Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Triazine-wingtips accelerated NHC-Pd catalysed carbonylative Sonogashira cross-coupling reaction

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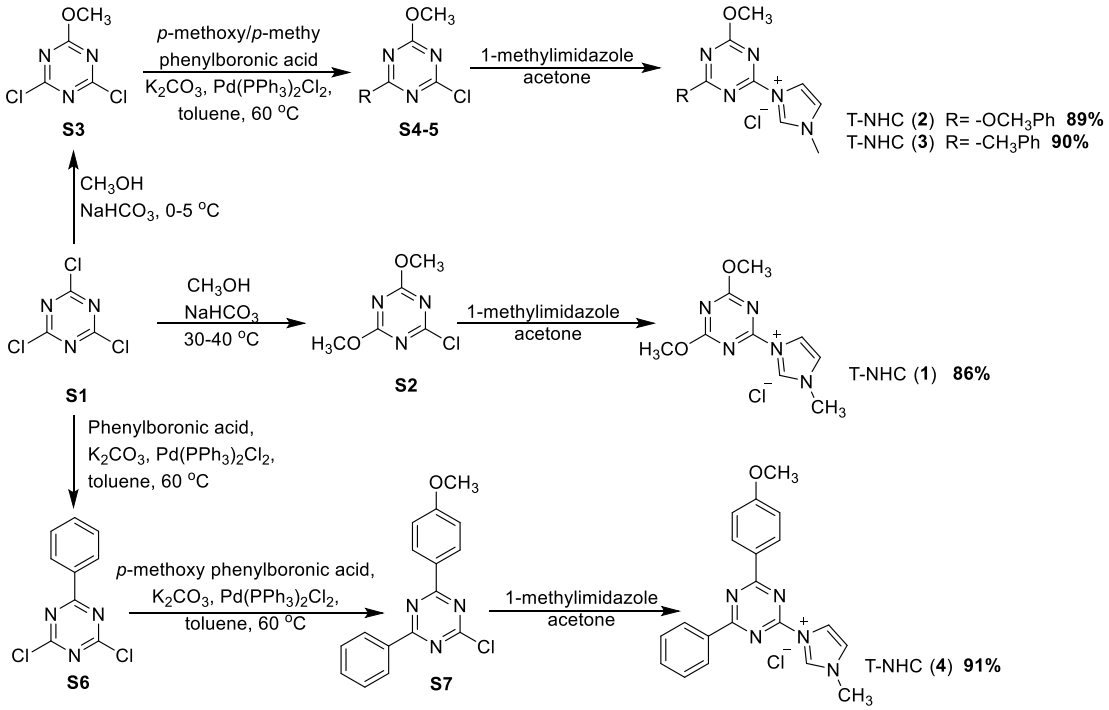
S-1 General experimental

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless-steel cannula. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point was between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker-400 MHz, 600 MHz Spectrometer (^{1}H: 400 MHz,^{13}C: 101 MHz and ^{1}H: 600 MHz, ^{13}C: 151 MHz), using $CDCl_3$, DMSO-d_6 and D_2O as the solvent at room temperature. The chemical shifts (δ) were expressed in ppm and the coupling constants (*J*) were expressed in Hz. High-resolution mass spectra (HRMS) were recorded on a Bruker MAXIS spectrometer.

S-2. Synthetic routes for NHC ligands



Scheme S1. Synthetic routes of T-NHCs (**1**-**4**)

The synthetic procedures of T-NHC (**1**). Firstly, in a 50 mL round bottom flask, **S1** 1.84 g (10 mmol), methanol (20 mL) and sodium bicarbonate (30 mmol, 2.52 g) were added in batches. After reacting for 10 hours at 40 °C, a white solid **S2** 1.58 g (90% yield) was obtained by recrystallization in petroleum ether and ethyl acetate (v/v = 20/1). And then acetone (10 mL) as solvent and reactant 1-methylimidazole (10 mmol, 821 mg) were added to react with **S2** (5 mmol, 875 mg). A white solid T-NHC (**1**) 1.11 g (yield: 86%) was collected with high purity.

T-NHC (1) (White solid was obtained in 86% isolated yield, 221 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 1H), 8.45 (s, 1H), 8.00 (s, 1H), 4.09 (s, 6H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, D_2O) δ 174.7, 163.0, 138.3, 126.5, 120.6, 58.1, 38.3. HRMS(ESI) m/z：[M-Cl]$^-$ calcd for $C_9H_{12}ClN_5O_2$, 222.0986; found, 222.0986.

The synthetic procedures of T-NHCs **(2**, **3**, **4)** were similar and the preparation process for T-NHC (**1**) was taken as an example. Firstly, in a 50 mL round bottom flask, **S1** (10 mmol, 1.84 g), methanol 20 mL and sodium bicarbonate (30 mmol, 2.52 g) were added in batches. After reacting for 6 hours at 0 °C, a white solid **S3** 1.58 g (yield: 90%) was obtained by recrystallization in petroleum ether and ethyl acetate (v/v = 20/1). To a 150 mL round-bottom flask containing **S3** (6 mmol, 1104 mg), 4-methoxyphenylboronic acid (760 mg, 5 mmol), $Pd(PPh_3)Cl_2$ (17.5 mg, 0.025 mmol), K_2CO_3 (1380 mg, 2 mmol) suspended in 50 mL toluene was added under nitrogen at 60 °C. It was purified by flash chromatography with dichloromethane and petroleum ether (v/v = 1/2) as elute. A white solid **S4** 1004 mg (yield: 80%) was collected. And then acetone (10 mL) as solvent and reactant 1-methylimidazole (5 mmol, 410 mg) were added to react with **S3** (2.5 mmol, 627 mg). A white solid T-NHC (**2**) 741 mg (yield: 89%) was collected with high purity.

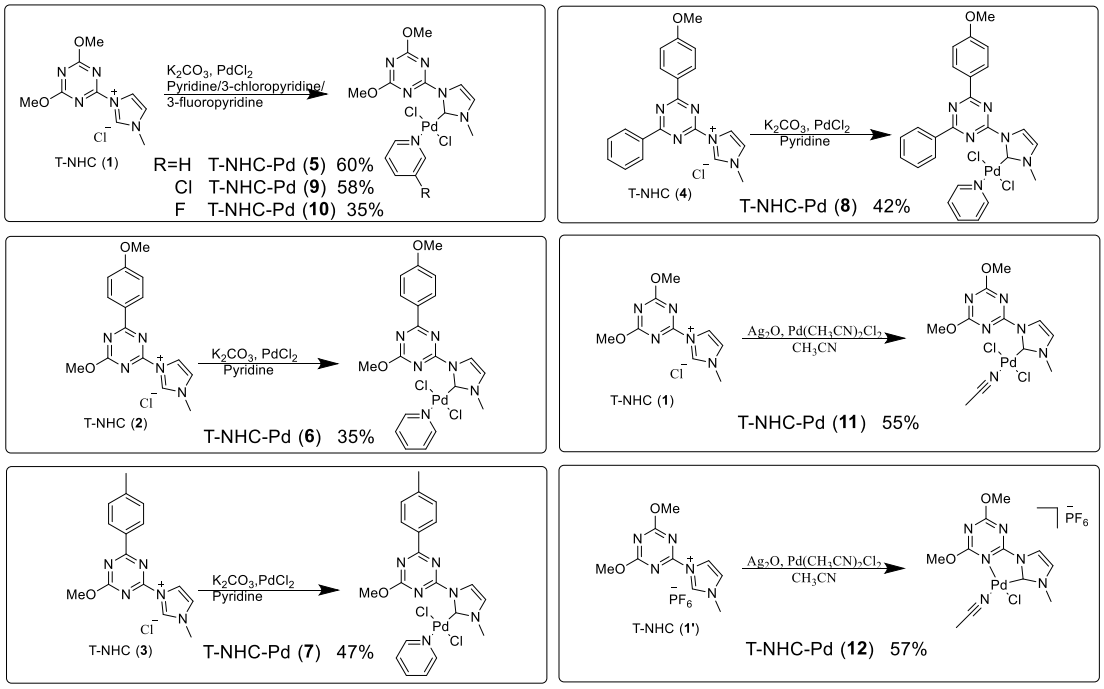
T-NHC (2) (White solid was obtained in 89% isolated yield, 1.49 g).^{1}H NMR (600 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.63 (s, 1H), 8.57 (d, J = 8.4 Hz, 2H), 8.06 (s, 1H), 7.15 (d, J = 8.5 Hz, 2H), 4.19 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 173.9, 171.8, 164.3, 160.7, 137.6, 131.5, 125.6, 125.3, 118.9, 114.4, 56.1, 55.7, 36.6. HRMS(ESI) m/z：[M-Cl]$^-$ calcd for $C_{15}H_{16}ClN_5O_2$, 298.1299; found, 298.1294.

T-NHC (3) (White solid was obtained in 90% isolated yield, 1.43 g).^{1}H NMR (600 MHz, DMSO-d_6) δ 10.54 (s, 1H), 8.65 (s, 1H), 8.51 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 1.9 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 4.21 (s, 3H), 4.05 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.4, 172.0, 160.8, 145.0, 137.6, 130.7, 129.6, 129.3, 125.3, 118.9, 56.2, 36.7, 21.3. HRMS(ESI) m/z：[M-Cl]$^-$ calcd for $C_{15}H_{16}ClN_5O$, 282.1349; found, 282.1350.

T-NHC (4) (White solid was obtained in 91% isolated yield, 1.73 g).^{1}H NMR (600 MHz, DMSO-d_6) δ 10.69 (s, 1H), 8.79 (s, 1H), 8.67 (dd, J = 17.4, 8.2 Hz, 4H), 8.10 (s, 1H), 7.74 (t, J

= 7.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 4.09 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.5, 172.4, 164.3, 159.9, 137.6, 134.1, 133.7, 131.5, 129.1, 129.0, 125.8, 125.3, 119.0, 114.4, 55.7, 36.7. HRMS(ESI) m/z：[M-Cl]$^-$ calcd for $C_{20}H_{18}ClN_5O$: 344.1506; found, 344.1509.

S-3. Synthetic routes for T-NHC-Pds (5-12) complexes:



Scheme S2. Synthetic routes of T-NHC-Pds (**5**-**12**) complexes

The synthetic procedures of T-NHC-Pds (**5**-**10**) were similar and the preparation process for T-NHC-Pd (**5**) was taken as an example. Complex T-NHC-Pd (**5**) 286 mg (yield: 60%) were prepared by the direct reaction of $PdCl_2$ (1 mmol, 177 mg), K_2CO_3 (2 mmol, 276 mg) and a triazine imidazolium salt T-NHC (**1**) (1 mmol, 257 mg) in pyridine at 45°C. The formed yellowish powder was filtered and the solution was evaporated to dryness and washed with ethyl ether.

T-NHC-Pd (5) (Yellow solid was obtained in 60% isolated yield, 286 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (dt, *J* = 5.0, 1.6 Hz, 2H), 8.05 (d, *J* = 2.3 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.40 - 7.35 (m, 2H), 7.03 (d, *J* = 2.3 Hz, 1H), 4.38 (s, 3H), 4.21 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 156.6, 150.6, 149.3, 138.2, 132.8, 125.0, 124.0, 120.9, 56.5, 39.5. HRMS(ESI) m/z：[M-Cl]$^+$ calcd for $C_{14}H_{17}Cl_2N_6O_2Pd$, 441.0056; found, 441.0058.

T-NHC-Pd (6) (Yellow solid was obtained in 35% isolated yield, 194 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 – 9.03 (m, 2H), 8.77 (d, *J* = 9.0 Hz, 2H), 8.13 (d, *J* = 2.3 Hz, 1H), 7.84 - 7.76 (m, 1H), 7.38 - 7.31 (m, 2H), 7.06 (d, *J* = 2.2 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 4.40 (s, 3H), 4.25

(s, 3H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 171.0, 163.1, 162.4, 156.1, 150.7, 137.0, 131.0, 126.3, 123.5, 122.8, 119.8, 112.9, 55.1, 54.5, 38.5. [M-Cl]$^+$ calcd for $C_{20}H_{21}Cl_2N_6O_2Pd$, 517.0371; found, 517.0368.

T-NHC-Pd (7) (Yellow solid was obtained in 47% isolated yield, 252 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 - 9.03 (m, 2H), 8.67 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 2.2 Hz, 1H), 7.83 - 7.76 (m, 1H), 7.34 (m, 2H), 7.11 - 7.05 (m, 3H), 4.40 (s, 3H), 4.27 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ175.2, 172.1, 163.5,157.3, 151.6, 144.3, 138.1, 132.0, 129.9, 129.3, 124.4, 123.9, 120.8, 56.2, 39.5, 21.8. HRMS(ESI) m/z: [M-Cl]$^+$ calcd for $C_{20}H_{21}Cl_2N_6OPd$, 501.0422; found, 501.0416.

T-NHC-Pd (8) (Yellow solid was obtained in 42% isolated yield, 248 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 - 9.02 (m, 2H), 8.90 - 8.79 (m, 4H), 8.27 (d, *J* = 2.2 Hz, 1H), 7.85 - 7.76 (m, 1H), 7.59 - 7.50 (m, 1H), 7.42 - 7.29 (m, 4H), 7.11 (d, *J* = 2.2 Hz, 1H), 6.91 - 6.81 (m, 2H), 4.42 (s, 3H), 3.85 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 172.1, 163.5 , 157.3, 151.6, 144.3, 138.1, 132.0, 129.9, 129.3, 124.4, 123.9, 120.8, 56.2, 39.5, 21.8. HRMS(ESI) m/z: [M-Cl]$^+$ calcd for $C_{25}H_{23}Cl_2N_6OPd$, 563.0579; found, 563.0579.

T-NHC-Pd (9) (Yellow solid was obtained in 58% isolated yield, 296 mg). ^{1}H NMR (400 MHz, $CDCl_3$ δ 9.09 (dd, *J* = 6.4, 1.5 Hz, 2H), 8.05 (d, *J* = 2.3 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.40 - 7.35 (m, 2H), 7.03 (d, *J* = 2.3 Hz, 1H), 4.38 (s, 3H), 4.21 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 156.5, 150.52, 149.27, 138.1, 132.7, 124.9, 123.8, 120.7, 39.5. HRMS(ESI) m/z：[M-Cl]$^+$ calcd for $C_{14}H_{16}Cl_3N_6O_2Pd$, 474.9669; found: 474.9663.

T-NHC-Pd (10) (Yellow solid was obtained in 35% isolated yield, 173 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (t, *J* = 2.9 Hz, 1H), 8.98 - 8.92 (m, 1H), 8.04 (d, *J* = 2.3 Hz, 1H), 7.55 (tdd, *J* = 7.4, 2.9, 1.4 Hz, 1H), 7.39 (dt, *J* = 8.6, 5.3 Hz, 1H), 7.04 (d, *J* = 2.3 Hz, 1H), 4.34 (s, 3H), 4.19 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 164.1, 160.5(d, ^{1} *J* = 254.52 Hz), 156.3, 147.5(d, ^{4} *J* = 4.04 Hz), 140.6, 140.3, 125.5 (d, ^{2} *J* = 18.18 Hz), 125.2(d, ^{3} *J* = 6.06 Hz), 124.0, 120.9, 56.5, 39.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ 122.11. HRMS(ESI) m/z：[M-Cl]$^+$ calcd for $C_{14}H_{16}Cl_2FN_6O_2Pd$, 458.9964; found, 458.9963.

The synthetic procedures of T-NHC-Pds (**11** and **12**) were similar and the preparation process for T-NHC-Pd (**11**) was taken as an example. To a dried Schlenk flask, T-NHC (**1**) (257 mg, 1 mmol) and Ag_2O (115 mg, 0.5 mmol) were added under nitrogen atmosphere. Subsequently, dried CH_3CN (3 mL) was added via syringe. The mixture was stirred at room temperature for 20 min. Then $PdCl_2(CH_3CN)_2$ (259 mg, 1 mmol) in anhydrous CH_3CN (3 mL) was added at the room temperature. The formed yellowish powder NHC-Pd (**11**) (242 mg, yield: 55%) was filtered and the solution was evaporated to dryness and recrystallized in CH_3CN and

petroleum ether (v/v = 1/2).

T-NHC (1') (White solid was obtained in 86% isolated yield, 315.8 mg). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.20 (s, 1H), 8.45 (t, *J* = 1.8 Hz, 1H), 7.99 - 7.87 (m, 1H), 4.11 (s, 6H), 3.99 (s, 3H).^{13}C NMR (151 MHz, DMSO-d_6) δ 172.91, 161.41, 137.43, 125.27, 118.94, 56.30, 36.65. HRMS(ESI) m/z：$[M\text{-}PF_6]^-$ calcd for $C_9H_{12}F_6N_5O_2P$, 222.0986; found, 222.0986.

T-NHC-Pd (11) (Yellow solid was obtained in 55% isolated yield, 241 mg). ^{1}H NMR (600 MHz, DMSO-d6) δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.71 (d, *J* = 2.1 Hz, 1H), 4.21 (s, 3H), 4.16 (s, 1H).^{13}C NMR (151 MHz, DMSO) δ 172.6, 163.4, 159.0, 125.4, 120.4, 99.5, 56.6, 38.9.

T-NHC-Pd (12) (Yellow solid was obtained in 60% isolated yield, 286 mg).^{1}H NMR (600 MHz, DMSO-d_6) δ 8.30 (d, *J* = 2.3 Hz, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 4.18 (s, 6H), 4.16 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.4, 163.1, 126.4, 120.8, 118.0, 56.5, 38.9, 1.1.

S-4. Single crystal X-ray analysis of T-NHC-Pds (5, 8, 9, 11 and 12).

Table S1. Summary of X-ray crystallographic data for T-NHC-Pd (**5**).

CCDC number	2005203
Empirical formula	$C_{14}H_{16}Cl_2N_6O_2Pd$
Formula weight	477.63
Temperature/K	152.99
Crystal system	triclinic
Space group	P-1
a/Å	8.6642(6)
b/Å	10.2036(8)
c/Å	10.5774(8)
α/°	80.779(2)
β/°	73.728(2)
γ/°	84.359(2)
Volume/Å^3	884.64(11)
Z	2
*ρ*calcg/cm^3	1.793
μ/mm‑1	11.439
F(000)	476.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuK*α* (*λ* = 1.54178)
2Θ range for data collection/°	8.794 to 136.414
Index ranges	-9 ≤ h ≤ 10, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	8178
Independent reflections	3158[R_{int}=0.0538, R_{sigma} =0.0559]
Data/restraints/parameters	3158/0/229
Goodness-of-fit on F^2	1.083
Final R indexes [*I* >= 2*σ* (*I*)]	R_1 = 0.0573, wR_2 = 0.1518
Final R indexes [all data]	R_1 = 0.0577, wR_2 = 0.1523
Largest diff. peak/hole / *e* Å^{-3}	3.30/-1.34

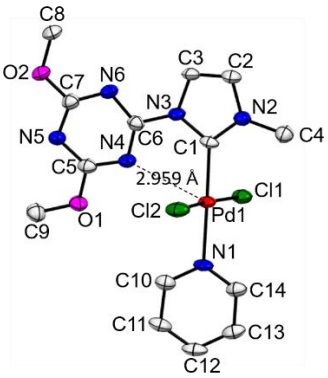


Figure S1. Single-crystal structure of T-NHC-Pd (**5**) (thermal ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity).

Table S2. Summary of X-ray crystallographic data for T-NHC-Pd (**8**).

CCDC number	2039570
Empirical formula	$C_{25}H_{22}Cl_2N_6OPd$
Formula weight	599.78
Temperature/K	152.99
Crystal system	triclinic
Space group	P-1
a/Å	8.7459(5)
b/Å	12.3604(6)
c/Å	12.4452(7)
α/°	75.518(2)
β/°	70.882(2)
γ/°	89.938(2)
Volume/Å^3	1225.96(12)
Z	2
*ρ*calcg/cm^3	1.625
μ/mm‑1	8.366
F(000)	604
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuK*α* (*λ* = 1.54178)
2Θ range for data collection/°	7.416 to 136.608
Index ranges	-10 ≤ h ≤ 9, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	19809
Independent reflections	4485[R_{int}=0.0354, R_{sigma} = 0.0255]
Data/restraints/parameters	4485/0/318
Goodness-of-fit on F^2	1.090
Final R indexes [*I* >= 2*σ* (*I*)]	*R1* = 0.0281, *wR2* = 0.0794
Final R indexes [all data]	*R1* = 0.0284, *wR2* = 0.0797
Largest diff. peak/hole / *e* Å^{-3}	1.53/-0.44

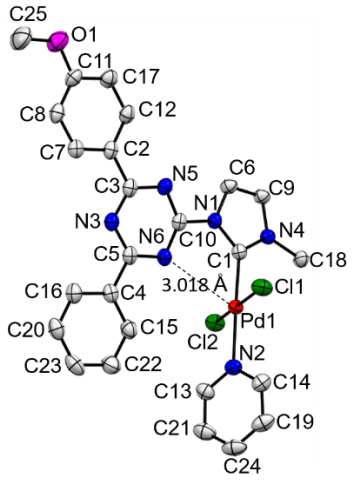


Figure S2. Single-crystal structure of T-NHC-Pd (**8**) (thermal ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity).

Table S3. Summary of X-ray crystallographic data for T-NHC-Pd (**9**).

CCDC number	2005204
Empirical formula	$C_{14}H_{15}Cl_3N_6O_2Pd$
Formula weight	512.07
Temperature/K	152.99
Crystal system	triclinic
Space group	P-1
a/Å	8.6323(4)
b/Å	10.3450(5)
c/Å	10.7361(5)
α/°	77.526(2)
β/°	78.814(2)
γ/°	83.699(2)
Volume/Å^3	916.02(8)
Z	2
*ρ*calcg/cm^3	1.857
μ/mm-1	12.409
F(000)	508.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuK*α* (*λ* = 1.54178)
2Θ range for data collection/°	8.776 to 136.524
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	14017
Independent reflections	3344[R_{int}=0.0420, R_{sigma} = 0.0309]
Data/restraints/parameters	3344/0/238
Goodness-of-fit on F^2	1.089
Final R indexes [*I* >= 2*σ* (*I*)]	R_1 = 0.0322, wR_2 = 0.0840
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0845
Largest diff. peak/hole / *e* Å^{-3}	2.55/-0.42

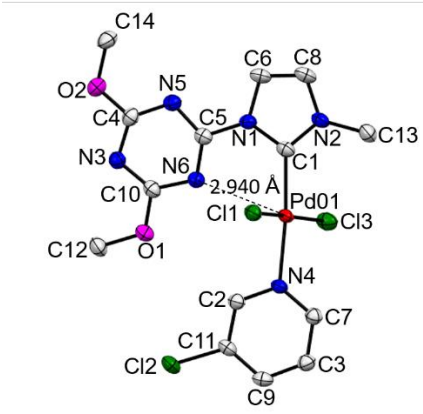


Figure S3. Single-crystal structure of T-NHC-Pd (**9**) (thermal ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity).

Table S4. Summary of X-ray crystallographic data for T-NHC-Pd (**11**).

CCDC number	2005201
Empirical formula	$C_{11}H_{14}Cl_2N_6O_2Pd$
Formula weight	439.58
Temperature/K	152.99
Crystal system	triclinic
Space group	P-1
a/Å	7.3845(4)
b/Å	10.3301(6)
c/Å	10.8624(6)
α/°	75.1030(10)
β/°	86.4900(10)
γ/°	88.6250(10)
Volume/Å3	799.23(8)
Z	2
ρcalcg/cm3	1.827
μ/mm‑1	12.593
F(000)	436.0
Crystal size/mm3	0.5 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.436 to 136.49
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	18183
Independent reflections	2888[Rint = 0.0340, Rsigma = 0.0245]
Data/restraints/parameters	2888/0/203
Goodness-of-fit on F2	1.124
Final R indexes [I >= 2σ (I)]	R1 = 0.0242, wR2 = 0.0629
Final R indexes [all data]	R1 = 0.0242, wR2 = 0.0629
Largest diff. peak/hole / e Å-3	0.43/-0.92

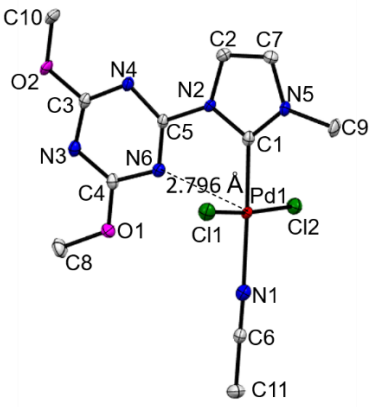


Figure S4. Single-crystal structure of T-NHC-Pd (**11**) (thermal ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity).

Table S5. Summary of X-ray crystallographic data for T-NHC-Pd (**12**).

CCDC number	2005202
Empirical formula	$C_{11}H_{14}ClF_6N_6O_2PPd$
Formula weight	549.10
Temperature/K	153.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.8588(10)
b/Å	23.213(3)
c/Å	10.2891(13)
α/°	90
β/°	103.435(4)
γ/°	90
Volume/Å^3	1825.6(4)
Z	4
*ρ*calcg/cm^3	1.998
μ/mm‑1	1.331
F(000)	1080.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	MoK*α* (*λ* = 0.71073)
2Θ range for data collection/°	5.374 to 52.846
Index ranges	-9 ≤ h ≤ 9, -29 ≤ k ≤ 29, -11 ≤ l ≤ 12
Reflections collected	21945
Independent reflections	3718 [R_{int} = 0.0253, R_{sigma} = 0.0166]
Data/restraints/parameters	3718/0/257
Goodness-of-fit on F^2	1.112
Final R indexes [I >= 2*σ* (I)]	R_1 = 0.0381, wR_2 = 0.0918
Final R indexes [all data]	R_1 = 0.0397, wR_2 = 0.0927
Largest diff. peak/hole / *e* Å^{-3}	1.70/-0.88

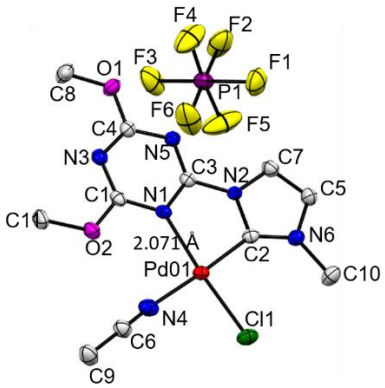
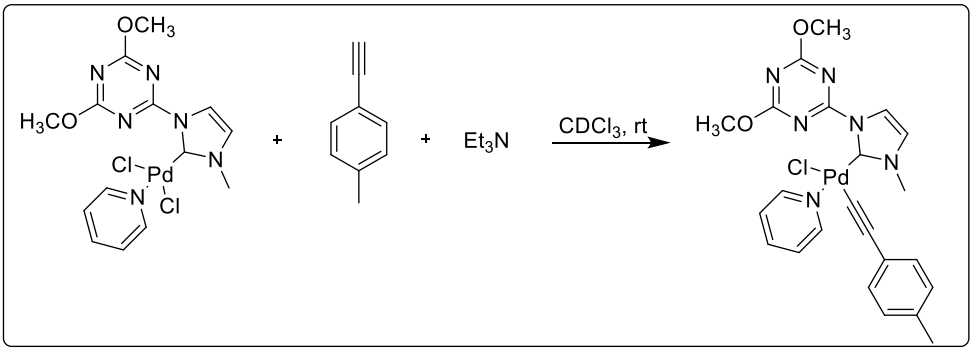


Figure S5. Single-crystal structure of T-NHC-Pd (**12**) (thermal ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity).

S-5. ^{1}H NMR experiment

The reaction procedures of ^{1}H NMR experiment (**S-5-1, S-5-3, S-5-4**) were similar and the preparation process for (**S-5-1**) was taken as an example. To a solution of complex T-NHC-Pd (**8**) (0.025 mmol) and the internal standard 4-phenyltoluene (0.025 mmol) in 5 mL $CDCl_3$, 4-ethynyltoluene (0.025 mmol) and then Et_3N (0.025 mmol) and were added. And then the ^{1}H NMR spectra of the reaction solution at different time were recorded.

S-5-1. ^{1}H NMR experiment of complex T-NHC-Pd (5) with *4*-ethynyltoluene and Et_3N.



To shed light on the activation of the alkynyl groups by T-NHC-Pd complexes, the interaction between complex T-NHC-Pd (**5**), 4-ethynyltoluene and Et_3N were studied by ^{1}H NMR experiment, which was considered as a powerful technique to investigate reaction process of an catalytic system. The broadened peak at δ 2.56 ppm was ascribed to the Et_3N-CH_2 resonance, which indicated that probably the presence of active H led to the broadening of the peak in **Figure S6 (a, b)**. The -CH_3 signal of Et_3N appeared at δ 1.05 ppm. With the procedding of the reaction, the chemical shifts of the two signals move to the lower field, from the initial δ 2.56 and 1.05 ppm to 2.89 and 1.25 ppm, respectively and then the movement almost ceased. And the peaks were sharpened gradually to the standard quartet shape of triethylamine, which is due to the protonation of triethylamine and finally generates Et_3N·HCl. There is an alkynyl H signal at δ 3.02 ppm. Its chemical shift remained unchanged with extension of the reaction time. However, the peak intensity was getting weaker, which is due to the consumption of 4-ethynyltoluene in the reaction system when its alkynyl group is coordinated with the palladium center. In addition, no evident chemical shifts in other places of the NMR spectra have been found.

In the process of ^{1}H NMR experiment, the color of the reaction is also visible to the naked eye, which changed gradually from the initial bright yellow to darker and finally to brown-black, as shown in **Figure S7**.

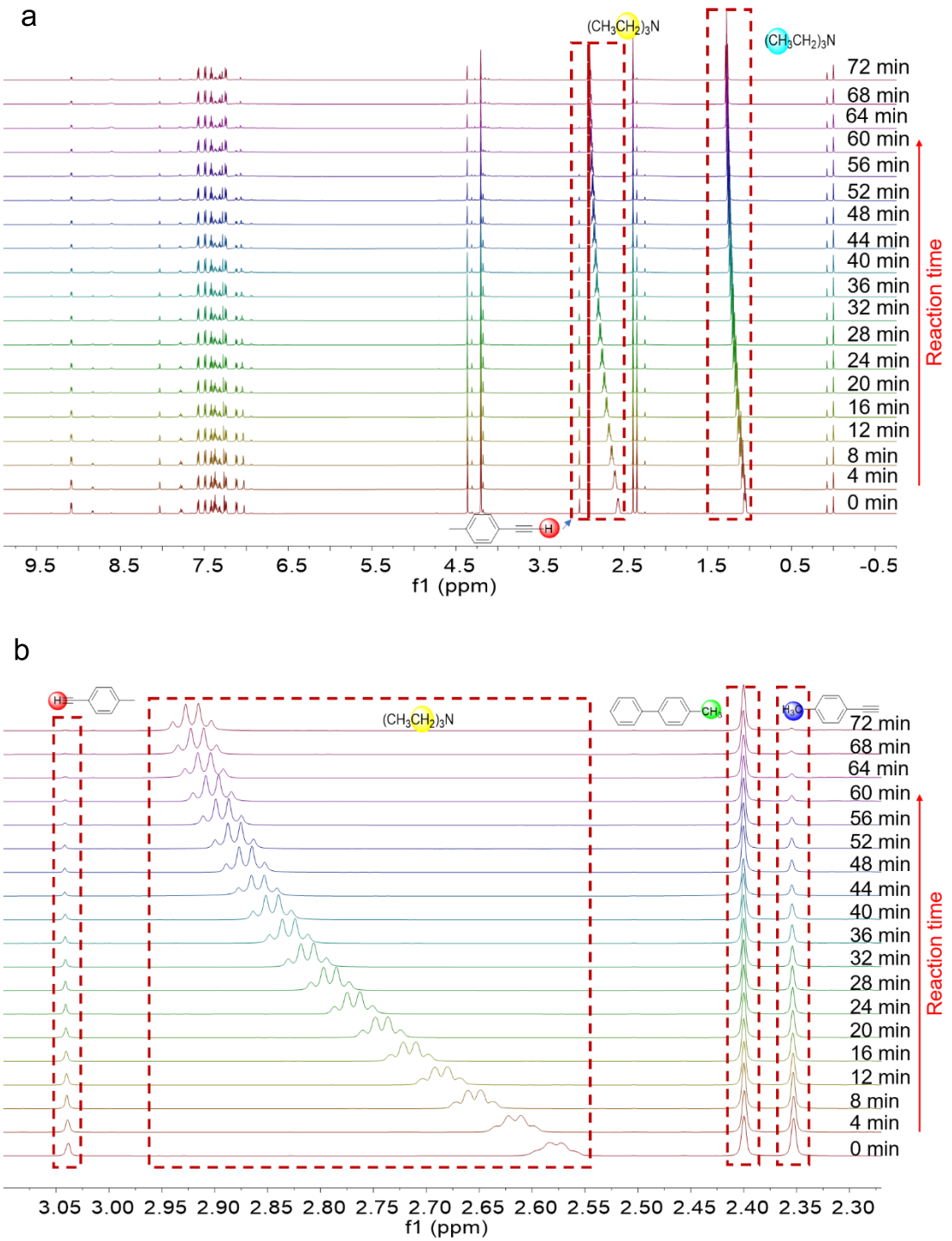


Figure S6. 600 MHz ^{1}H NMR spectra for a complex T-NHC-Pd (**5**) solution with the addition of 4-ethynyltoluene and Et_3N in $CDCl_3$.

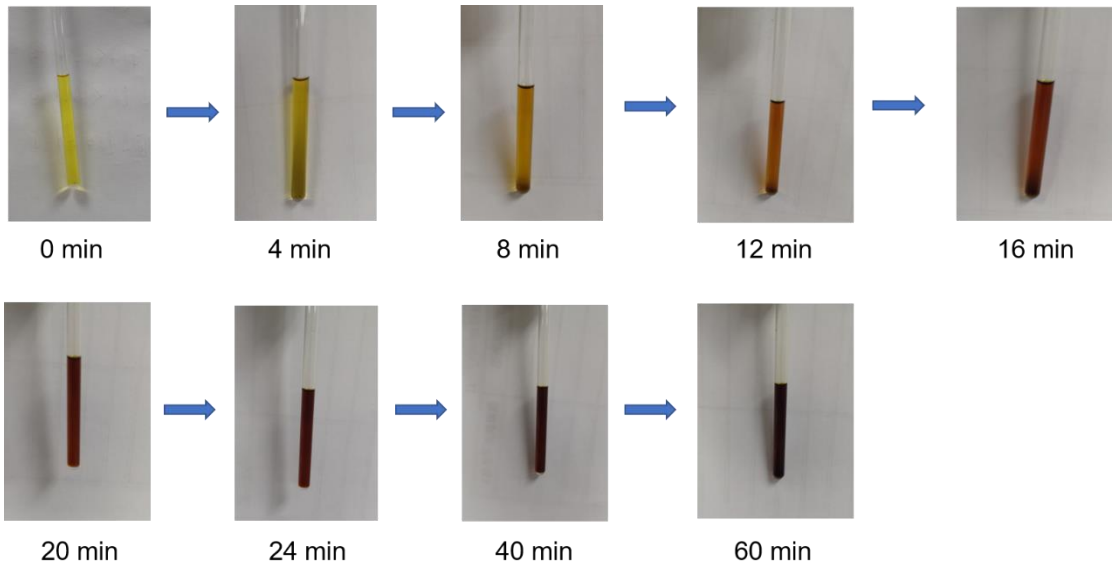


Figure S7. Reaction time dependence of the color of the complex T-NHC-Pd (**5**) solution with the addition of 4-ethynyltoluene and Et_3N in $CDCl_3$.

S-5-2. HR-ESI-MS detection of intermediates in the reaction system in S-5-1.

The ^1H NMR titration experiment was also investigated by ESI-MS analysis, in which the ion peak at m/z 521.0921 is corresponding to $C_{23}H_{23}N_6O_2Pd^+$

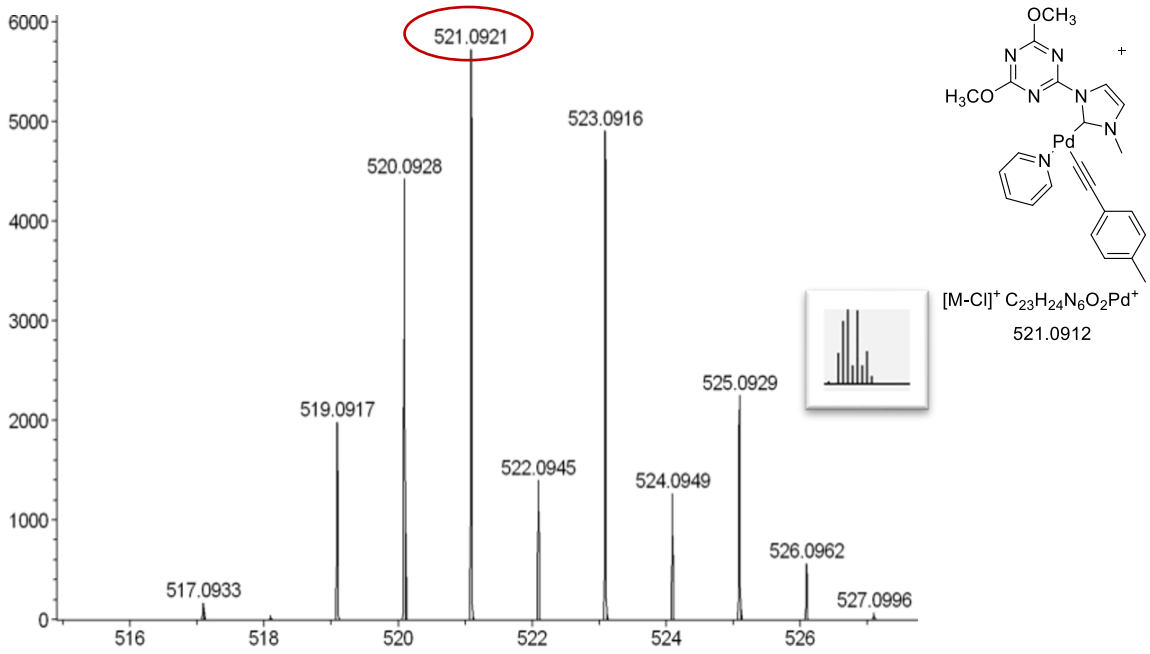
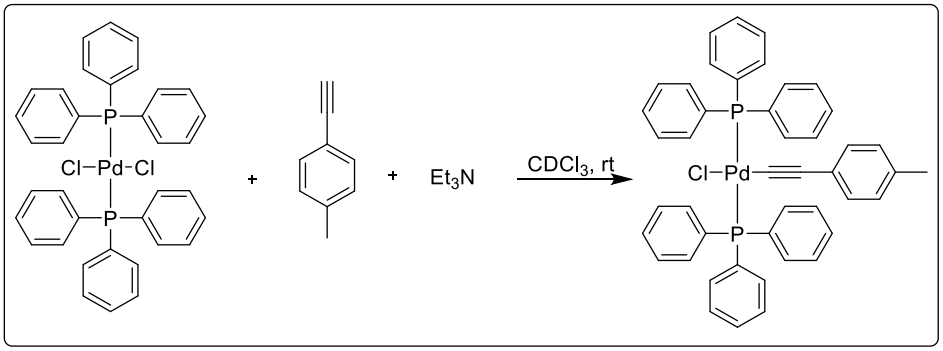
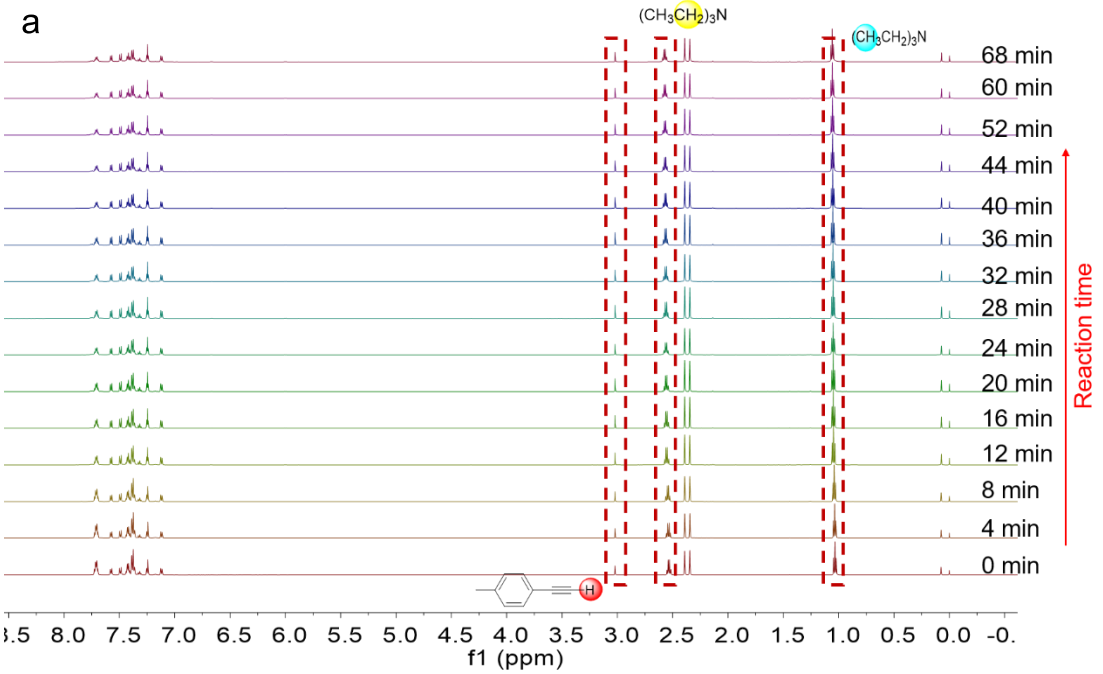


Figure S8. ESI(+)-MS spectrum of the organometallic Pd complex.

S-5-3. ^{1}H NMR experiment of $PdCl_2(PPh_3)$ with *4*-ethynyltoluene and Et_3N.

Additionally, we also examined the reaction with the classic $PdCl_2(PPh_3)$ palladium complex as catalyst under the same condition. As displayed in **Figure S9**, the chemical shifts and peak shapes of the two protons in triethylamine almost retained with the reaction time consumed. The peak integration values of the protons in 4-ethynyltoluene changed hardly with the reaction proceeding as we observed in the catalytic system of $PdCl_2(PPh_3)$. The solution color also remained its initial bright yellow as shown in **Figure S10**.





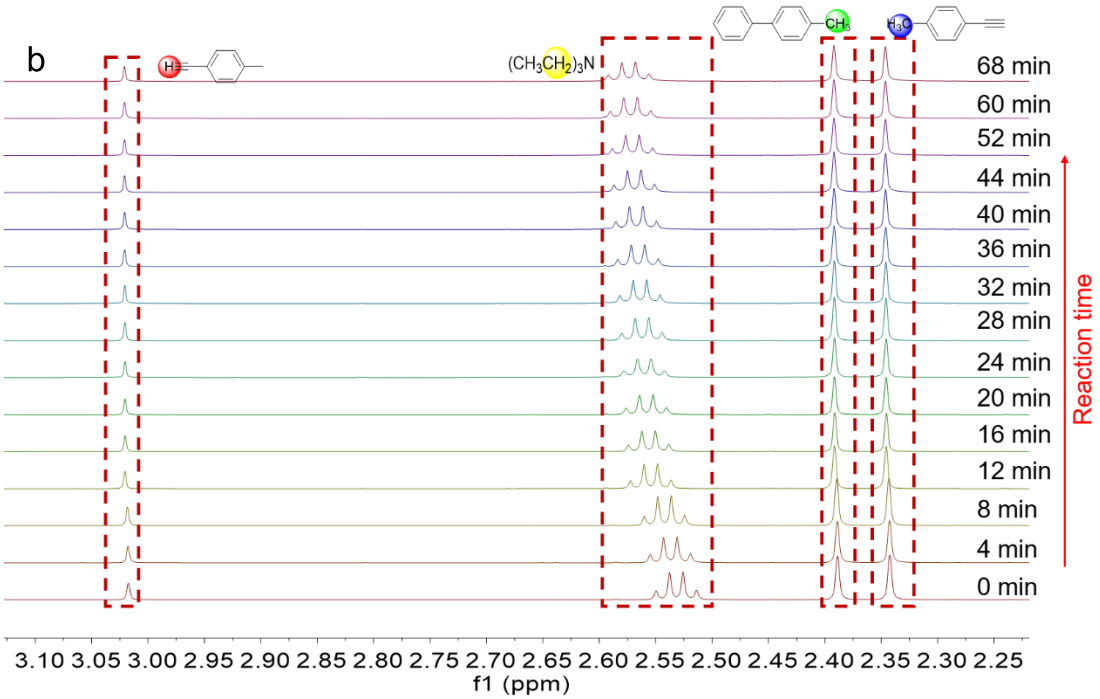


Figure S9. 600 MHz ^{1}H NMR spectra for a $PdCl_2(PPh_3)$ solution with the addition of 4-ethynyltoluene and Et_3N in $CDCl_3$.

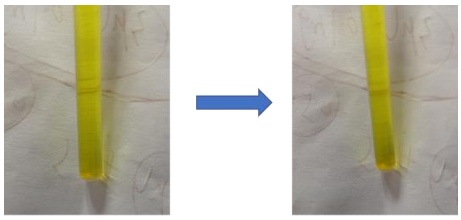


Figure S10. Reaction time dependence of the color of the complex $PdCl_2(PPh_3)$ solution with the addition of 4-ethynyltoluene and Et_3N in $CDCl_3$.

S-5-4. ^{1}H NMR titration experiment of NHC-Pd with *4*-ethynyltoluene and Et_3N.

Next, in order to further prove that the addition of the triazine ring promotes the deprotonation process, we compared complex T-NHC-Pd (**5**) with other well-known palladium complexes. Firstly, the NHC-Pd complex reported by the Orpen group was employed for ^{1}H NMR investigation under same condition. It was found that there is no obvious chemical shift movement and peak broadening for the protons in triethylamine and 4-ethynyltolueneas shown in **Figure S11**, and the color of the reaction solution kept the initial bright yellow and no obvious change was observed with reaction proceeding (**Figure S12**).

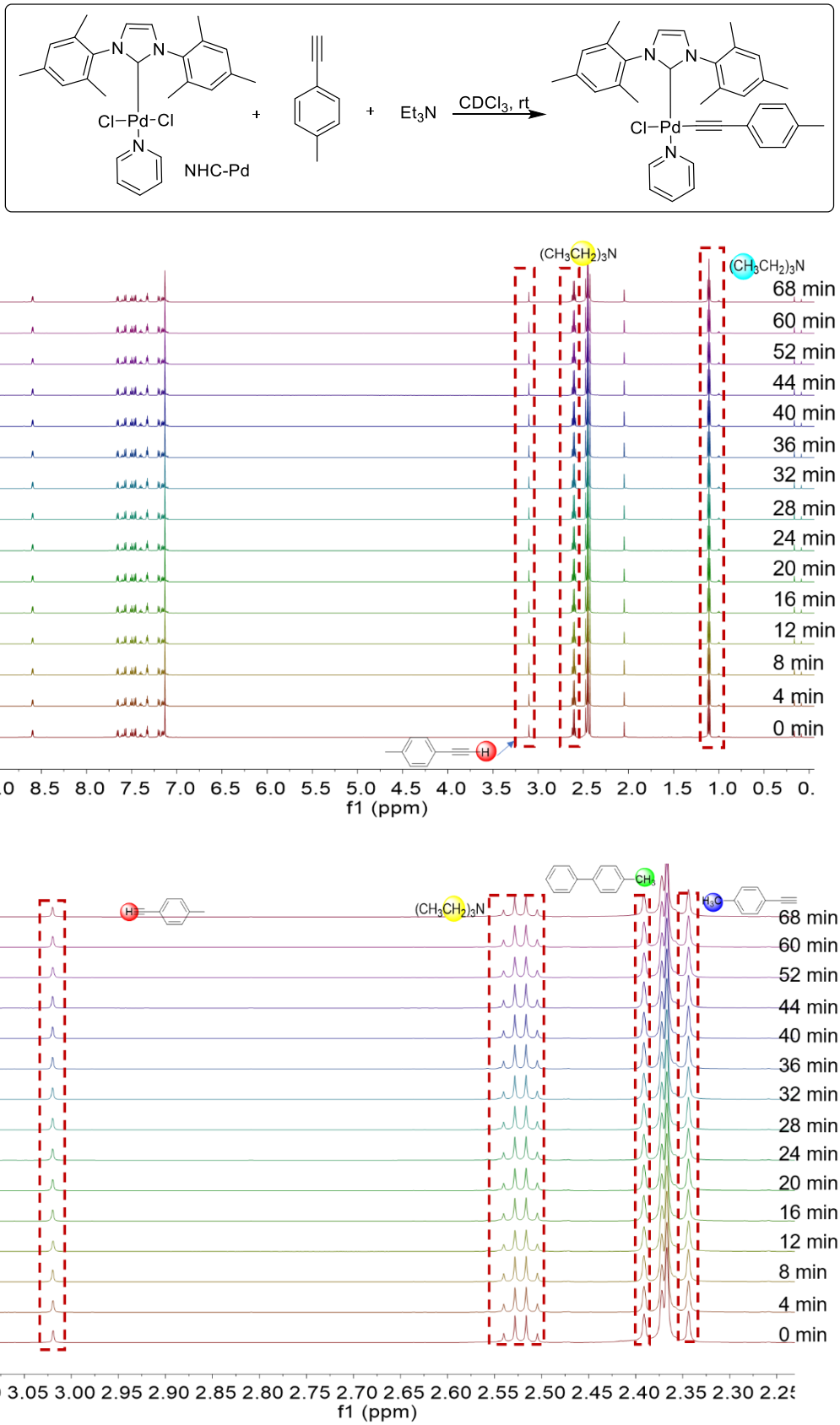


Figure S11. 600 MHz ^{1}H NMR spectra for a NHC-Pd solution with the addition of 4-ethynyltoluene and Et_3N in $CDCl_3$.

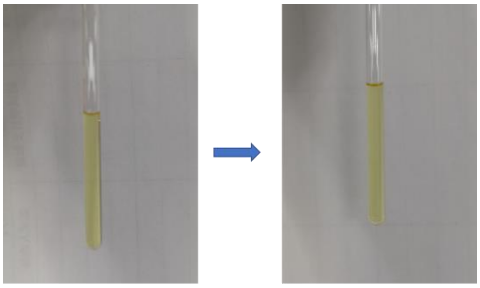


Figure S12. Reaction time dependence of the color of the complex NHC-Pd solution with the addition of 4-ethynyltoluene and Et_3N in $CDCl_3$.

S-5-5. Comparison of the catalytic performance

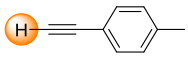
In order to be able to clearly observe the speed of the reaction of the three different palladium complexes with 4-ethynyltoluene, we made a broken line statistics chart, the horizontal coordinate is the reaction time, and the vertical coordinate is the concentration of 4-ethynyltoluene. It can be seen from the **Figure S13** that at a same reaction time, the palladium complex T-NHC-Pd (**5**) containing the triazine-based NHC ligand has the highest rate for consumption of 4-ethynyltoluene.

The ^1H NMR experiment procedures of T-NHC-Pd (**5**), NHC-Pd and $PdCl_2(PPh_3)$ were similar and the preparation process for T-NHC-Pd (**5**) was taken as an example. To a solution of complex T-NHC-Pd (**5**) (0.025 mmol) and the internal standard 4-phenyltoluene (0.025 mmol) in 5 mL $CDCl_3$, 4-ethynyltoluene (0.025 mmol) and Et_3N (0.025 mmol) were added.

The initial concentration of 4-ethynyltoluene: $c=n/v=0.025$ mmol/5 mL$=5*10^{-3}$ mmol/mL$= 5*10^{-3}$mol/L (vertical coordinate is the concentration of 4-ethynyltoluene).

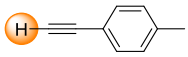
And then the ^1H NMR spectra of the reaction solution at different time were recorded. Using the internal standard 4-phenyltoluene as a reference, the ethynyl hydrogen signals of compound 4-ethynyltoluene were integrated at different time. The integrated value of the ethynyl hydrogen signals of the 4-ethynyltoluene corresponds to the 4-ethynyltoluene concentration in the solution (horizontal coordinate was the reaction time). And we displayed the dependence of 4-ethynyltoluene concentration on the reaction time in **Figure S13** based on the data in **Table S6**, **S7**, **S8**. At the same time, we also calculated the average reaction rates of the reactions and they were shown in **Figure S14**.

Table S6. Calculated 4-ethynyltoluene concentrations at different reaction time with T-NHC-Pd (**5**) as precatalyst in the ^{1}H NMR experiments.

Time (min)	 Integrated value of alkynyl hydrogen	4-ethynyltoluene (mol/L)
0	1.00	$5.00*10^{-3}$
4	0.91	$4.55*10^{-3}$
8	0.83	$4.15*10^{-3}$
12	0.75	$3.75*10^{-3}$
16	0.68	$3.40*10^{-3}$
28	0.62	$3.10*10^{-3}$
40	0.53	$2.65*10^{-3}$
52	0.48	$2.40*10^{-3}$
60	0.42	$2.10*10^{-3}$

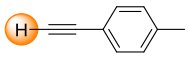
[a] Reaction conditions: T-NHC-Pd (**5**) (0.025 mmol), 4-ethynyltoluene (0.025 mmol), Et_3N (0.025 mmol), $CDCl_3$ (5 mL), internal standard 4-phenyltoluene (0.025 mmol), RT, 60 min.

Table S7. Calculated 4-ethynyltoluene concentrations at different reaction time with $PdCl_2(PPh_3)$ as precatalyst in the ^{1}H NMR experiments.

Time (min)	 Integrated value of alkynyl hydrogen	4-ethynyltoluene (mol/L)
0	1.00	$5.00*10^{-3}$
4	0.98	$4.90*10^{-3}$
8	0.96	$4.80*10^{-3}$
20	0.93	$4.65*10^{-3}$
32	0.92	$4.60*10^{-3}$
40	0.92	$4.60*10^{-3}$
52	0.92	$4.60*10^{-3}$
60	0.92	$4.60*10^{-3}$

[a] Reaction conditions: $PdCl_2(PPh_3)$ (0.025 mmol), 4-ethynyltoluene (0.025 mmol), Et_3N (0.025 mmol), $CDCl_3$ (5 mL), internal standard 4-phenyltoluene (0.025 mmol), RT, 60 min.

Table S8. Calculated 4-ethynyltoluene concentrations at different reaction time with NHC-Pd as precatalyst in the ^{1}H NMR experiments.

Time (min)	 Integrated value of alkynyl hydrogen	4-ethynyltoluene (mol/L)
0	1.00	$5.00*10^{-3}$
4	0.98	$4.90*10^{-3}$
8	0.97	$4.85*10^{-3}$
20	0.97	$4.85*10^{-3}$
32	0.97	$4.85*10^{-3}$
40	0.96	$4.80*10^{-3}$
52	0.96	$4.80*10^{-3}$
60	0.95	$4.80*10^{-3}$

[a] Reaction conditions: NHC-Pd (0.025 mmol), 4-ethynyltoluene (0.025 mmol), Et_3N (0.025 mmol), $CDCl_3$ (5 mL), internal standard 4-phenyltoluene (0.025 mmol), RT, 60 min.

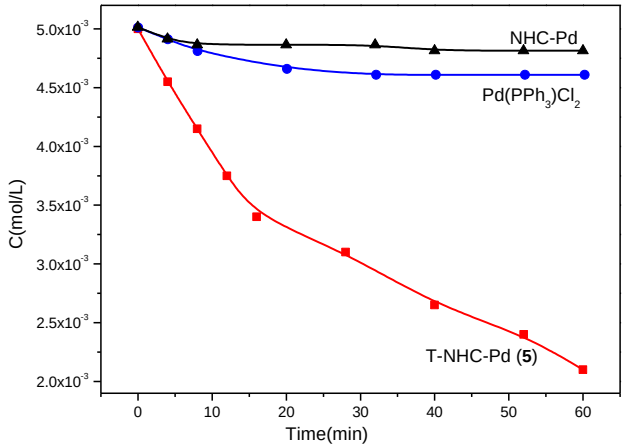
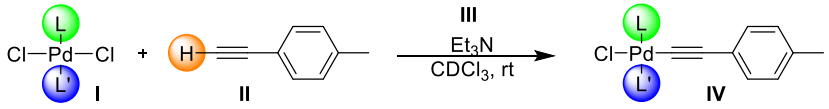


Figure S13. Comparison of the catalytic performance of complex T-NHC-Pd (**5**) with other catalyst precursors of NHC-Pd and $PdCl_2(PPh_3)$.



(1). L=T-NHC, L'=Py, $\bar{v}$=4.8*10^{-5} mol.L^{-1}.min^{-1};
(2). L, L'=PPh_3, $\bar{v}$=6.7*10^{-6} mol.L^{-1}.min^{-1};
(3). L=NHC, L'=Py, $\bar{v}$=4.2*10^{-6} mol.L^{-1}.min^{-1}.

Figure S14. Catalyst T-NHC-Pd (**5**) promoted the deprotonation of terminal alkyne.

The average reaction rates of the reactions were calculated as follows:

(1) for precatalyst T-NHC-Pd (**5**):

Concentration of 4-ethynyltoluene after 60 minutes reaction is:

c=n/v=0.025*(1.00-0.42) mmol/5 mL=2.9*10^{-3} mmol/mL=2.9*10^{-3} mol/L

the average reaction rate is:

$\bar{v}$=c/t=2.9*10^{-3} mol/L/60min=4.8*10^{-5} mol/L/min

(2) for precatalyst $PdCl_2(PPh_3)$:

c=n/v=0.025*(1.00-0.92) mmol/5 mL=4*10^{-4} mmol/mL=4*10^{-4} mol/L

$\bar{v}$=c/t=4*10^{-4} mol/L/60 min=6.7*10^{-6} mol/L/min

(3) for precatalyst NHC-Pd:

c=n/v=0.025*(1.00-0.95) mmol/5 mL=2.5*10^{-4} mmol/mL=2.5*10^{-4} mol/L

$\bar{v}$=c/t=2.5*10^{-4} mol/L/60min=4.2*10^{-6} mol/L/min

S-6 Optimization of Sonogashira carbonylation coupling reaction between1a and 2a

S-6.1 Optimization of solvents in the titled reaction between 1a and 2a

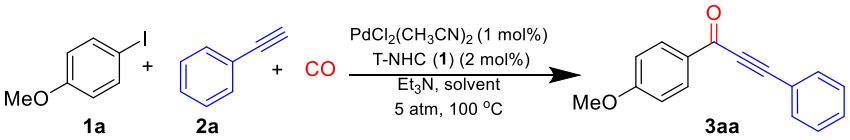


Table S9. Optimization of solvents in the titled reaction between **1a** and **2a**

Entry	[Pd]	[L]	Solvent	Base	Yield(%)
1	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	DMF	Et_3N	trace
2	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	CH_3CN	Et_3N	42
3	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	DMSO	Et_3N	trace
4	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	Et_3N	79
5	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	1,4-dioxane	Et_3N	45
6	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	H_2O	Et_3N	25
7	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	PEG-400	Et_3N	trace

[a] Reaction conditions: 4-iodoanisole (1 mmol), phenylacetylene (1.2 mmol), toluene (1 mL), Et_3N (1.4 mmol, 1.4 equiv.), $PdCl_2(CH_3CN)_2$ (1 mol%), T-NHC (**1**) (2 mol%), CO (5 atm), 100 °C, 8 h. [b] Determined by GC analysis of the reaction mixture using biphenyl as an internal standard.

The Pd catalysed carbonylation was carried out using a high-pressure steel autoclave with heating jacket (from WATTCAS, **Figure S15**). For each carbonylation procedure, seven reactions were carried out in a parallel reaction modulor, a spare vial was used to monitor the reaction temperature. The pressure of CO can be adjusted (1-20 atm).

Figure S15. High-pressure steel autoclave and parallel reaction modulor.

S-6.2 Optimization of bases in the titled reaction of 1a and 2a

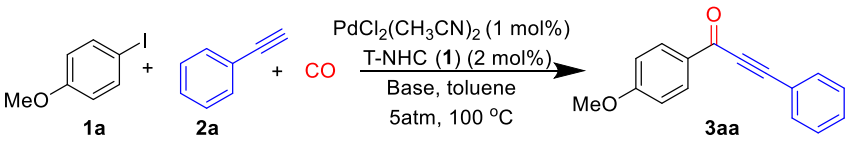


Table S10. Optimization of different bases in the titiled reaction between **1a** and **2a**

Entry	[Pd]	[L]	Solve	Base	Tempreture (°C)	Yield(%)
1	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	Cs_2CO_3	100	47
2	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	CH_3COOCs	100	53
3	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	K_2CO_3	100	43
4	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	Li_2CO_3	100	trace
5	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	KOH	100	41
6	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	DIPEA	100	46
7	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	Et_3N	100	79
8	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	DBU	100	17
9	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	DBN	100	10
10	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	^tBuOK	100	5
11	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	aniline	100	40
12	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	Toluene	benzamide	100	12

[a] Reaction conditions: 4-iodoanisole (1 mmol), phenylacetylene (1.2 mmol), Et_3N (1.4 mmol, 1.4 equiv.), toluene (1 mL), $PdCl_2(CH_3CN)_2$ (1 mol%), T-NHC (**1**) (2 mol%), CO (5 atm), 100 °C, 8 h. [b] Determined by GC analysis of the reaction mixture using biphenyl as an internal standard.

S-6.3 Optimization of palladium sources and ligands in the titled reaction of 1a and 2a

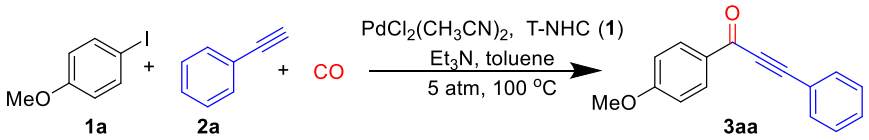


Table S11. Optimization of palladium to ligand ratio in the titled reaction between **1a** and **2a**

Entry	$PdCl_2(CH_3CN)_2$ (mol%)	T-NHC (**1**) (mol%)	Yield (%)
1	2	2	52
2	2	4	68
3	4	2	52
4	6	2	60
5	2	6	55
6	0.5	1	53
7	1	2	79
8	3	6	67
9	/	2	trace
10	1	/	58

[a] Reaction conditions: **1a** 4-iodoanisole (1 mmol), **2a** phenylacetylene (1.2 mmol), toluene (1 mL), Et_3N (1.4 mmol, 1.4 equiv.), $PdCl_2(CH_3CN)_2$ (0.5-6 mol%), T-NHC (**1**) (1-6 mol%), CO (5 atm), 100 °C, 8 h. [b] Conversion and yield were determined by GC-MS using 1,1'-biphenyl as internal standard.

S-6.4 Optimization of palladium sources and ligands in the titled reaction of 1a and 2a

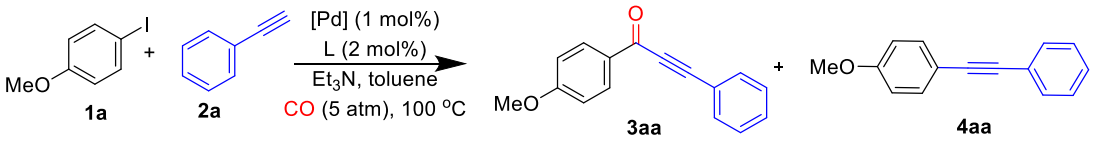


Table S12. Optimization of Pd sources and ligands in the titled reaction between **1a** and **2a**

Entry	[Pd]	L	Yield (%)	
			3aa	**4aa**
1	$PdCl_2(CH_3CN)_2$	T-NHC (**1**)	79	1
2	$Pd(OAc)_2$	T-NHC (**1**)	71	1
3	$Pd_2(DBA)_3$	T-NHC (**1**)	86	6
4	$Pd(PPh_3)_4$	T-NHC (**1**)	30	3
5	$PdCl_2(PPh_3)_2$	T-NHC (**1**)	24	13
6	$PdCl_2$(dppf)	T-NHC (**1**)	75	<1
7	$PdCl_2$	T-NHC (**1**)	93	<1
8	$PdCl_2$	PPh_3	52	18
9	$PdCl_2$	Xantphos	77	5
10	$PdCl_2$	dppf	75	7
11	$PdCl_2$	dppp	65	1
12	$PdCl_2$	IPr·HCl	86	5
13	$PdCl_2$	T-NHC (**2**)	92	<1
14	$PdCl_2$	T-NHC (**3**)	94	<1
15	$PdCl_2$	T-NHC (**4**)	95	<1

[a] Reaction conditions: **1a** 4-iodoanisole (1 mmol), **2a** phenylacetylene (1.2 mmol), toluene (1 mL), Et_3N (1.4 mmol, 1.4 equiv.) [Pd] (1 mol%), L (2 mol%), CO (5 atm), 100 °C, 8 h. [b] Conversion and yield were determined by GC-MS using 1,1'-biphenyl as internal standard.

In the $Pd(CH_3CN)_2Cl_2$ / T-NHC (**1**) catalytic system, toluene and Et_3N were screened as the optimized solvent and base, respectively, giving a yield of 79% for 1,3-ynone (**Table S12**, entry 1). Moreover, other palladium sources, including $Pd(OAc)_2$, $Pd_2(DBA)_3$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf) and $PdCl_2$, can also promote the reaction in such catalytic system, but it is more inclined to have no carbonylation product 4aa (**Table S12**, entries 2-7). And the results showed that the highest yield of **3aa** (93%) was obtained with good regioselectivity when $PdCl_2$ was used as the Pd source. We then turned our attention to investigate the effect of various ligands with $PdCl_2$ as the Pd precursor (entries 8-15). It was obvious that when P-containing ligands PPh_3, Xantphos, dppf, dppp were added in the catalytic system, only 52% 77%, 75% and 65% yields of **3aa** were obtained, respectively (**Table S12**, entries 8-11). Comparingly, the N-containing ligands IPr·HCl, T-NHC (**2**), T-NHC (**3**) and T-NHC (**4**) were

added in the catalytic system, which gave yields of 86%, 92%, 94% and 95%, respectively (**Table S12**, entries 12-15).

The stock solutions prepared by the step-wise diluting Pd precatalyst with toluene. For instance, T-NHC-Pd (**5**) (4.7mg, 0.01mmol) was dissolved in 100 mL of toluene solution, and 100 ppm of T-NHC-Pd (**5**) in toluene was prepared. Then, 1 ml of 100ppm T-NHC-Pd (**5**) solution was diluted with 9 mL toluene, and 10 ppm T-NHC-Pd (**5**) solution was prepared. In the reaction, 1mL of 10 ppm stock solution was added to the mixture of 1mmol of aryl iodides, 1.2 mmol of alkynes and 1.4 mmol of triethylamine in reaction vials. No special precautions for the preparation of the catalyst stock solutions were not taken, and the catalysts were handled in air. In order to avoid the contamination of residue Pd in each experiment, the following general procedure was used: A test glass tube and a stirrer bar coated with PTFE were treated with aqua regia (1:3 concd aq HCl–concd aq HNO_3) for 30 min and then washed sequentially with pure water and acetone, and dried with heating.

S-6.5 Optimization of Pd sources in the titled reaction of 1a and 2a

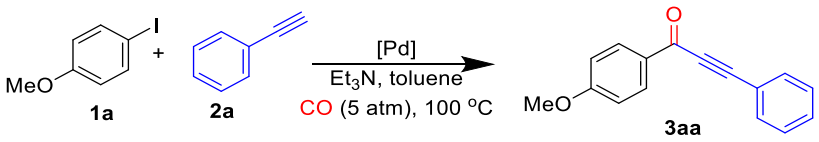


Table S13. Optimization of the amount of Pd sources in the titled reaction of **1a** and **2a**

Entry	Catalyst	Pd (mol%)	Yield (%)	TON	TOF(h^{-1})
1	T-NHC-Pd (**5**)	1	97	/	/
2	T-NHC-Pd (**5**)	0.1	97	/	/
3	T-NHC-Pd (**5**)	0.01	95	$9.5*10^3$	1188
4	T-NHC-Pd (**5**)	0.001	83	$7.0*10^4$	10375
5	T-NHC-Pd (**6**)	1	90	/	/
6	T-NHC-Pd (**6**)	0.1	89	/	/
7	T-NHC-Pd (**6**)	0.01	86	$8.9*10^3$	1113
8	T-NHC-Pd (**6**)	0.001	86	$8.6*10^4$	10750
9	T-NHC-Pd (**7**)	1	97	/	/
10	T-NHC-Pd (**7**)	0.1	96	/	/
11	T-NHC-Pd (**7**)	0.01	96	$9.6*10^3$	1200
12	T-NHC-Pd (**7**)	0.001	90	$9.0*10^4$	11250
13	T-NHC-Pd (**8**)	1	98	/	/
14	T-NHC-Pd (**8**)	0.1	96	/	/
15	T-NHC-Pd (**8**)	0.01	95	$9.5*10^3$	1188
16	T-NHC-Pd (**8**)	0.001	95	$9.5*10^4$	11875
17	T-NHC-Pd (**8**)	0.0001	60	$6.0*10^{-5}$	75000
18	T-NHC-Pd (**9**)	1	98	/	/
19	T-NHC-Pd (**9**)	0.1	96	/	/
20	T-NHC-Pd (**9**)	0.01	96	$9.6*10^3$	1200
21	T-NHC-Pd (**9**)	0.001	85	$8.5*10^4$	10625
22	T-NHC-Pd (**10**)	1	96	/	/
23	T-NHC-Pd (**10**)	0.1	96	/	/
24	T-NHC-Pd (**10**)	0.01	96	$9.6*10^3$	1200
25	T-NHC-Pd (**10**)	0.001	89	$8.9*10^4$	11125
26	T-NHC-Pd (**11**)	1	80	/	/
27	T-NHC-Pd (**11**)	0.001	70	$7.0*10^4$	8750
28	T-NHC-Pd (**12**)	1	78	/	/
29	T-NHC-Pd (**12**)	0.001	65	$6.5*10^4$	8125
30	$PdCl_2$+T-NHC (**4**)	0.001	35	$3.5*10^4$	4375
31	NHC-Pd	0.001	65	$6.5*10^4$	8125

[a] Reaction conditions: 4-iodoanisole (1 mmol), phenylacetylene (1.2 mmol), toluene (1 mL), [Pd] T-NHC-Pd (**5**-**12**) (1-0.001 mol%), $PdCl_2$, NHC-Pd (0.001 mol%), T-NHC (**4**) (0.002 mol%), CO (5 atm), 100 °C, 8 h. [b] Determined by GC analysis of the reaction mixture using biphenyl as an internal standard.

S-6.6 Optimization of the reaction time in combination with the catalyst loading in the titled reaction of 1a and 2a

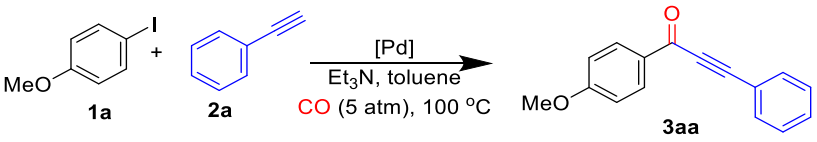


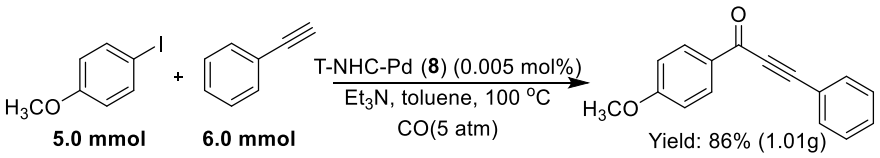
Table S14. Optimization of the reaction time in combination with the catalyst loading in the titled reaction of **1a** and **2a**

Entry	Catalyst	Pd (mol%)	Time (h)	Yield (%)
1	T-NHC-Pd (**8**)	1	4	80
2	T-NHC-Pd (**8**)	1	6	96
3	T-NHC-Pd (**8**)	1	8	98
4	T-NHC-Pd (**8**)	0.1	4	80
5	T-NHC-Pd (**8**)	0.1	6	92
6	T-NHC-Pd (**8**)	0.1	8	98
7	T-NHC-Pd (**8**)	0.01	4	75
8	T-NHC-Pd (**8**)	0.01	6	90
9	T-NHC-Pd (**8**)	0.01	8	95
10	T-NHC-Pd (**8**)	0.001	4	68
11	T-NHC-Pd (**8**)	0.001	6	85
12	T-NHC-Pd (**8**)	0.001	8	95
13	T-NHC-Pd (**8**)	0.001	10	95
14	T-NHC-Pd (**8**)	0.001	12	96
15	T-NHC-Pd (**8**)	0.0001	8	60
16	T-NHC-Pd (**8**)	0.0001	12	60
17	T-NHC-Pd (**8**)	0.0001	16	62

[a] Reaction conditions: 4-iodoanisole (1 mmol), phenylacetylene (1.2 mmol), toluene (1 mL), T-NHC-Pd (**8**) (1-0.0001 mol%), CO (5 atm), 100 °C, 4-16 h. [b] Determined by GC analysis of the reaction mixture using biphenyl as an internal standard.

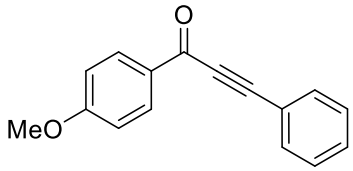
S-6.7 The scale-up reaction of 1a and 2a

The large-scale reaction was performed using 5.0 mmol of starting materials, affording 1.01g of 1-(4-methoxy)-3-ynone with 86% yield. The gram-scale experimental procedure was as follows: In 25 mL reaction tube, 4-iodoanisole (5.0 mmol), phenylacetylene (6.0 mmol) and Et_3N (7.0 mmol) were added. Then, 5 mL stock solution containing 10 ppm T-NHC-Pd (**8**) was added. The reaction tube was loaded in autoclave. After being charged, released and refilled CO (5 atm) for three times, the reaction was stirred at 100 °C for 12 hours. The reaction was cool down to room temperature. The solvents were evaporated completely. The residue was separated by flash chromatography with dichloromethane and petroleum ether (v/v = 1/2) as elute. A yellow solid 3aa 1.01 g (yield: 86%) was collected.

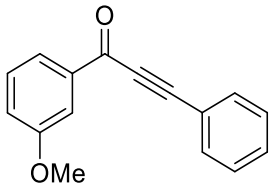


Scheme S3. The scale-up reaction.

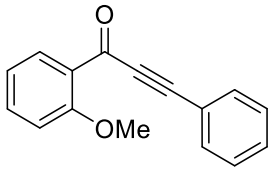
S-7 NMR-Data of 1,3-ynone products



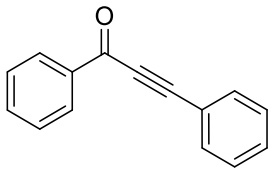
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (3aa).[1] (Yellow solid was obtained in 95% isolated yield, 224 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.71 - 7.64 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 164.5, 132.9, 132.0, 130.6, 130.3, 128.6, 120.4, 113.9, 92.3, 86.9, 55.6.



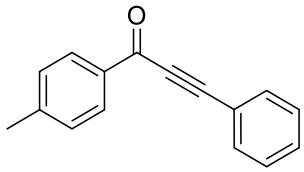
1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-one (3ba).[1] (Yellow solid was obtained in 81% isolated yield, 191 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.81 - 7.74 (m, 3H), 7.59 - 7.55 (m, 1H), 7.51 (q, *J* = 7.3 Hz, 3H), 7.29 - 7.24 (m, 1H), 3.96 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 159.8, 138.2, 133.1, 130.8, 129.7, 128.7, 122.8, 120.9, 120.1, 112.8, 93.0, 87.0, 55.5.



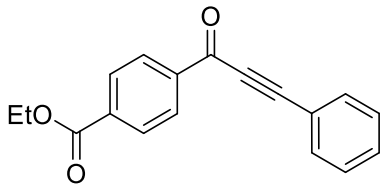
1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one(3ca).[1] (Yellow solid was obtained in 86% isolated yield, 203 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.65 - 7.60 (m, 2H), 7.56 - 7.51 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 159.8, 135.1, 133.0, 132.6, 130.5, 128.6, 126.8, 120.7, 120.3, 112.3, 91.6, 89.3, 56.0.



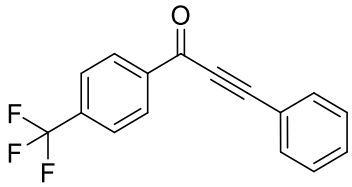
1,3-diphenylprop-2-yn-1-one(3da).[2] (Yellow solid was obtained in 90% isolated yield, 185 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.51 (dt, *J* = 21.1, 7.5 Hz, 3H), 7.43 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 137.0, 134.2, 133.2, 130.9, 129.7, 128.8, 128.7, 120.2, 100.1, 93.2, 87.0.



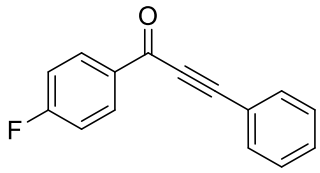
3-phenyl-1-(*p*-tolyl)prop-2-yn-1-one(3ea).[2] (Yellow solid was obtained in 91% isolated yield, 200 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 - 8.09 (m, 2H), 7.71 - 7.65 (m, 2H), 7.51 - 7.45 (m, 1H), 7.42 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.32 (s, 2H), 2.44 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 144.2, 133.5, 132.0, 129.6, 128.6, 128.3, 127.6, 119.2, 91.5, 85.9, 20.8.



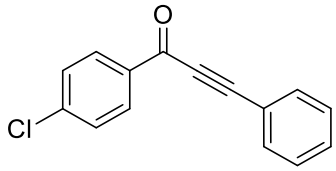
ethyl 4-(3-phenylpropioloyl)benzoate (3fa).[3] (Yellow solid was obtained in 80% isolated yield, 223 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.73 - 7.67 (m, 2H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 165.7， 139.9 , 135.1, 133.3, 131.2, 129.9, 129.5, 128.8, 119.9, 94.2, 86.9, 61.6, 14.4.



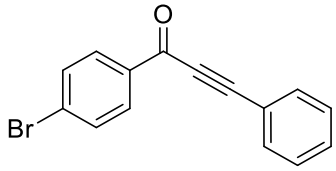
3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (3ga).[4] (Yellow solid was obtained in 48% isolated yield, 132 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.73 - 7.67 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 139.4, 135.3(q, ^{2} *J* = 33.2 Hz), 133.2, 131.2, 129.8, 128.8, 125.7(q, ^{3} *J* = 4.53 Hz), 124.4(q, ^{1} *J* = 271.8 Hz), 119.6, 94.5, 86.6.



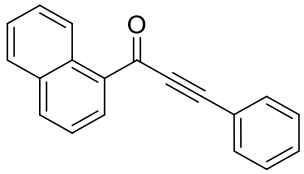
1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one (3ha).[4] (Yellow solid was obtained in 79% isolated yield, 177.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 - 8.22 (m, 2H), 7.72 - 7.65 (m, 2H), 7.50 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.22 - 7.16 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 167.3(d, ^{1} *J* = 256.7 Hz), 133.4(d, ^{4} *J* = 1.51 Hz), 133.0, 132.2(d, ^{3} *J* = 10.6 Hz),130.9, 128.7, 120.0, 115.9 (d, ^{2} *J* = 21.1 Hz), 93.3, 86.6.



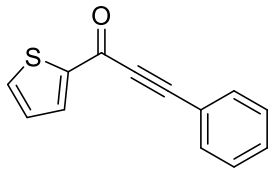
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (3ia).[4] (Yellow solid was obtained in 78% isolated yield, 187 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 - 8.12 (m, 2H), 7.72 - 7.65 (m, 2H), 7.49 (d, *J* = 8.5 Hz, 3H), 7.43 (t, *J* = 7.6 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 140.7, 135.3, 133.13, 131.0, 130.9, 129.0, 128.7, 119.9, 93.6, 86.6.



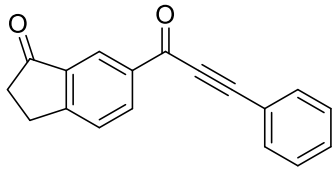
1-(4-bromophenyl)-3-phenylprop-2-yn-1-one (3ja).[4] (White solid was obtained in 74% isolated yield, 187 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 - 8.05 (m, 2H), 7.71 - 7.64 (m, 4H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 135.7, 133.1, 132.0, 131.0, 130.9, 129.5, 128.7, 119.9, 99.9, 93.7, 86.5.



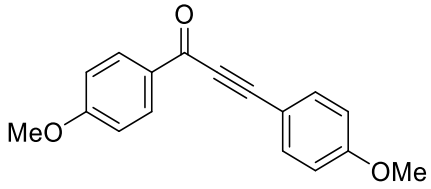
1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one (3ka).[2] (Yellow solid was obtained in 94% isolated yield, 241 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.26 (d, *J* = 8.7 Hz, 1H), 8.66 (dd, *J* = 7.2, 1.1 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.69 (td, *J* = 8.6, 7.8, 3.5 Hz, 3H), 7.64 - 7.55 (m, 2H), 7.52 - 7.46 (m, 1H), 7.43 (t, *J* = 7.4 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 135.2, 134.6, 133.9, 133.0, 130.8, 130.7, 129.0, 128.7, 128.6, 126.8, 126.1, 124.5, 120.4, 91.8, 88.6.



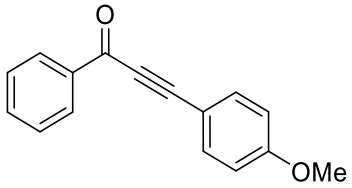
3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (3la).[2] (Yellow solid was obtained in 74% isolated yield, 157 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.73 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.69 - 7.63 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.19 (dd, *J* = 4.7, 4.0 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 144.9, 135.2, 135.1, 133.0, 130.8, 128.7, 128.3, 119.9, 91.7, 86.5.



6-(3-phenylpropioloyl)-2,3-dihydro-1H-inden-1-one (3ma). (Yellow solid was obtained in 60% isolated yield, 156 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.6 Hz, 1H), 8.39 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.74 - 7.67 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 - 7.47 (m, 1H), 7.46 - 7.40 (m, 2H), 3.28 - 3.19 (m, 2H), 2.82 - 2.74 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.7, 177.0, 160.8, 137.6, 136.6, 134.4, 133.3, 131.1, 128.8, 127.2, 126.0, 119.9, 94.0, 86.7, 36.6, 26.3. HRMS(ESI) m/z：$[M+Na]^+$ calcd for $C_{18}H_{12}NaO_2$: 283.0735. Found: 283.0736.

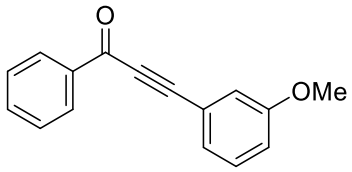


1,3-bis(4-methoxyphenyl)prop-2-yn-1-one (3ab).[5] (Yellow solid was obtained in 99% isolated yield, 263 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.3, 161.5, 134.9, 131.8, 130.4, 114.4, 113.8, 112.1, 93.4, 86.8, 55.5, 55.4.

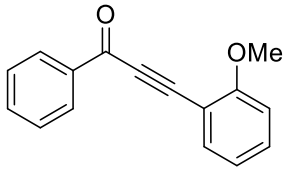


3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (3db).[6] (Yellow solid was obtained in 94% isolated yield, 222 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 - 8.19 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C

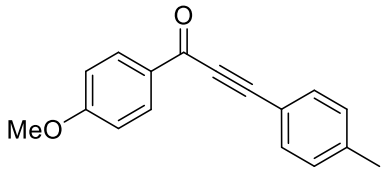
NMR (151 MHz, $CDCl_3$) δ 177.0, 160.7, 136.0, 134.1, 132.8, 128.4, 127.5, 113.4, 110.8, 93.3, 85.8, 54.4.



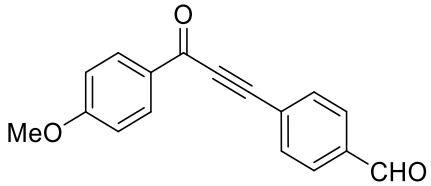
3-(3-methoxyphenyl)-1-phenylprop-2-yn-1-one (3dc).[7] (Yellow solid was obtained in 94% isolated yield, 222 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.3 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.19 (s, 1H), 7.06 - 7.01 (m, 1H), 3.84 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 159.4, 136.8, 134.1, 129.8, 129.6, 128.6, 125.6, 121.0, 117.6, 93.0, 86.6, 55.4.



3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one (3dd).[8] (Yellow solid was obtained in 97% isolated yield, 228 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.3 Hz, 2H), 7.61 (td, *J* = 6.0, 2.9 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.47 - 7.42 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 161.9, 137.1, 135.0, 133.8, 132.6, 129.7, 128.5, 120.7, 110.8, 109.4, 91.2, 90.5, 55.9.

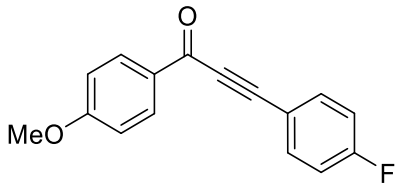


1-(4-methoxyphenyl)-3-(*p*-tolyl)prop-2-yn-1-one (3ae).[9] (Yellow solid was obtained in 94% isolated yield, 235 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.4, 141.3, 133.0, 131.9, 130.4, 129.4, 117.2, 113.8, 92.9, 86.7, 55.6, 21.7.

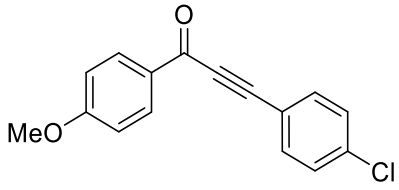


4-(3-(4-methoxyphenyl)-3-oxoprop-1-yn-1-yl)benzaldehyde (3af). Reaction was carried out at 120 ^{o}C. (Yellow solid was obtained in 44% isolated yield, 101 mg). ^{1}H NMR (600 MHz, $CDCl_3$)

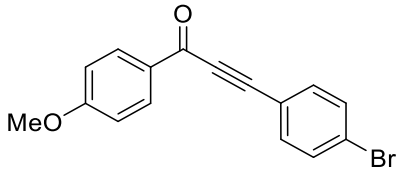
δ 10.05 (s, 1H), 8.17 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.2, 176.2, 164.9, 137.1, 133.4, 132.1, 130.1, 129.7, 126.4, 114.1, 90.1, 89.4, 55.7. HRMS(ESI) m/z：[M+Na]$^+$calcd for $C_{17}H_{12}NaO_3$: 287.0684. Found: 287.0680.



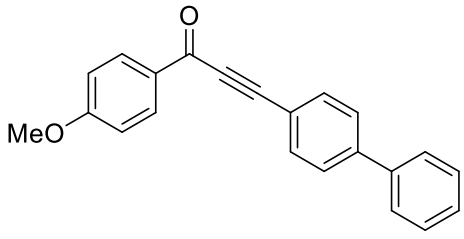
3-(4-fluorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one (3ag).[10] (Yellow solid was obtained in 79% isolated yield, 107 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.71 - 7.63 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 7.01 - 6.94 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 164.5 (d, ^{1} *J* = 253.7 Hz), 135.25 (d, ^{3} *J* = 9.1 Hz), 131.9, 130.2, 116.5 (d, ^{4} *J* = 3.0 Hz), 116.2 (d, ^{2} *J* = 22.7 Hz),113.9, 91.2, 86.8, 55.6.



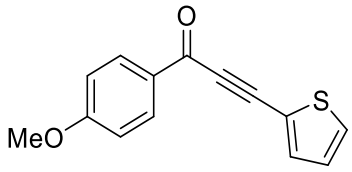
3-(4-chlorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one (3ah).[11] (Yellow solid was obtained in 80% isolated yield, 216 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 9.3, 2.2 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 164.6, 136.9, 134.1, 132.0, 130.1, 129.1, 118.8, 113.9, 90.8, 87.6, 55.6.



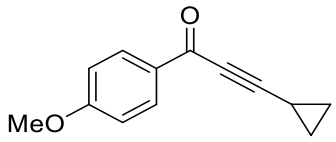
3-(4-bromophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one (3ai).[12] (Yellow solid was obtained in 75% isolated yield, 236 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 - 8.12 (m, 2H), 7.59 - 7.53 (m, 2H), 7.53 - 7.49 (m, 2H), 7.02 - 6.95 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.43, 164.62, 134.2, 132.0, 130.1, 125.3, 119.3, 113.7, 90.8, 87.7, 55.6.



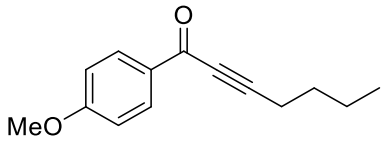
3-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)prop-2-yn-1-one (3aj). (Yellow solid was obtained in 56% isolated yield, 175 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 164.6, 143.5, 139.9, 133.6, 132.1, 130.5, 129.1, 128.2, 127.4, 127.2, 119.2, 114.0, 92.5, 87.7, 55.7. HRMS(ESI) m/z：$[M+H]^+$calcd for $C_{22}H_{17}O_2$: 313.1223. Found: 313.1223.



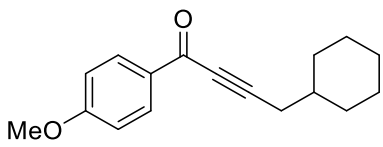
1-(4-methoxyphenyl)-3-(thiophen-2-yl)prop-2-yn-1-one (3ak).[12] Reaction was carried out at 120 °C. (Brown solid was obtained in 75% isolated yield, 181 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.49 (d, *J* = 5.1 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 164.5, 136.4, 131.8, 131.3, 130.1, 127.7, 120.1, 113.9, 91.6, 86.2, 55.6.



3-cyclopropyl-1-(4-methoxyphenyl)prop-2-yn-1-one (3al).[13] (Yellow liquid was obtained in 75% isolated yield, 150 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (t, *J* = 8.8 Hz, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 4.05 - 3.57 (m, 3H), 1.04 - 0.86 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 164.2, 131.7, 130.3, 113.7, 100.0, 75.4, 55.5, 9.8.



1-(4-methoxyphenyl)hept-2-yn-1-one (3am).[7] (Yellow liquid was obtained in 75% isolated yield, 107 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 - 8.02 (m, 2H), 6.97 - 6.87 (m, 2H), 3.85 (t, *J* = 2.1 Hz, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.68 - 1.57 (m, 2H), 1.47 (q, *J* = 7.5 Hz, 2H), 1.01 - 0.86 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 164.2, 131.8, 130.3, 113.7, 95.9, 79.6, 55.5, 29.9, 22.0, 18.8, 13.5.

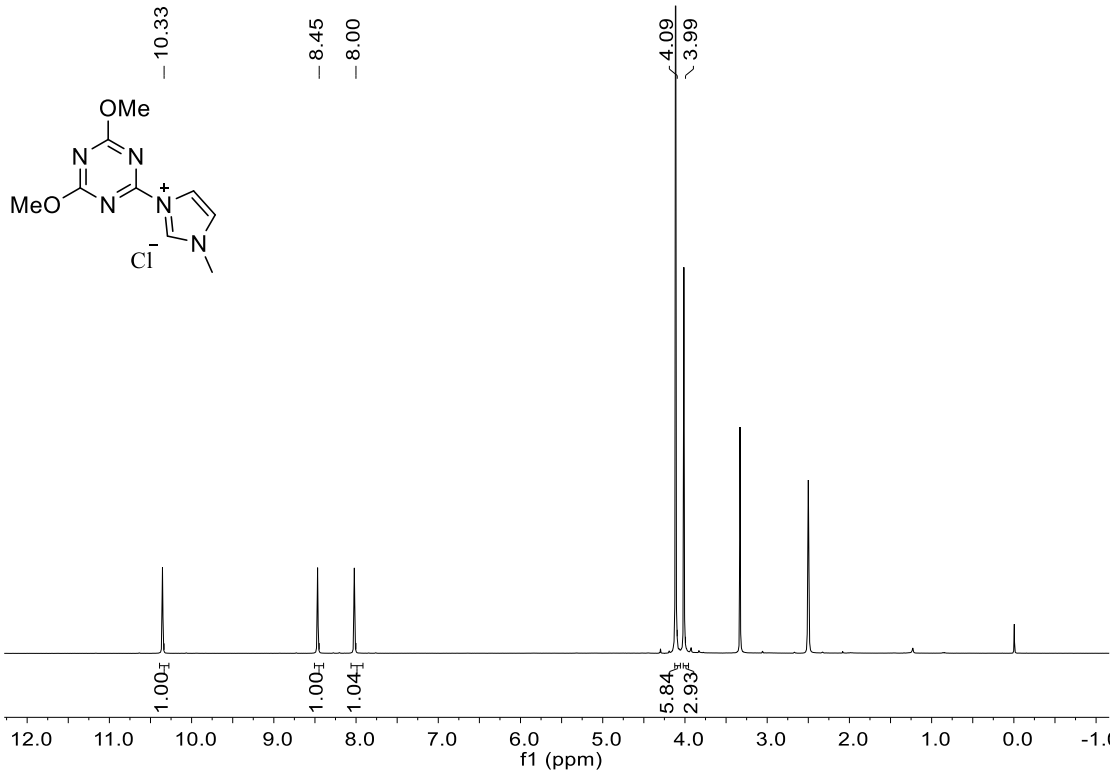


4-cyclohexyl-1-(4-methoxyphenyl)but-2-yn-1-one (3an). (Yellow liquid was obtained in 76% isolated yield, 190 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.37 (d, *J* = 6.7 Hz, 2H), 1.91 - 1.82 (m, 2H), 1.74 (m, 2H), 1.69 - 1.59 (m, 2H), 1.32 - 1.22 (m, 2H), 1.21 - 1.13 (m, 1H), 1.11 - 1.03 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.0, 164.3, 131.9, 130.4, 113.8, 95.0, 80.6, 55.6, 37.0, 32.9, 27.0, 26.1, 26.1. HRMS(ESI) m/z：$[M+H]^+$calcd for $C_{17}H_{21}O_2$: 257.1536. Found: 257.1541.

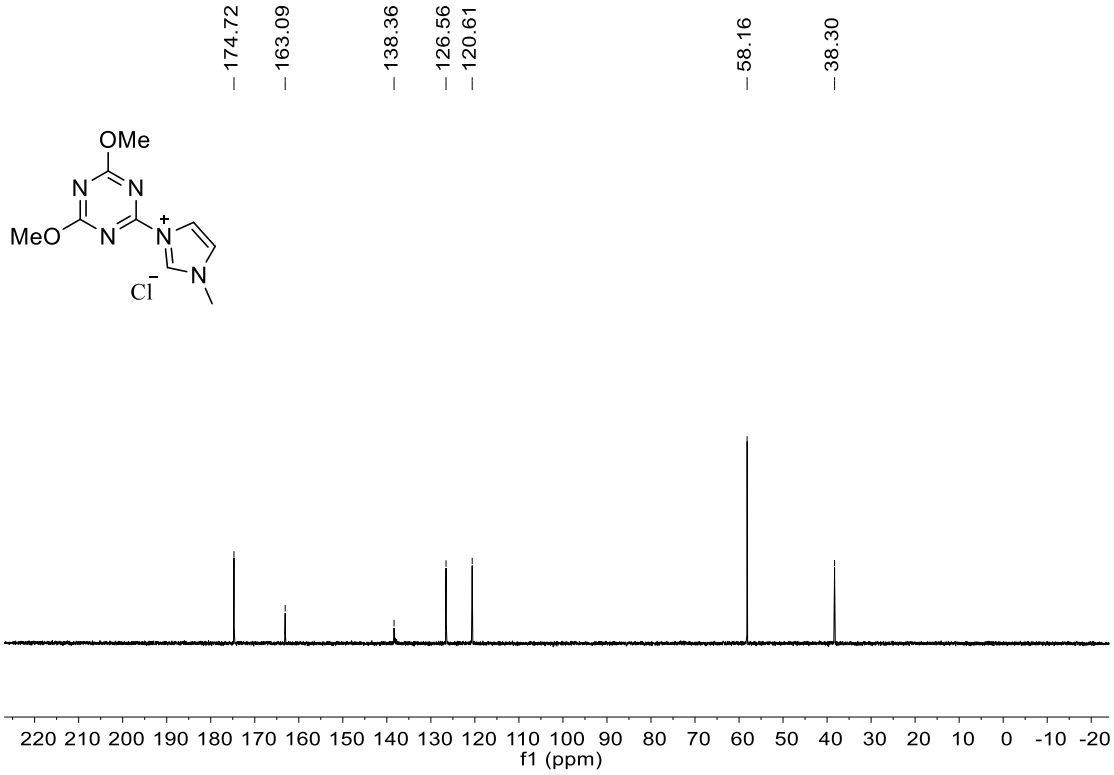
S-8 NMR spectrum of products

S-8-1 NMR Spectrum of T-NHCs and T-NHC-Pds

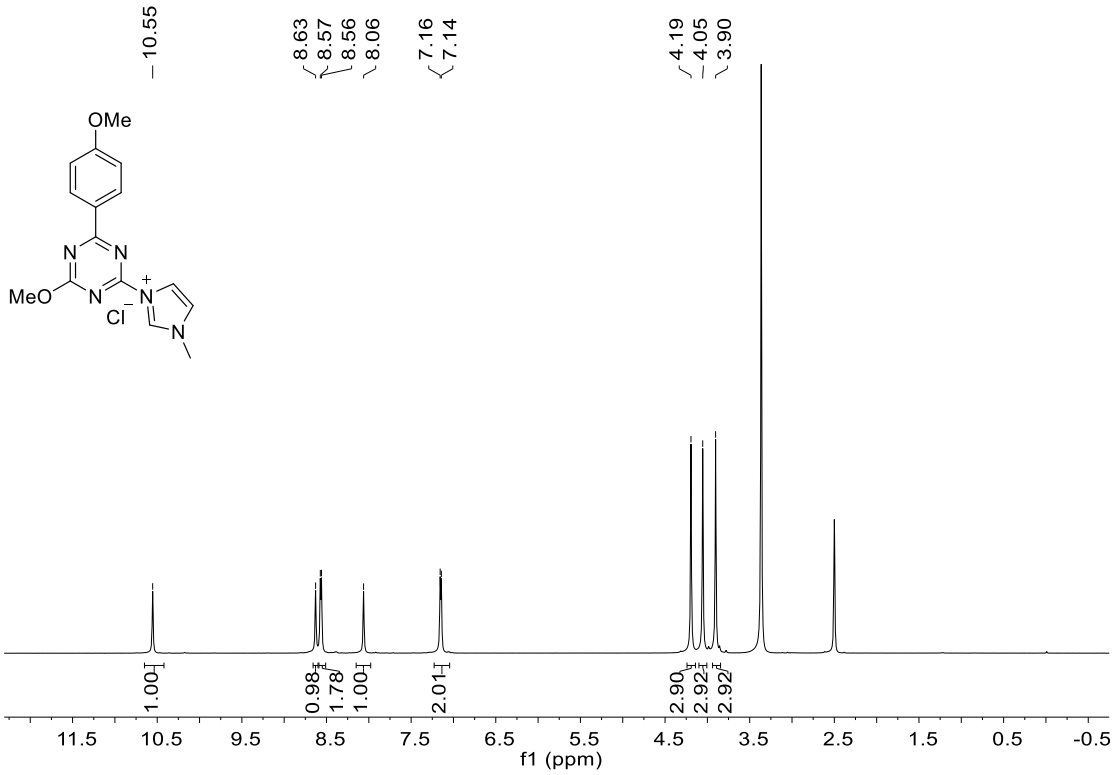
^{1}H NMR of compound T-NHC (**1**)



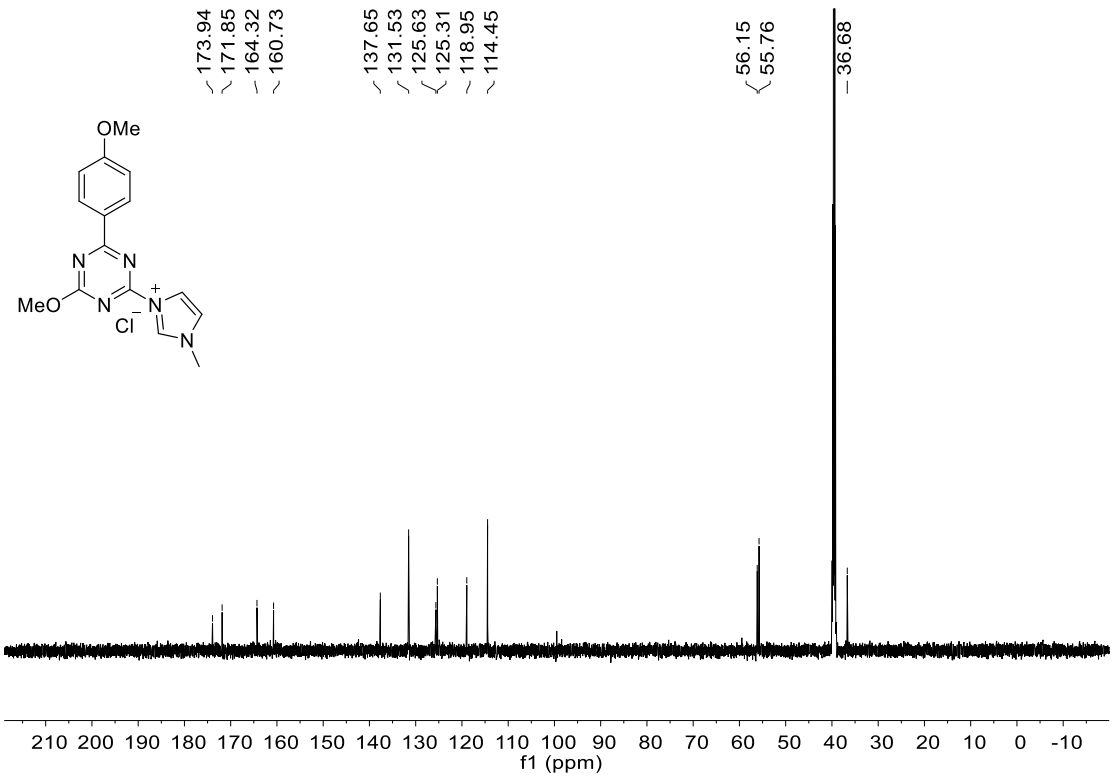
^{13}C NMR of compound T-NHC (**1**)



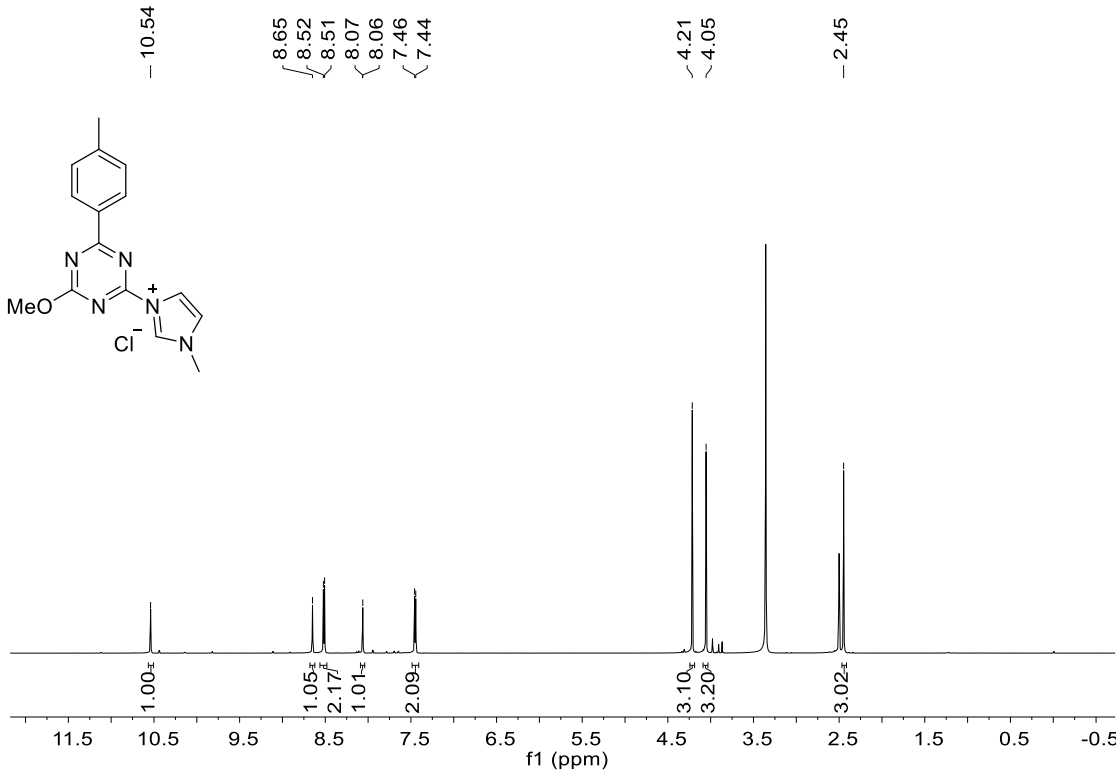
^{1}H NMR of compound T-NHC (**2**)



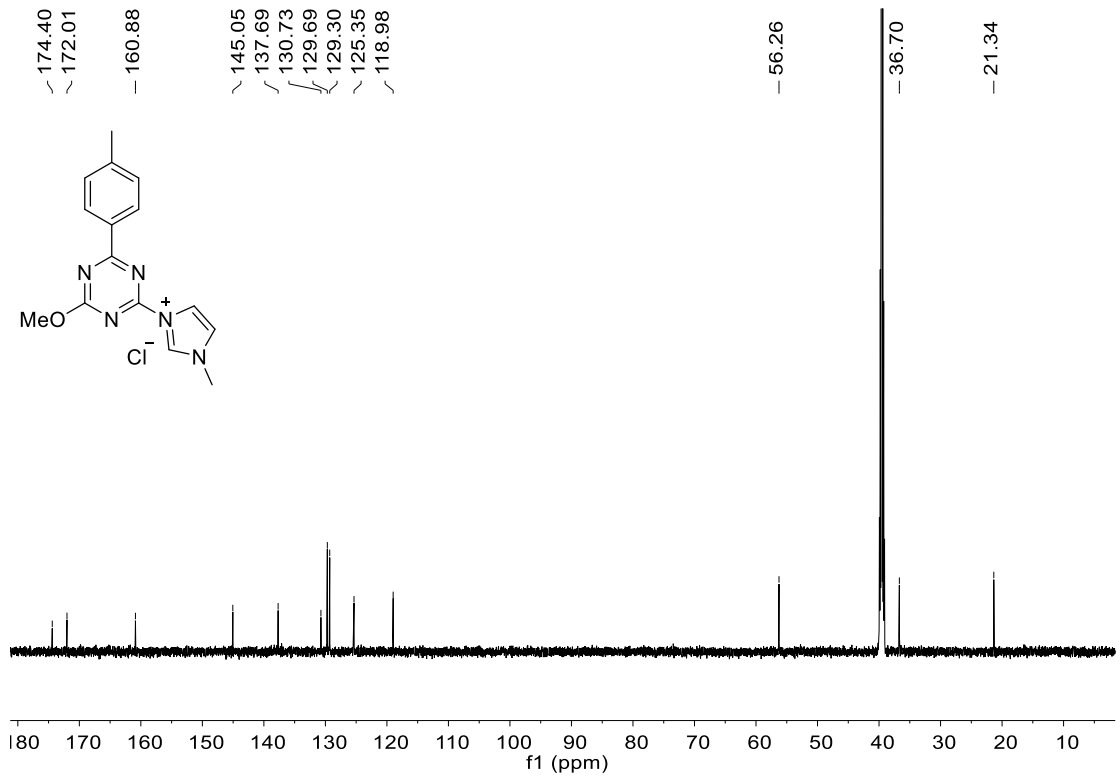
^{13}C NMR of compound T-NHC (**2**)



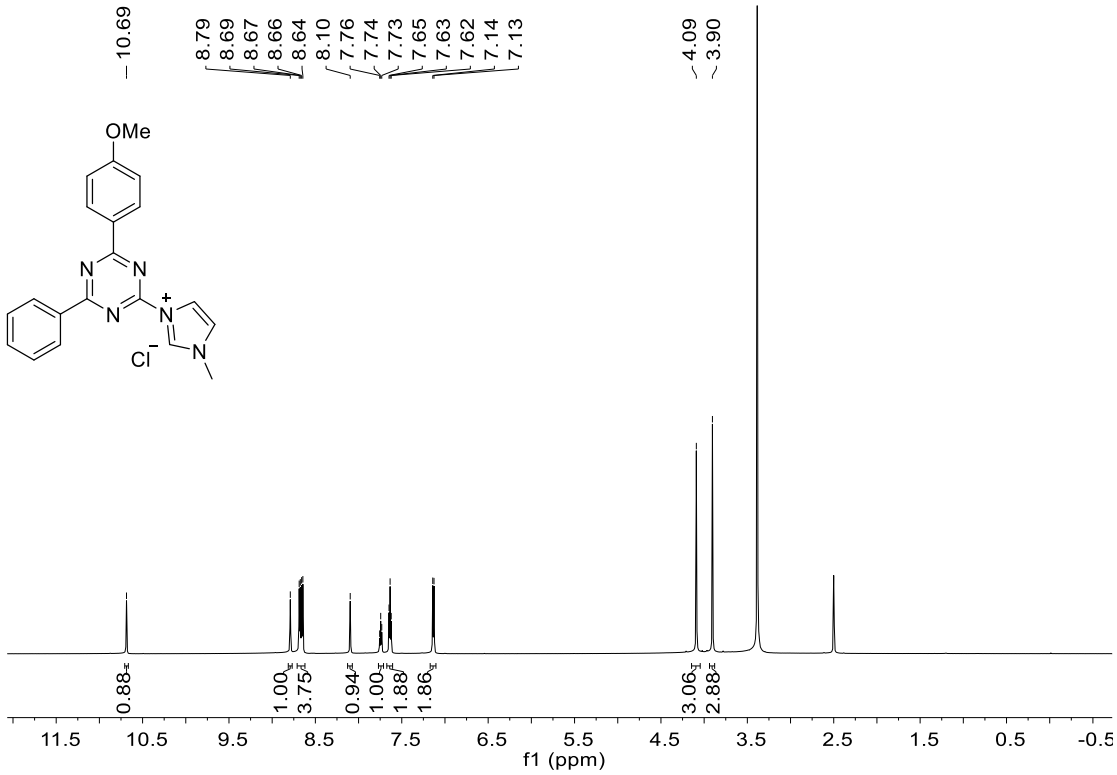
^{1}H NMR of compound T-NHC (**3**)



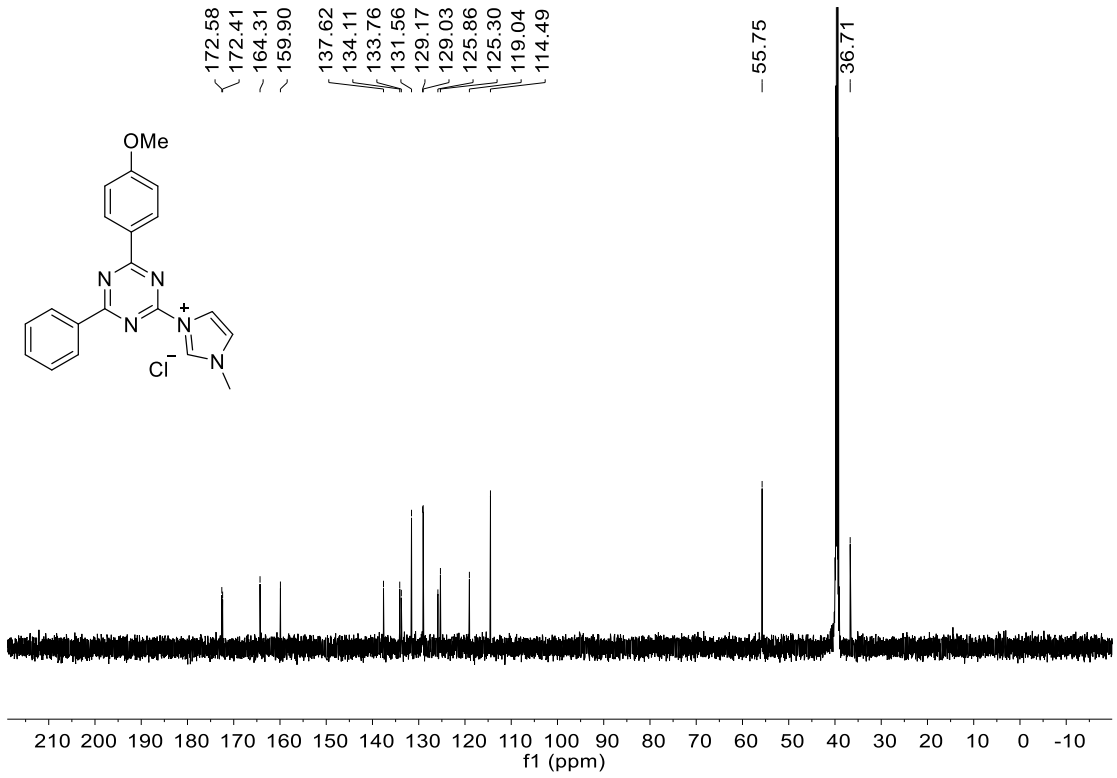
^{13}C NMR of compound T-NHC (**3**)



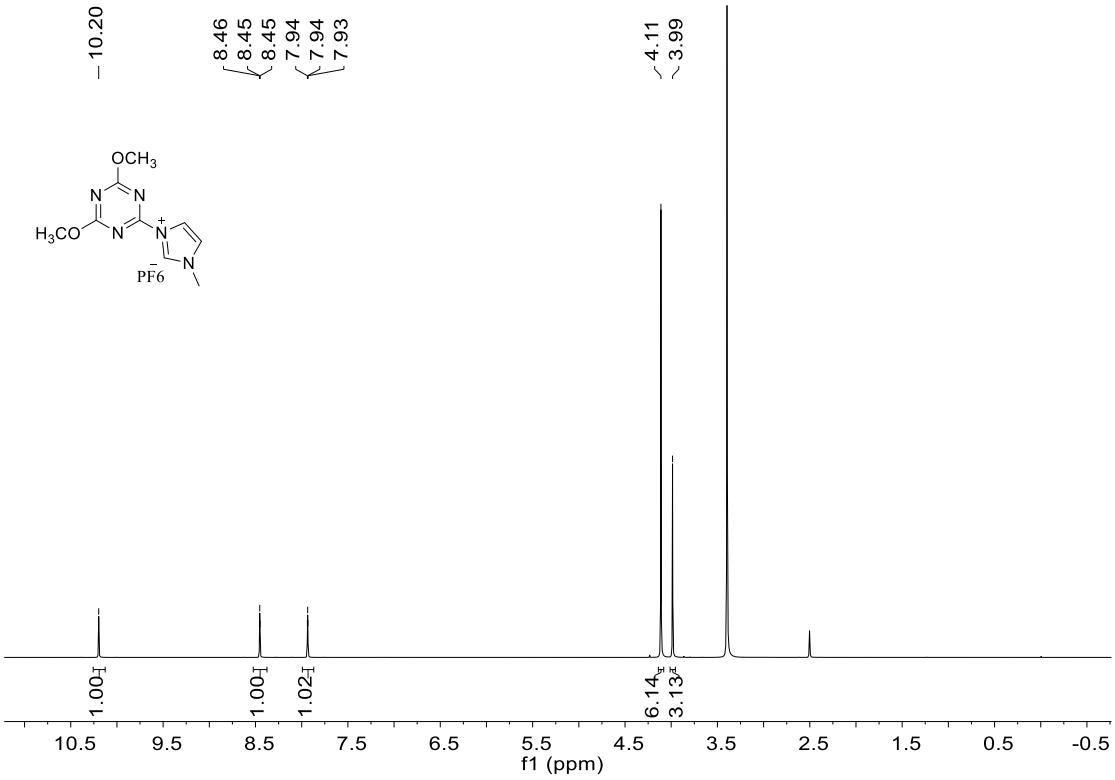
^{1}H NMR of compound T-NHC (**4**)



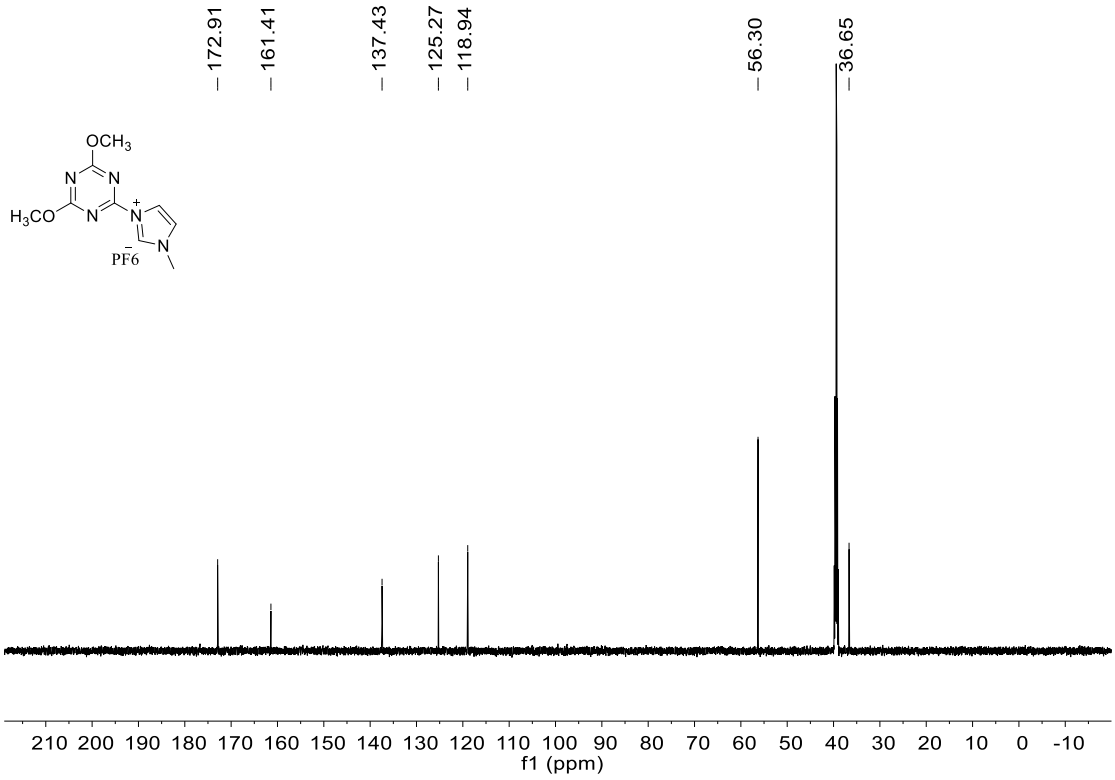
^{13}C NMR of compound T-NHC (**4**)



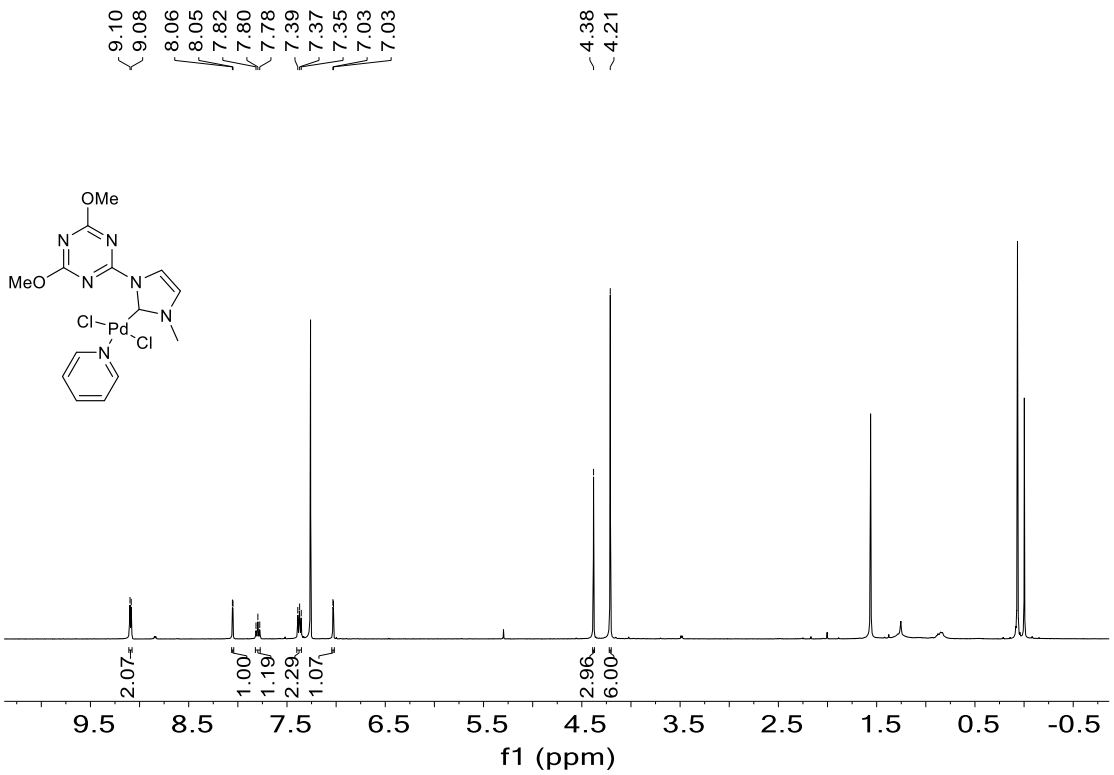
^{1}H NMR of compound T-NHC (**1'**)



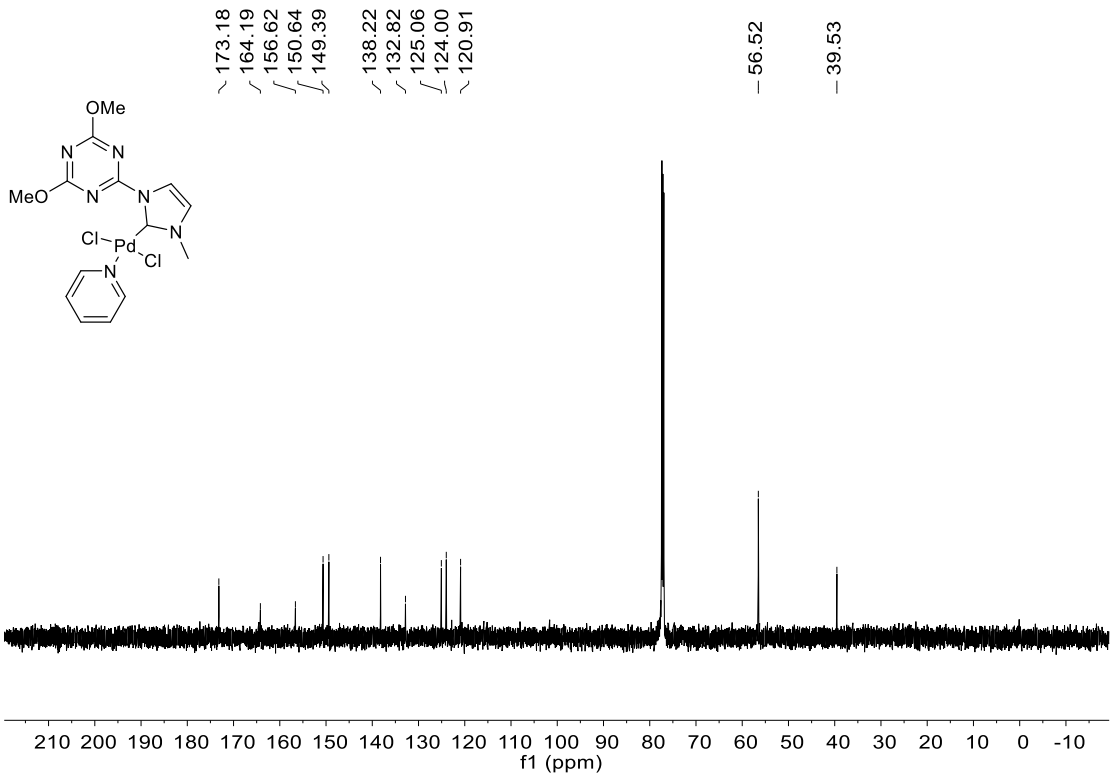
^{13}C NMR of compound T-NHC (**1'**)



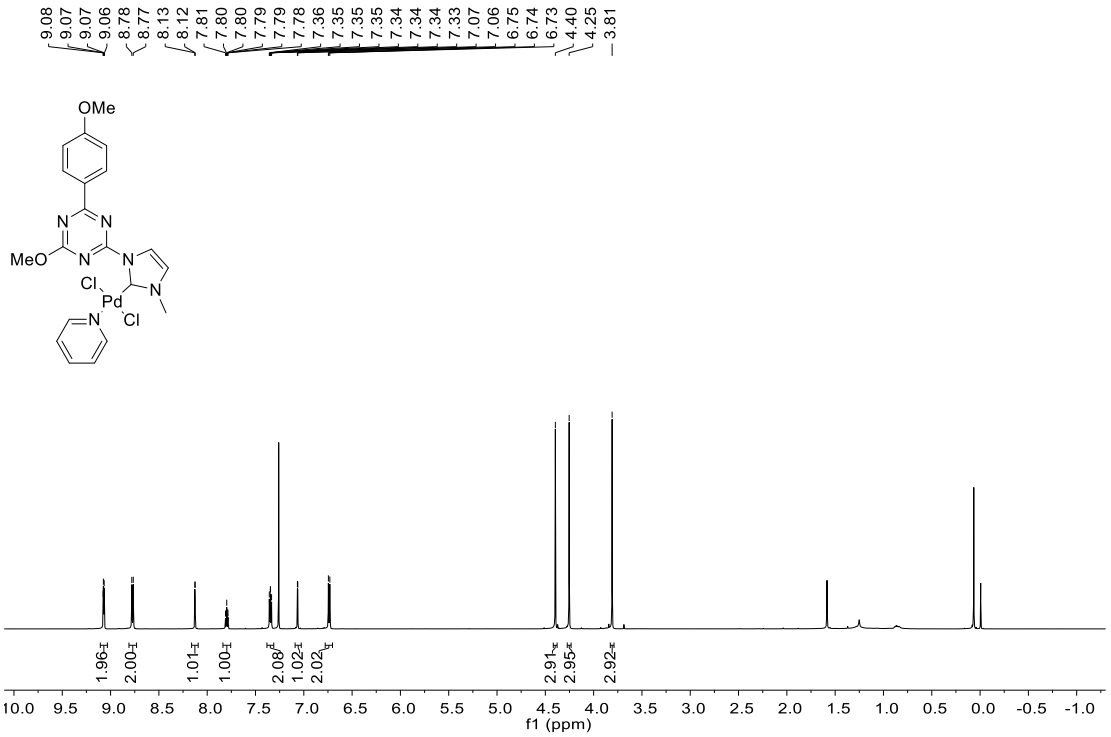
^{1}H NMR of complex T-NHC-Pd (**5**)



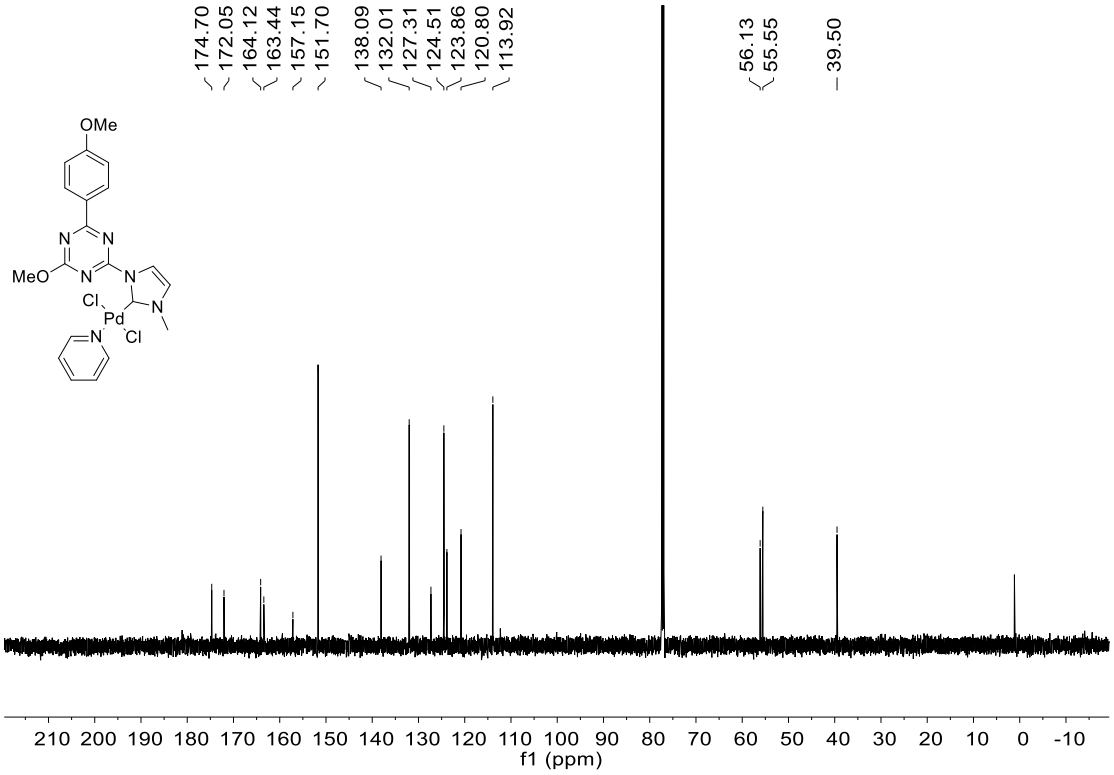
^{13}C NMR of complex T-NHC-Pd (**5**)



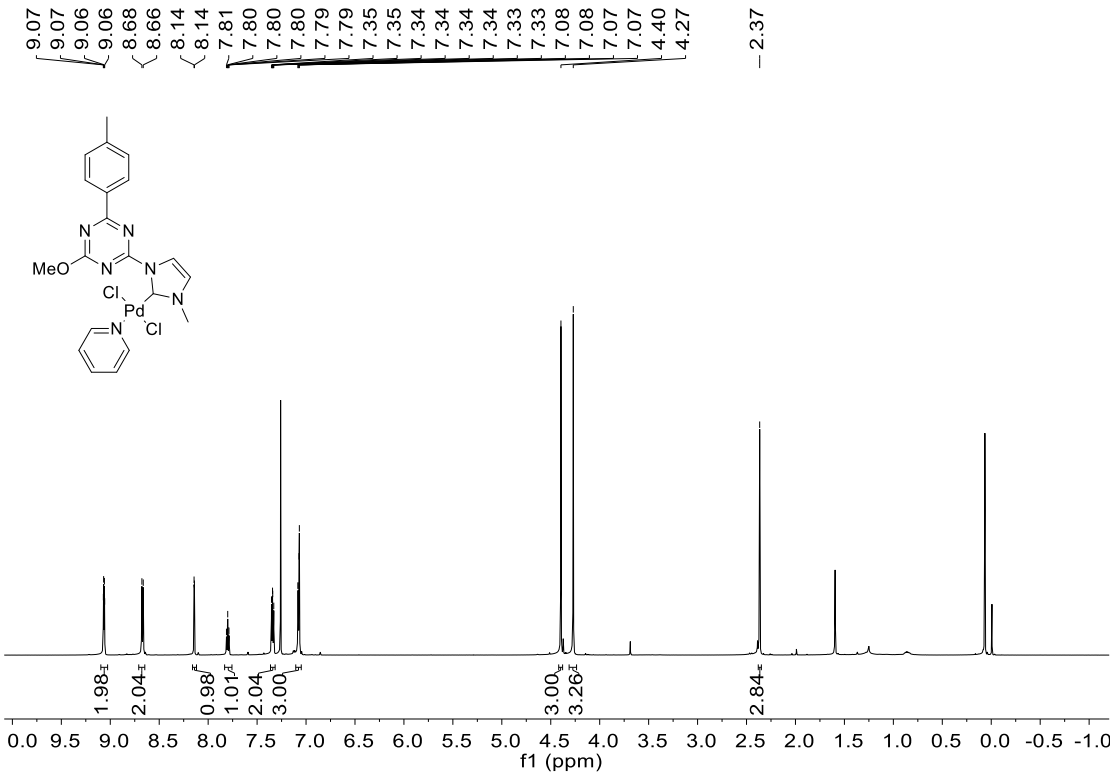
^{1}H NMR of complex T-NHC-Pd (**6**)



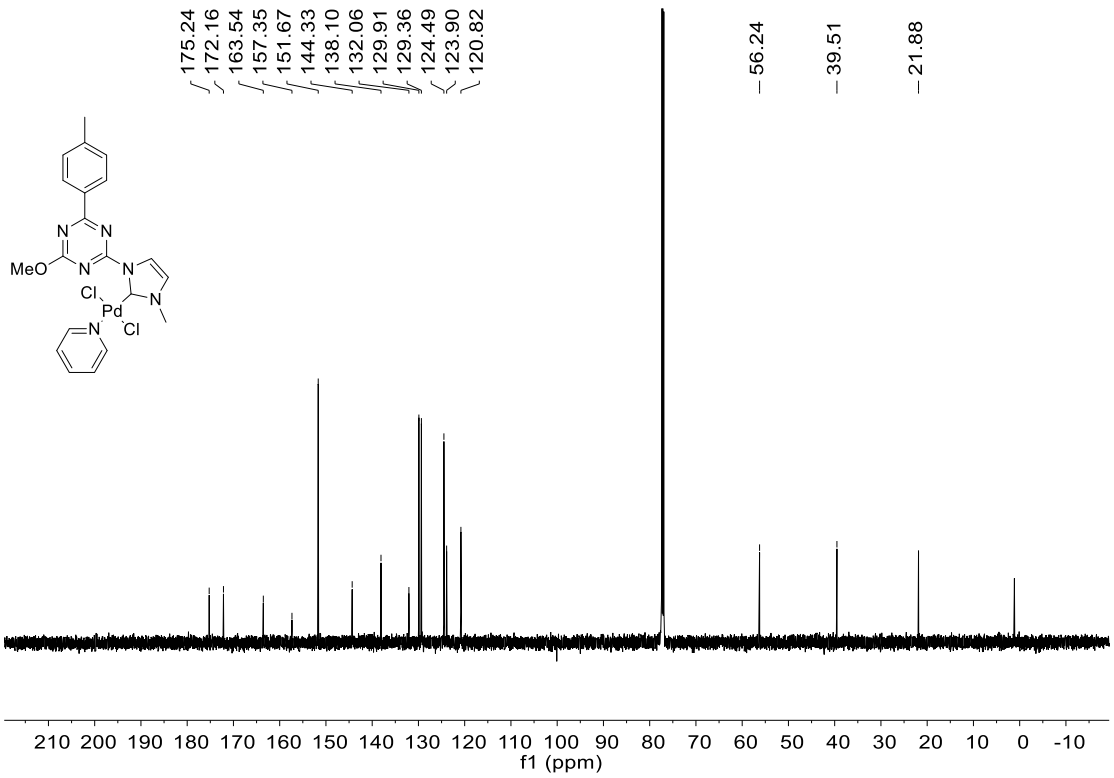
^{13}C NMR of complex T-NHC-Pd (**6**)



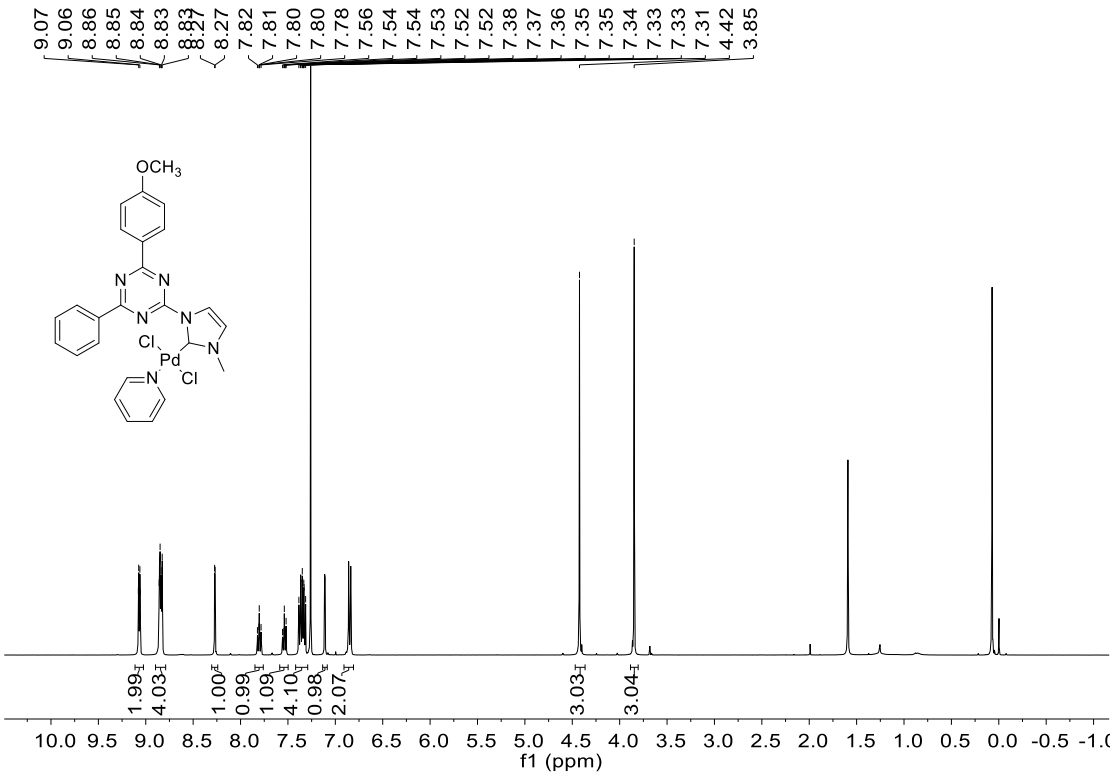
^{1}H NMR of complex T-NHC-Pd (**7**)



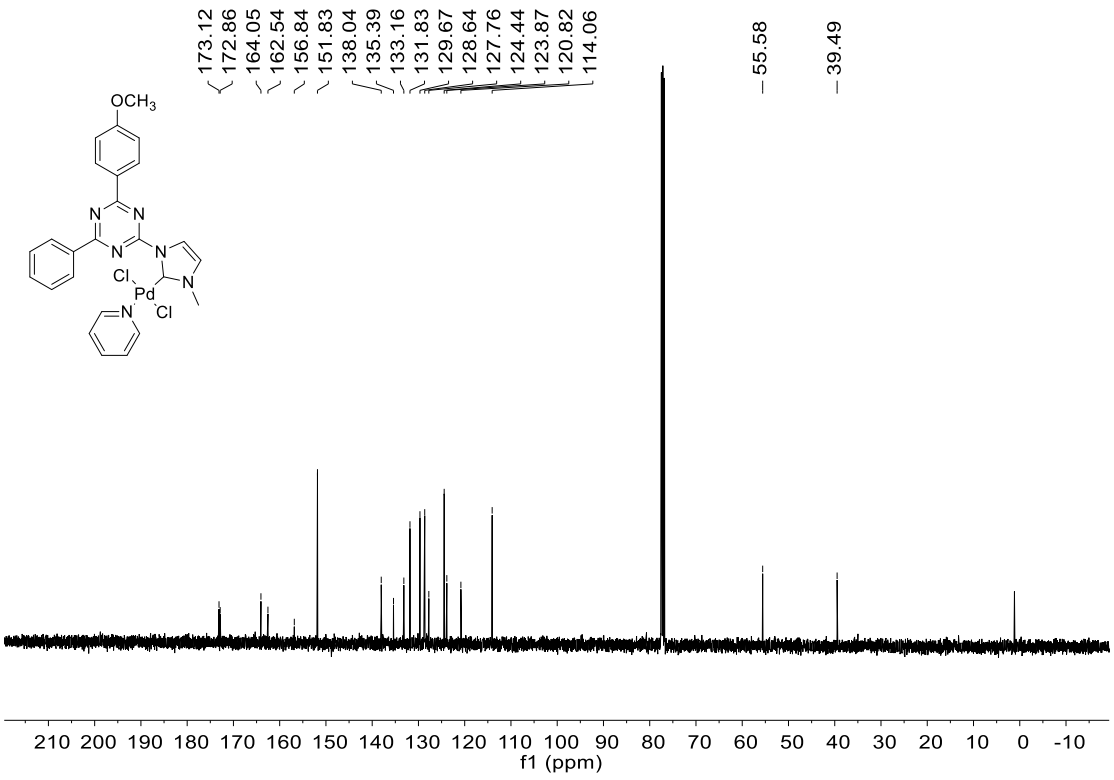
^{13}C NMR of complex T-NHC-Pd (**7**)



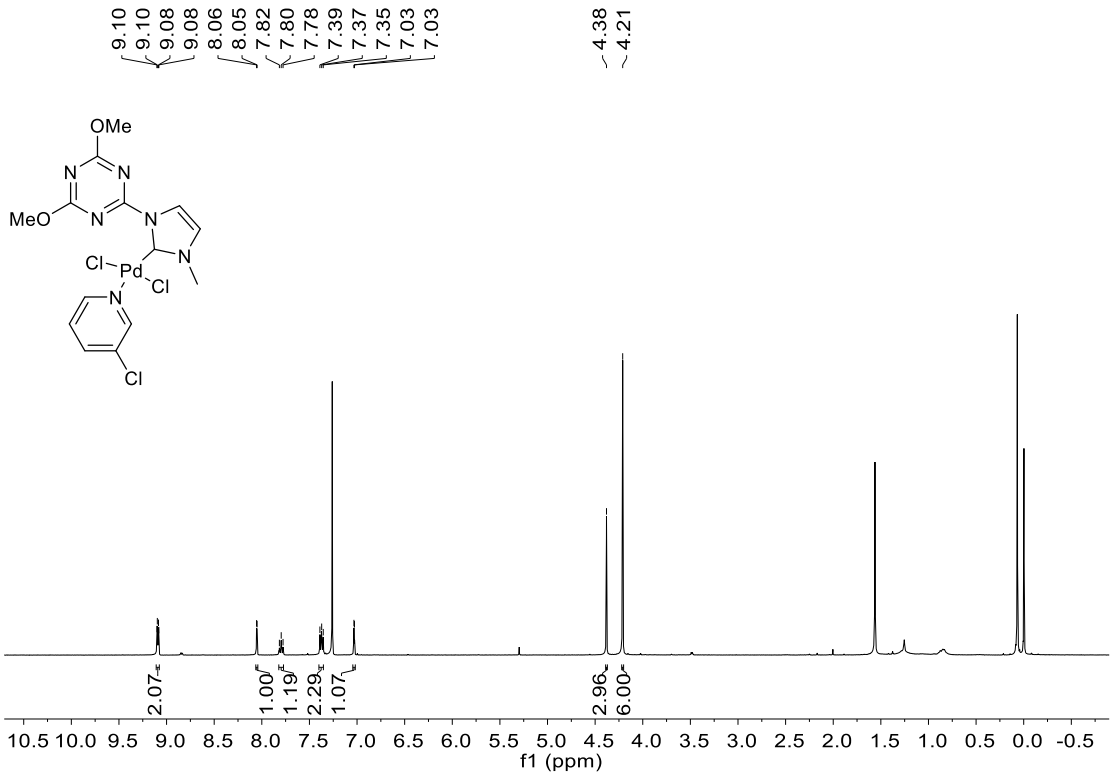
^{1}H NMR of complex T-NHC-Pd (**8**)



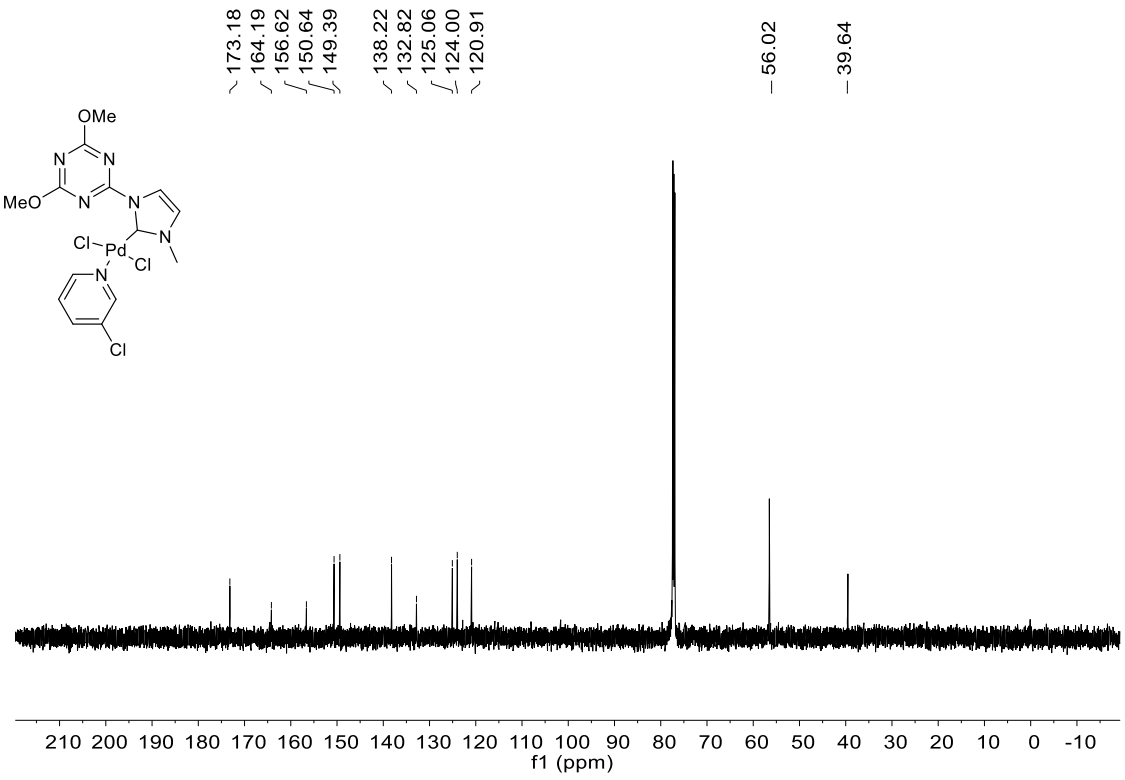
^{13}C NMR of complex T-NHC-Pd (**8**)



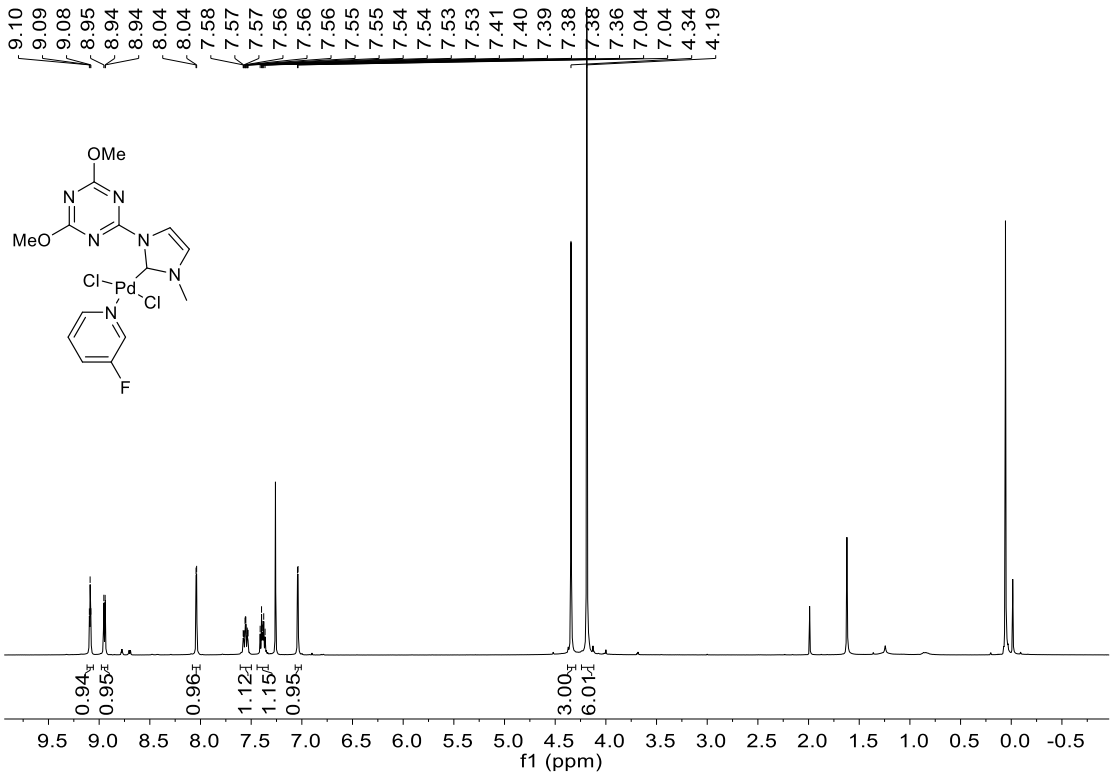
^{1}H NMR of complex T-NHC-Pd (**9**)



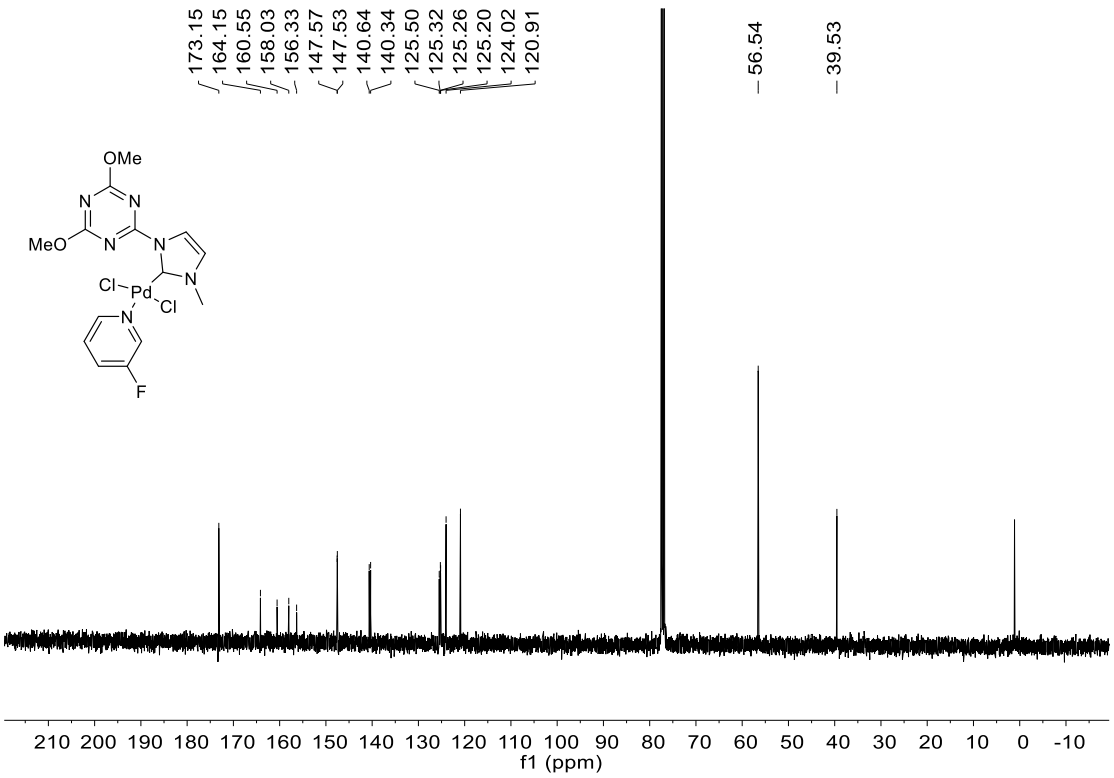
^{13}C NMR of complex T-NHC-Pd (**9**)



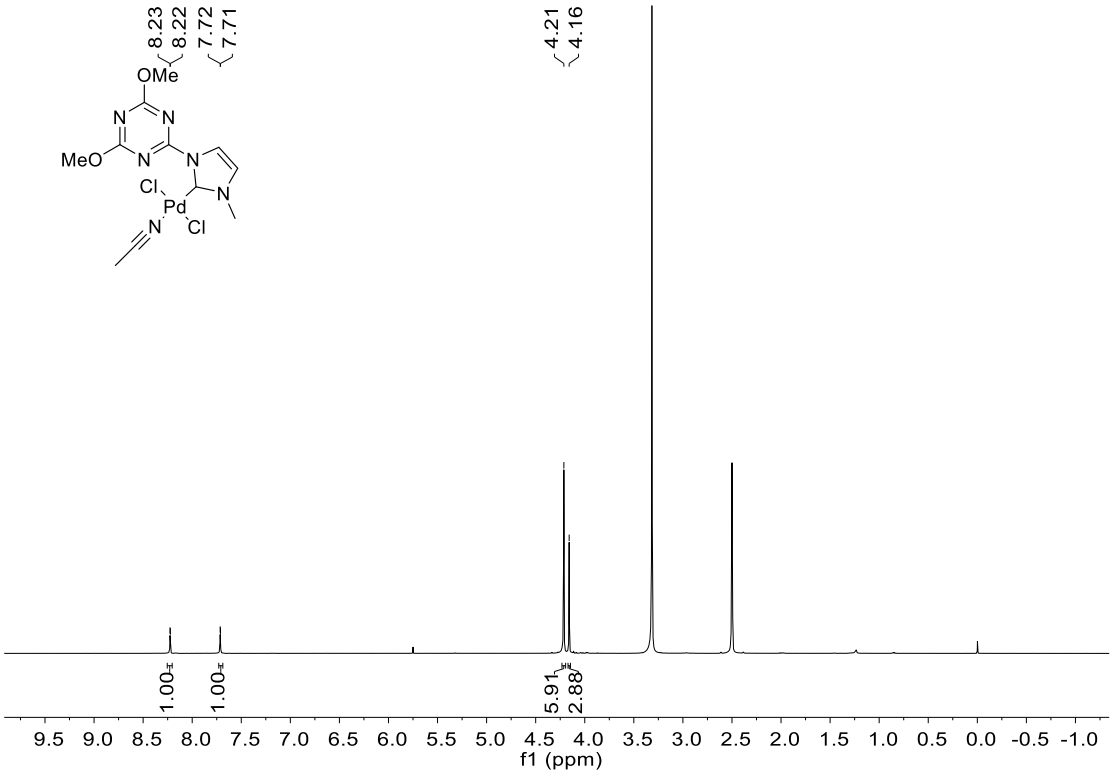
^{1}H NMR of complex T-NHC-Pd (**10**)



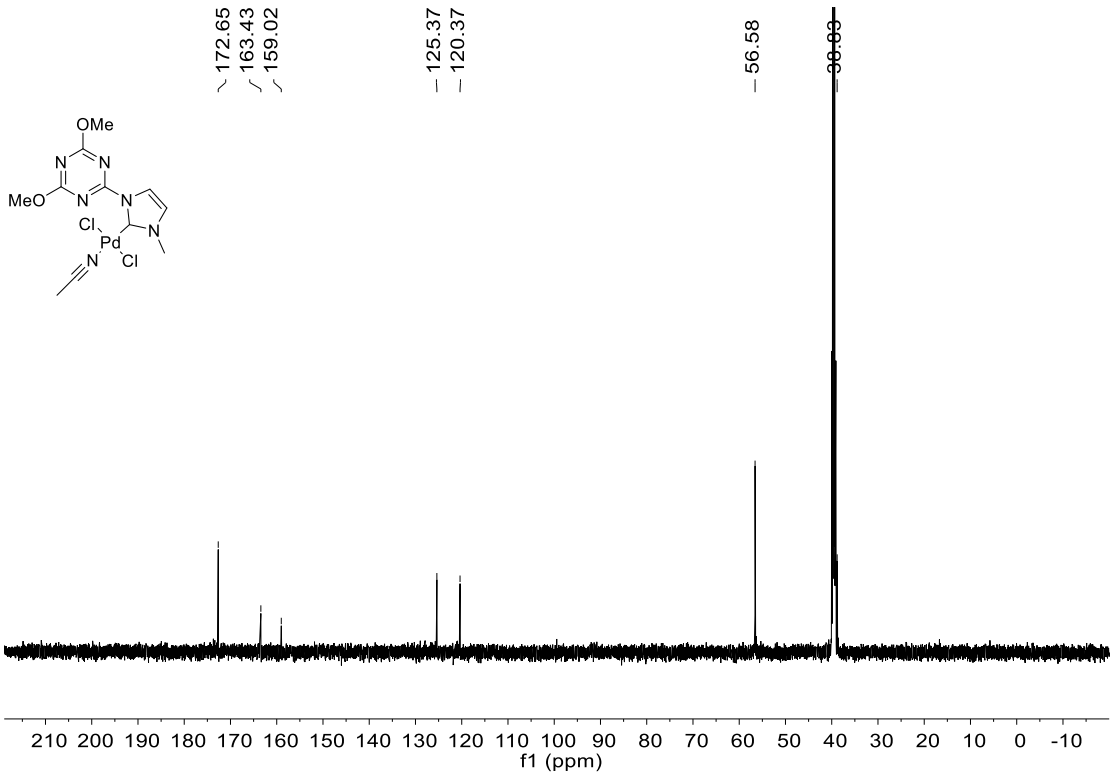
^{13}C NMR of complex T-NHC-Pd (**10**)



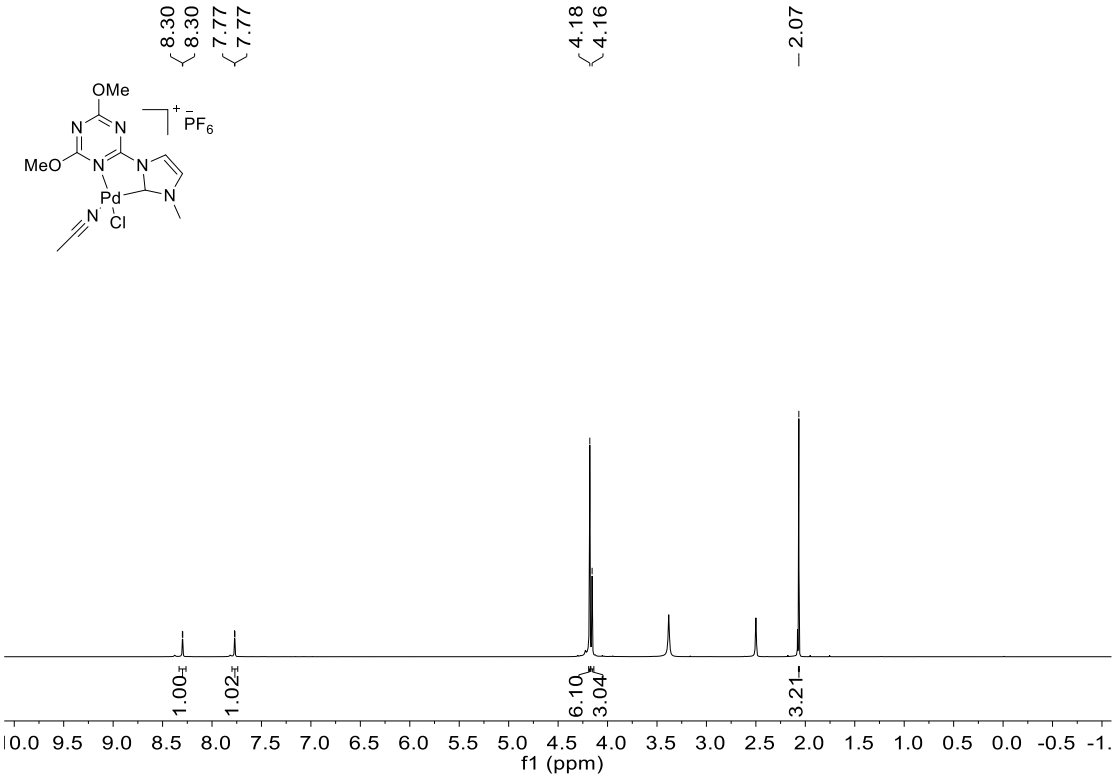
^{1}H NMR of complex T-NHC-Pd (**11**)



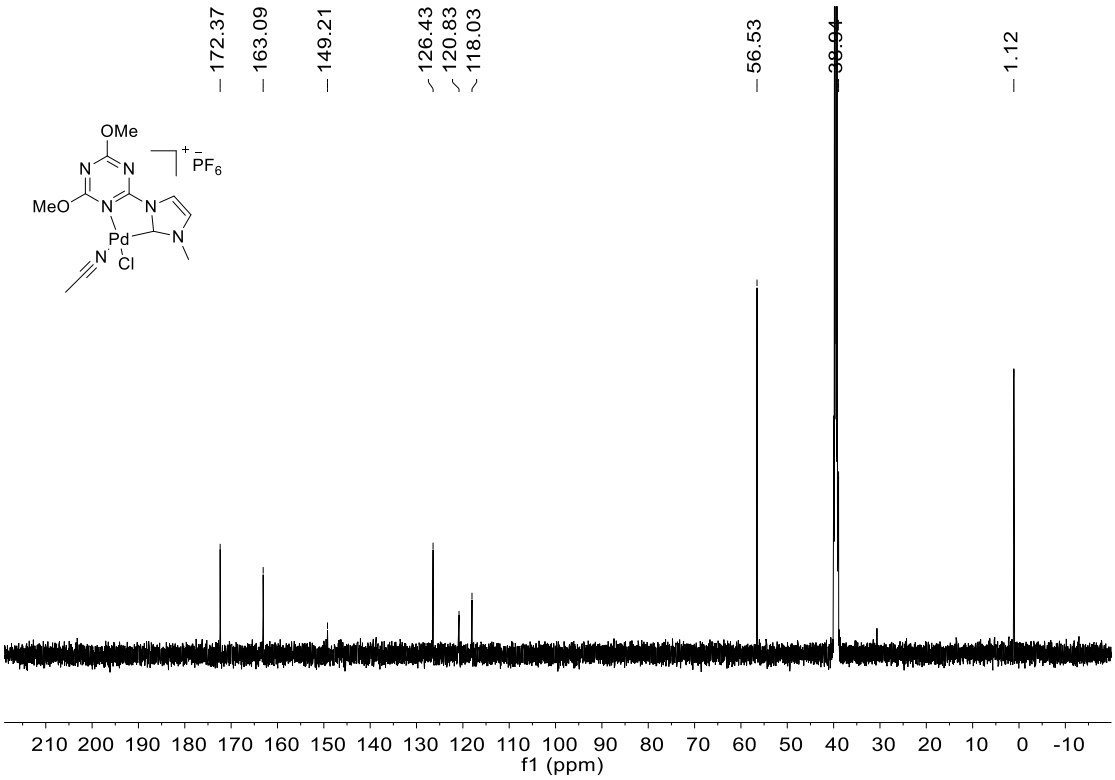
^{13}C NMR of complex T-NHC-Pd (**11**)



^{1}H NMR of complex T-NHC-Pd (**12**)

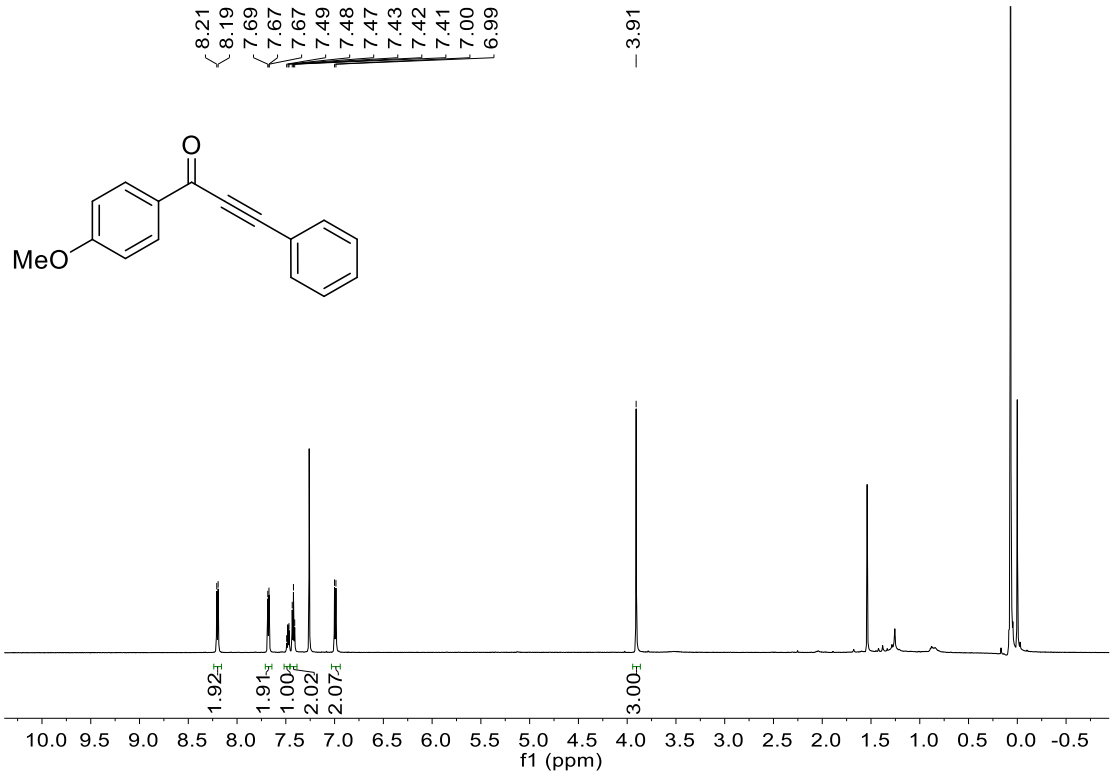


^{13}C NMR of complex T-NHC-Pd (**12**)

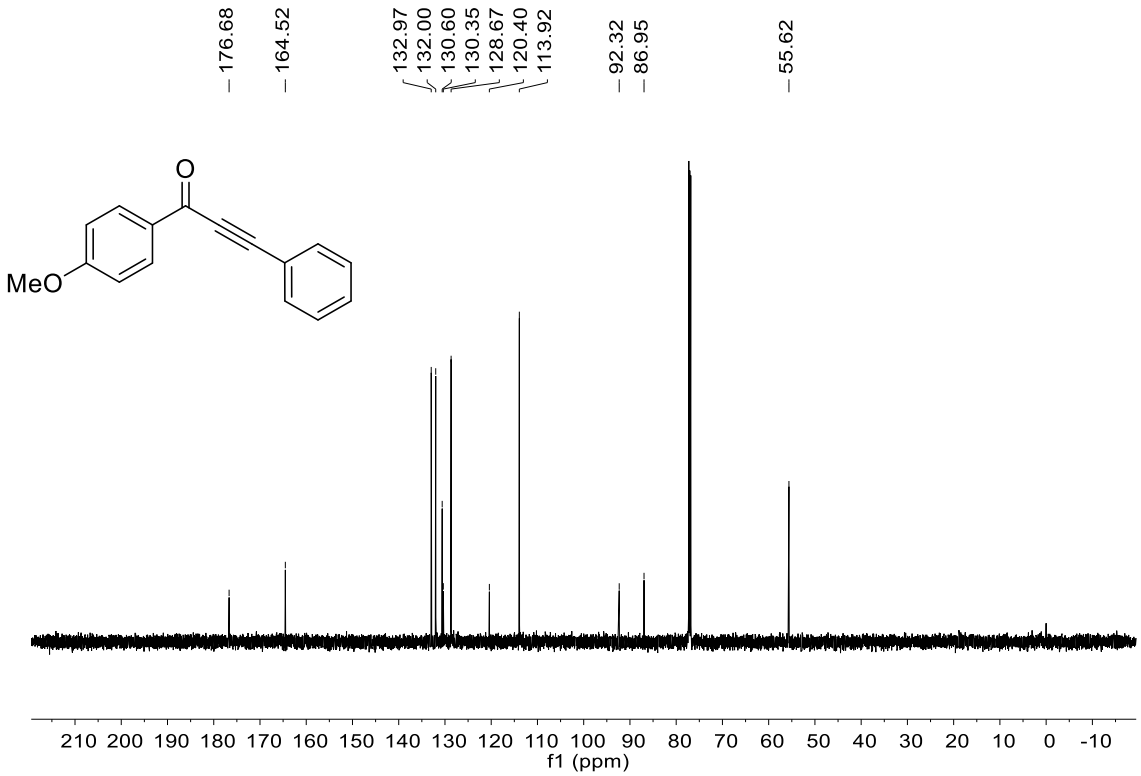


S-8-2 NMR Spectrum of 1,3-ynone products

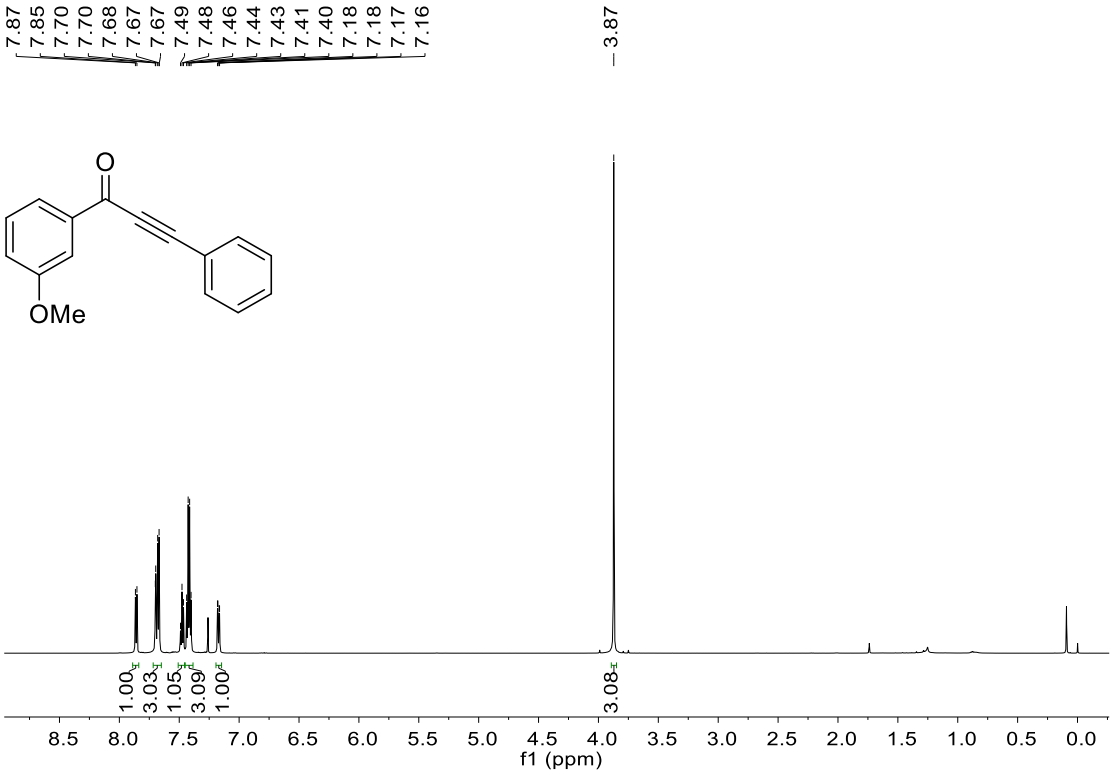
^{1}H NMR of compound 3aa



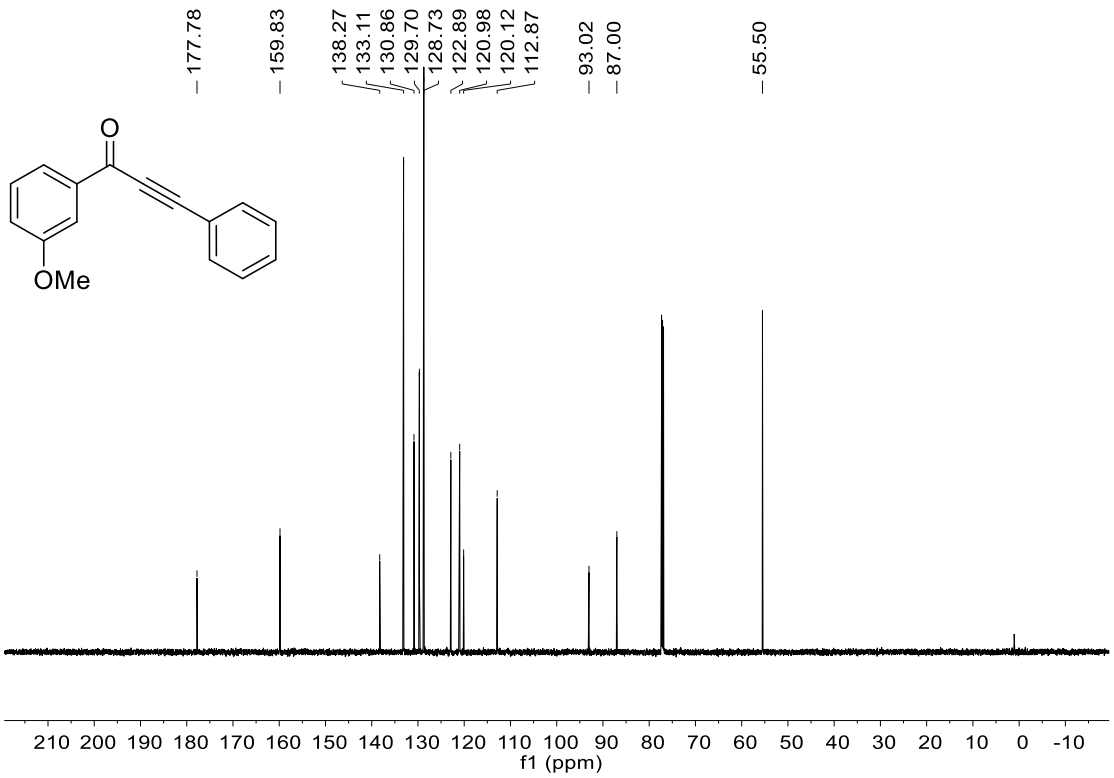
^{13}C NMR of compound 3aa



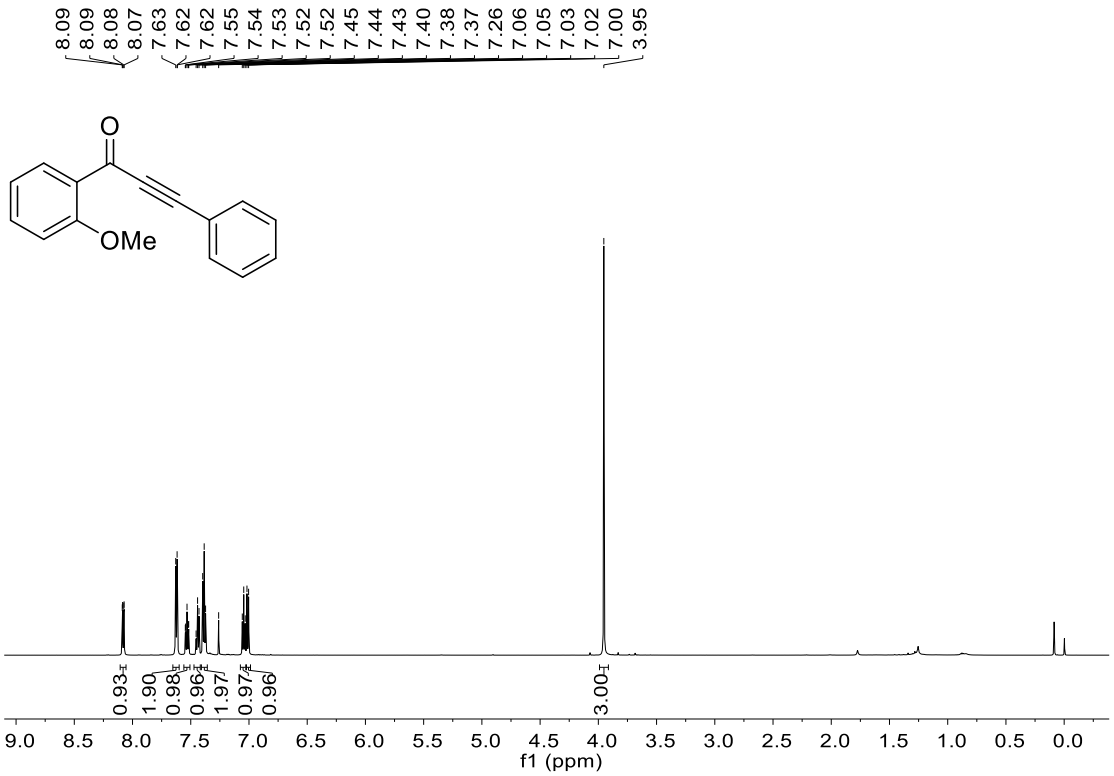
^{1}H NMR of compound 3ba



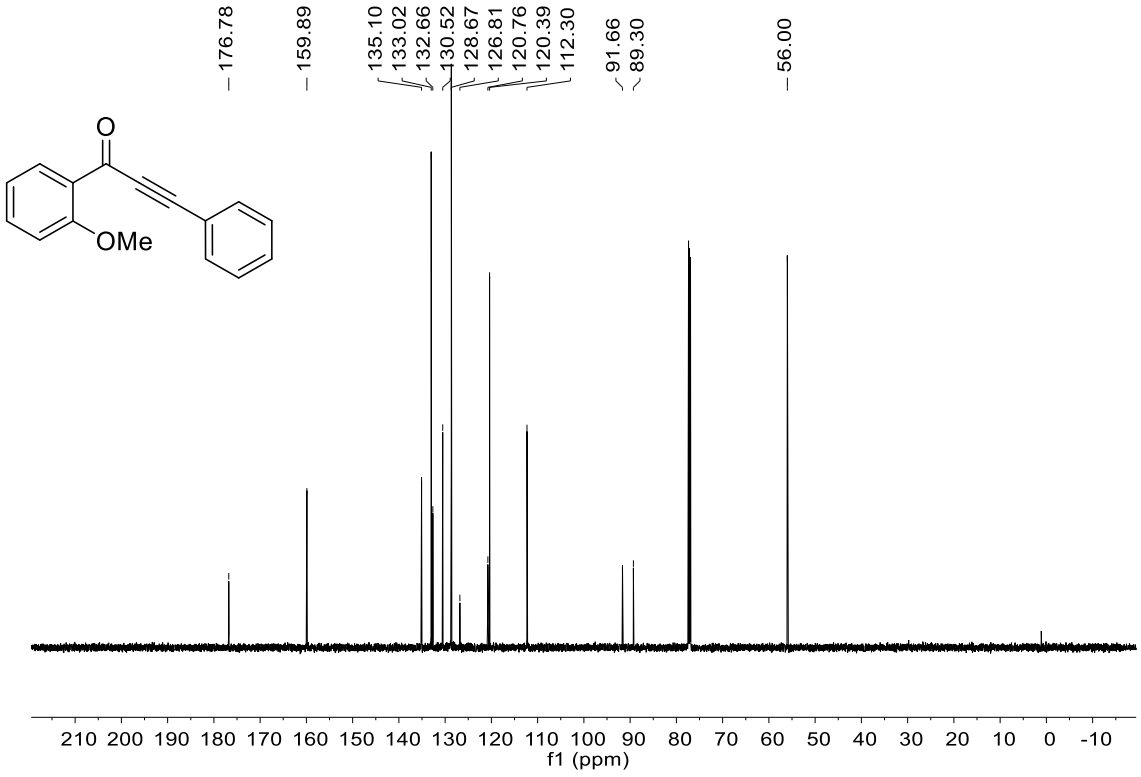
^{13}C NMR of compound 3ba



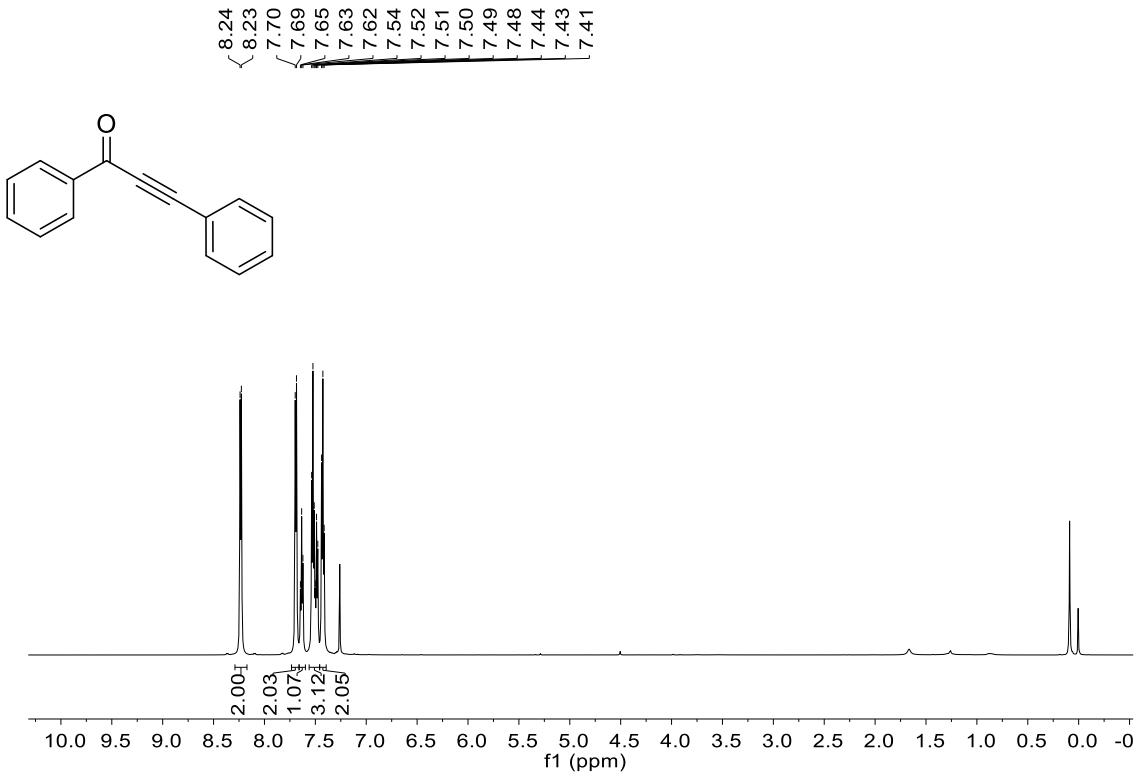
^{1}H NMR of compound 3ca



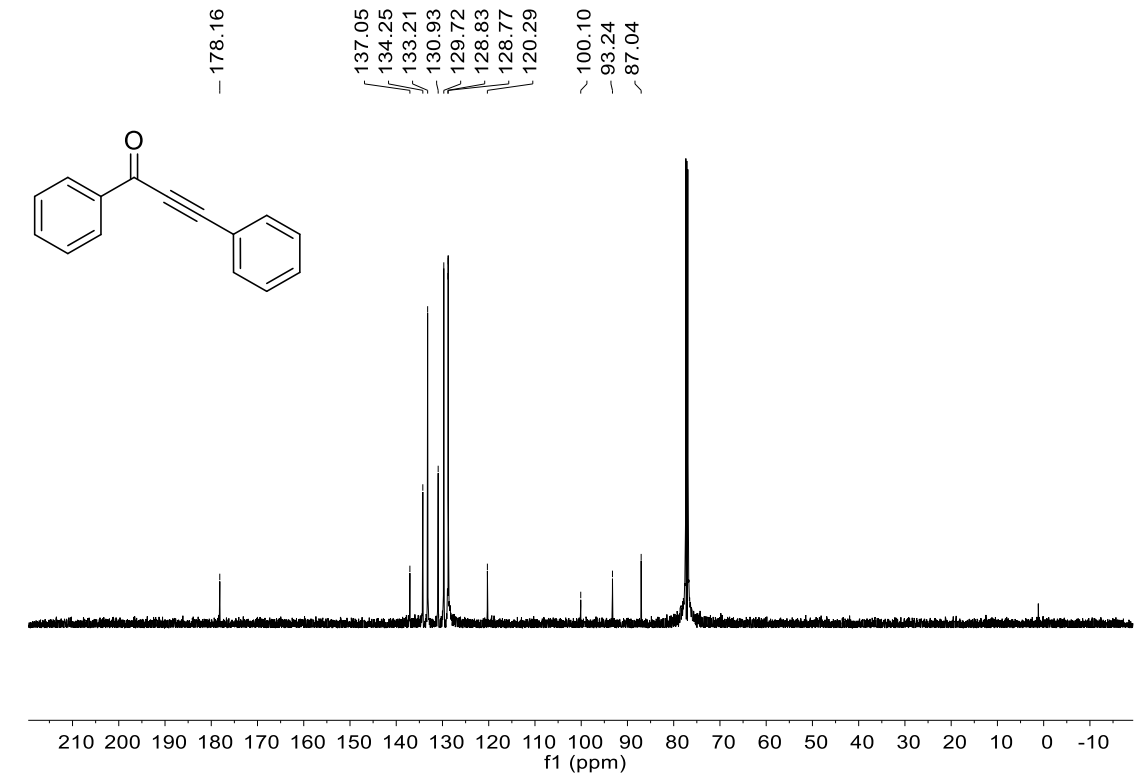
^{13}C NMR of compound 3ca



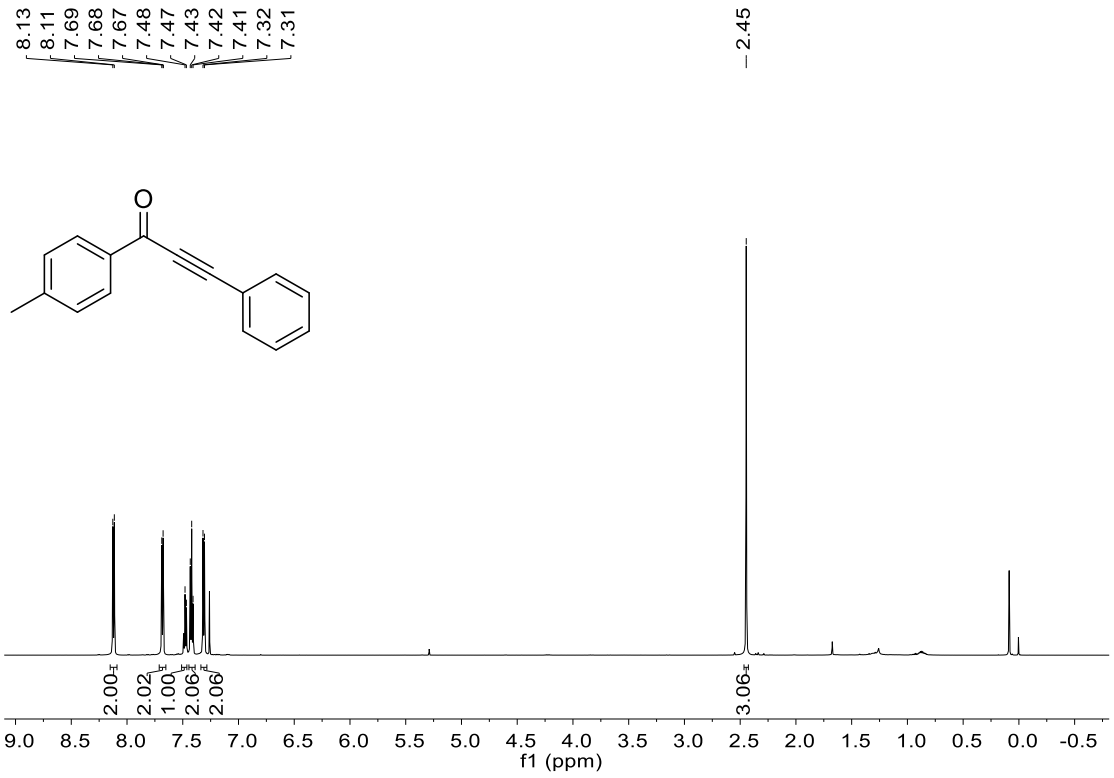
^{1}H NMR of compound 3da



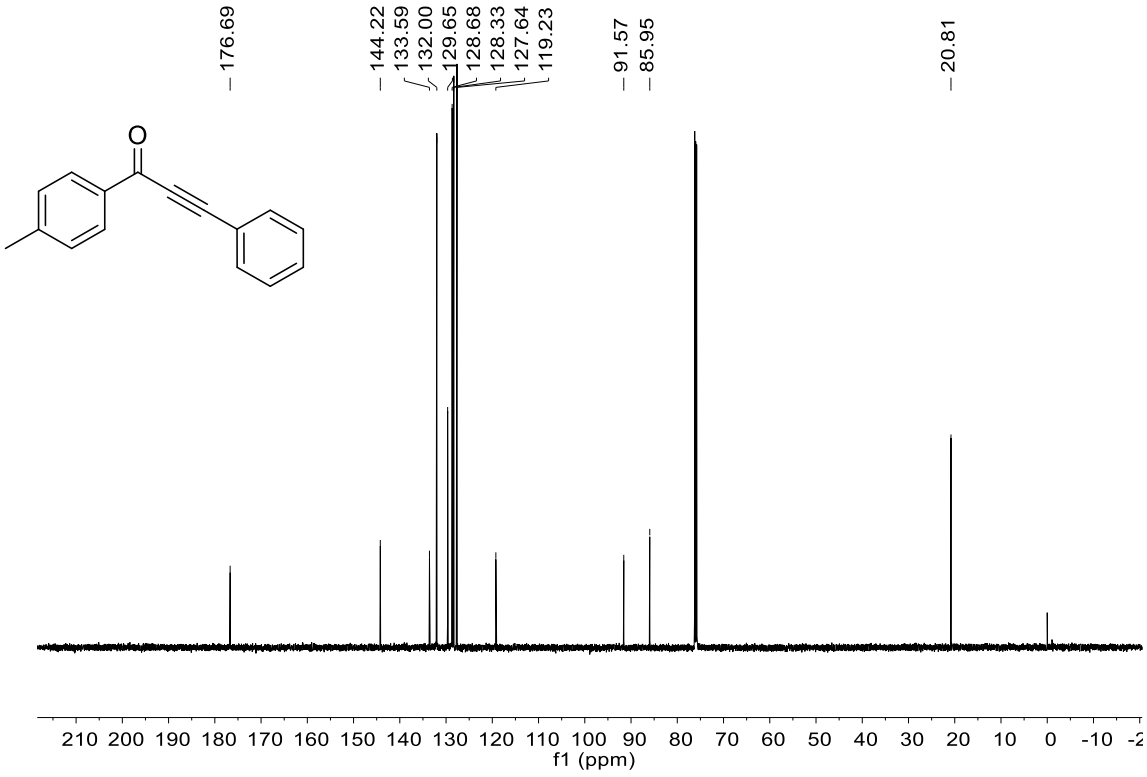
^{13}C NMR of compound 3da



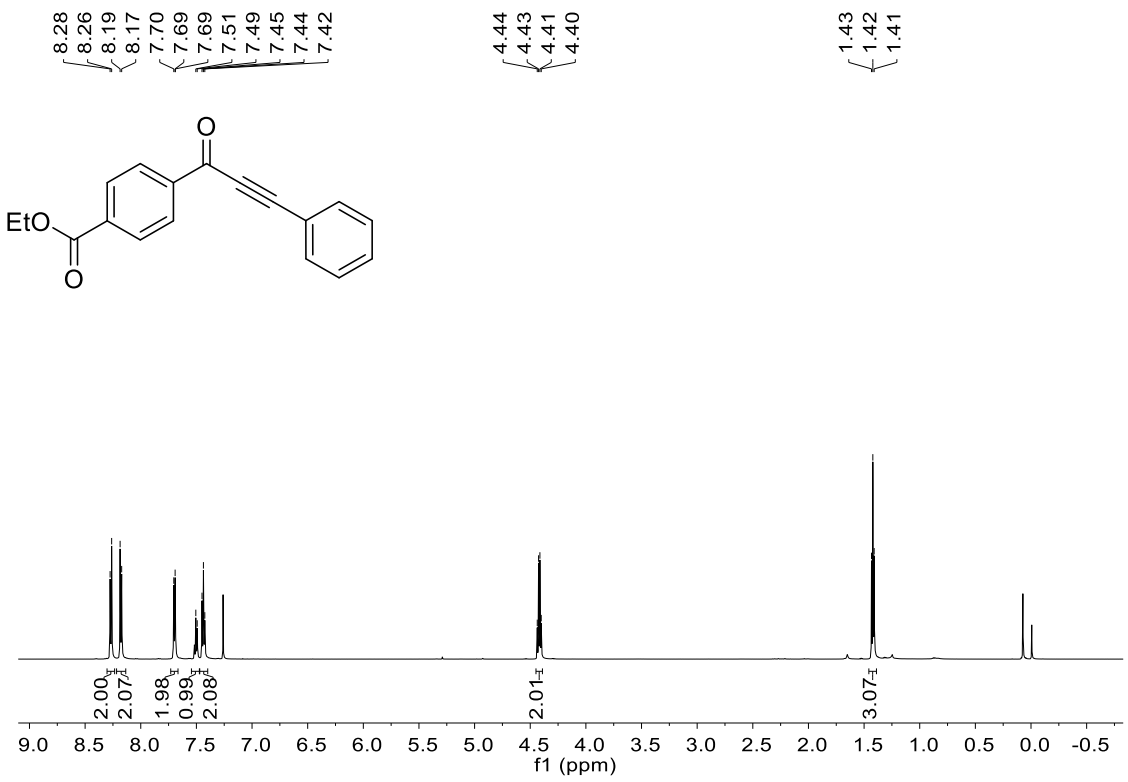
^{1}H NMR of compound 3ea



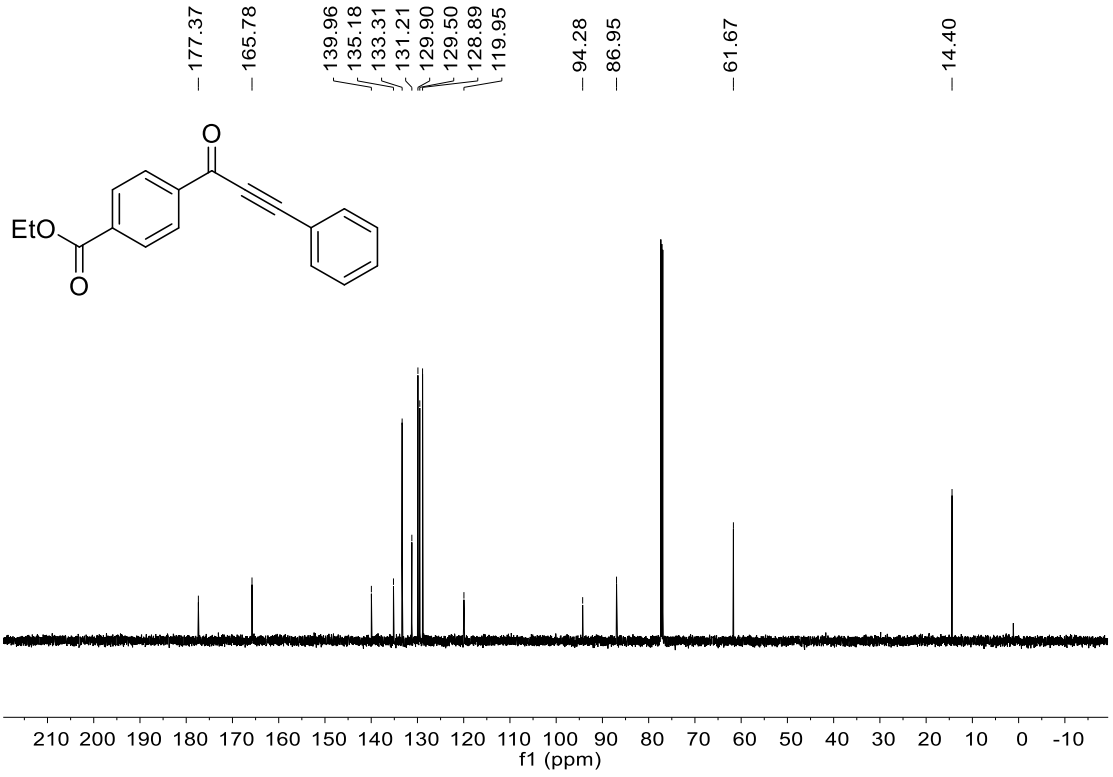
^{13}C NMR of compound 3ea



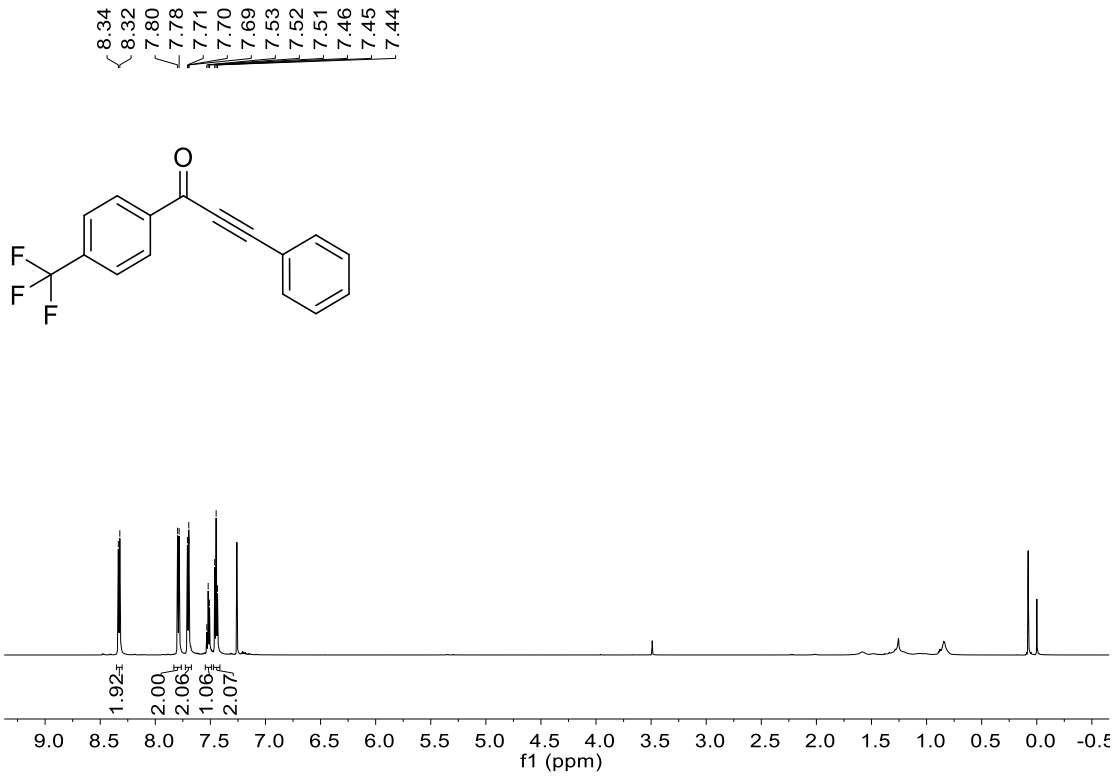
^{1}H NMR of compound 3fa



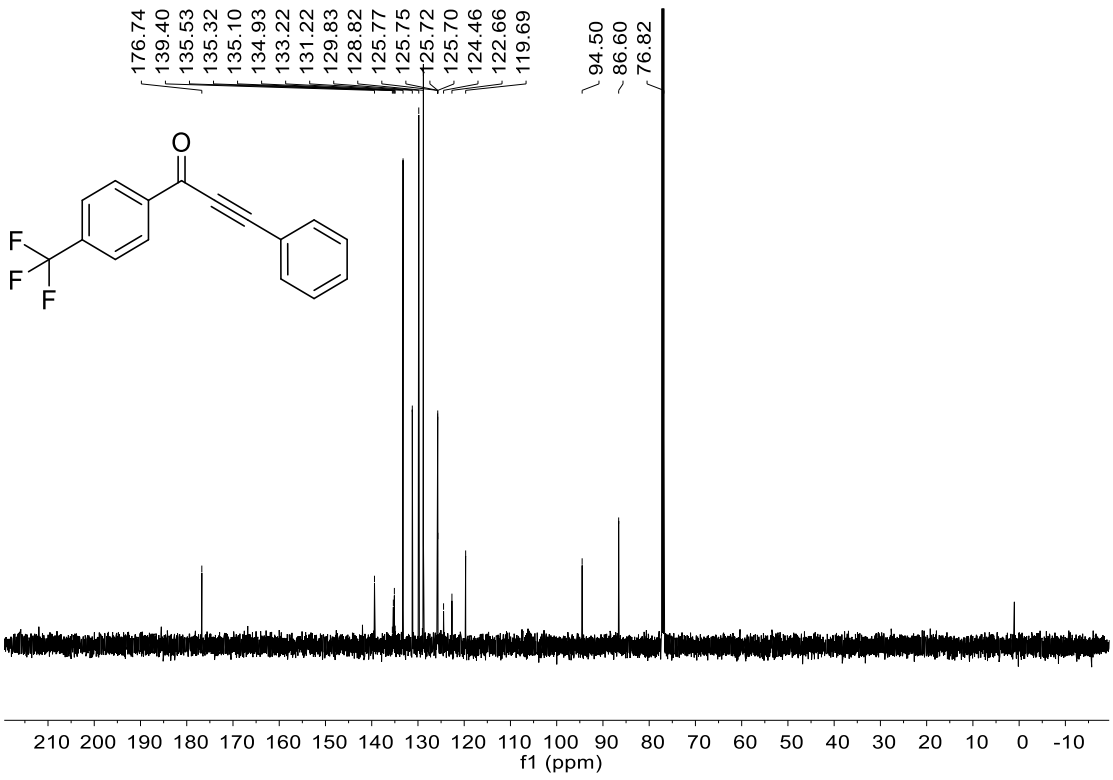
^{13}C NMR of compound 3fa



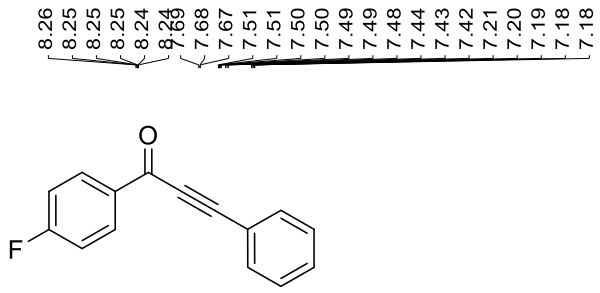
^{1}H NMR of compound 3ga

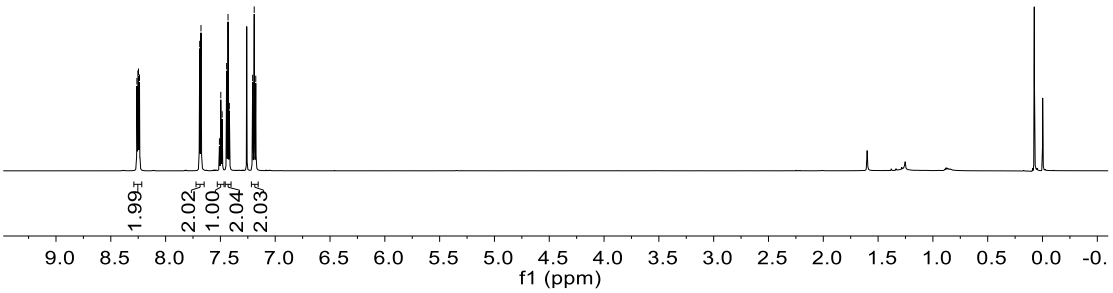


^{13}C NMR of compound 3ga

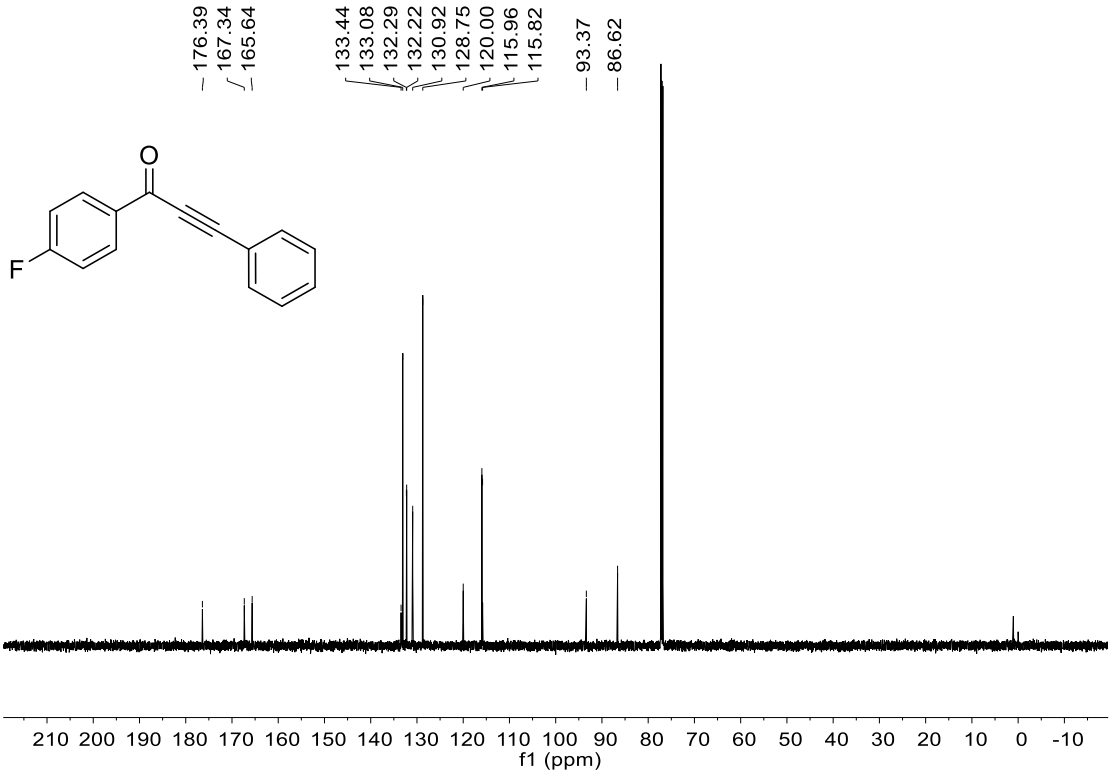


^{1}H NMR of compound 3ha

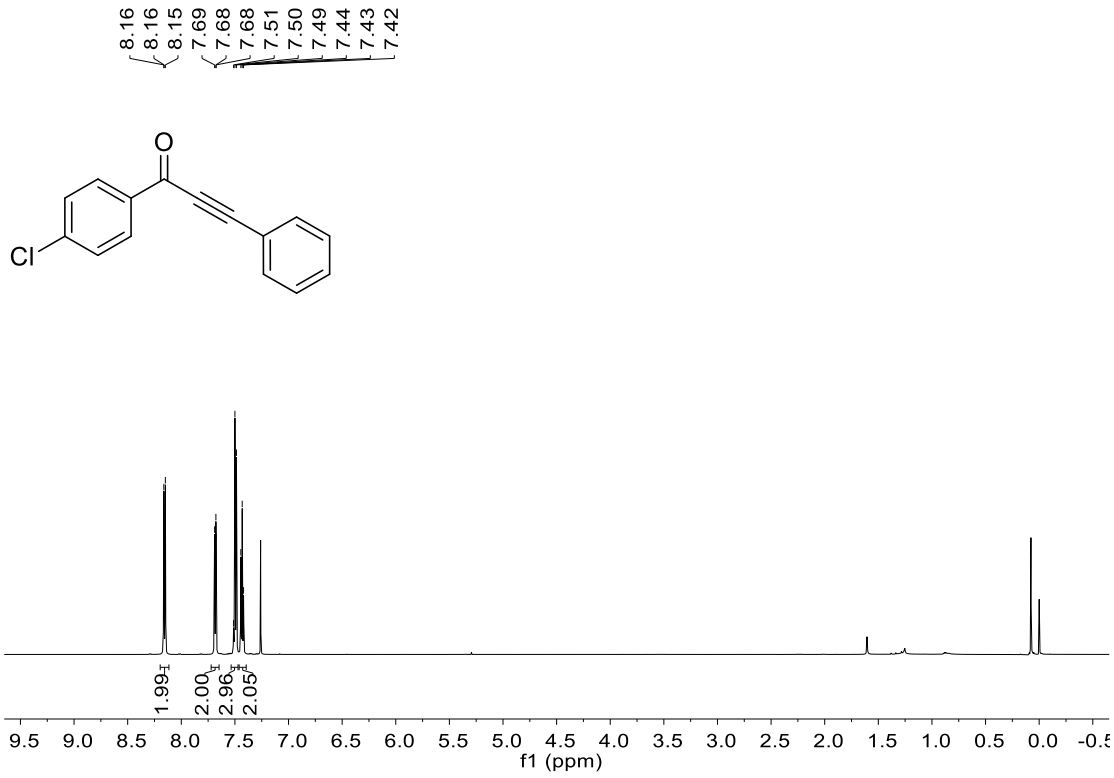




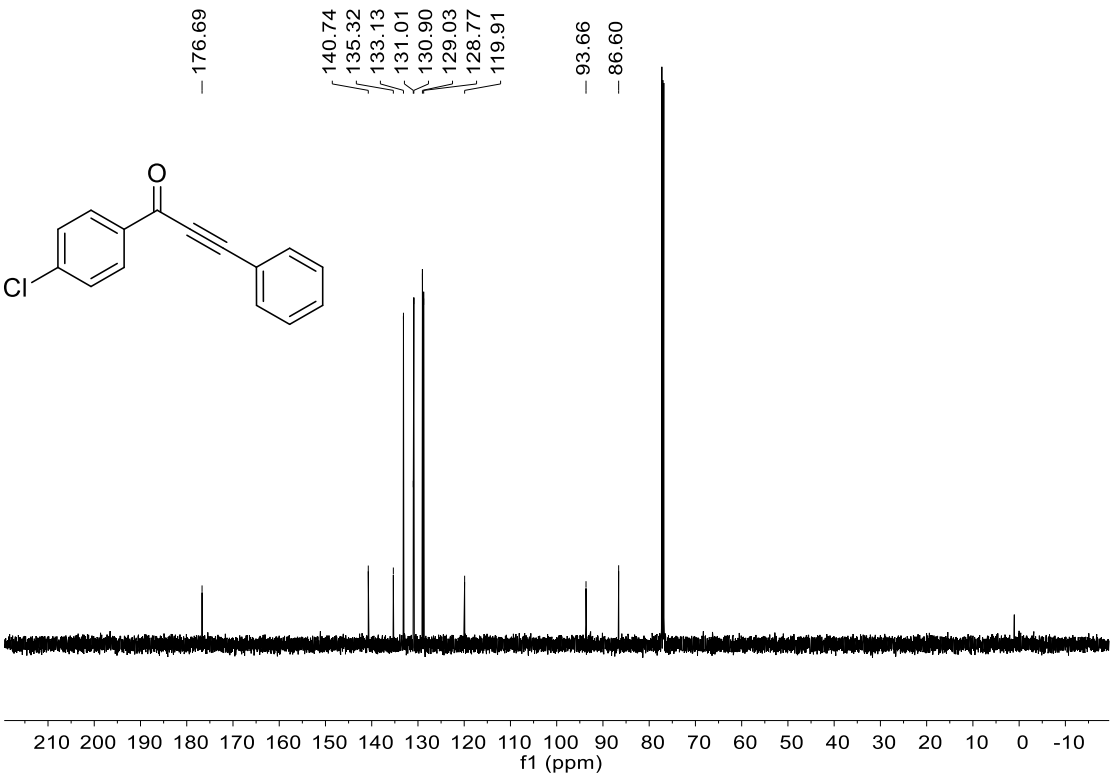
^{13}C NMR of compound 3ha



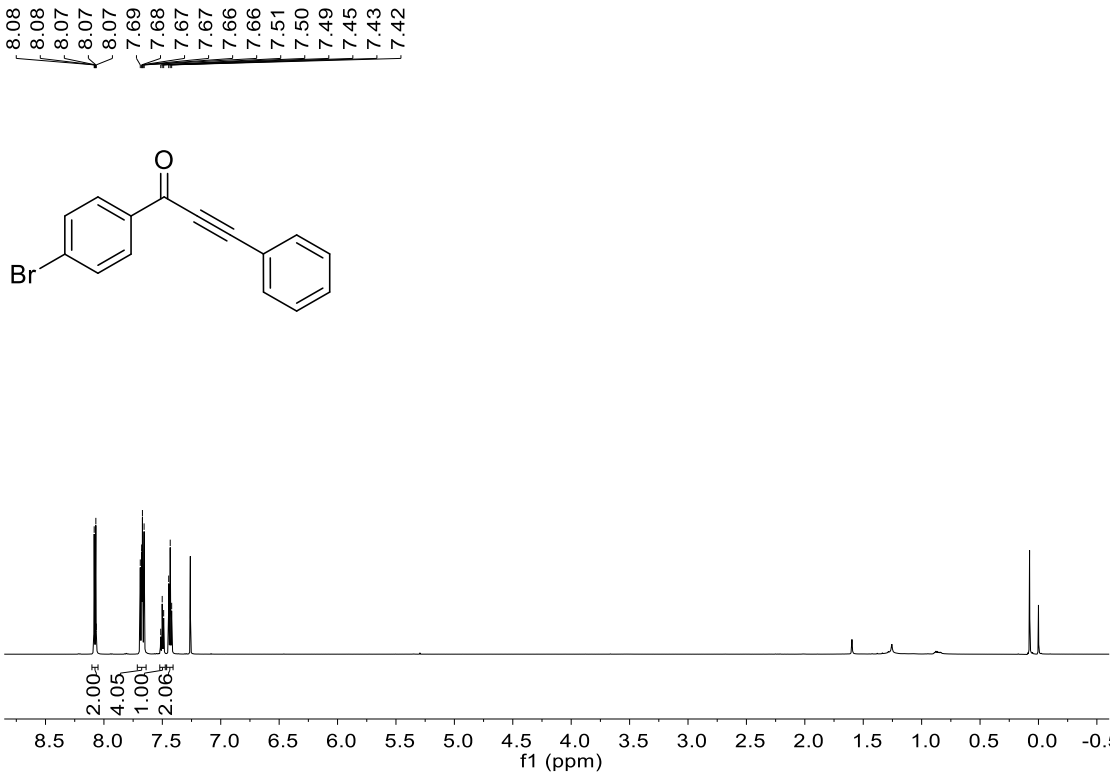
^{1}H NMR of compound 3ia



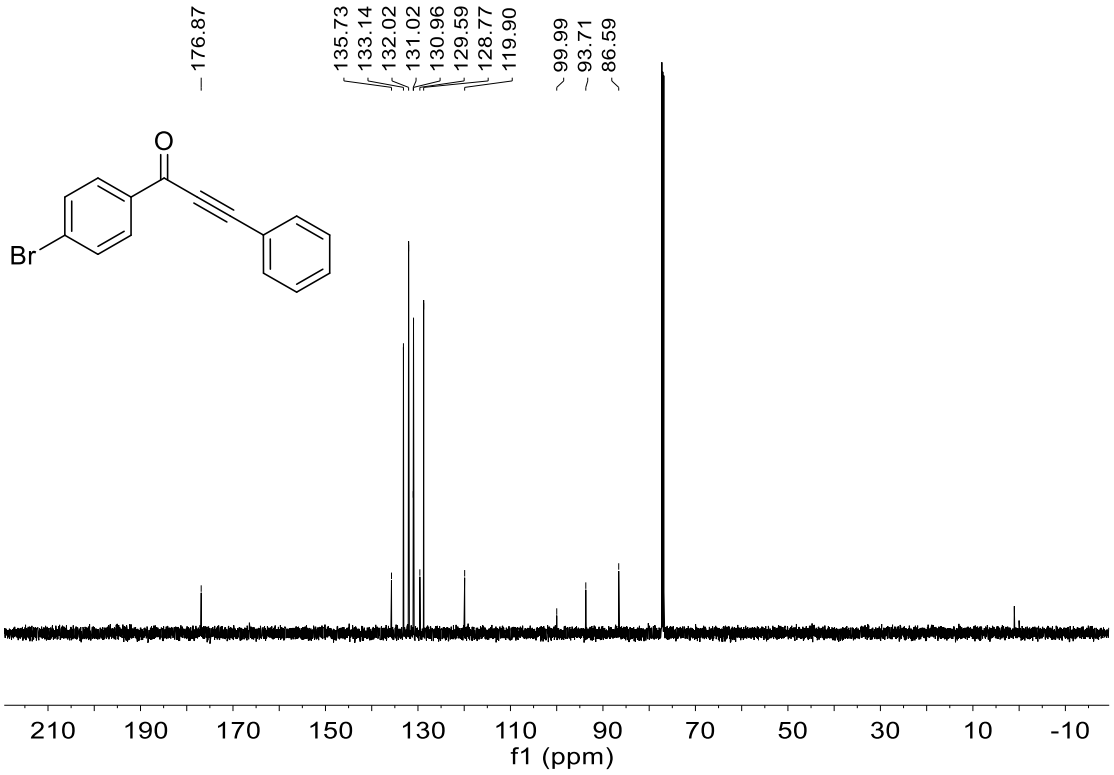
^{13}C NMR of compound 3ia



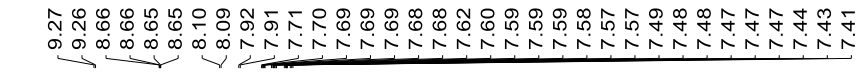
^{1}H NMR of compound 3ja

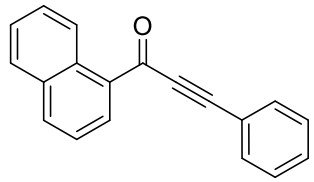


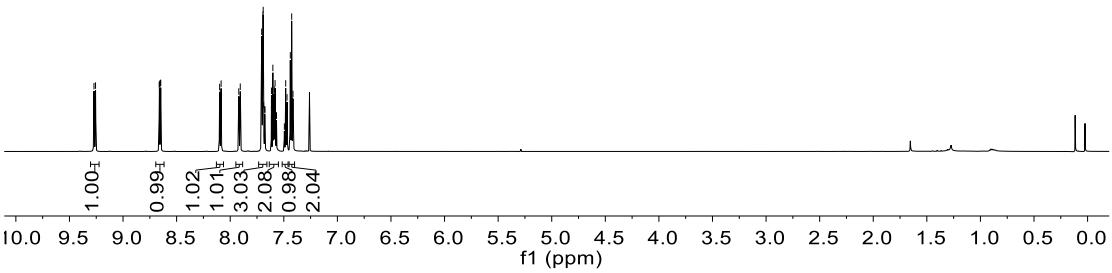
^{13}C NMR of compound 3ja



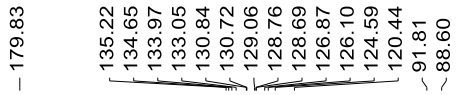
^{1}H NMR of compound 3ka

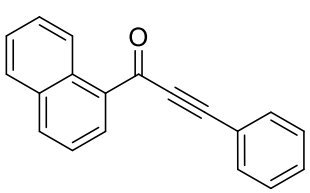




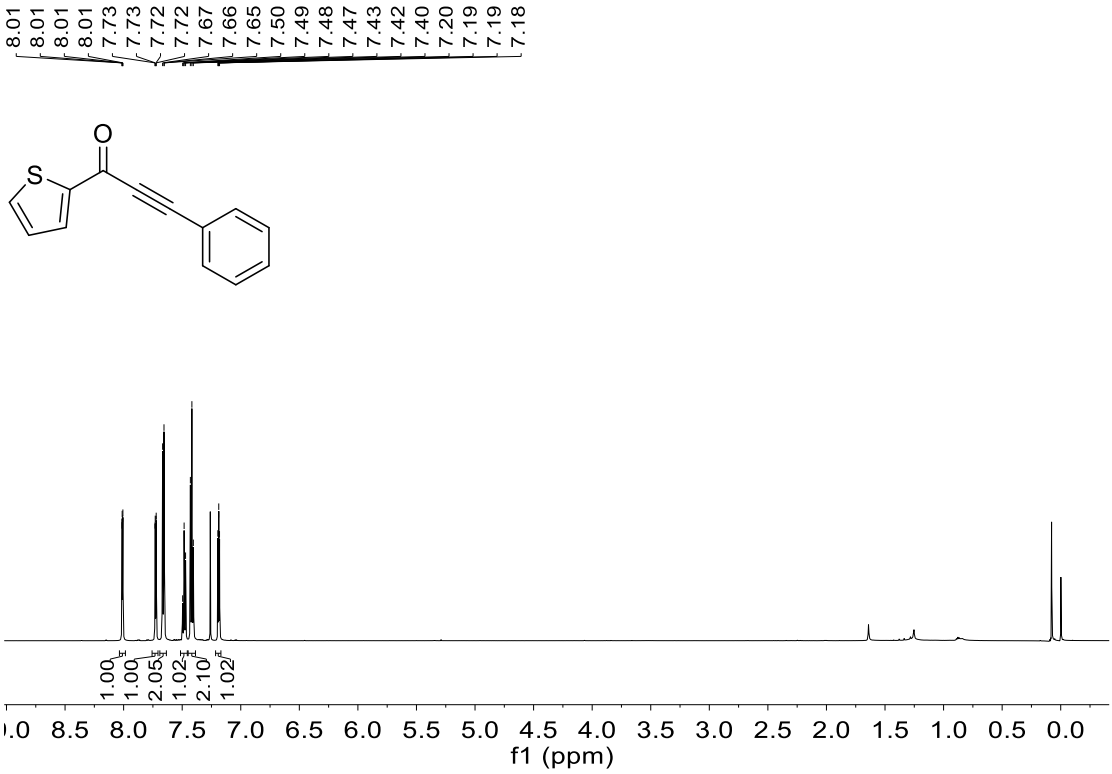


^{13}C NMR of compound 3ka

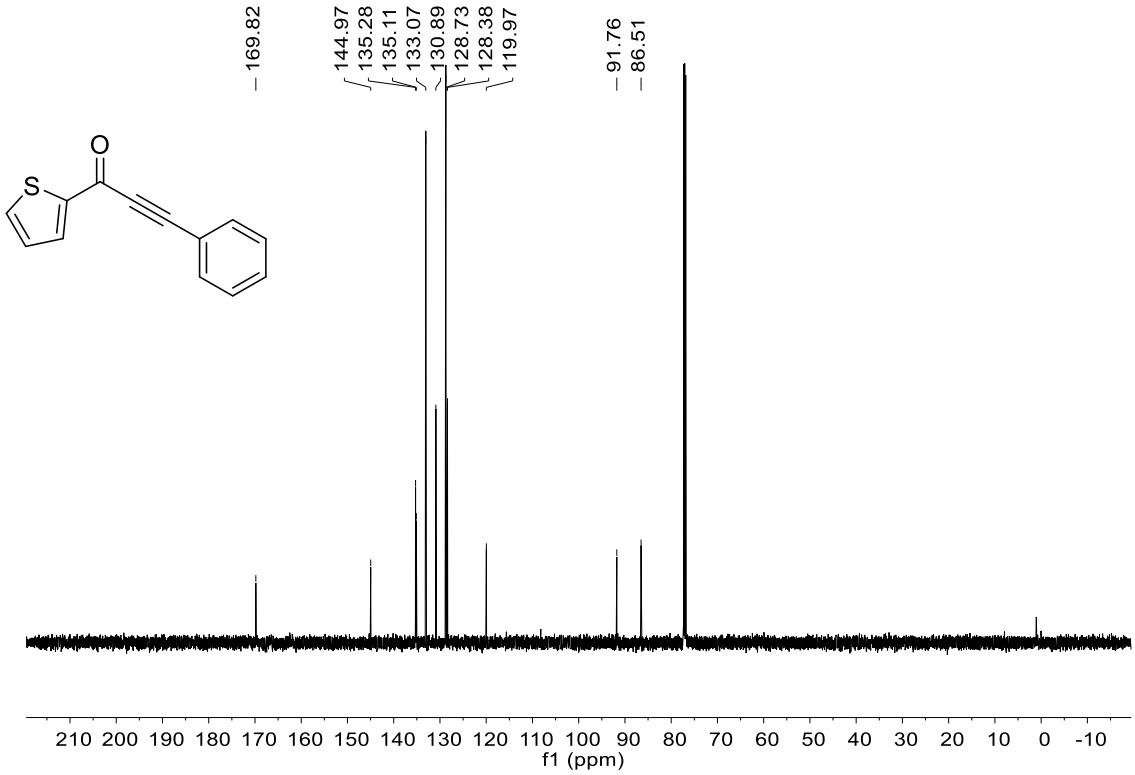




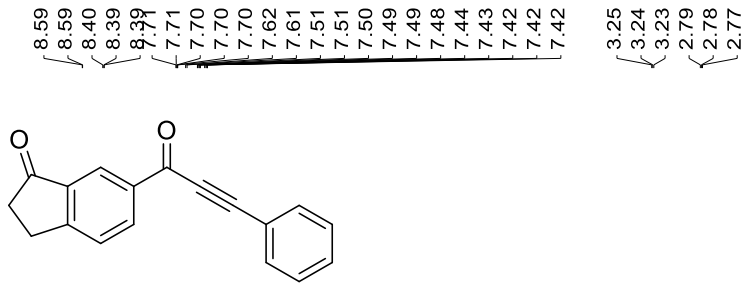
^{1}H NMR of compound 3la

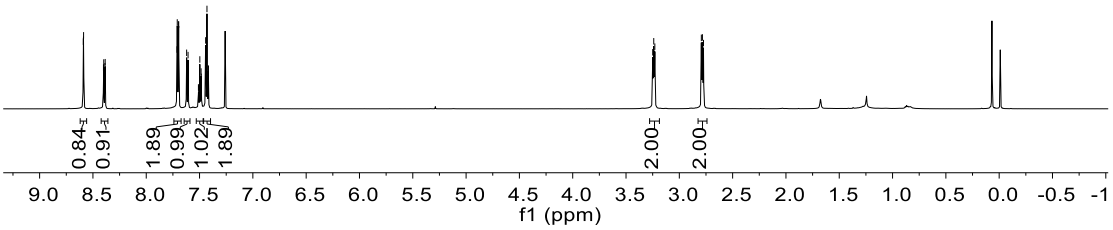


^{13}C NMR of compound 3la

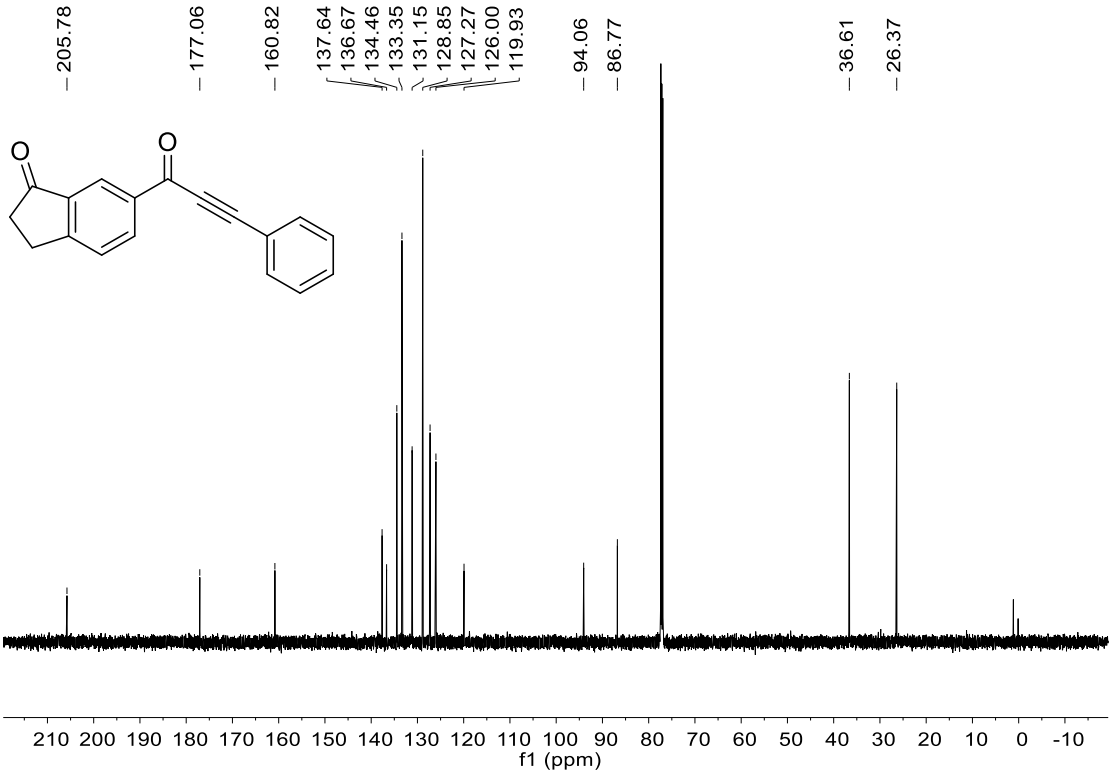


^{1}H NMR of compound 3ma

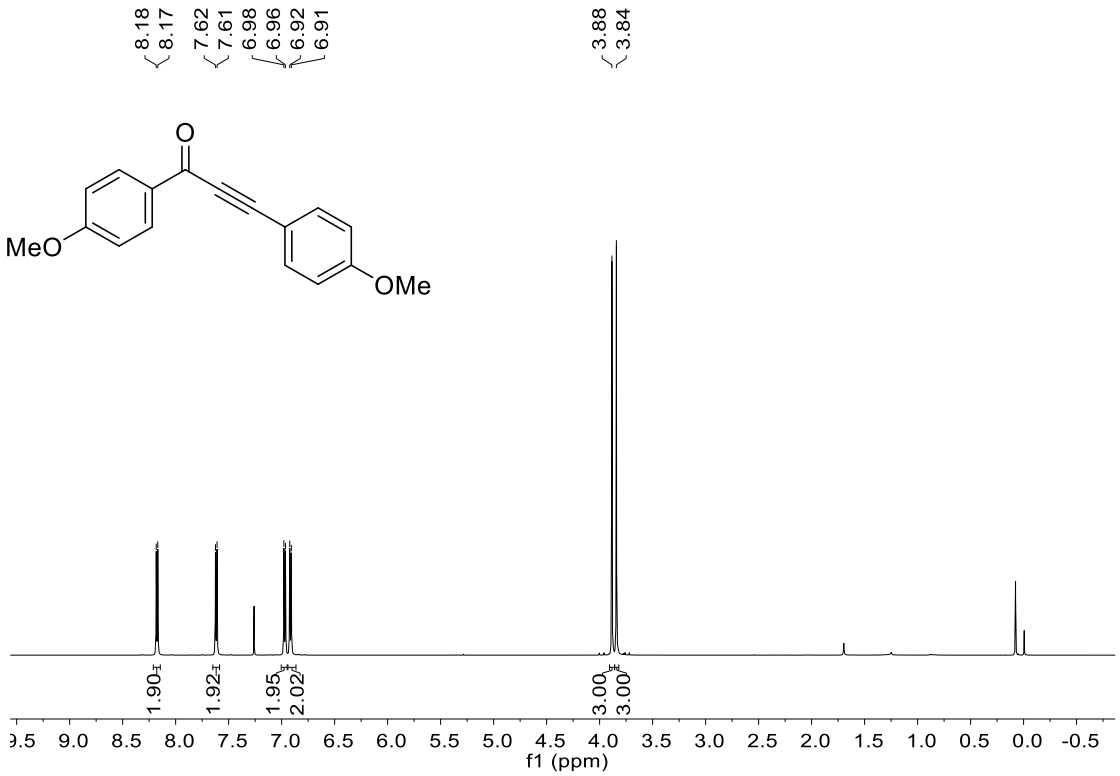




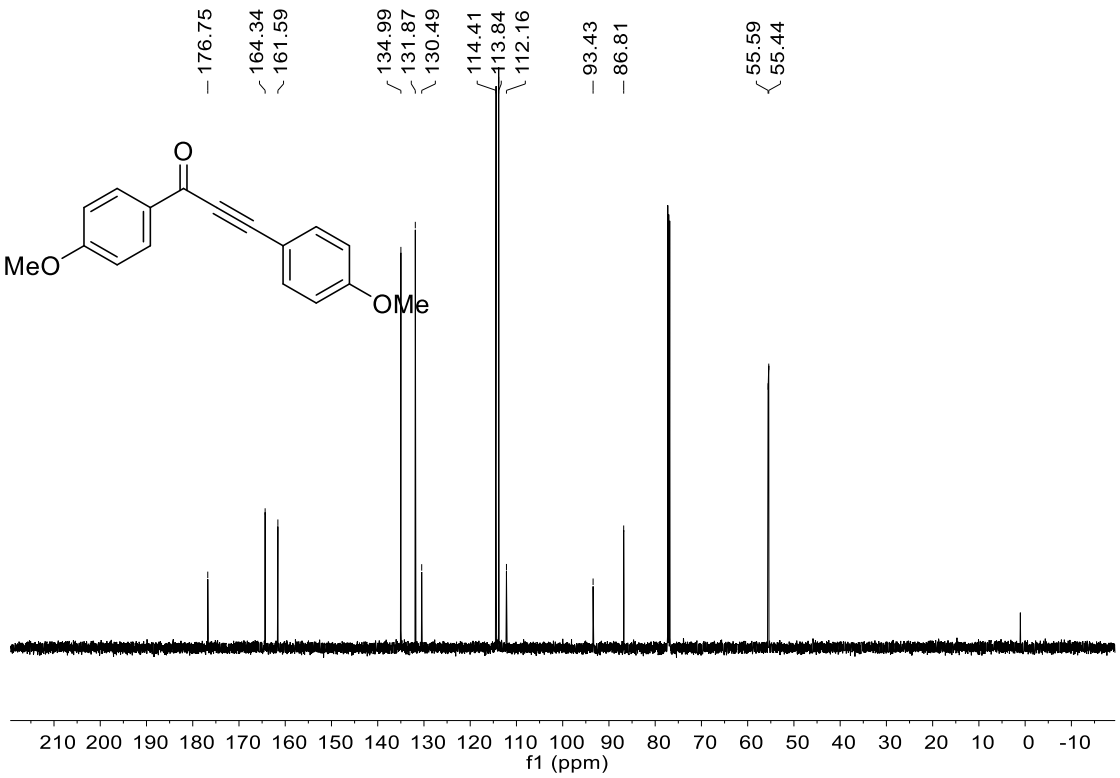
^{13}C NMR of compound 3ma



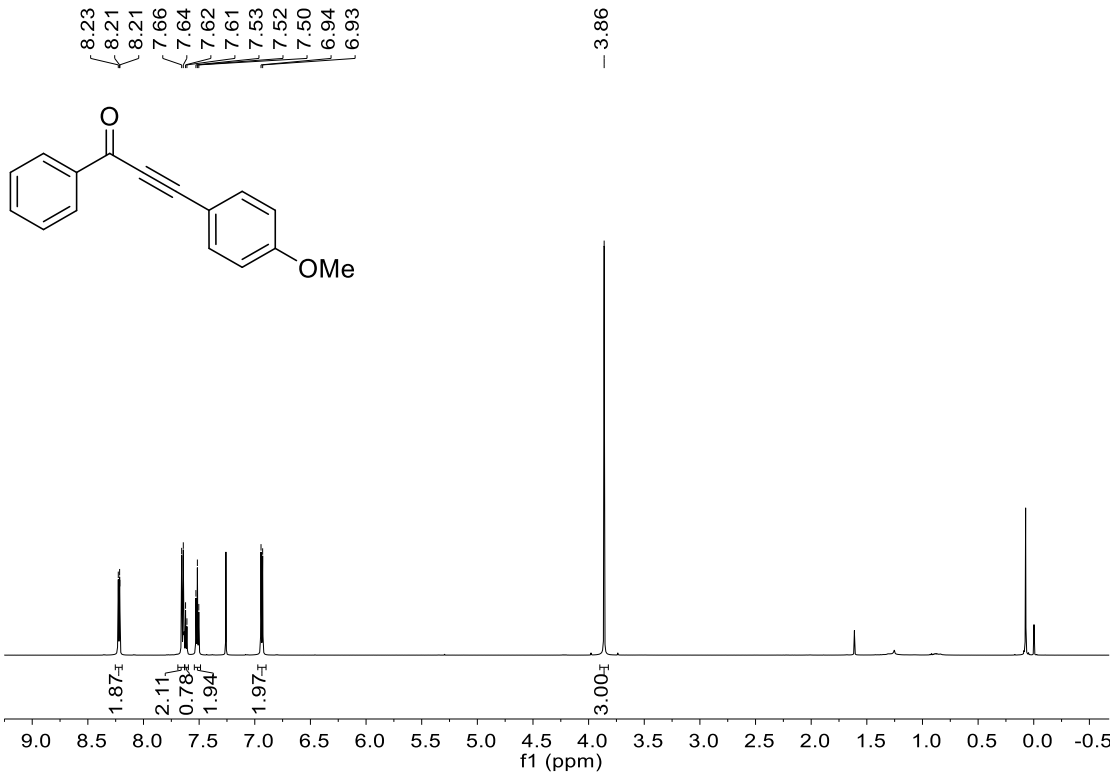
^{1}H NMR of compound 3ab



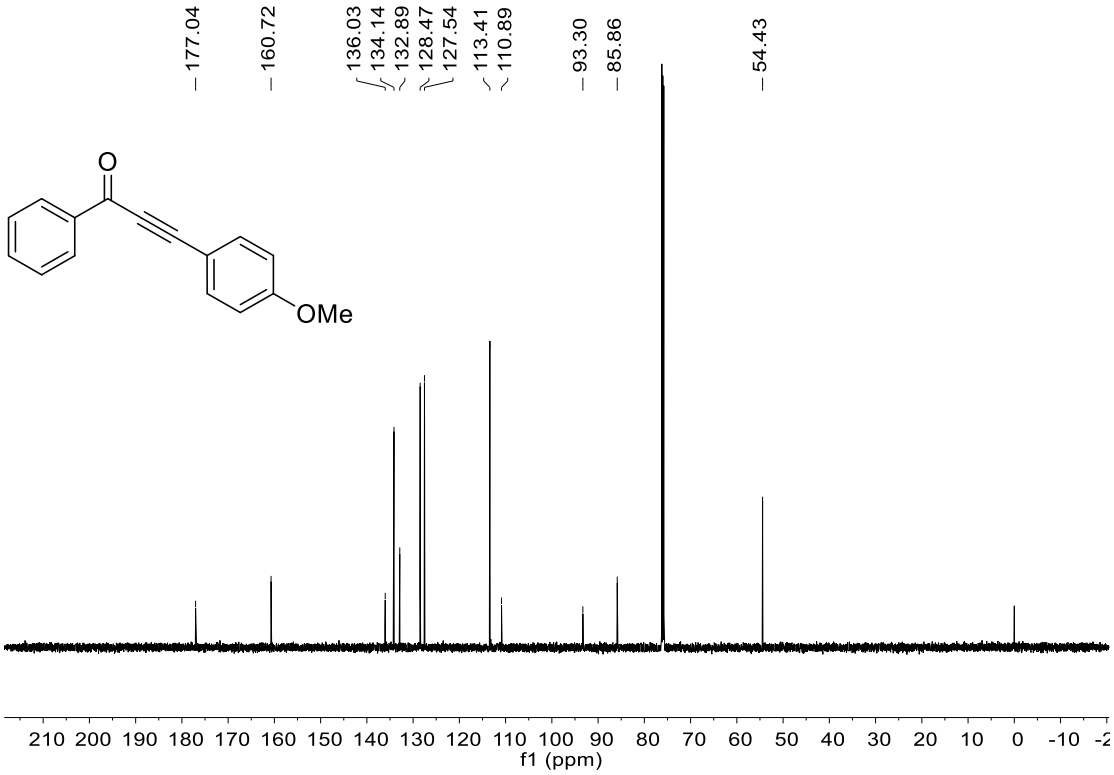
^{13}C NMR of compound 3ab



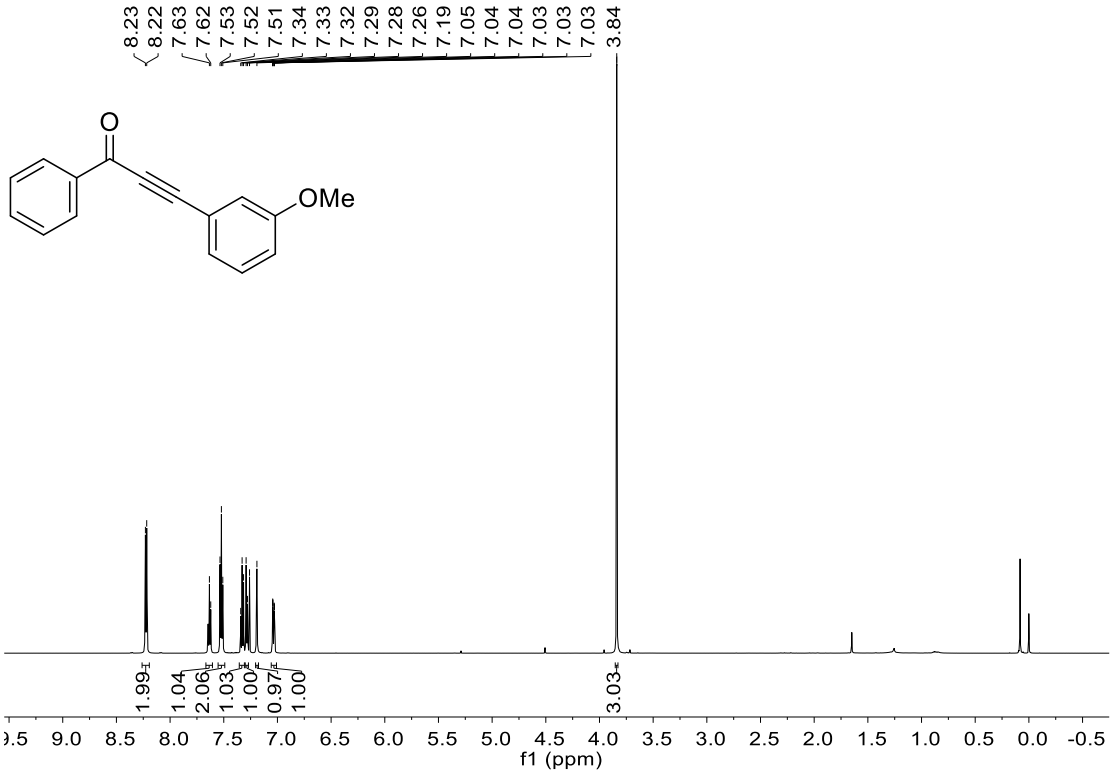
^{1}H NMR of compound 3db



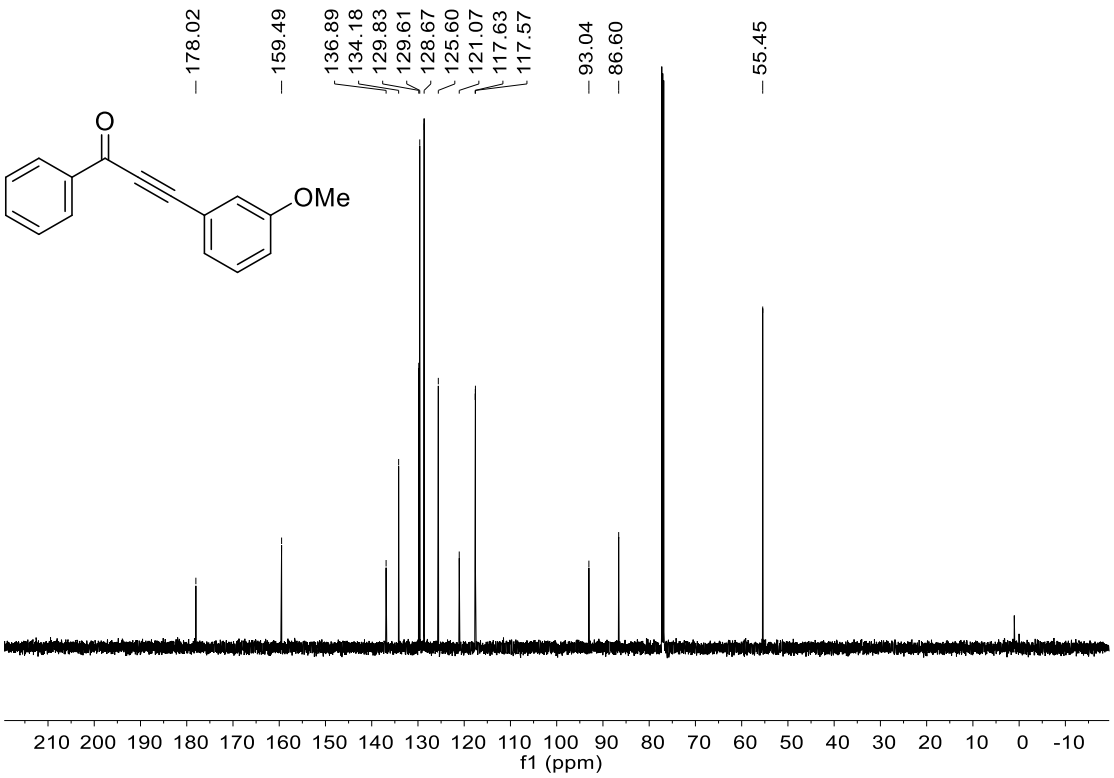
^{13}C NMR of compound 3db



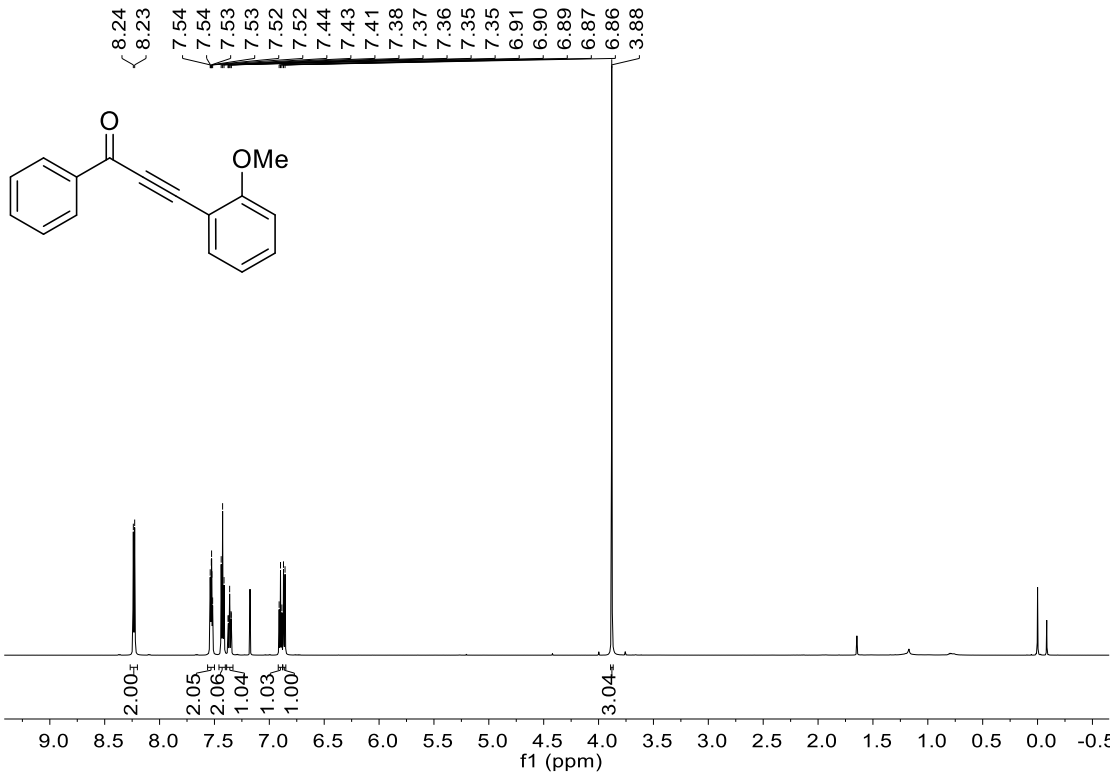
^{1}H NMR of compound 3dc



^{13}C NMR of compound 3dc



^{1}H NMR of compound 3dd



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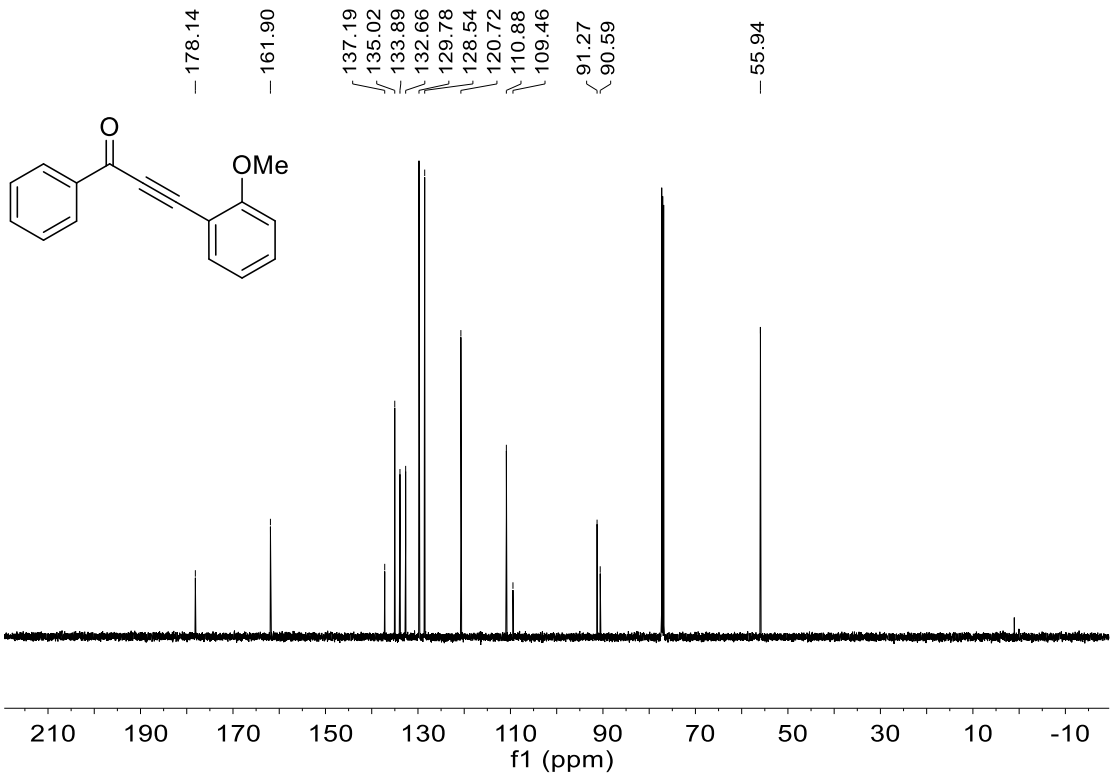
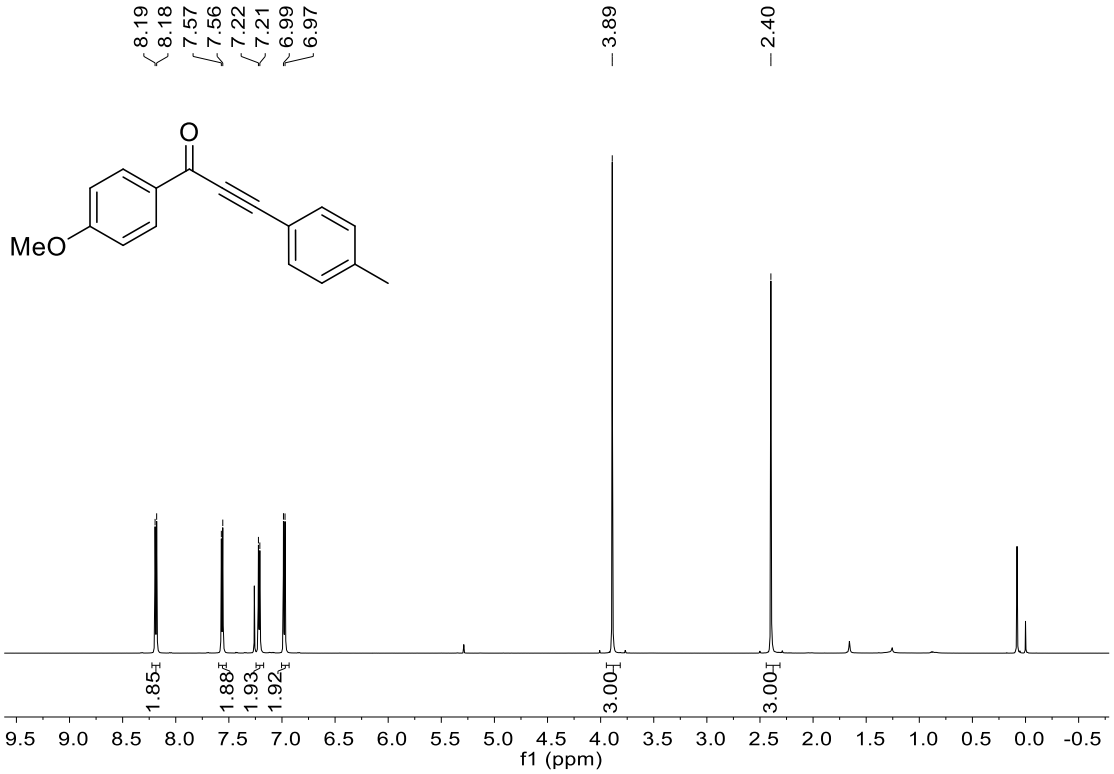
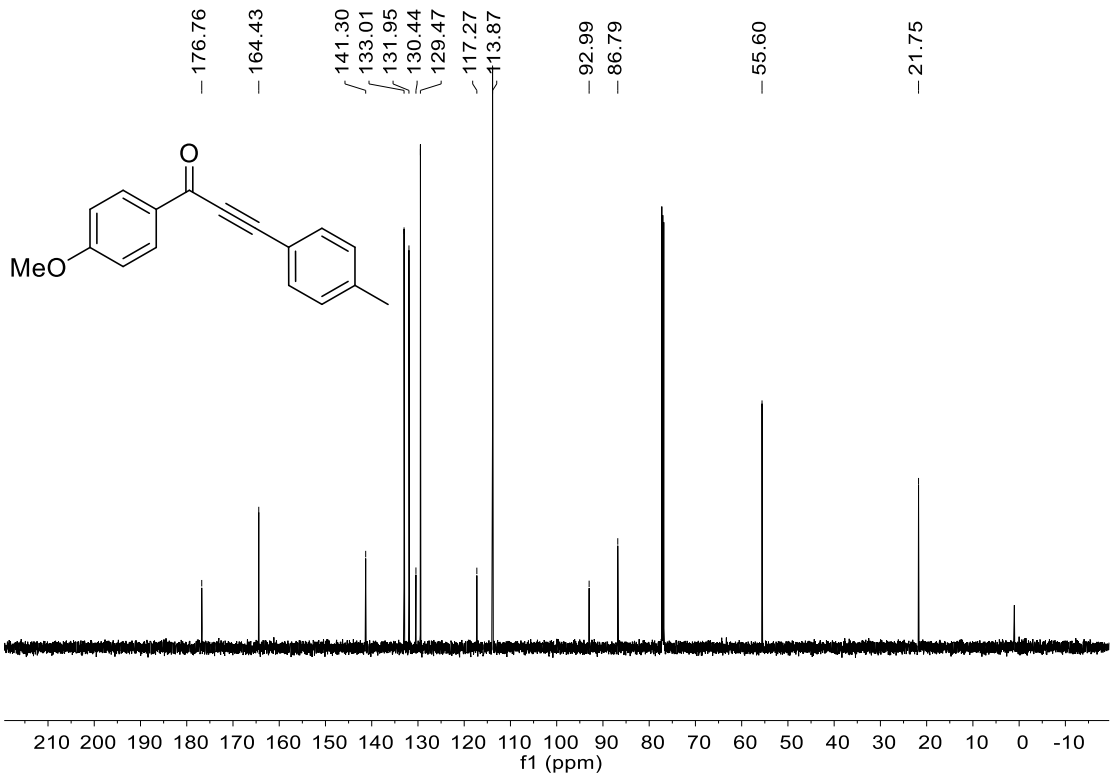


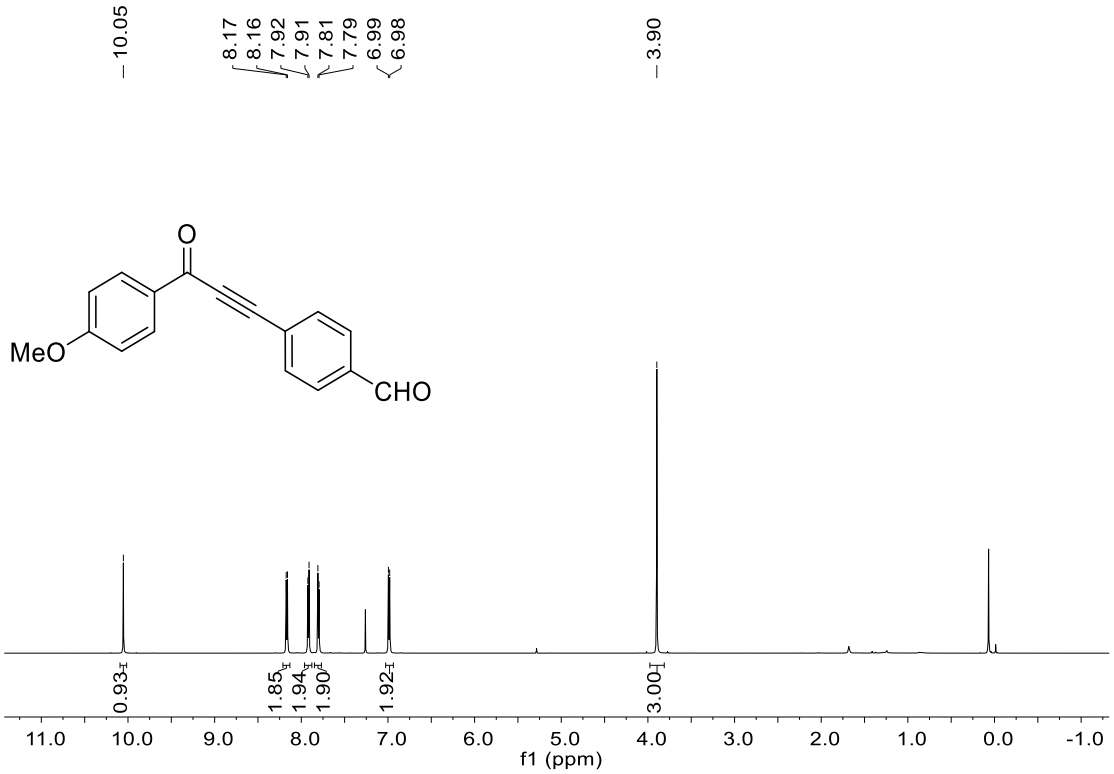
^{1}H NMR of compound 3ae



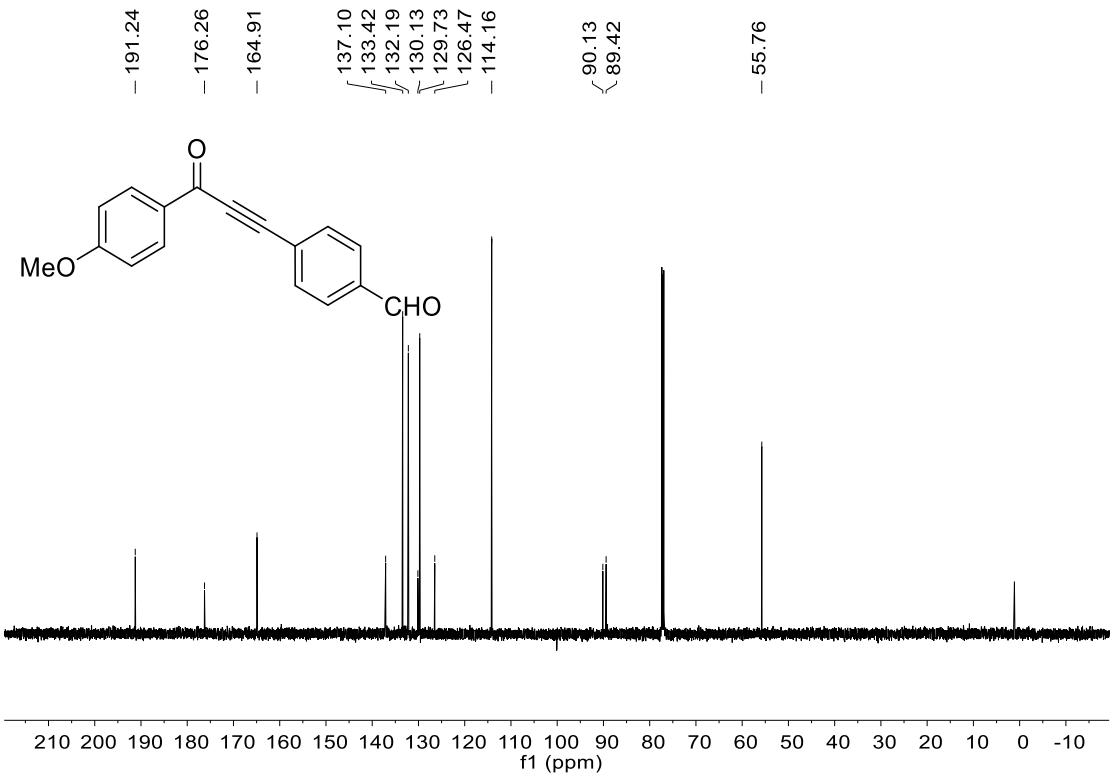
^{13}C NMR of compound 3ae



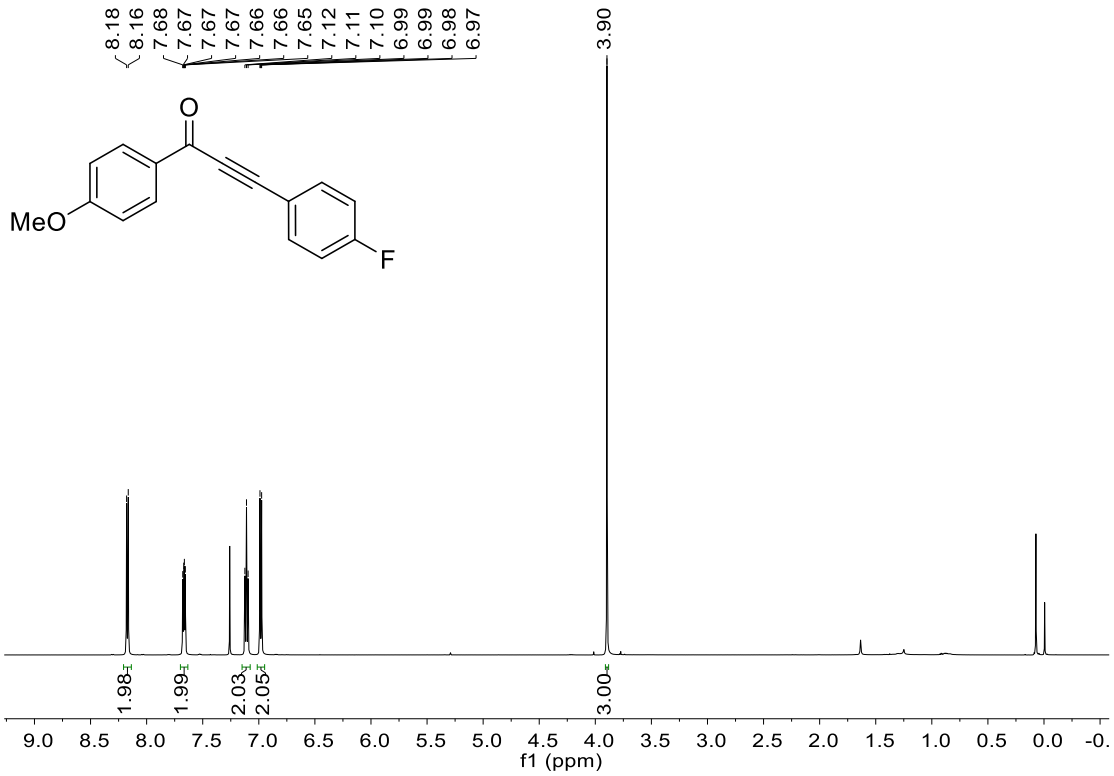
^{1}H NMR of compound 3af



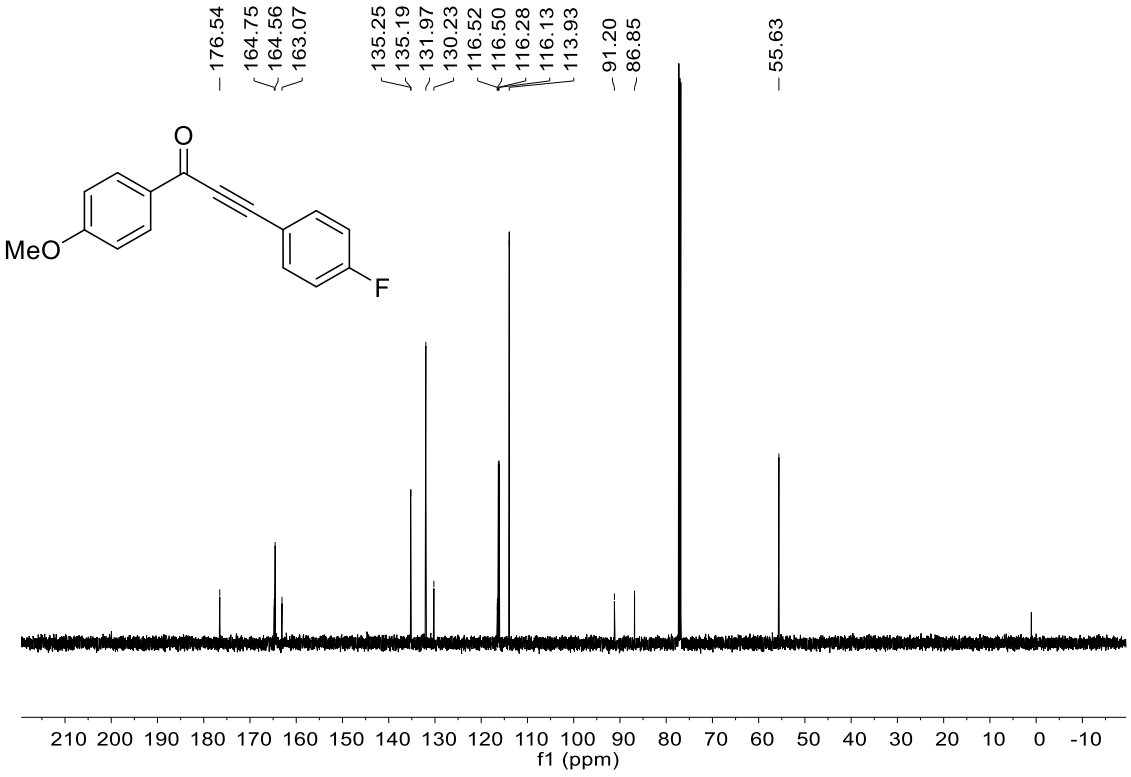
^{13}C NMR of compound 3af



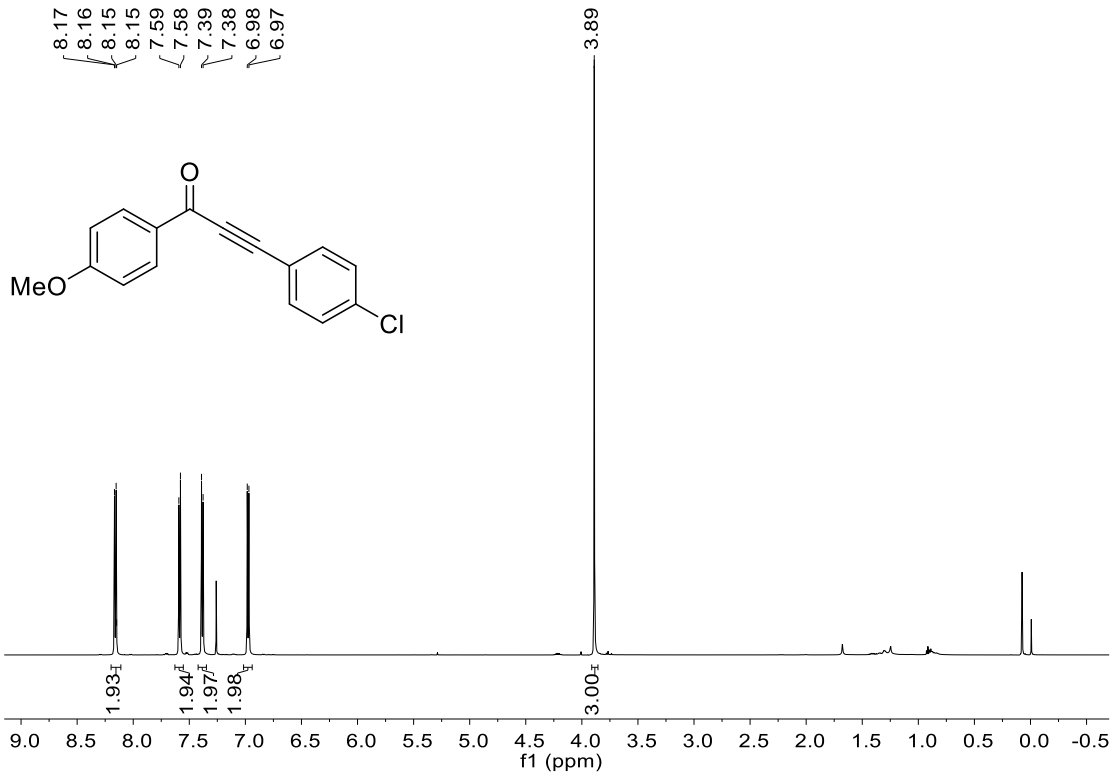
^{1}H NMR of compound 3ag



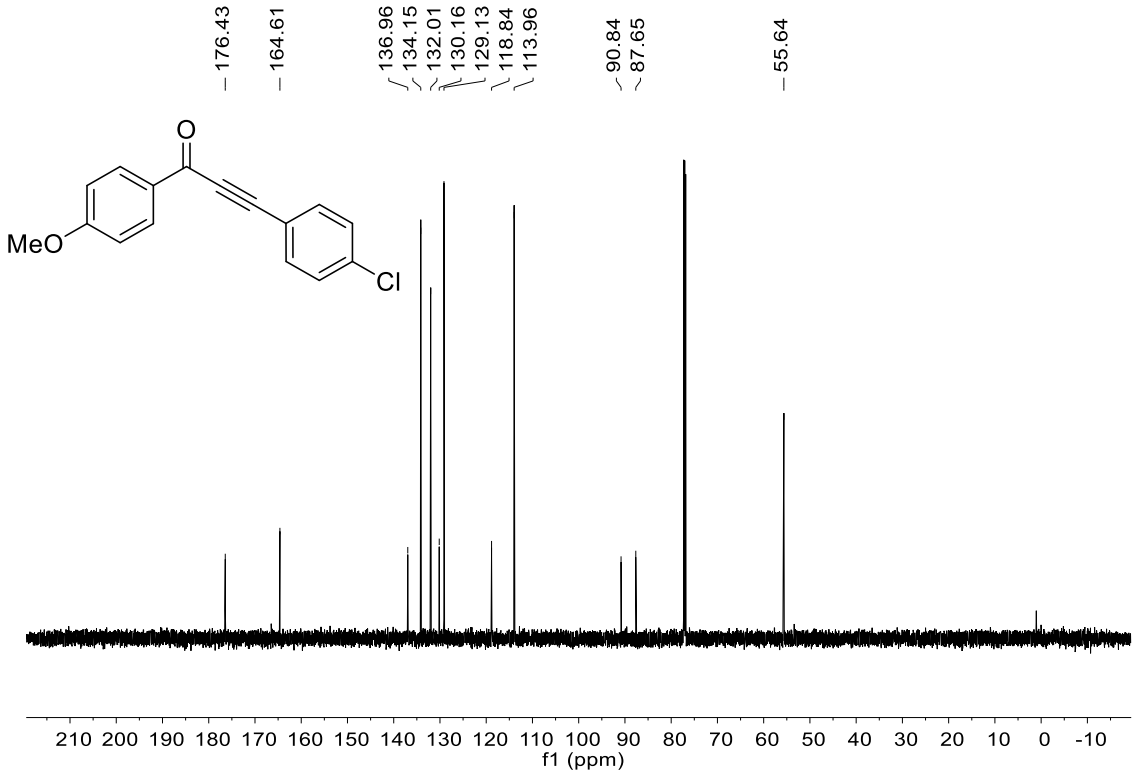
^{13}C NMR of compound 3ag



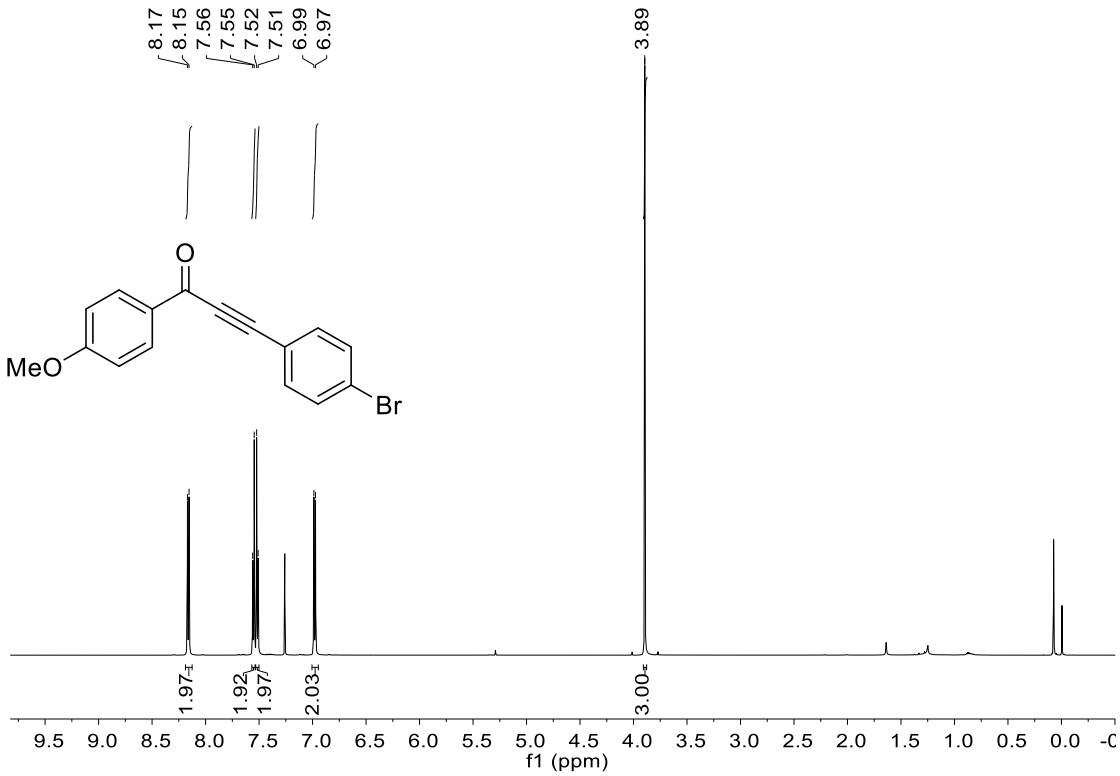
^{1}H NMR of compound 3ah



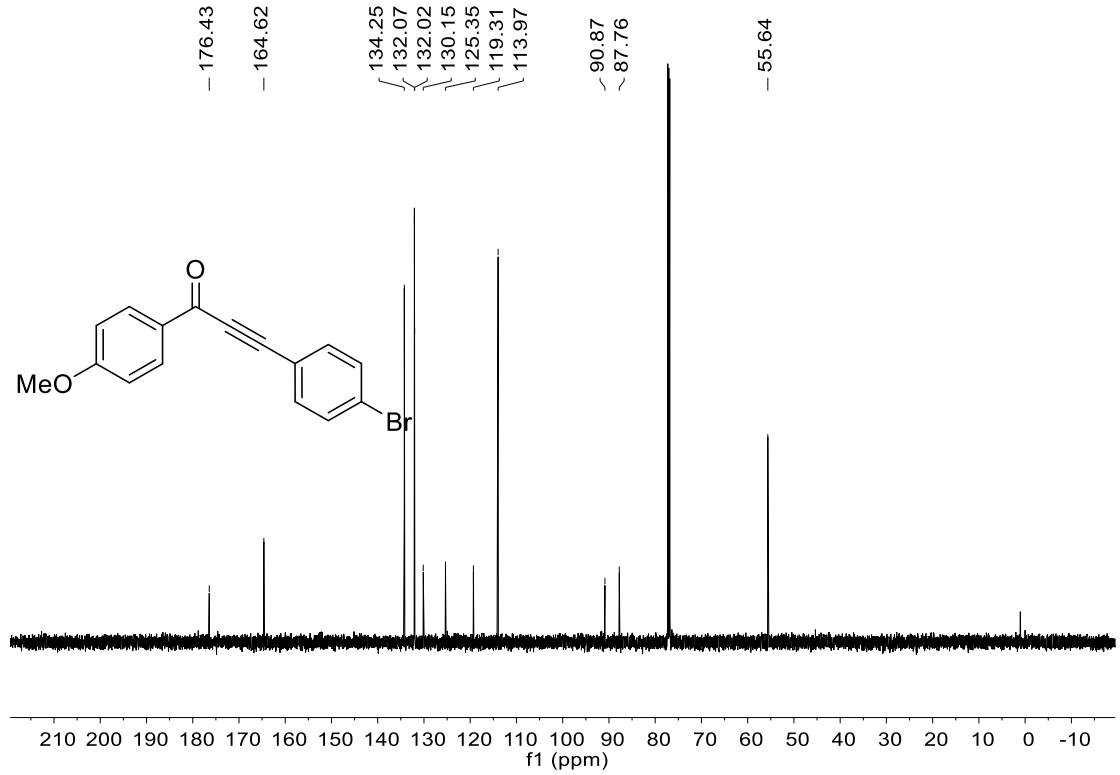
^{13}C NMR of compound 3ah



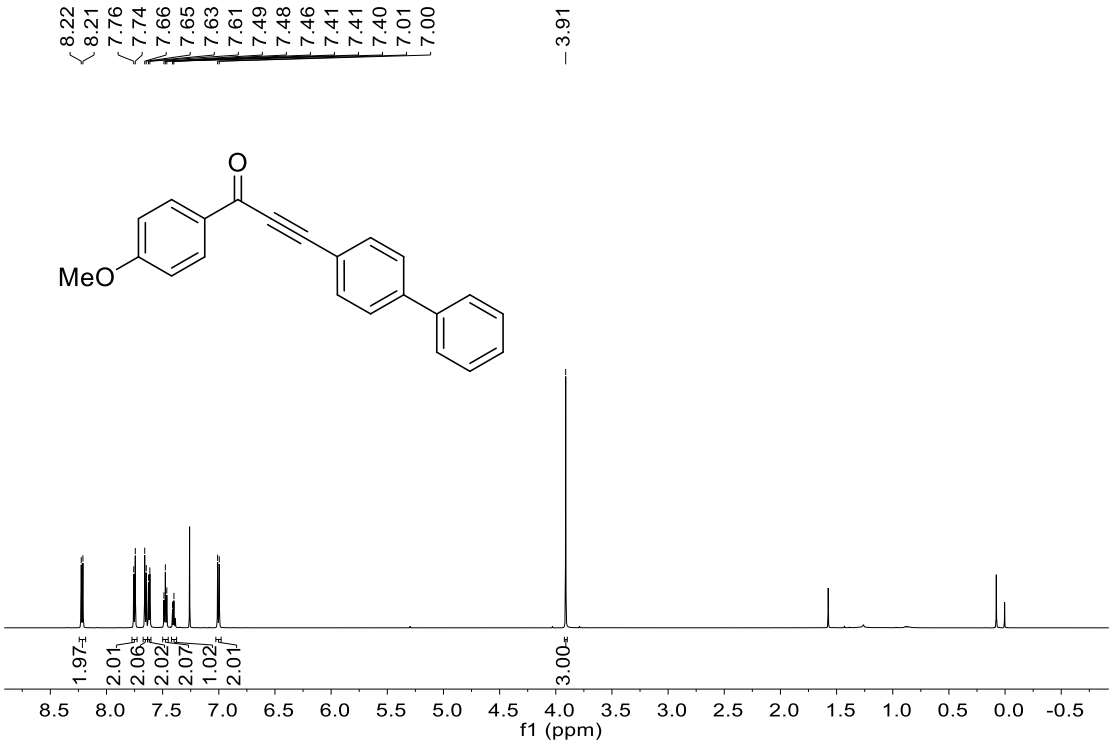
^{1}H NMR of compound 3ai



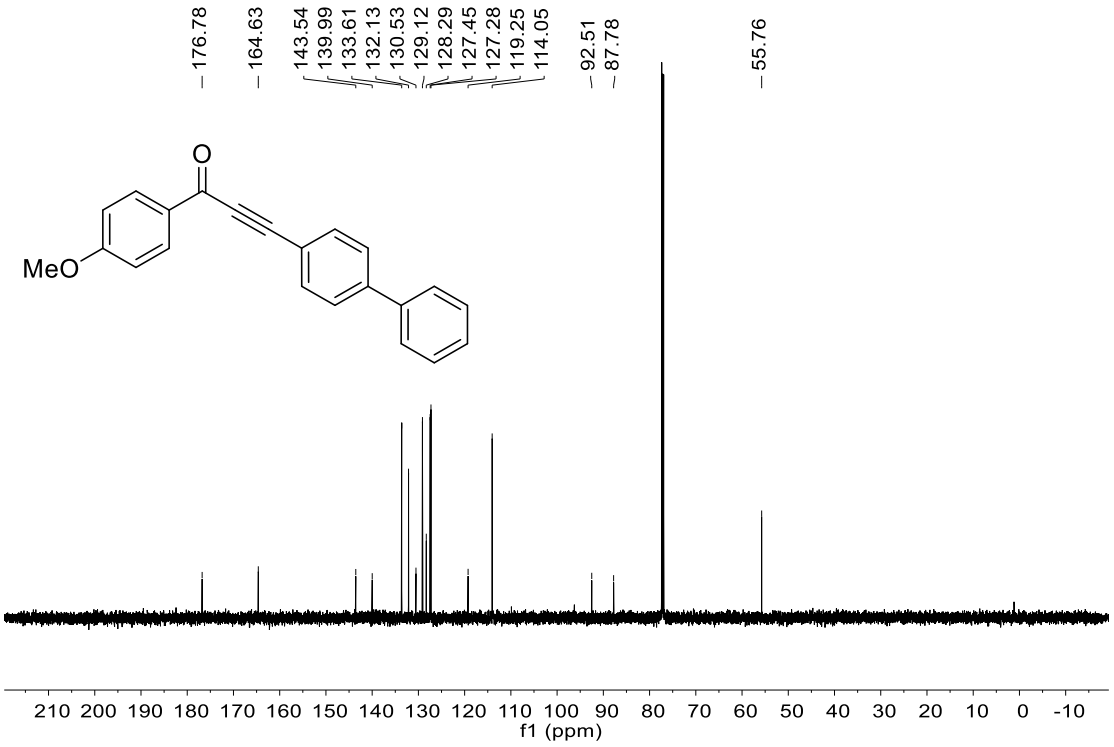
^{13}C NMR of compound 3ai



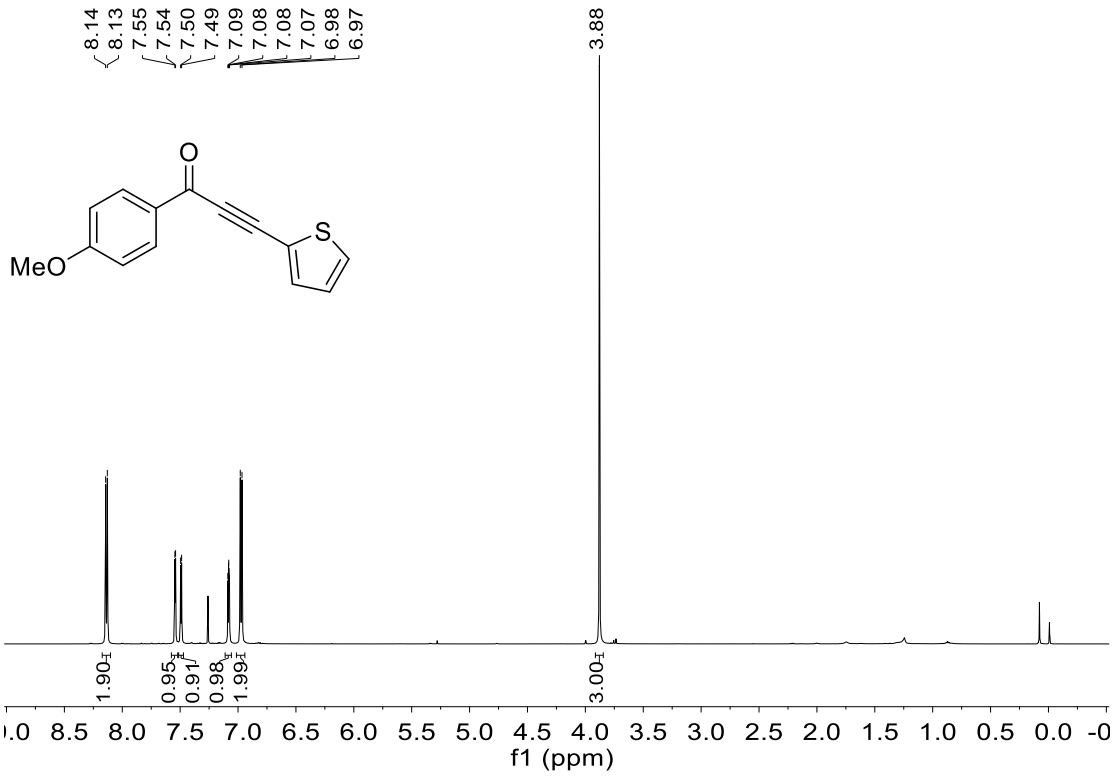
^{1}H NMR of compound 3aj



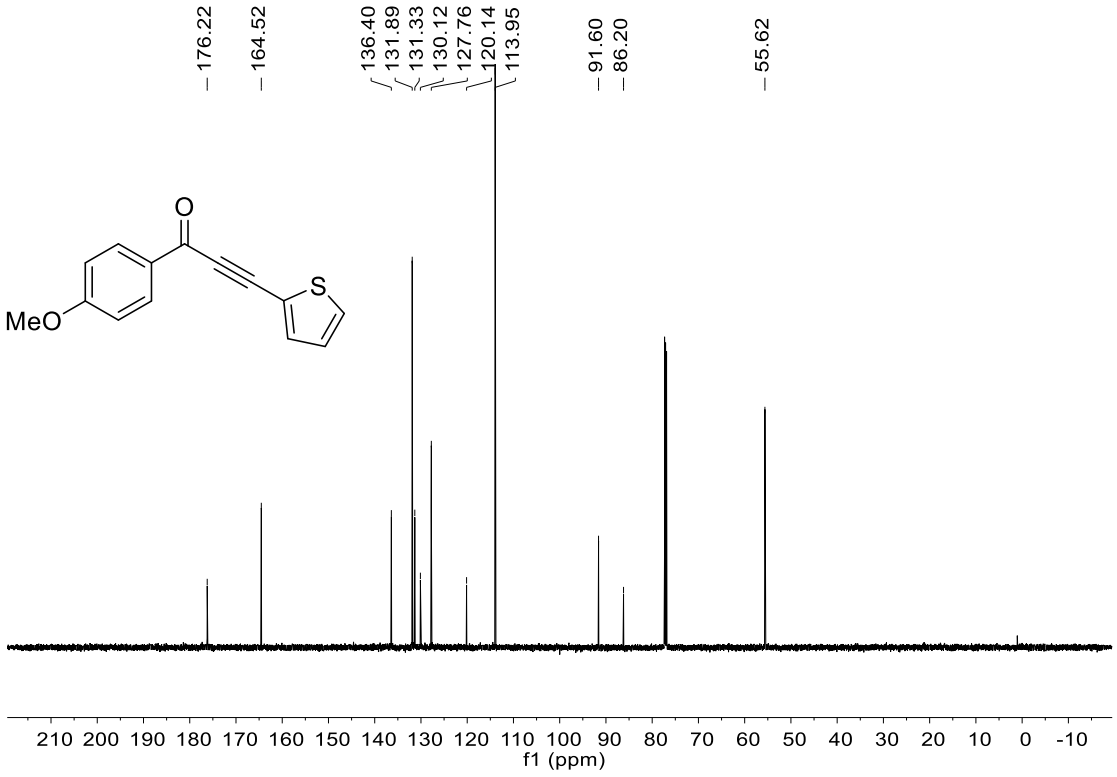
^{13}C NMR of compound 3ai



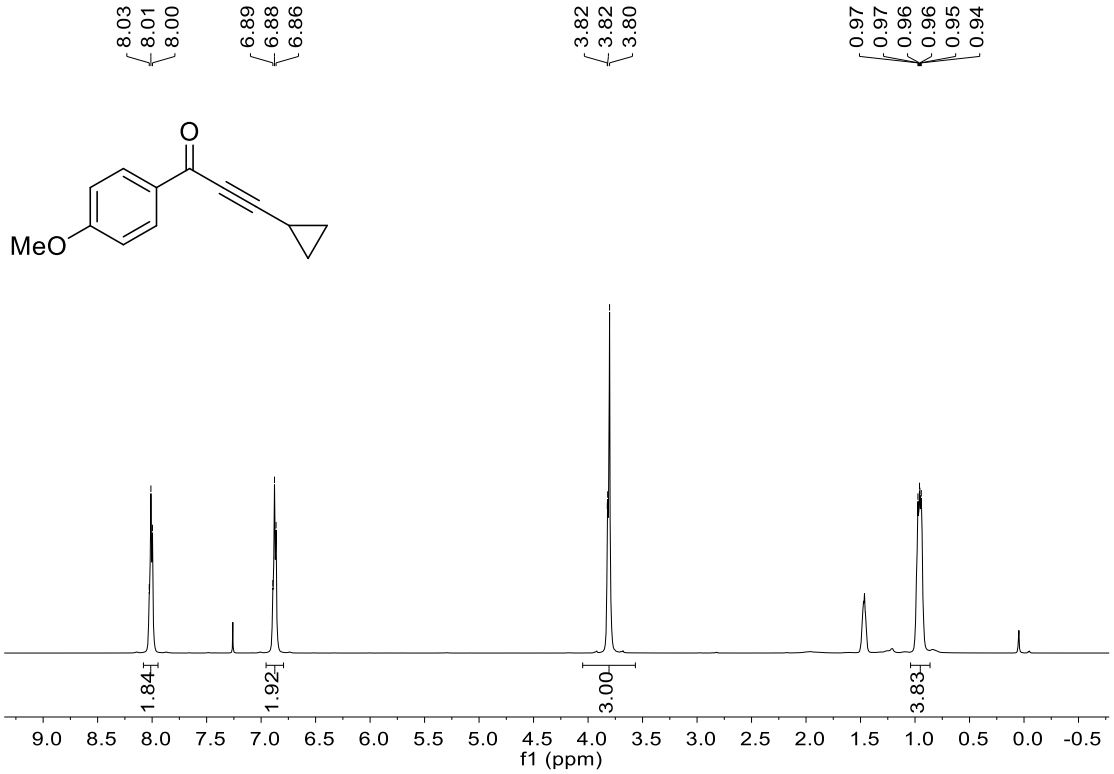
^{1}H NMR of compound 3ak



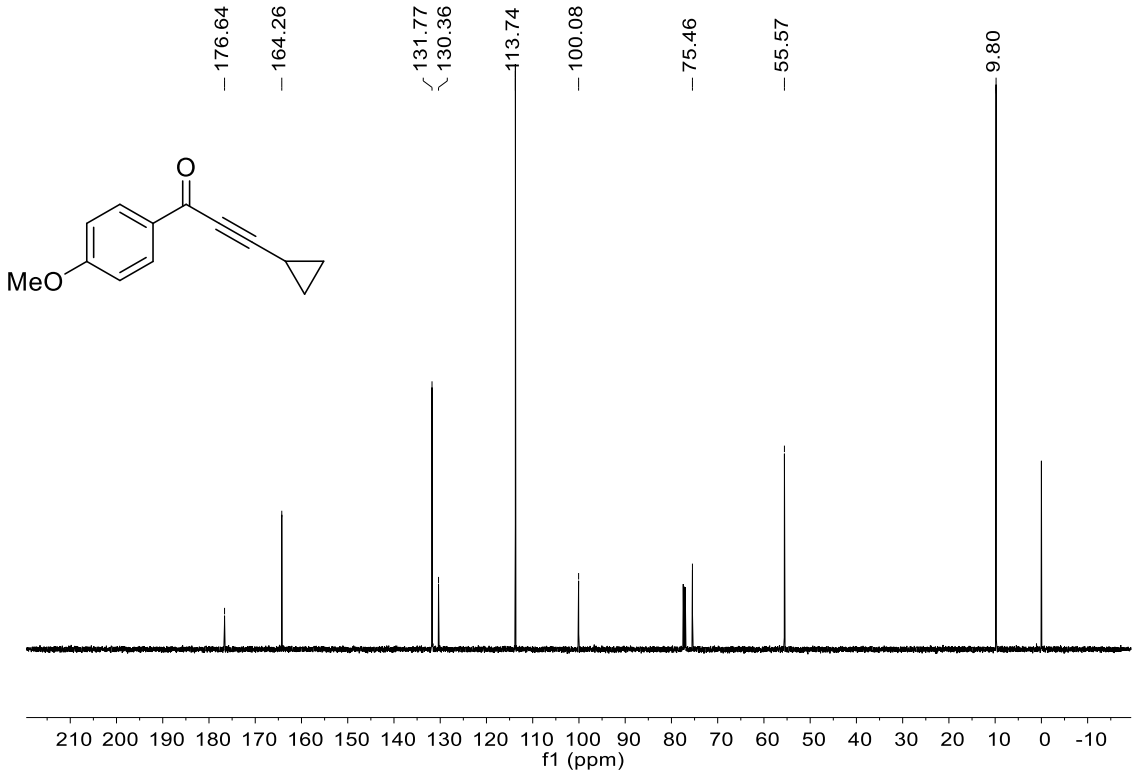
^{13}C NMR of compound 3ak



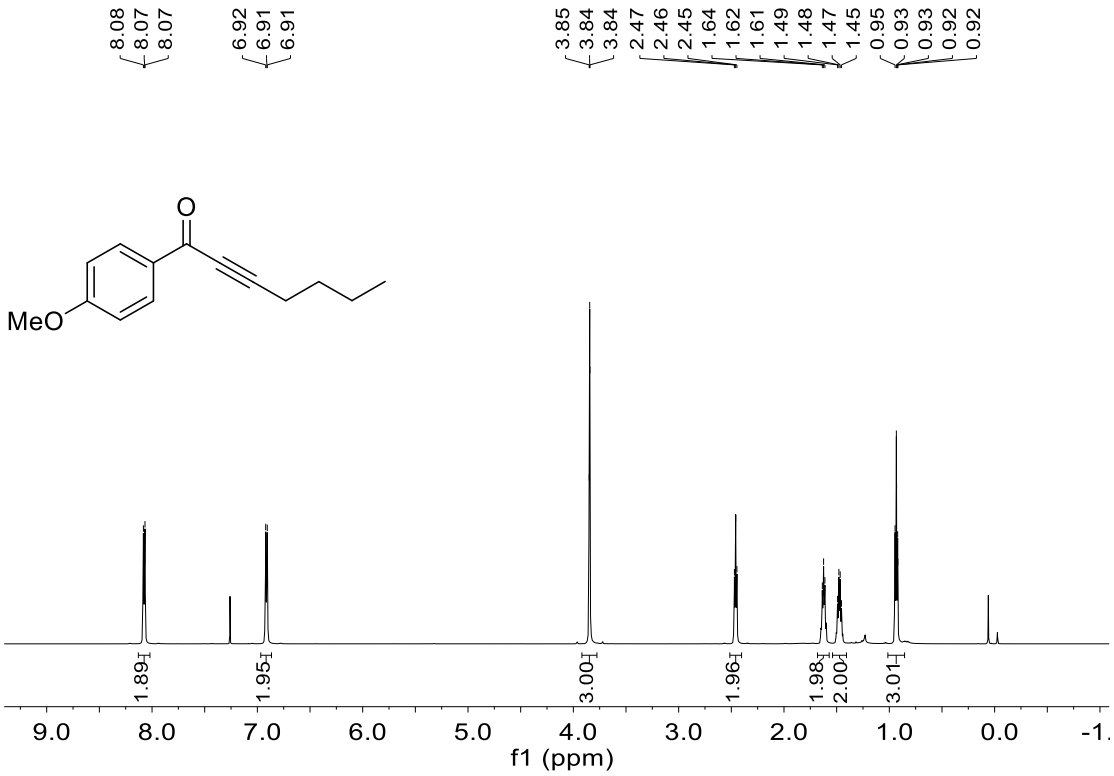
^{1}H NMR of compound 3al



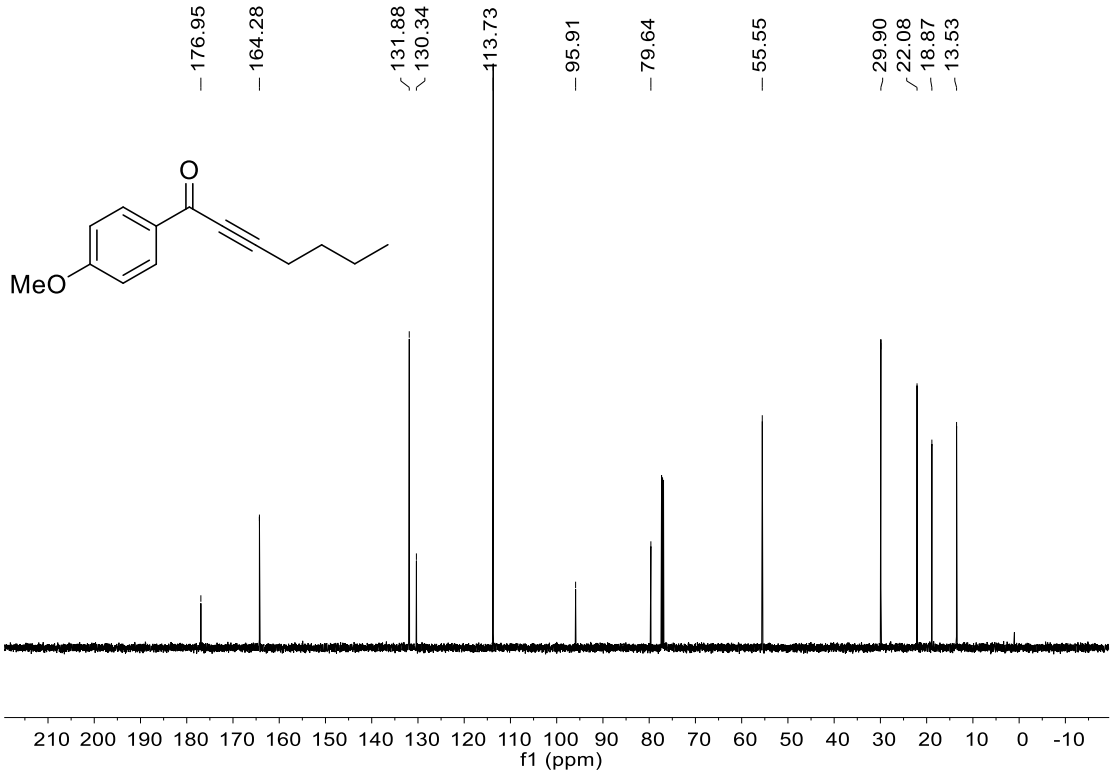
^{13}C NMR of compound 3al



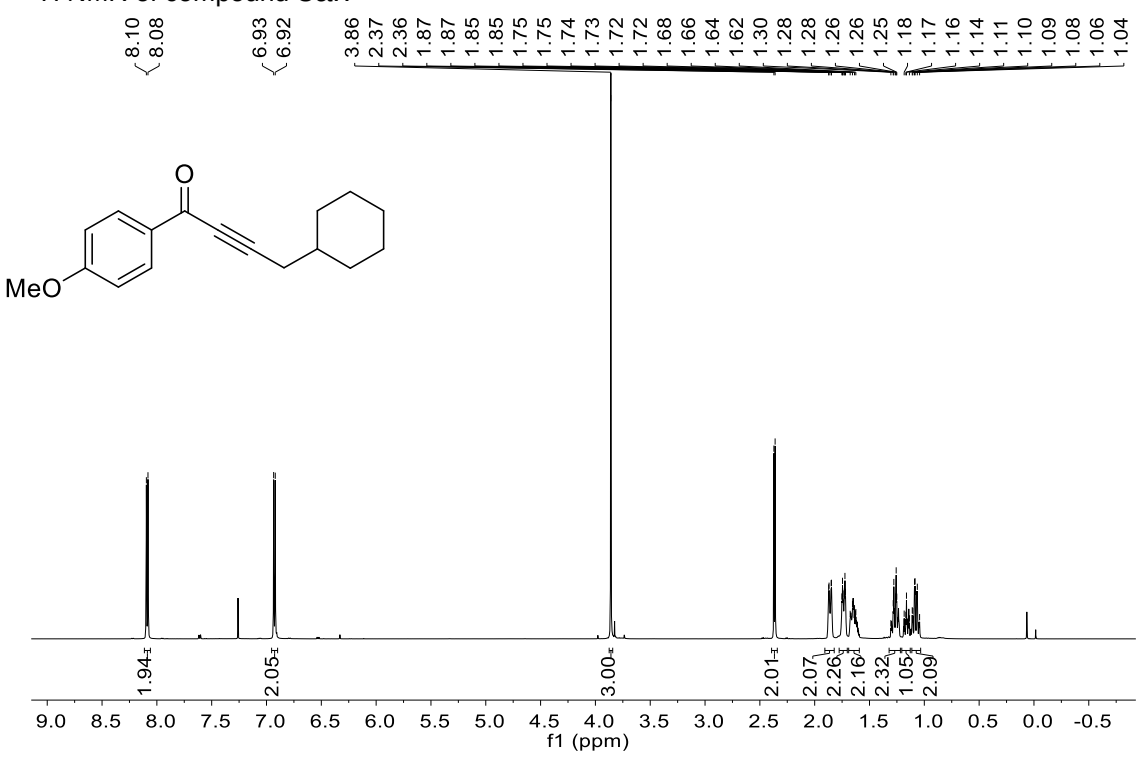
^{1}H NMR of compound 3am



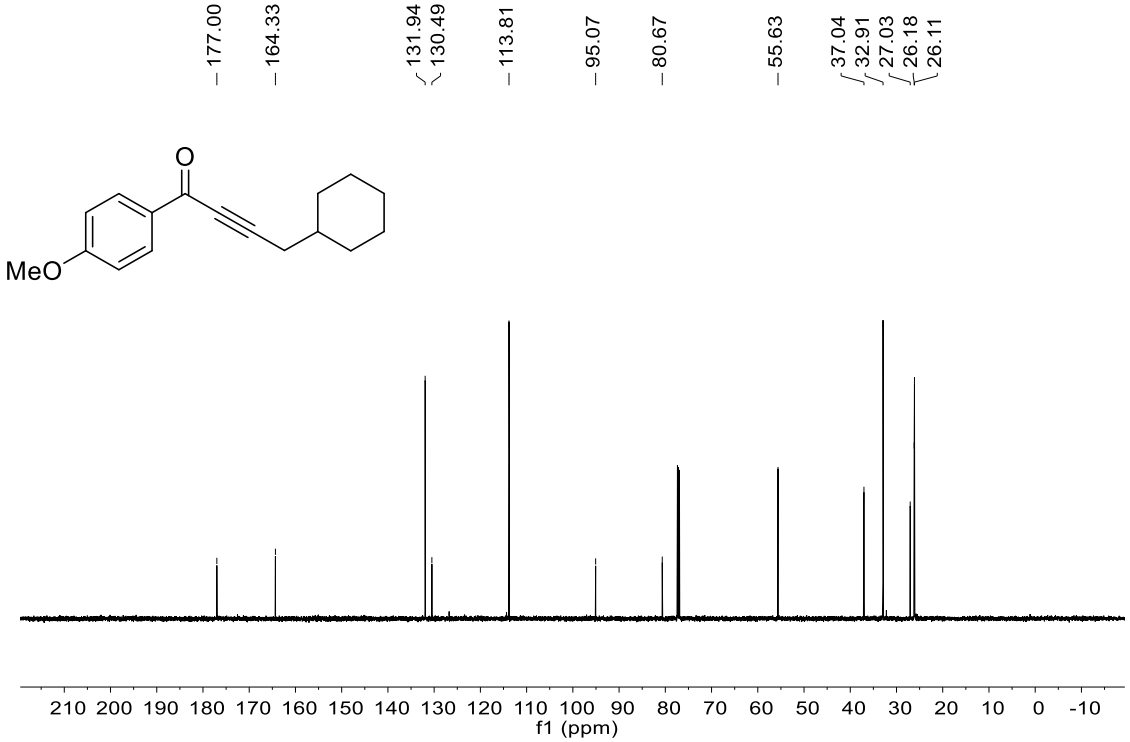
^{13}C NMR of compound 3am



^{1}H NMR of compound 3an



^{1}H NMR of compound 3an



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