Supplementary Information

1. Experimental Section

1.1 General considerations

The chemical reagents were purchased from TCI Shanghai Co. Ltd., Alfa Aesar China, Nine Ding Chemistry Shanghai Co. Ltd., Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, and used as received. Diethyl ether was distilled from sodium. DMF was distilled from drying over $CaSO_4$. Both diethyl ether and DMF were stored over 4Å molecular sieves under N_2. Purification of the compounds was carried out by flash chromatography on silica gel. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker ARX 400 spectrometer. The ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. CHN elemental analysis was performed on a Vario EL III Element Analyzer. The amount of Pd in the organic phase was quantified using an inductive coupled plasma atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC-mass spectrometry (GC-MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. HPLC-MS (ESI) was performed on a TSQ Quantum Access Max-HPLC (Thermo-Fisher).

1.2 X-ray Crystallography

Intensity data were collected on a Bruker SMARTAPEX II diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction included

absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by fullmatrix least-squares using SHELXS-97 (Sheldrick, 1990), with all non-hydrogen atoms refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. The crystal data and refinement details are given in S. Table 1.

S. Table 1 Crystal data and structure refinement for **L4-Pd**, **L1-Au**, and **L3-Au**

	L4-Pd	**L1-Au**	**L3-Au**
Empirical formula	$C_{27}H_{21}Cl_2I_1N_1P_2Pd_1$	$C_{28}H_{30}O_1Au_1Cl_1N_1P_2$ ($C_1F_3S_1O_3$)	$C_{33}H_{32}Au_1Cl_1N_1P_2$ ($C_1F_3S_1O_3$)
Formula weight	725.59	839.96	886.02
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_1/c$	*Pbca*
a (Å)	9.2622(7)	18.0468(4)	17.0157(4)
b (Å)	18.5110(15)	13.1909(3)	15.2244(4)
c (Å)	9.5911(8)	14.8731(3)	27.1217(7)
α (°)	90	90	90
β (°)	112.413(2)	112.0830	90
γ (°)	90	90	90
V (Å^3)	1520.2(2)	3280.86(12)	7026.0(3)
Z	2	4	8
d_{calc} (Mg/m^3)	1.585	1.701	1.675
μ (Mo-K_α) (mm^{-1})	1.922	4.778	4.465
T (K)	296(2)	296(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073
Total reflections	17622	37403	78591
Unique reflections (R_{int})	5326 (0.0482)	5778 (0.0378)	6180 (0.0753)
R_1 [I>2σ(*I*)]	0.0727	0.0460	0.0321
wR_2 (all data)	0.2215	0.1386	0.0797
F(000)	706	1648	3488
Goodness-of-fit on F^2	1.062	1.038	1.033

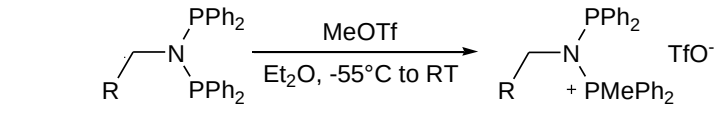
1.3 General procedures for Pd-catalyzed carbonylative Sonogashira reaction with the involvement of L1

In a typical experiment, the commercial precatalyst $PdCl_2(CH_3CN)_2$ (0.0025 mmol) was mixed with 3 mL DMF, **L1** (0.15 mmol), iodobenzene (5 mmol), phenylacetylene (6

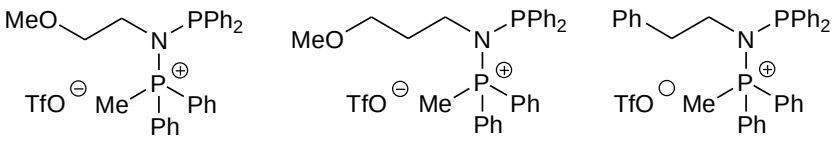
mmol), and Et_3N (7.5 mmol) sequentially in a 50 mL sealed Teflon-lined stainless steel autoclave. After flushing three times with CO, the autoclave was purged with CO at a pressure of 1.0 MPa. The obtained mixture in the autoclave was stirred vigorously at 90 ^oC for 1.5 h. Upon completion, the reaction mixture was cooled to room temperature and then extracted with diethyl ether (3 mL × 3). The ether fractions were combined, and then analyzed by GC to determine the conversions (1-dodecane as internal standard) and the selectivities (normalization method). The structures of obtained products were further confirmed by GC-Mass. The structures of the obtained products were further confirmed by ^{1}H-NMR and ^{13}C-NMR. During the recycling uses, the remaining slurry containing the Pd-catalyst, [Bmim]BF_4, and the formed ammonium salt (Et_3N·HI) obtained after extraction by diethyl ether was used directly without further treatment for the next run. Due to the stoichiometric consumption of the base, Et_3N (7.5 mmol) was added additionally per pass. All manipulations were conducted in air.

1.4 Synthesis and characterization

The diphosphinoamines were prepared according to the methods published in Ref. 13(a,b). The general method for the preparation of **L1~L3** is as follows.



Diphosphinoamines **L1 ~ L3**

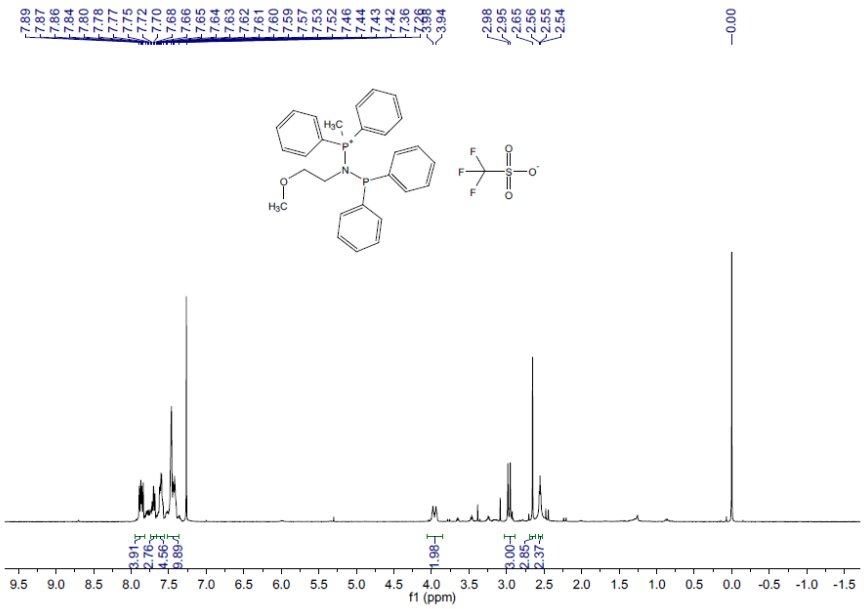


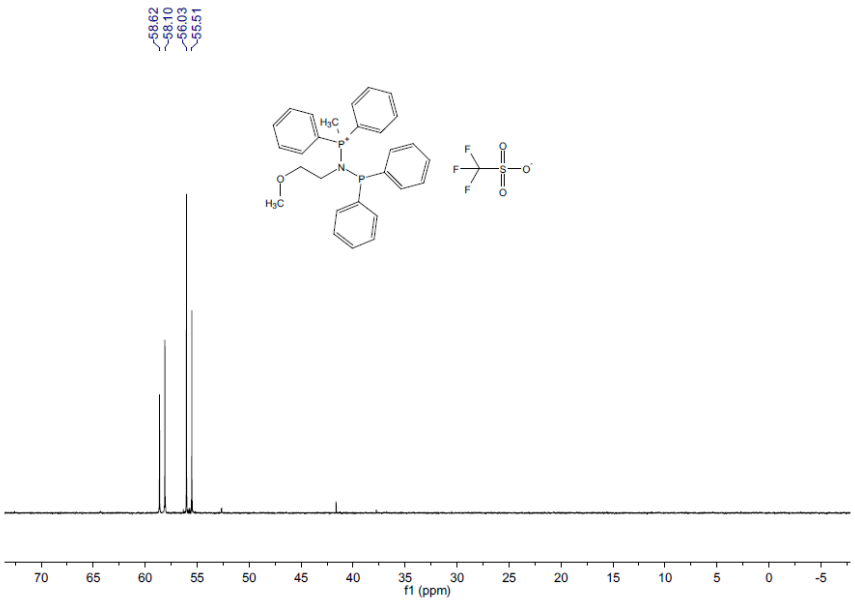
L1 **L2** **L3**

A solution of the corresponding diphosphinoamine (5 mmol, 1 equiv) in diethyl ether (75 mL) was added dropwise to the solution of MeOTf (5 mmol, 1 equiv) in diethyl ether (20 mL) during 30 min at -55 ℃ under N_2 atmosphere. The reaction

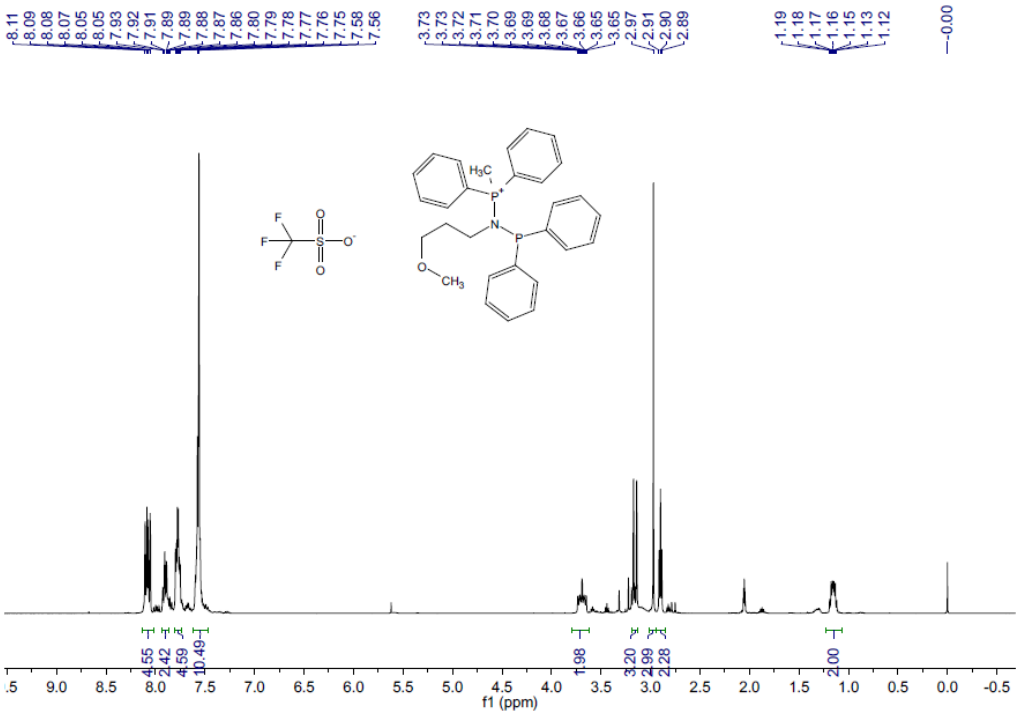
mixture was stirred at -55 ℃ for 1 h and then warmed up to room temperature overnight. After filteration and drying in vacuo, the ligand was collected as a white solid.

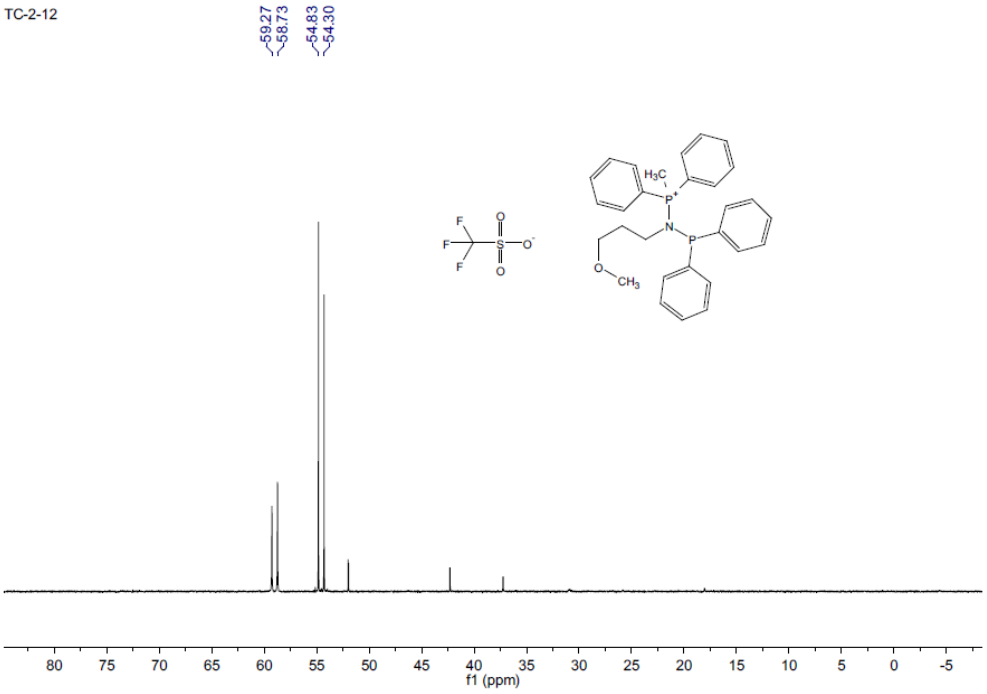
L1 was obtained in 92% yield as a white solid. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.89-7.84 (4H, m), 7.70 (2H, t, $^{3}J_{HH}$ = 8 Hz), 7.62-7.57 (4H, m), 7.46-7.42 (10H, m), 3.96 (2H, m), 2.97 (3H, d, $^{2}J_{PH}$ = 12 Hz), 2.65 (3H, s), 2.55 (2H, t, $^{3}J_{HH}$ = 4 Hz). ^{31}P NMR (δ, ppm, $CDCl_3$): 58.5(d, $^{2}J_{PP}$ = 83Hz), 55.8(d, $^{2}J_{PP}$ = 83Hz). HPLC-MS (ESI) for $C_{28}H_{30}NOP_2^+$ ($[M]^+/z$): Found 458.2 (Exact mass calcd. 458.2).



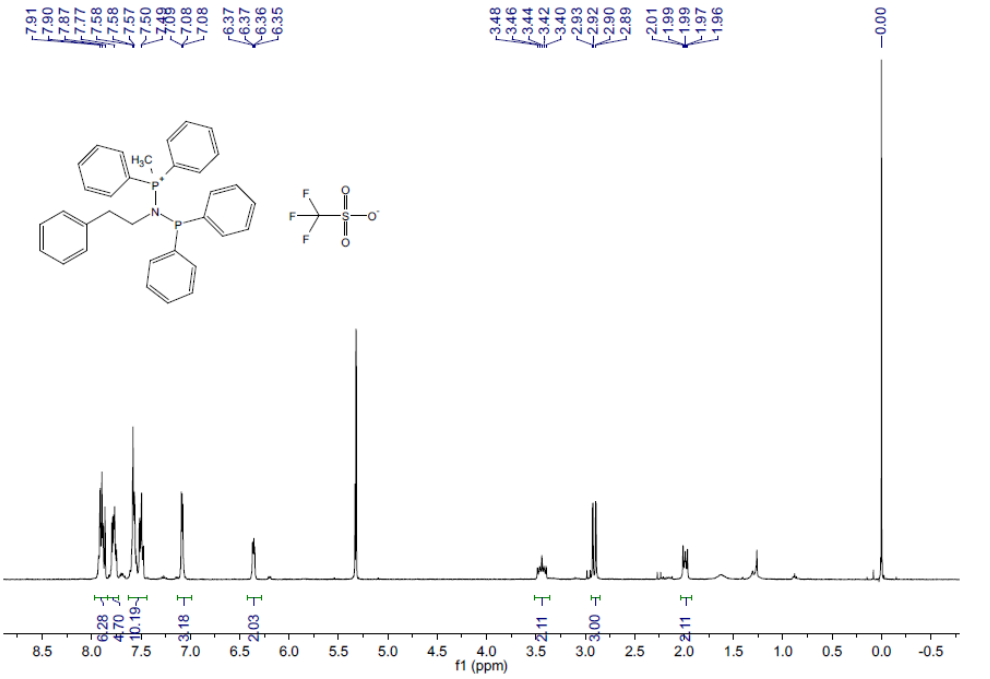


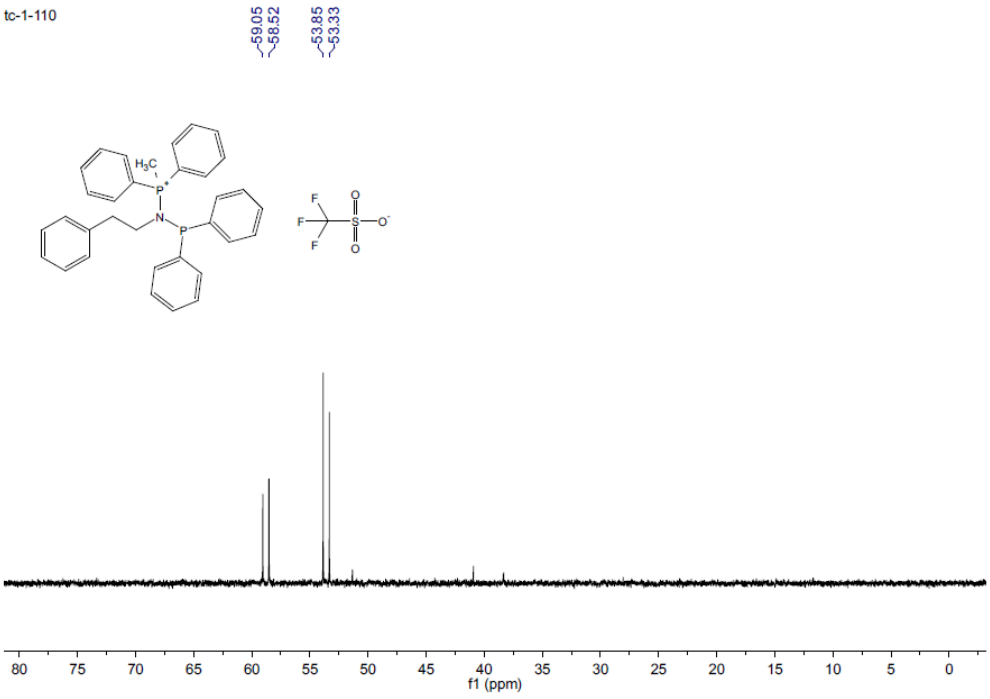
L2 was obtained in 82% yield as a white solid. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.11-8.05 (4H, m), 7.93-7.89 (2H, m), 7.80-7.75 (4H, m), 7.60-7.55 (10H, m), 3.73-3.65 (2H, m), 3.16 (3H, d, $^{2}J_{PH}$=12 Hz), 2.97 (3H, s), 2.90 (2H, t, $^{3}J_{HH}$ = 4 Hz),1.19-1.12 (2H, m). ^{31}P-NMR (δ, ppm, $CDCl_3$): 59.0 (d, $^{2}J_{PP}$ = 86 Hz), 54.6 (d, $^{2}J_{PP}$ = 86 Hz). HPLC-MS (ESI) for $C_{29}H_{32}NOP_2^+$ $(M)^+/z$): Found 472.2 (Exact mass calcd. 472.2).

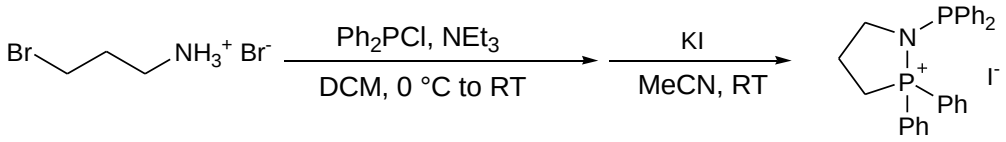




L3 was obtained in 86% yield as a white solid. ^{1}H NMR (δ, ppm, CD_2Cl_2): 7.93-7.86 (6H, m), 7.80-7.75 (4H, m), 7.59-7.54 (6H, m), 7.52-7.47 (4H, m), 7.09-7.08 (3H, m), 6.37-6.35 (2H, m), 3.48-3.40 (2H, m), 2.91 (3H, dd, $^{2}J_{PH}$ = 4, 12 Hz), 2.01-1.96 (2H, m). ^{31}P NMR (δ, ppm, CD_2Cl_2): 58.8(d, $^{2}J_{PP}$ = 86 Hz), 53.6(d, $^{2}J_{PP}$ = 86 Hz). HPLC-MS (ESI) for $C_{33}H_{32}NP_2^+$ $(M]^+/z$): Found 504.2 (Exact mass calcd. 504.2).

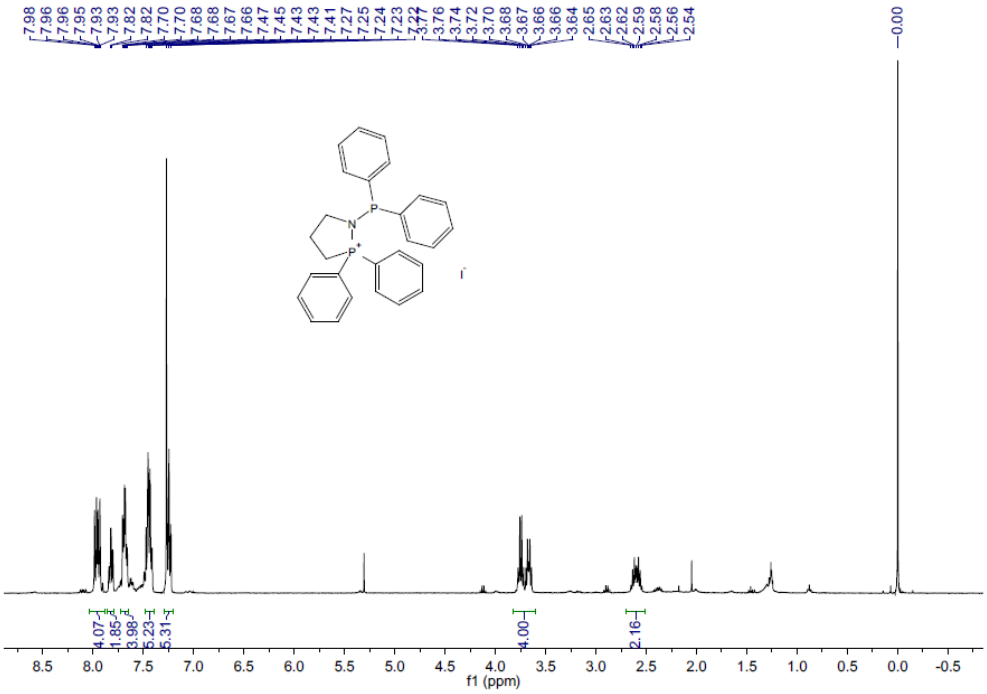


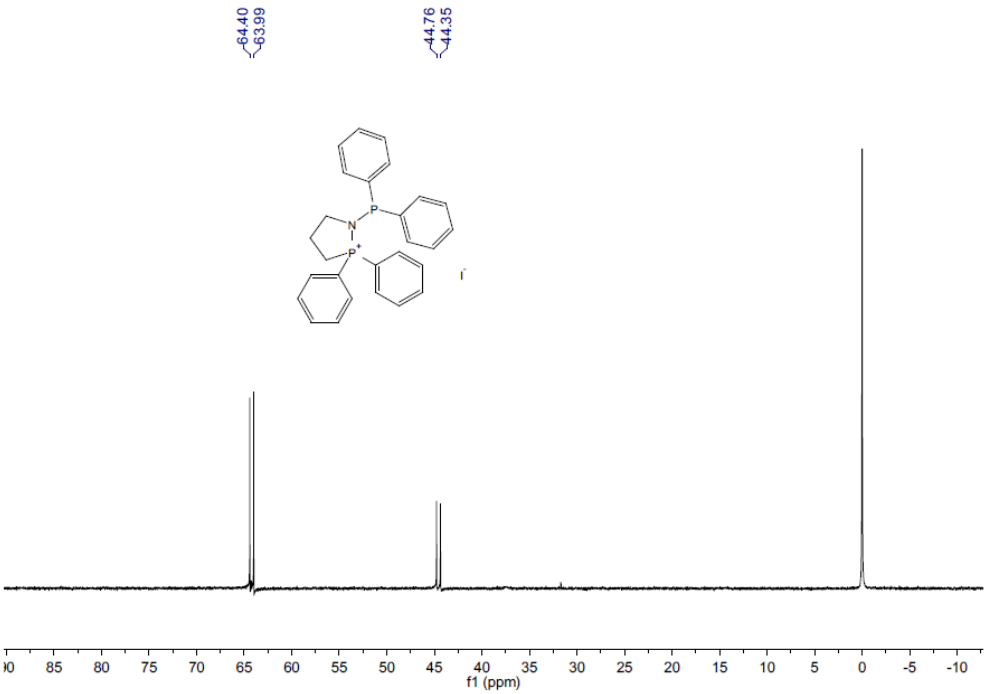




L4

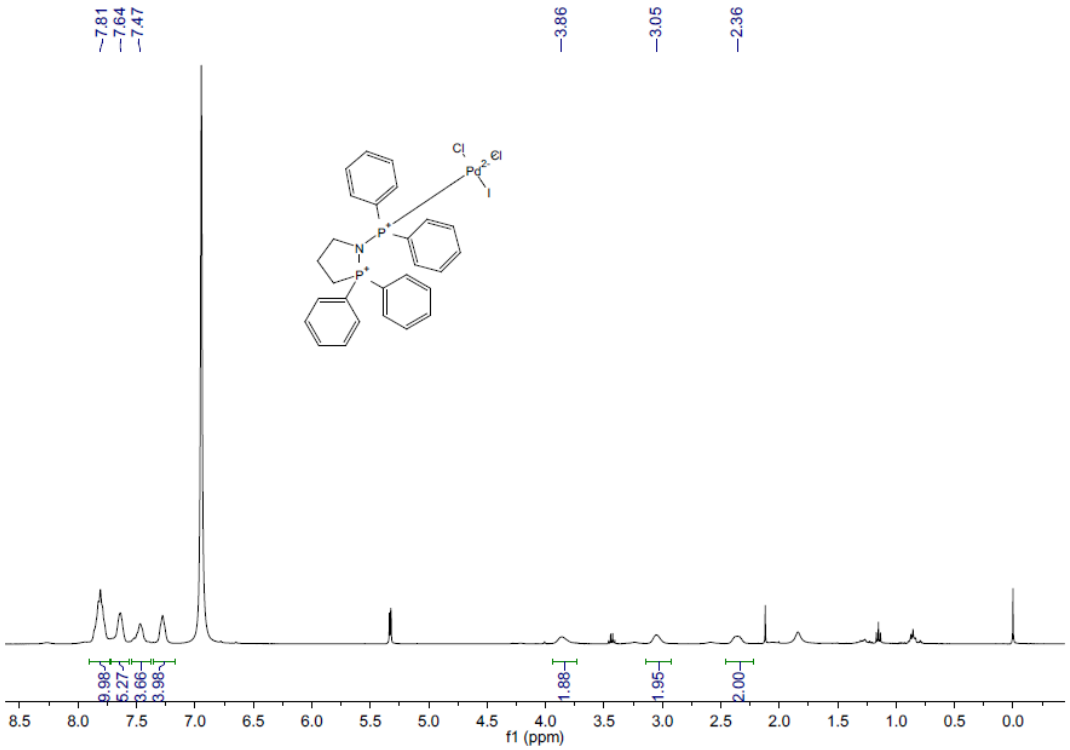
L4 was obtained in 70% yield as a white solid. To a suspension of 3-bromopropylamine hydrobromide (5 mmol, 1 equiv) in dichloromethane (30 mL), a solution of triethylamine (15.5 mmol, 3.1 equiv) in dichloromethane (10 mL) was added dropwise under vigorous stirring in N_2 atmosphere. After 20 min, the mixture was cooled to 0 ℃ and then a solution of diphenylchlorophosphine (10.1 mmol, 2.02 equiv) in dichloromethane (15 mL) was added dropwise during 30 min at 0 ℃. The reaction mixture was stirred at 0 ℃ for 1 h and then warmed up to room temperature overnight. The solvent was removed in vacuo. The residue was dissolved in tetrahydrofuran (30 mL) to filter off triethylamine hydrohalide. After removal of tetrahydrofuran in vacuo, the collected residue was dissolved in acetonitrile and then excess KI was added. After fifltration, the filtrate was evaporated in vacuo. The obtained residue was then dissolved in dichloromethane and the precipitates were filtered off. The solution was dried in vacuoto give the residue which was crystallized in acetonitrile-ethyl acetate. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.98-7.93 (4H, m), 7.82-7.80 (2H, m), 7.70-7.67 (4H, m), 7.47-7.41 (5H, m), 7.27-7.22 (5H, m), 3.77-3.64 (4H, m), 2.65-2.54 (2H, m). ^{31}P NMR (δ, ppm, $CDCl_3$): 64.2 (d, $^{2}J_{PP}$ = 66 Hz), 44.4 (d, $^{2}J_{PP}$ = 66 Hz).

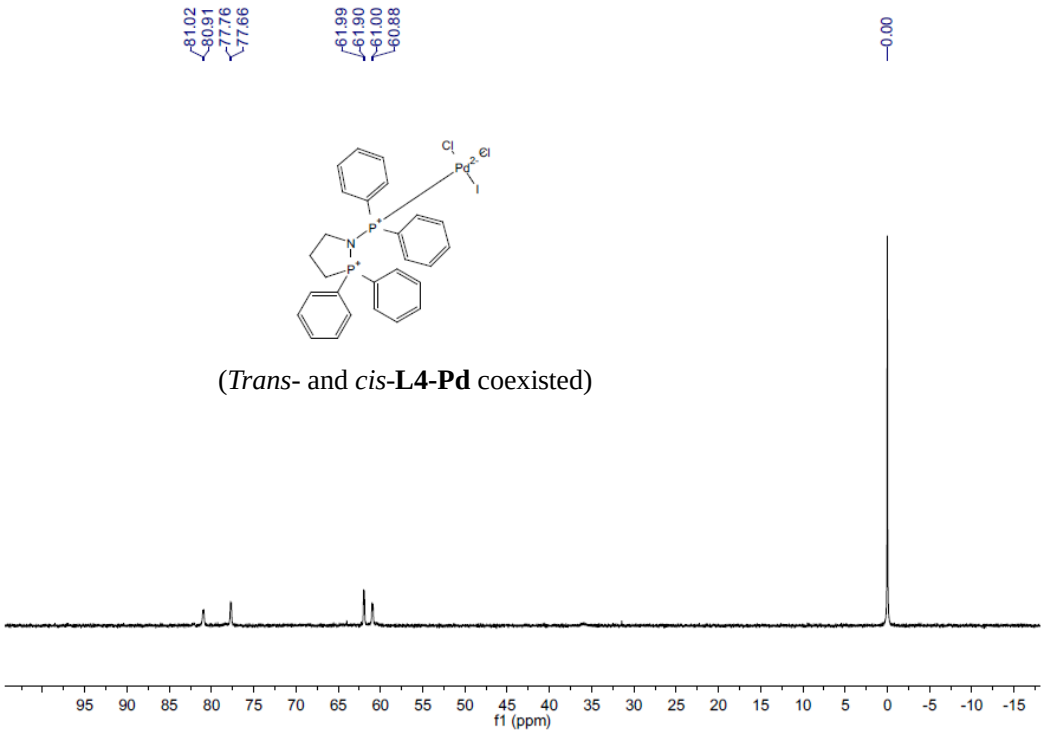




L4-Pd: To a solution of $PdCl_2(CH_3CN)_2$ (0.2 mmol, 1 equiv) dissolved in dry dichloromethane (4 mL) was added **L4** (0.2 mmol, 1 equiv). The obtained mixture was stirred at room temperature for 1 h. Then the reaction solution was treated with diethyl ether (50 mL) to precipitate a brown solid in 93% yield as the product of **L4-Pd**. ^{1}H

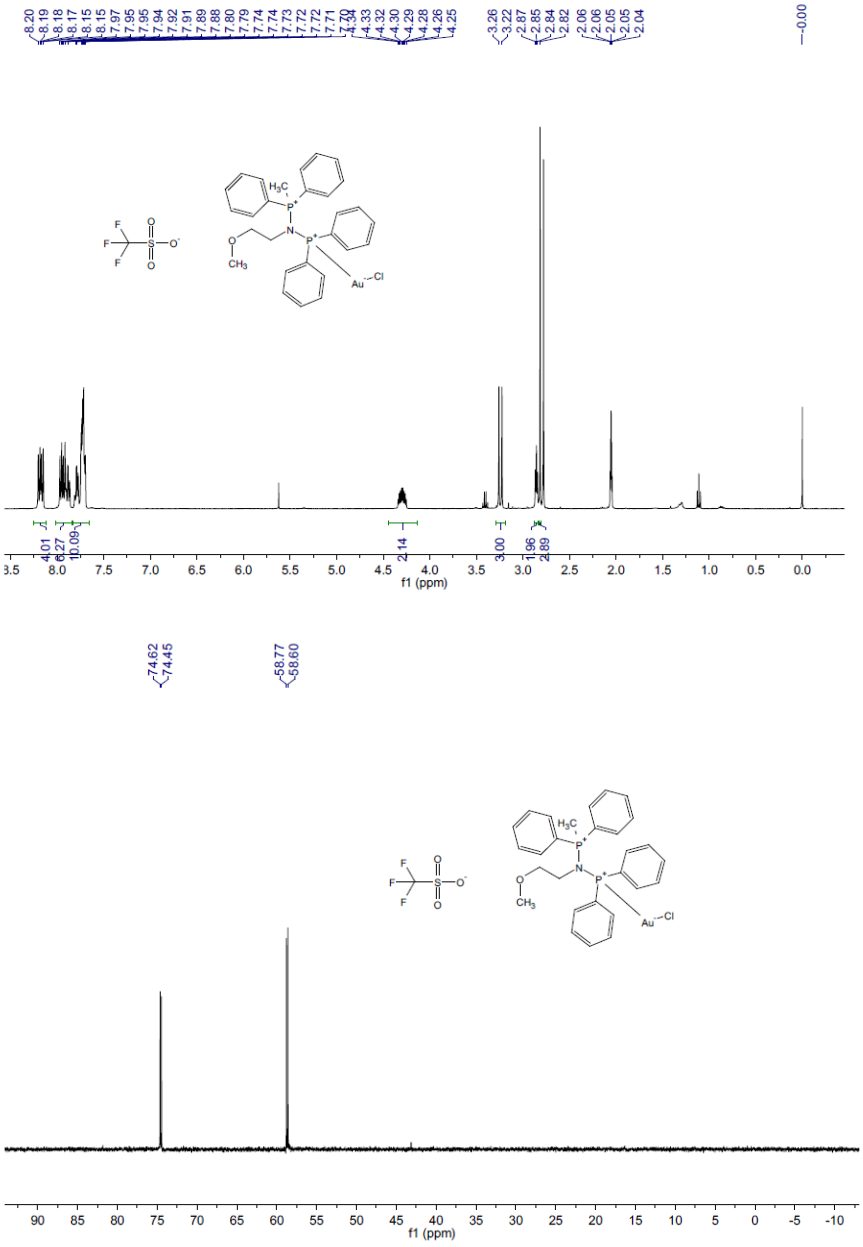
NMR (δ, ppm, $CDCl_3$): 7.81 (9H, br), 7.64 (5H, br), 7.47 (3H, br), 7.28 (3H, br), 3.88 (2H, br), 3.05 (2H, br), 2.36 (2H, br). ^{31}P NMR (δ, ppm, $CDCl_3$): 80.97 (d, $^{2}J_{PP}$ = 19 Hz), 77.70 (d, $^{2}J_{PP}$ = 16 Hz), 61.95 (d, $^{2}J_{PP}$ = 16 Hz), 60.94 (d, $^{2}J_{PP}$ = 19 Hz).



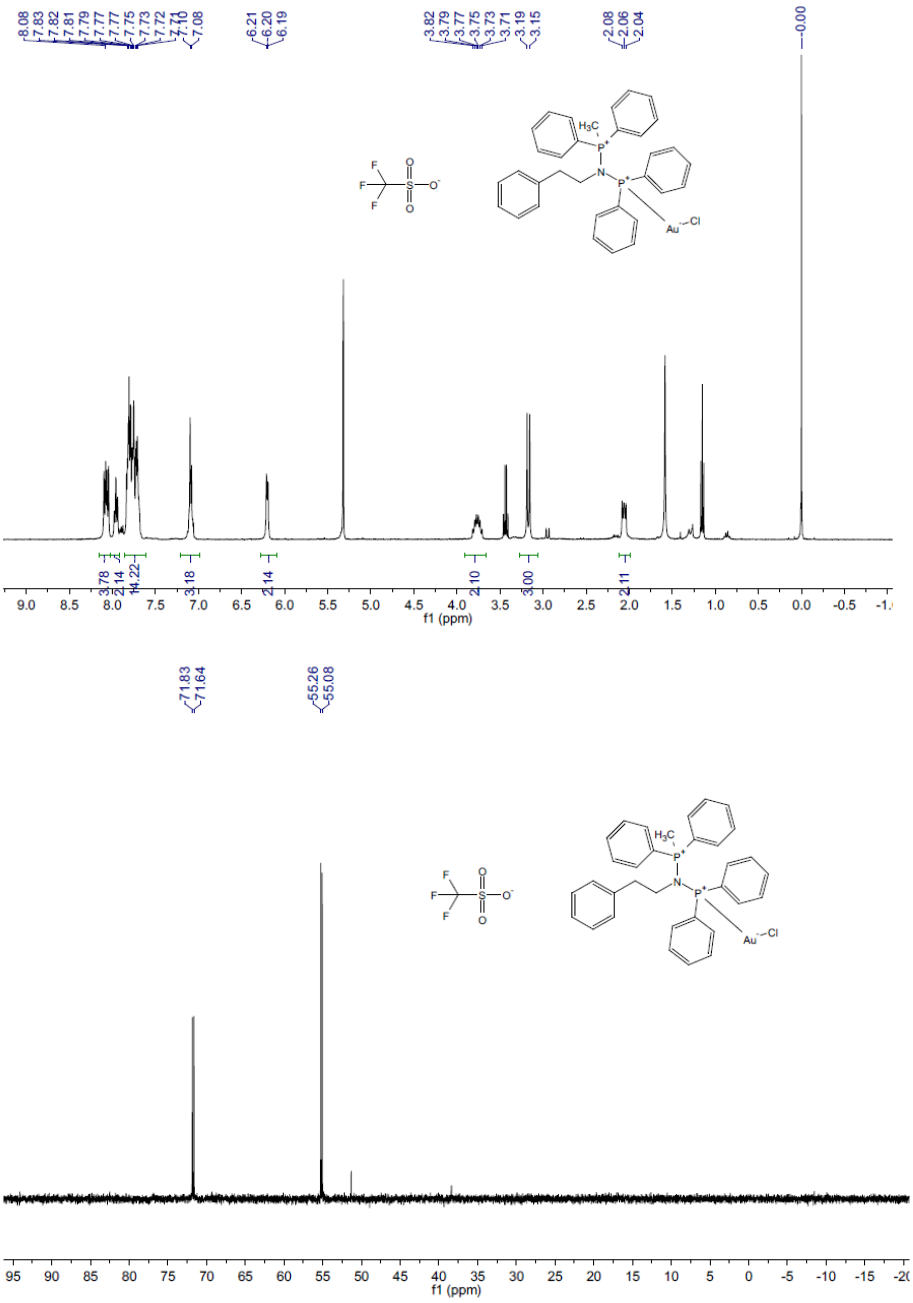


(*Trans*- and *cis*-**L4-Pd** coexisted)

L1-Au: To a solution of AuCl(tht) (0.2 mmol, 1 equiv) dissolved in dry dichloromethane (4 mL) was added **L1** (0.2 mmol, 1 equiv). The obtained mixture was stirred at room temperature for 4 h. Then the reaction solution was treated with diethyl ether (50 mL) for recrystallization. After standing-by for 24 h, the precipitated white micro-crystallines were collected as the product of **L1-Au** (Yield 50%). ^{1}H NMR (δ, ppm, CD_2Cl_2): 8.20-8.15 (4H, m), 7.97-7.87 (6H, m), 7.82-7.70 (10H, m), 4.34-4.25 (2H, m), 3.24 (3H, d, $^{2}J_{PH}$ = 16 Hz), 2.85 (2H, t, $^{3}J_{HH}$ = 5Hz), 2.82 (3H, s). ^{31}P NMR (δ, ppm, CD_2Cl_2): 74.5 (d, $^{2}J_{PP}$ = 28 Hz), 58.7 (d, $^{2}J_{PP}$ = 28 Hz).

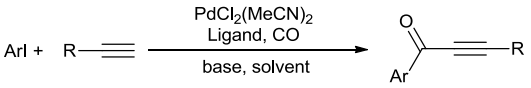


L3-Au: According to the similar procedures for the preparation of **L1-Au** as mentioned above, **L3-Au** was obtained in 60% yield as the white crystals. ^{1}H NMR (δ, ppm, CD_2Cl_2): 8.10-8.04 (4H, m), 7.98-7.94 (2H, m), 7.84-7.69 (14H, m), 7.10-7.08 (3H, m), 6.21-6.19 (2H, m), 3.82-3.71 (2H, m), 3.14 (3H, d, $^{2}J_{PH}$ = 16 Hz), 2.06 (2H, t, $^{3}J_{HH}$ = 8 Hz). ^{31}P NMR (δ, ppm, CD_2Cl_2): 71.7 (d, $^{2}J_{PP}$ = 31 Hz), 55.2 (d, $^{2}J_{PP}$ = 31 Hz).

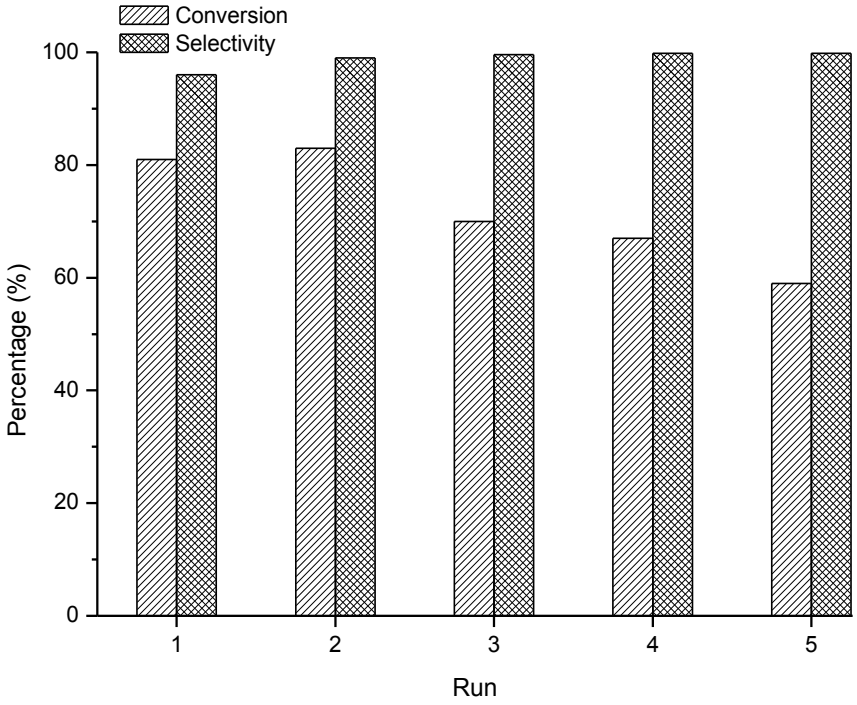


2 Results and discussion

General procedure for the carbonylative Sonogashira coupling:

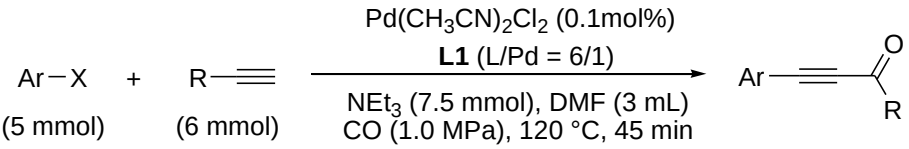


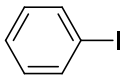
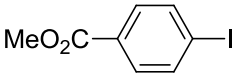
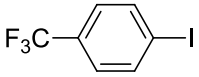
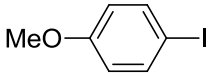
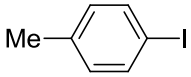
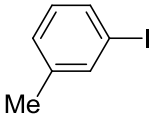
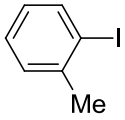
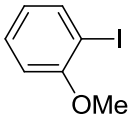
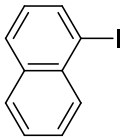
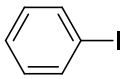
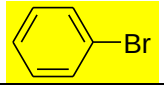
The generality of $PdCl_2(CH_3CN)_2$-**L1** for carbonylative Sonogashira reaction was performed according to the procedures as decribed blow. The $PdCl_2(MeCN)_2$ (0.005 mmol, 0.001 equiv) was mixed with DMF (3 mL), **L1** (0.03 mmol, 0.006 equiv), Et_3N (7.5 mmol, 1.5 equiv), iodobenzene (5 mmol, 1 equiv) and phenylacetylene (6 mmol, 1.2 equiv) sequentially in a 50 mL sealed Teflon-lined stainless steel autoclave. After flushing three times with CO, the autoclave was purged with CO at a pressure of 1.0 MPa. The resultant mixture in the autoclave was stirred vigorously at 120 ℃ for 45 min. Then the obtained mixture was cooled to room temperature and then diluted with EtOAc (20 mL). The EtOAc phase was washed with water (20 mL×5). Then the mixture was concentrated and directly subjected to a short silica gel column chromatograph using petroleum ether/ethyl acetate (from 70:1 to 20:1) as the eluent to afford the product. The structures of the obtained products were further confirmed by ^{1}H NMR and ^{13}C NMR spectra.



S. Fig. 1 The recycling uses of $PdCl_2(MeCN)_2$-**L1** dissolved in $[Bmim]BF_4$ (Pd 0.05 mol%, **L1** 1mol%, PhI 10 mmol, phenylacetylene 12 mmol, Et_3N 15 mmol, CO 2.0 MPa, $[Bmim]BF_4$ 6 mL, 120 ^oC, 2 h)

S. Table 2 The generality of $PdCl_2(CH_3CN)_2$-**L1** for carbonylative Sonogashira reaction



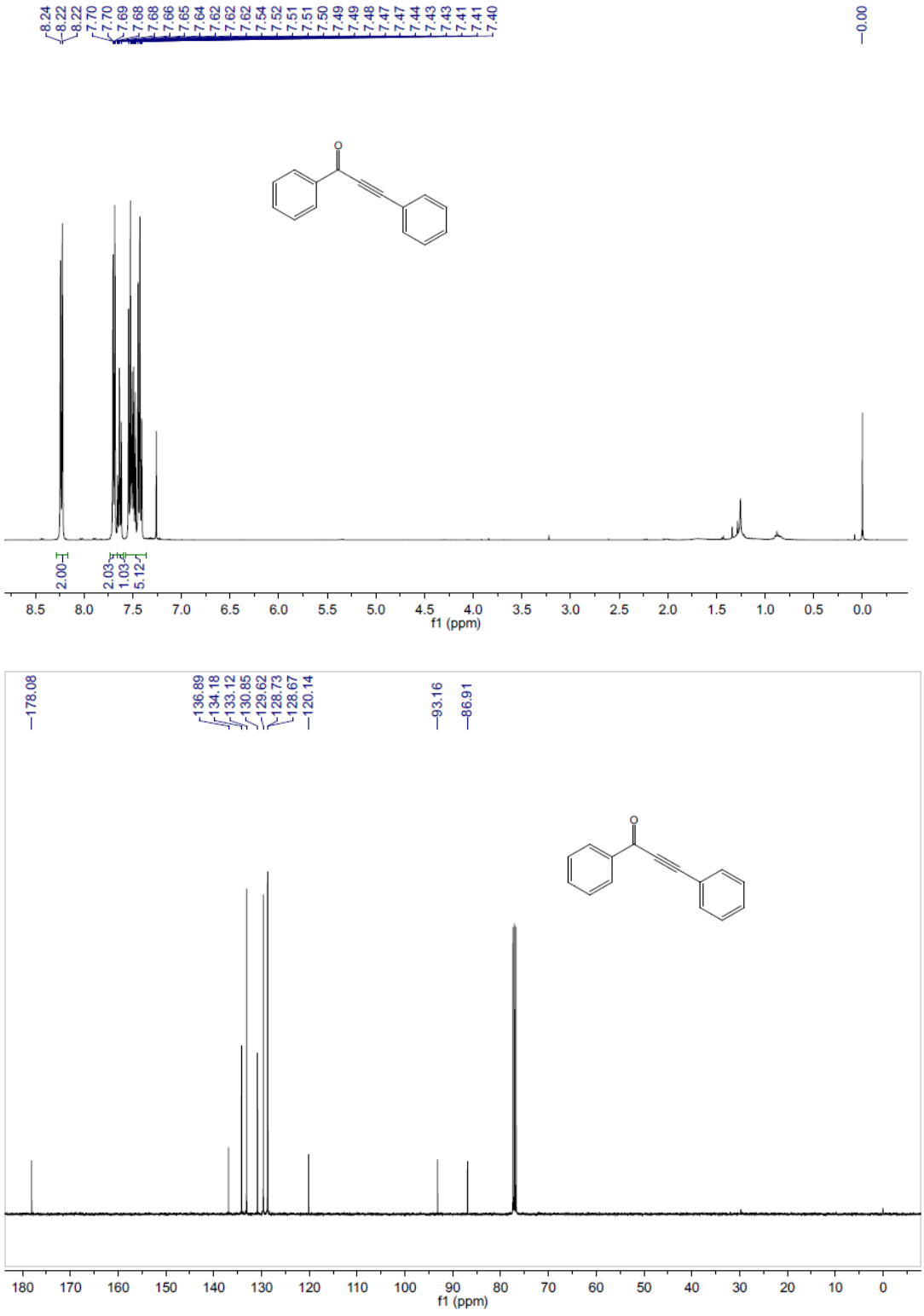
Entry	ArX	R	Yield (%)[a]
1		Ph	83 (93[b])
2		Ph	87
3		Ph	82
4		Ph	60
5		Ph	86
6		Ph	78
7		Ph	75
8		Ph	52
9		Ph	75
10		*n*-C_6H_{13}	17
11		Ph	--

[a] Isolated yield; [b] Determined by GC analysis.

NMR data for the products of carbonylative Sonogashira reaction:

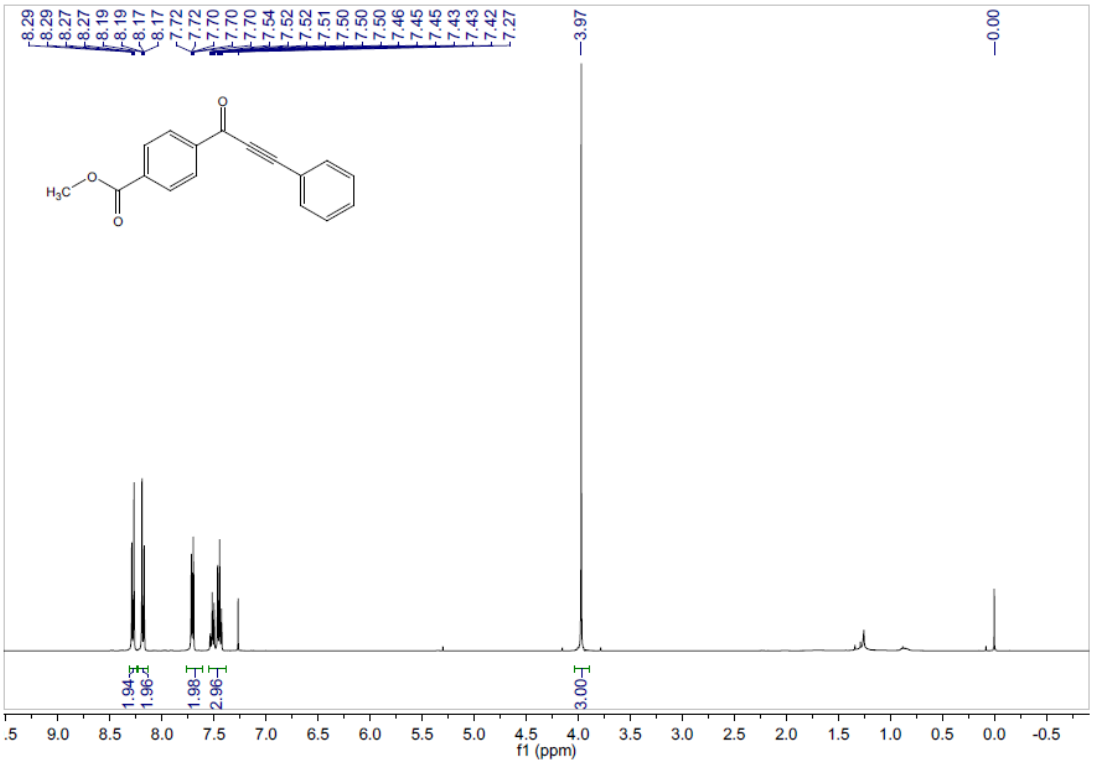
Yellow oil.

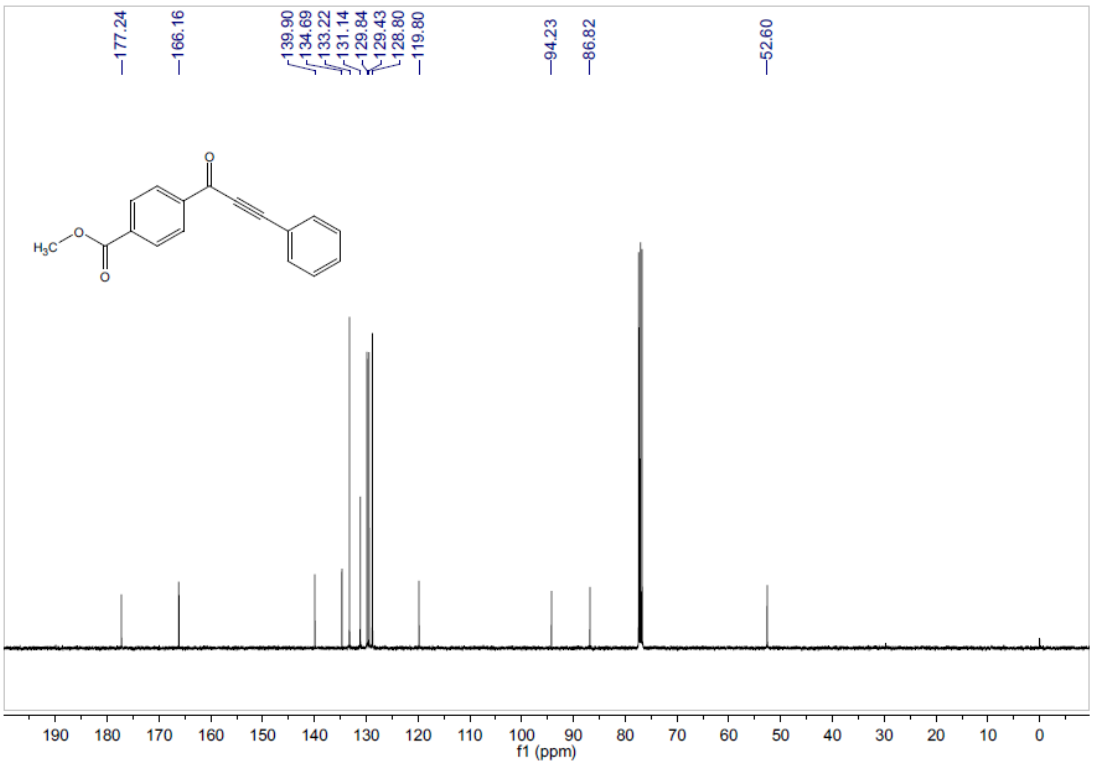
^{1}H NMR (δ, ppm, $CDCl_3$): 8.24-8.22 (2H, m), 7.70-7.68 (2H, m), 7.66-7.62 (2H, m), 7.54-7.40 (3H, m). ^{13}C NMR (δ, ppm, $CDCl_3$): 178.1, 136.9, 134.2, 133.1, 130.9, 129.6, 128.7, 128.7, 120.1, 93.2, 86.9.



Yellow solid.

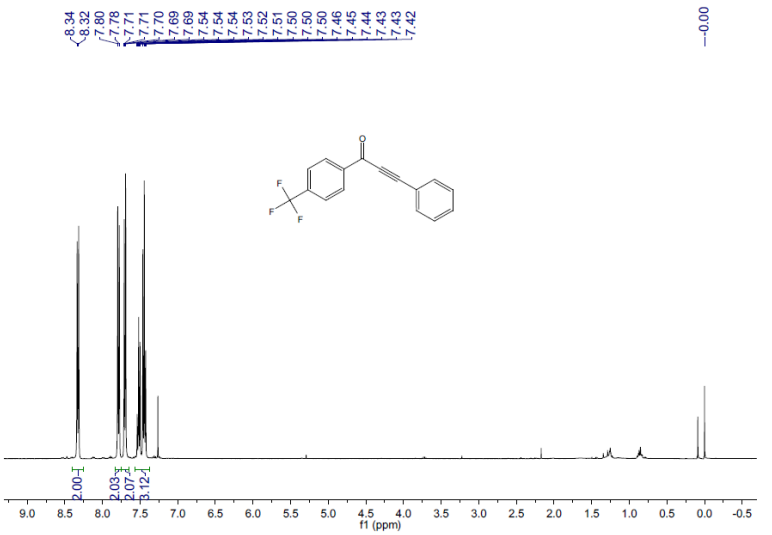
^{1}H NMR (δ, ppm, $CDCl_3$): 8.29-8.27 (2H, m), 8.19-8.17 (2H, m), 7.72-7.70 (2H, m), 7.54-7.42 (3H, m), 3.97 (3H, s). ^{13}C NMR (δ, ppm, $CDCl_3$): 177.2, 166.2, 139.9, 134.7, 133.2, 131.1, 129.8, 129.4, 128.8, 119.8, 94.2, 86.8, 52.6.

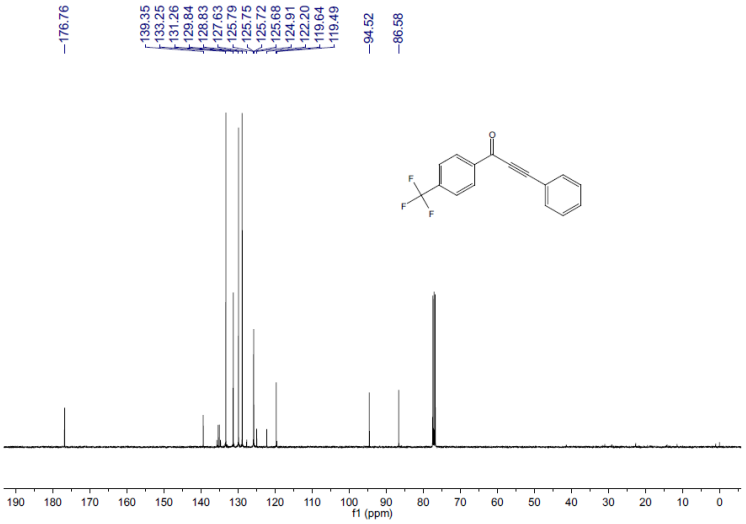


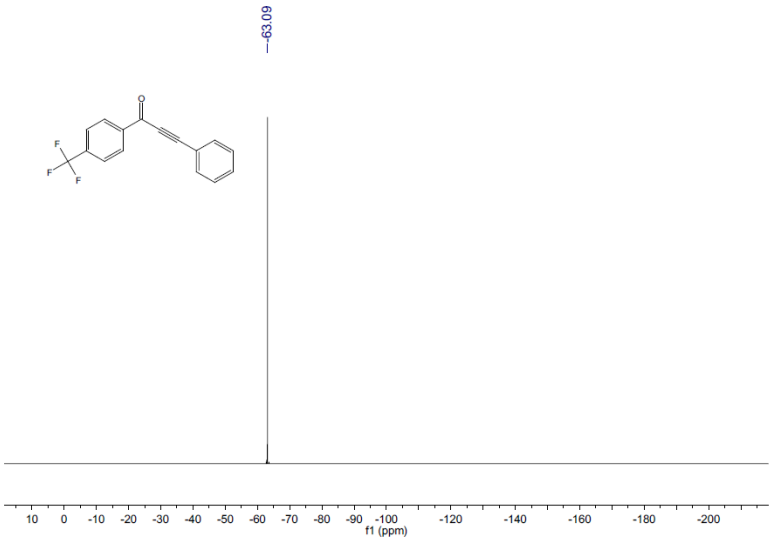


Yellow solid.

^{1}H NMR (δ, ppm, $CDCl_3$): 8.33 (2H, d, $^{3}J_{HH}$ = 8Hz), 7.79 (2H, d, $^{3}J_{HH}$ = 8Hz), 7.71-7.69 (2H, m), 7.54-7.42 (3H, m). ^{13}C NMR (δ, ppm, $CDCl_3$): 176.8, 139.4, 133.3, 131.3, 129.8, 128.8, 125.73 (q, $^{1}J_{FC}$ = 4Hz), 124.9, 122.2, 119.6, 94.5, 86.6. ^{19}F NMR (δ, ppm, $CDCl_3$): -63.1 (s).

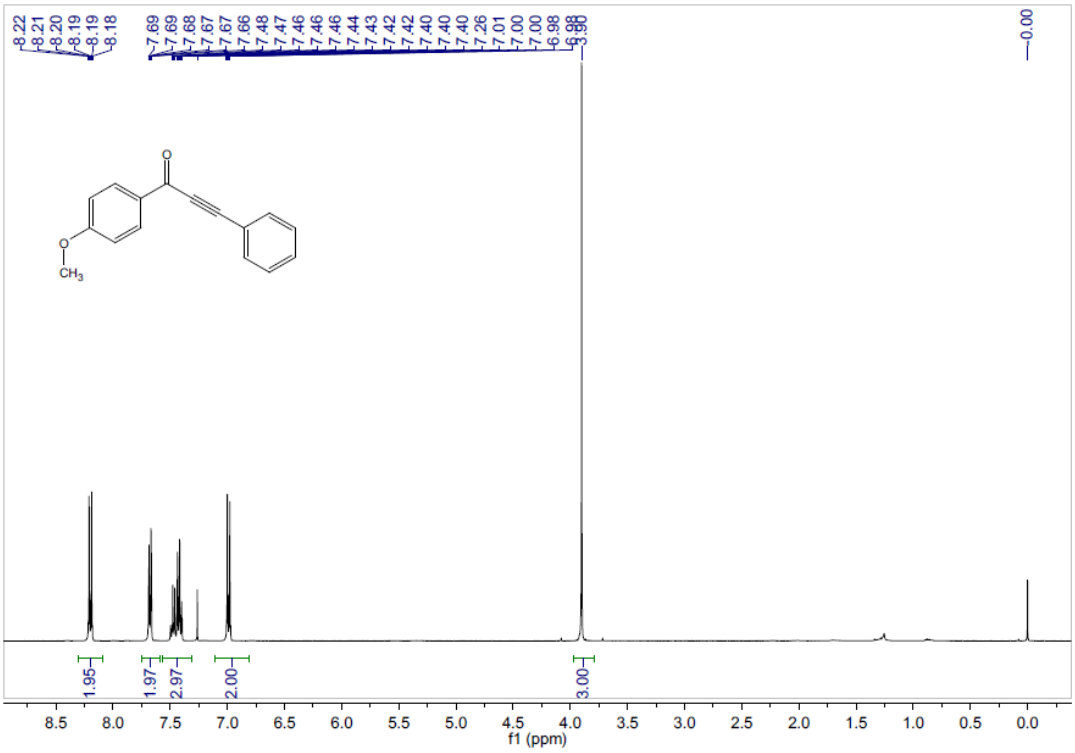


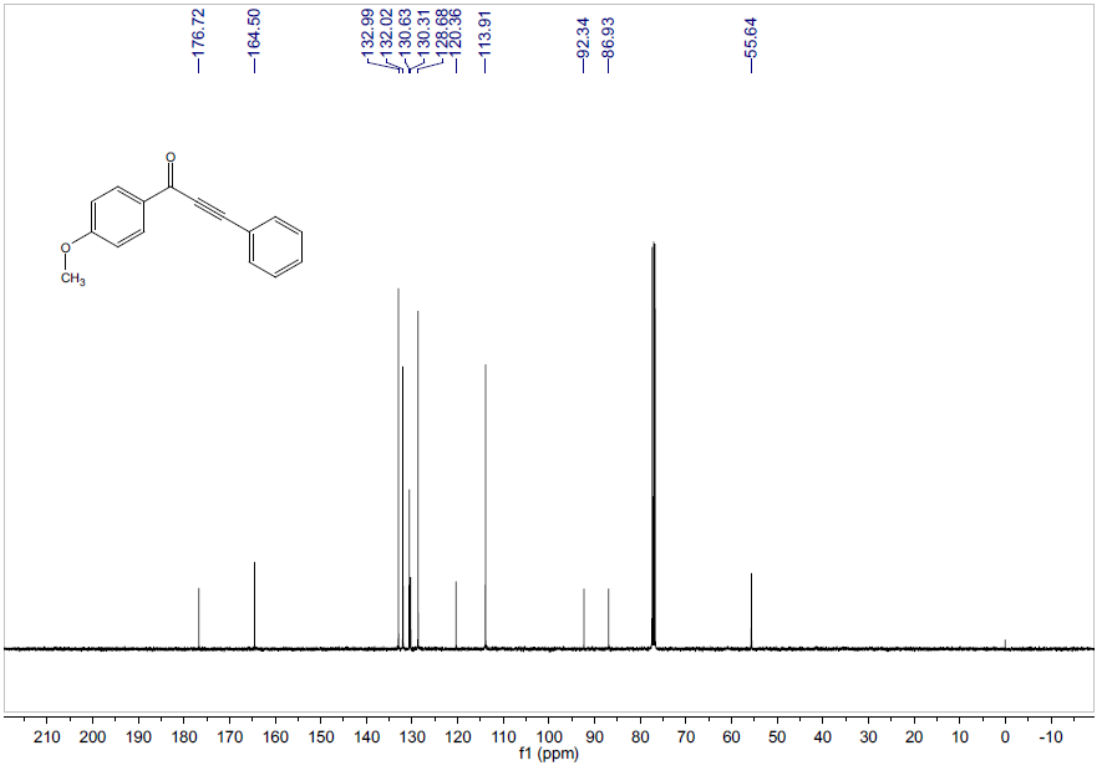




Yellow solid.

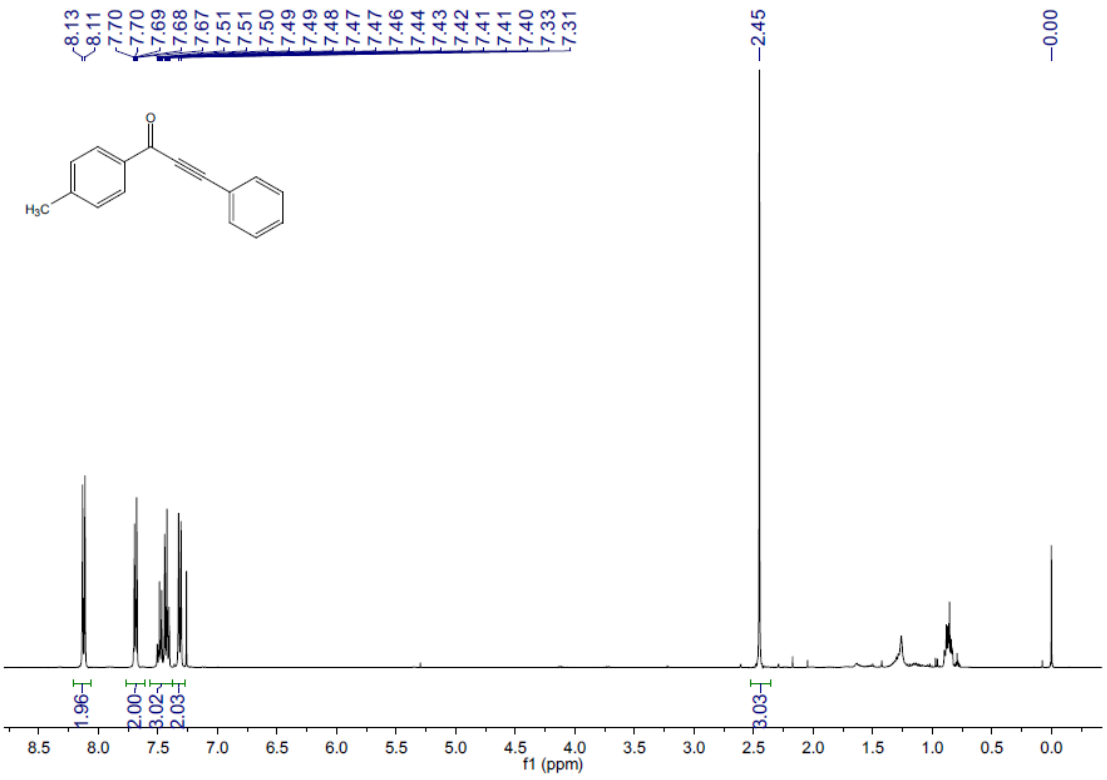
^{1}H NMR (δ, ppm, $CDCl_3$): 8.22-8.18 (2H, m), 7.69-7.66 (2H, m), 7.48-7.40 (3H, m), 7.01-6.97 (2H, m), 3.90 (3H, s). ^{13}C NMR (δ, ppm, $CDCl_3$): 176.7, 164.5, 133.0, 132.0, 130.6, 130.3, 128.7, 120.4, 113.9, 92.3, 86.9, 55.6.

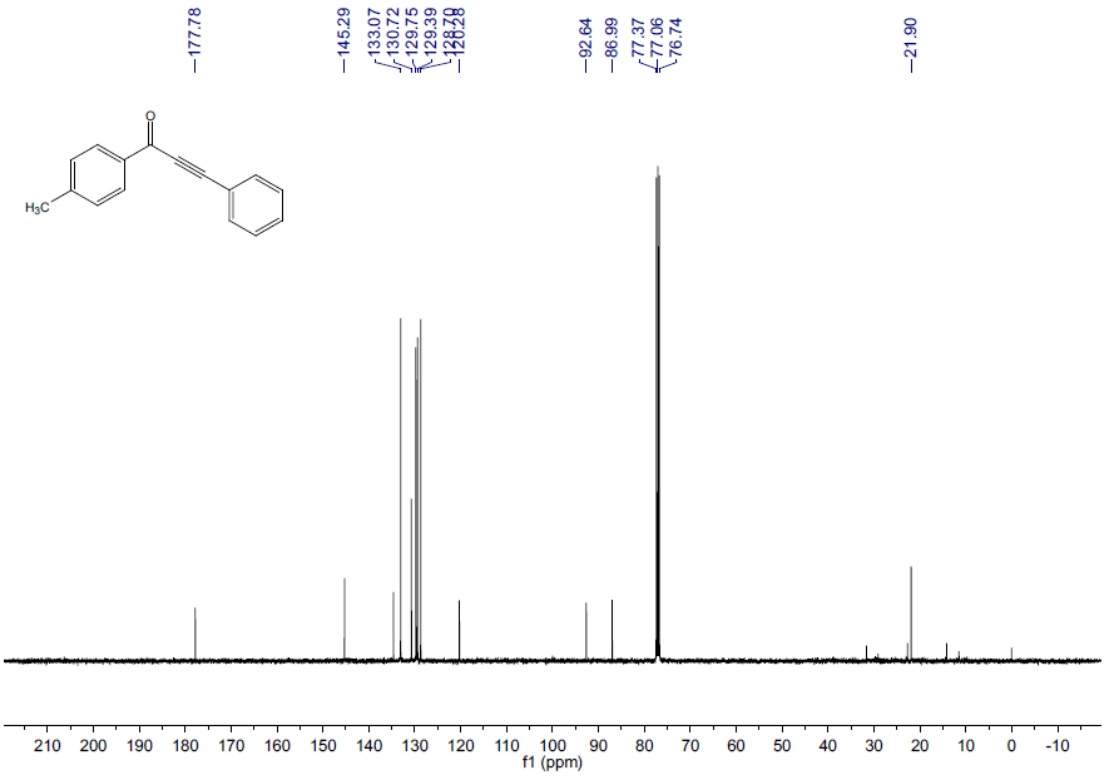




Yellow solid.

^{1}H NMR (δ, ppm, $CDCl_3$): 8.12 (2H, d, $^{3}J_{HH}$ = 8Hz), 7.70-7.67 (2H, m), 7.51-7.40 (3H, m), 7.32 (2H, d, $^{3}J_{HH}$ = 8Hz), 2.45 (3H, s). ^{13}C NMR (δ, ppm, $CDCl_3$): 177.8, 145.3, 134.6, 133.0, 130.1, 129.8, 129.4, 128.7, 120.28, 92.6, 87.0, 21.9.

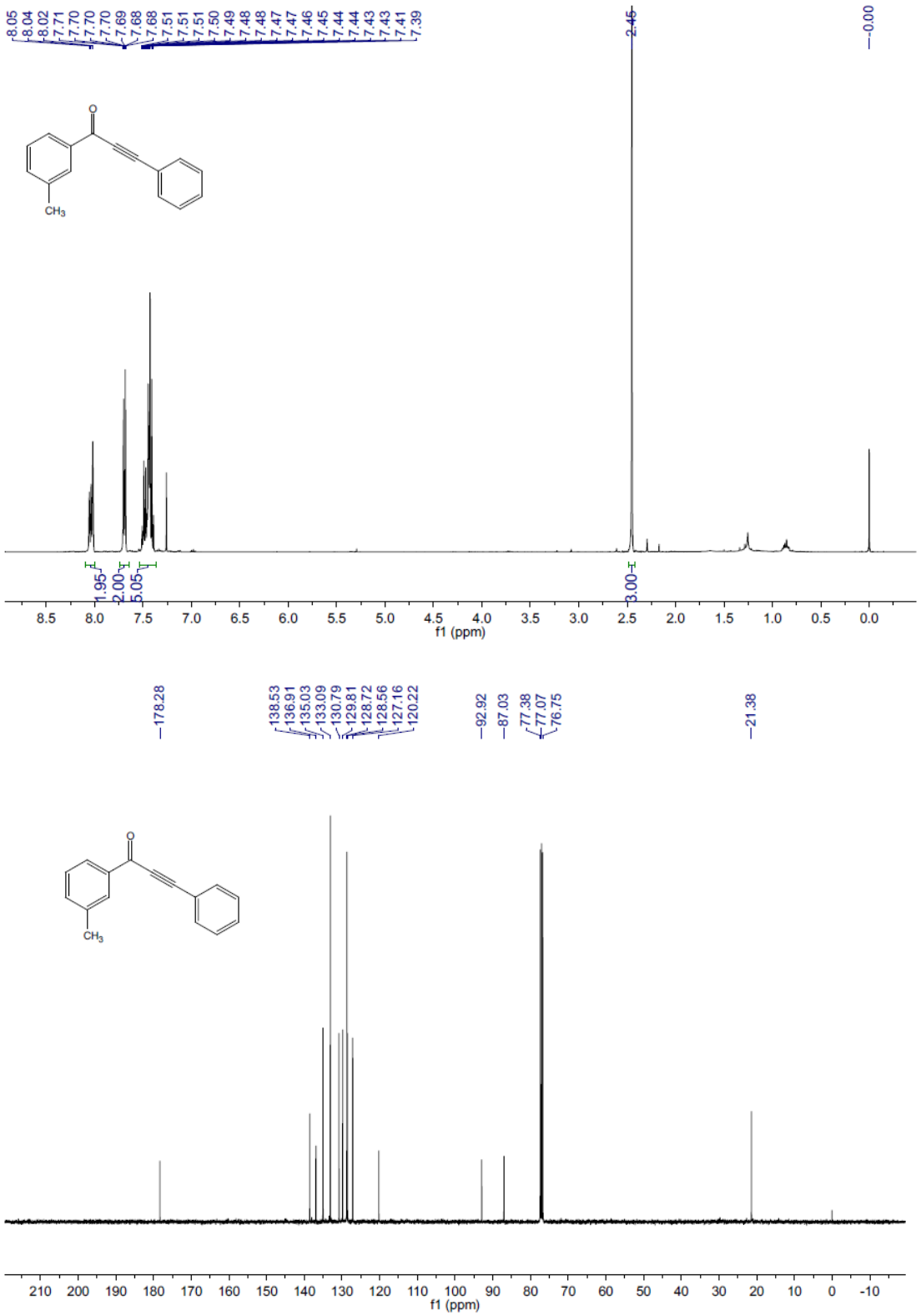




Yellow solid.

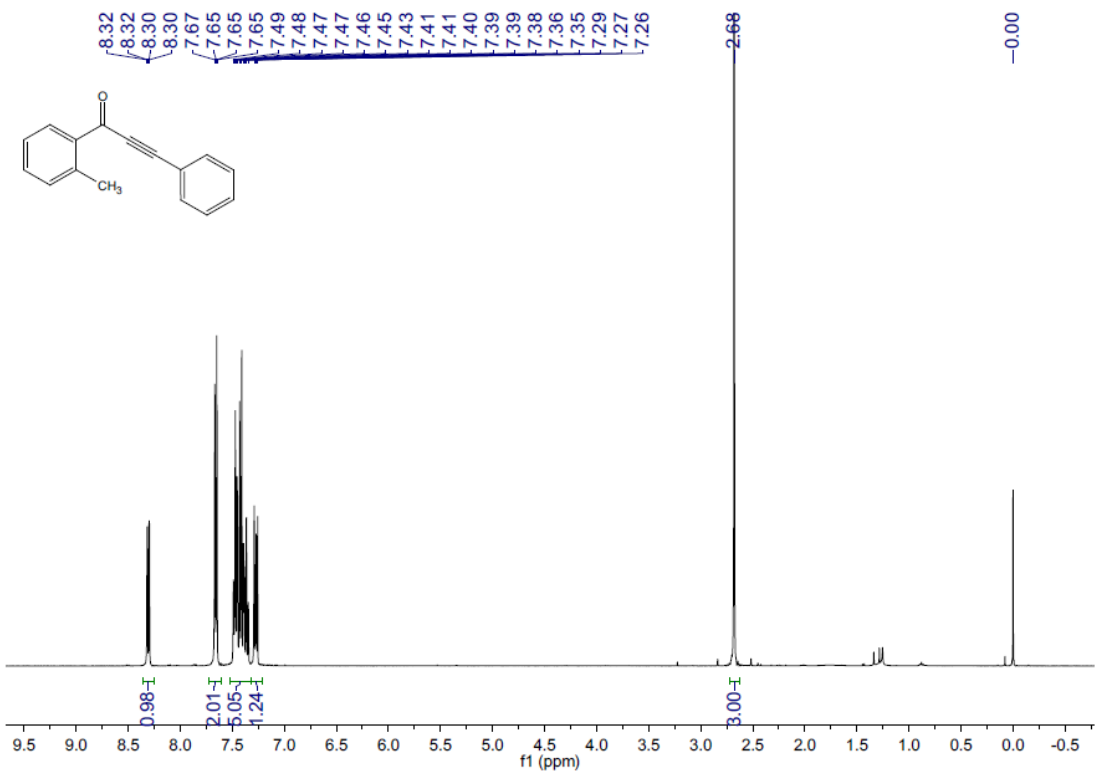
^{1}H NMR (δ, ppm, $CDCl_3$): 8.05-8.02 (2H, m), 7.71-7.68 (2H, m), 7.51-7.39 (2H, m), 2.45 (3H, s).

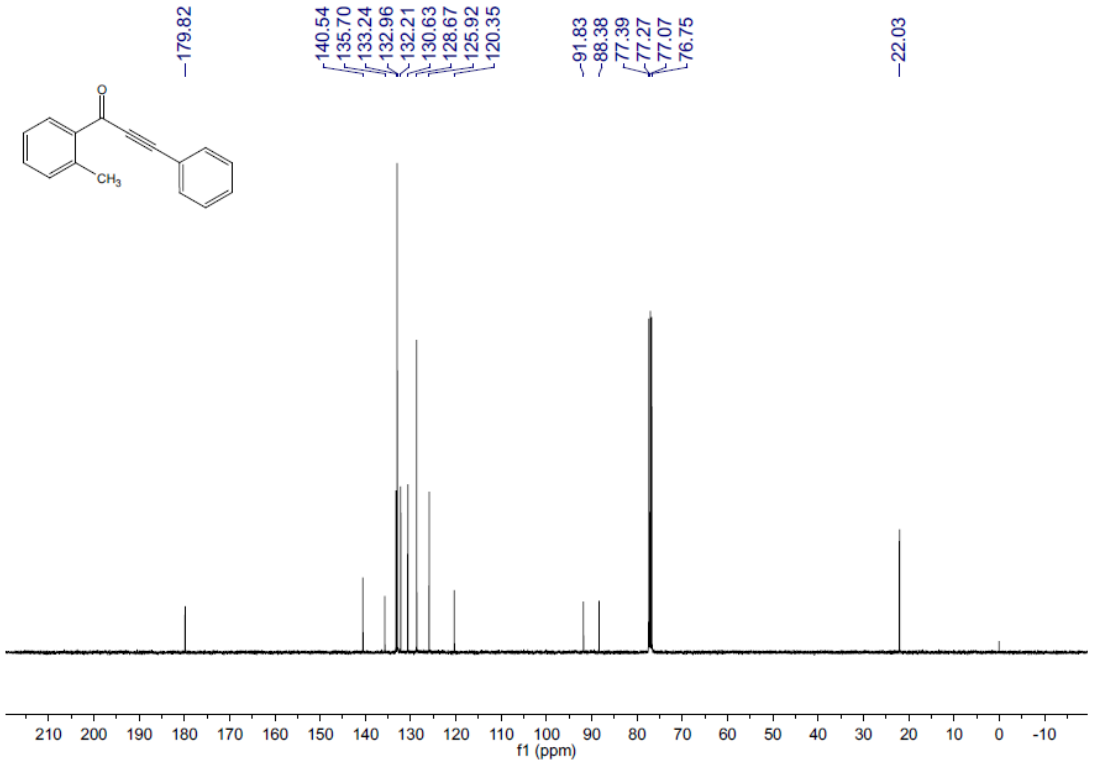
^{13}C NMR (δ, ppm, $CDCl_3$): 178.3, 138.5, 136.9, 135.0, 133.1, 130.8, 129.8, 128.7, 128.6, 127.2, 120.2, 92.9, 87.0, 21.4.



Yellow oil.

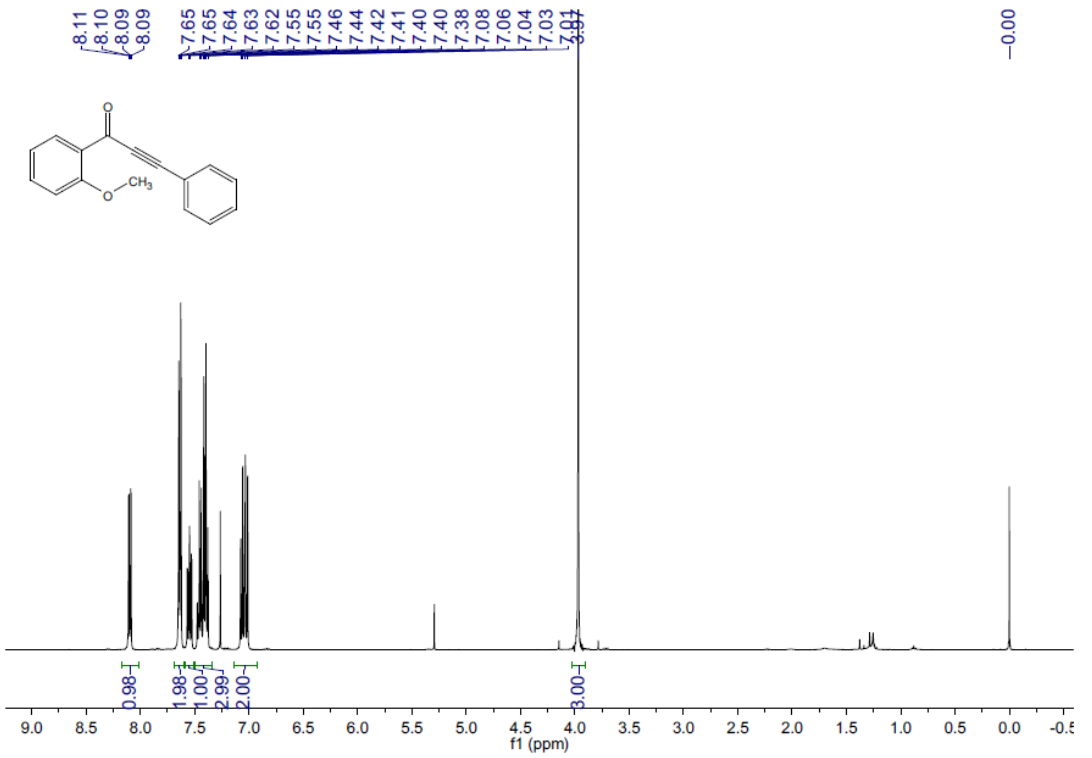
^{1}H NMR (δ, ppm, $CDCl_3$): 8.31 (1H, dd, $^{3}J_{HH}$ = 1, 8Hz), 7.67-7.65 (2H, m), 7.49-7.35 (5H, m), 7.29-7.26 (1H, m), 2.68 (3H, s). ^{13}C NMR (δ, ppm, $CDCl_3$): 179.8, 140.5, 135.7, 133.2, 133.0, 132.2, 130.6, 128.7, 125.9, 120.35, 91.8, 88.4, 22.0.

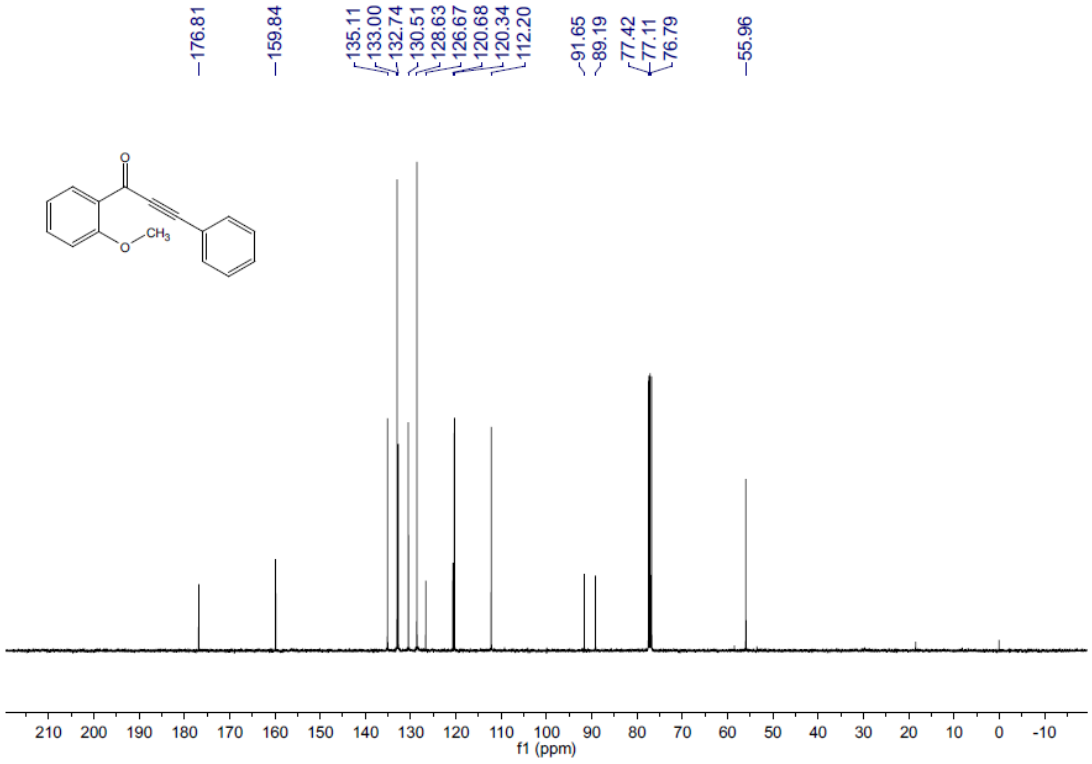




Yellow oil.

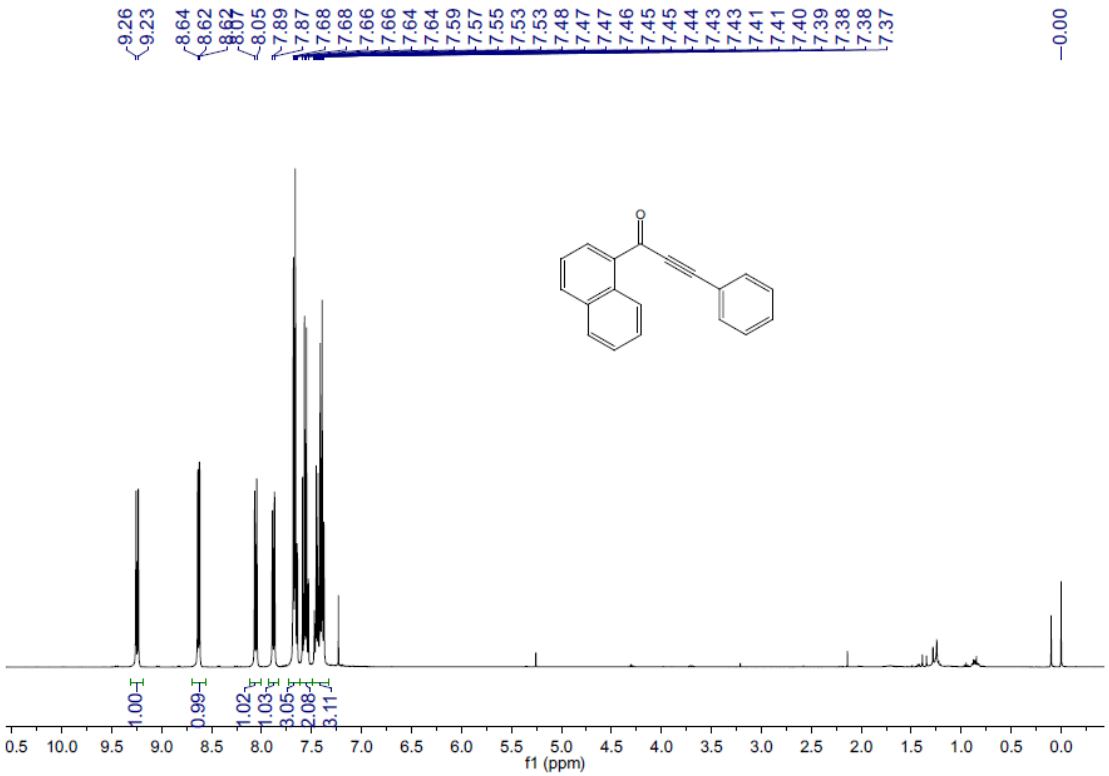
^{1}H NMR (δ, ppm, $CDCl_3$): 8.10 (1H, dd, $^{3}J_{HH}$ = 2, 8Hz), 7.65-7.62 (2H, m), 7.55-7.54 (1H, m), 7.48-7.38 (3H, m), 7.08-7.01 (2H, m), 3.97 (3H, s). ^{13}C NMR (δ, ppm, $CDCl_3$): 176.8, 159.8, 135.1, 133.0, 132.7, 130.5, 128.6, 126.7, 120.7, 120.3, 112.2, 91.7, 89.2, 56.0.

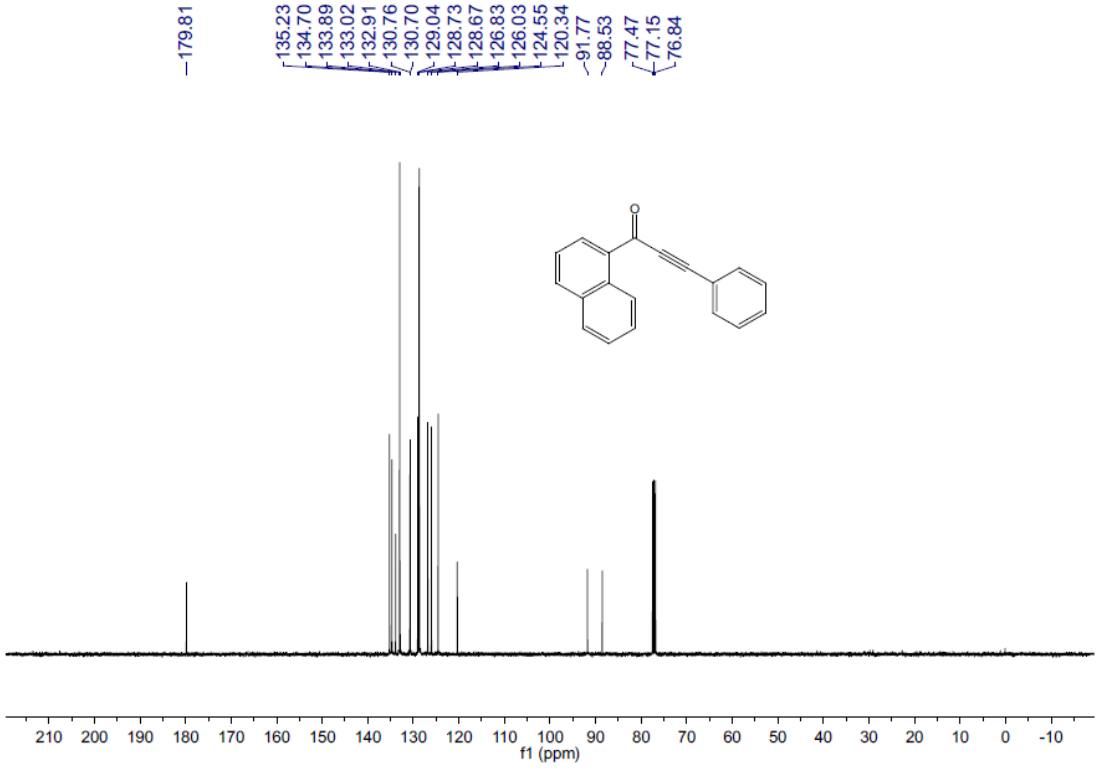




Yellow solid.

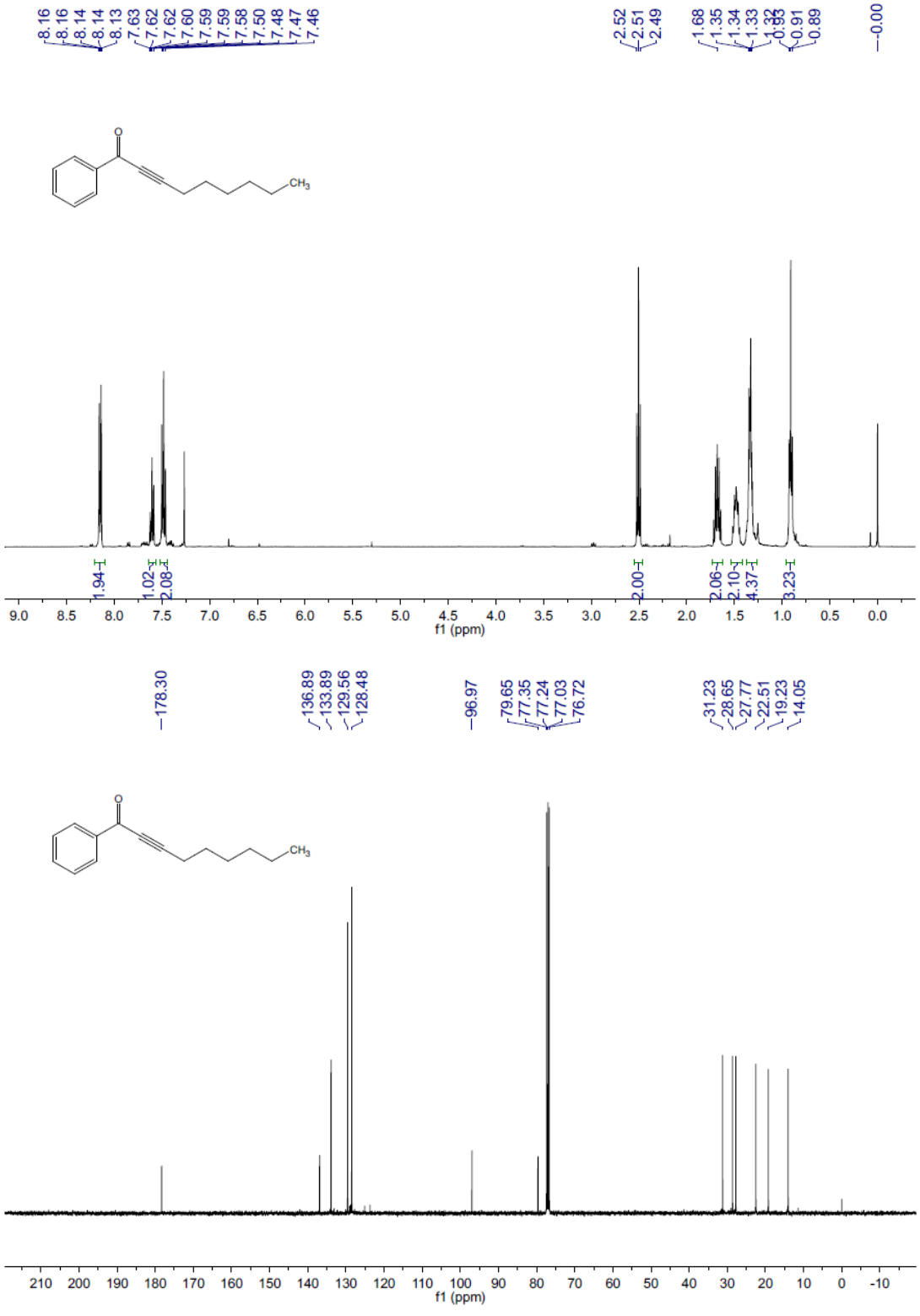
^{1}H NMR (δ, ppm, $CDCl_3$): 9.25 (1H, d, $^{3}J_{HH}$ = 12Hz), 8.63 (1H, dd, $^{3}J_{HH}$ = 1, 7Hz), 8.06 (1H, d, $^{3}J_{HH}$ = 8Hz), 7.88 (1H, d, $^{3}J_{HH}$ = 8Hz), 7.68-7.64 (3H, m), 7.59-7.53 (2H, m), 7.48-7.37 (3H, m). ^{13}C NMR (δ, ppm, $CDCl_3$): 179.8, 135.2, 134.7, 133.9, 133.0, 132.9, 130.8, 130.7, 129.0, 128.8, 128.7, 126.8, 126.0, 124.6, 120.3, 91.8, 88.5.





Yellow oil.

^{1}H NMR (δ, ppm, $CDCl_3$): 8.16-8.13 (2H, m), 7.63-7.58 (1H, m), 7.50-7.46 (2H, m), 2.51 (2H, t, $^{3}J_{HH}$ = 4Hz), 1.72-1.64 (2H, m), 1.52-1.44 (2H, m), 1.35-1.31 (4H, m), 0.91 (3H, t, $^{3}J_{HH}$ = 8Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 178.3, 136.9, 133.9, 129.6, 128.5, 97.0, 79.7, 31.2, 28.7, 27.8, 22.5, 19.2, 14.0.



References

13 (a) K. Blanna, A. Bollmanna, H. de Boda, J. T. Dixona, E. Killiana, P. Nongodlwanaa, M. C. Maumelaa, H. Maumelaa, A. E. McConnella, D. H. Morgana, M. J. Overetta, M. Prétoriusa, S. Kuhlmannb and P. Wasserscheid, *J. Catal.*, 2007, **249**, 244; (b) I. M. Aladzheva, D. I. Lobanov, O. V. Bykhovskaya, P. V. Petrovskii, K. A. Lyssenko and T. A. Mastryukova, *Heteroatom Chem.*, 2003, **14**, 596; (c) A.-M. Caminade, E. Ocando, J.-P. Majoral, M. Cristante and G. Bertrand, *Inorg. Chem.*, 1986, **25**, 712; (d) G. Ewart, A. P. Lane, J. Mckechnie and D. S. Payne, *J. Chem. Soc.*, 1964, 1543; (e) H. Schindlbauer, L. Golser and V. Hilzensauer, *Chem. Ber.*, 1964, **97**, 1150; (f) D. S. Payne, J. A. A. Mokuolu and J. C. Speakman, *Chem. Commun.*, 1965, **23**, 599; (g) D. S. McGuinness, M. Overett, R. P. Tooze, K. Blann, J. T. Dixon and A. M. Z. Slawin, *Organometallics*, 2007, **26**, 1108.