Supporting Information

Metal-Free Carbonyl C(sp^2)-H Oxidative Alkynylation of Aldehydes With Hypervalent Iodine Reagents Leading to Ynones

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(A) Typical experimental procedure

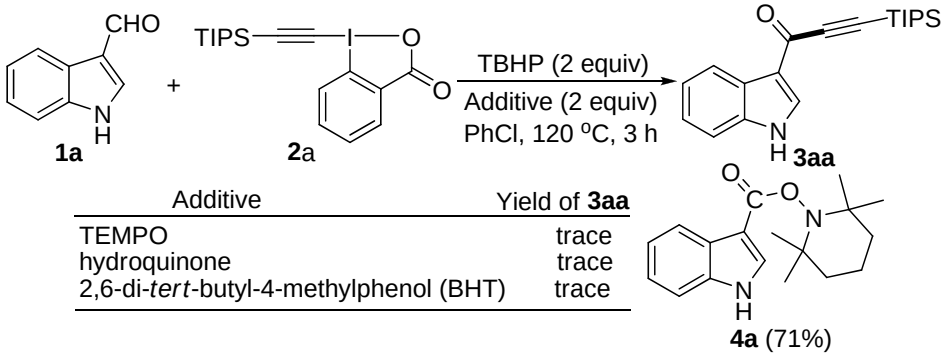
(a) Synthesis of Enynyl Benziodoxolones 2:

All enynyl benziodoxolones **2** were prepared accordding to the known methods.[1]

(b) Typical Experimental Procedure for the Synthesis of Ynones:

To a Schlenk tube were added aldehyde **1** (0.2 mmol), enynyl benziodoxolone **2** (1.5 equiv), TBHP (2 equiv; 5 M in decane) and PhCl (3 mL). Then the tube was charged with argon, and was stirred at 120 ^{o}C for 3 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with saturated $NaHCO_3$ solution. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **3**.

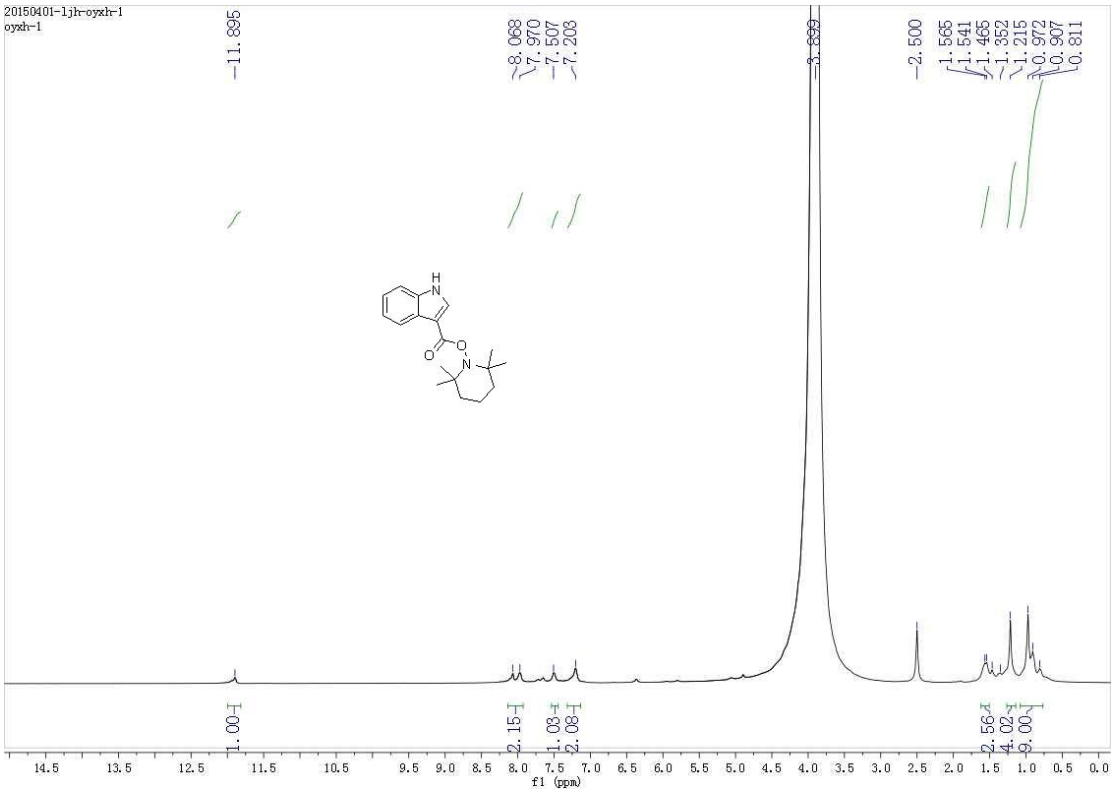
(c) Control Experiments



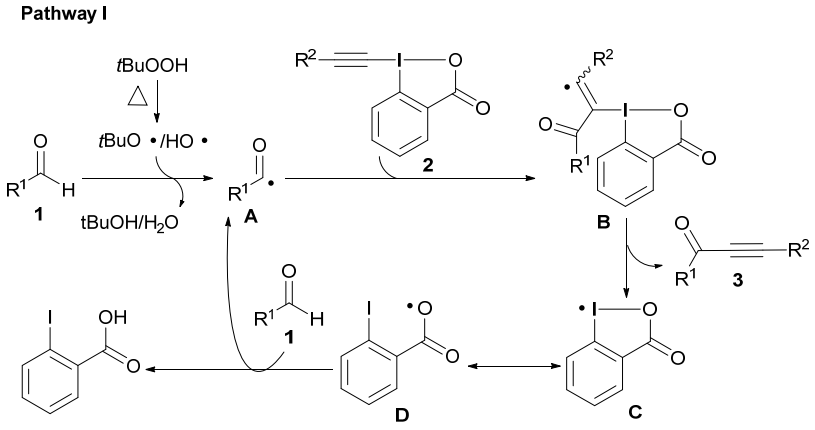
Additive	Yield of **3aa**
TEMPO	trace
hydroquinone	trace
2,6-di-*tert*-butyl-4-methylphenol (BHT)	trace

Scheme S1. Control Experiments.

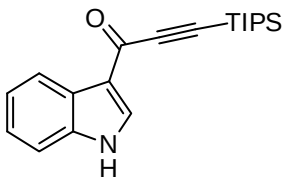
2,2,6,6-tetramethylpiperidin-1-yl 1*H*-indole-3-carboxylate (4a)



(d) Possible mechanism

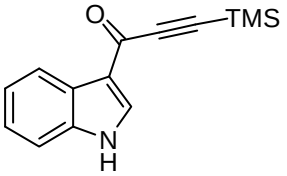


(B) Analytical data



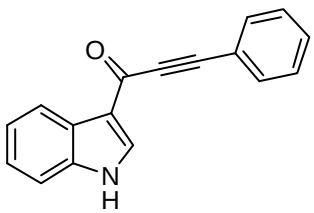
1-(1*H*-Indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3aa):

Light yellow solid, mp 148.5-150.2 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.98 (s, 1H), 8.44-8.36 (d, *J* = 4.8 Hz, 1H), 8.13 (d, *J* = 2.8 Hz, 1H), 7.54-7.45 (d, *J* = 6.4 Hz, 1H), 7.33-7.26 (m, 2H), 1.15-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 137.0, 136.2, 125.0, 124.2, 123.1, 122.2, 119.8, 112.1, 104.3, 92.3, 18.6, 11.1; (EI, 70 eV) *m/z* (%): 325 (M^+, 42), 282 (100), 254 (36), 144 (28); HRMS *m/z* (ESI) calcd for $C_{20}H_{28}NOSi$ ($[M+H]^+$) 326.1935, found 326.1943.



1-(1*H*-Indol-3-yl)-3-(trimethylsilyl)prop-2-yn-1-one (3ab):

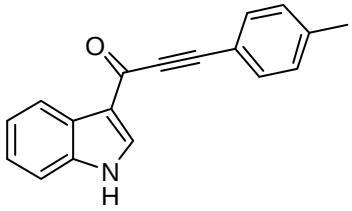
Light yellow solid, mp 134.5-135.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.56 (s, 1H), 8.42 (d, *J* = 6.4 Hz, 1H), 8.20 (s, 1H), 7.56 (d, *J* = 6.4 Hz, 1H), 7.34-7.29 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 137.1, 137.1, 124.9, 124.1, 123.1, 121.9, 119.1, 112.4, 102.0, 95.5, -0.7; IR (KBr, cm^{-1}): 1692, 1676; LRMS (EI, 70 eV) *m/z* (%): 241 (M^+, 75), 226 (70), 198 (100), 83 (62); HRMS *m/z* (ESI) calcd for $C_{14}H_{16}NOSi$ ($[M+H]^+$) 242.0996 found 242.1004.



1-(1*H*-Indol-3-yl)-3-phenylprop-2-yn-1-one (3ac):

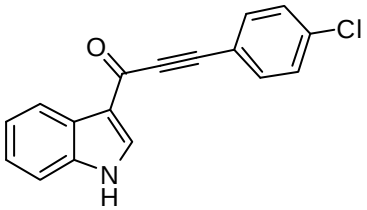
Yellow solid, mp 184.1-185.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, DMSO) δ: 12.32 (s, 1H), 8.51 (d, *J* = 3.2

Hz, 1H), 8.19 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 6.8 Hz 2H), 7.58-7.49 (m, 4H), 7.30-7.23 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ: 171.1, 138.4, 137.7, 133.4, 131.3, 129.6, 125.3, 124.2, 123.2, 121.7, 120.5, 118.8, 113.3, 88.2, 87.5; HRMS *m/z* (ESI) calcd for $C_{17}H_{12}NO$ ($[M+H]^+$) 246.0913, found 246.0921.



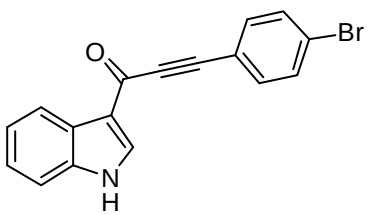
1-(1*H*-Indol-3-yl)-3-p-tolylprop-2-yn-1-one (3ad):

Light yellow solid, mp 197.7-198.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, DMSO) δ: 12.30 (s, 1H), 8.50 (d, *J* = 2.8 Hz, 1H), 8.19 (d, *J* =2.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.40-7.19 (m, 4H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ: 171.2, 141.4, 138.2, 137.6, 133.4, 130.1, 125.3, 124.1, 123.0, 121.7, 118.8, 117.4, 113.2, 88.0, 87.9, 21.8; HRMS *m/z* (ESI) calcd for $C_{18}H_{14}NO$ ($[M+H]^+$) 260.1070, found 260.1077.



3-(4-Chlorophenyl)-1-(1*H*-indol-3-yl)prop-2-yn-1-one (3ae):

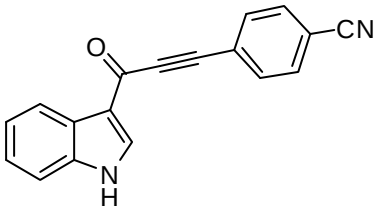
Light yellow solid, mp 181.2-182.9 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, DMSO) δ: 12.35 (s, 1H), 8.54 (d, *J* = 3.2 Hz, 1H), 8.18 (d, *J* = 6.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.81-7.53 (m, 3H), 7.37-7.18 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ: 170.8, 138.6, 137.7, 136.1, 135.1, 129.7, 125.3, 124.2, 123.1, 121.7, 119.4, 118.8, 113.2, 88.9, 86.0; HRMS *m/z* (ESI) calcd for $C_{17}H_{11}{}^{35}ClNO$ ($[M+H]^+$) 280.0524, found 280.0531.



3-(4-Bromophenyl)-1-(1*H*-indol-3-yl)prop-2-yn-1-one (3af):

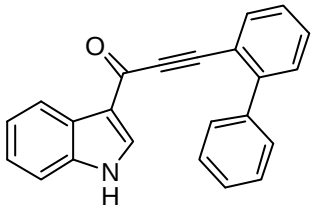
Light yellow solid, mp 204.5-205.9 ^{o}C

(uncorrected); ^{1}H NMR (400 MHz, DMSO) δ: 12.43 (s, 1H), 8.53 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 3H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.30-7.23 (m, 3H); ^{13}C NMR (100 MHz, DMSO) δ: 170.8, 138.6, 137.7, 135.2, 132.6, 125.2, 124.9, 124.2, 123.1, 121.7, 119.7, 118.8, 113.2, 89.0, 86.1; HRMS *m/z* (ESI) calcd for $C_{17}H_{11}{}^{79}BrNO$ ($[M+H]^+$) 324.0019, found 324.0025.



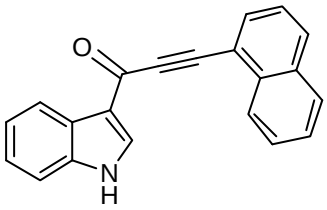
4-(3-(1*H*-Indol-3-yl)-3-oxoprop-1-ynyl)benzonitrile (3ag):

Light yellow solid, mp 228.2-229.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.41 (s, 1H), 8.57 (d, *J* = 2.4 Hz 1H), 8.17 (s, 1H), 7.98-7.90 (m, 4H), 7.54 (d, *J* = 7.2 Hz 1H), 7.30-7.24 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ: 170.4, 139.0, 137.7, 134.1, 133.2, 125.4, 125.2, 124.3, 123.3, 121.7, 118.8, 113.3, 113.2, 90.7, 85.0; HRMS *m/z* (ESI) calcd for $C_{18}H_{11}N_2O$ ($[M+H]^+$) 271.0866, found 271.0874.



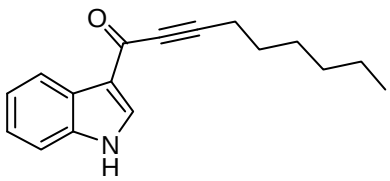
3-(Biphenyl-2-yl)-1-(1*H*-indol-3-yl)prop-2-yn-1-one (3ah):

Light yellow solid, mp 237.5.1-238.9 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, DMSO) δ: 12.24 (s, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 3H), 7.64-7.46 (m, 7H), 7.27-7.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ: 170.8, 145.5, 140.2, 137.6, 137.5, 134.9, 131.5, 130.3, 129.7, 129.0, 128.7, 128.4, 125.1, 124.2, 123.1, 121.6, 119.0, 118.8, 113.1, 90.7, 87.0; HRMS *m/z* (ESI) calcd for $C_{23}H_{16}NO$ ($[M+H]^+$) 322.1226, found 322.1234.



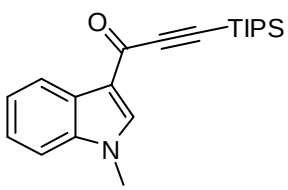
1-(1*H*-Indol-3-yl)-3-(naphthalen-1-yl)prop-2-yn-1-one (3ai):

Light yellow solid, mp 167.8-168.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, DMSO) δ: 12.35 (s, 1H), 8.57 (d, *J* = 2.8 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 6.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.68-7.62 (m 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.33-7.23 (m, 2H); ^{13}C NMR (100MHz, DMSO) δ: 171.0, 138.2, 137.7, 133.5, 133.4, 133.3, 131.7, 129.4, 128.6, 127.7, 126.3, 125.7, 125.4, 124.3, 123.2, 121.7, 118.9, 117.8, 113.3, 93.0, 85.3; HRMS *m/z* (ESI) calcd for $C_{21}H_{14}NO$ ($[M+H]^{+}$) 296.1070, found 296.1077.



1-(1*H*-Indol-3-yl)non-2-yn-1-one (3aj):

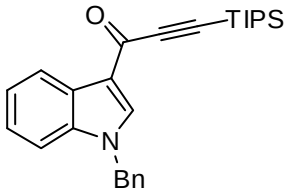
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (s, 1H), 8.46-8.35 (m, 1H), 8.07 (s, 1H), 7.48-7.42 (m, 1H), 7.30 (d, *J* = 8.8 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.65-1.60 (m, 2H), 1.47-1.40 (m, 2H), 1.30 (d, *J* = 3.6 Hz, 4H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 136.7, 135.4, 125.0, 124.0, 122.9, 122.2, 119.7, 111.7, 91.6, 80.5, 31.2, 28.7, 27.9, 22.5, 19.02, 14.0; LRMS (EI, 70 eV) *m/z* (%): 253 (M^{+}, 63), 236 (47), 224 (30), 196 (64), 144 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{20}N_2O$ ($[M+H]^{+}$) 254.1539, found 254.1546.



1-(1-Methyl-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ba):

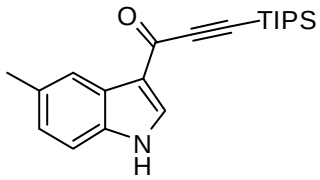
Yellow solid, mp 101.4-103.5 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (t, *J* = 4.4 Hz, 1H), 7.84 (s, 1H), 7.32-7.28 (m, 3H), 3.84 (s,

3H), 1.24-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8, 138.9, 137.7, 125.7, 123.8, 123.0, 122.5, 118.4, 109.8, 104.5, 91.1, 33.7, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 339 (M^+, 55), 296 (100), 268 (32), 158 (55); HRMS *m/z* (ESI) calcd for $C_{21}H_{30}NOSi$ ($[M+H]^+$) 340.2091, found 340.2099.



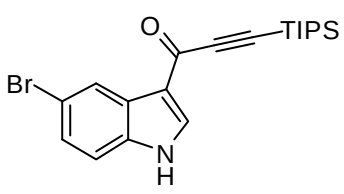
1-(1-Benzyl-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ca):

Light yellow solid, mp 84.0-85.5 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 6.8, 1H), 7.85 (s, 1H), 7.39-7.21 (m, 8H), 5.30 (s, 2H), 1.22-1.01 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 138.0, 137.3, 134.9, 129.1, 128.4, 127.7, 125.9, 123.9, 123.1, 122.6, 118.9, 110.2, 104.4, 91.3, 50.9, 18.6, 11.1; HRMS *m/z* (ESI) calcd for $C_{27}H_{34}NOSi$ ($[M+H]^+$) 416.2404, found 416.2414.



1-(5-Methyl-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ea):

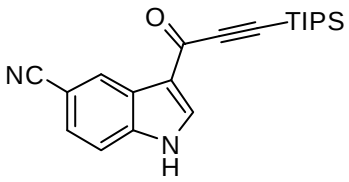
Yellow solid, mp 181.3-182.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.64 (s, 1H), 8.20 (s, 1H), 8.07 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 2.46 (s, 3H), 1.17-1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 135.8, 135.1, 132.8, 125.6, 125.2, 121.8, 119.4, 111.5, 104.4, 21.5, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 339 (M^+, 55), 296 (100), 268 (32), 158 (55); HRMS *m/z* (ESI) calcd for $C_{21}H_{30}NOSi$ ($[M+H]^+$) 340.2091, found 340.2099.



1-(5-Bromo-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3fa):

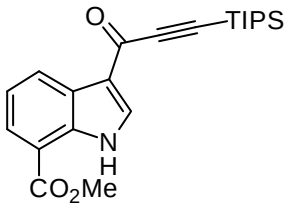
Light yellow solid, mp 207.3-208.7 ^{o}C (uncorrected);

^{1}H NMR (400 MHz, DMSO) δ: 12.37 (s, 1H), 8.27 (s, 1H), 8.17 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 1.19-1.06 (m, 21H); ^{13}C NMR (100 MHz, DMSO) δ: 169.9, 137.5, 135.8, 126.3, 123.0, 117.4, 115.4, 114.9, 104.3, 90.9, 79.3, 18.4, 10.6; HRMS *m/z* (ESI) calcd for $C_{20}H_{27}{}^{79}BrNOSi$ ($[M+H]^+$) 404.1040, found 404.1047.



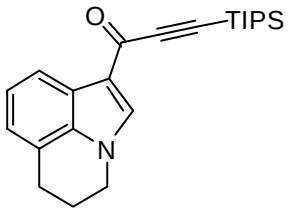
3-(3-(Triisopropylsilyl)propioloyl)-1*H*-indole-5-carbonitrile (3ga):

Yellow solid, mp 180.8-182.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.56 (s, 1H), 8.78 (s, 1H), 8.24 (d, *J* = 3.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 1.19-1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 138.7, 137.4, 127.6, 127.0, 124.9, 119.9, 119.6, 113.2, 106.0, 103.5, 94.3, 18.5, 11.0; HRMS *m/z* (ESI) calcd for $C_{21}H_{27}N_2OSi$ ($[M+H]^+$) 351.1887, found 351.1895.



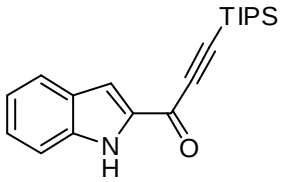
Methyl 3-(3-(triisopropylsilyl)propioloyl)-1*H*-indole-7-carboxylate (3ha):

Yellow solid, mp 153.2-155.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.45 (s, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 3.2 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 4.00 (s, 3H), 1.22-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.5, 167.4, 136.5, 135.6, 128.1, 126.1, 125.9, 122.5, 119.8, 113.2, 104.0, 92.1, 52.2, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 383 (M^+, 34), 340 (98), 294 (38), 207 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{30}NO_3Si$ ($[M+H]^+$) 384.1989 found 384.1998.



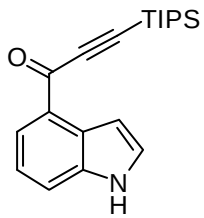
1-(5,6-Dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-1-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ia):

Light yellow solid, mp 85.8-87.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.21 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 6.0 Hz, 2H), 2.29-2.23 (m, 2H), 1.25-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 135.8, 134.9, 123.7, 123.3, 122.3, 121.1, 119.9, 118.8, 104.7, 90.9, 45.1, 24.2, 22.7, 18.6, 11.2; LRMS (EI, 70 eV) *m/z* (%): 368 (M^+, 64), 322 (100), 294 (38), 184 (56); HRMS *m/z* (ESI) calcd for $C_{23}H_{32}NOSi$ ($[M+H]^+$) 366.2248, found 366.2255.



1-(1*H*-Indol-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ja):

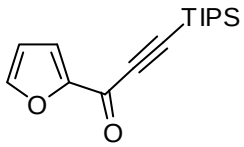
Light yellow solid, mp 158.0-159.1 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.20 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.44-7.35 (m, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 1.23-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 138.0, 136.7, 127.4, 127.2, 123.5, 121.3, 113.4, 112.3, 102.9, 96.6, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 77), 282 (100), 254 (52), 113 (34); HRMS *m/z* (ESI) calcd for $C_{20}H_{28}NOSi$ ($[M+H]^+$) 326.1935, found 326.1942.



1-(1*H*-Indol-4-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ka):

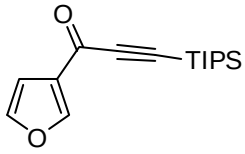
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (s, 1H), 8.18 (d, *J* = 7.2, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.49-7.44 (m, 1H), 7.41 (d, *J* = 2.8 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 1.26-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.6, 136.6, 128.9, 127.7, 127.0, 126.3, 121.0, 117.5,

104.4, 104.2, 95.7, 18.6, 11.2; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 51), 282 (100), 254 (40), 116 (47); HRMS *m/z* (ESI) calcd for $C_{20}H_{28}NOSi$ ($[M+H]^+$) 326.1935, found 294.1493.



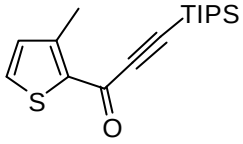
1-(Furan-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3la):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 1.2 Hz, 1H), 7.36 (t, *J* = 2.8, 1H), 6.58 (d, *J* = 3.6, 1H), 1.19-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1, 153.3, 148.1, 121.3, 112.6, 102.3, 96.8, 18.5, 11.0; LRMS (EI, 70 eV) *m/z* (%): 276 (M^+, 4), 26 (34), 288 (100), 177 (66); HRMS *m/z* (ESI) calcd for $C_{16}H_{24}O2Si$ ($[M+H]^+$) 277.1618, found 277.1624.



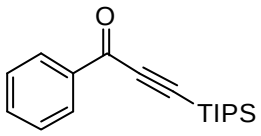
1-(Furan-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ma):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (s, 1H), 7.45 (s, 1H), 6.83 (s, 1H), 1.14-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.6, 150.3, 144.6, 129.3, 108.4, 103.4, 94.5, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 276 (M^+, 4), 233 (100), 245 (43), 217 (52); HRMS *m/z* (ESI) calcd for $C_{16}H_{25}O_2Si$ ($[M+H]^+$) 277.1618, found 277.1625.



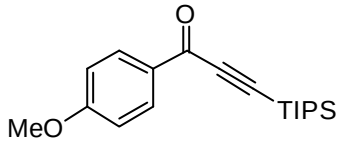
1-(3-Methylthiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3na):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 4.8 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 2.62 (s, 3H), 1.20-1.10 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 146.3, 137.4, 133.1, 132.8, 104.3, 95.7, 28.1, 18.5, 11.1; LRMS (EI, 70 eV) *m/z* (%): 306 (M^+, 13), 291 (5), 263 (100), 235 (41); HRMS *m/z* (ESI) calcd for $C_{16}H_{25}O_2Si$ ($[M+H]^+$) 277.1618, found 277.1625.



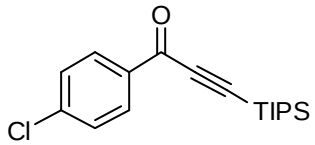
1-Phenyl-3-(triisopropylsilyl)prop-2-yn-1-one (3oa):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 1.24-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.5, 136.8, 134.1, 129.6, 128.6, 103.1, 98.0, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 286 (M^+, 14) 243 (100), 215 (37), 187(49); HRMS *m/z* (ESI) calcd for $C_{18}H_{27}OSi$ ($[M+H]^+$) 287.1826, found 287.1833.



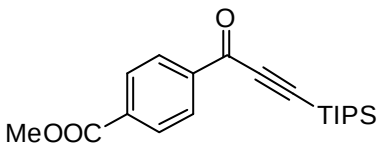
1-(4-Methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (3pa):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 1.25-1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.1, 164.4, 131.8, 130.1, 113.8, 103.2, 96.7, 55.5, 18.5, 11.0; LRMS (EI, 70 eV) *m/z* (%): 316 (M^+, 10) 273 (100), 245 (3), 135 (52); HRMS *m/z* (ESI) calcd for $C_{19}H_{28}O_2Si$ ($[M+H]^+$) 317.1931, found 317.1938.



1-(4-Chlorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (3qa):

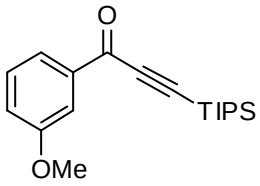
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 1.29-1.11 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.1, 140.7, 135.2, 130.8, 129.0, 102.6, 98.8, 18.5, 11.1; LRMS (EI, 70 eV) *m/z* (%): 322 (M^++2, 1), 320 (M^+, 3), 221 (63), 139 (73); HRMS *m/z* (ESI) calcd for $C_{18}H_{26}{}^{35}ClOSi$ ($[M+H]^+$) 321.1436, found 321.1443.



Methyl 4-(3-(triisopropylsilyl)propioloyl)benzoate (3ra):

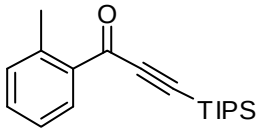
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ:

8.23 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H), 1.27–1.13 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 166.1, 139.8, 134.6, 129.8, 129.4, 102.8, 99.6, 52.5, 18.5, 11.1; LRMS (EI, 70 eV) *m/z* (%): 344 (M^+, 2), 301 (100), 273(42), 245 (60); HRMS *m/z* (ESI) calcd for $C_{20}H_{29}O_3Si$ ($[M+H]^+$) 345.1880, found 345.1887.



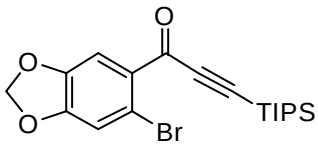
1-(3-Methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (3sa):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 1.20-1.10 (m, 22H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 159.8, 138.1, 129.6, 122.6, 121.3, 112.7, 103.1, 97.9, 55.5, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 316 (M^+, 24), 273 (100), 245 (43), 217 (52); HRMS *m/z* (ESI) calcd for $C_{19}H_{29}O_2Si$ ($[M+H]^+$) 317.1931, found 317.1938.



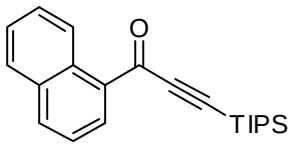
1-*o*-Tolyl-3-(triisopropylsilyl)prop-2-yn-1-one (3ta):

Light yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.29 (d, *J* = 7.6, 1H), 7.44 (t, *J* = 7.6, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* =7.6 Hz, 1H), 2.64 (s, 3H), 1.21-1.10 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.2, 140.6, 135.4, 133.4, 132.9, 132.1, 125.8, 104.5, 96.3, 22.0, 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 300 (M^+, 1), 257 (100), 229 (41), 185 (66); HRMS *m/z* (ESI) calcd for $C_{19}H_{29}OSi$ ($[M+H]^+$) 301.1982, found 301.1989.



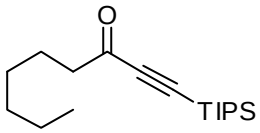
1-(6-Bromobenzo[d][1,3]dioxol-5-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ua):

Light yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.62 (s, 1H), 7.11 (s, 1H), 6.09 (s, 2H), 1.21-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.0, 151.6, 147.2, 130.2, 115.0, 112.7, 103.6, 102.7, 98.5, 18.5, 11.1; LRMS (EI, 70 eV) *m/z* (%): 410 (M^++2, 40), 408 (M^+, 38) 367 (100), 286 (94), 258 (42); HRMS *m/z* (ESI) calcd for $C_{19}H_{26}{}^{79}BrO_3Si$ ($[M+H]^+$) 409.0829, found 409.0837.



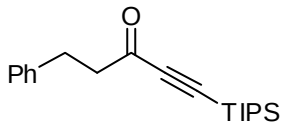
1-(Naphthalen-1-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3va):

Light yellow solid, mp 146.7-148.5 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.20 (d, *J* = 8.8 Hz, 1H), 8.62 (d, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.69-7.63 (m, 1H), 7.59-7.53 (m, 2H), 1.21-1.15 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.2, 135.0, 134.6, 133.8, 132.8, 130.7, 128.9, 128.5, 126.7, 126.0, 124.4, 104.6, 96.2 18.6, 11.1; LRMS (EI, 70 eV) *m/z* (%): 337 (M^+, 18), 299 (100), 237 (41), 127 (29); HRMS *m/z* (ESI) calcd for $C_{22}H_{29}OSi$ ($[M+H]^+$) 337.1982, found 337.1990.



1-(Triisopropylsilyl)non-1-yn-3-one (3wa):

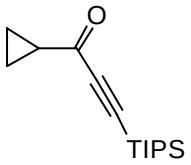
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.56 (t, *J* = 7.6 Hz, 2H), 1.74-1.66 (m, 2H), 1.35-1.27 (m, 6H), 1.17-1.09 (m, 21H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.2, 104.2, 95.4, 45.6, 31.5, 28.6, 24.2, 22.4, 18.5, 14.0, 11.0; LRMS (EI, 70 eV) *m/z* (%): 294 (M^+, 1) 251 (100), 223 (20), 167 (66); HRMS *m/z* (ESI) calcd for $C_{18}H_{35}OSi$ ($[M+H]^+$) 295.2452, found 295.2459.



5-Phenyl-1-(triisopropylsilyl)pent-1-yn-3-one (3xa):

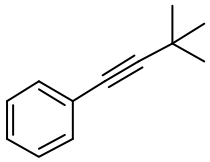
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 6.4 Hz, 3H), 3.0-2.96 (m, 2H), 2.95-2.85 (m, 2H), 1.12-

1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.6, 140.2, 128.6, 128.3, 126.3, 104.0, 96.1, 47.2, 30.1, 18.5, 11.0; LRMS (EI, 70 eV) *m/z* (%): 314 (M^+, 10), 271 (81), 245 (100), 91 (43); HRMS *m/z* (ESI) calcd for $C_{20}H_{31}OSi$ ($[M+H]^+$) 315.2139, found 315.2147.



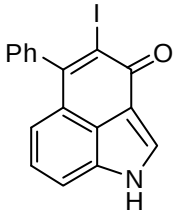
1-Cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-one (3ya):

Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.06-2.02 (m, 1H), 1.27-1.25 (m, *4*H), 1.12-1.02(m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.2, 101.9, 94.9, 24.6, 18.5, 11.0, 10.8; (EI, 70 eV) *m/z* (%): 250 (M^+, 3), 235 (2), 207 (100), 179 (48); HRMS *m/z* (ESI) calcd for $C_{15}H_{27}OSi$ ($[M+H]^+$) 251.1826, found 251.1833.



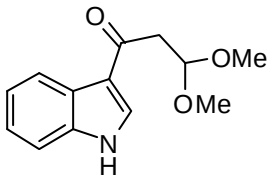
(3,3-Dimethylbut-1-ynyl)benzene (3zc):

Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 6.8 Hz, 2H), 7.27-7.24 (m, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.5, 128.1, 127.4, 124.1, 98.5, 79.0, 31.0, 27.9; LRMS (EI, 70 eV) *m/z* (%): 158 (M^+, 36), 143 (100), 128 (48), 115 (13); HRMS *m/z* (ESI) calcd for $C_{12}H_{15}$ ($[M+H]^+$) 159.1168, found 159.1175.



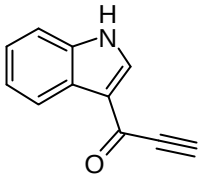
4-Iodo-5-phenylbenzo[*cd*]indol-3(1*H*)-one (5):

Light yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) δ: 9.53 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 2.8 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 3H), 7.42-7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.6, 138.6, 137.0, 135.2, 131.6, 129.7, 129.0, 128.4, 125.5, 124.3, 123.3, 122.2, 113.4, 112.1, 90.0; HRMS *m/z* (ESI) calcd for $C_{17}H_{11}INO$ ($[M+H]^+$) 371.9880, found 371.9888.



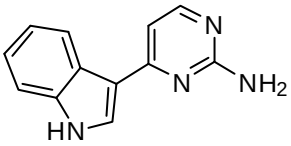
1-(1*H*-Indol-3-yl)-3,3-dimethoxypropan-1-one (6):

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.98 (s, 1H), 8.38 (d, *J* = 2.34 Hz, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.23-7.16 (m, 2H), 4.91 (s, 1H), 3.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.0, 137.3, 135.3, 125.9, 123.5, 122.4, 121.9, 117.5, 112.7, 102.7, 53.6, 43.4; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_3$ ($[M+H]^+$) 234.1125, found 234.1132.



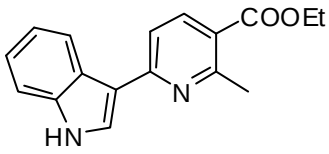
1-(1*H*-indol-3-yl)prop-2-yn-1-one (7):

Light yellow oil; ^{1}H NMR (400 MHz, acetone-D6) δ: 11.28 (s, 1H), 8.32 (s, 1H), 8.27 (d, *J* = 6.6 Hz, 1H), 7.60-7.49 (m, 1H), 7.34-7.23 (m, 2H), 3.94 (s, 1H); ^{13}C NMR (100 MHz, acetone-D6) δ: 170.4, 136.9, 125.1, 123.8, 122.6, 121.6, 118.9, 112.4, 112.3, 81.5, 76.3; HRMS *m/z* (ESI) calcd for $C_{11}H_8NO$ ($[M+H]^+$)170.0600, found 170.0611.



4-(1*H*-indol-3-yl)pyrimidin-2-amine (8):

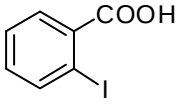
White solid; mp 187.2-189.0 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, DMSO-D6) δ: 11.66 (s, 1H), 8.59 (d, *J* = 7.6 Hz, 1H), 8.18-8.10 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.19-7.10 (m, 2H), 7.01 (d, *J* = 5.2 Hz, 1H), 6.39 (s, 2H); ^{13}C NMR (100 MHz, DMSO-D6) δ: 164.1, 163.3, 157.6, 137.6, 128.8, 125.9, 123.0, 122.58, 120.9, 114.3, 112.4, 105.9; LRMS (EI, 70 eV) *m/z* (%): 210 (M^+, 100), 169 (63), 140 (12), 91 (43); HRMS *m/z* (ESI) calcd for $C_{12}H_{10}N_4$ ($[M+H]^+$) 211.0978, found 211.0986.



Ethyl 6-(1H-indol-3-yl)-2-methylnicotinate (9):

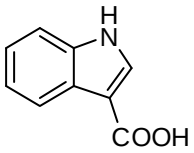
White solid; mp 216.3-217.5 ^{o}C (uncorrected);^{1}H

NMR (400 MHz, DMSO-D6) δ: 11.40 (s, 1H), 8.26 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 2.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.95-6.79 (m, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-D6) δ:166.7, 159.3, 158.2, 138.9, 137.8, 128.5, 125.9, 122.7, 122.6, 121.1, 120.5, 116.9, 115.2, 112.5, 61.2, 25.6, 14.7; LRMS (EI, 70 eV) *m/z* (%): 280 (M^+, 100), 252 (46), 235 (30), 207 (17); HRMS *m/z* (ESI) calcd for $C_{17}H_{16}N_2O_2$ ($[M+H]^+$) 281.1285, found 281.1292.



2-iodobenzoic acid (10):

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08-8.02 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H); (EI, 70 eV) *m/z* (%): 248 (M^+, 3), 235 (2), 207 (100), 179 (48).



1*H*-indole-3-carboxylic acid (11):

Light yellow solid, ^{1}H NMR (400 MHz, Acetone-D6) δ: 11.02 (s, 1H), 8.18 (t, *J* = 4.4 Hz, 1H), 8.10 (d, *J* = 2.8 Hz, 1H), 7.53 (t, J = 4.4 Hz, 1H), 7.25-7.20 (m, 2H); ^{13}C NMR (100 MHz, Acetone-D6) δ: 166.5, 136.9, 132.4, 126.5, 122.6, 121.3, 121.1, 112.1,107.6.

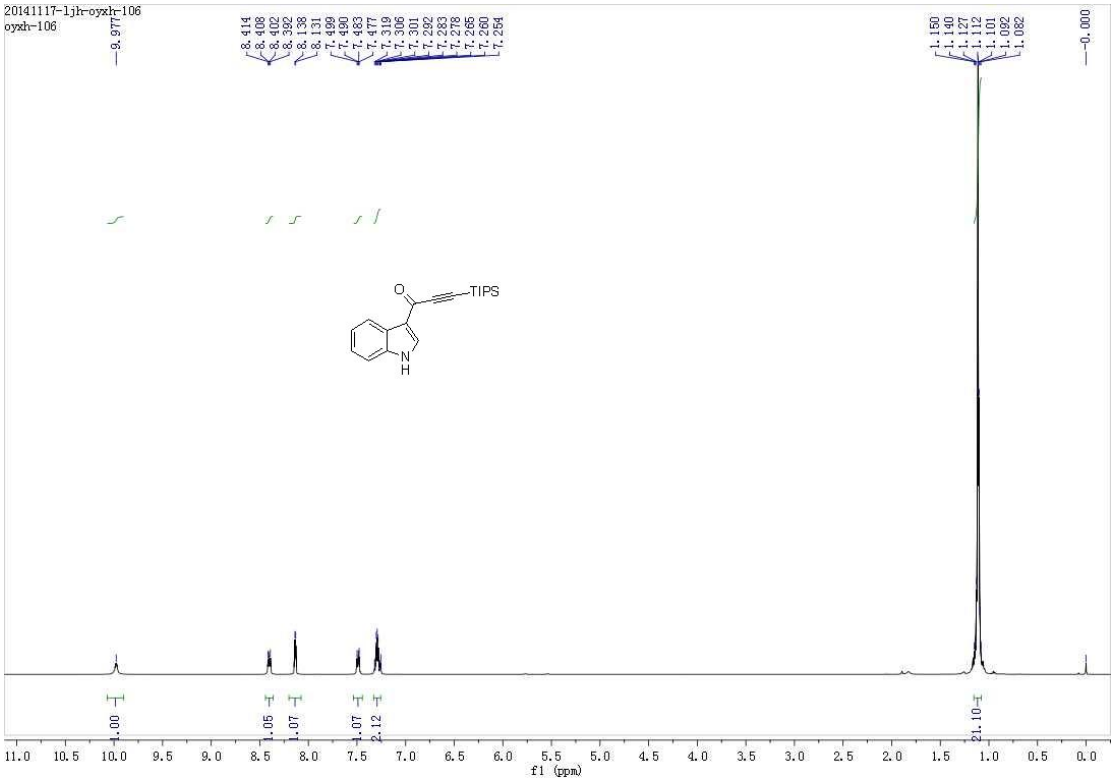
(C) Reference

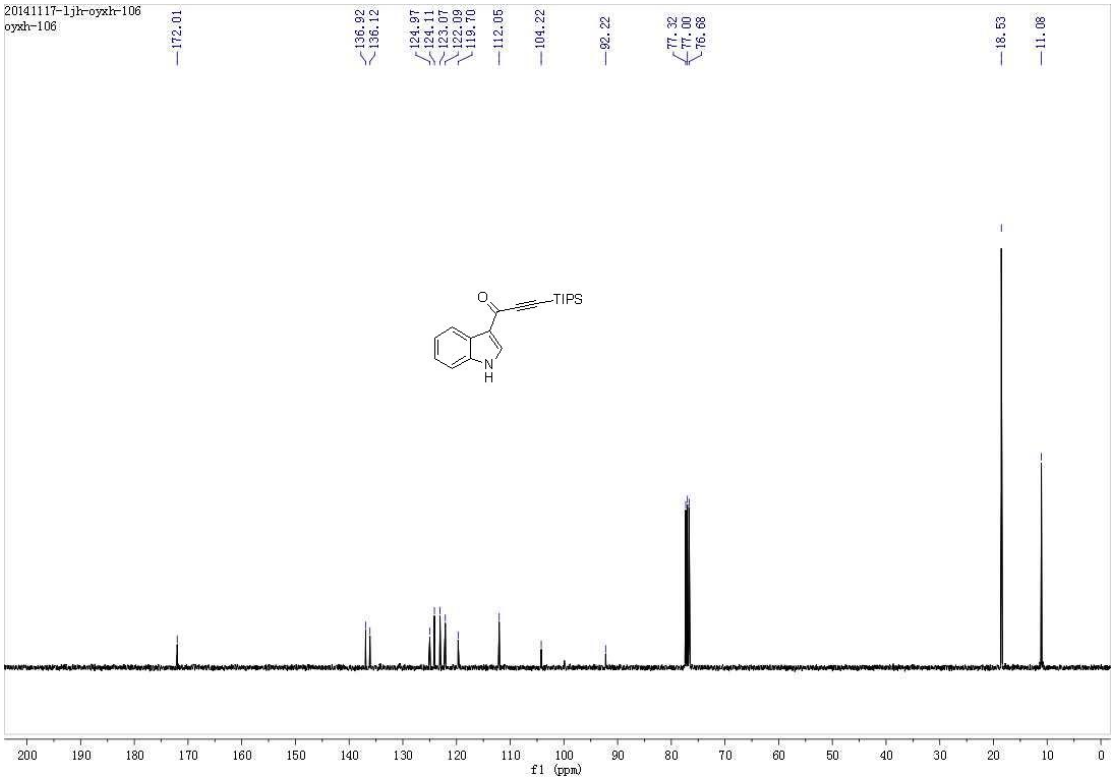
[1] a) J. P. Brand, C Chevalley, R. Scopelliti, J. Waser, *Chem. Eur. J.* **2012**, *18*, 5655; b) D. F. Gonzlez, J. P. Brand, R. Mondire, J. Waser, *Adv. Synth. Catal.* **2013**, *355*, 1631; c) H. Huang, G. Zhang, L. Gong, S. Zhang, Y. Chen, *J. Am. Chem. Soc.* **2014**, *136*, 2280; d) B. Lu, J. Wu, N. Yoshikai, *J. Am. Chem. Soc.* **2014**, *136*, 11598; e) T.

Kitamura, M. Kotani, Y. Fujiwara, *Synthesis* **1998**, *10*, 1416; f) X. Liu, Z. Wang, X. Cheng, C. Li, *J. Am. Chem. Soc*. **2012**, *134*, 14330

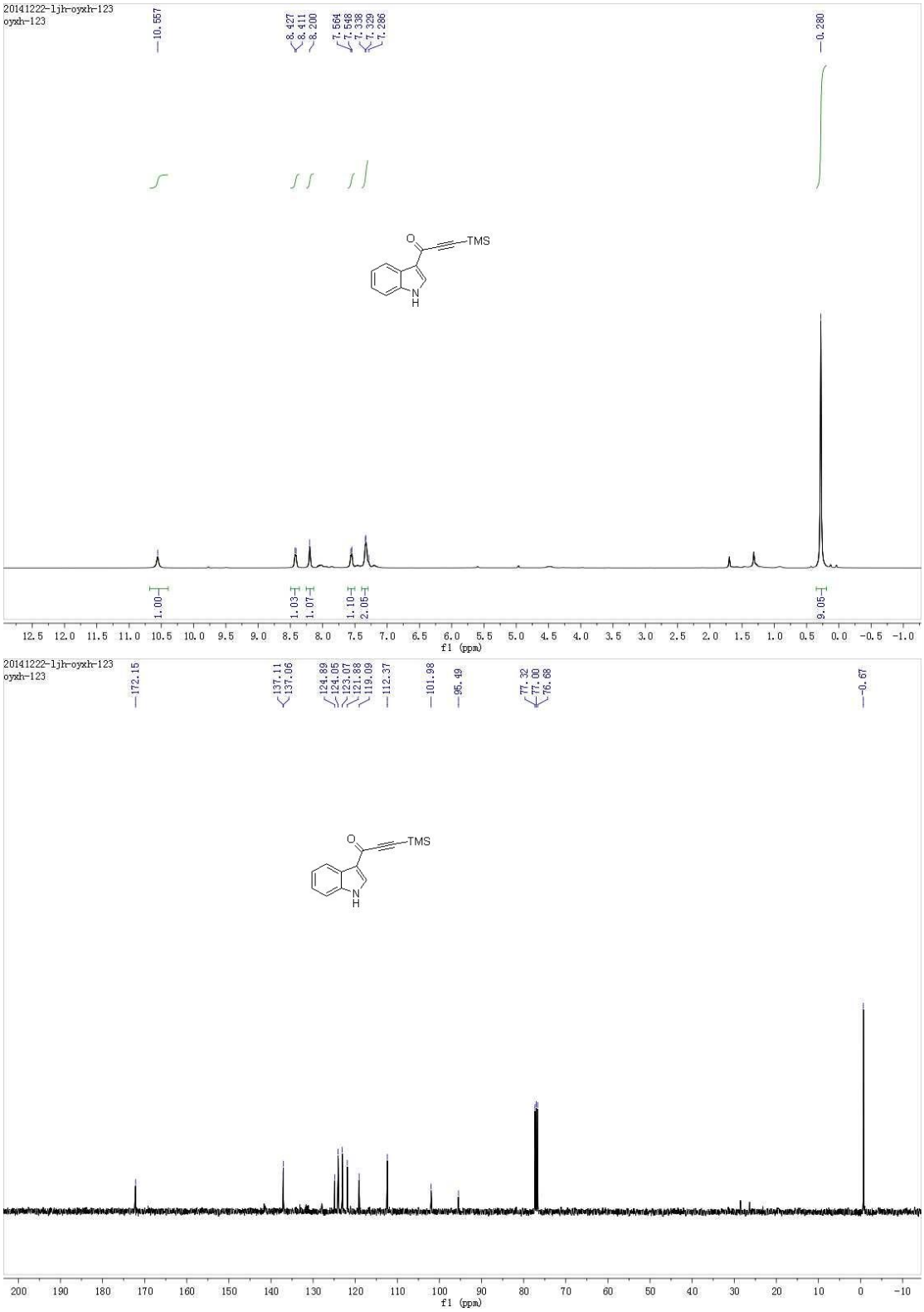
(D) Spectra

1-(1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3aa)

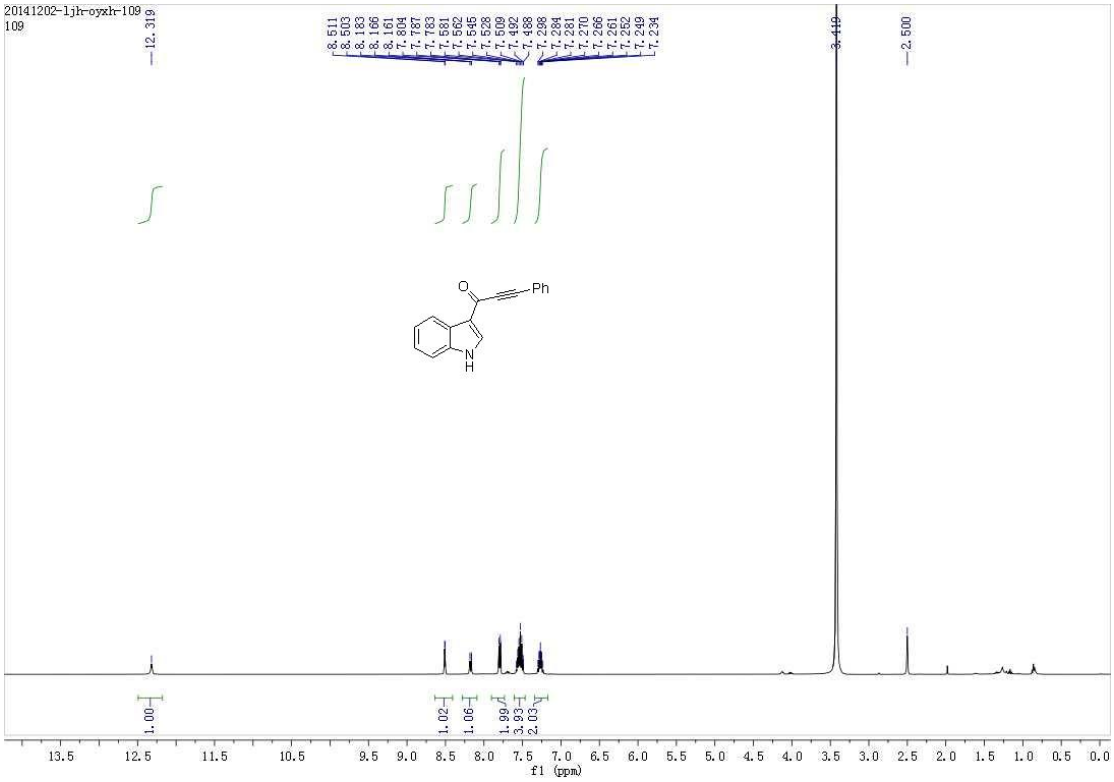


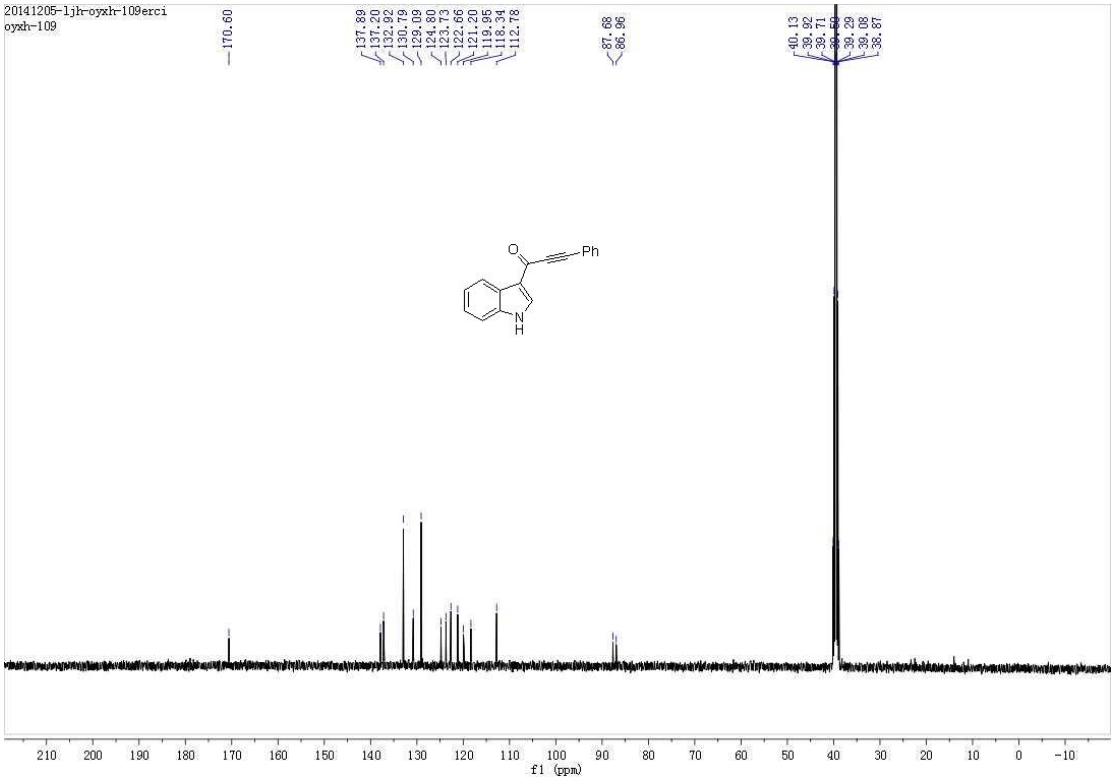


1-(1*H*-indol-3-yl)-3-(trimethylsilyl)prop-2-yn-1-one (3ab)

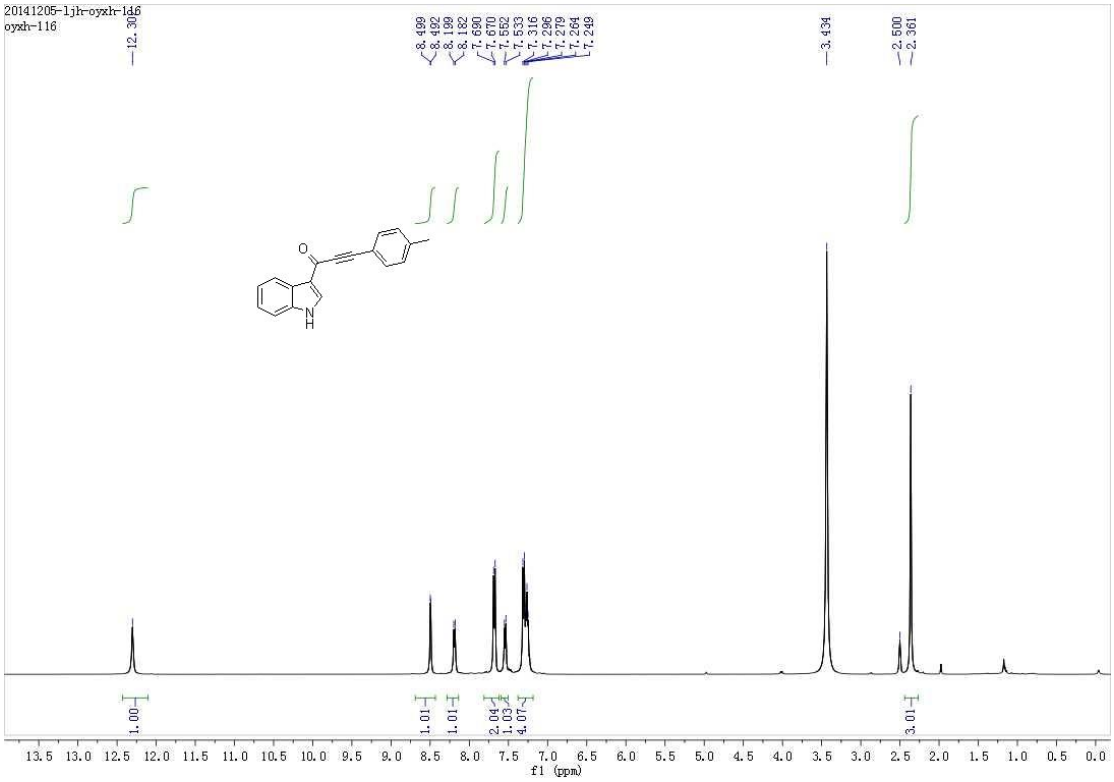


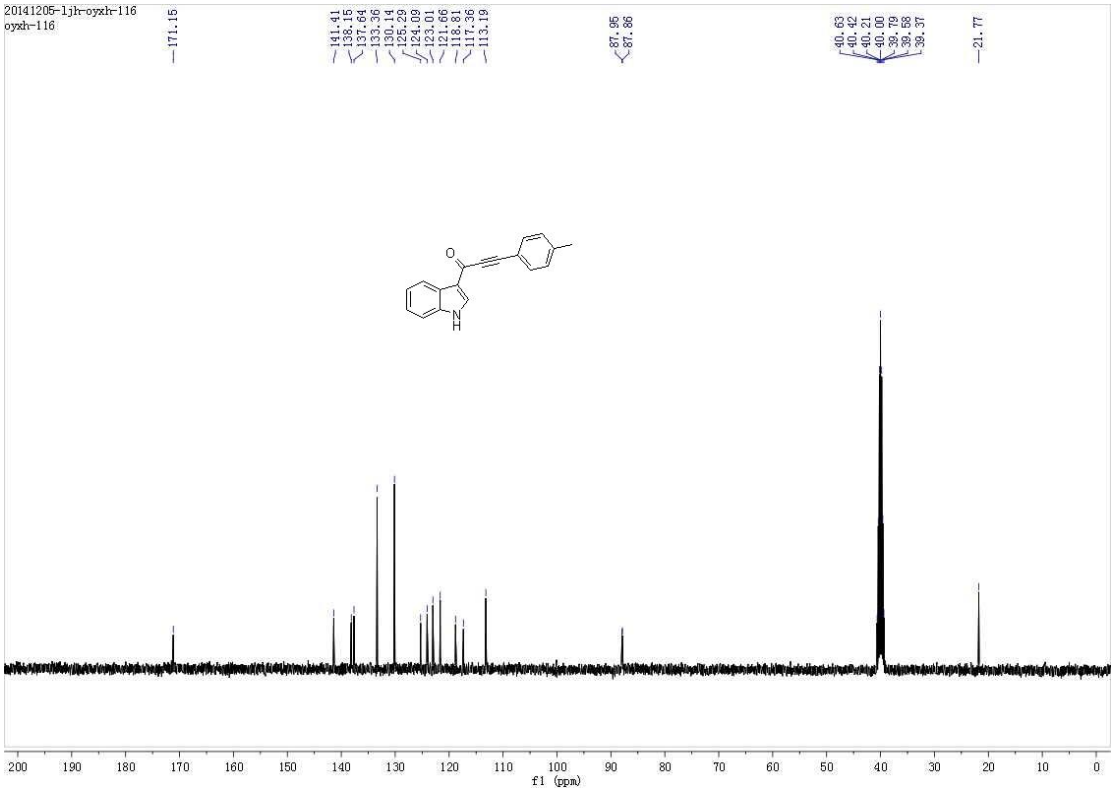
1-(1*H*-indol-3-yl)-3-phenylprop-2-yn-1-one (3ac)



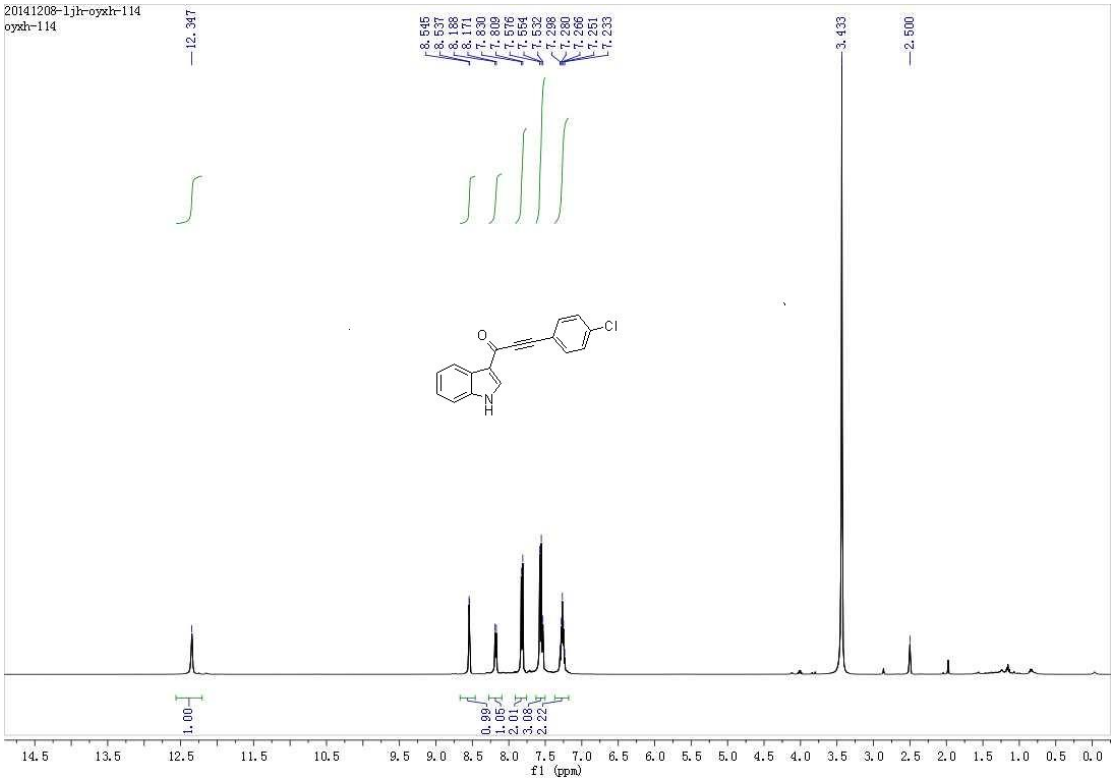


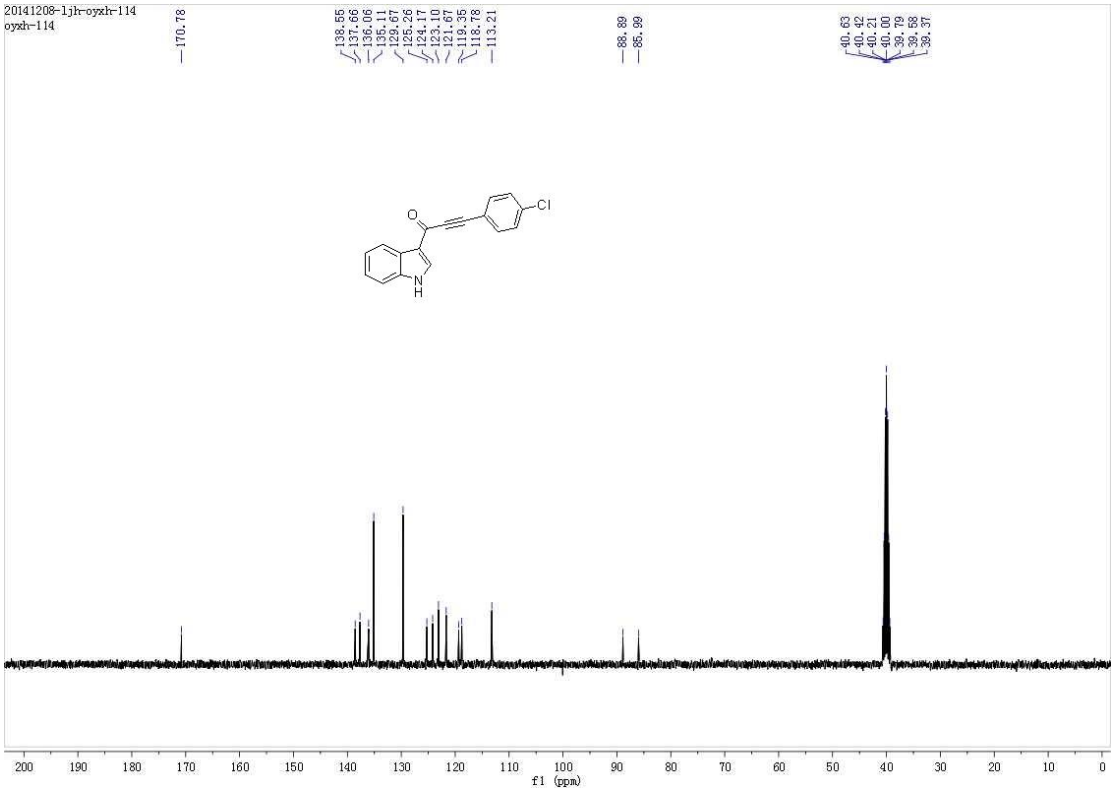
1-(1*H*-indol-3-yl)-3-p-tolylprop-2-yn-1-one (3ad)



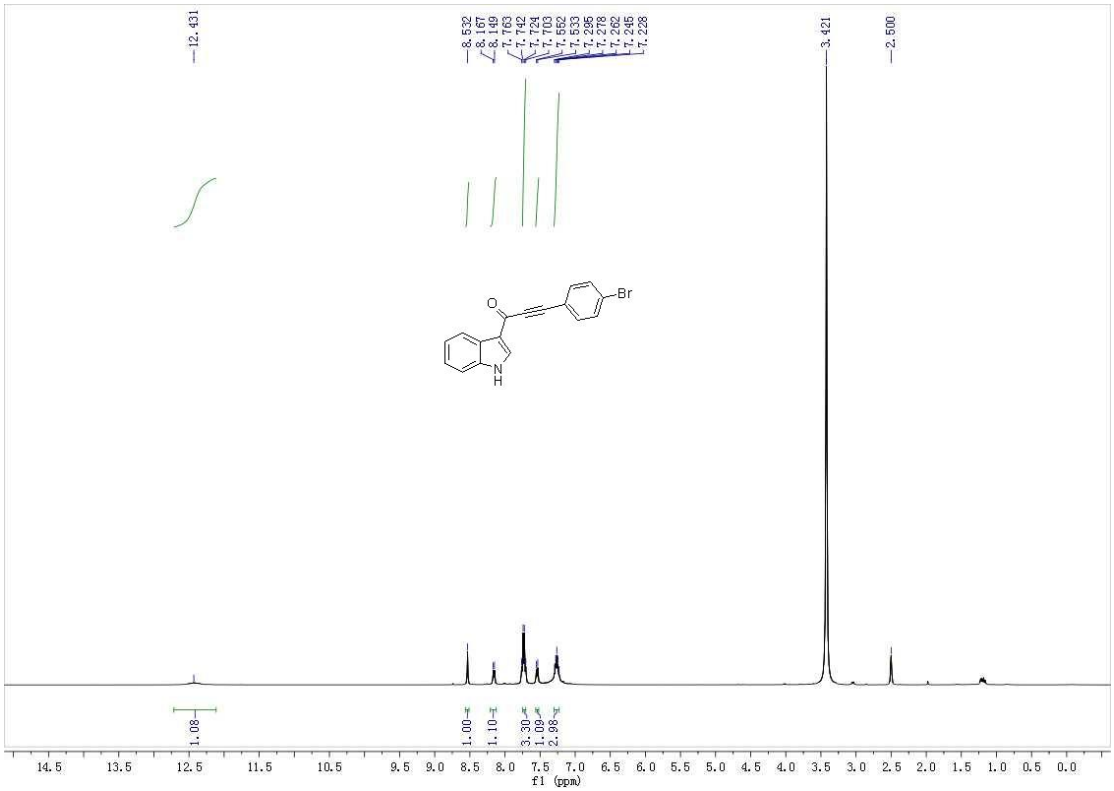


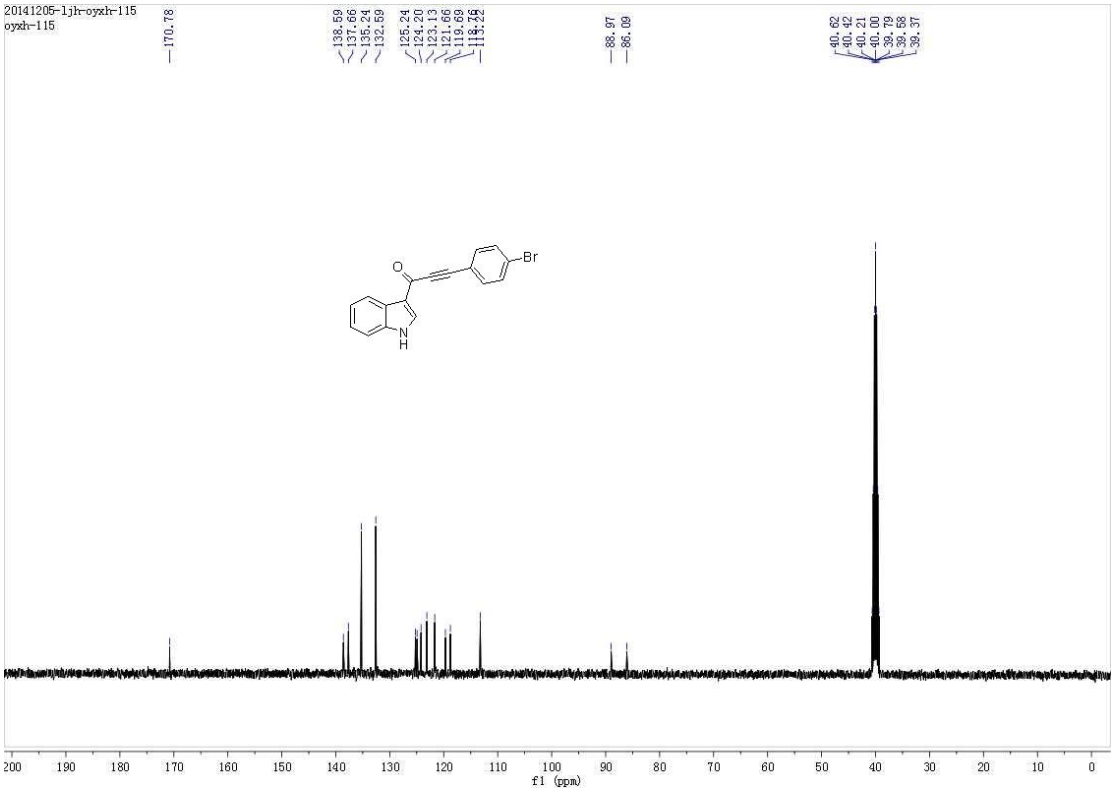
3-(4-chlorophenyl)-1-(1*H*-indol-3-yl)prop-2-yn-1-one (3ae)



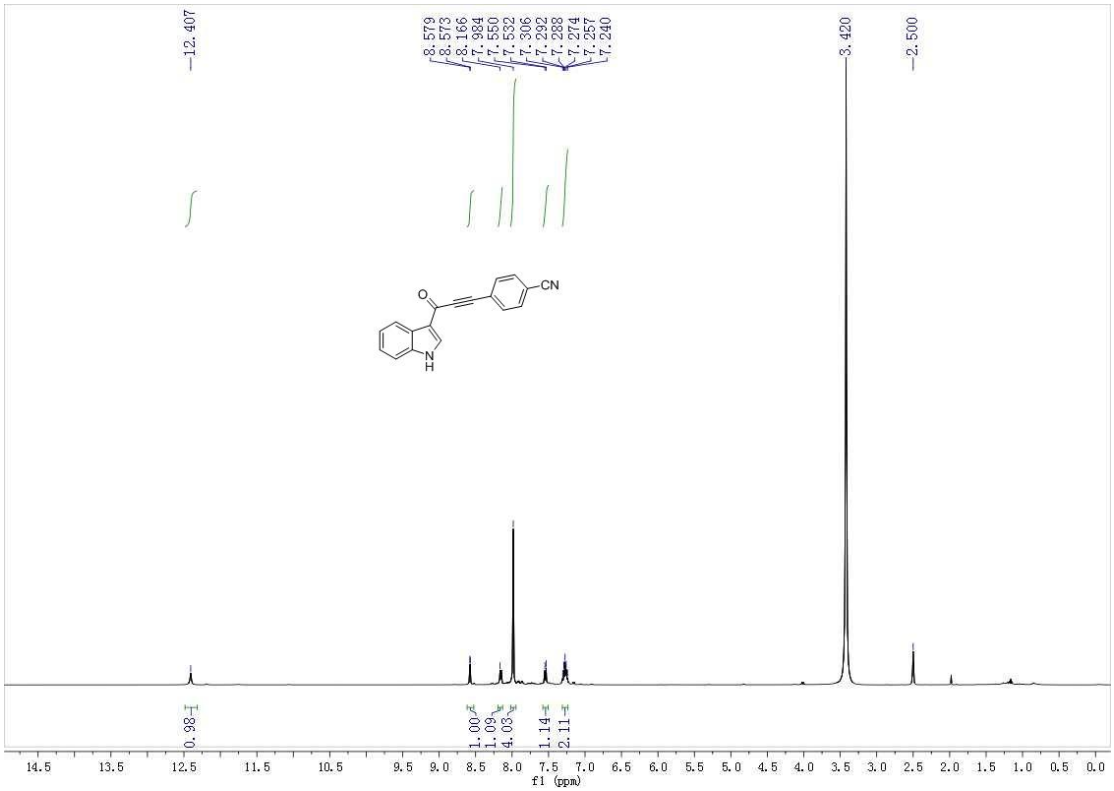


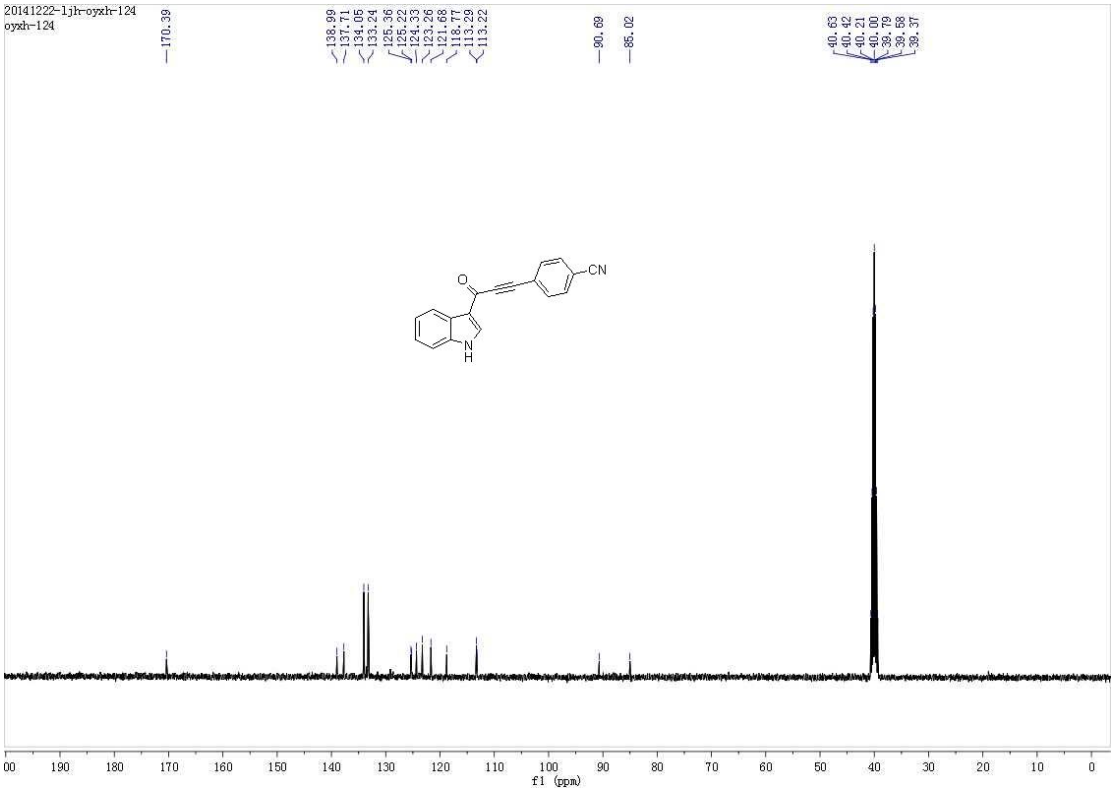
3-(4-bromophenyl)-1-(1*H*-indol-3-yl)prop-2-yn-1-one (3af)



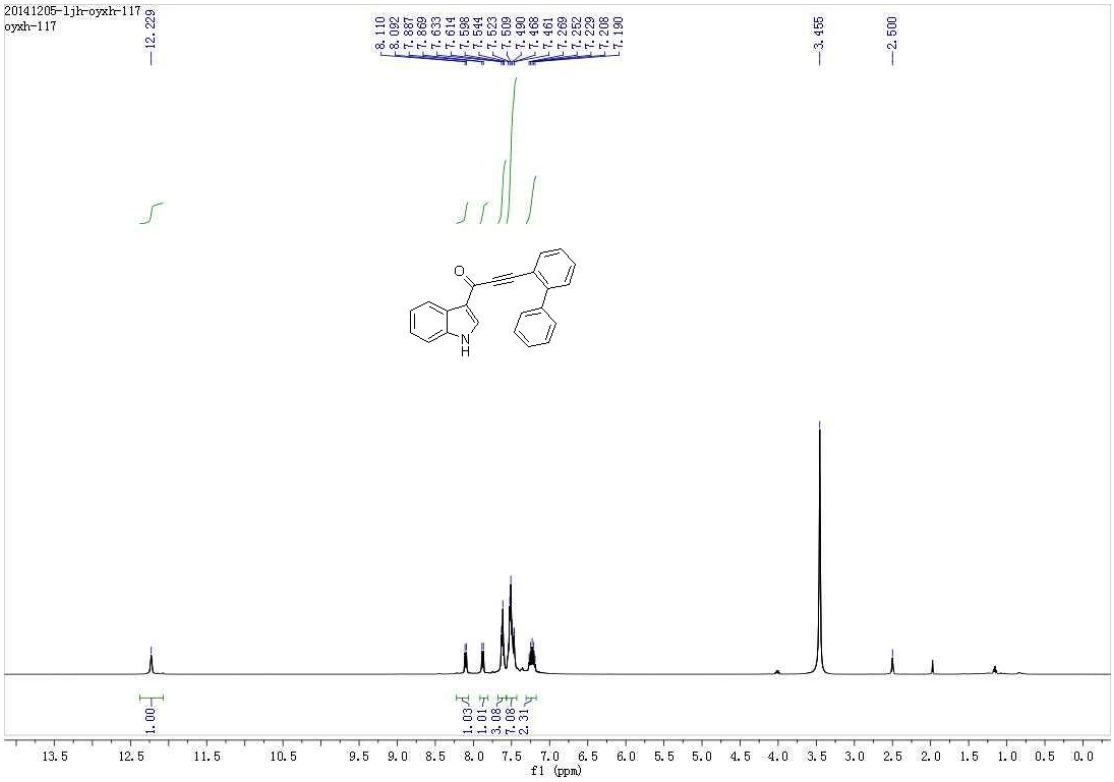


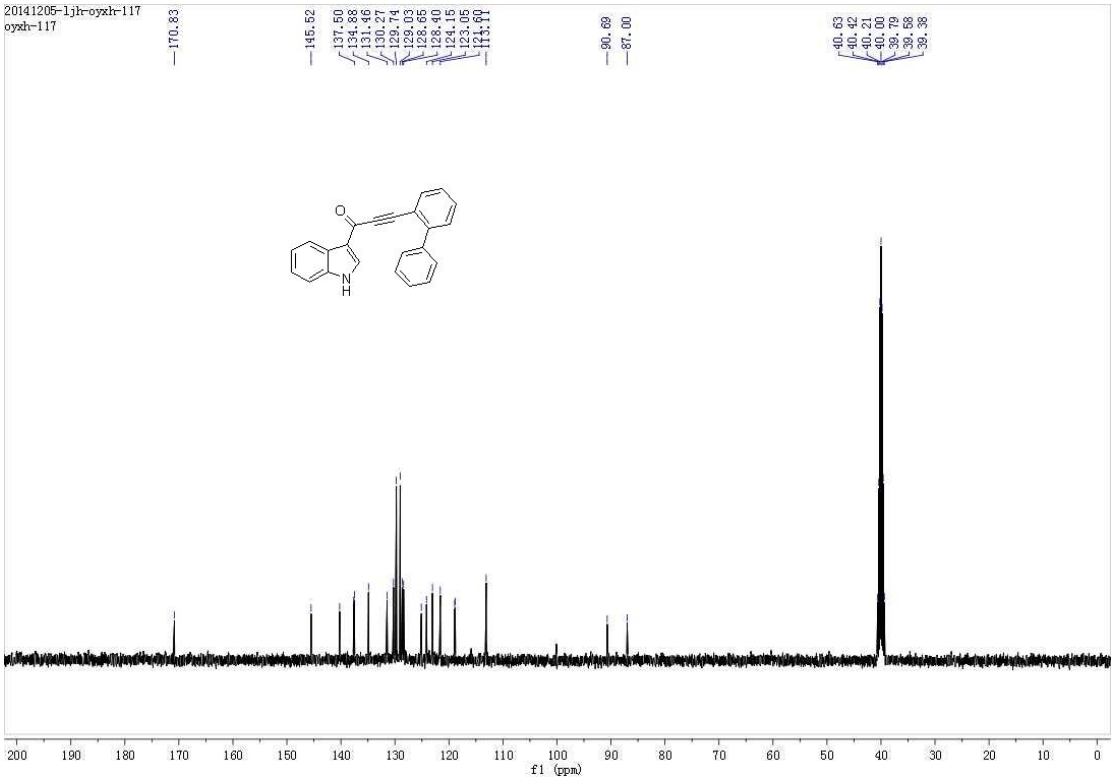
4-(3-(1*H*-indol-3-yl)-3-oxoprop-1-ynyl)benzonitrile (3ag)



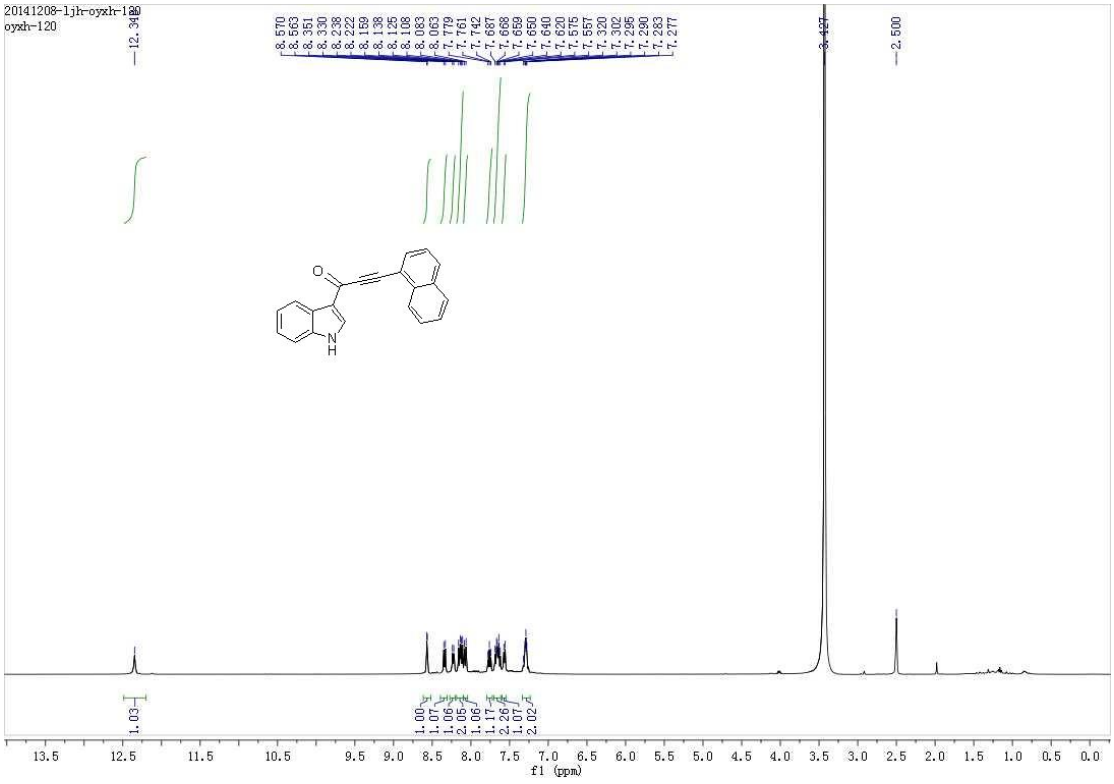


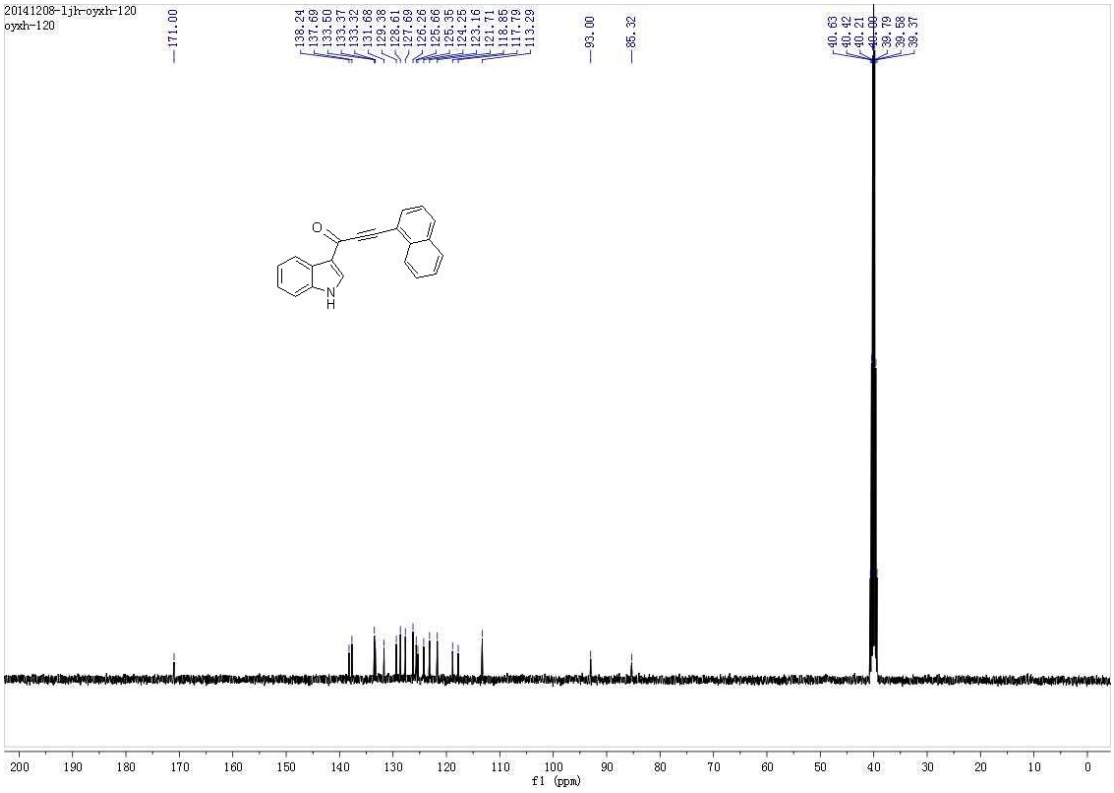
3-(biphenyl-2-yl)-1-(1*H*-indol-3-yl)prop-2-yn-1-one (3ah)



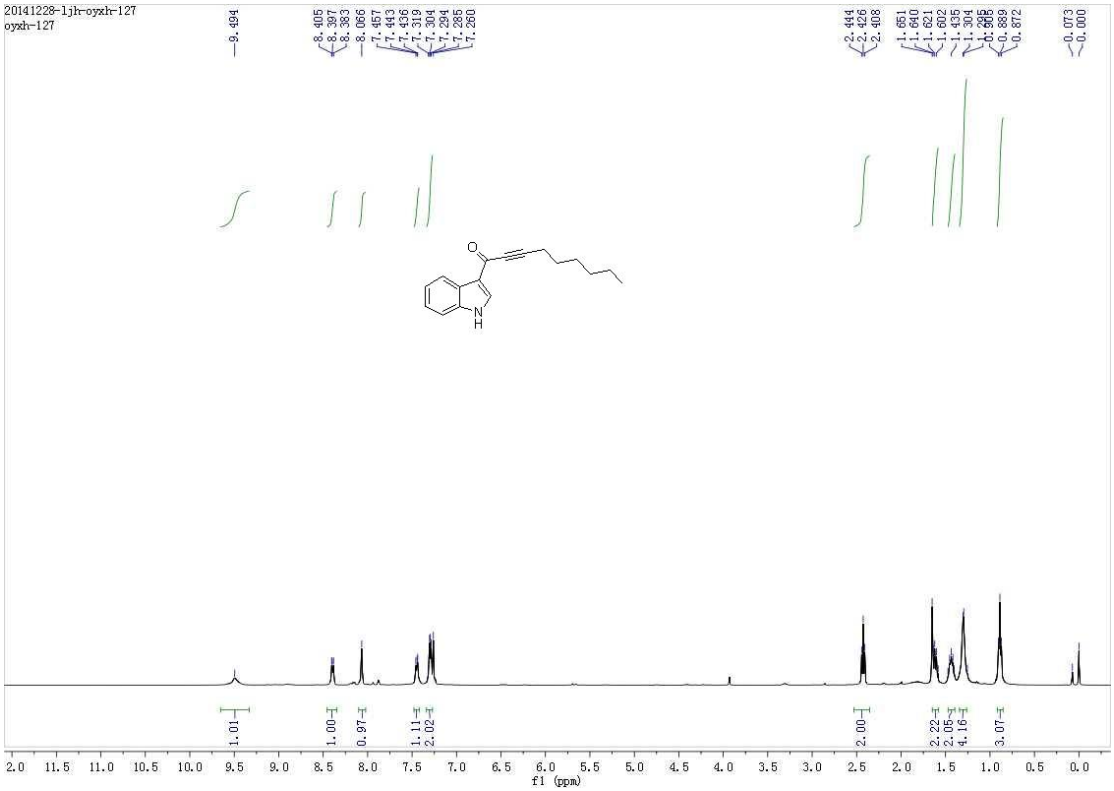


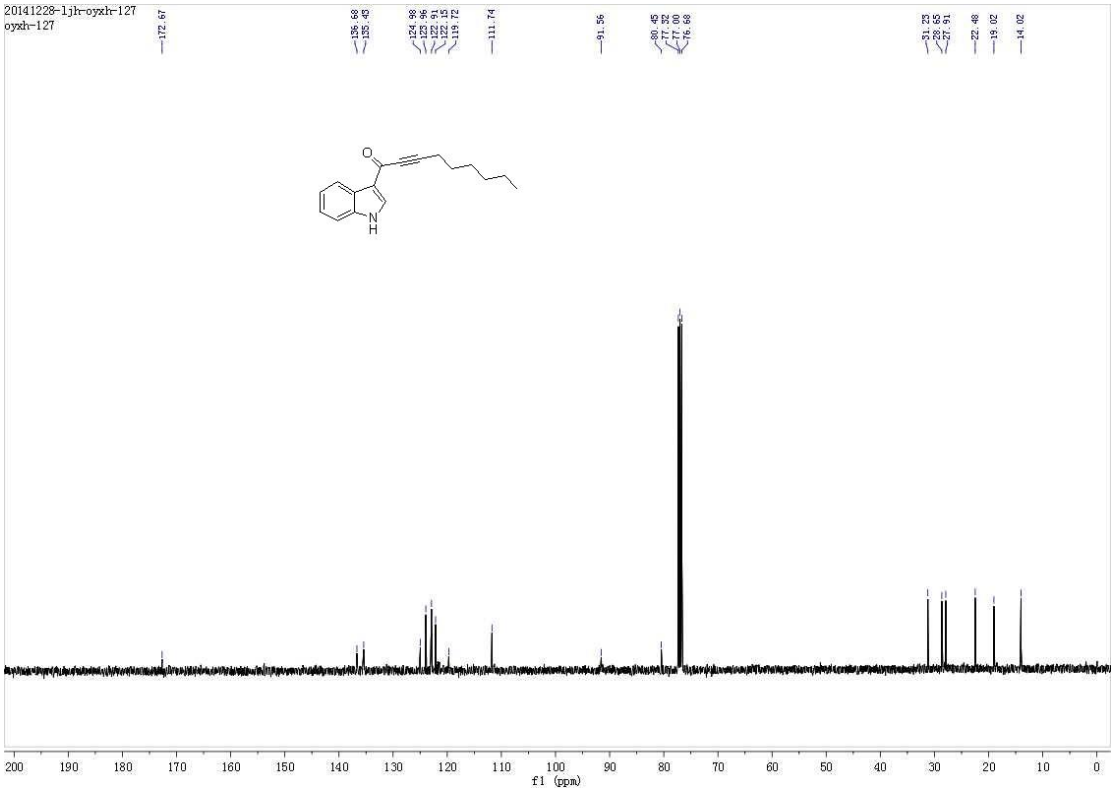
1-(1*H*-indol-3-yl)-3-(naphthalen-1-yl)prop-2-yn-1-one (3ai)



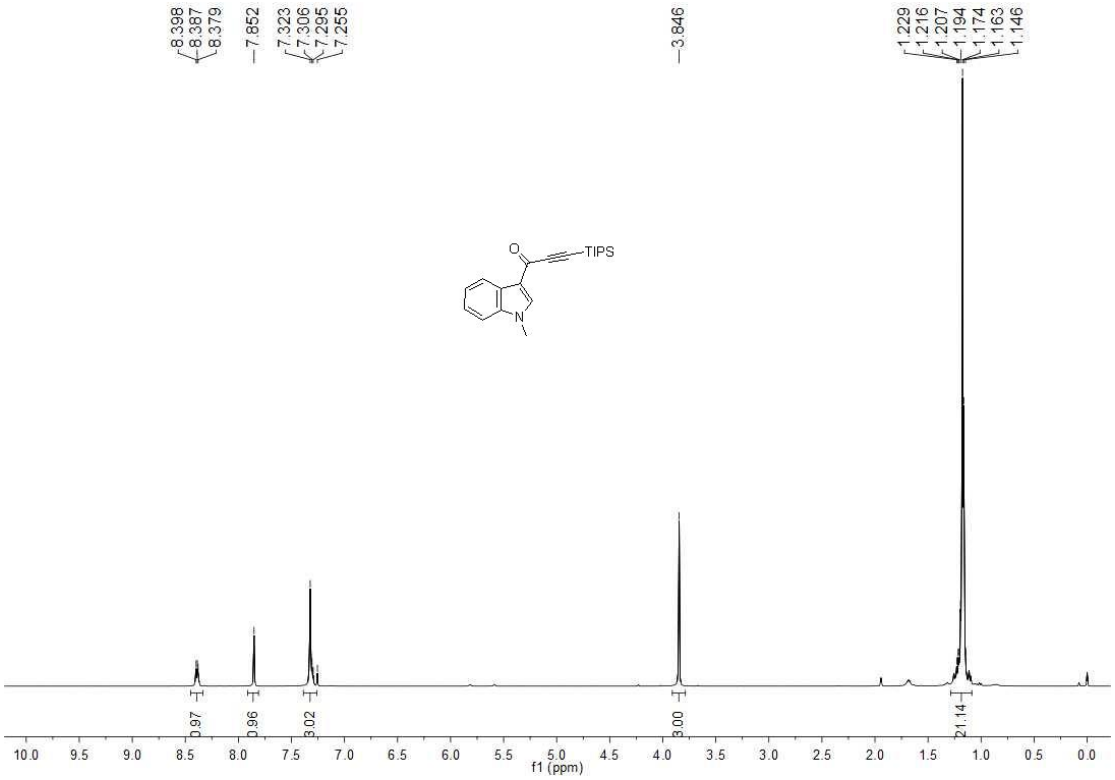


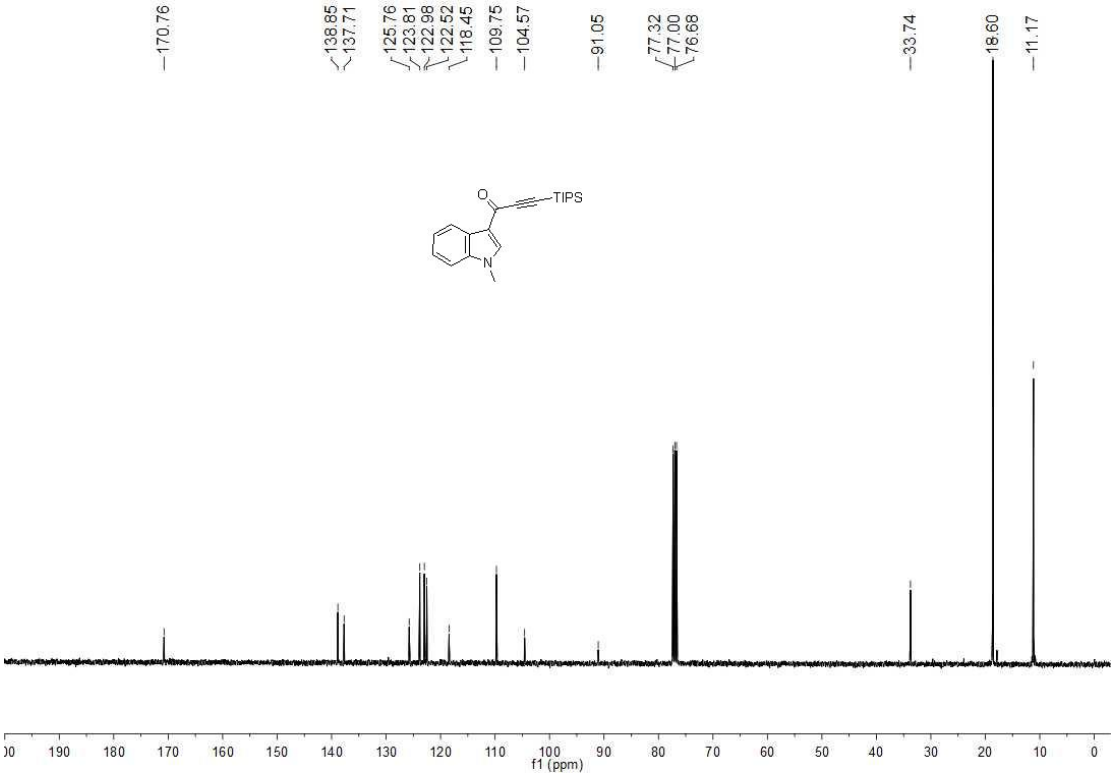
1-(1*H*-indol-3-yl)non-2-yn-1-one (3aj)



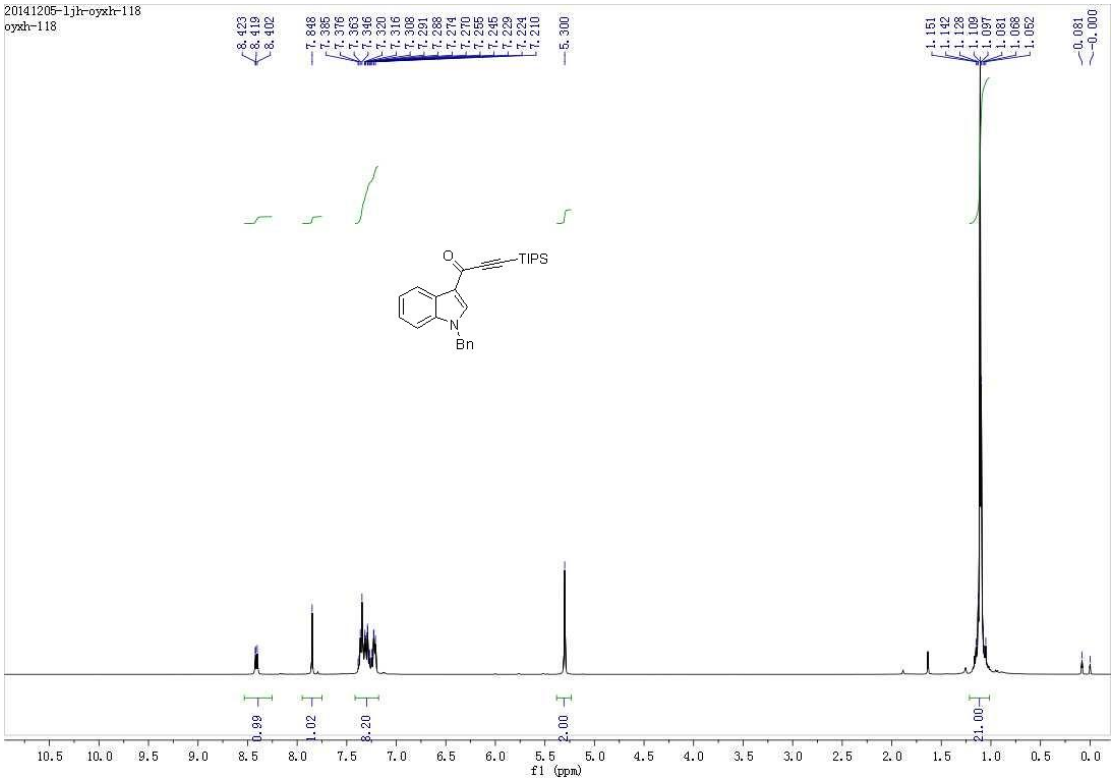


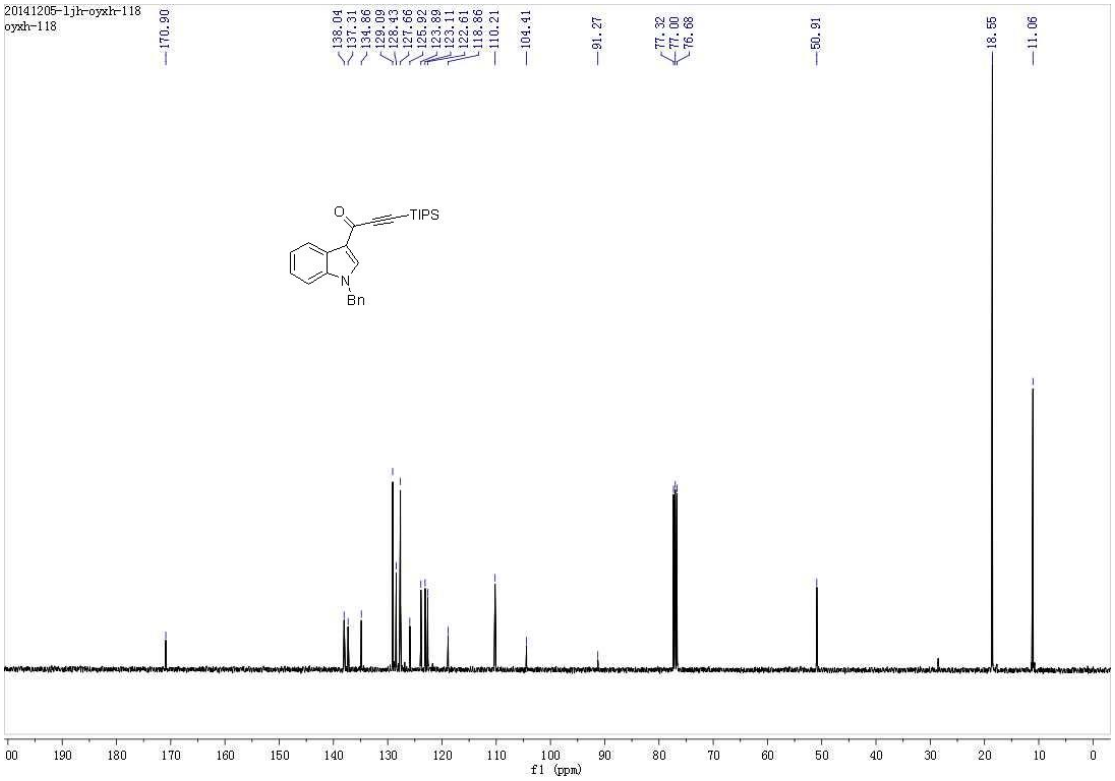
1-(1-methyl-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ba)



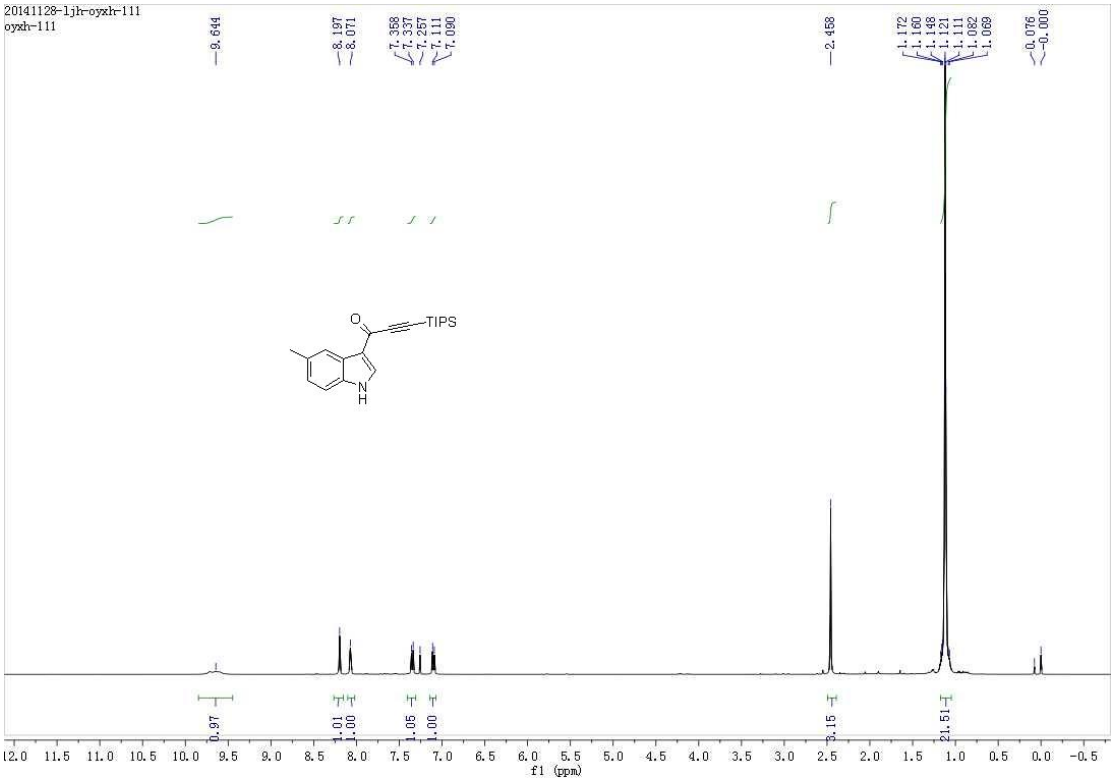


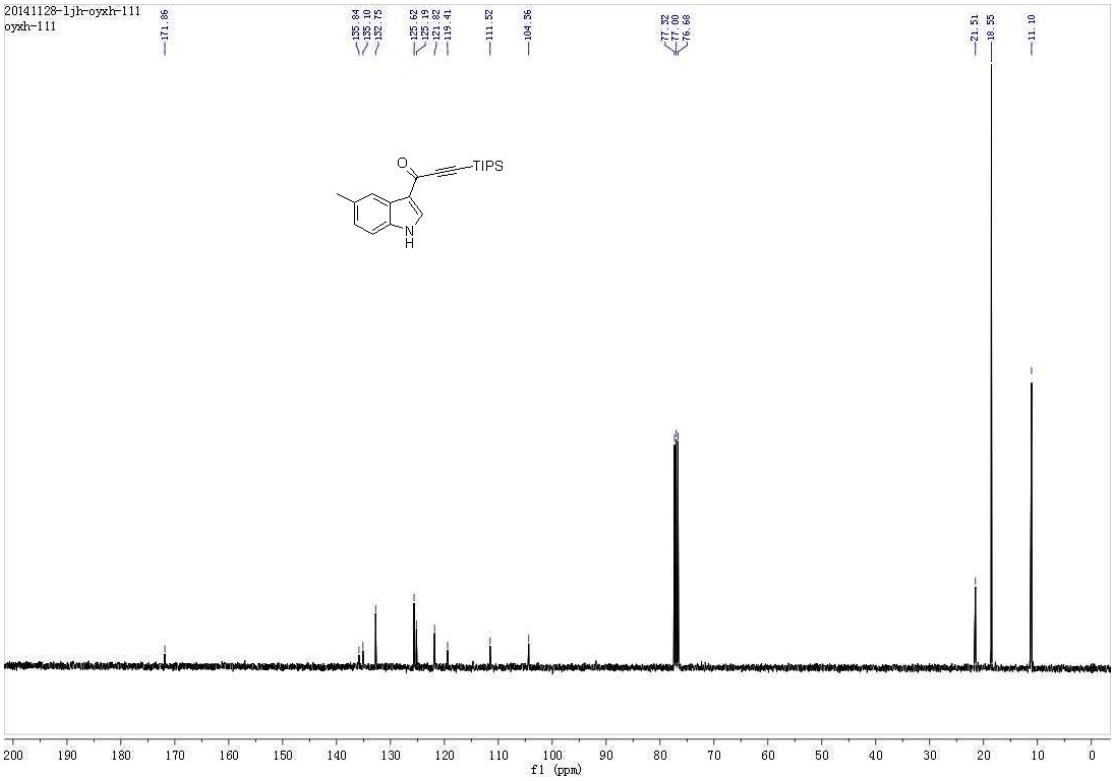
1-(1-benzyl-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ca)



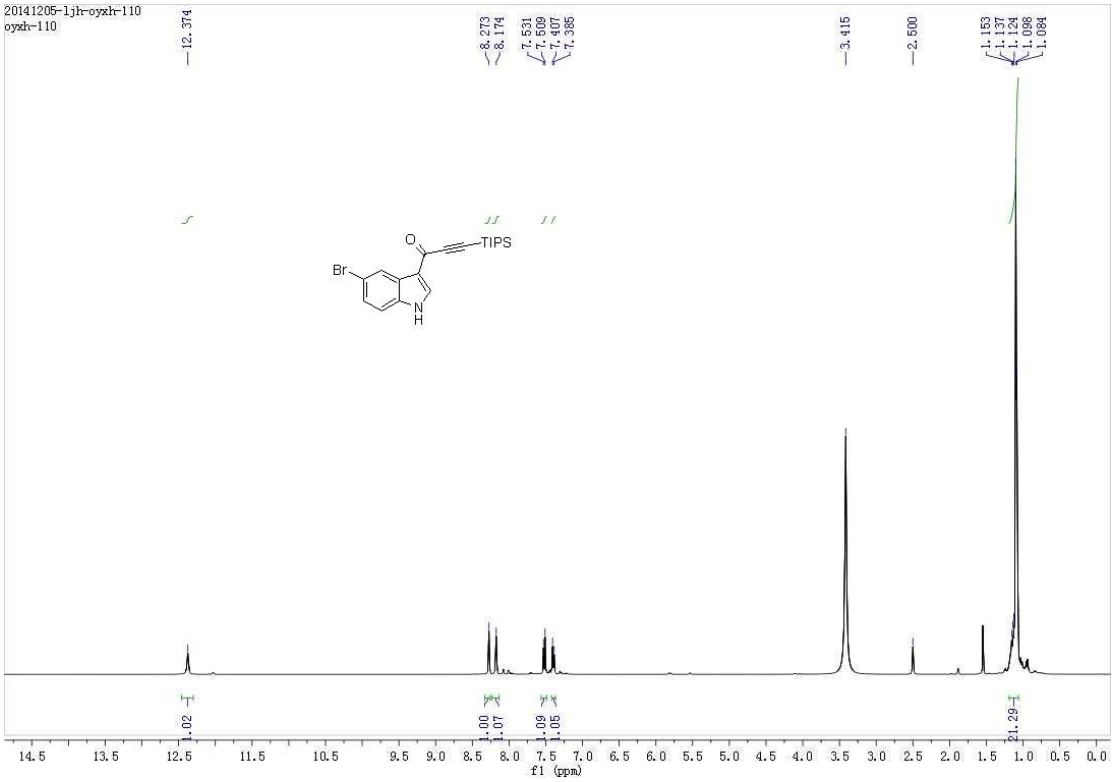


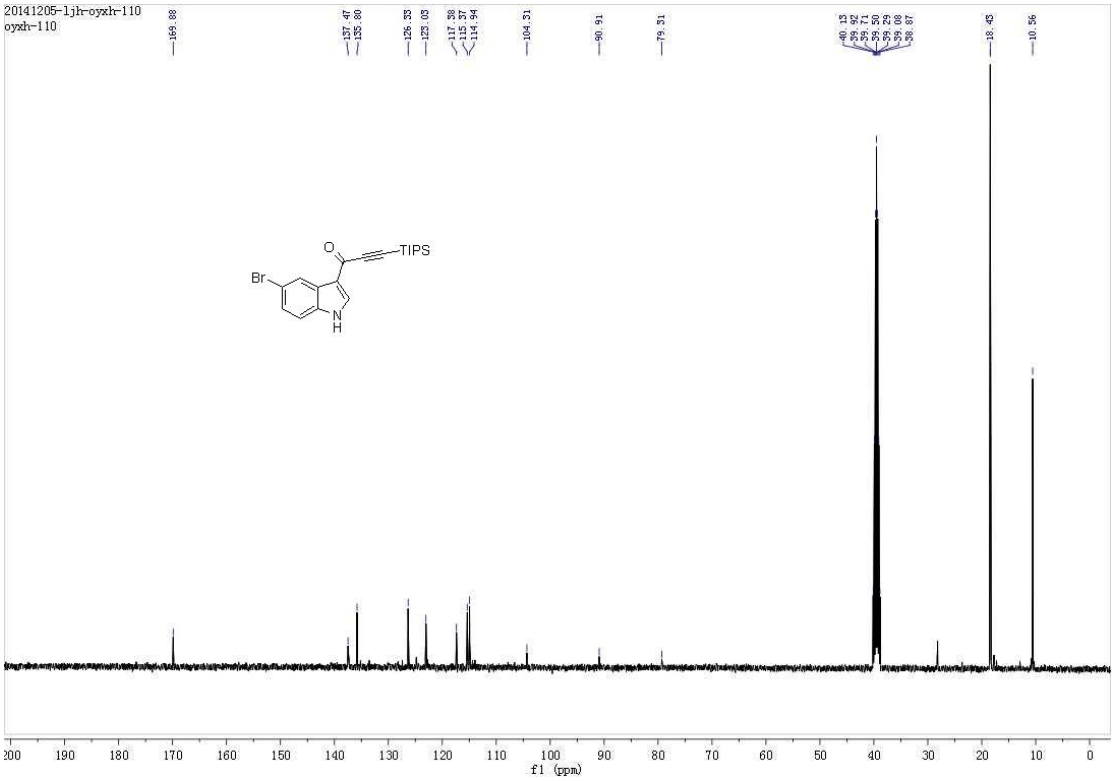
1-(5-methyl-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ea)



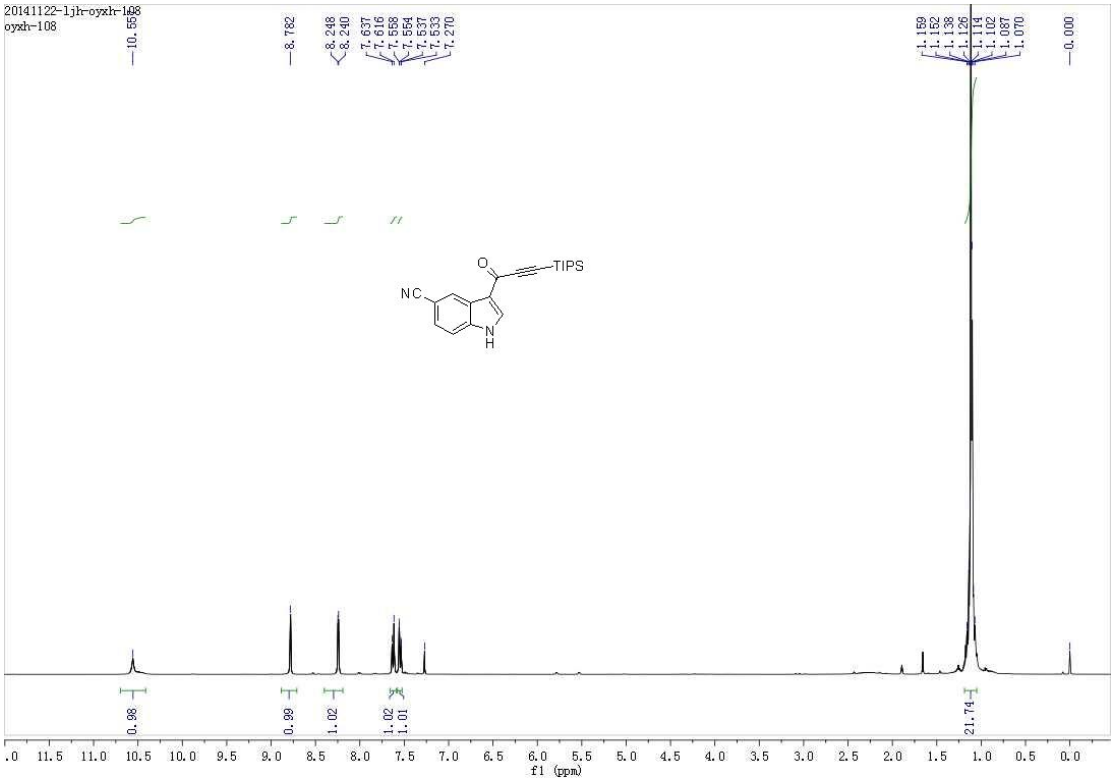


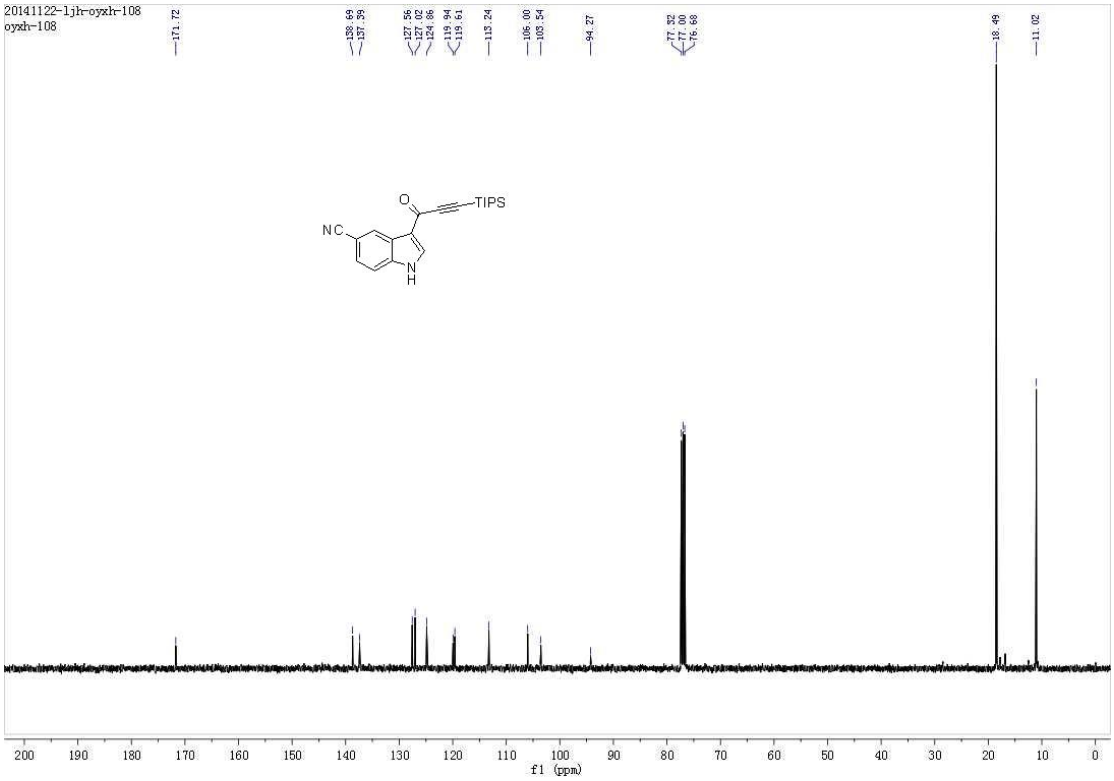
1-(5-bromo-1*H*-indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3fa)



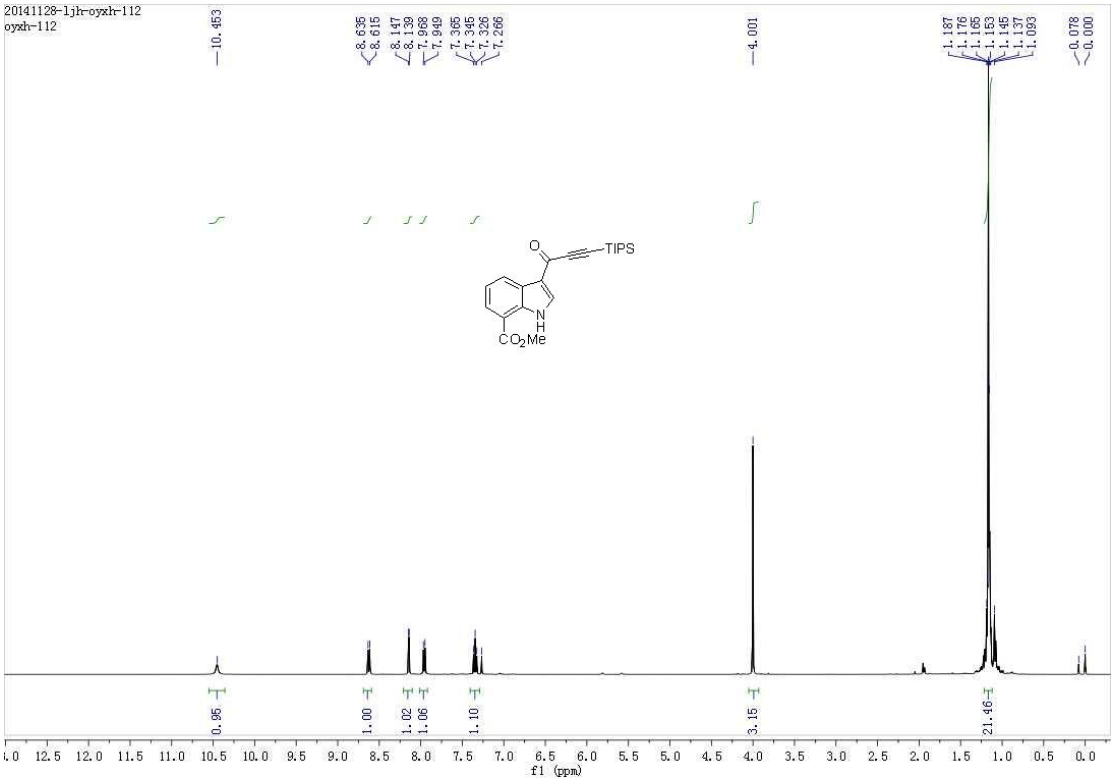


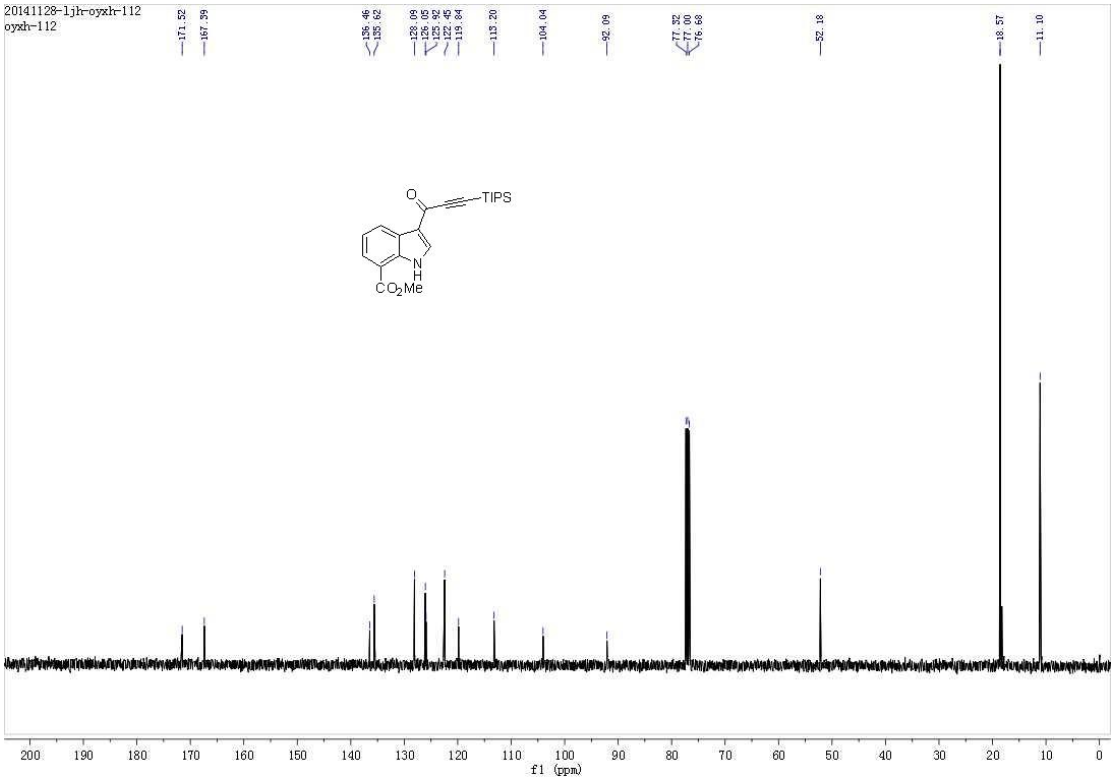
3-(3-(triisopropylsilyl)propioloyl)-1H-indole-5-carbonitrile (3ga)



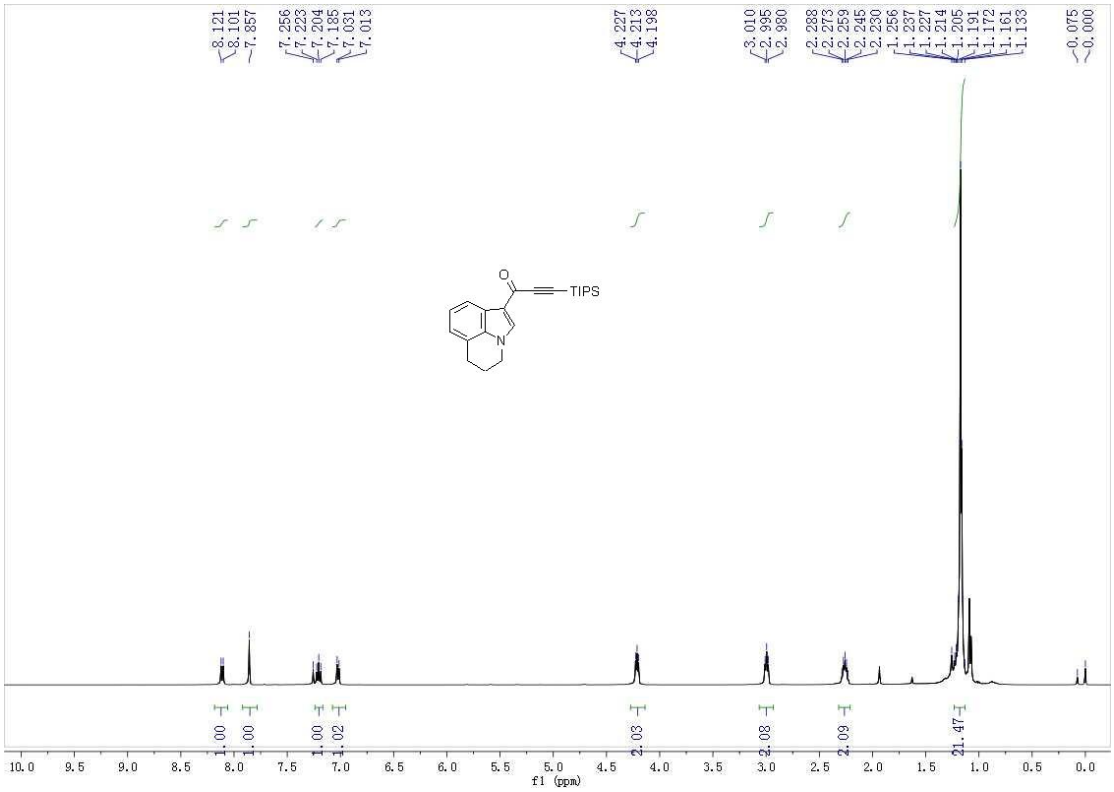


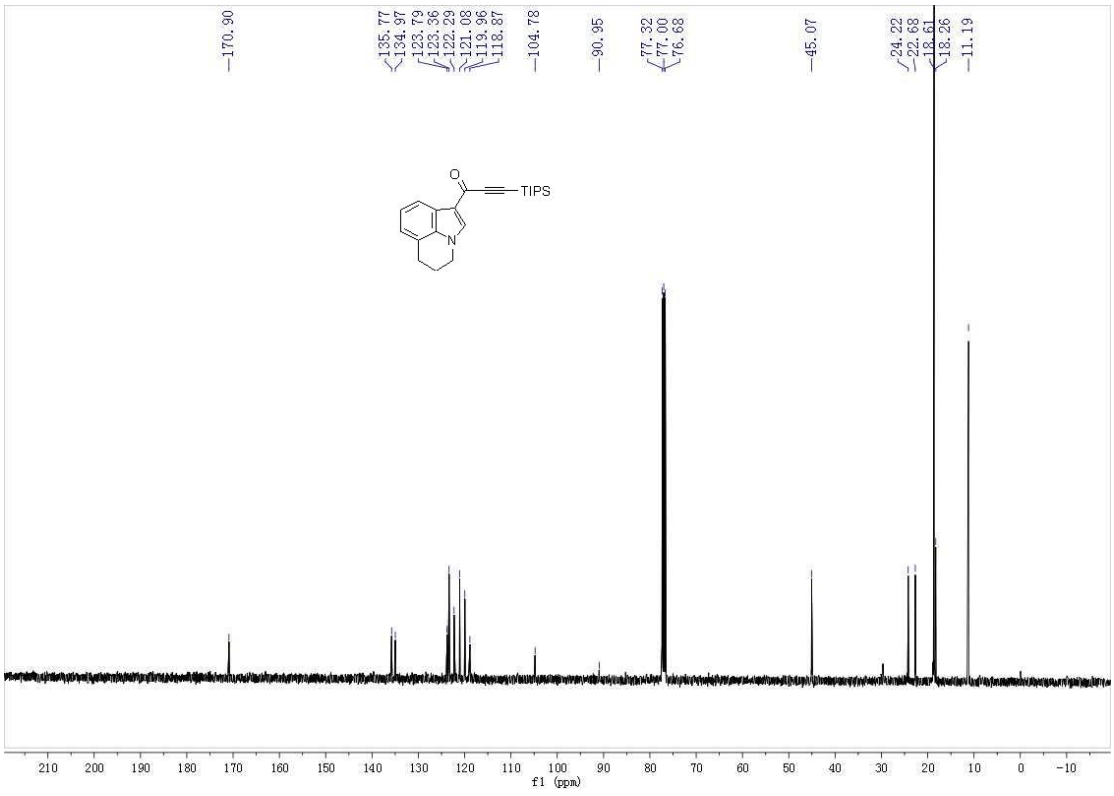
methyl 3-(3-(triisopropylsilyl)propioloyl)-1*H*-indole-7-carboxylate (3ha)



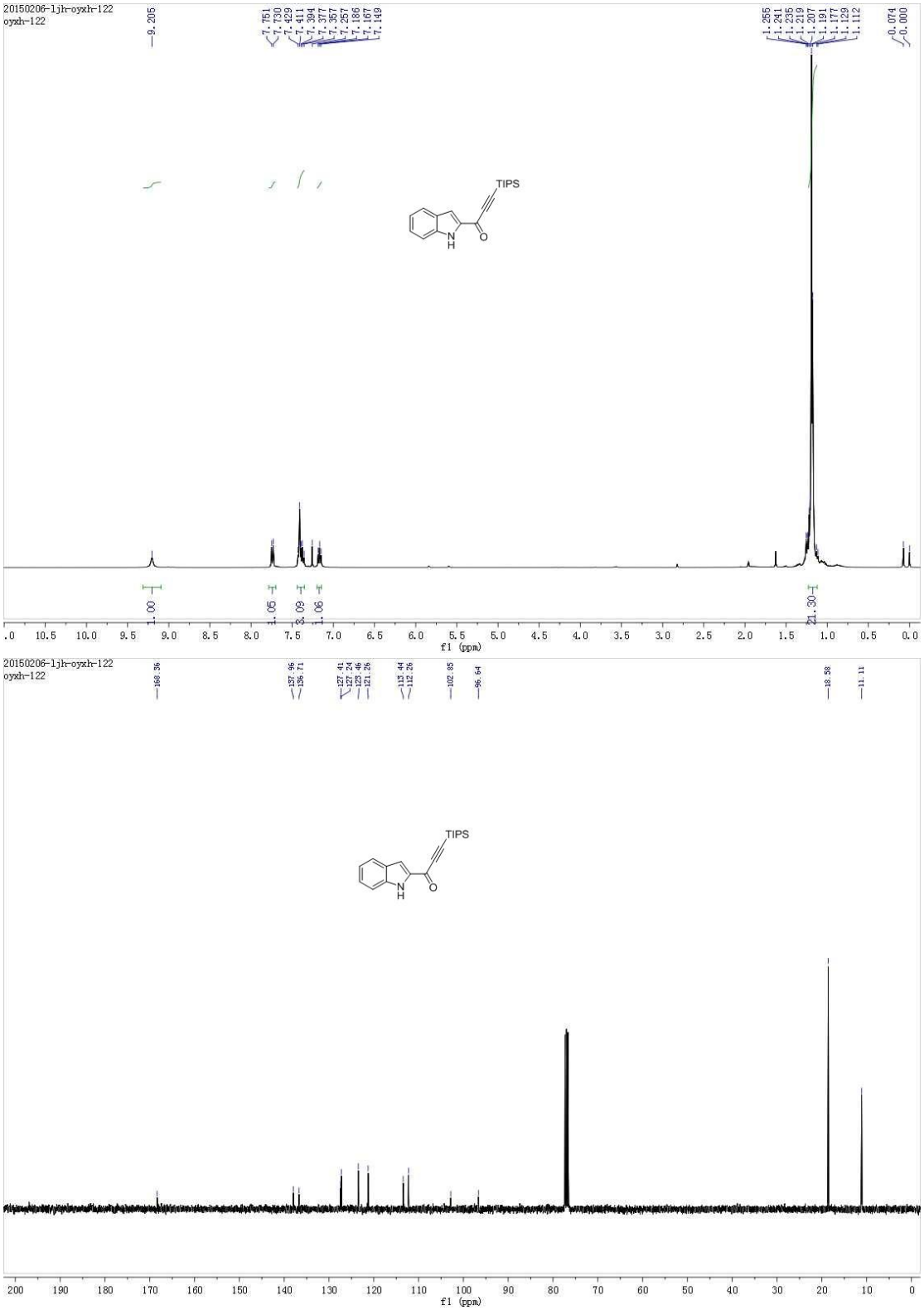


1-(5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-1-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ia)

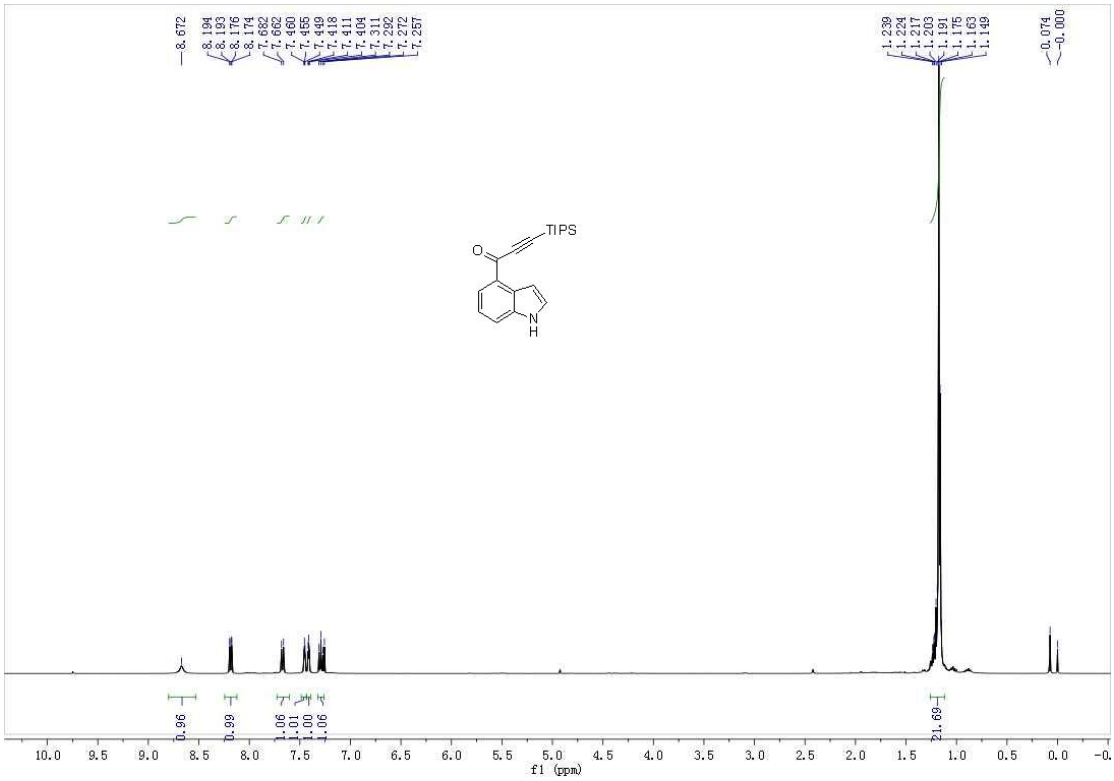


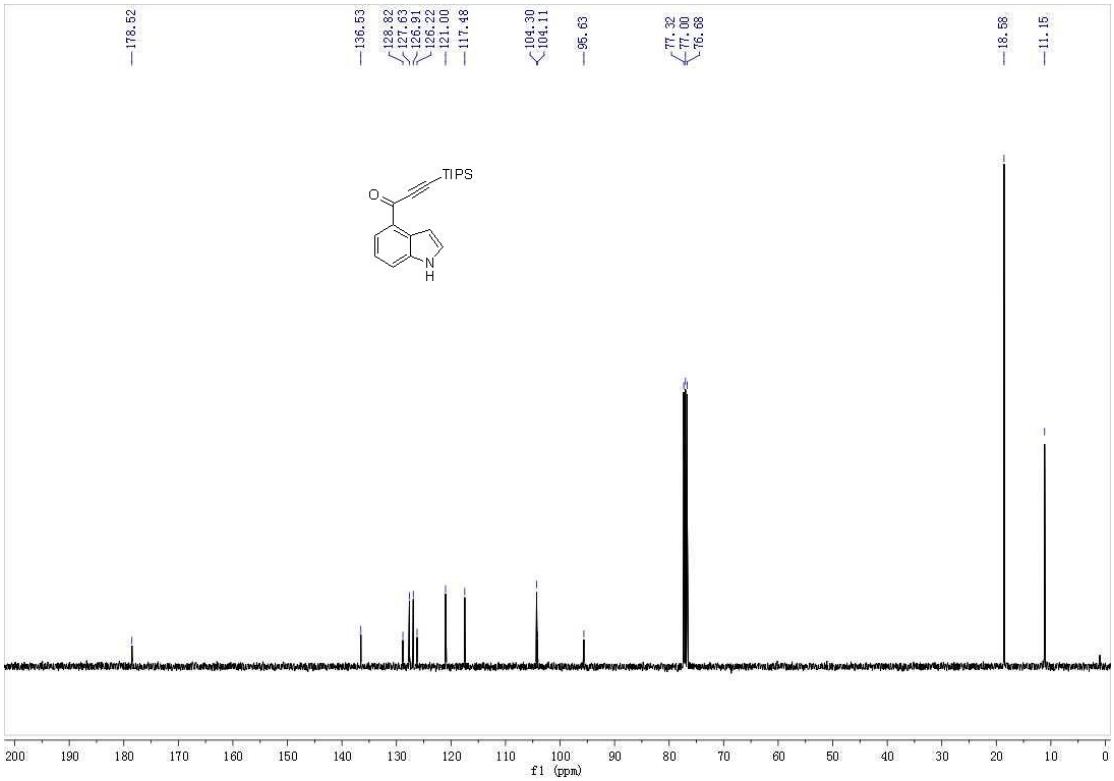


1-(1*H*-indol-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ja)

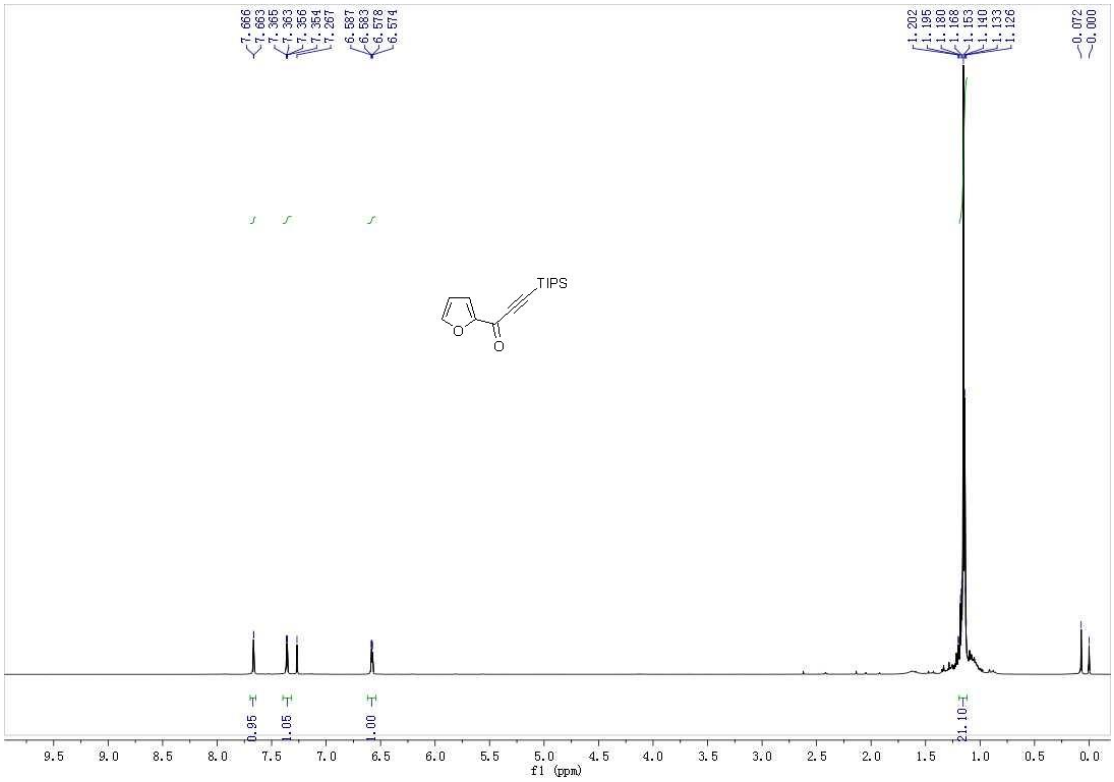


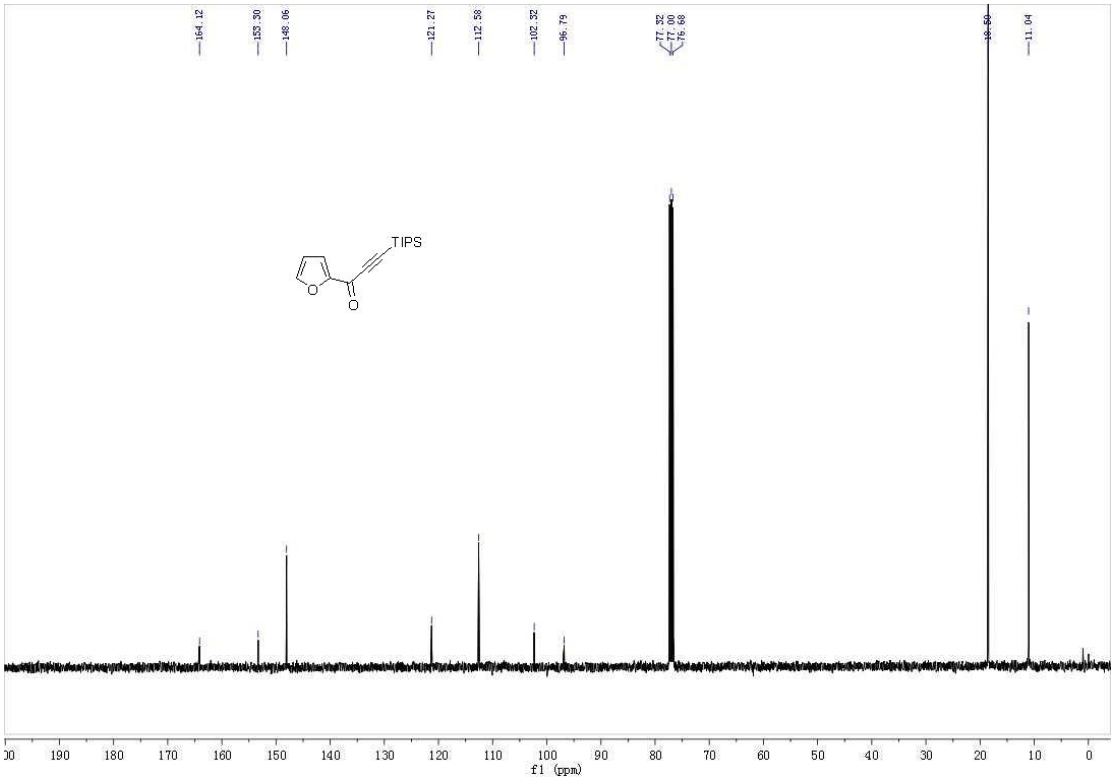
1-(1*H*-indol-4-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ka)



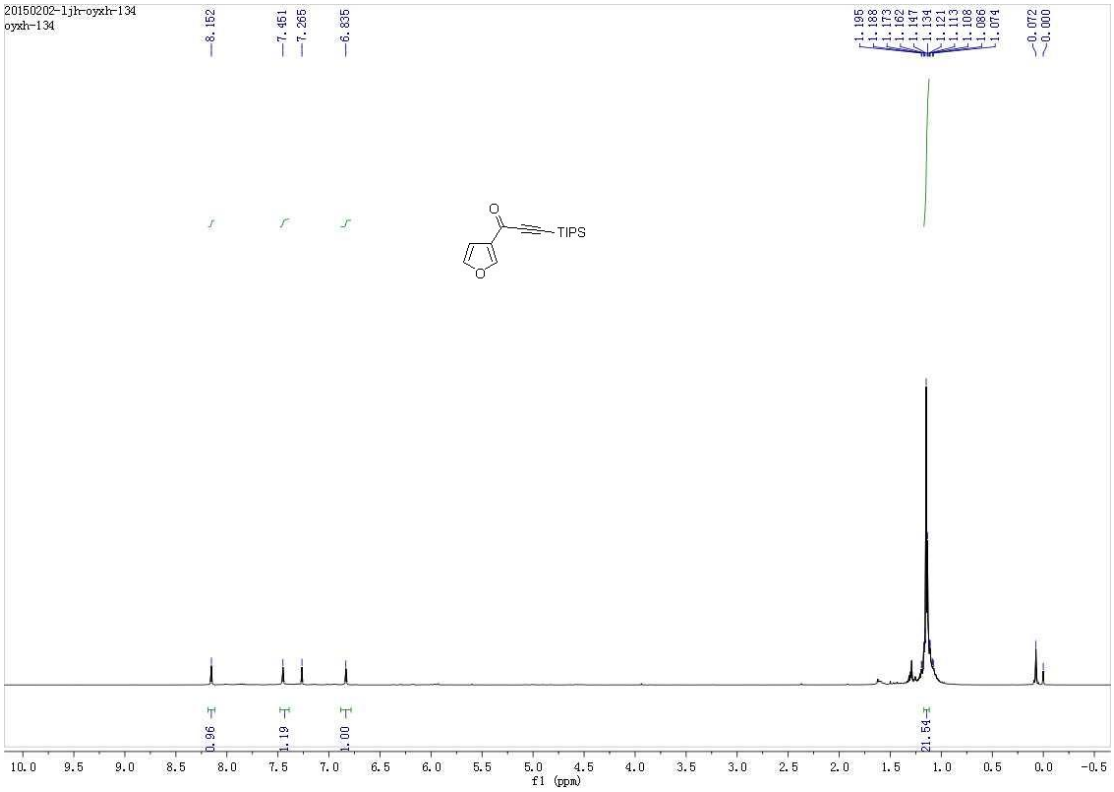


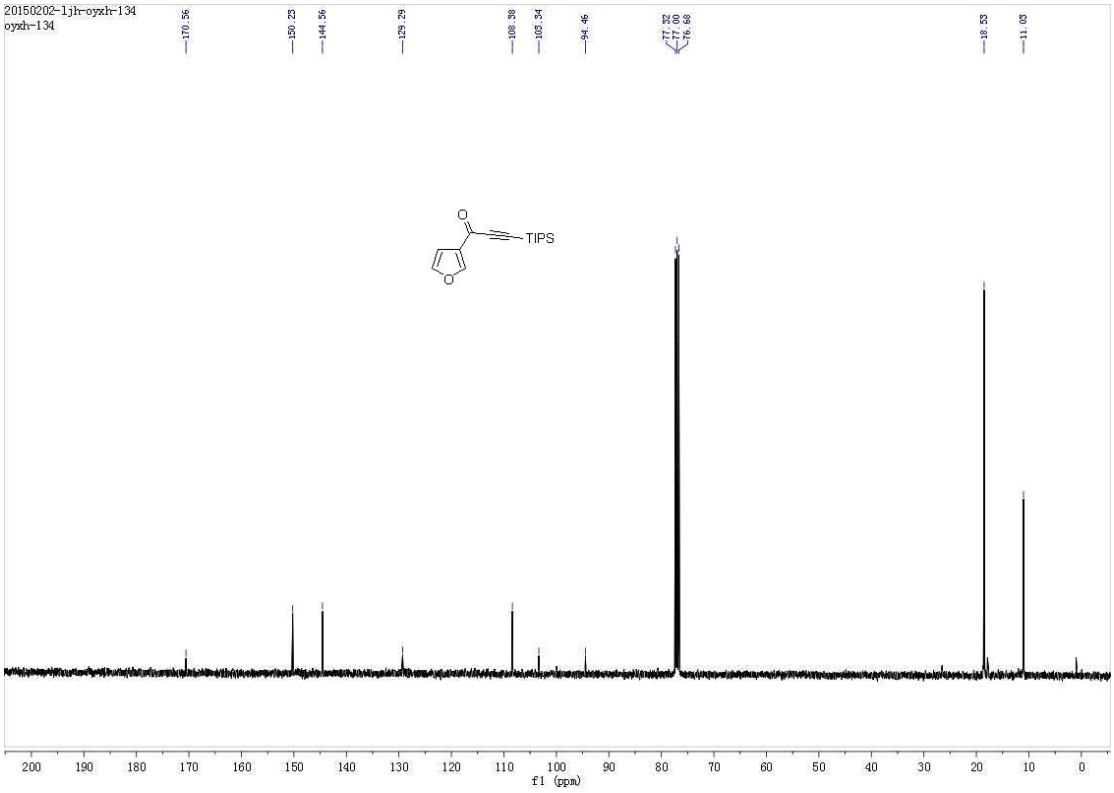
1-(furan-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3la)



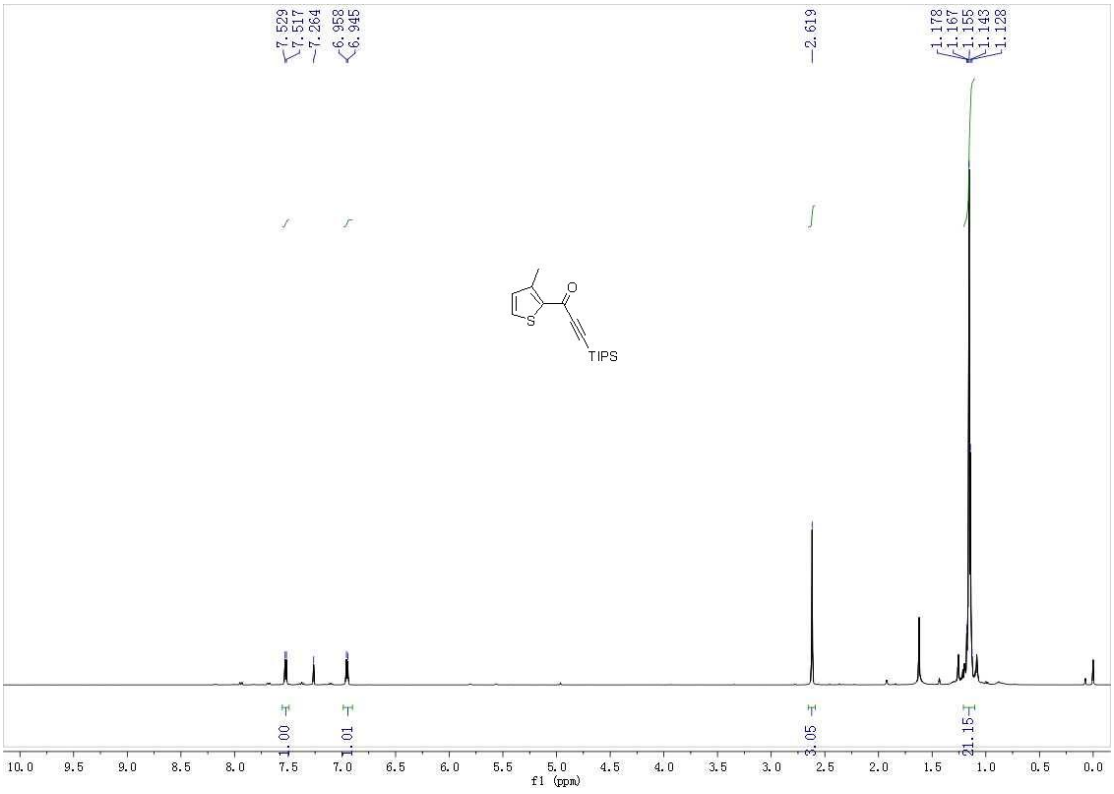


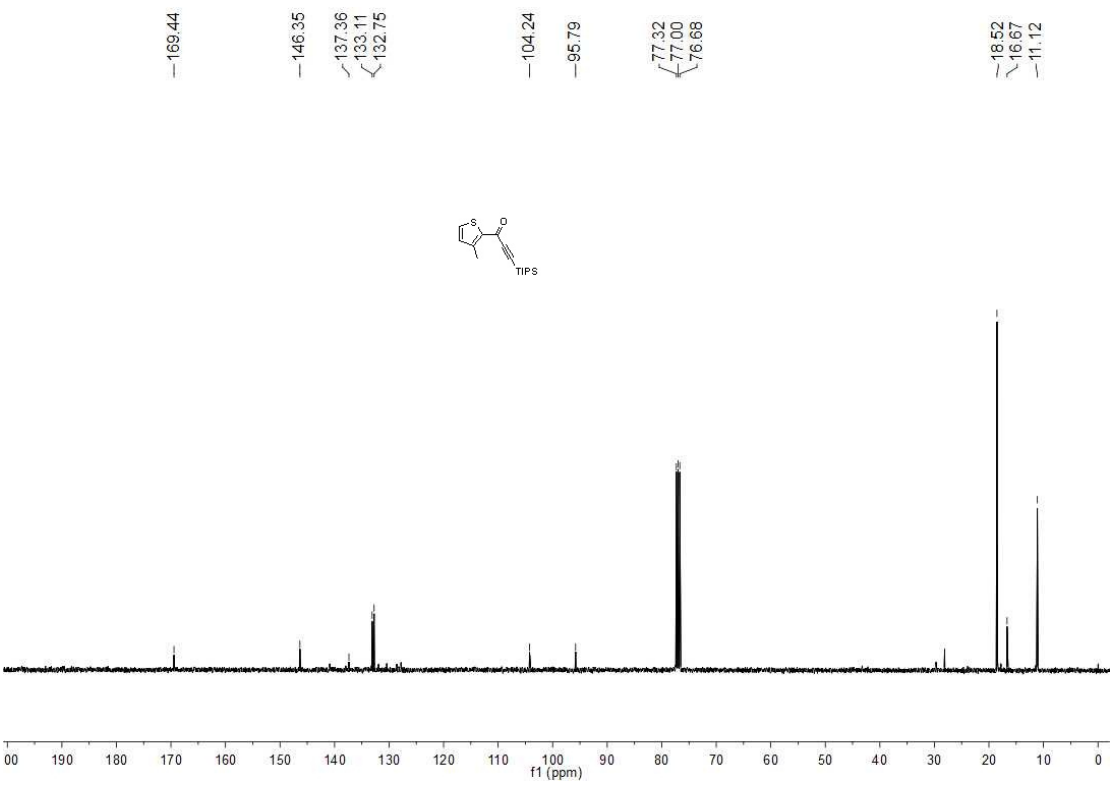
1-(furan-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ma)



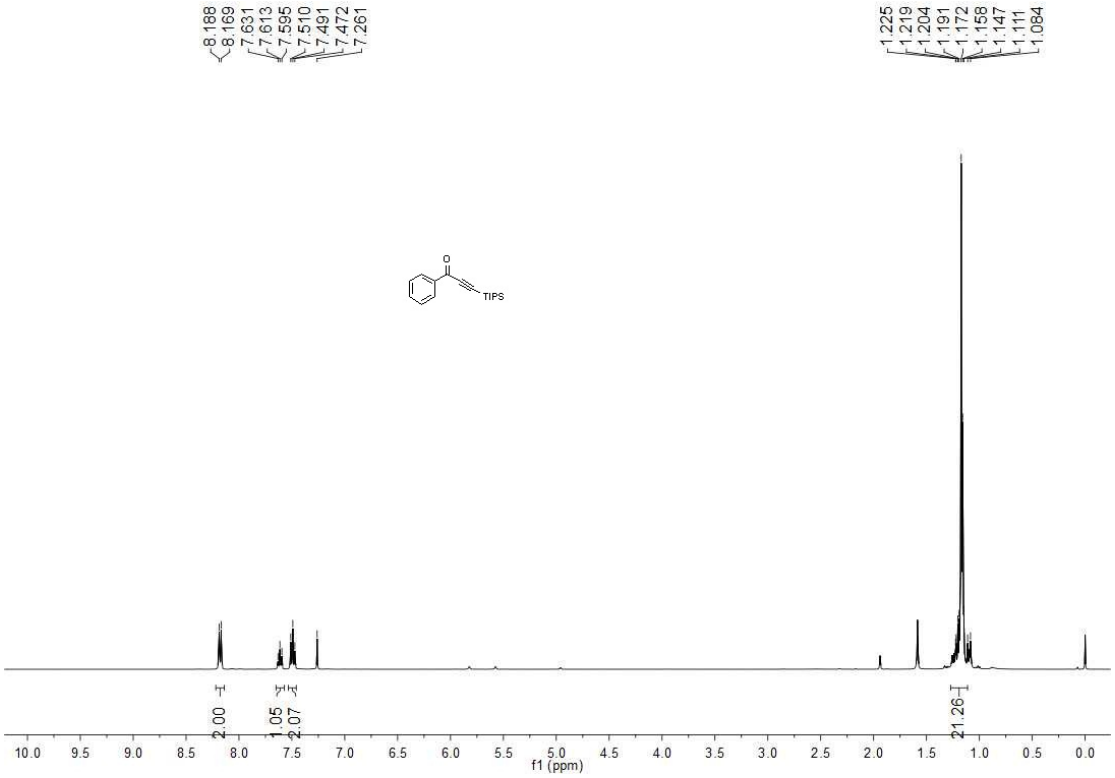


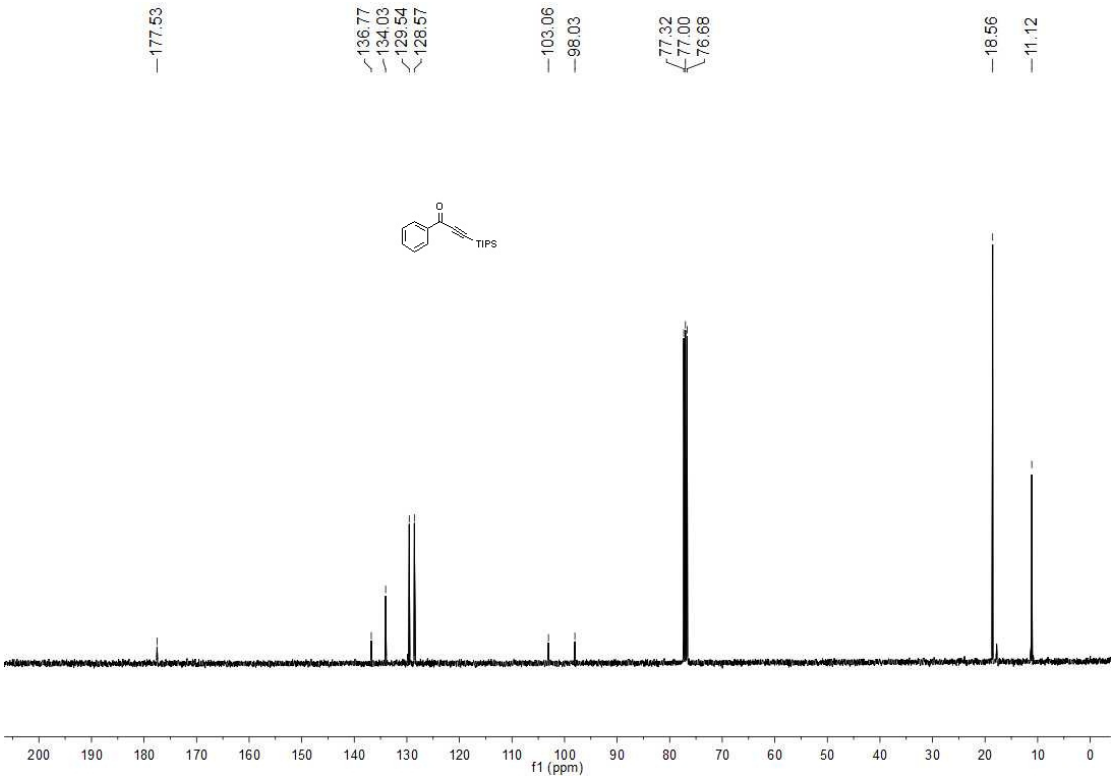
1-(3-methylthiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3na)



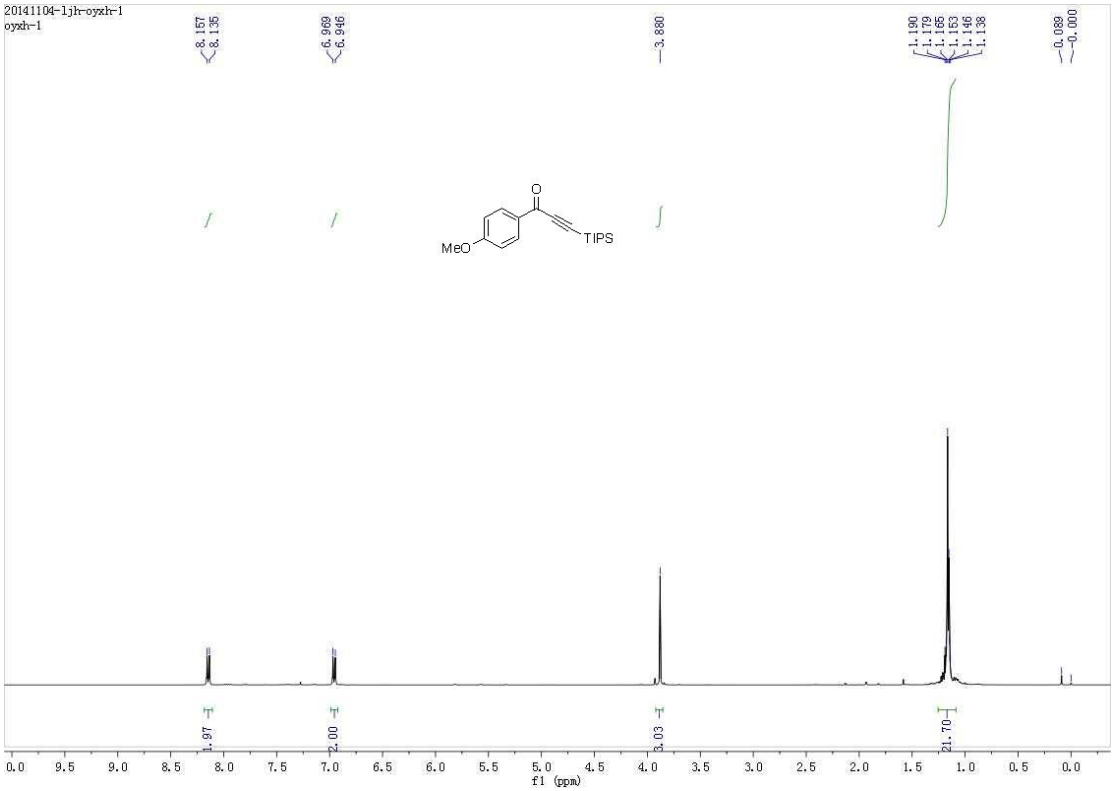


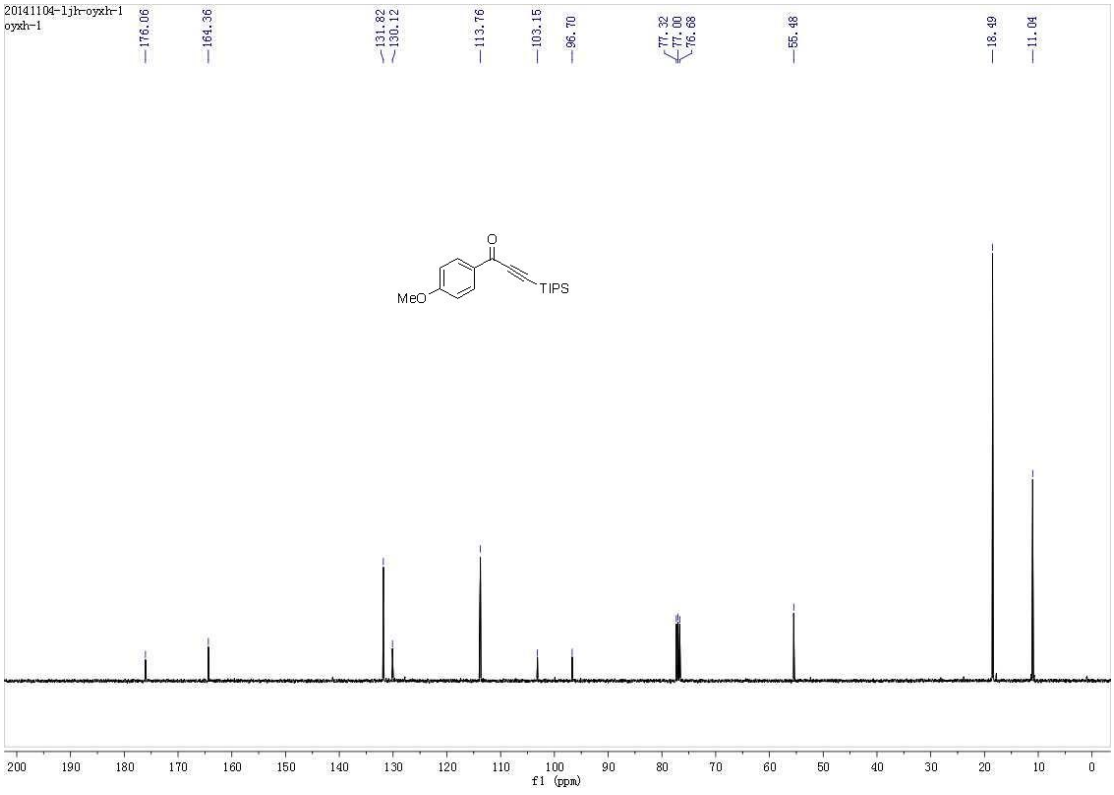
1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-one (3oa)



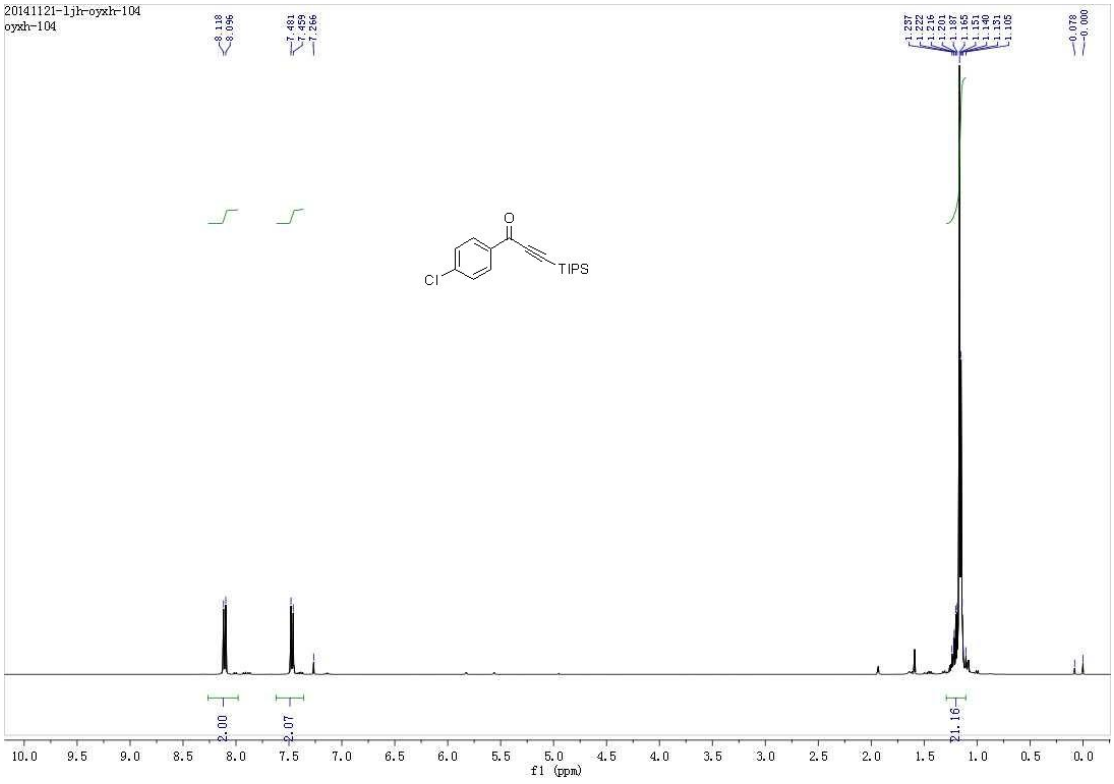


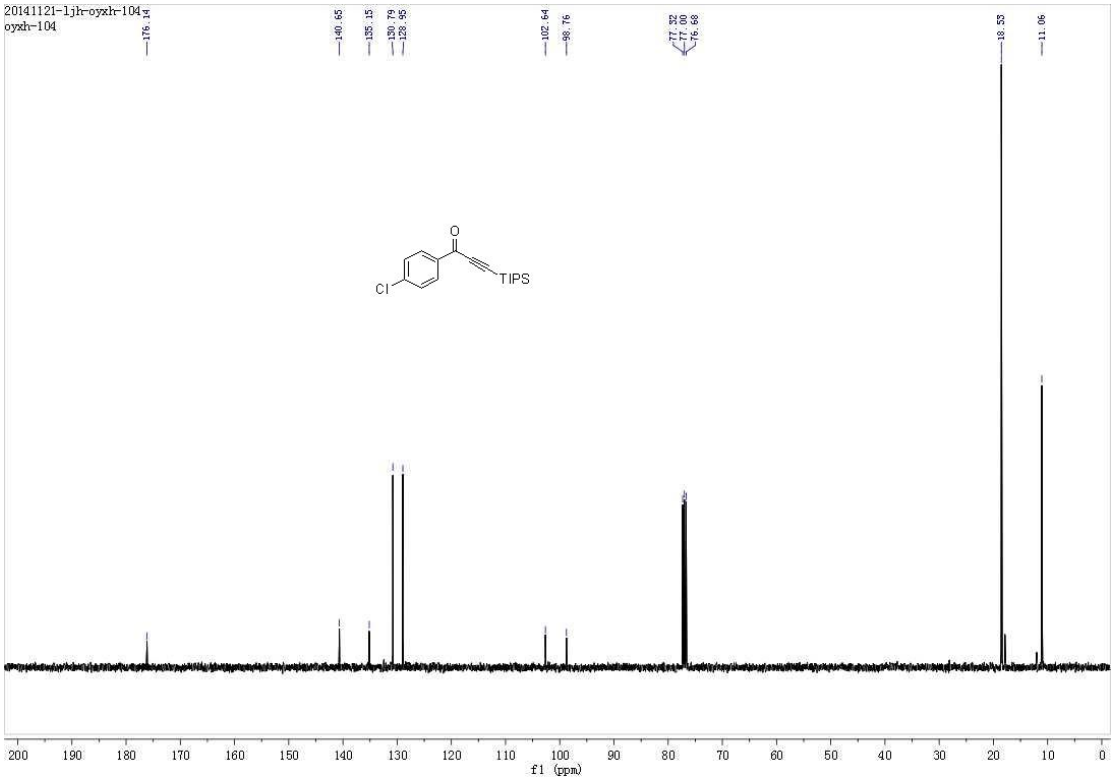
1-(4-methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (3pa)



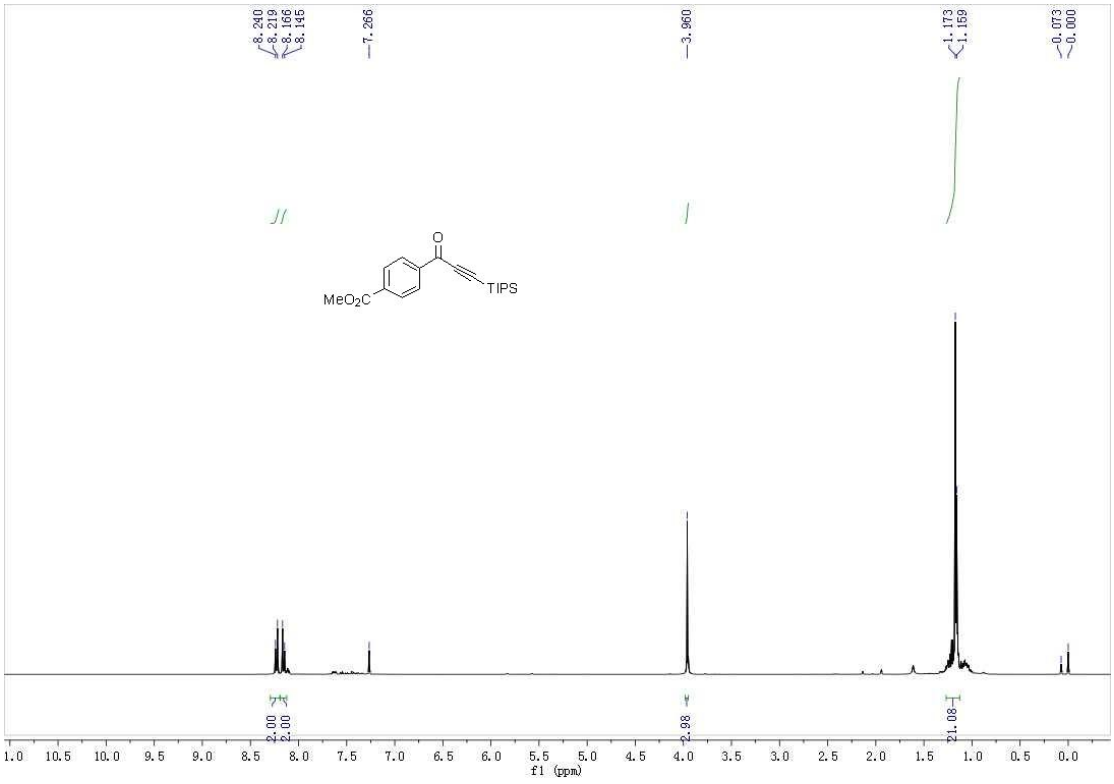


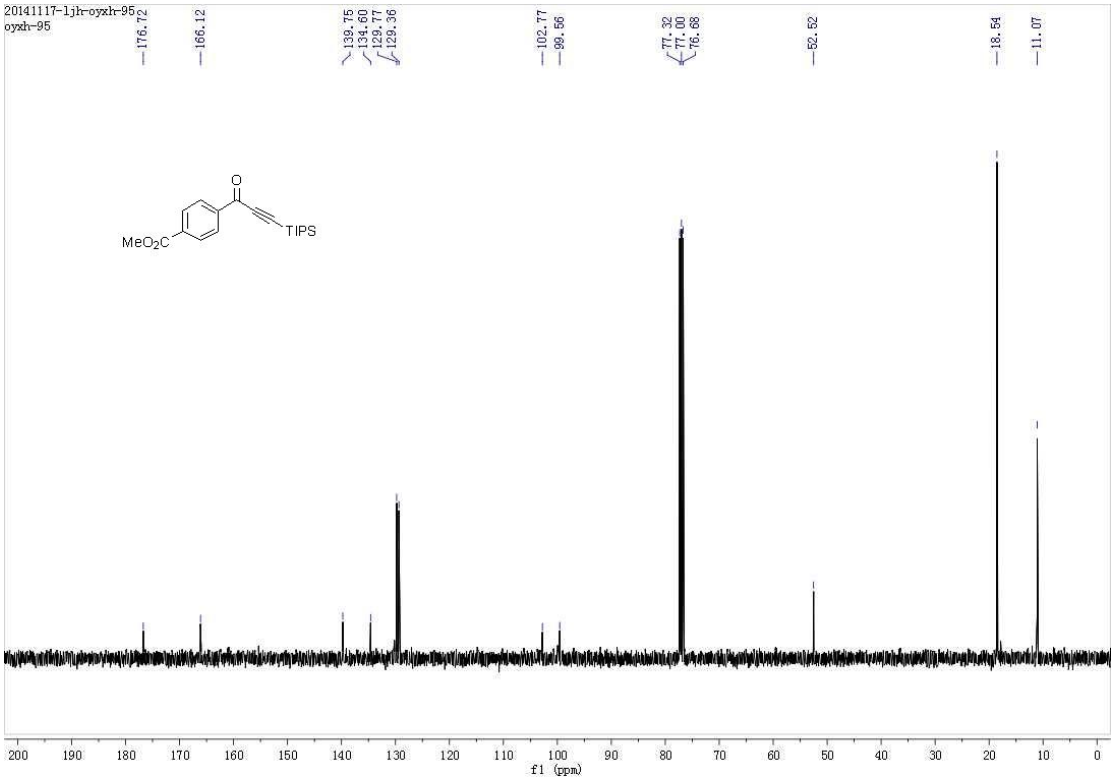
1-(4-chlorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (3qa)



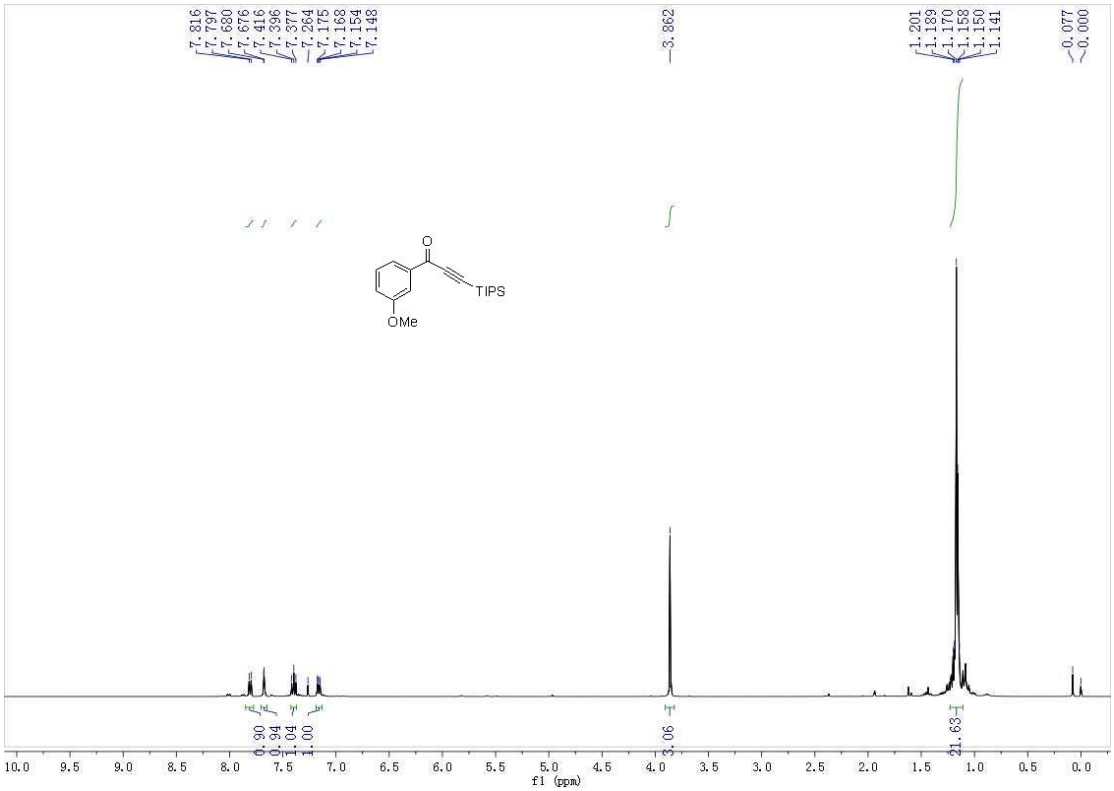


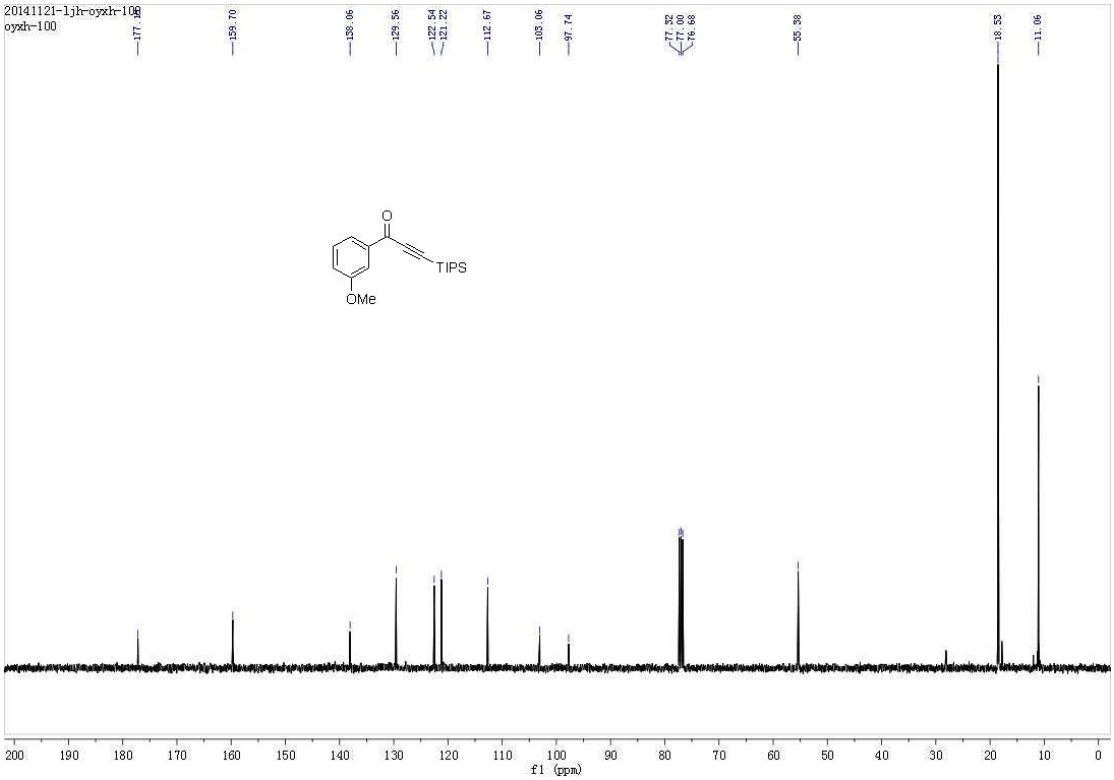
methyl 4-(3-(triisopropylsilyl)propioloyl)benzoate (3ra)



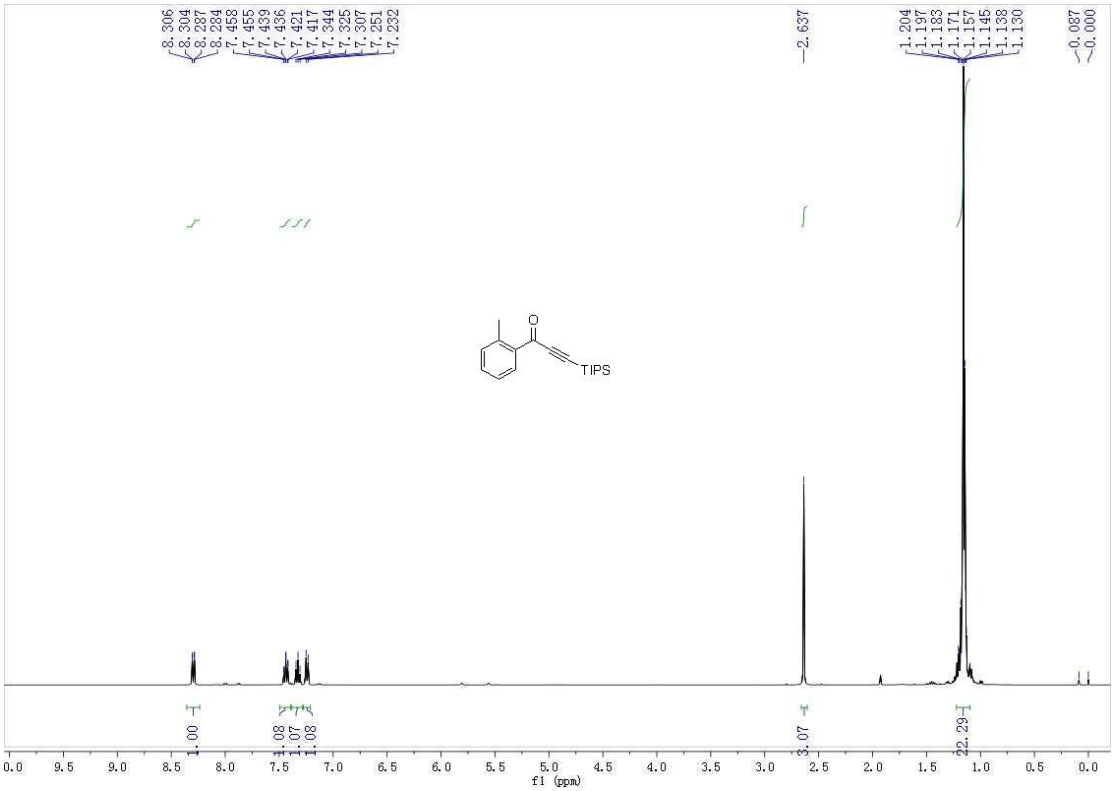


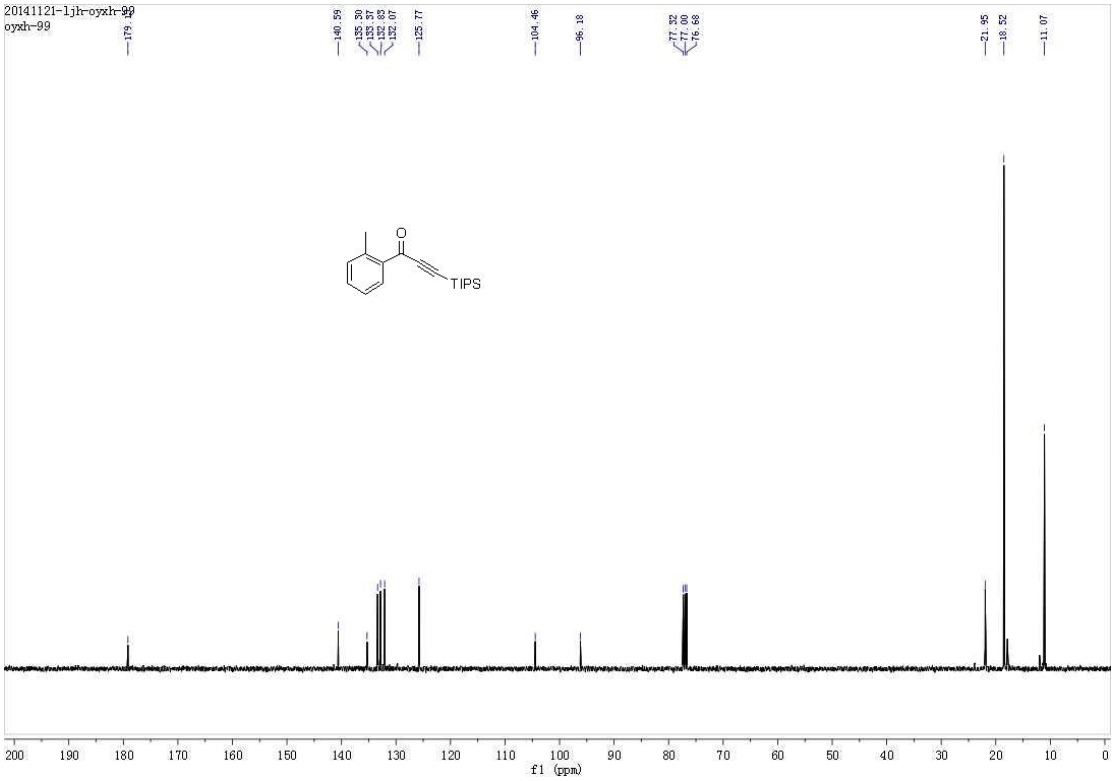
1-(3-methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (3sa)



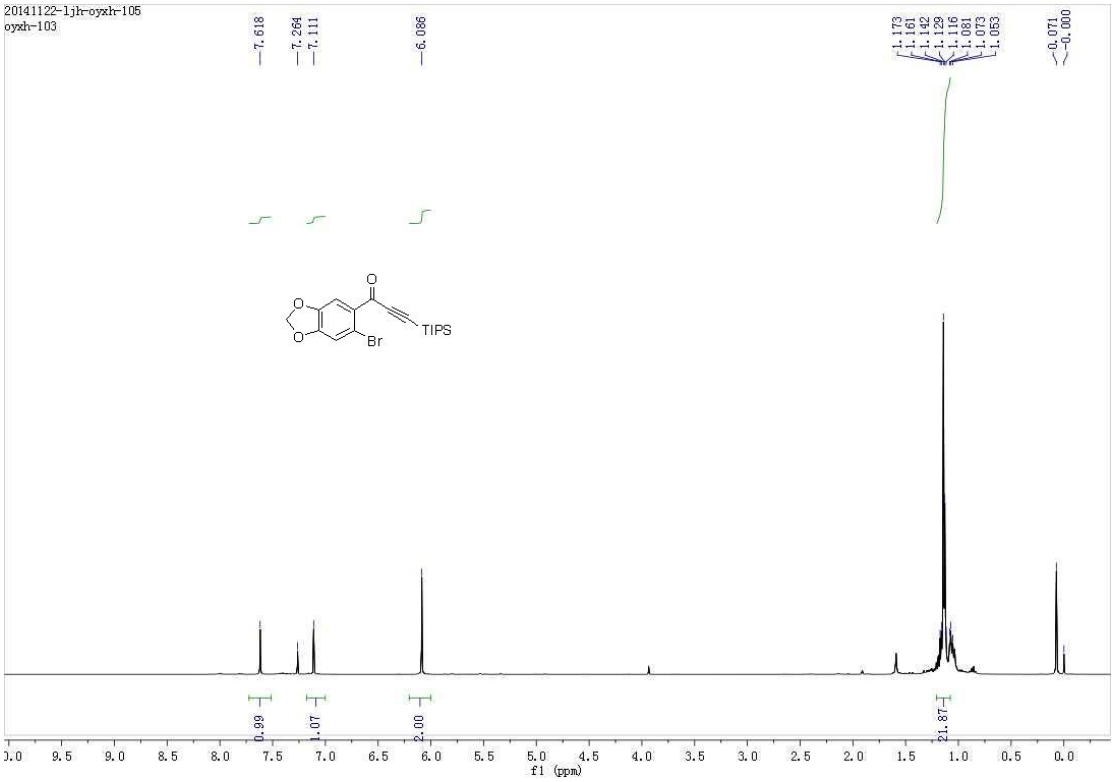


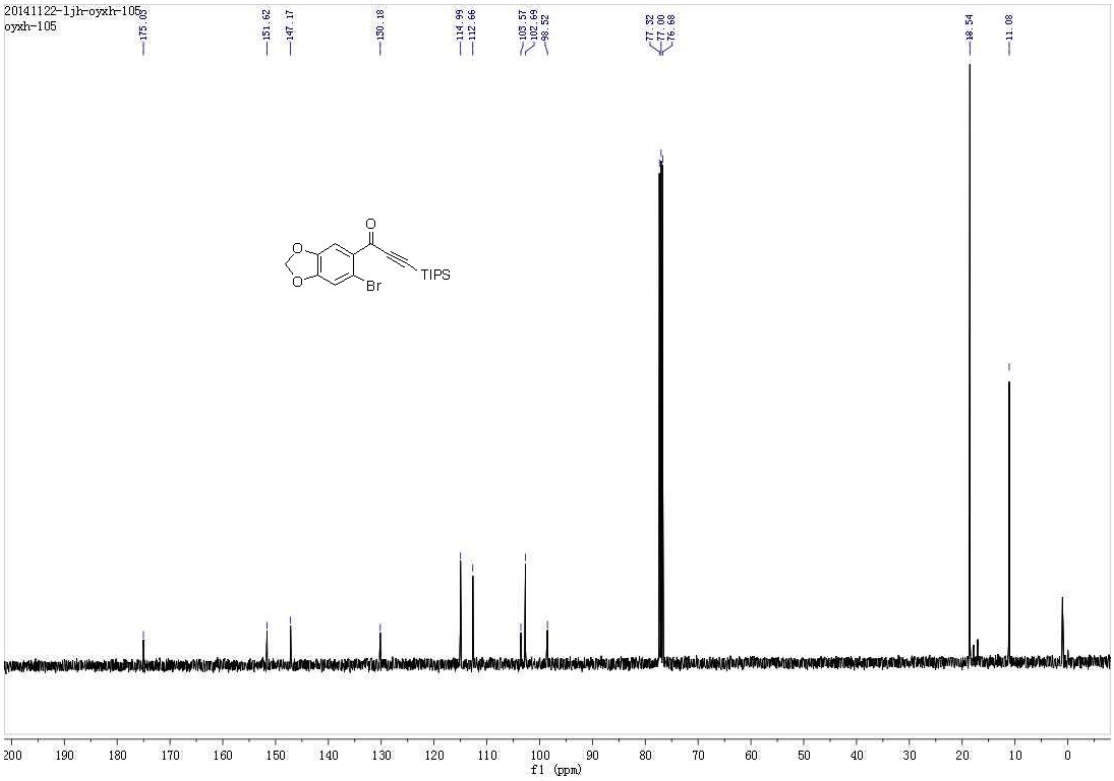
1-o-tolyl-3-(triisopropylsilyl)prop-2-yn-1-one (3ta)



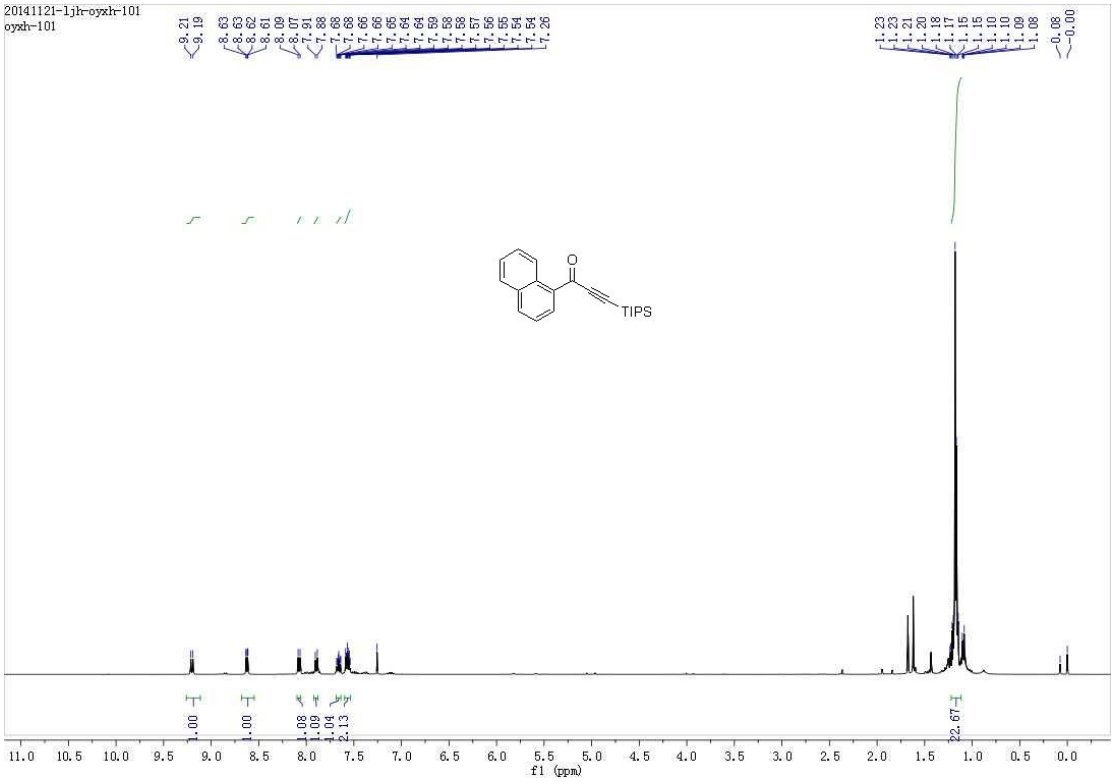


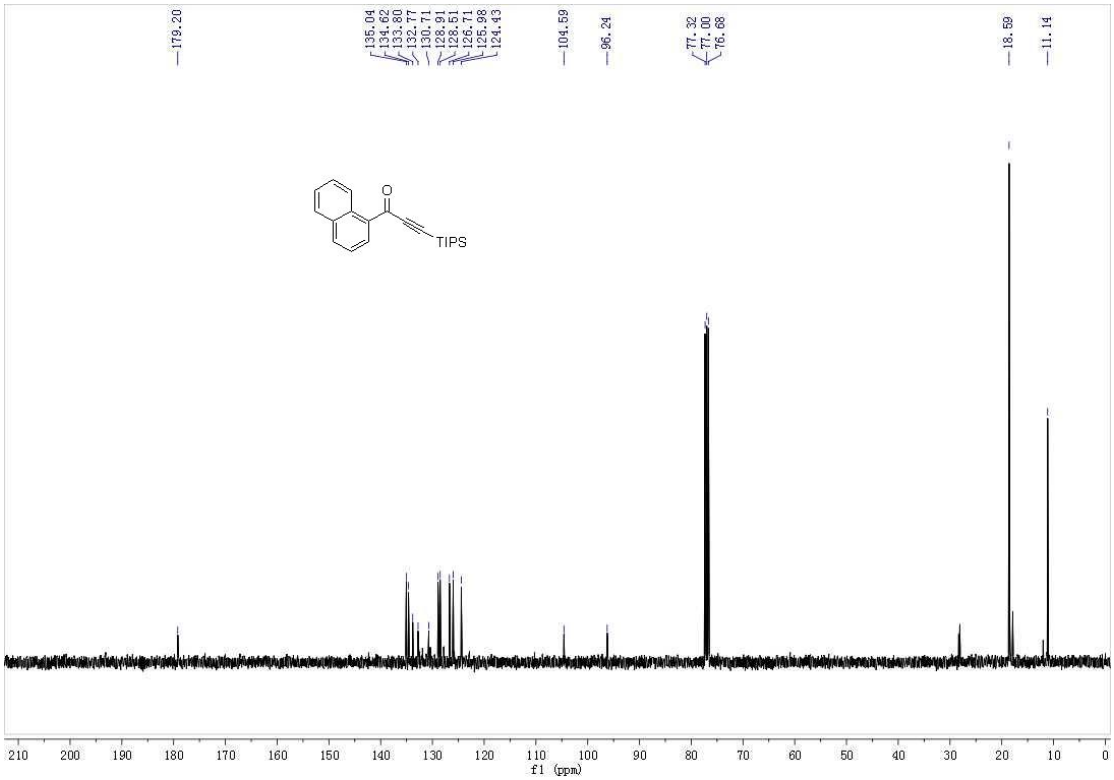
1-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3ua)



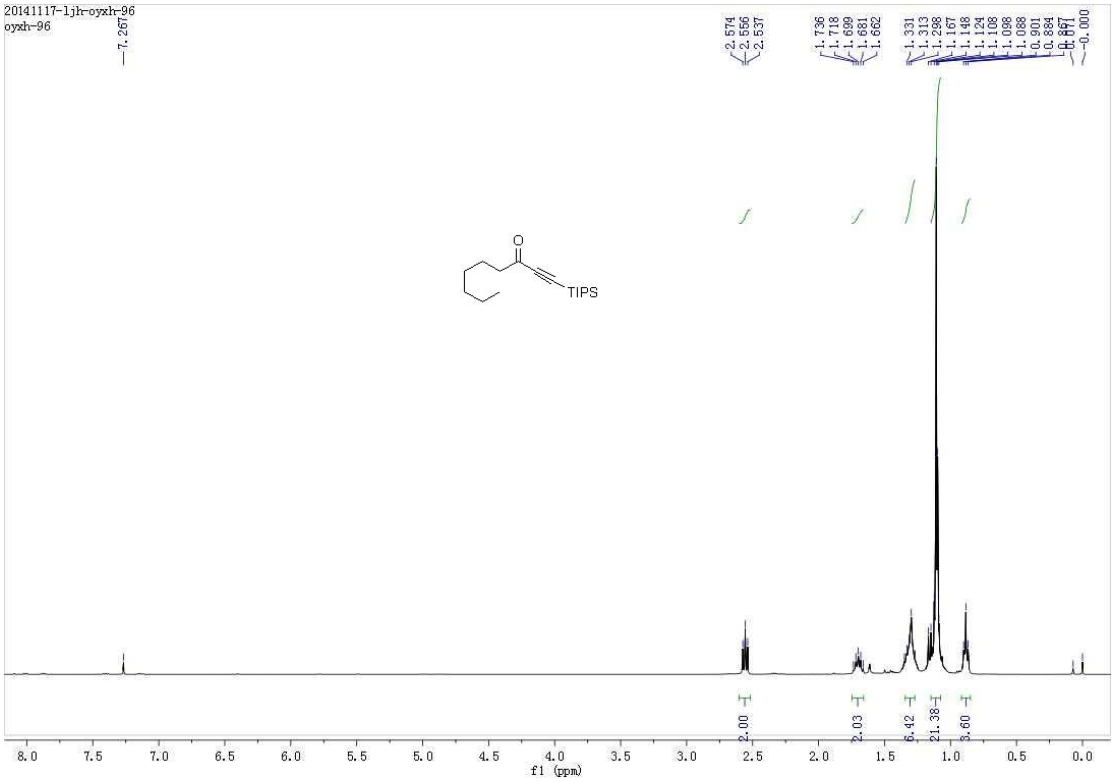


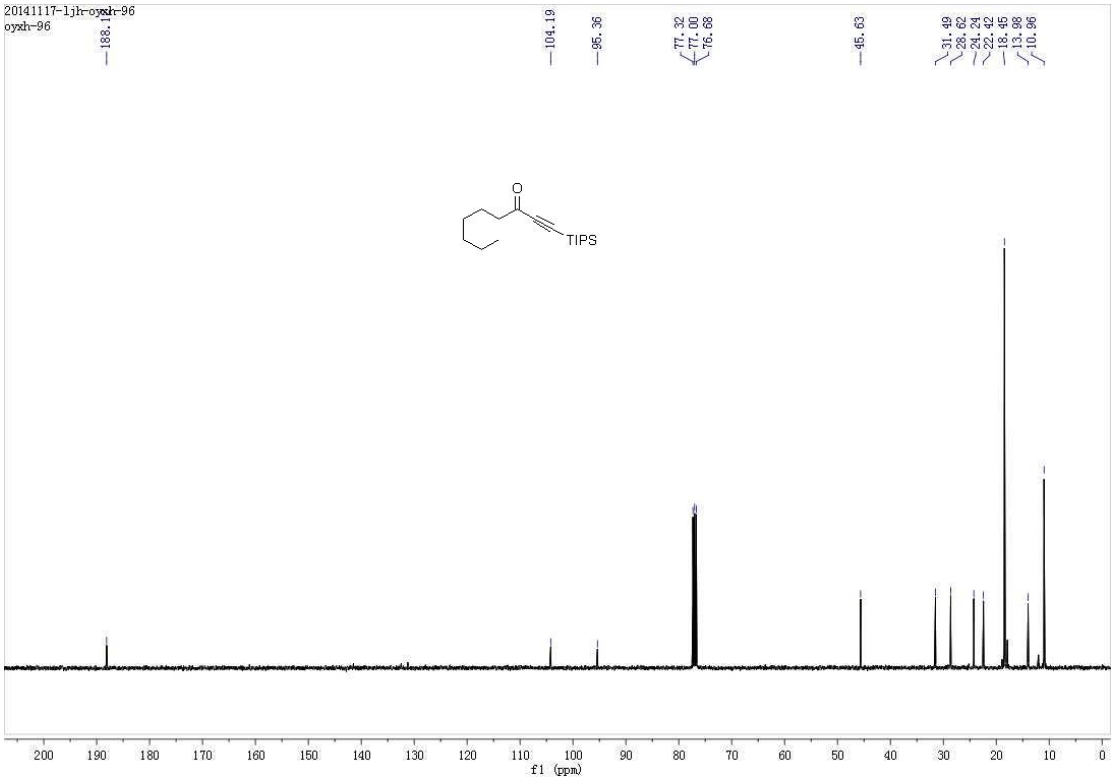
1-(naphthalen-1-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (3va)



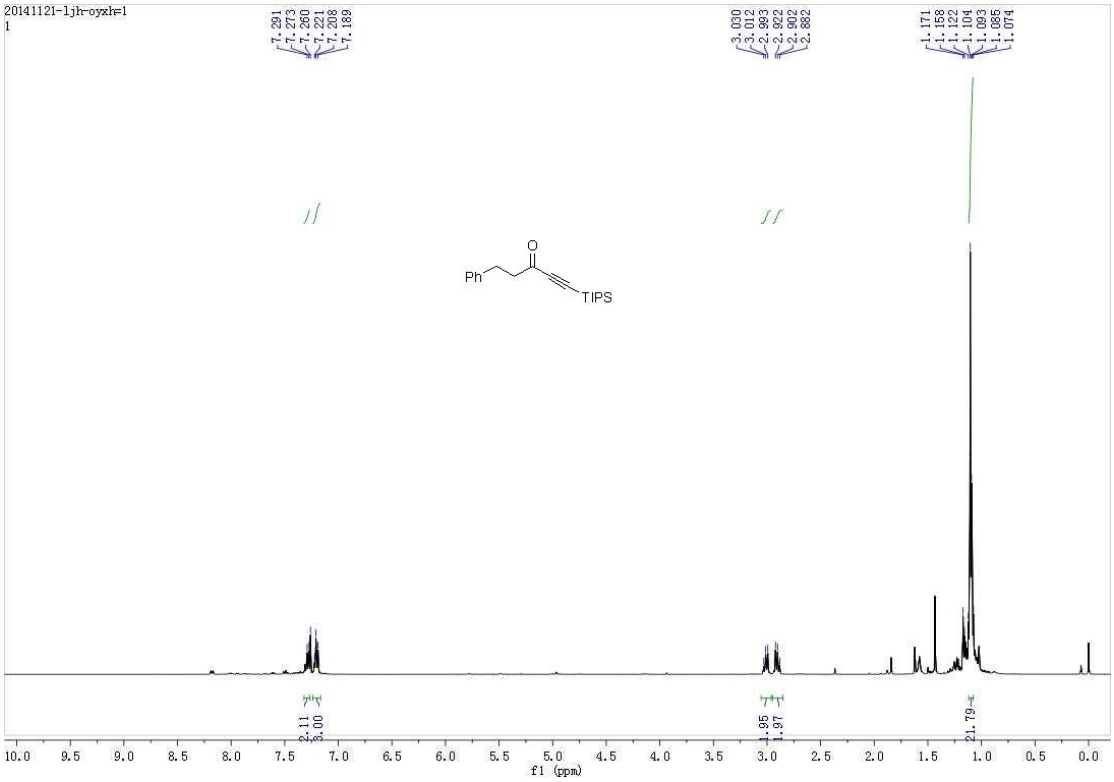


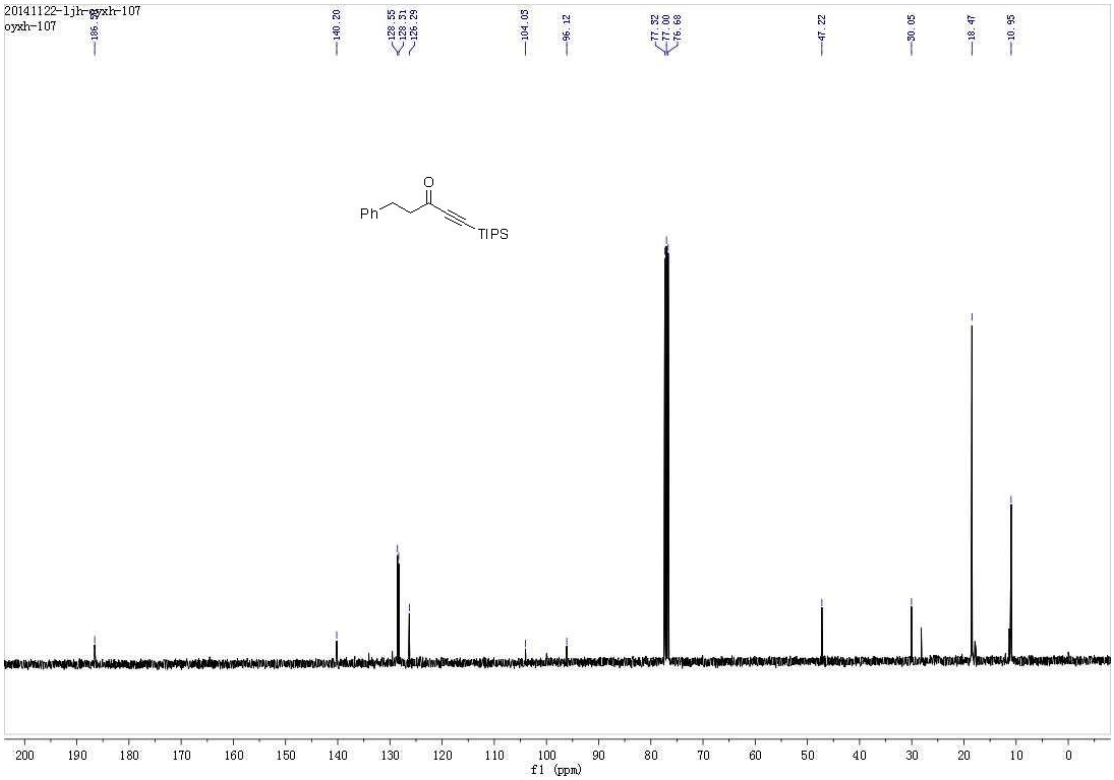
1-(triisopropylsilyl)non-1-yn-3-one (3wa)



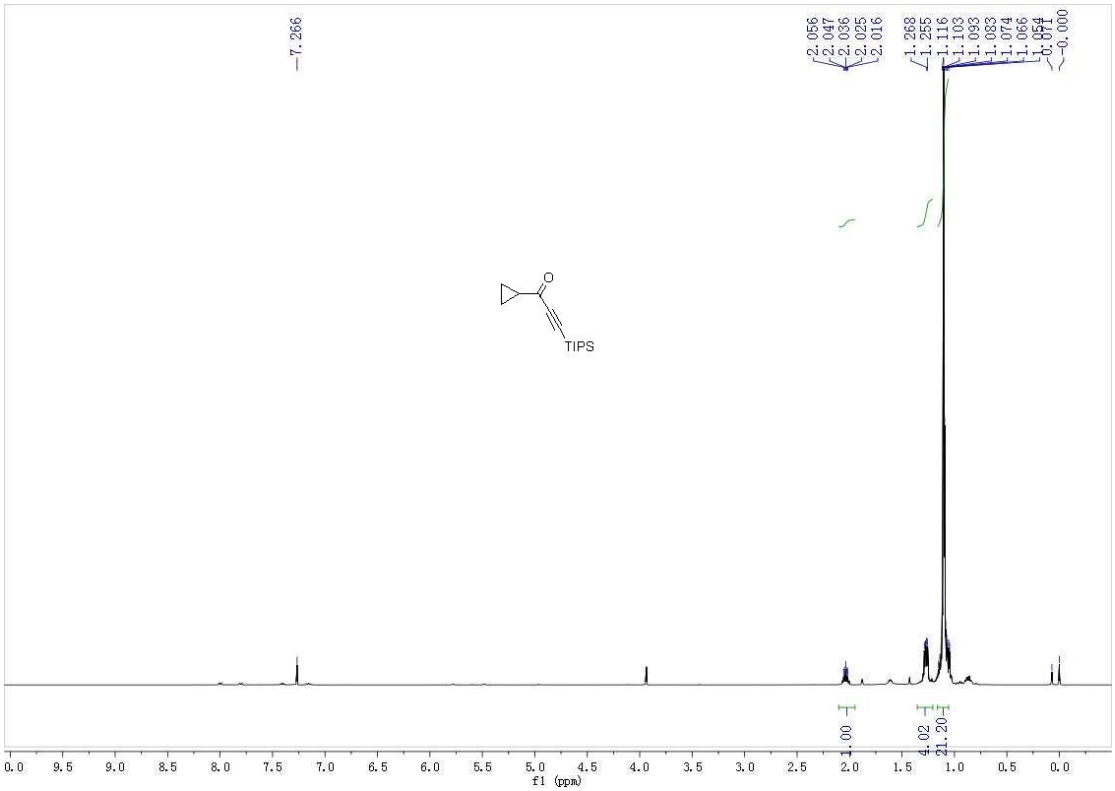


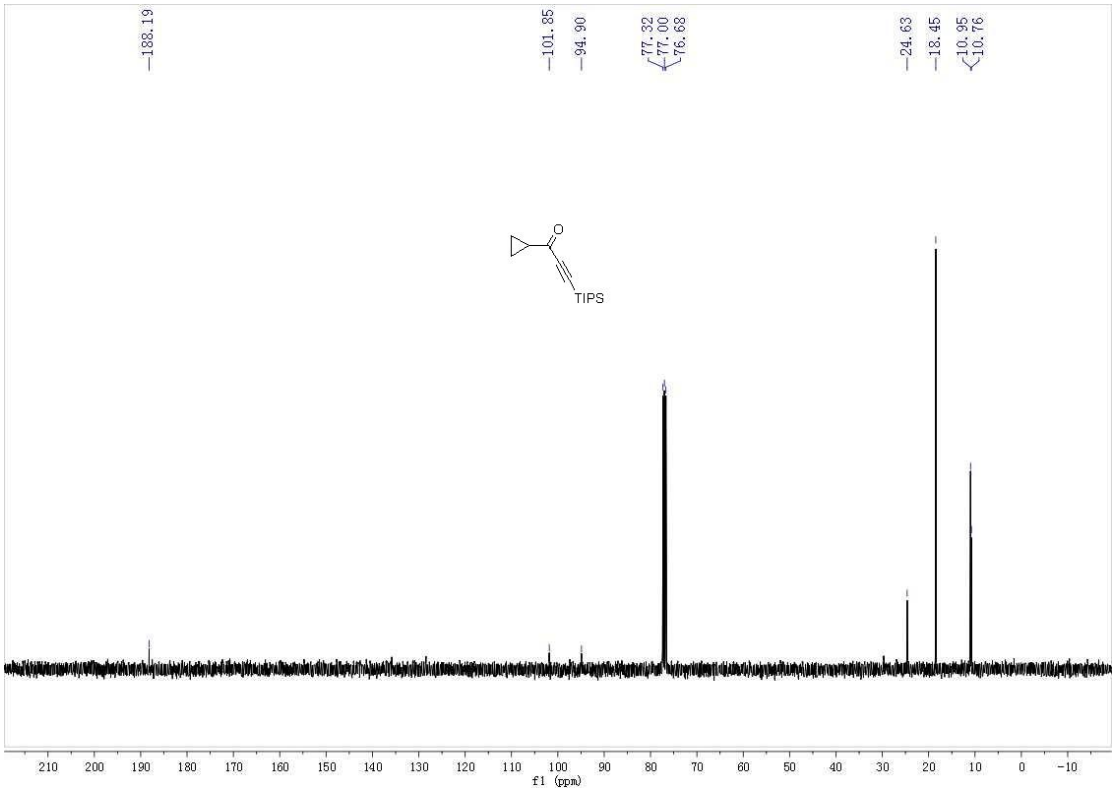
5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-one (3xa)



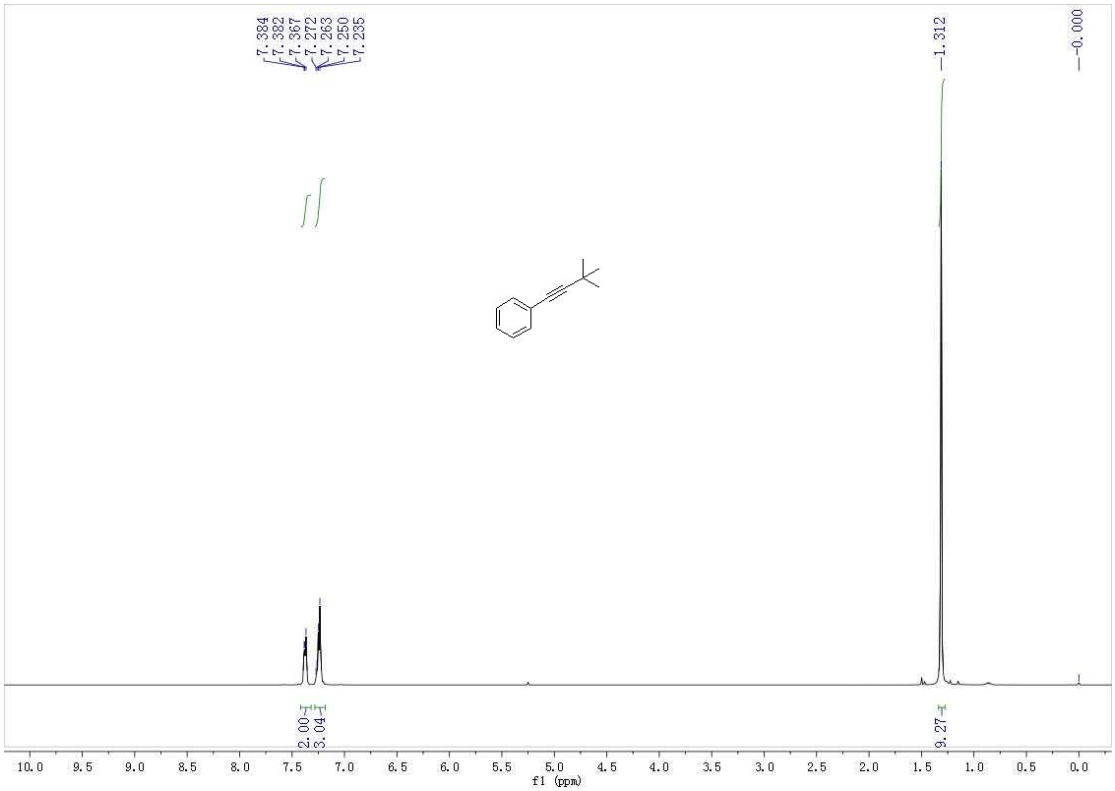


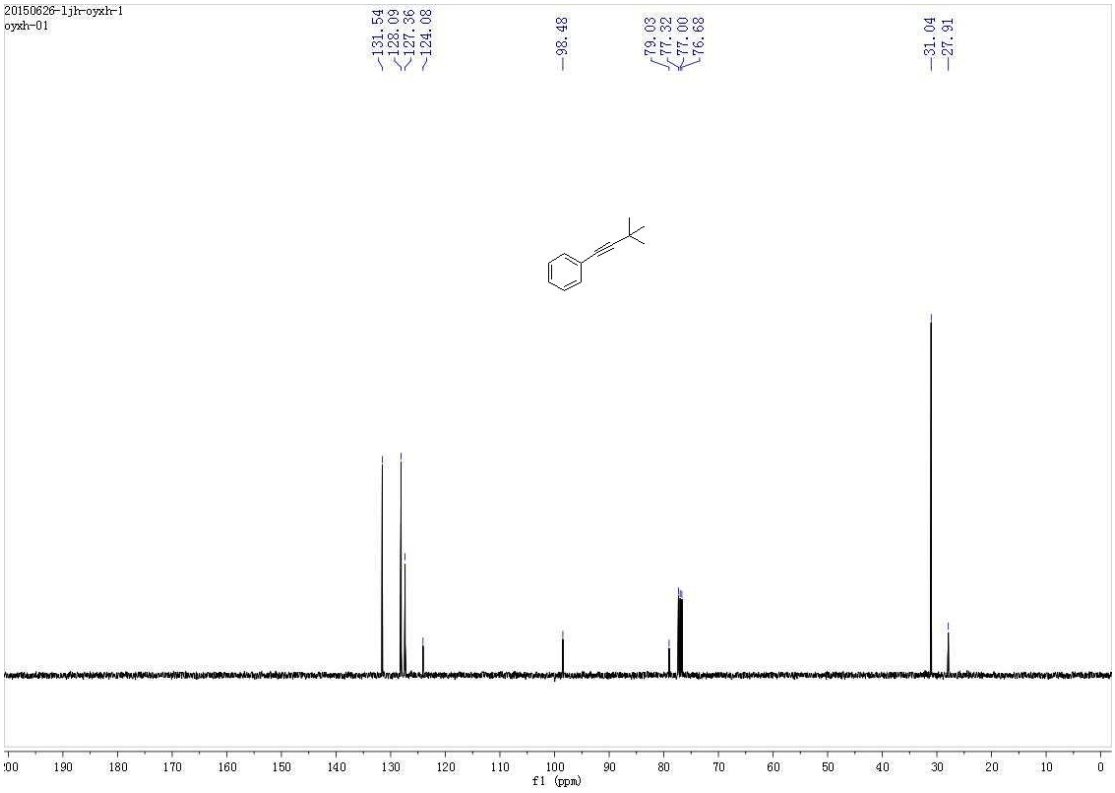
1- cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-one (3ya)



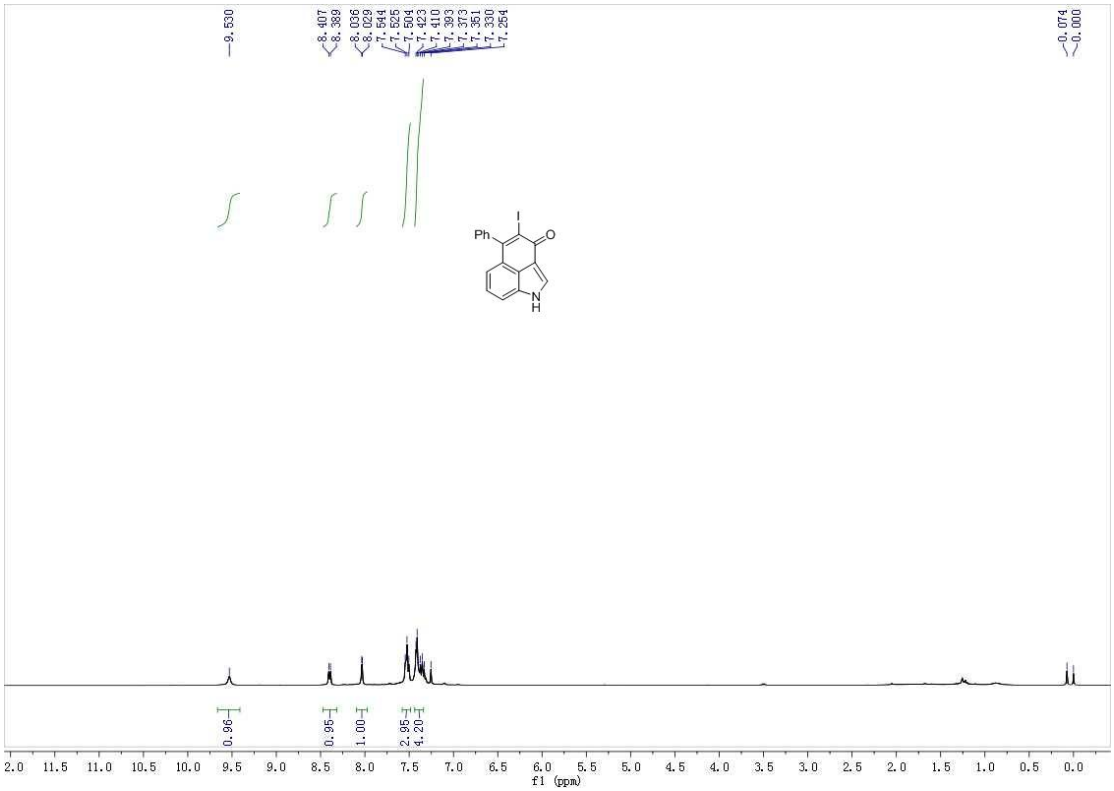


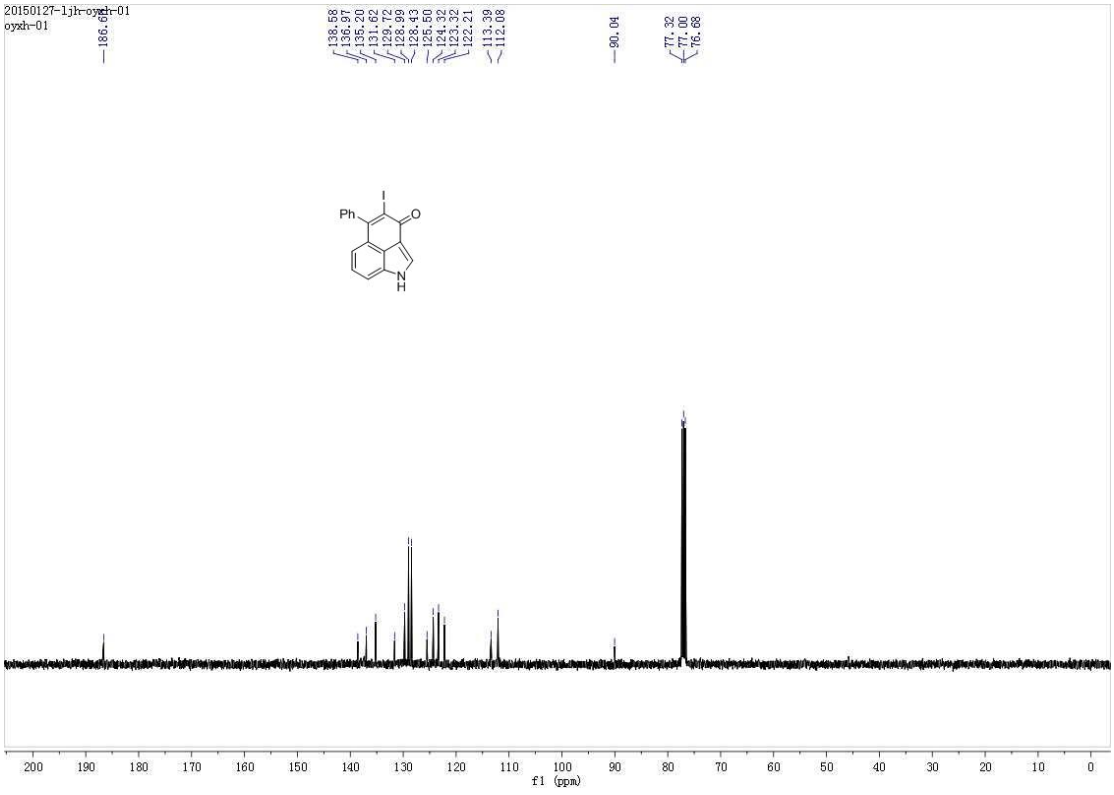
(3,3-dimethylbut-1-ynyl)benzene (3zc)



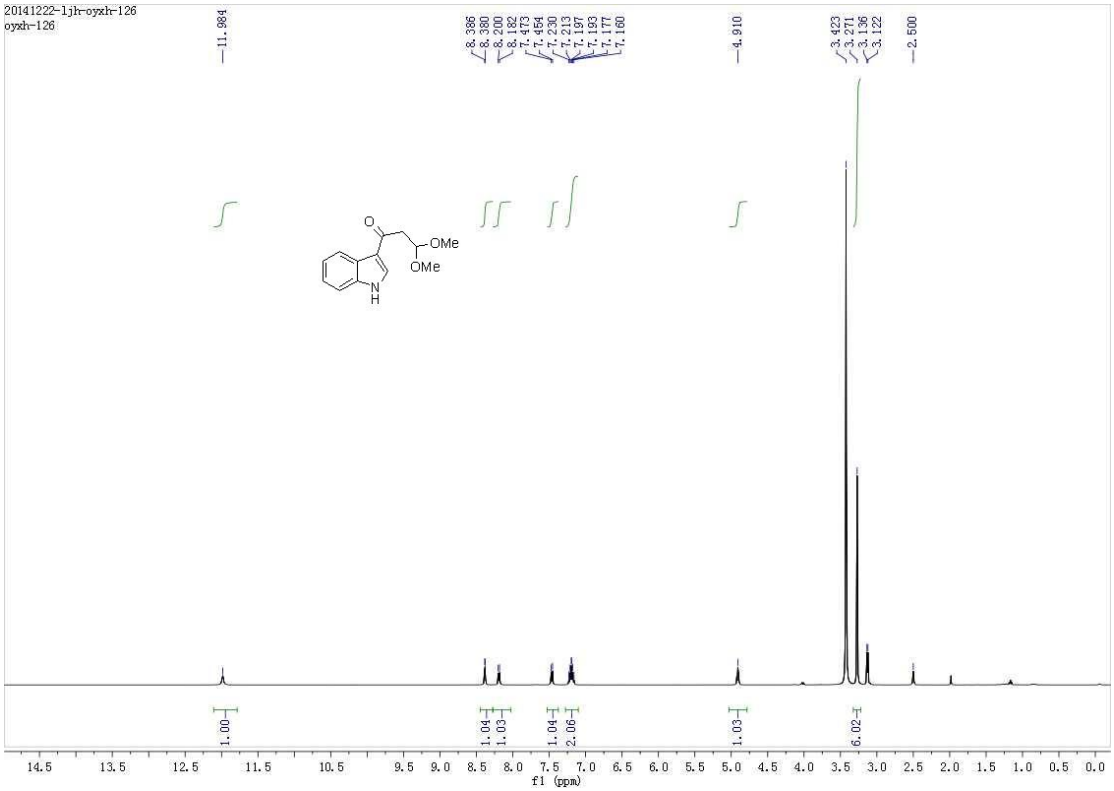


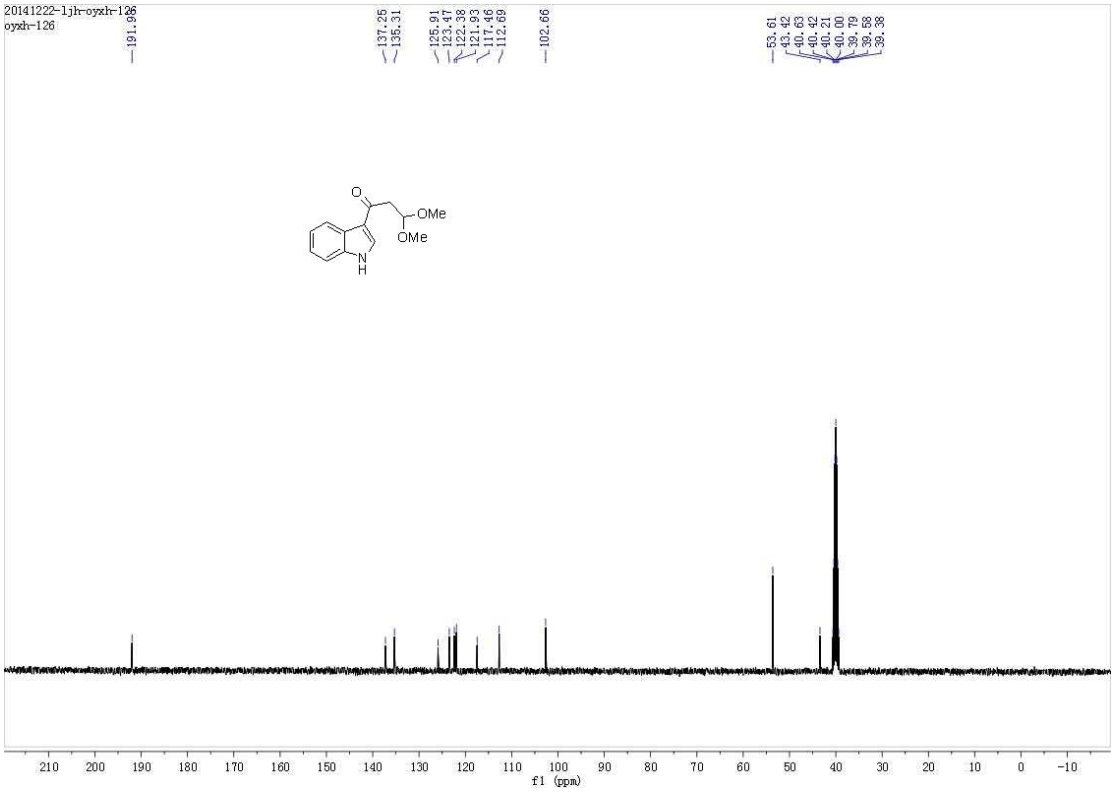
4-iodo-5-phenylbenzo[*cd*]indol-3(1*H*)-one (5)



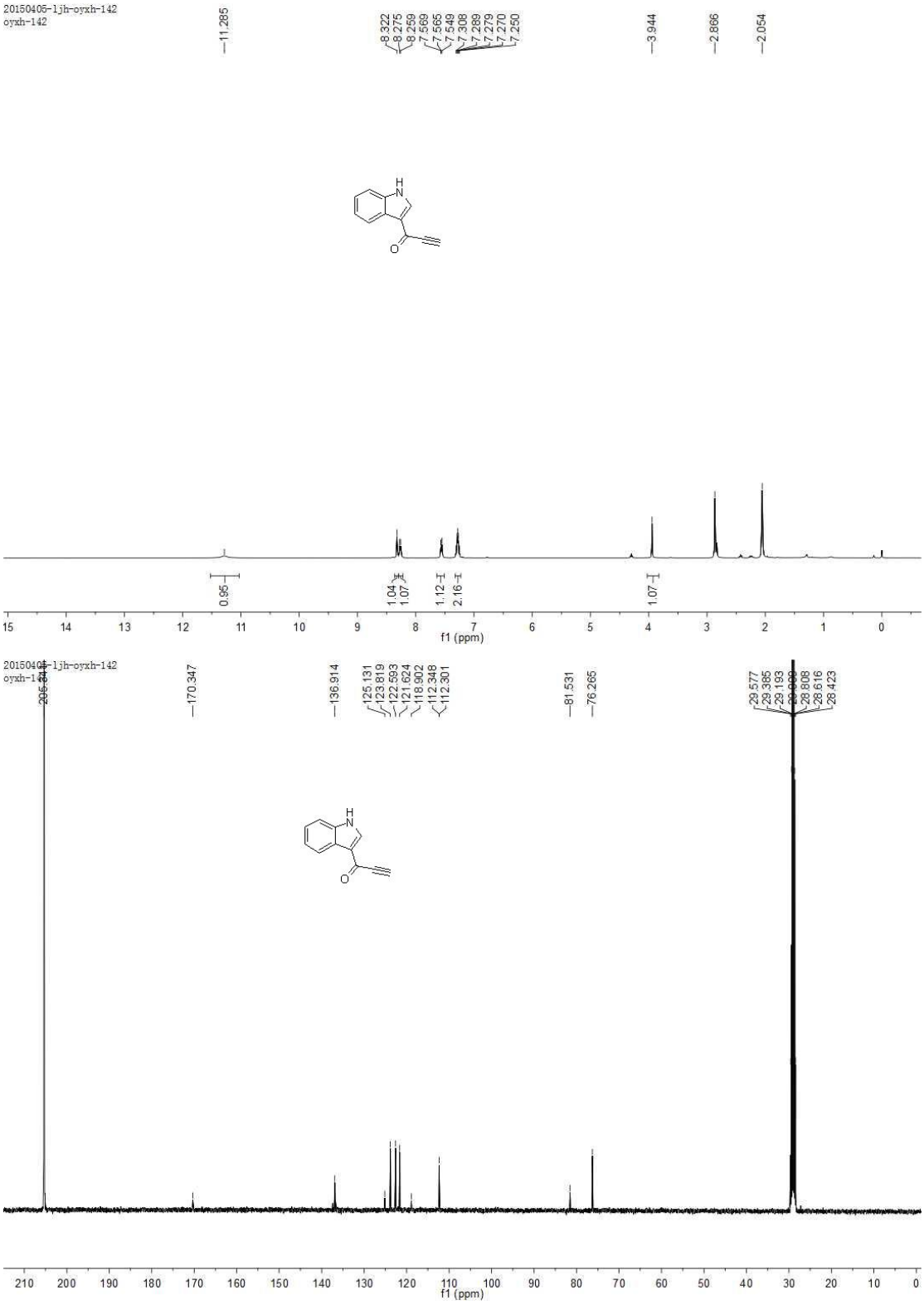


1-(1*H*-indol-3-yl)-3,3-dimethoxypropan-1-one (6)

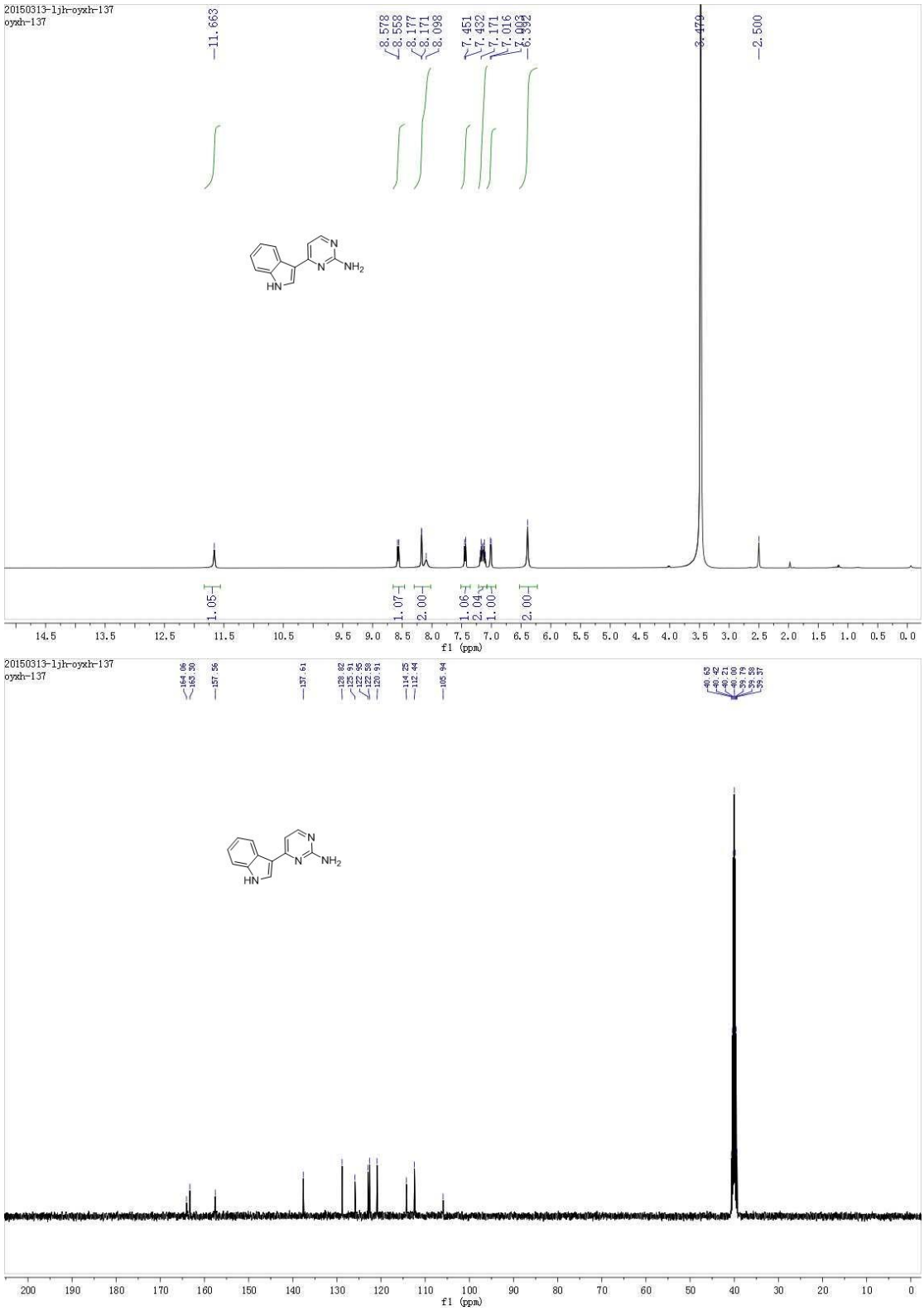




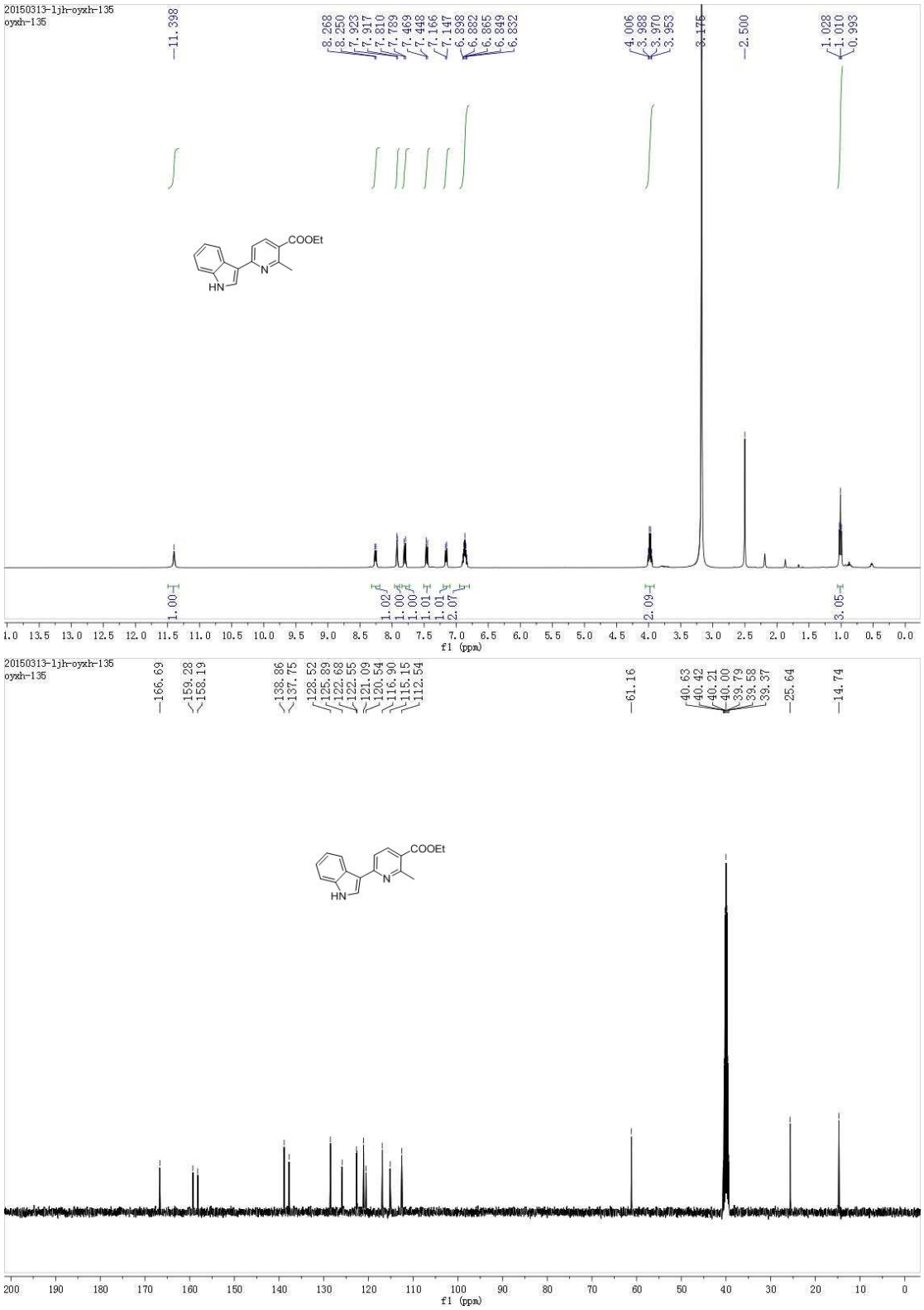
1-(1*H*-indol-3-yl)prop-2-yn-1-one (7)



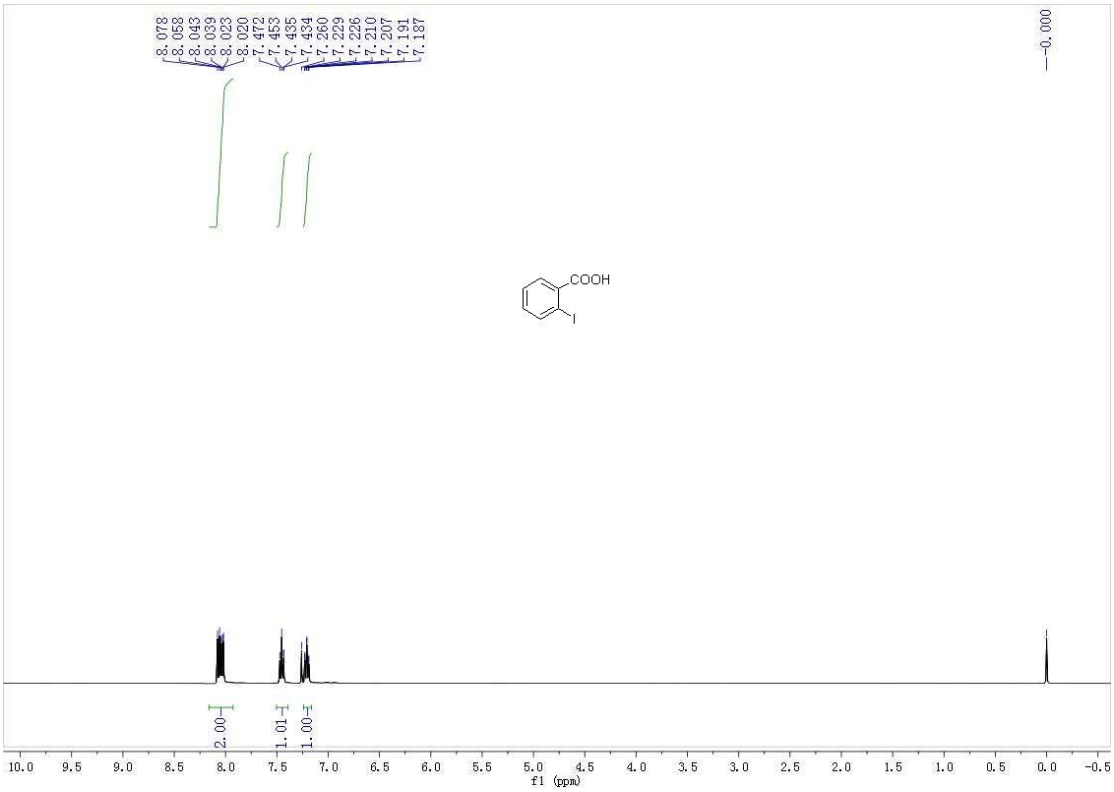
4-(1*H*-indol-3-yl)pyrimidin-2-amine (8)



ethyl 6-(1*H*-indol-3-yl)-2-methylnicotinate (9)



2-iodobenzoic acid (10)



1*H*-indole-3-carboxylic acid (11)