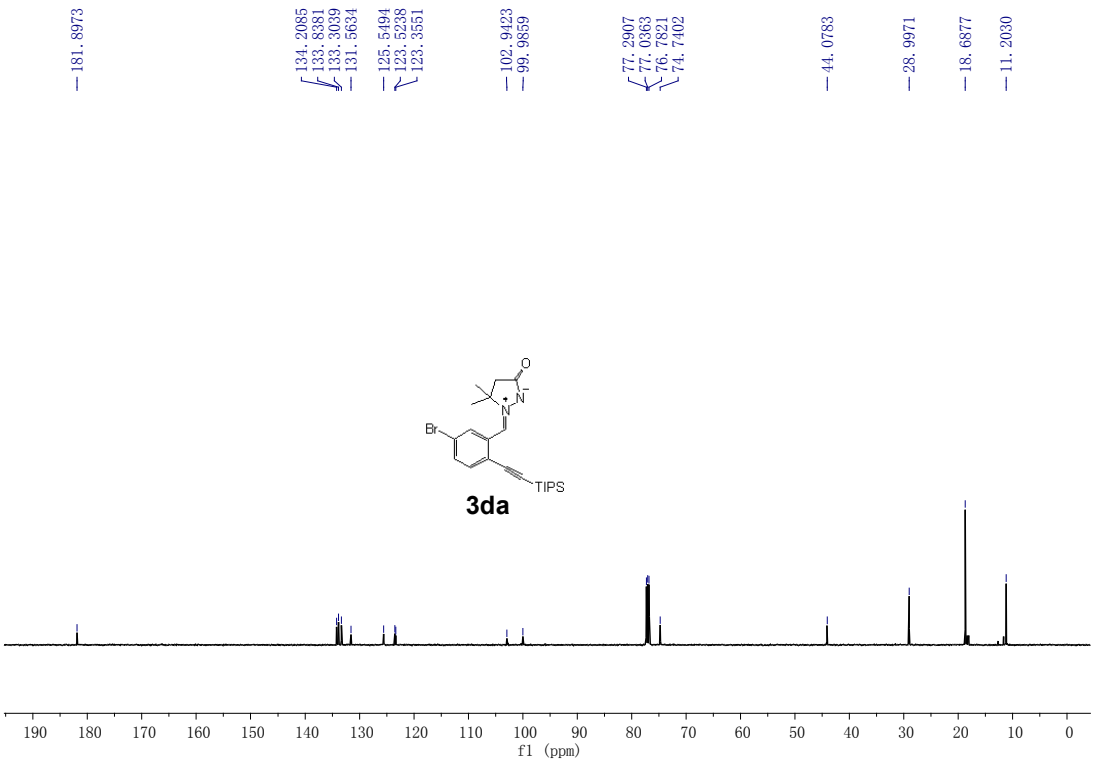
7.4023
2.7412
1.7043
1.1468
1.1386
1.1120
1.0902
Br
TIPS
3da
0.98
0.89
1.00
0.99
2.08
6.24
21.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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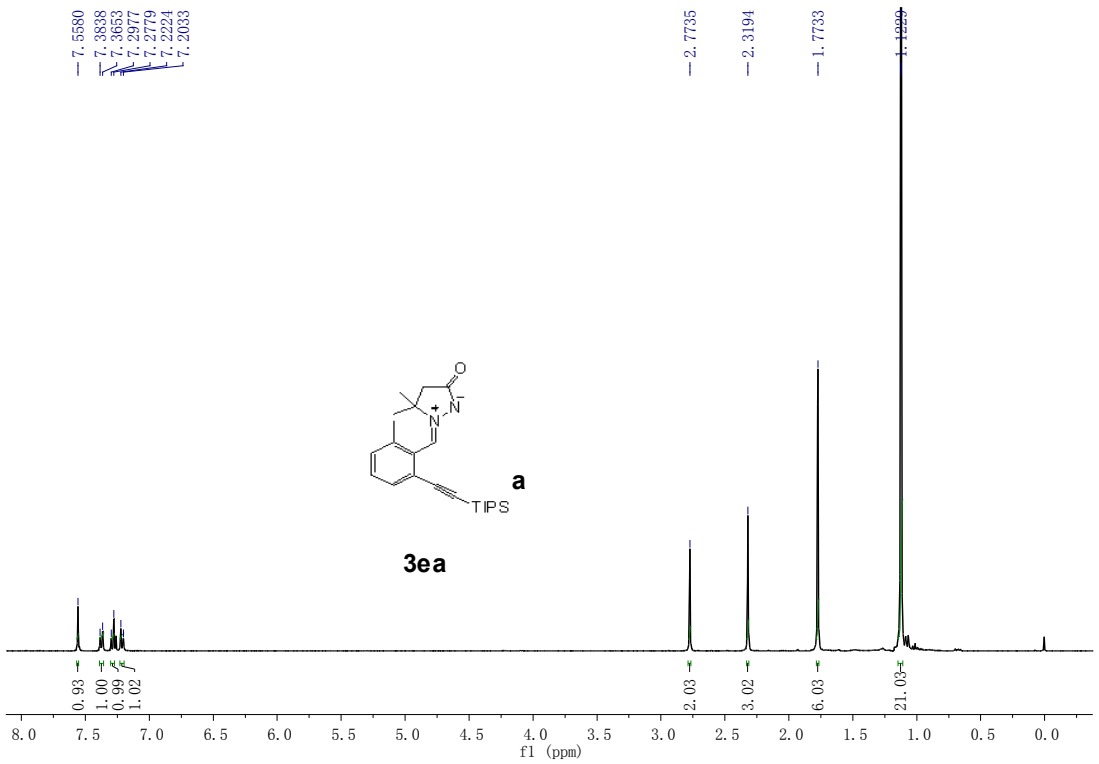
77.0363
76.7821
74.7402
44.0783
28.9971
18.6877
11.2030
O
N
Br
TIPS
3da
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.2033
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2.3194
1.7733
1.1290
O
N
a
TIPS
3ea
0.93
1.00
0.99
1.02
2.03
3.02
6.03
21.03
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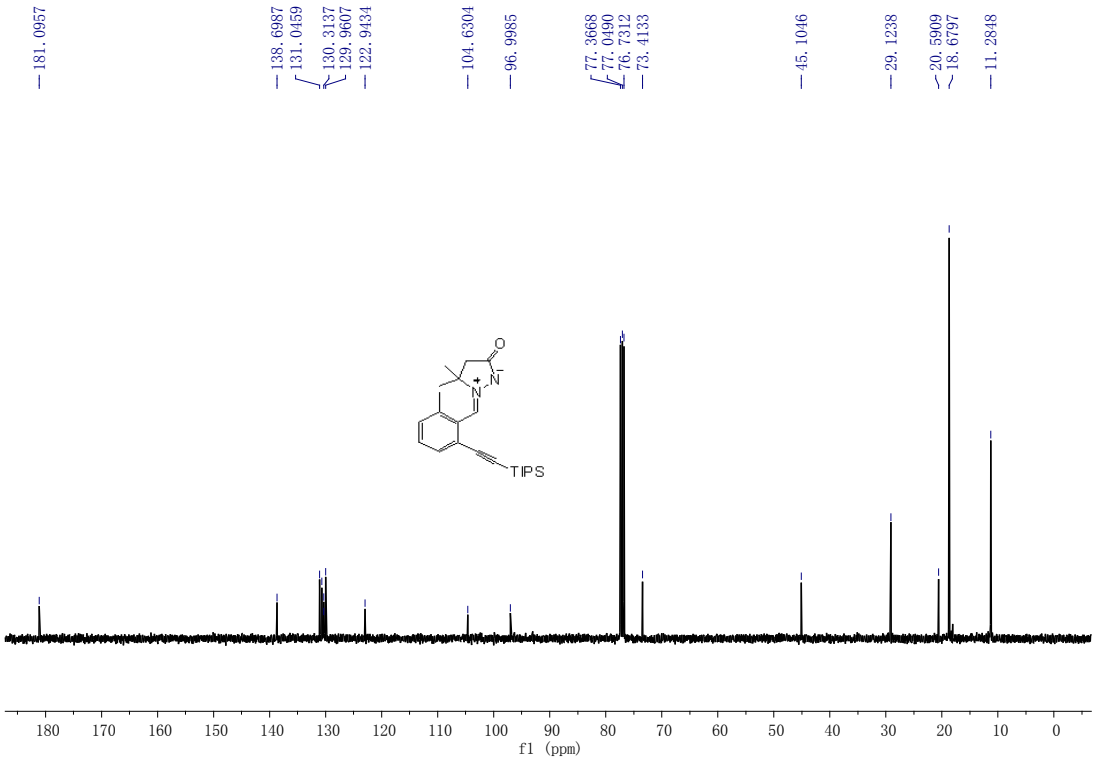
f1 (ppm)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29.1238
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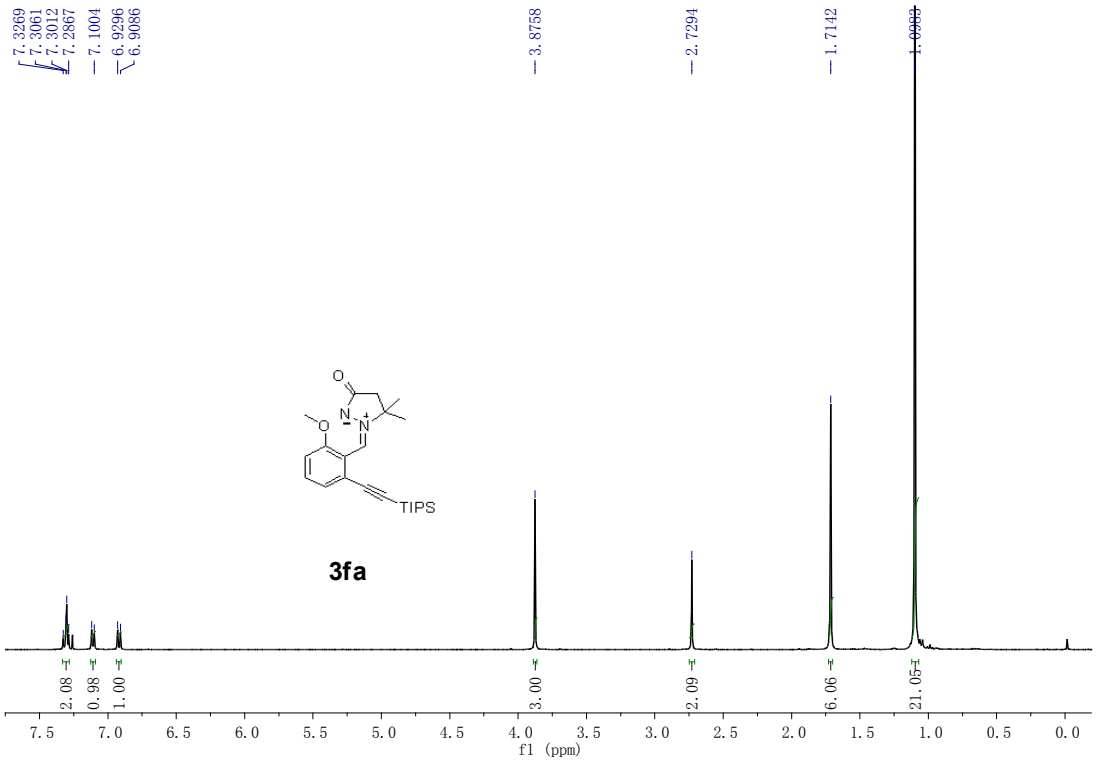
TIPS
f1 (ppm)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6.9086
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TIPS
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1.00
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2.09
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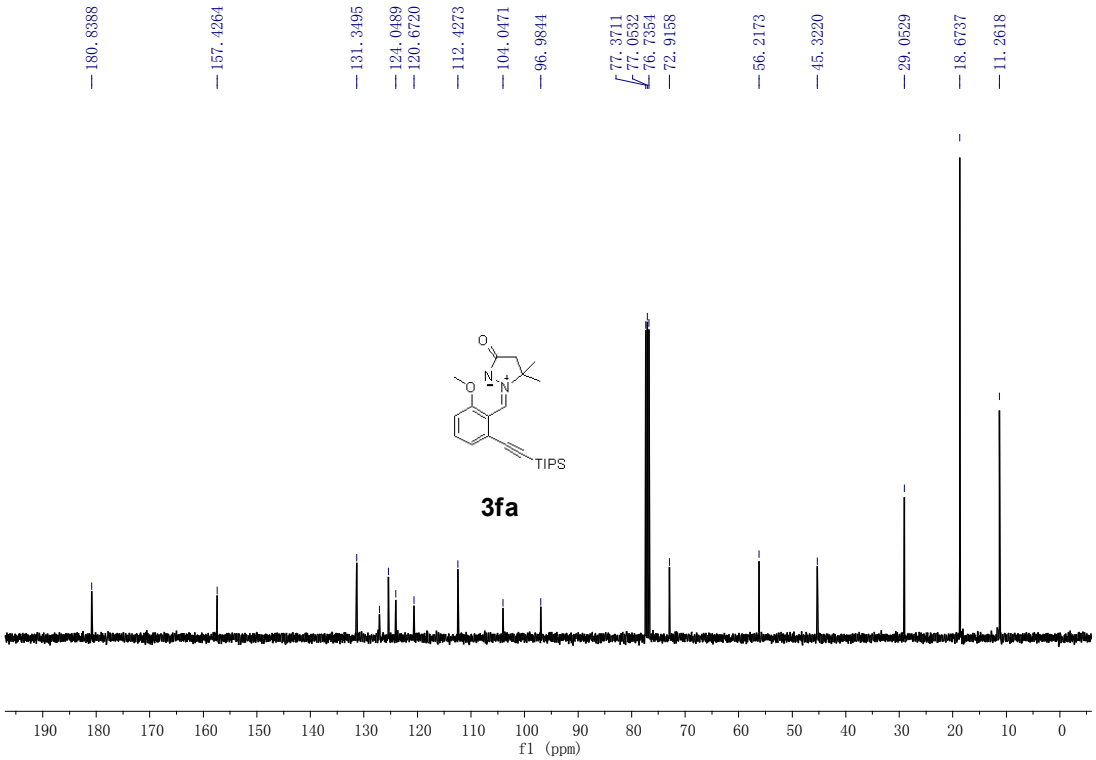
21.05
f1 (ppm)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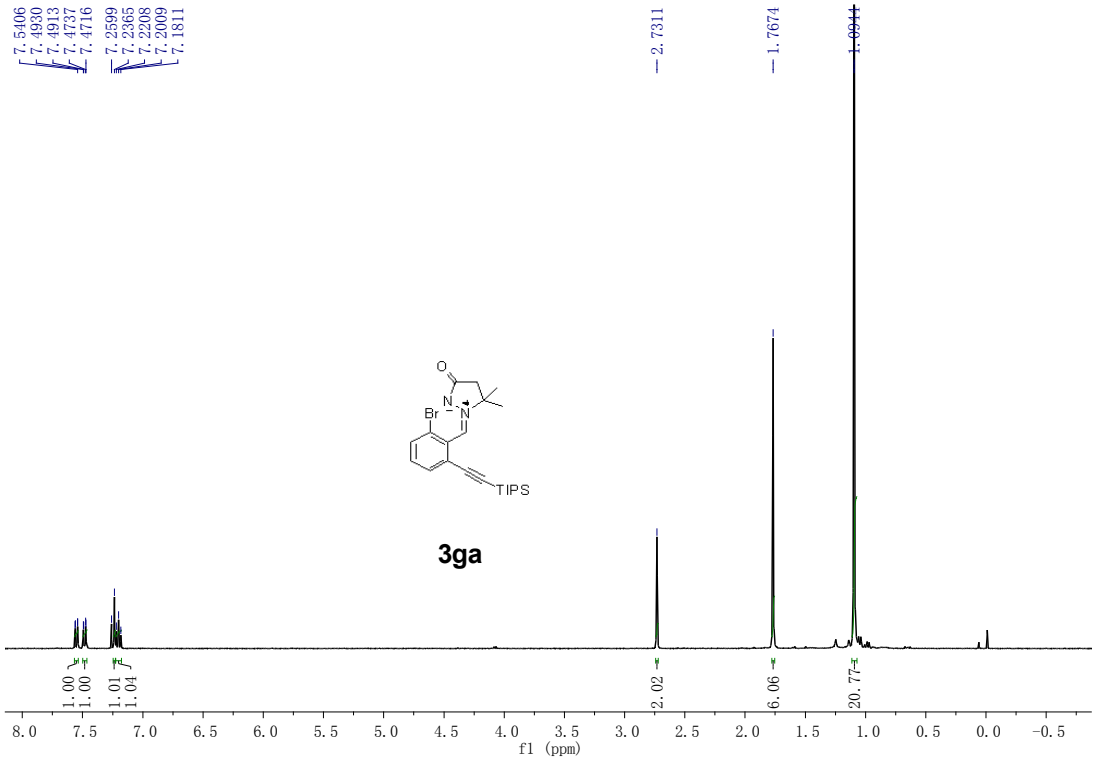
45.3220
29.0529
18.6737
11.2618
TIPS
3fa
f1 (ppm)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7.2009
7.1811
2.7311
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TIPS
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2.02
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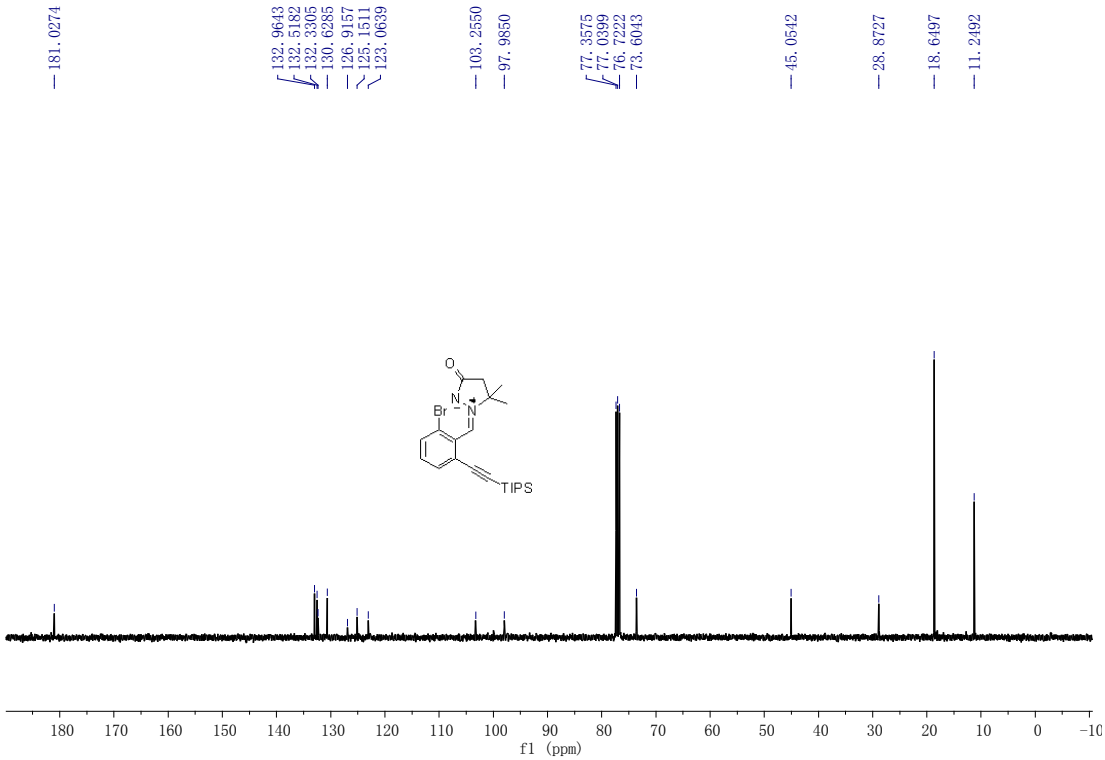
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77.3575
77.0399
76.7222
73.6043
45.0542
28.8727
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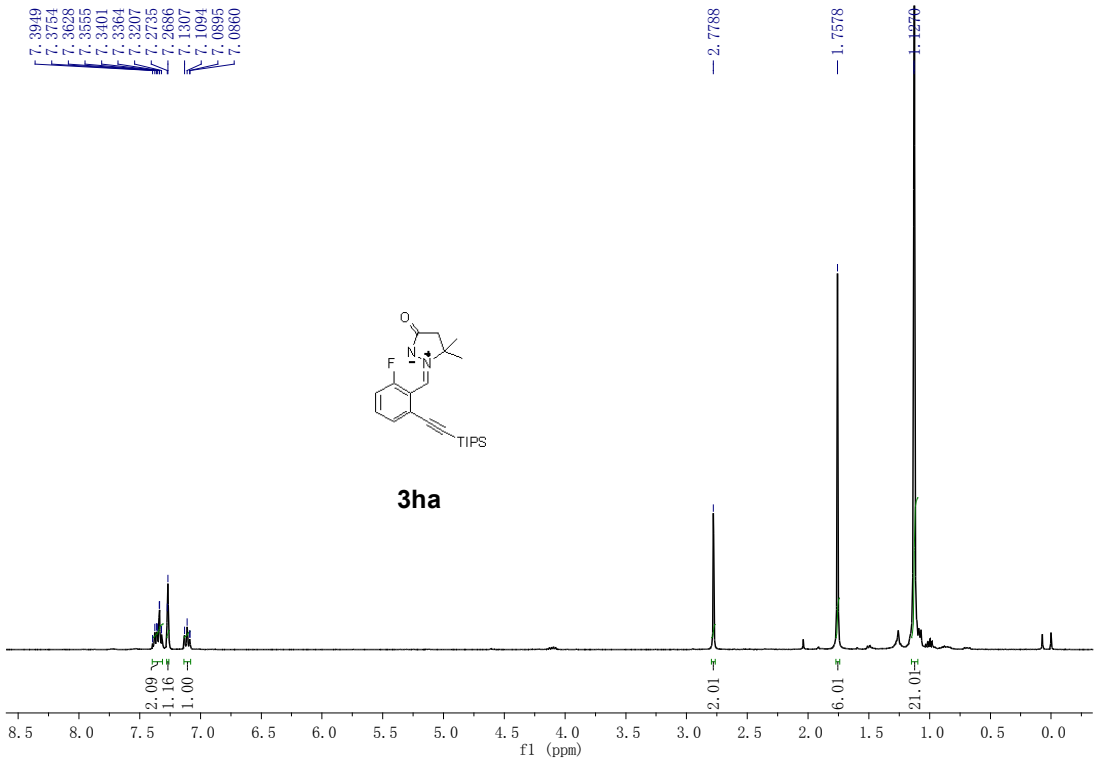
O
N
N
Br
TIPS
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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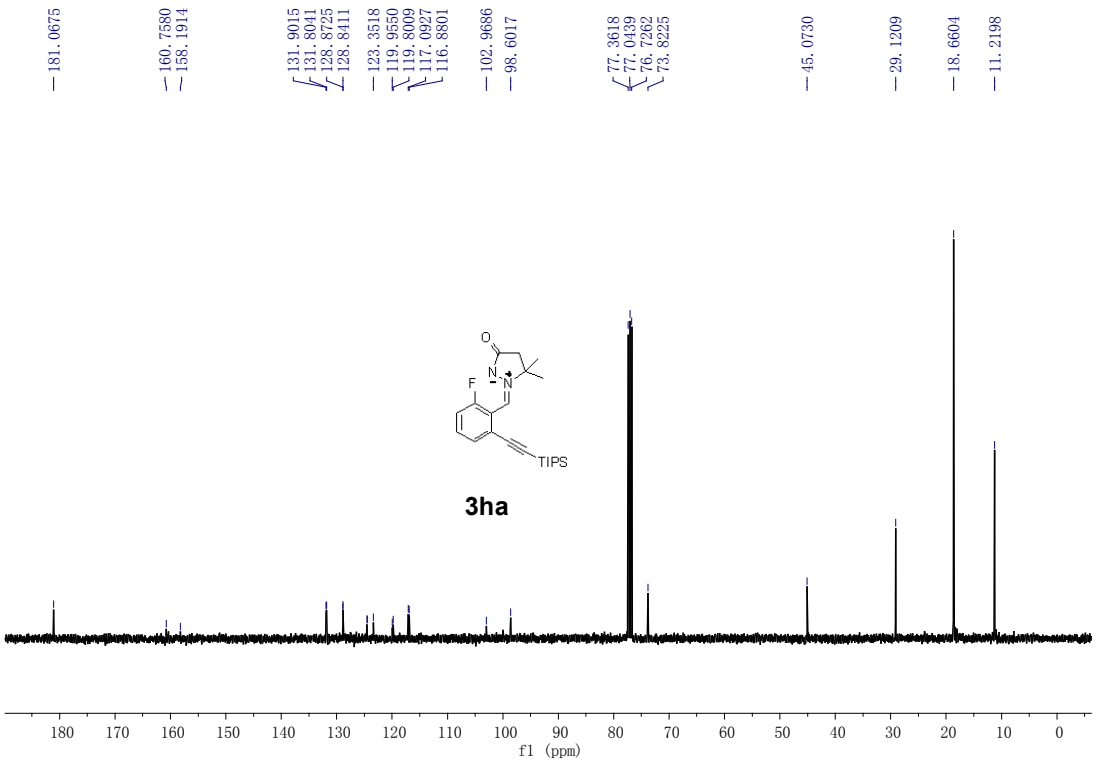
7.1094
7.0895
7.0860
2.7788
1.7578
1.1970
O
N
N
F
TIPS
2.09
1.16
1.00
2.01
6.01
21.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ha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102.9686
98.6017
77.3618
77.0439
76.7262
73.8225
45.0730
29.1209
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O
N
F
N
TIPS
3ha
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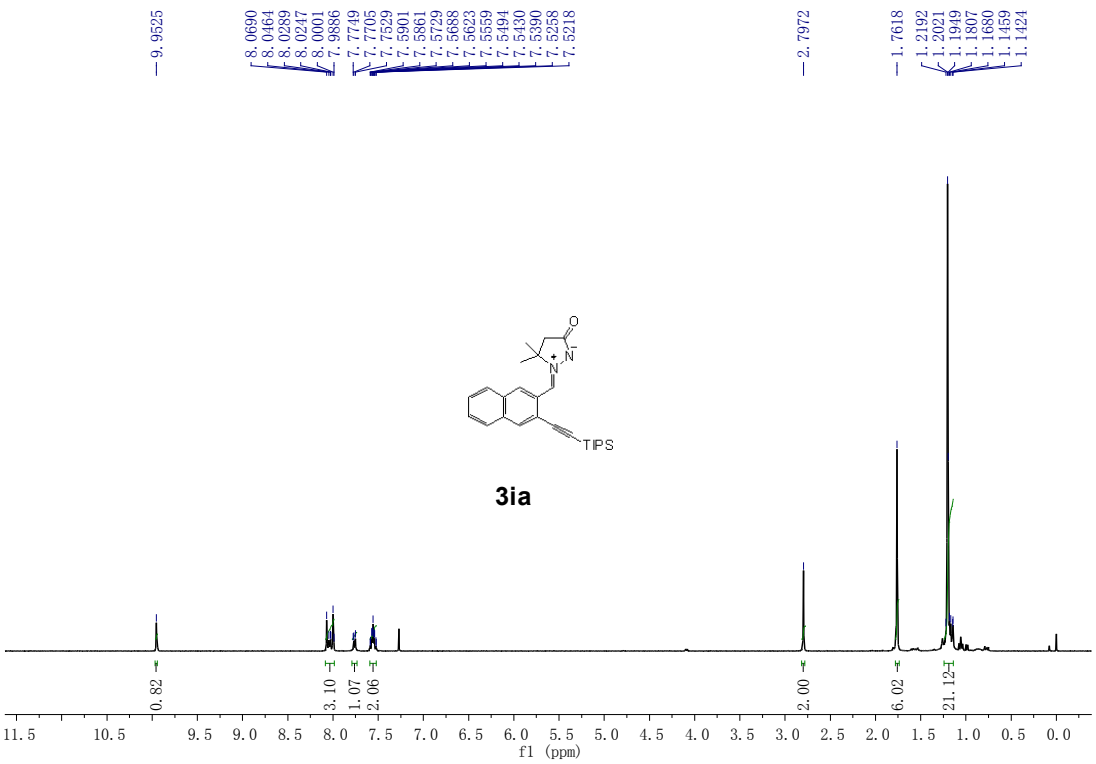
f1 (ppm)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7.5623
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7.5494
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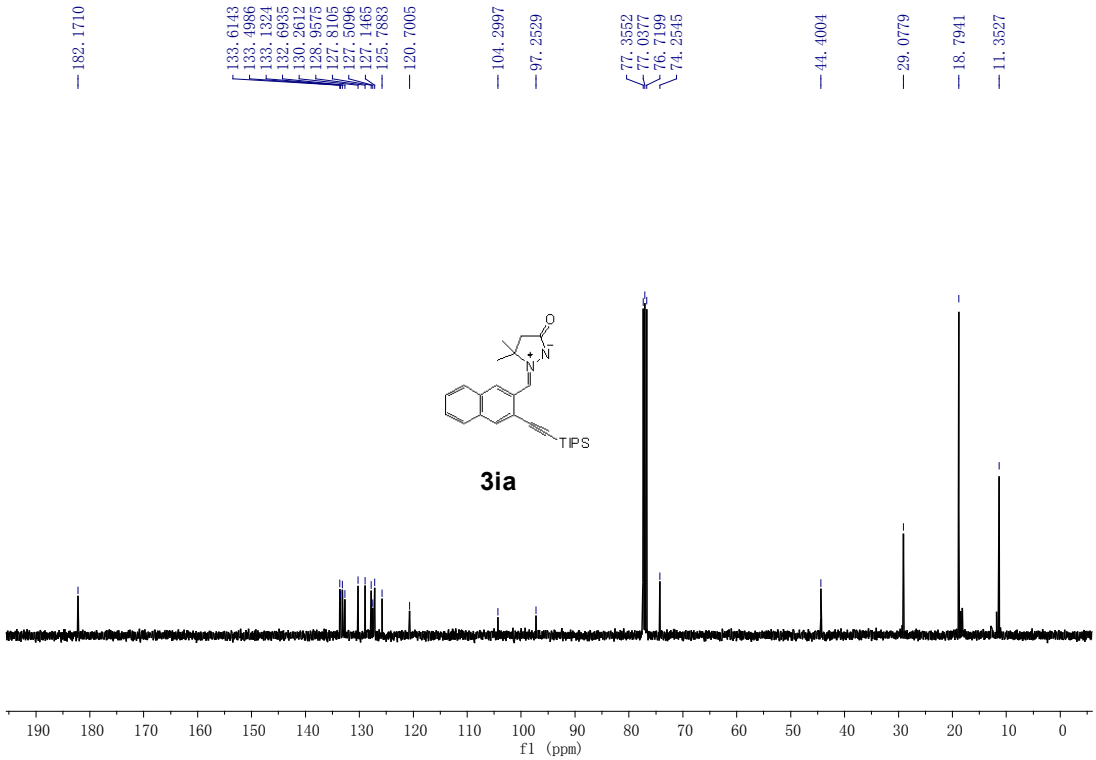
1.1680
1.1459
1.1424
O
N
N
TIPS
3ia
0.82
3.10
1.07
2.06
2.00
6.02
21.12
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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104.2997
97.2529
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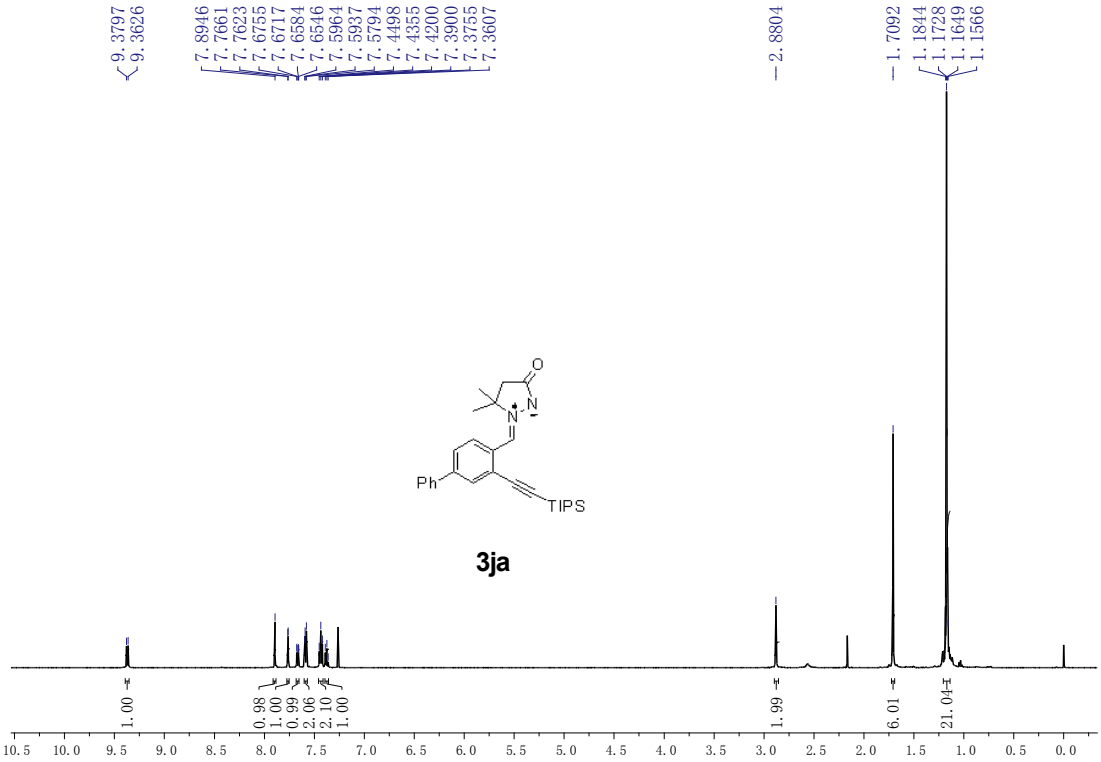
74.2545
44.4004
29.0779
18.7941
11.3527
TIPS
3ia
f1 (ppm)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7.5794
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7.3755
7.3607
2.8804
1.7092
1.1844
1.1728
1.1649
1.1566
Ph
TIPS
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0.98
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2.10
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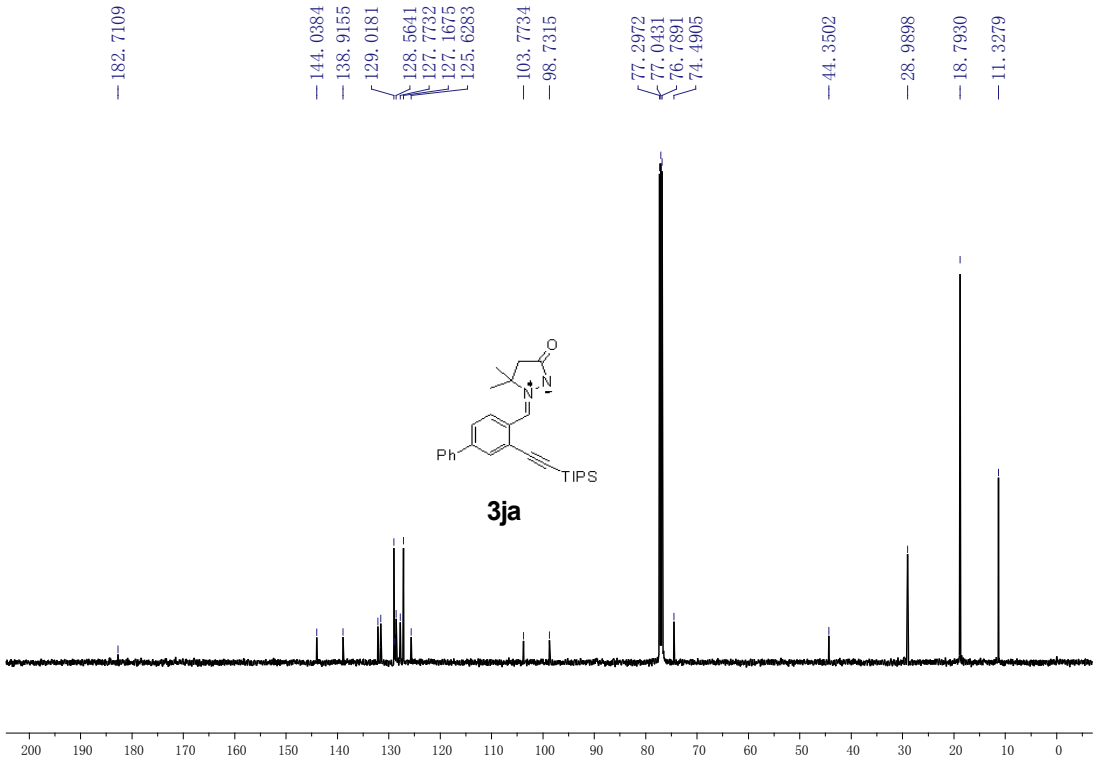
1.99
6.01
21.04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76.7891
74.4905
44.3502
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N
Ph
TIPS
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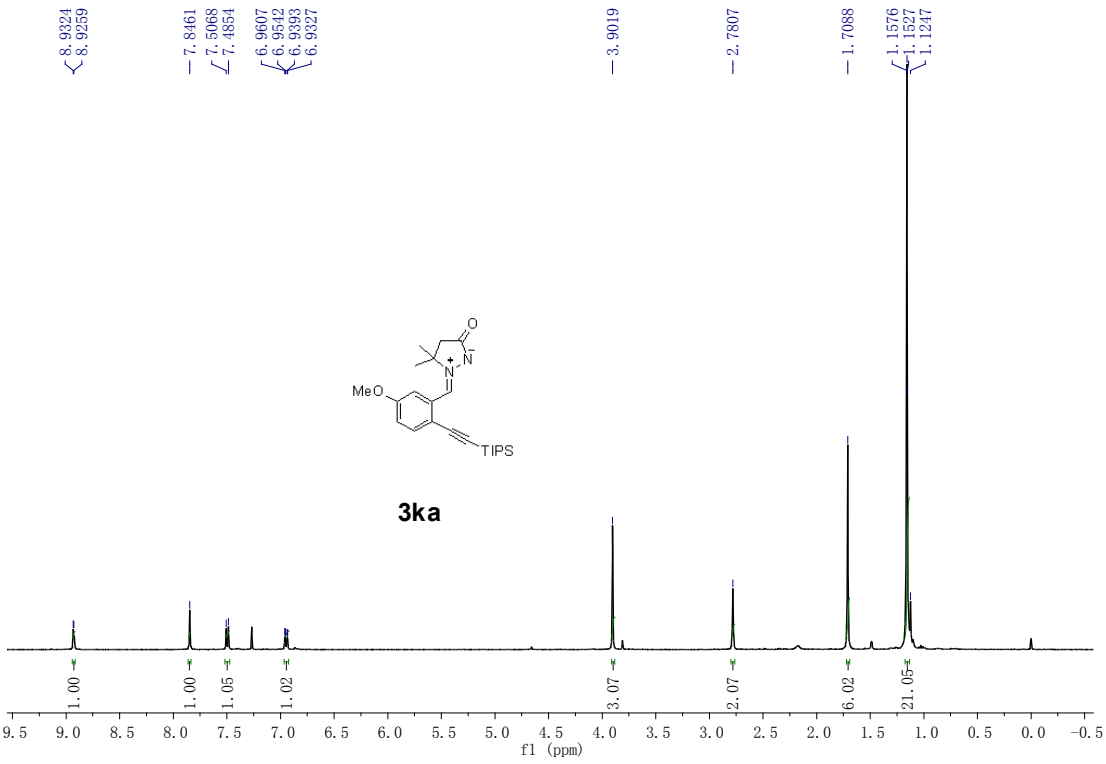
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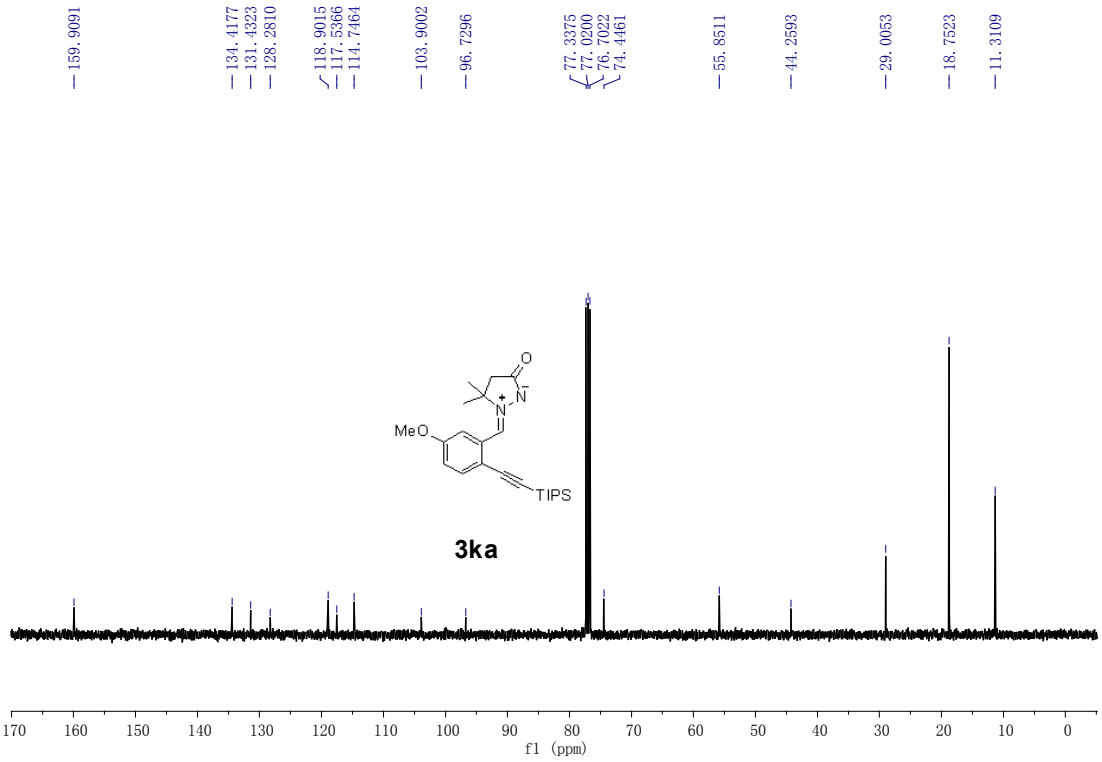
2.7807
1.7088
1.1576
1.1527
1.1247
O
N
MeO
TIPS
3ka
1.00
1.00
1.05
1.02
3.07
2.07
6.02
21.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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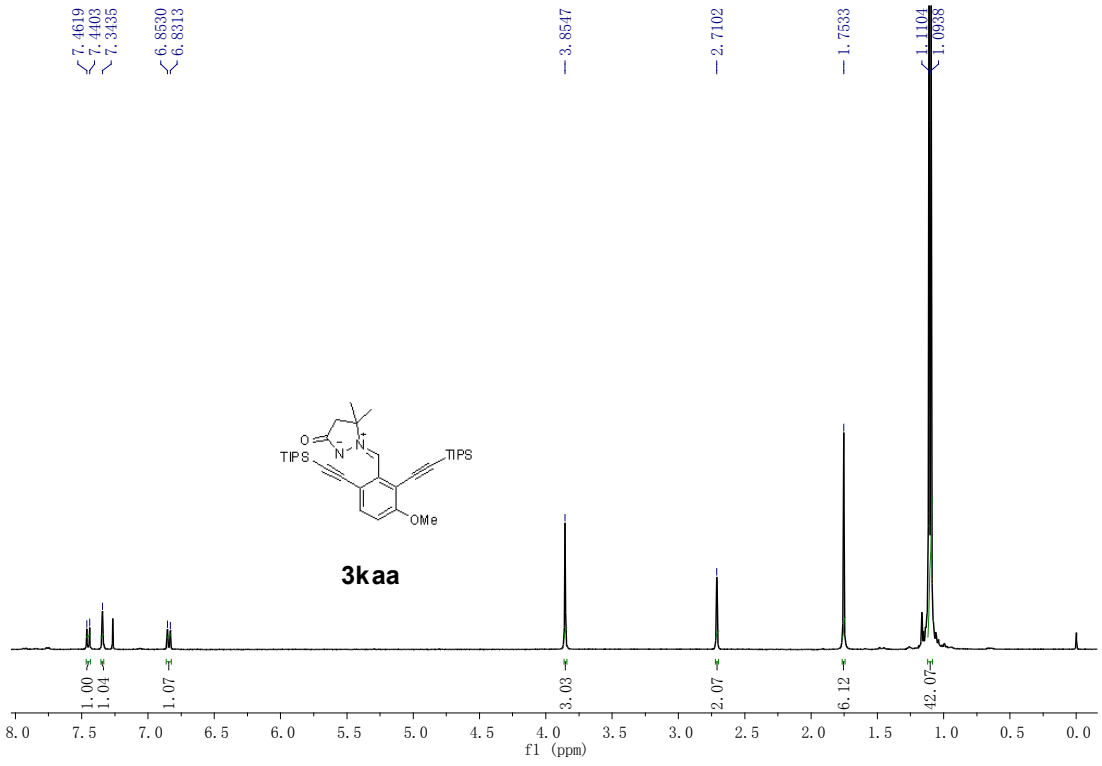
MeO
TIPS
3ka
f1 (ppm)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1.1104
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TIPS
TIPS
OMe
3kaa
1.00
1.04
1.07
3.03
2.07
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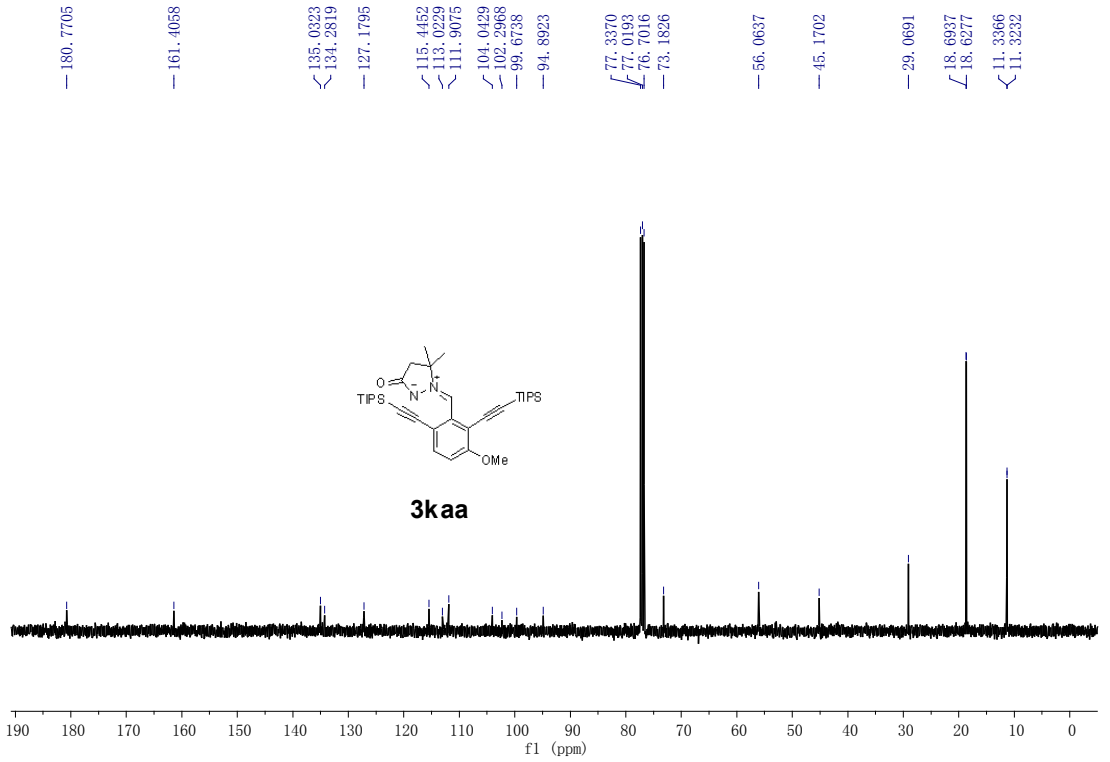
f1 (ppm)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77.0193
76.7016
73.1826
56.0637
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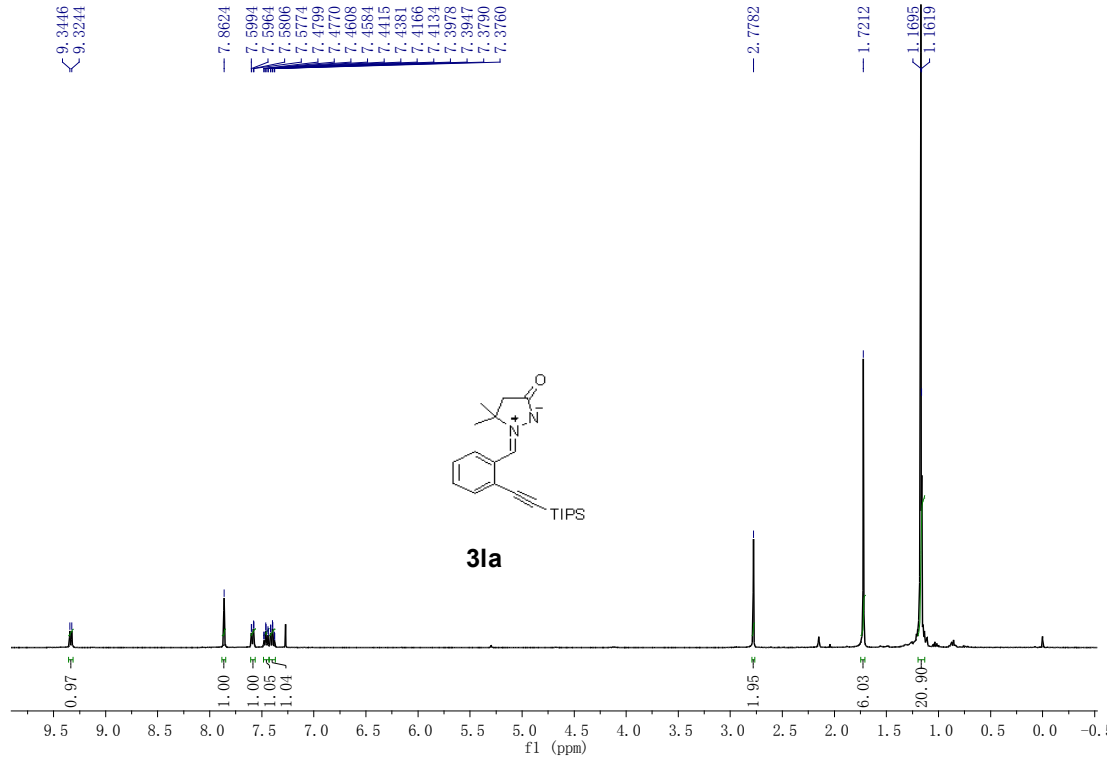
TIPS
TIPS
OMe
3kaa
f1 (ppm)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7.3947
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1.00
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1.95
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20.90
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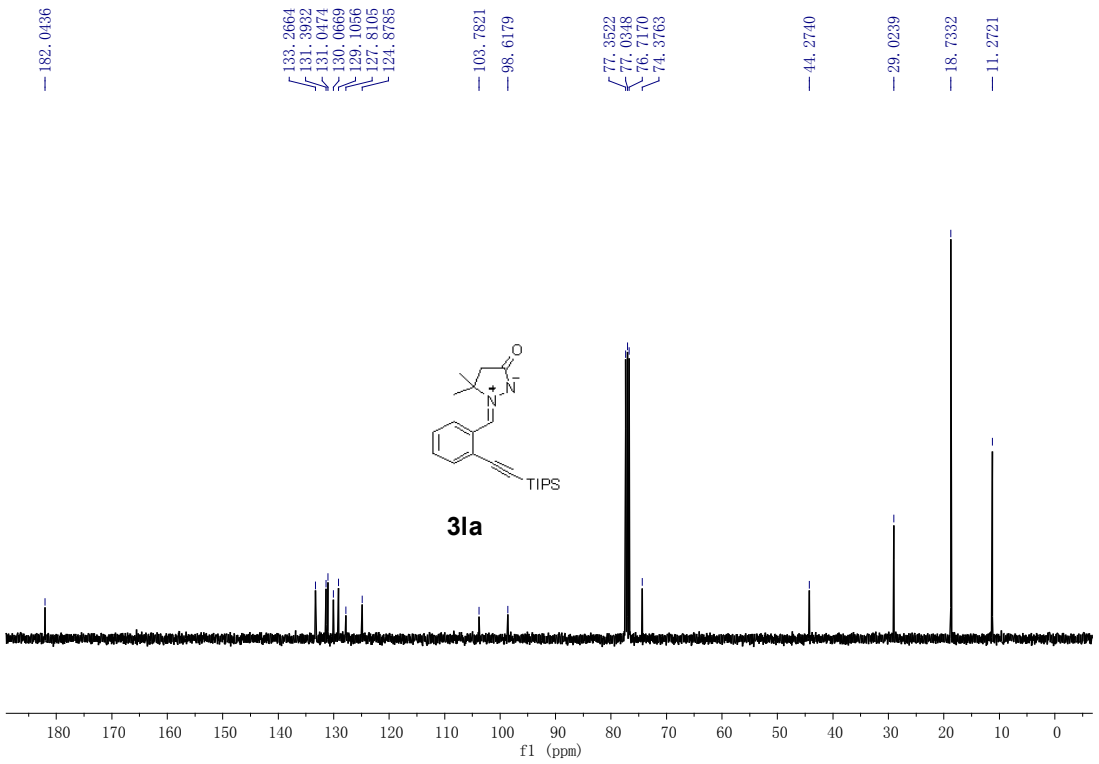
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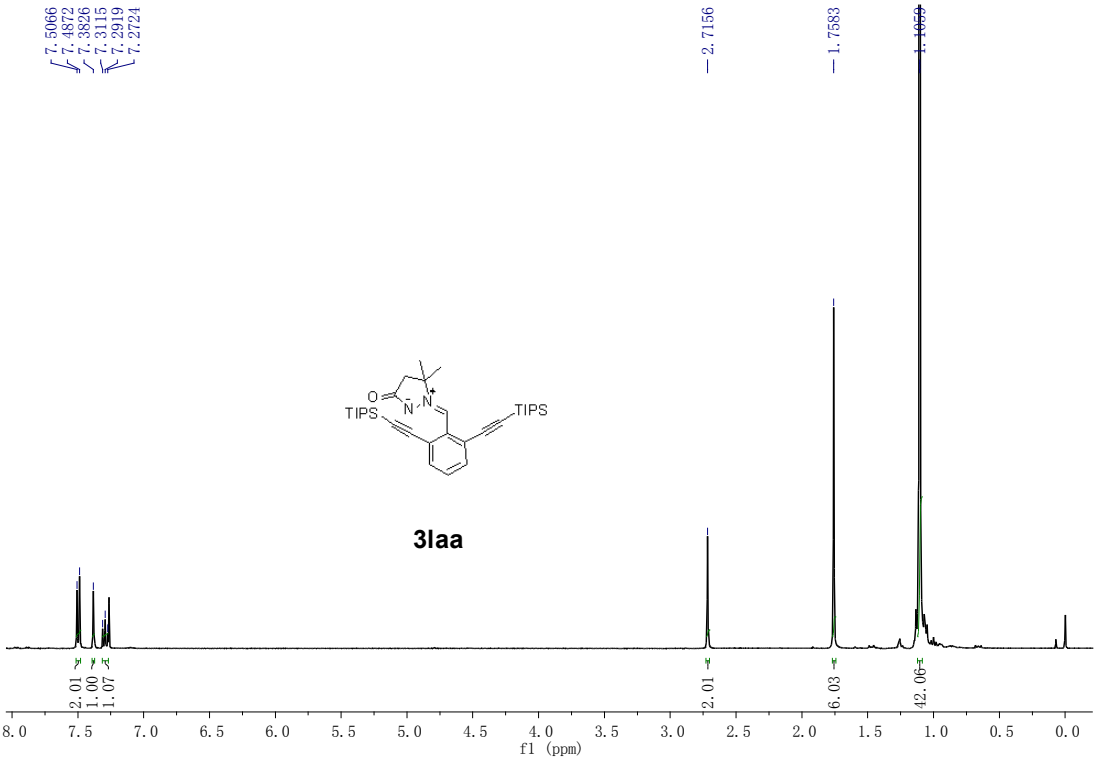
f1 (ppm)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TIPS
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2.01
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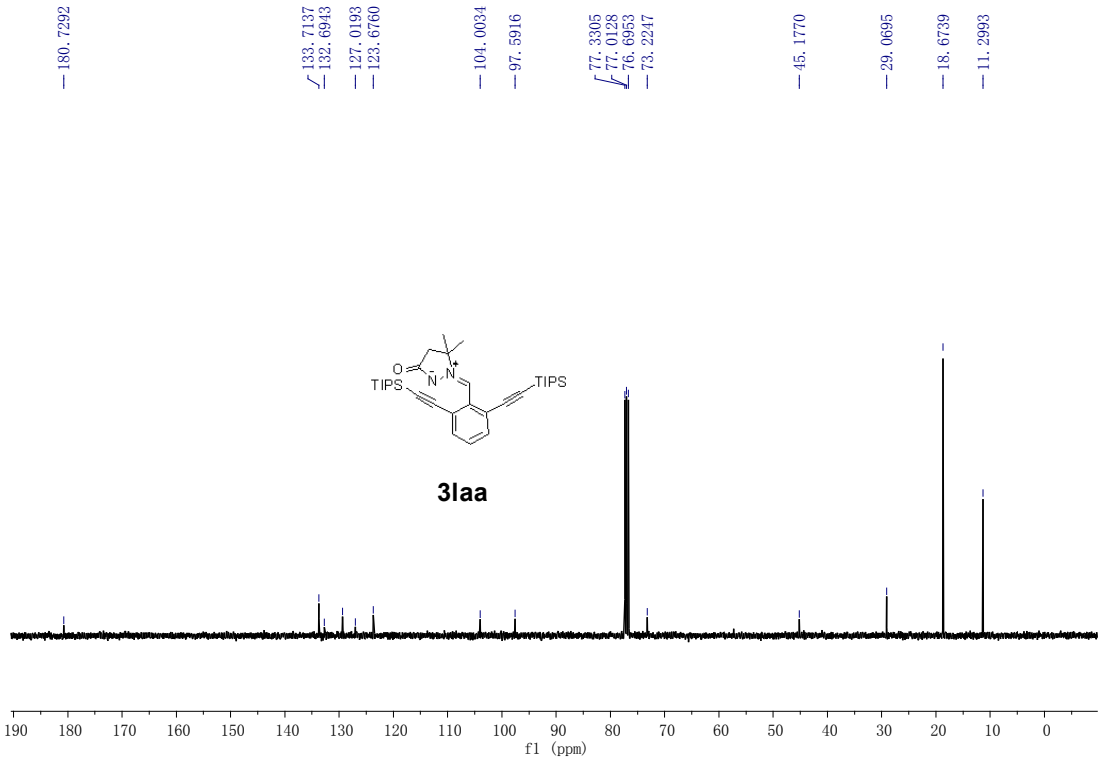
42.06
f1 (ppm)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TIPS
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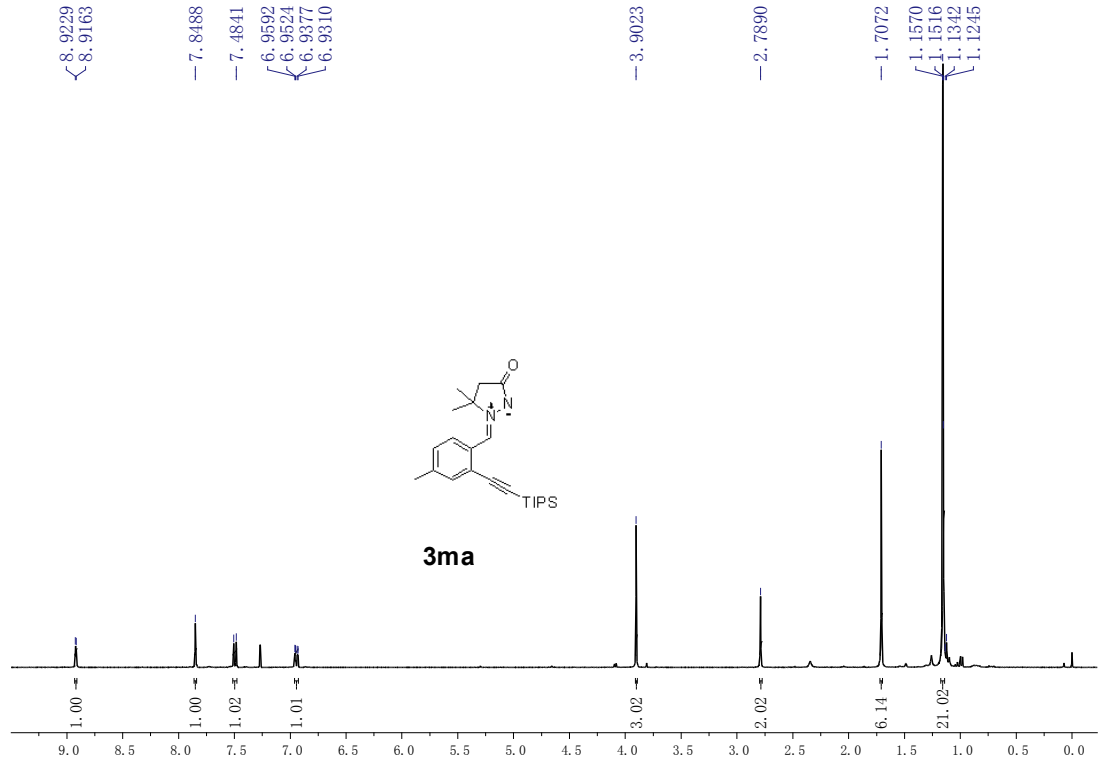
f1 (ppm)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2.7890
1.7072
1.1570
1.1516
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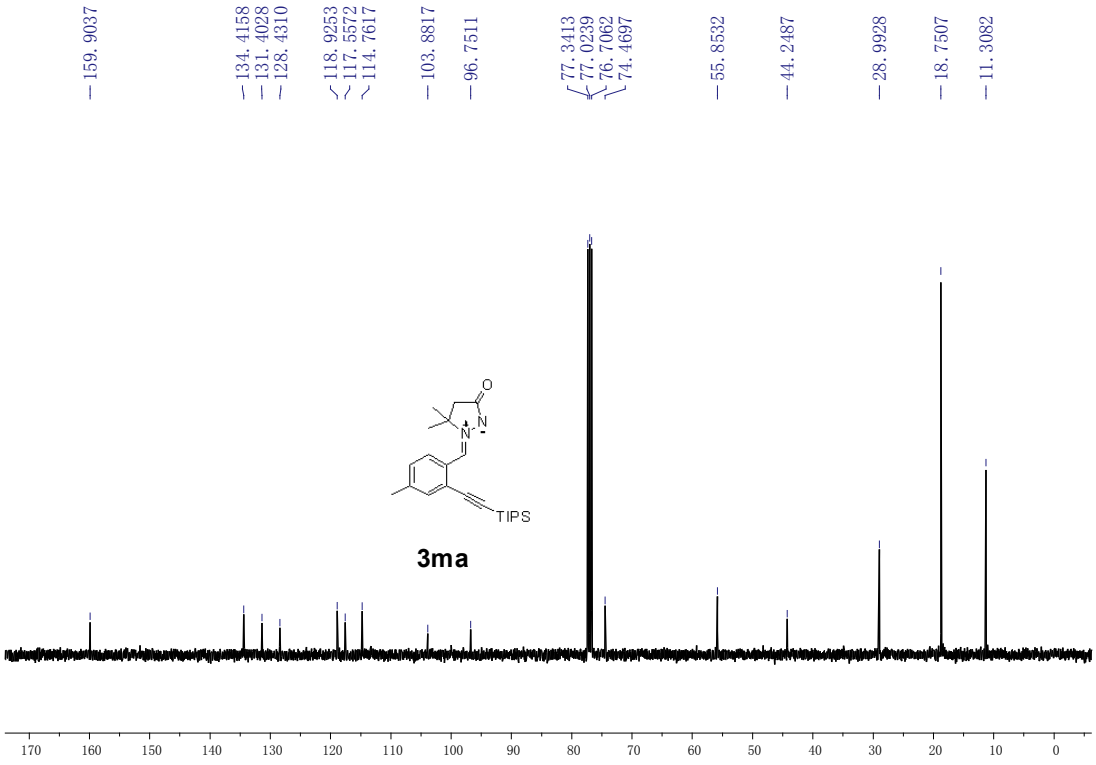
21.02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76.7062
74.4697
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TIPS
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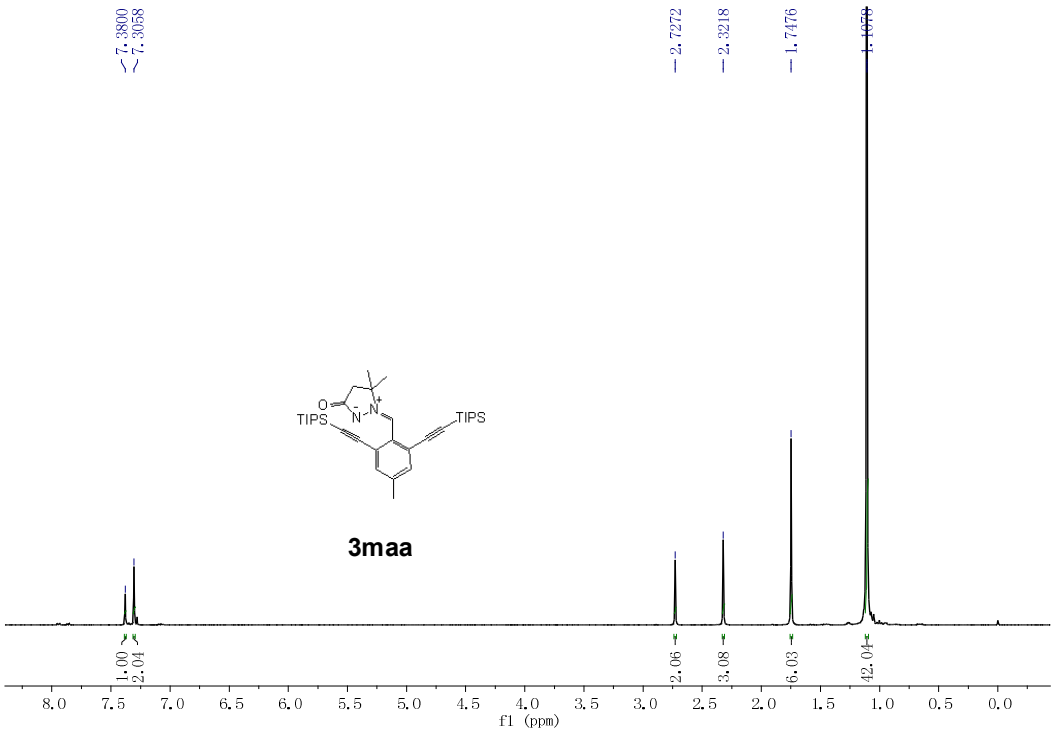
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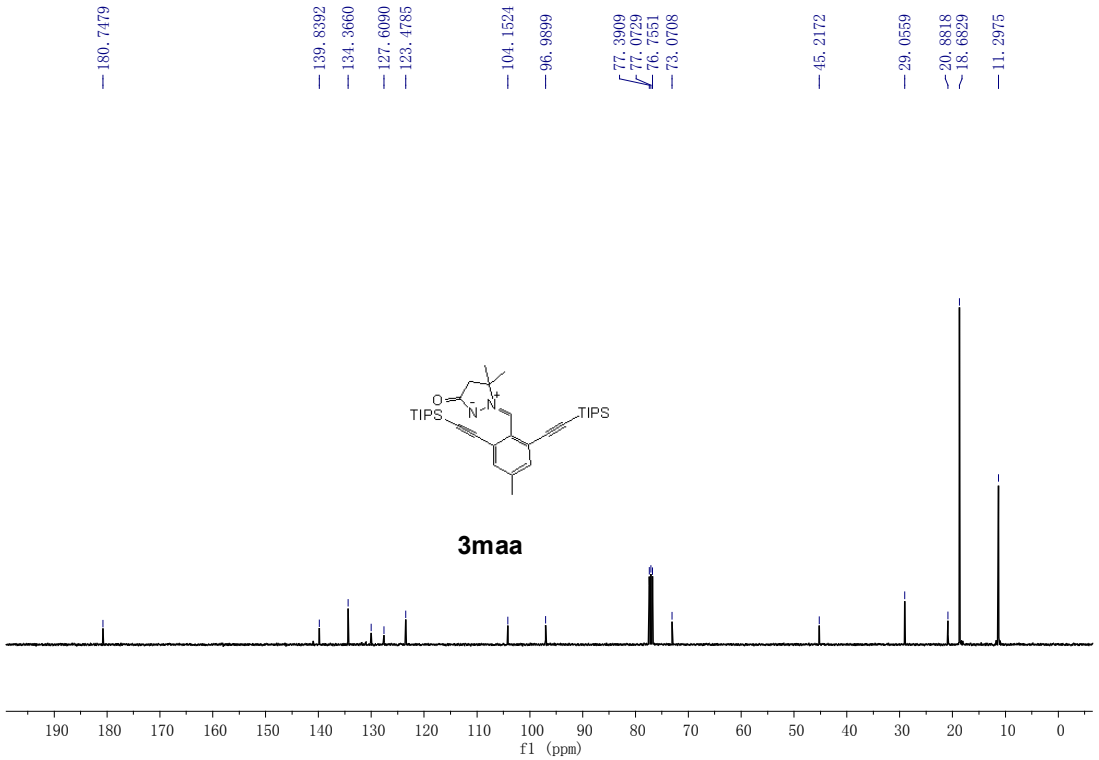
1.1678
TIPS
TIPS
3maa
1.00
2.04
2.06
3.08
6.03
42.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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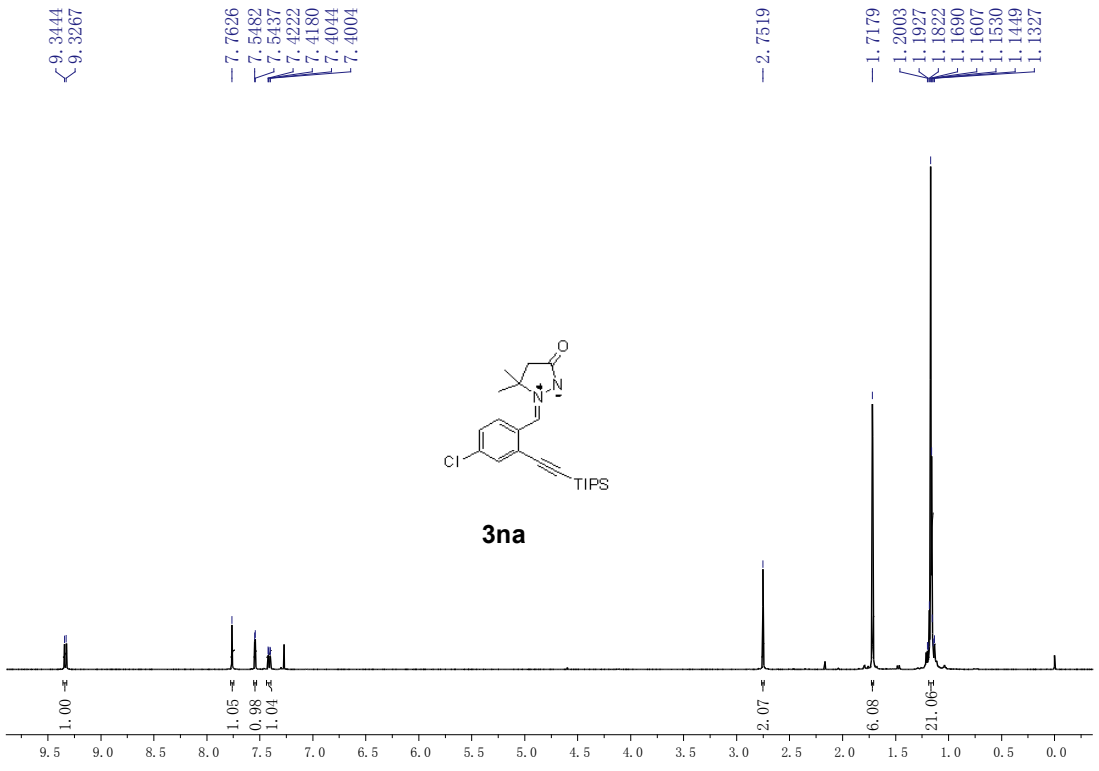
TIPS
3maa
f1 (ppm)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1.1822
1.1690
1.1607
1.1530
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Cl
TIPS
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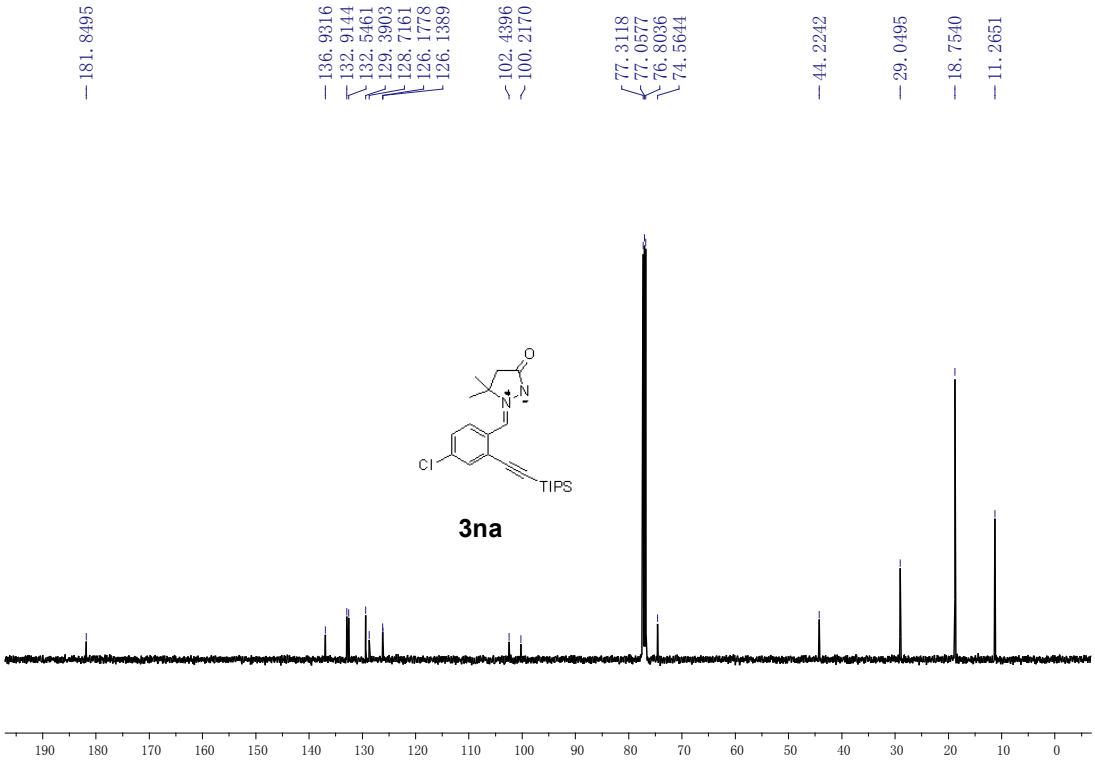
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74.5644
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29.0495
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11.2651
O
N
N
Cl
TIPS
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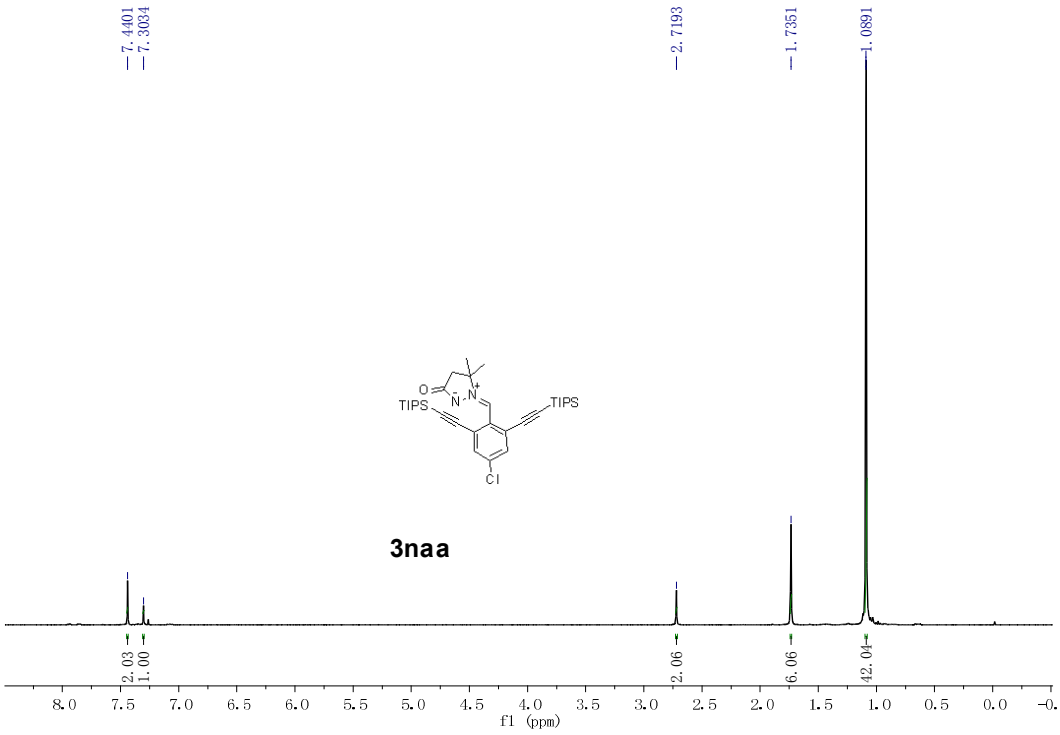
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N
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TIPS
Cl
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1.00
2.06
6.06
42.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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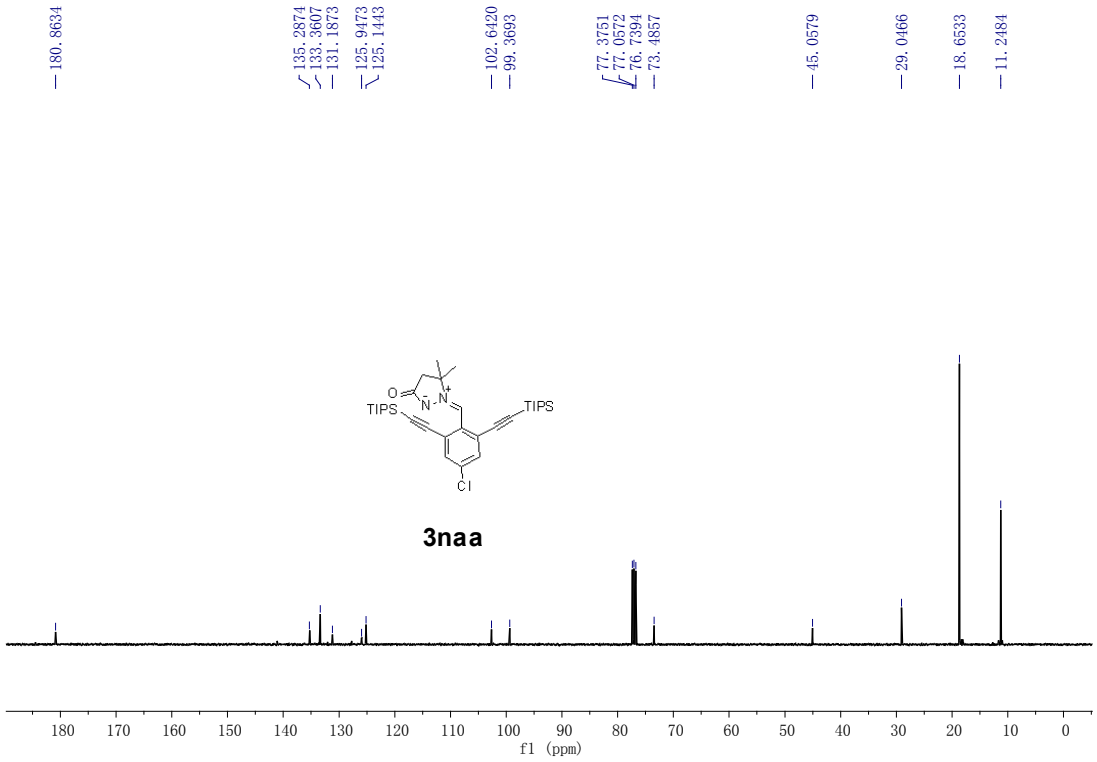
-0.
f1 (ppm)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TIPS
TIPS
Cl
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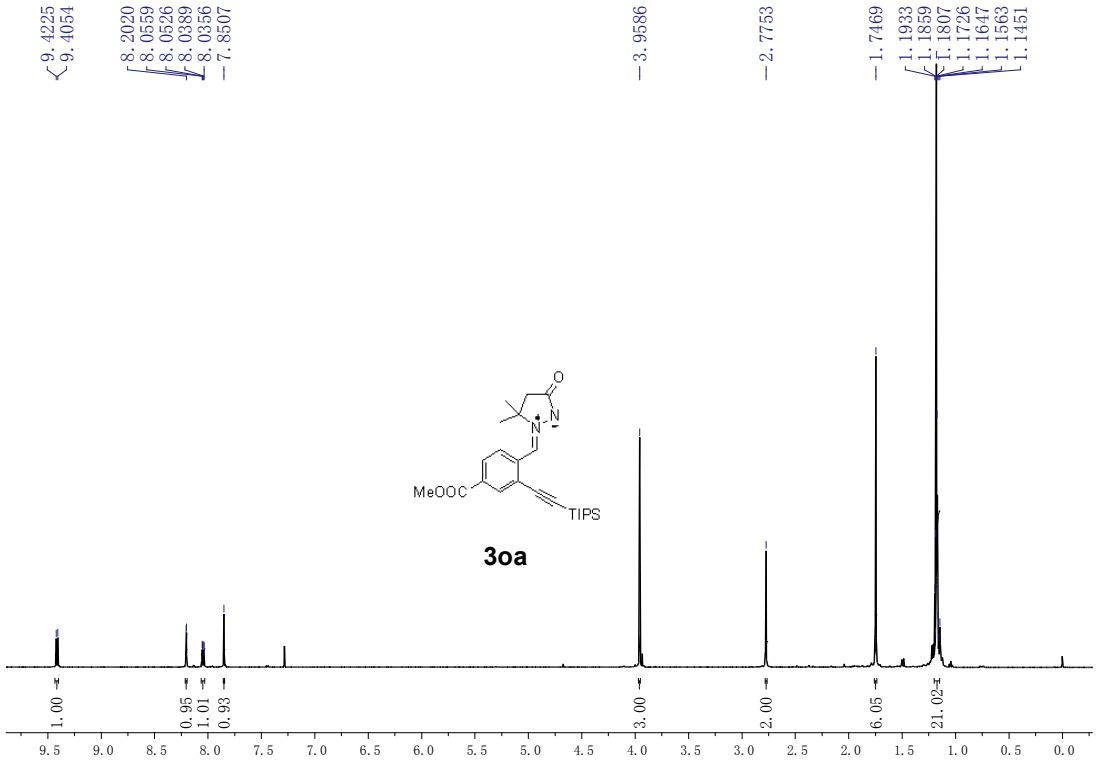
f1 (ppm)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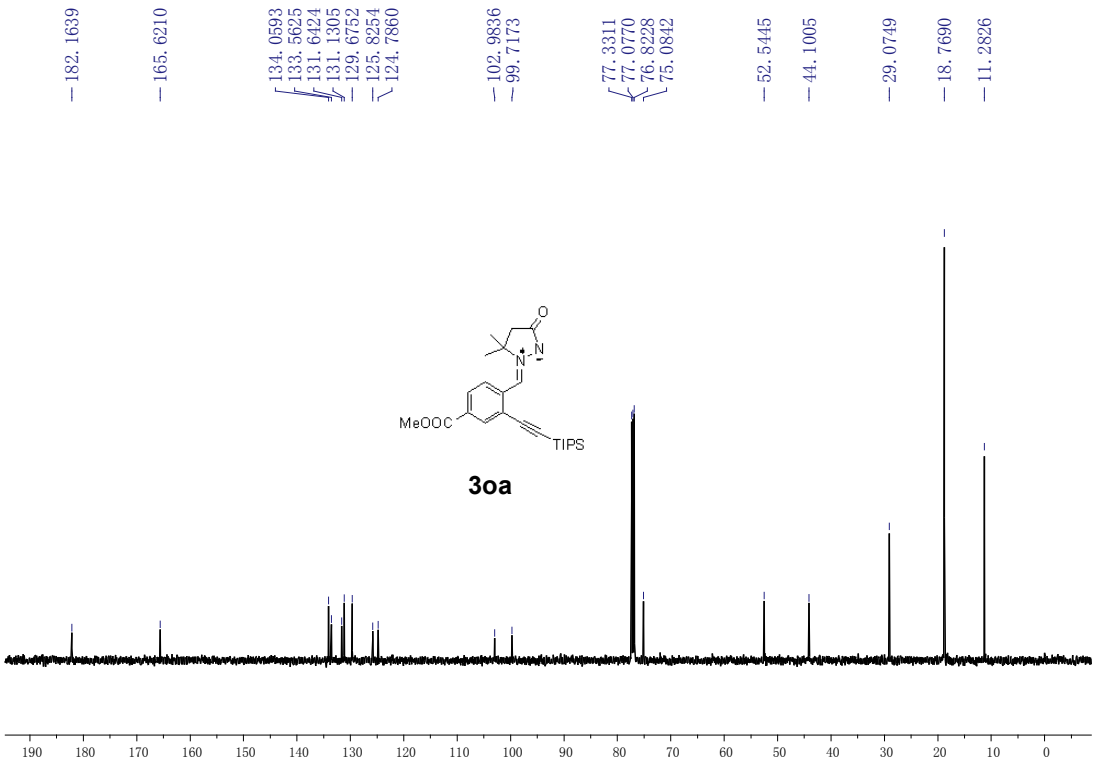
1.1563
1.1451
MeOOC
TIPS
3oa
1.00
0.95
1.01
0.93
3.00
2.00
6.05
21.02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77.0770
76.8228
75.0842
52.5445
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11.2826
MeOOC
TIPS
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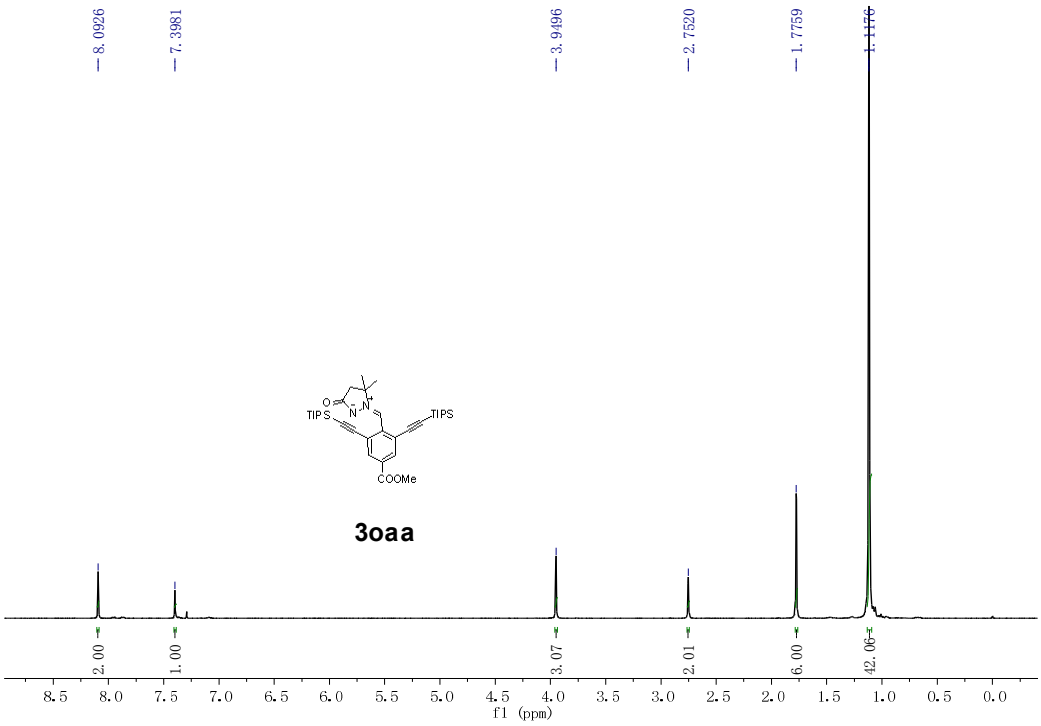
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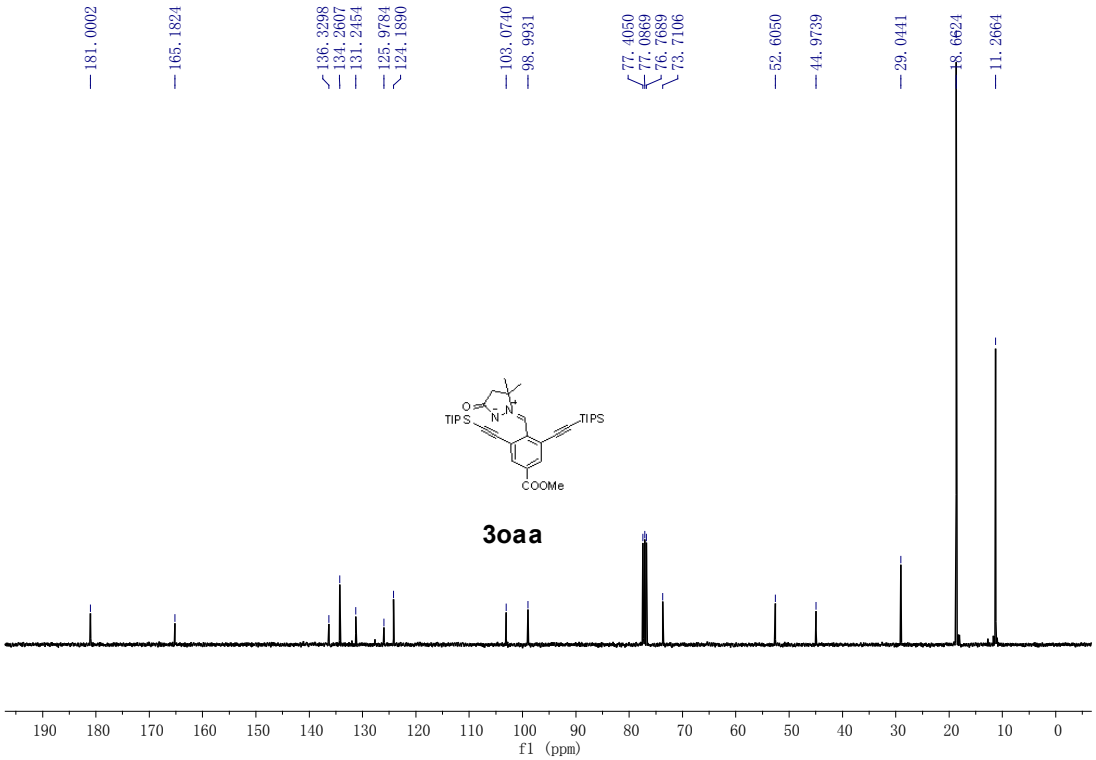
1.1176
TIPS
TIPS
COOMe
3oaa
2.00
1.00
3.07
2.01
6.00
42.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.7689
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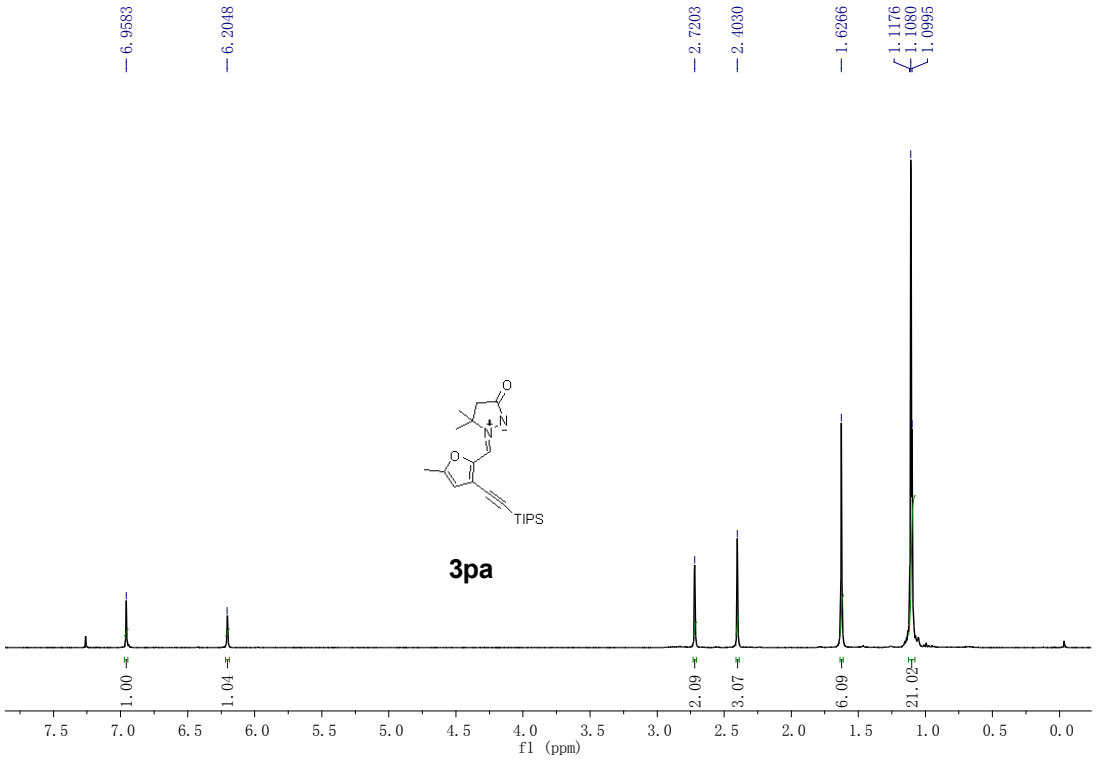
11.2664
TIPS
TIPS
COOMe
3oaa
f1 (ppm)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TIPS
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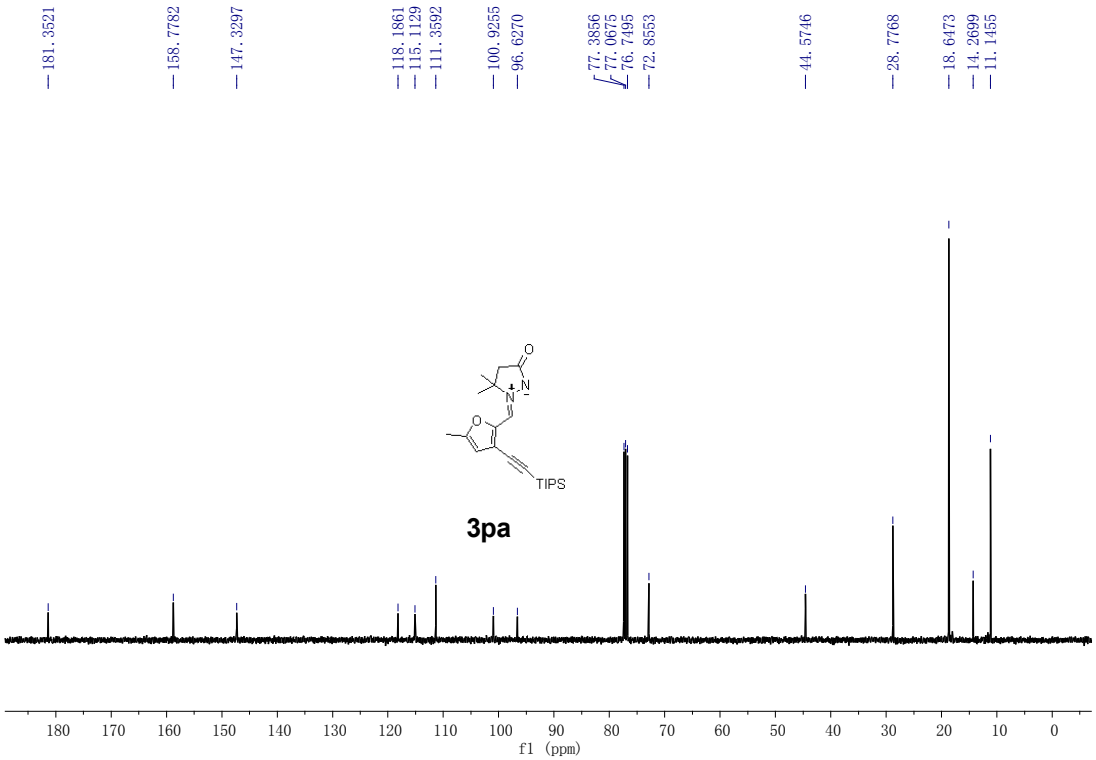
1.04
2.09
3.07
6.09
21.02
f1 (ppm)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115.1129
111.3592
100.9255
96.6270
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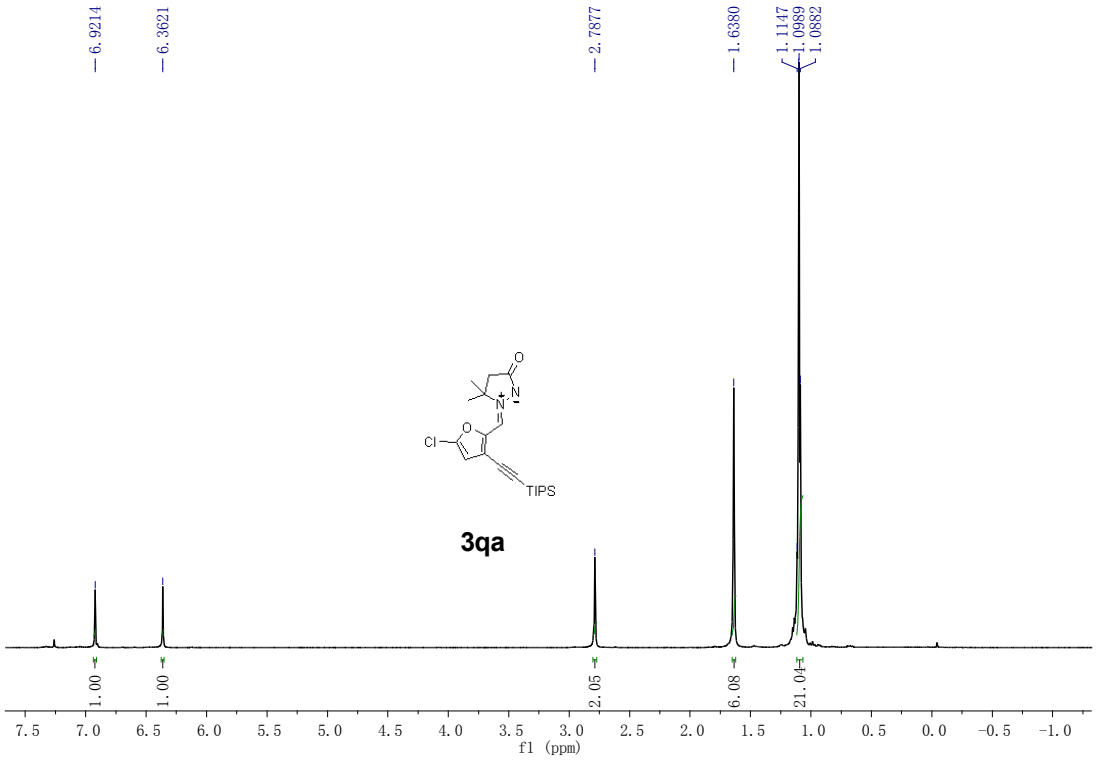
44.5746
28.7768
18.6473
14.2699
11.1455
TIPS
3pa
f1 (ppm)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2.7877
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Cl
TIPS
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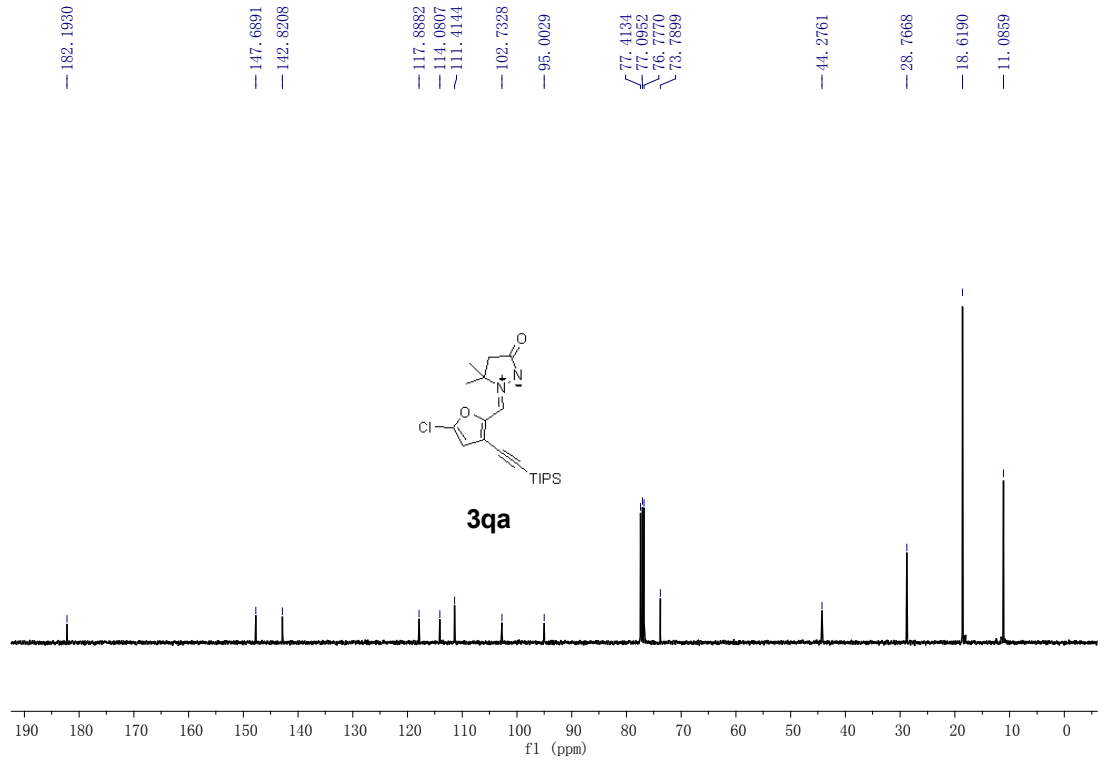
1.00
2.05
6.08
21.04
f1 (ppm)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Cl
TIPS
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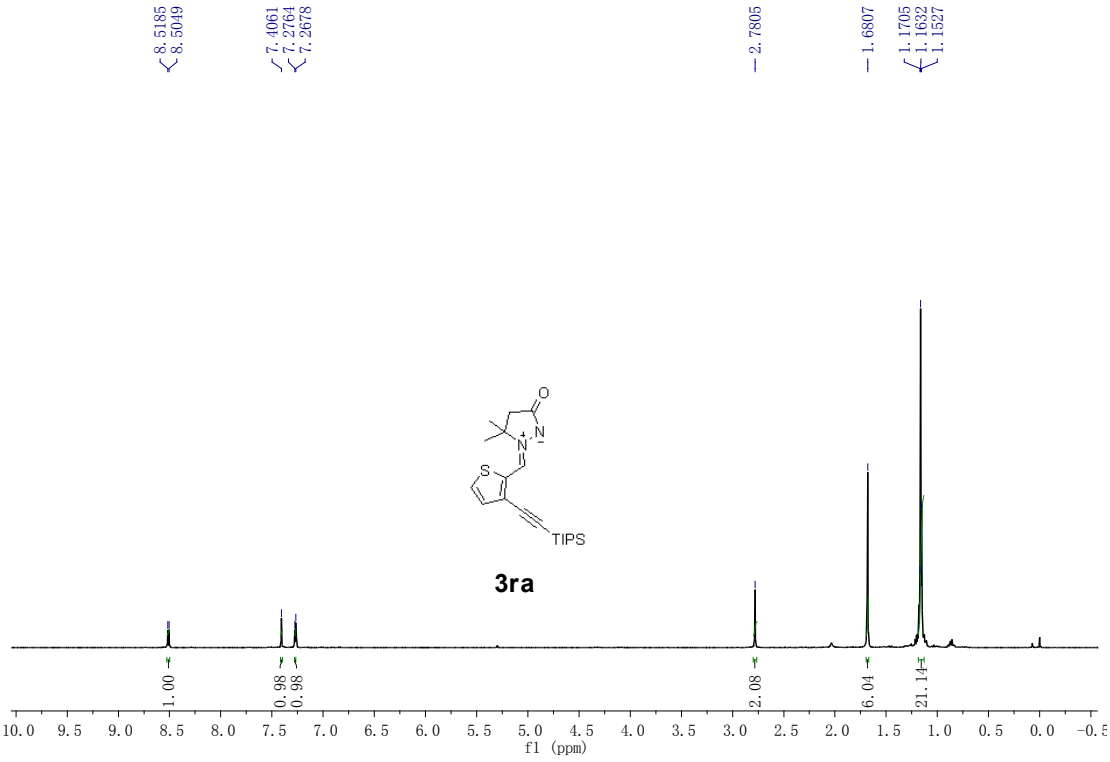
f1 (ppm)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TIPS
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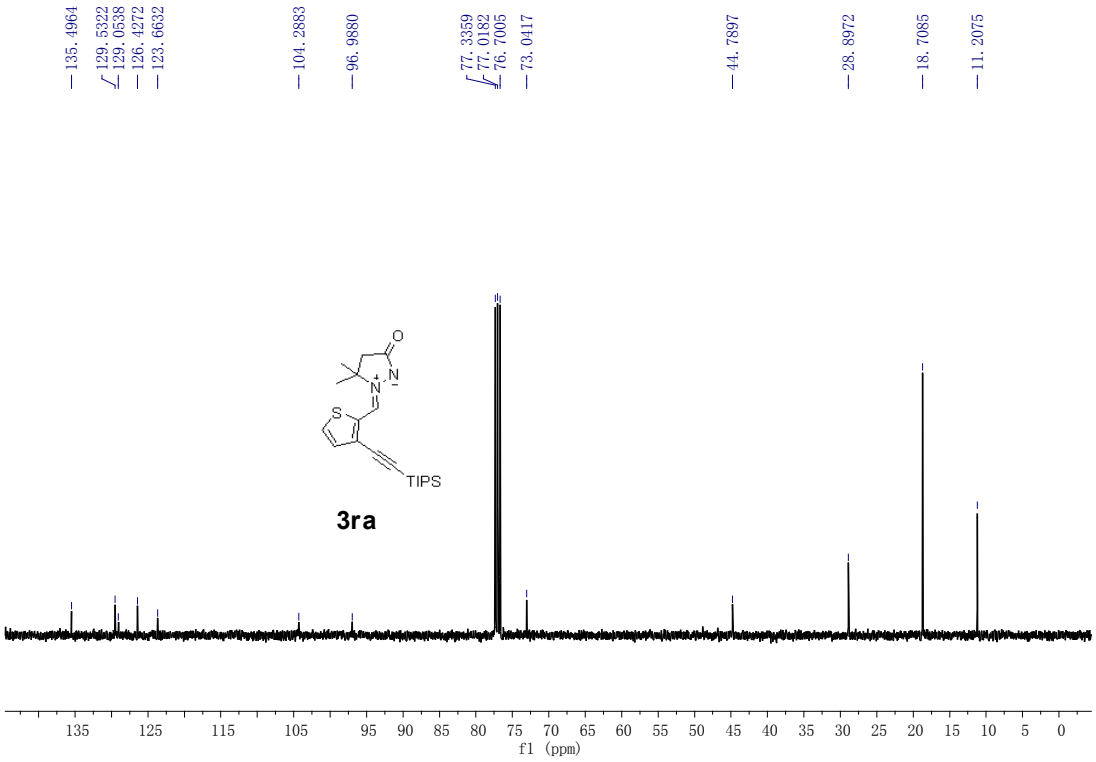
f1 (ppm)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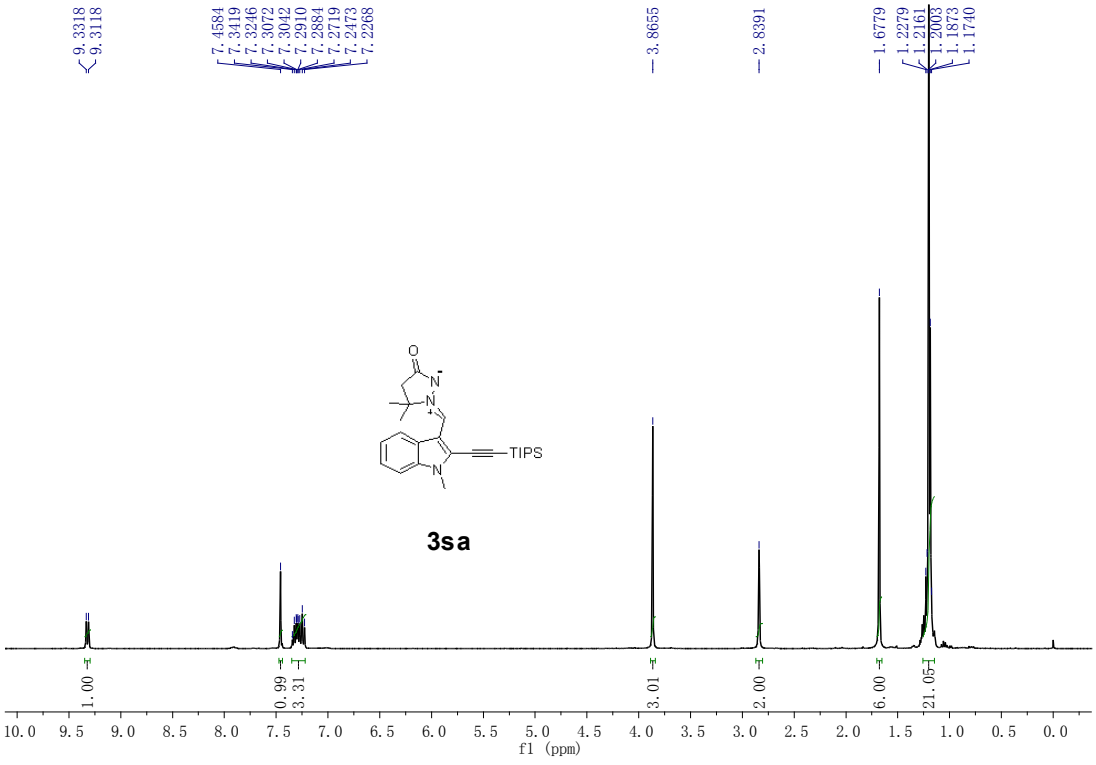
TIPS
3ra
f1 (ppm)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7.4584
7.3419
7.3246
7.3072
7.3042
7.2910
7.2884
7.2719
7.2473
7.2268
3.8655
2.8391
1.6779
1.2279
1.2161
1.2003
1.1873
1.1740
TIPS
3sa
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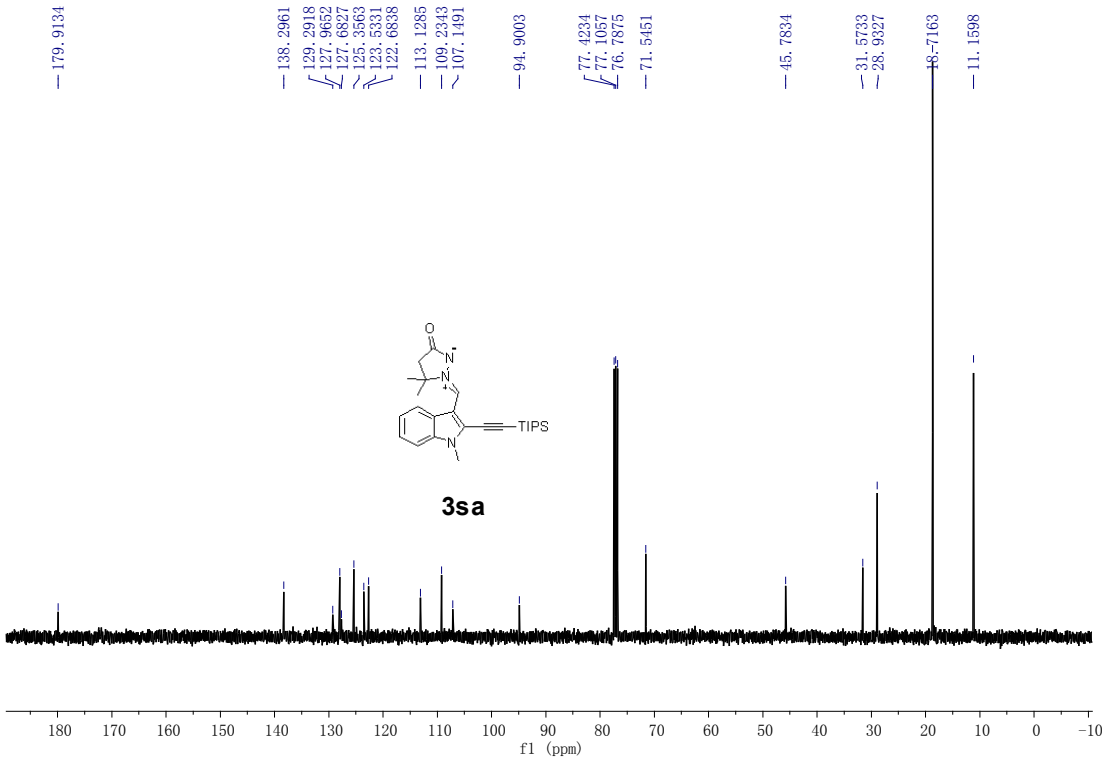
0.99
3.31
3.01
2.00
6.00
21.05
f1 (ppm)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127.6827
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123.5331
122.6838
113.1285
109.2343
107.1491
94.9003
77.4234
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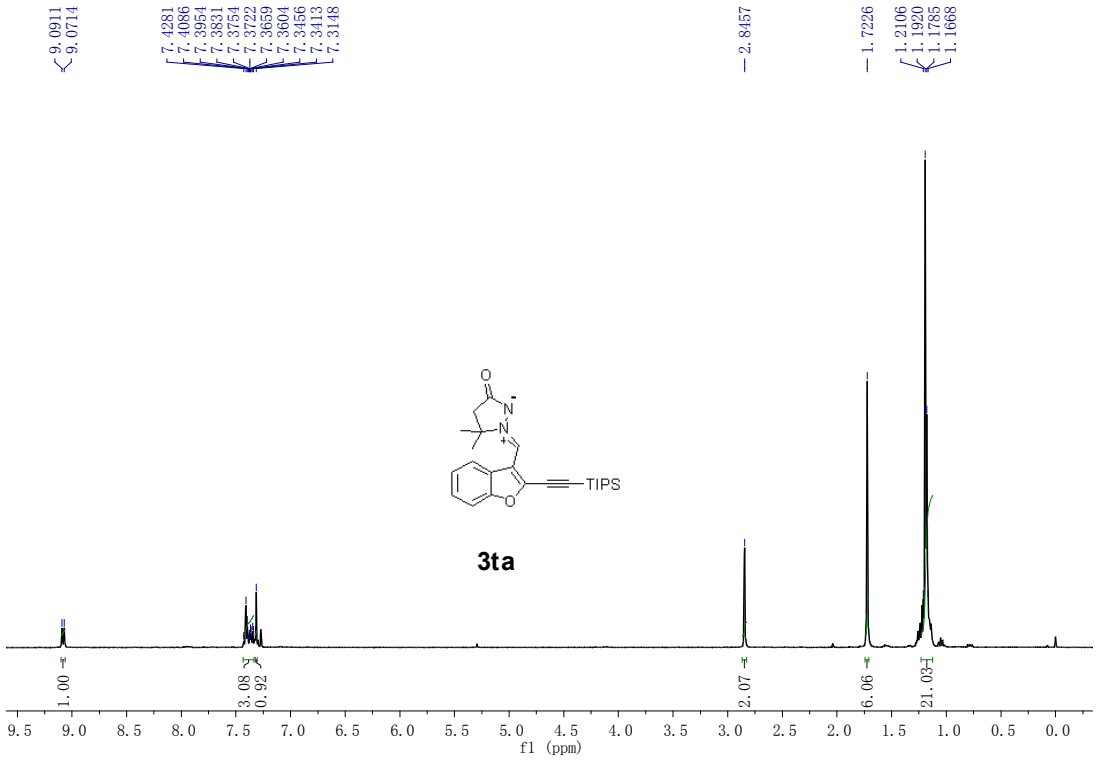
11.1598
TIPS
3sa
f1 (ppm)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7.4281
7.4086
7.3954
7.3831
7.3754
7.3722
7.3659
7.3604
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7.3413
7.3148
2.8457
1.7226
1.2106
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TIPS
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3.08
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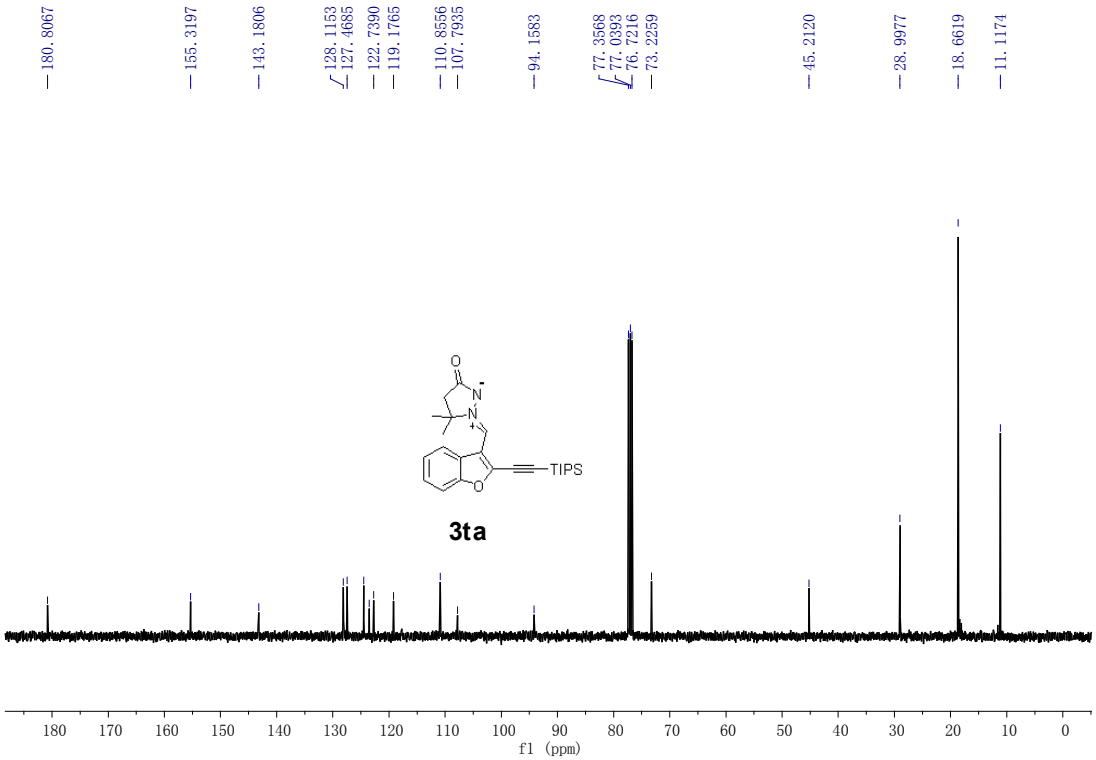
2.07
6.06
21.03
f1 (ppm)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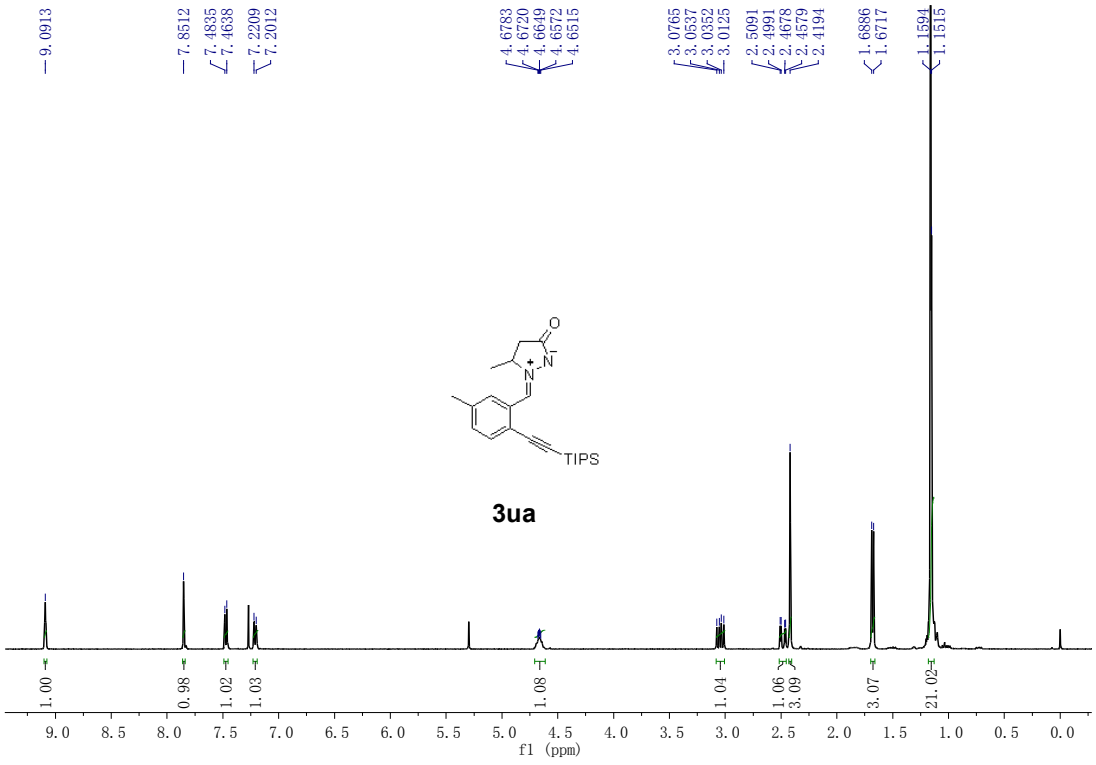
TIPS
3ta
f1 (ppm)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7.4835
7.4638
7.2209
7.2012
4.6783
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4.6649
4.6572
4.6515
3.0765
3.0537
3.0352
3.0125
2.5091
2.4991
2.4678
2.4579
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1.6886
1.6717
1.1594
1.1515
TIPS
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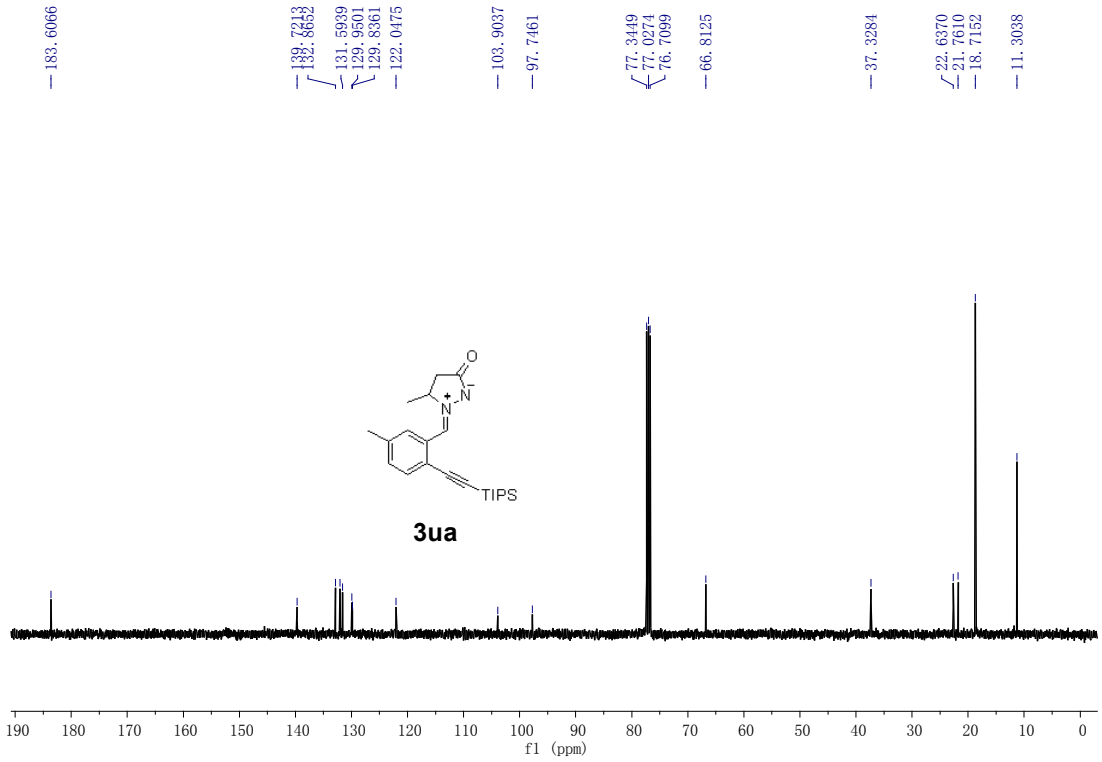
1.02
1.03
1.08
1.04
1.06
3.09
3.07
21.02
f1 (ppm)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66.8125
37.3284
22.6370
21.7610
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O
N
N
TIPS
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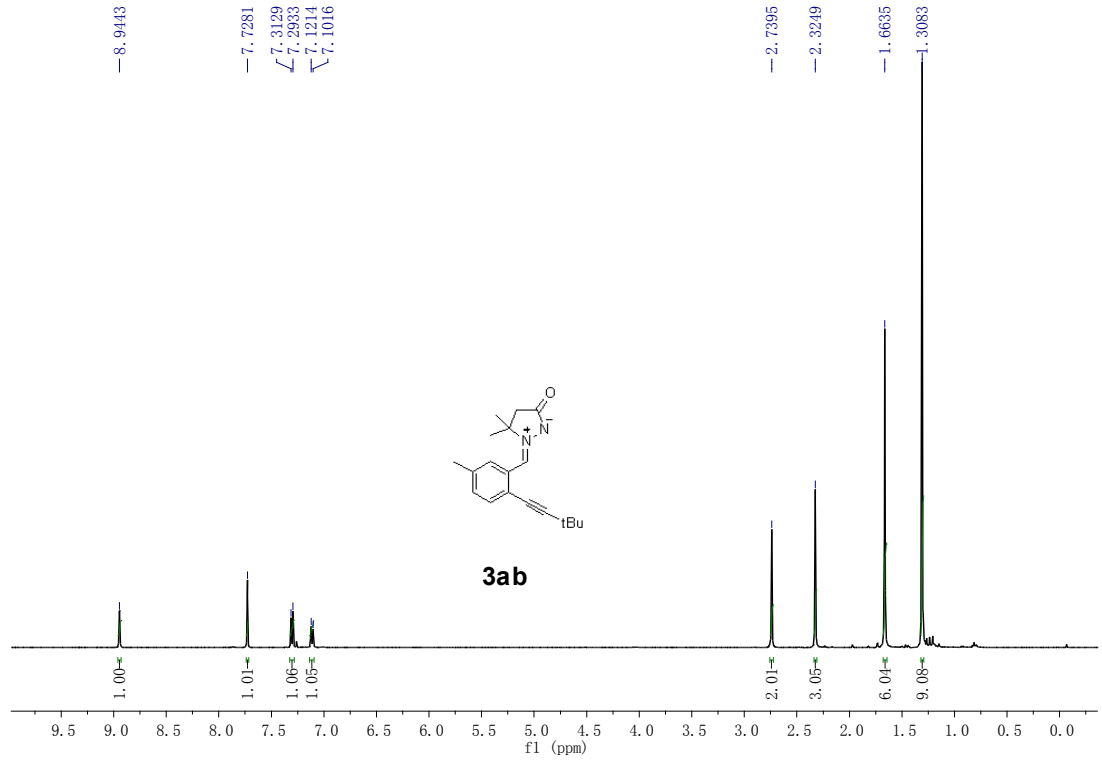
f1 (ppm)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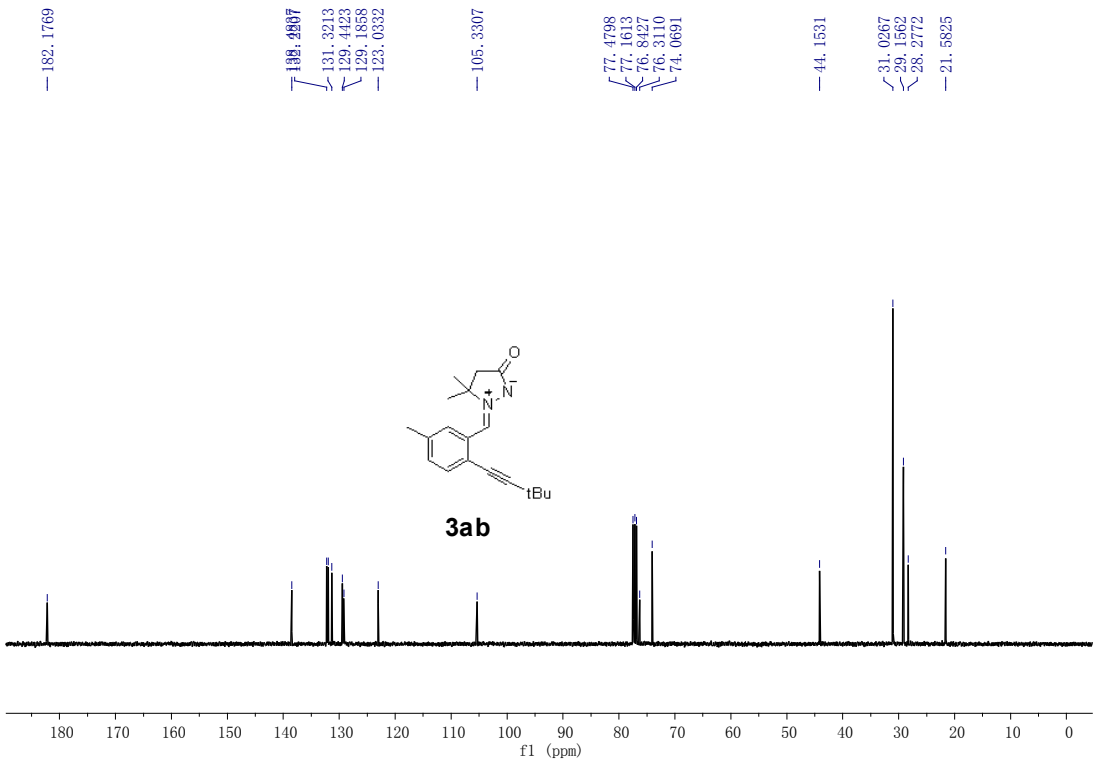
N
N
tBu
3ab
1.00
1.01
1.06
1.05
2.01
3.05
6.04
9.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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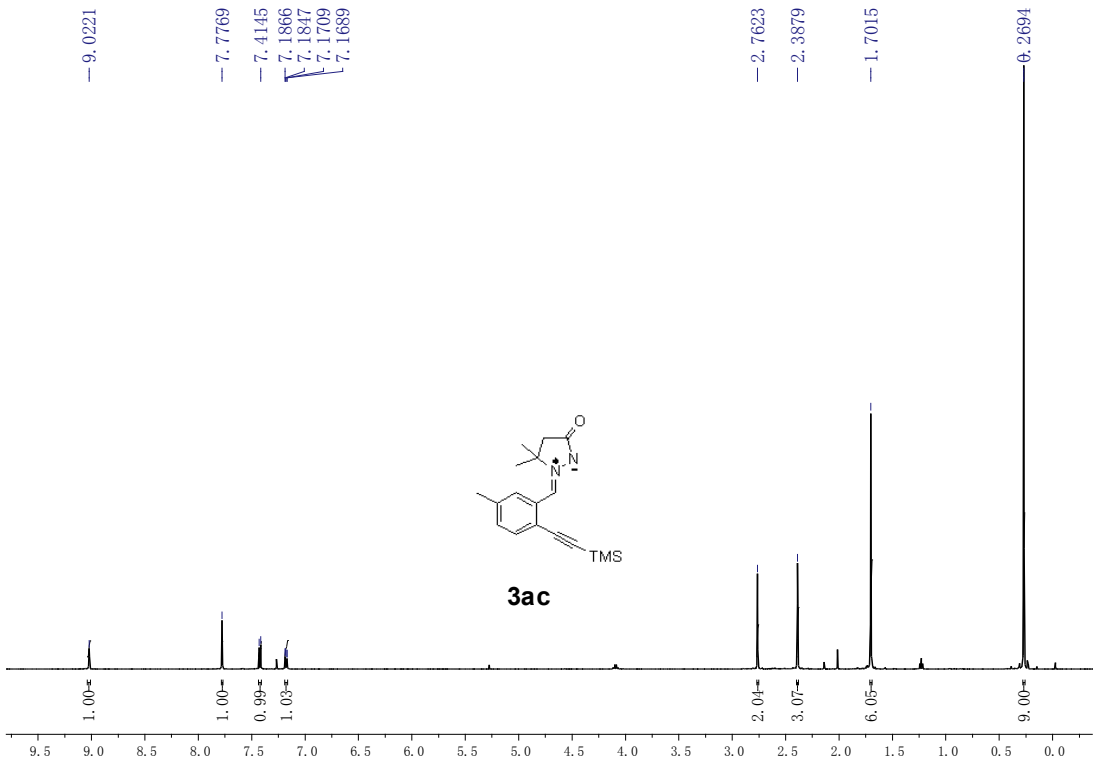
21.5825
tBu
3ab
f1 (ppm)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1.03
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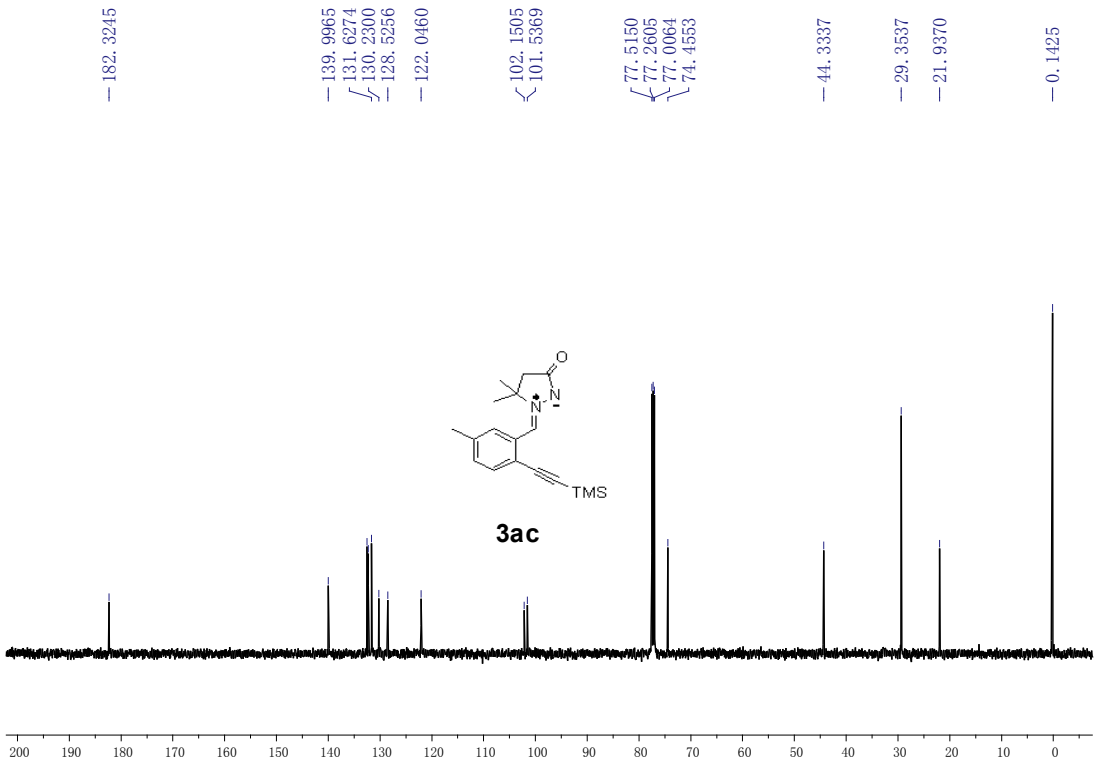
3.07
6.05
9.00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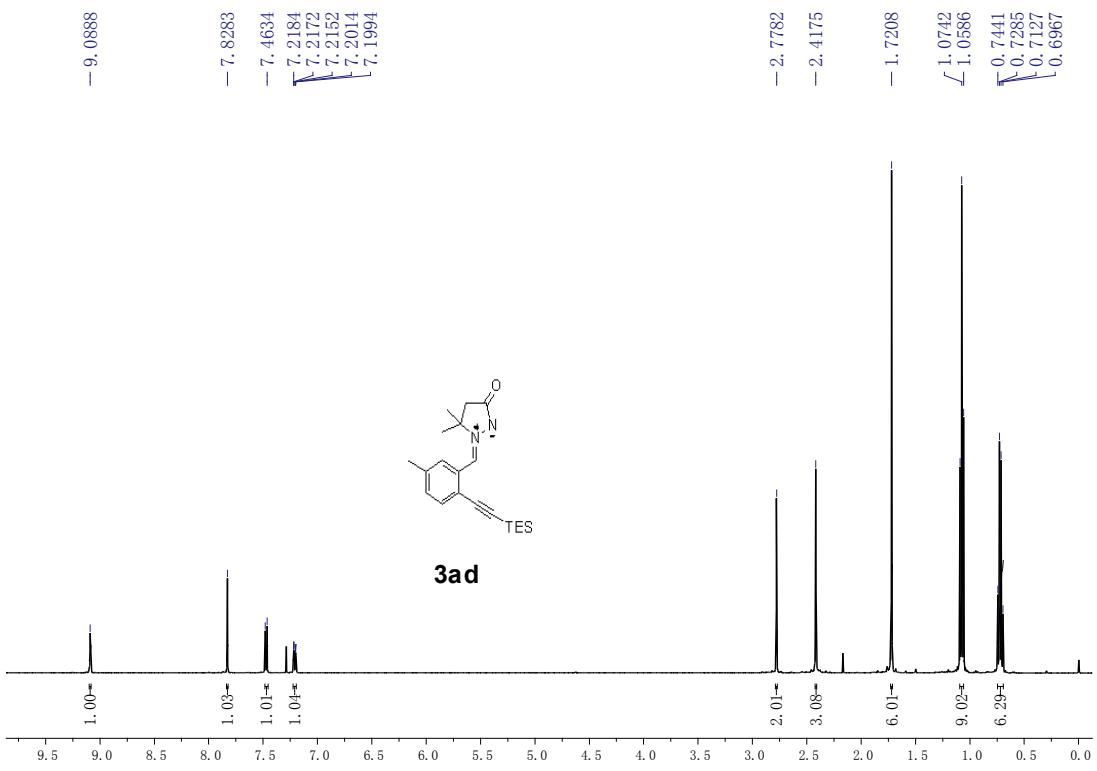
3ac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2.01
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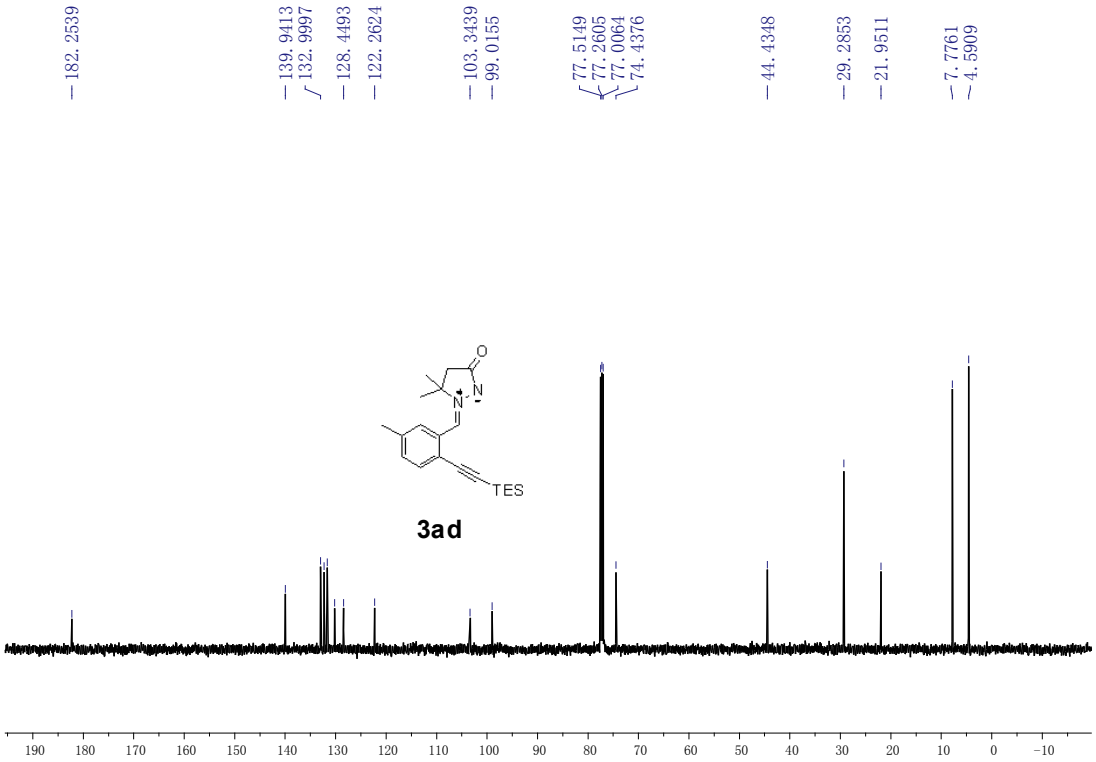
6.01
9.02
6.29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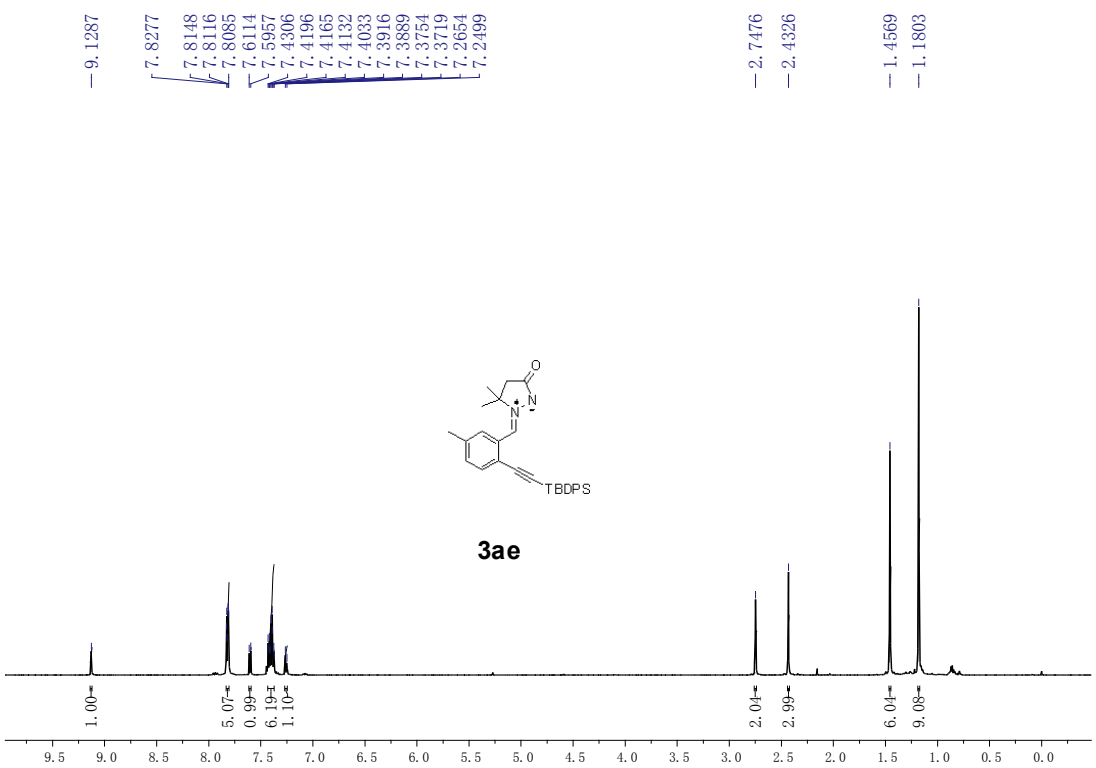
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7.4132
7.4033
7.3916
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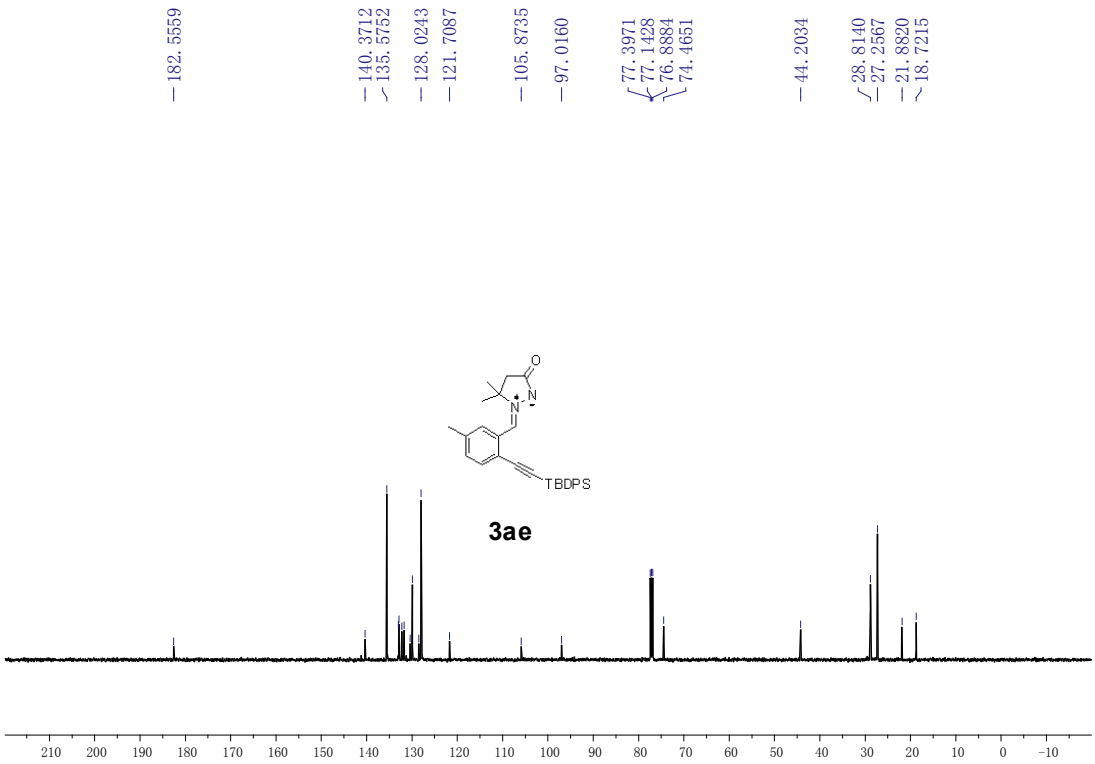
TBDPS
3ae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74.4651
44.2034
28.8140
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N
TBDPS
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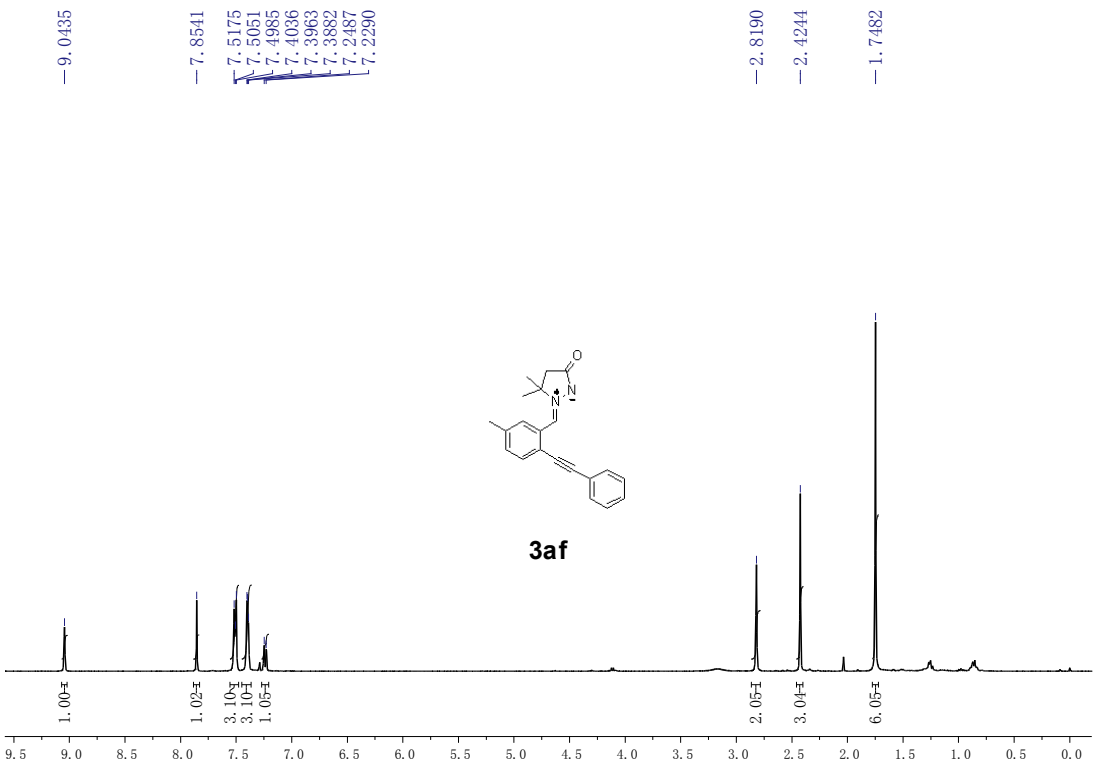
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7.2487
7.2290
2.8190
2.4244
1.7482
O
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3af
1.00
1.02
3.10
3.10
1.05
2.05
3.04
6.05
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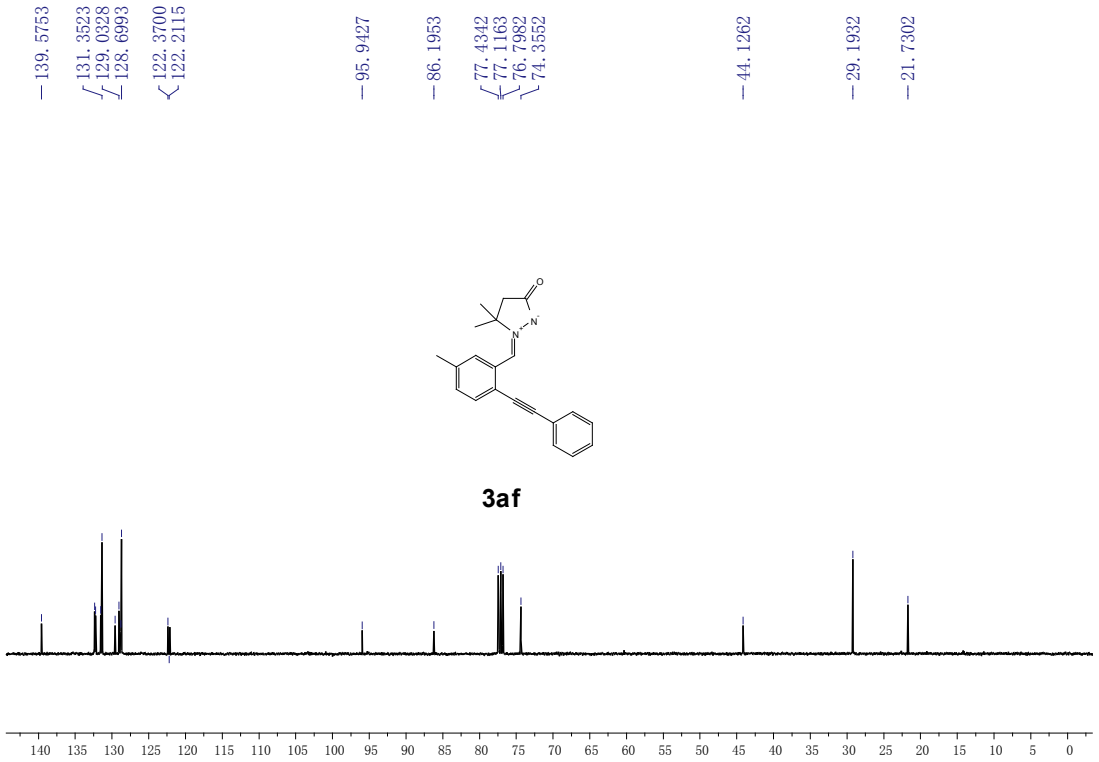
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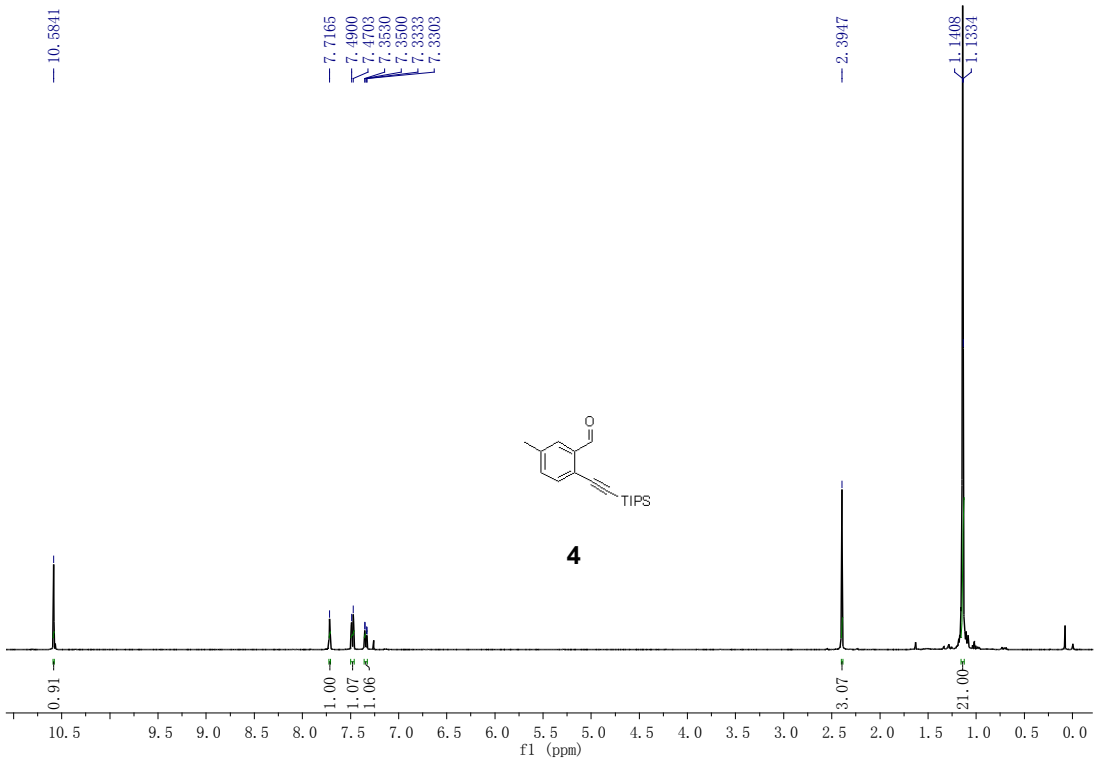
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1.1334
O
TIPS
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0.91
1.00
1.07
1.06
3.07
21.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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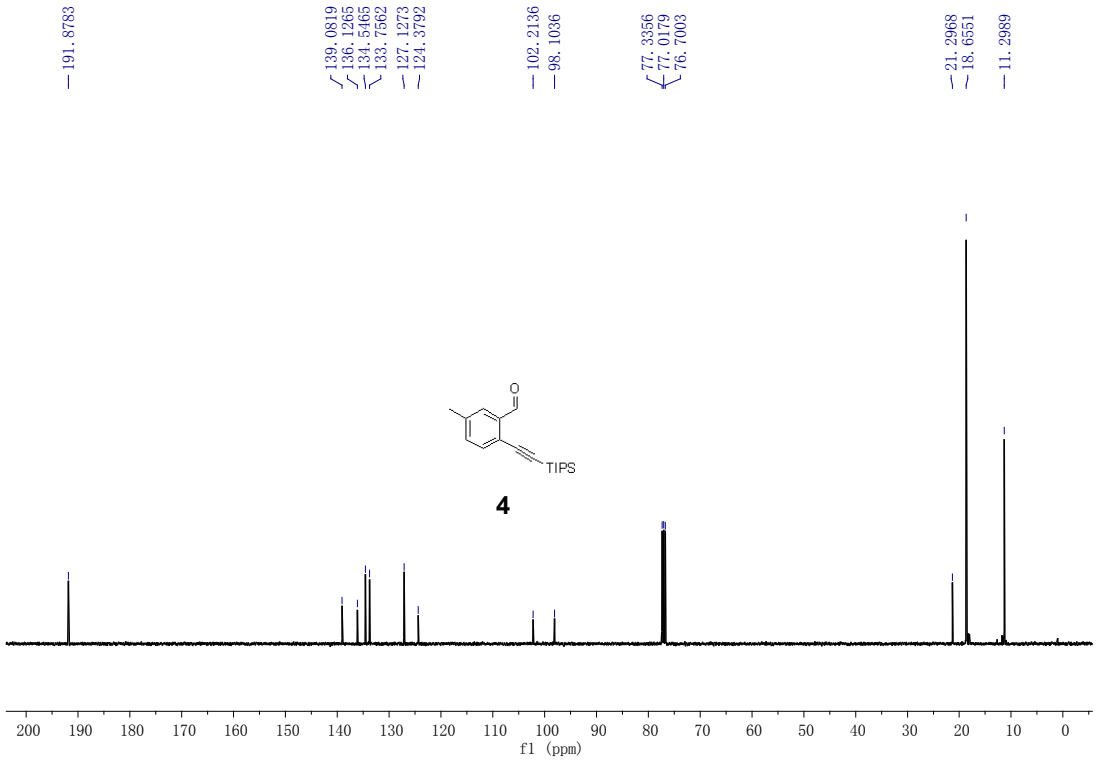
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77.0179
76.7003
21.2968
18.6551
11.2989
O
TIPS
4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)