Sonogashira reactions of alkyl halides catalyzed by NHC [CNN] pincer nickel(II) complexes

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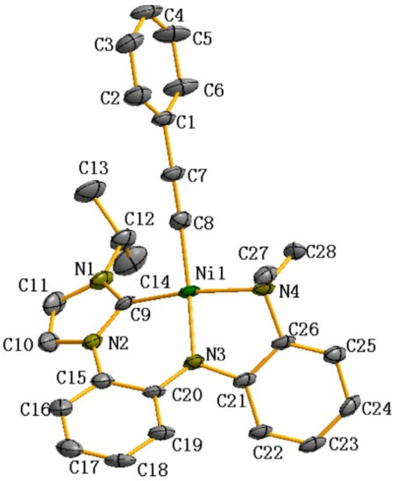
Contents

SI. X-ray crystallographic data of complex 9



Complex **9**. Red crystals, $C_{28}H_{28}N_4Ni$ = 479.25 g mol^{-1}, monoclinic, P2(1)/c, *a* = 11.193(1), *b* =8 .695(1), *c* = 24.486(1) Å, β = 94.64(1) °, V = 2375.4(1) Å^3, Z = 4, Calculated density = 1.340 g/cm^3, Reflections collected = 13102, Reflections unique = 4133, R(int) = 0.1210, R_1 (I > 2σ(I)) = 0.0833, wR_2(I>2σ(I)) = 0.2237, R_1(all data) = 0.0950, wR_2(all data) = 0.2359. Selected distances [Å] and angles [deg]: Ni1-N3 1.875(3), Ni1-N4 2.003(3), Ni1-C8 1.852(3), Ni1-C9 1.853(3), C7-C8 1.224(5); N4-Ni1-N3 84.91(11), C8-Ni1-N4 94.65(13), C9-Ni1-N3 89.84(13), C8-Ni1-C9 92.96(14), C8-Ni1-N3 167.47(16), C9-Ni1-N4 168.48(14), C7-C8-Ni1 173.8(4).

SII. IR, ^{1}H and ^{13}C NMR spectra of pincer complex 9

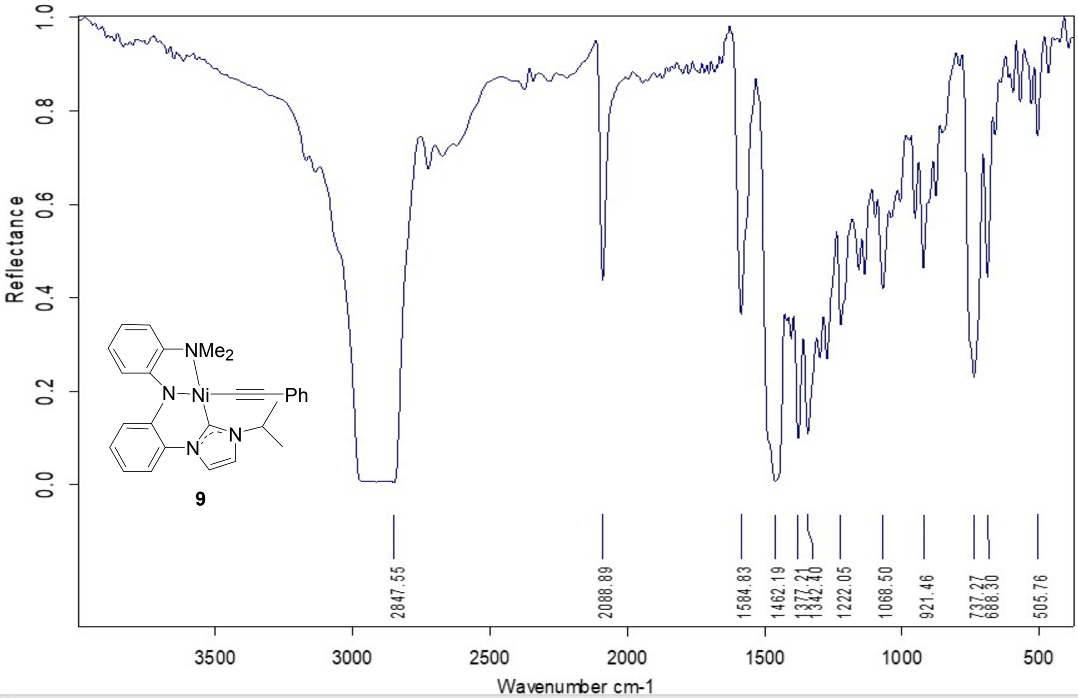


Figure S1. IR spectrum of complex **9**

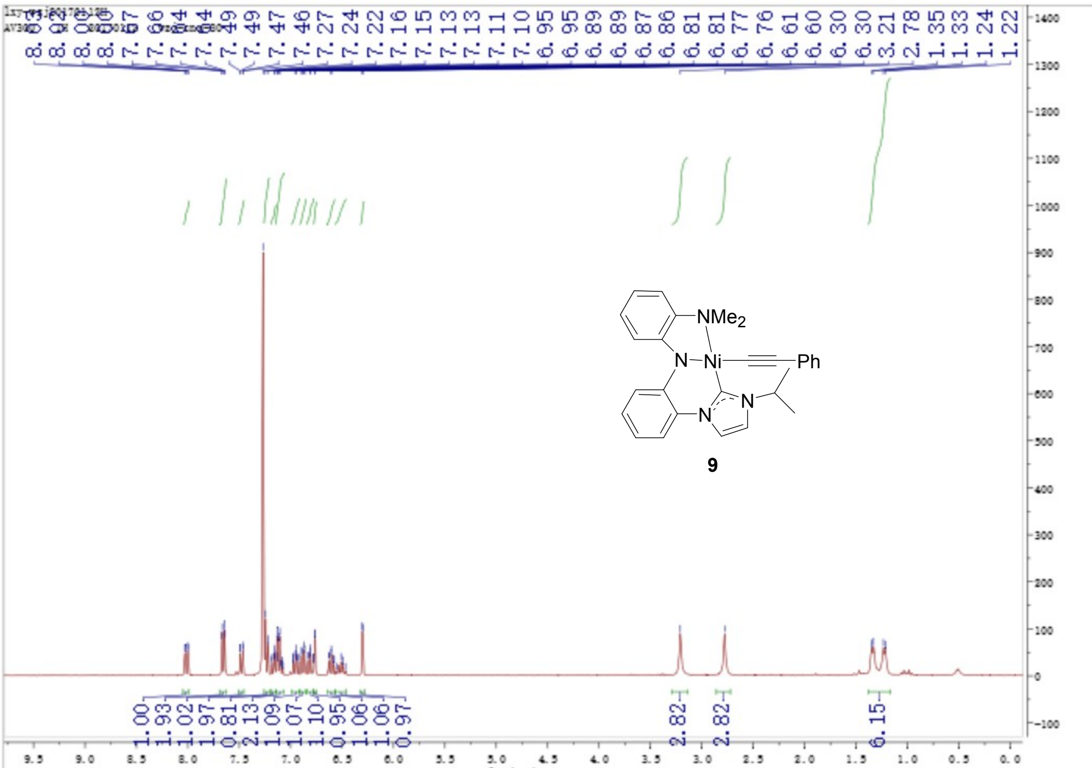


Figure S2. ^{1}H NMR spectrum of complex **9** (C_6D_6)

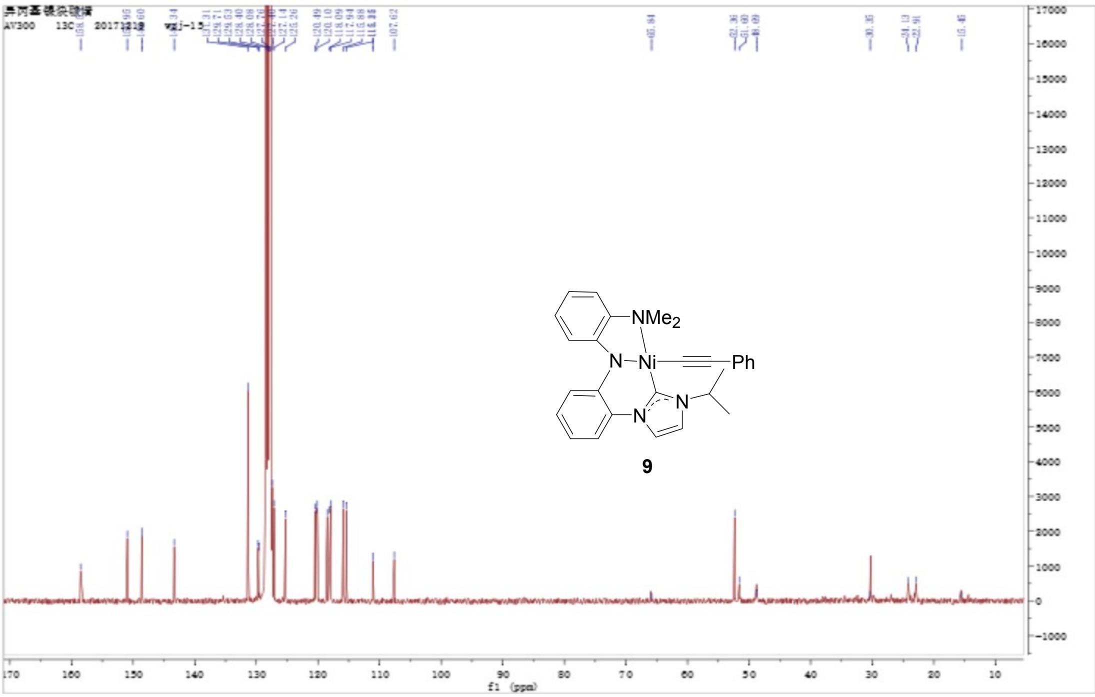


Figure S3. ^{13}C NMR spectrum of complex **9** (C_6D_6)

Note：The peaks at 15.4 and 66.0 ppm belong to Et_2O.

SIII. ^{1}H and ^{13}C NMR Spectra of the catalytic products

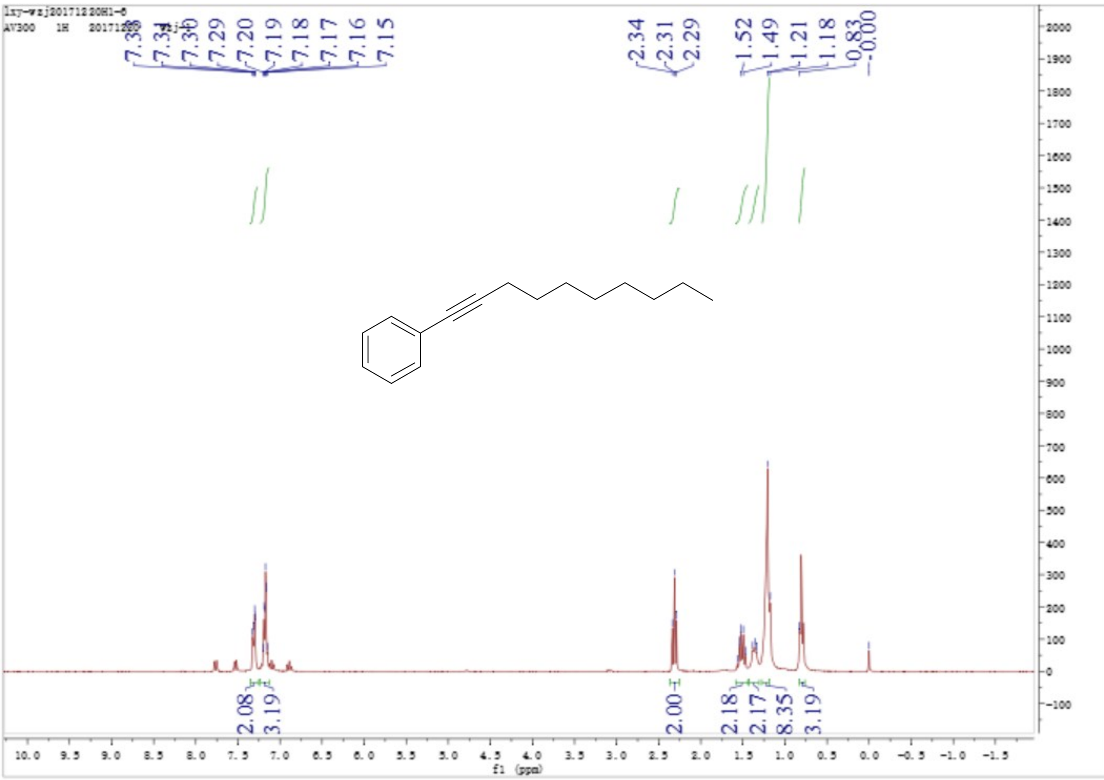


Figure S4. ^{1}H NMR spectrum of dec-1-ynyl-benzene ($CDCl_3$)

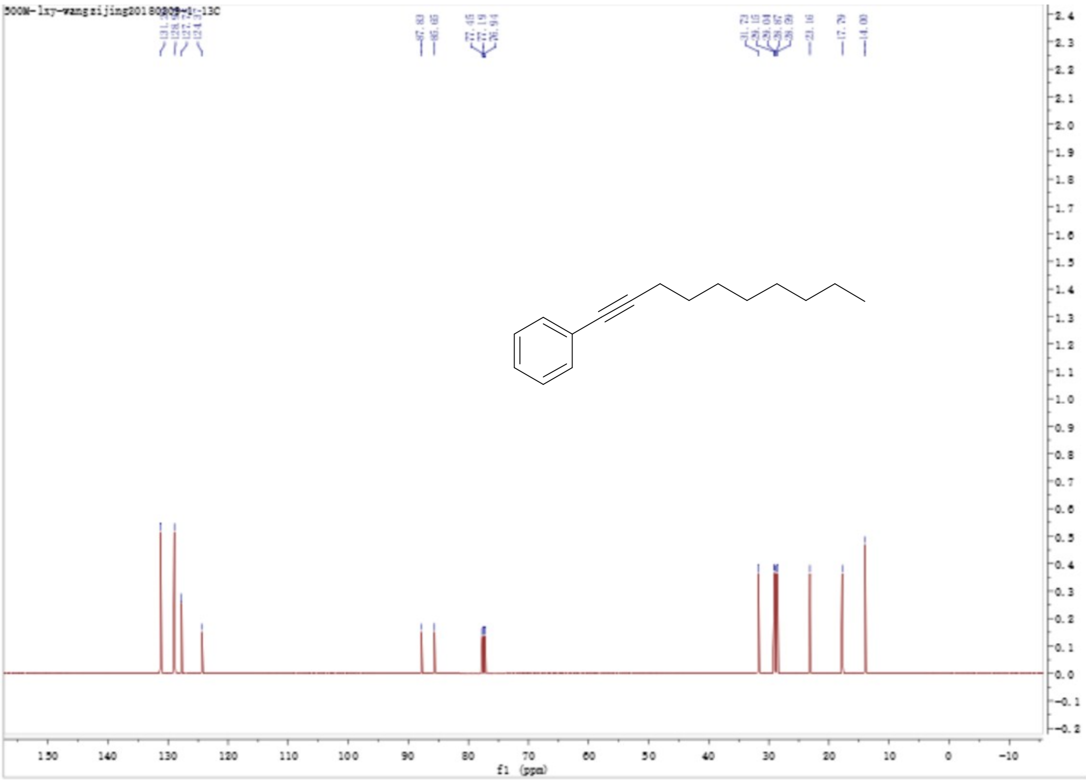


Figure S5. ^{13}C NMR spectrum of dec-1-ynyl-benzene ($CDCl_3$)

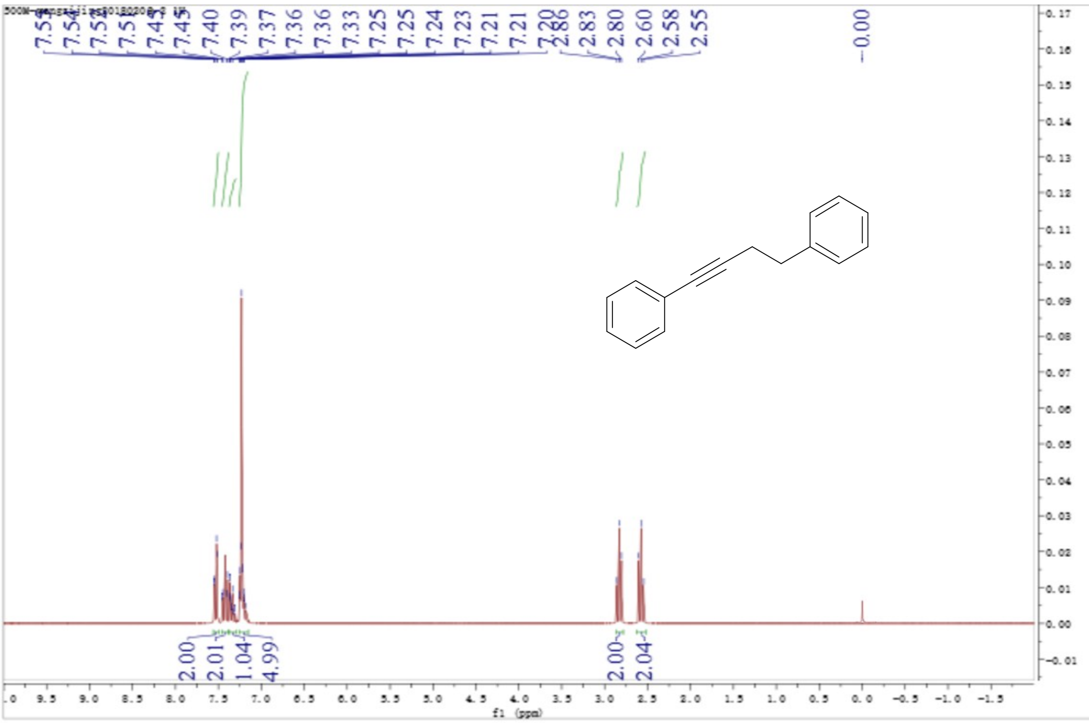


Figure S6. ^{1}H NMR spectrum of but-1-yne-1,4-diyldibenzene ($CDCl_3$)

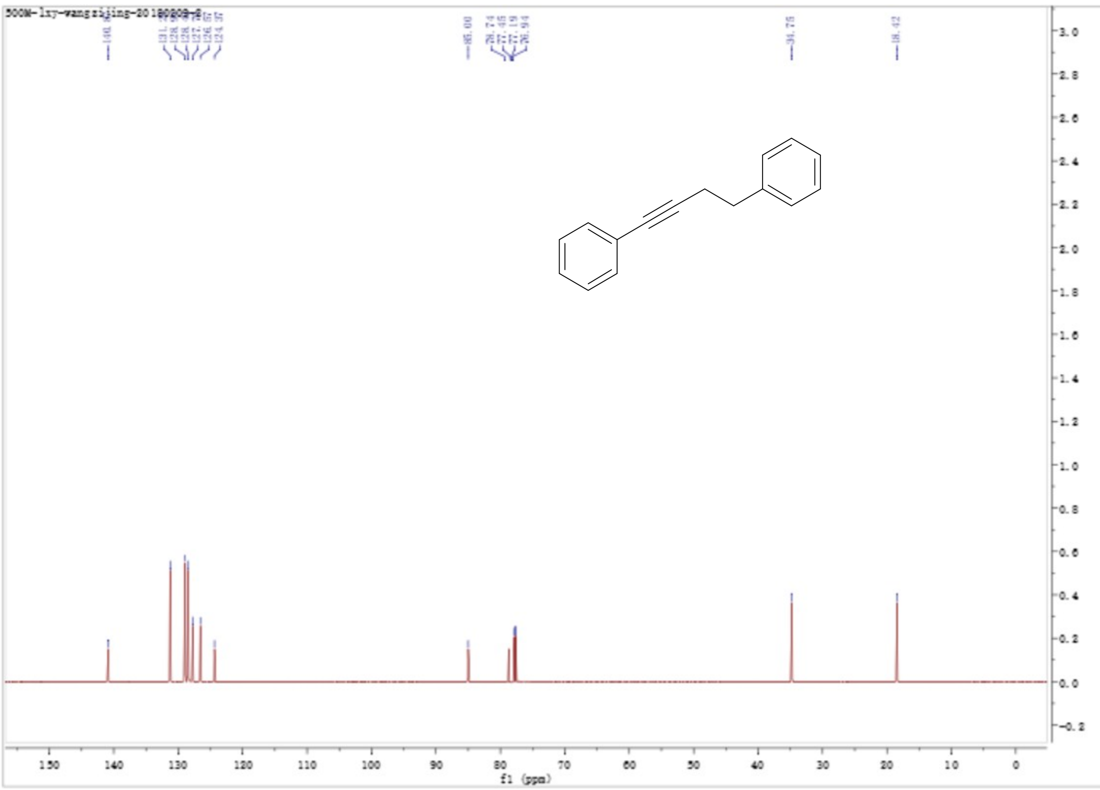


Figure S7. ^{13}C NMR spectrum of but-1-yne-1,4-diyldibenzene ($CDCl_3$)

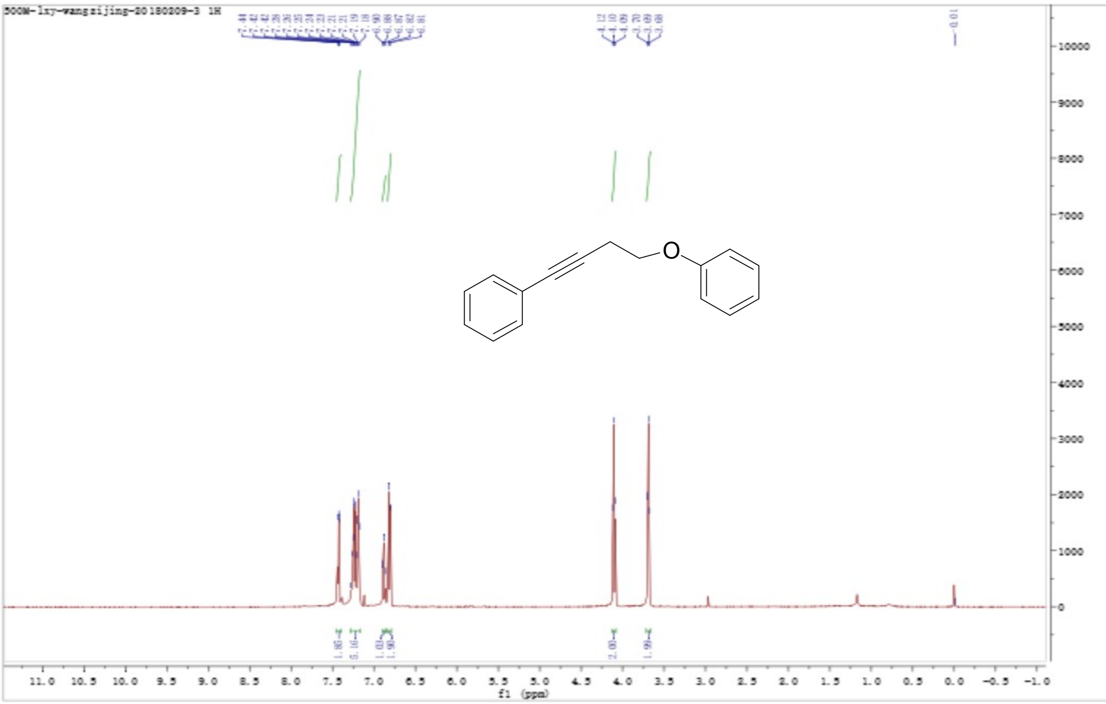


Figure S8. ^{1}H NMR spectrum of (4-phenoxybut-1-yn-1-yl)benzene ($CDCl_3$)

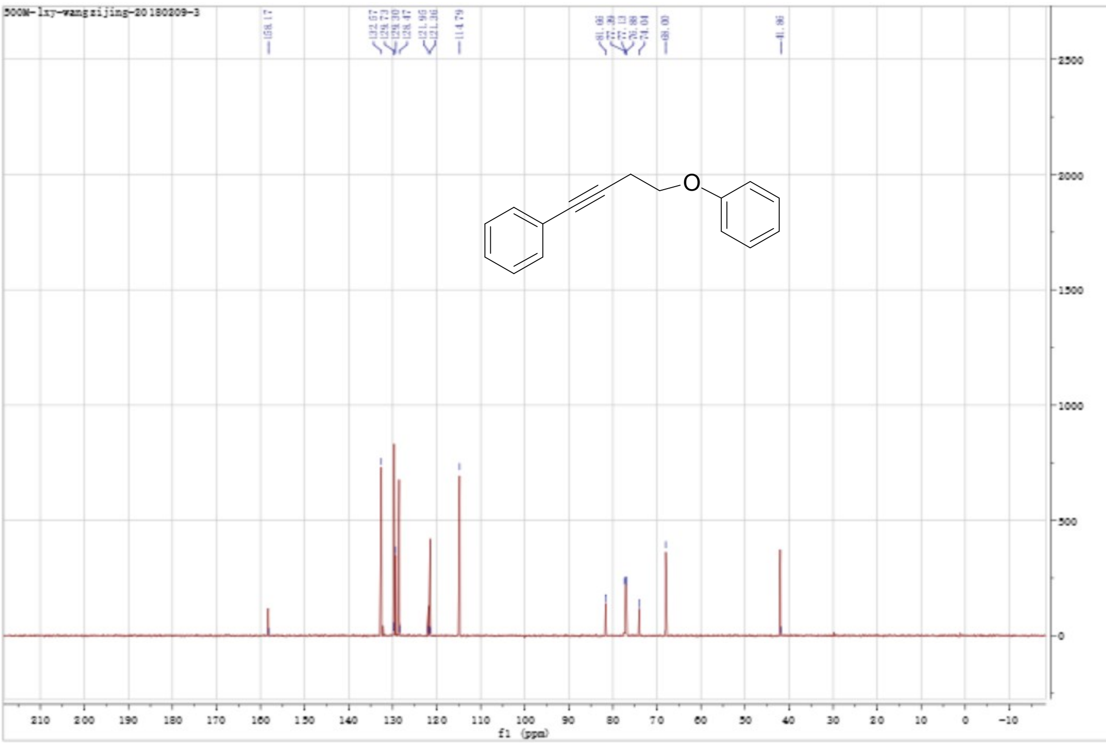


Figure S9. ^{13}C NMR spectrum of (4-phenoxybut-1-yn-1-yl)benzene ($CDCl_3$)

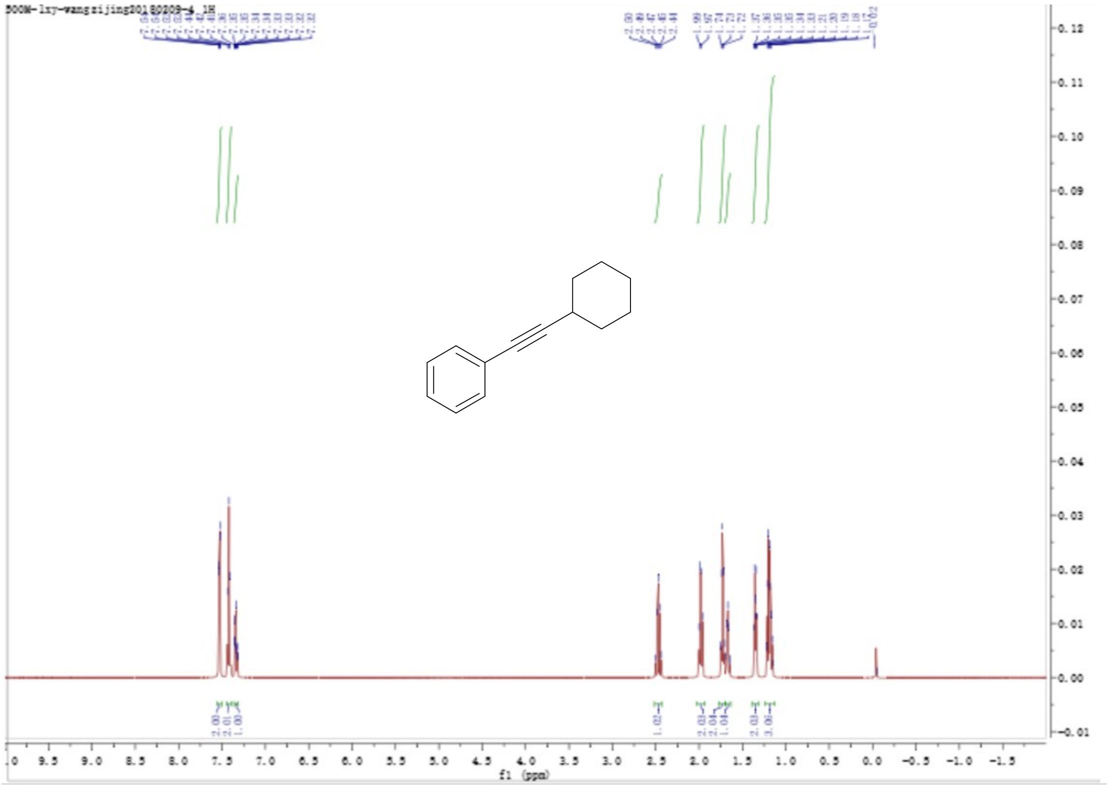


Figure S10. ^{1}H NMR spectrum of cyclohexylethynyl-benzene ($CDCl_3$)

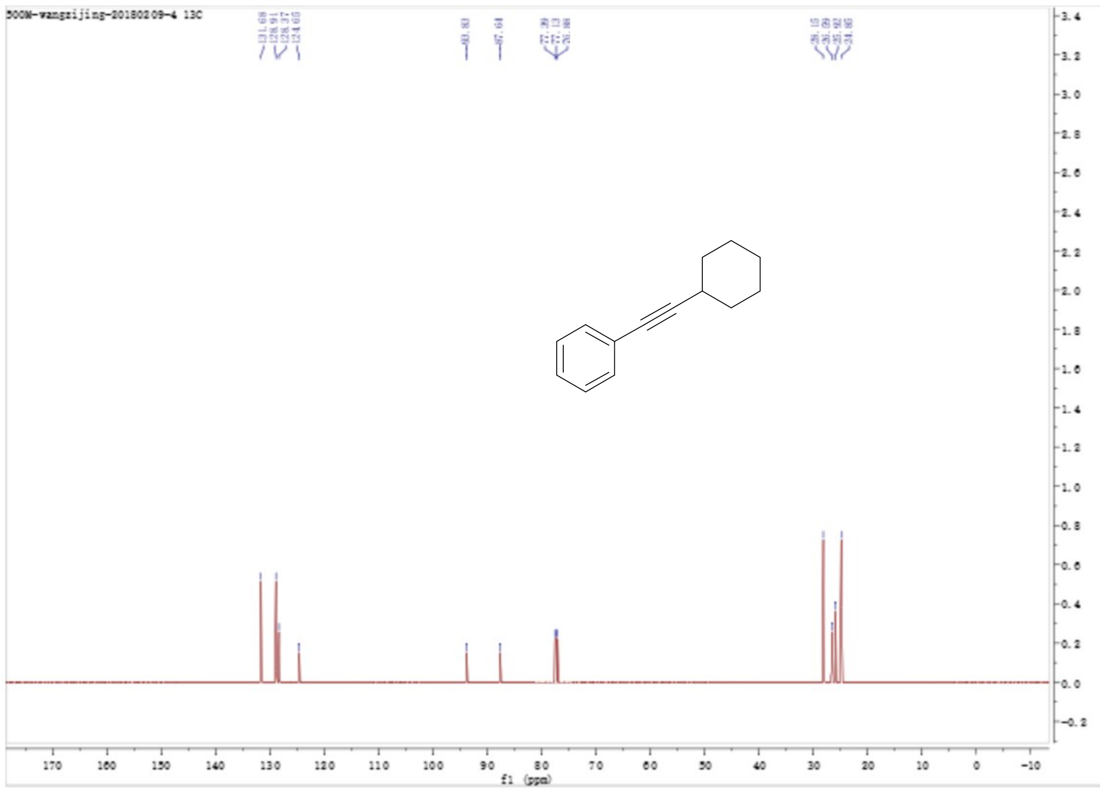


Figure S11. ^{13}C NMR spectrum of cyclohexylethynyl-benzene ($CDCl_3$)

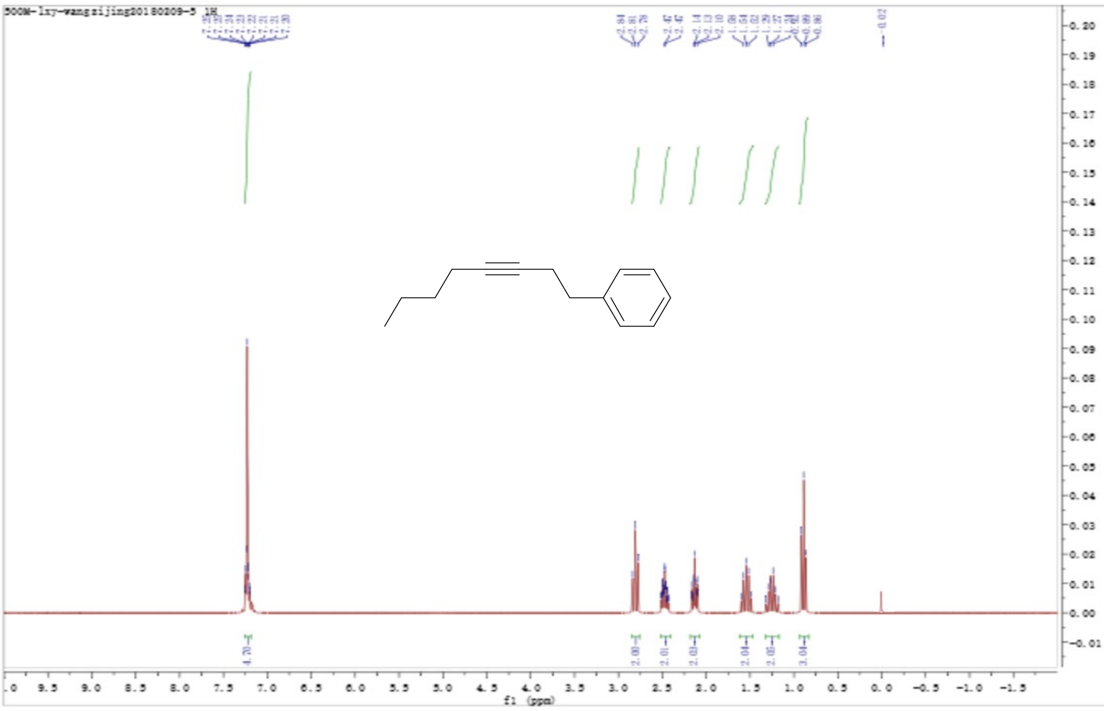


Figure S12. ^{1}H NMR spectrum of oct-3-ynyl-benzene ($CDCl_3$)

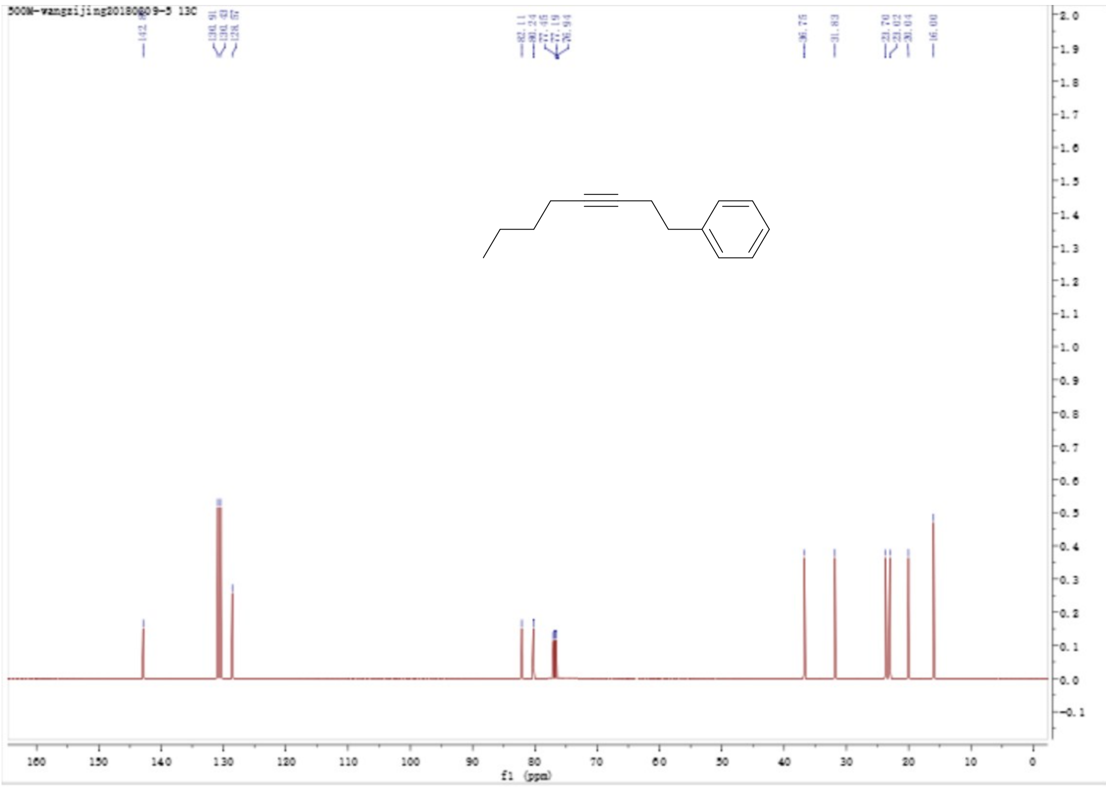


Figure S13. ^{13}C NMR spectrum of oct-3-ynyl-benzene ($CDCl_3$)

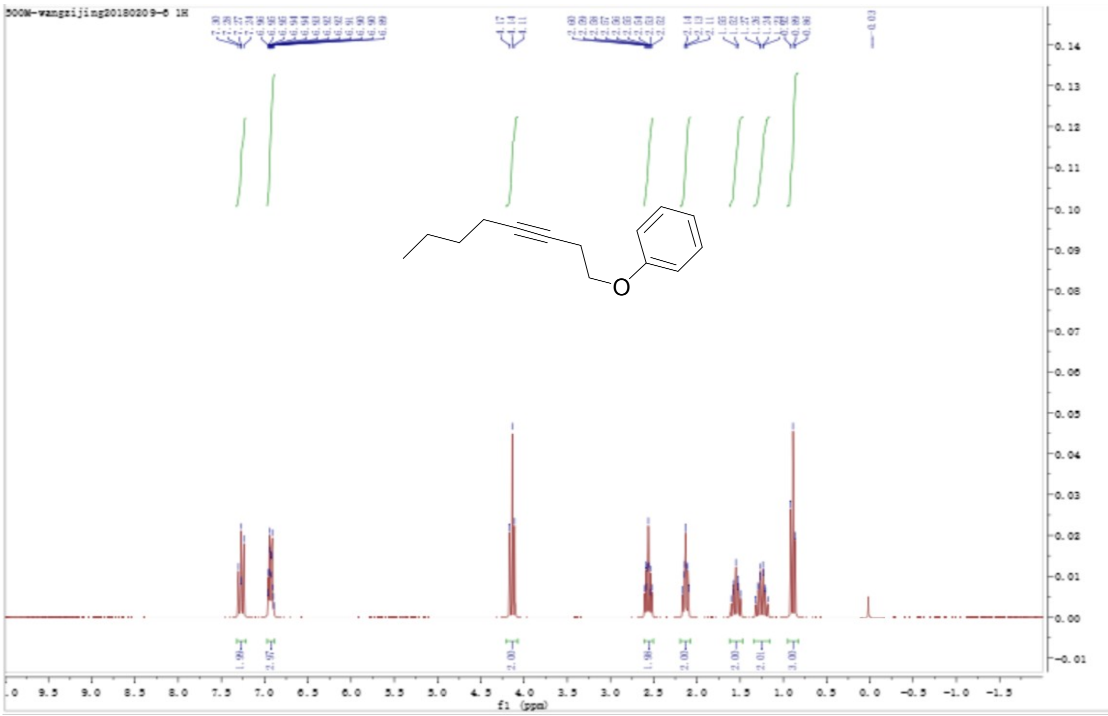


Figure S14. ^{1}H NMR spectrum of oct-3-ynyloxy-benzene ($CDCl_3$)

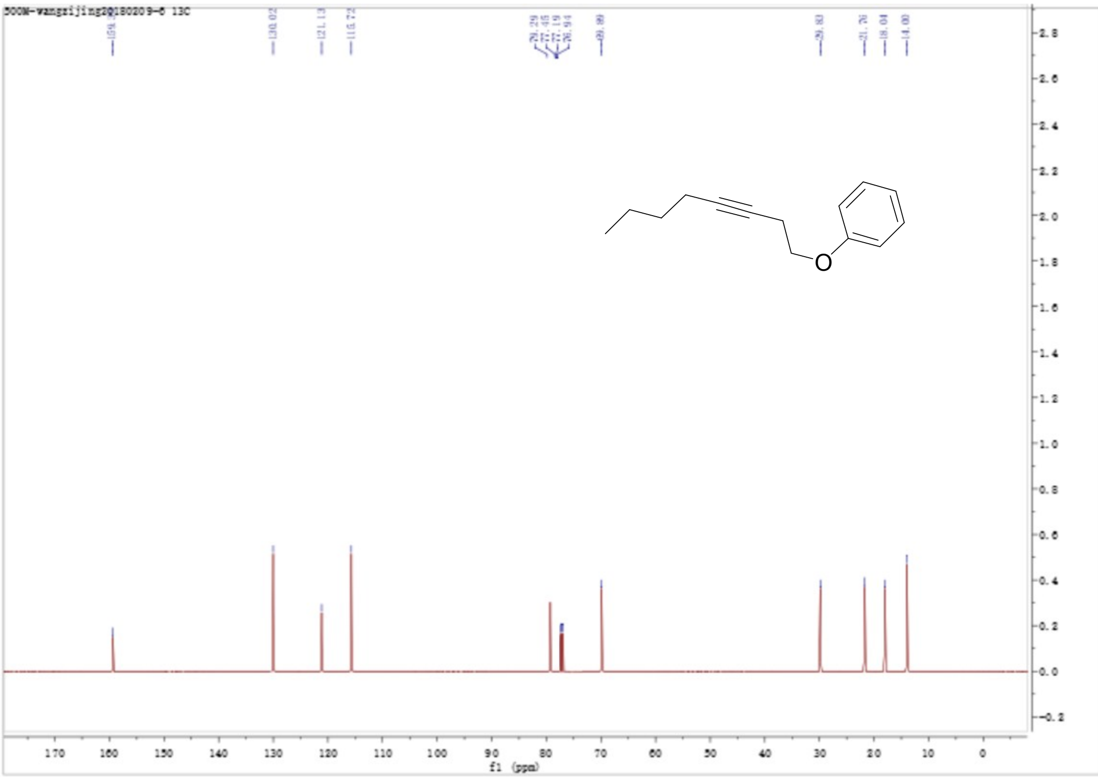


Figure S15. ^{13}C NMR spectrum of oct-3-ynyloxy-benzene ($CDCl_3$)

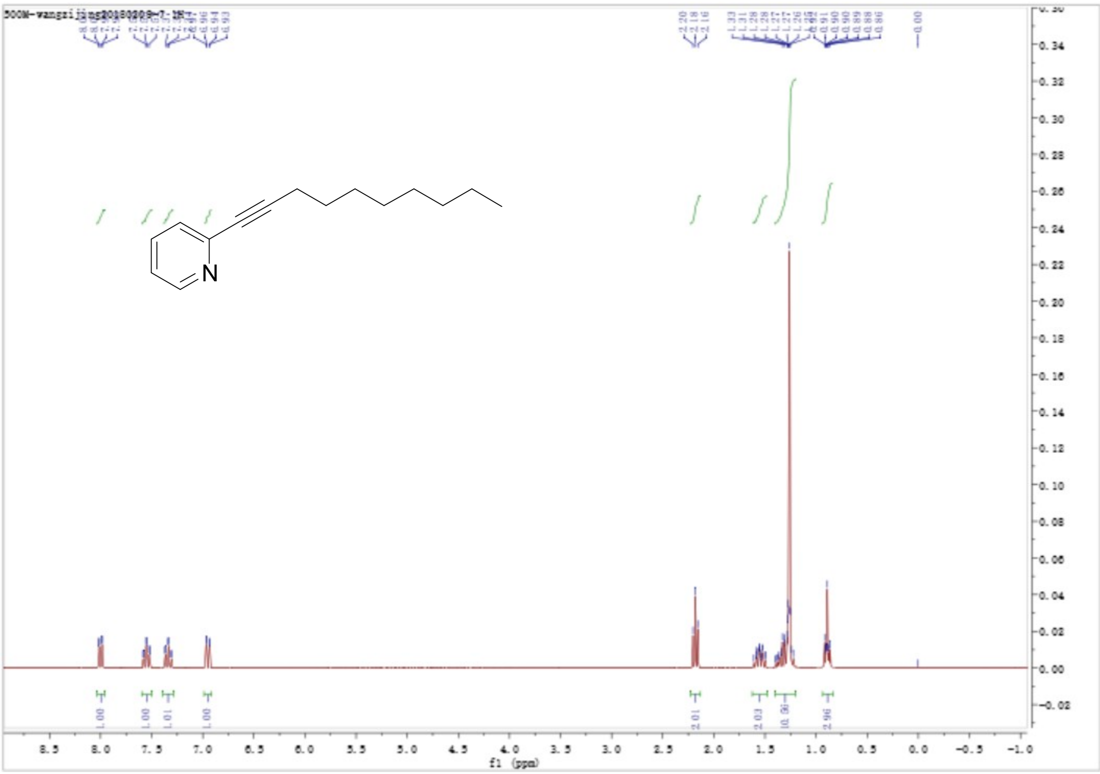


Figure S16. ^{1}H NMR spectrum of 2-dec-1-ynyl-pyridine ($CDCl_3$)

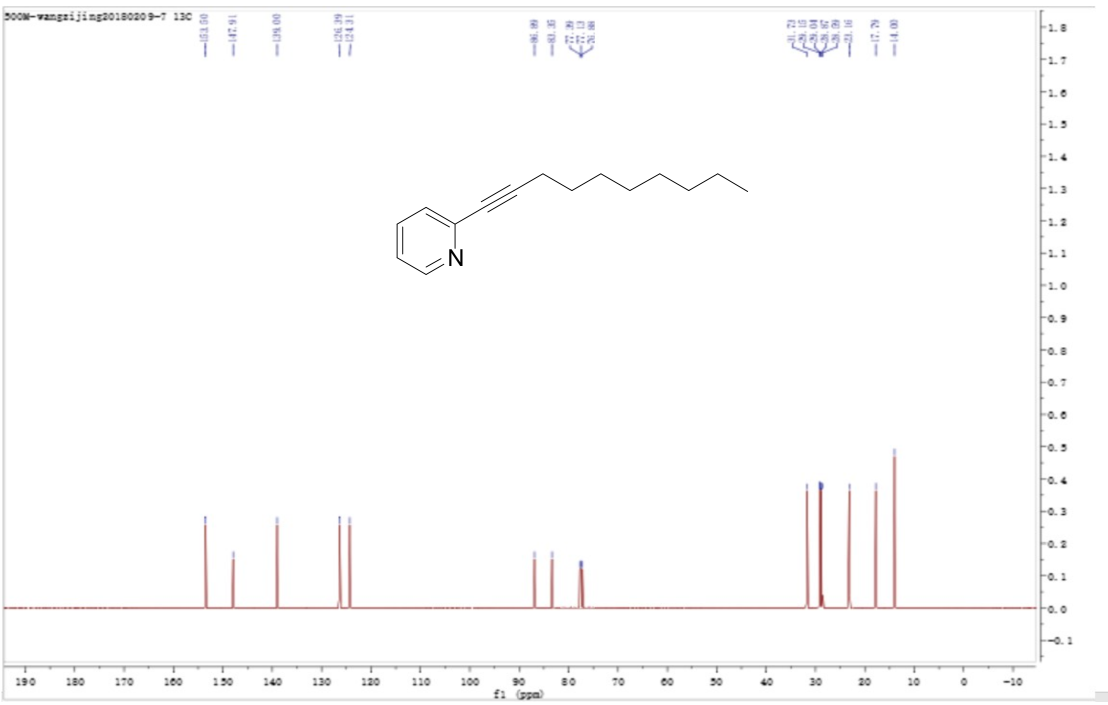


Figure S17. ^{13}C NMR spectrum of 2-dec-1-ynyl-pyridine ($CDCl_3$)

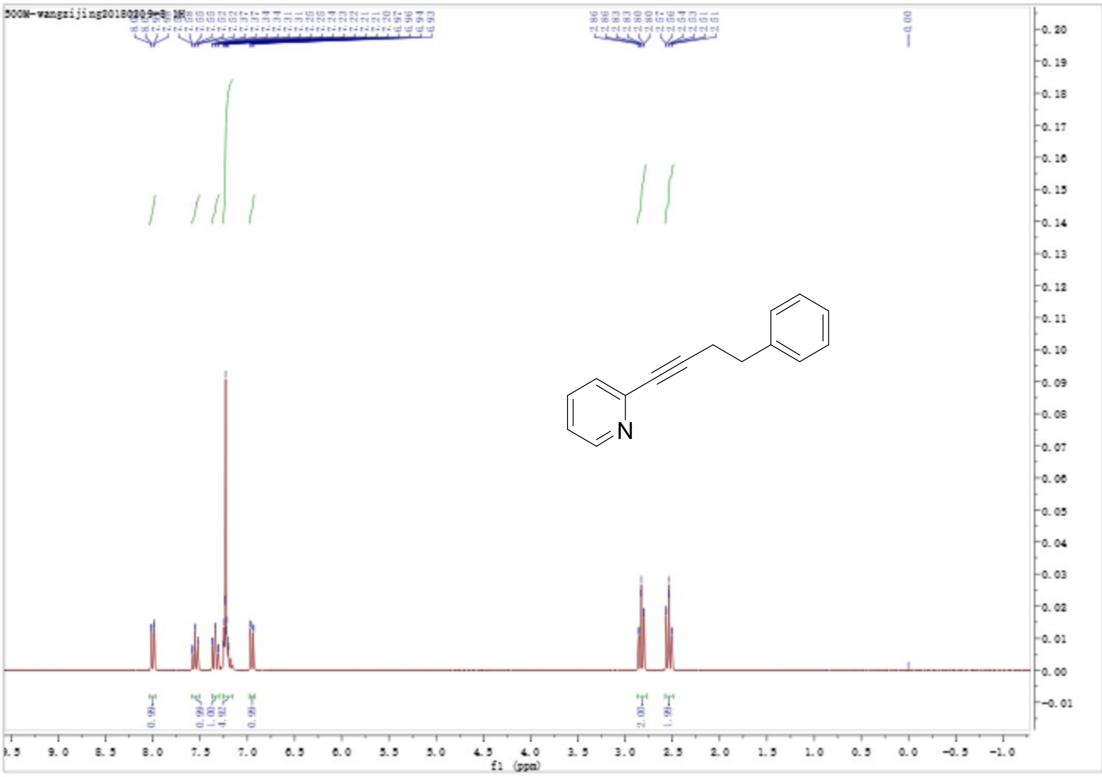


Figure S18. ^{1}H NMR spectrum of 2-(4-phenyl-but-1-ynyl)-pyridine ($CDCl_3$)

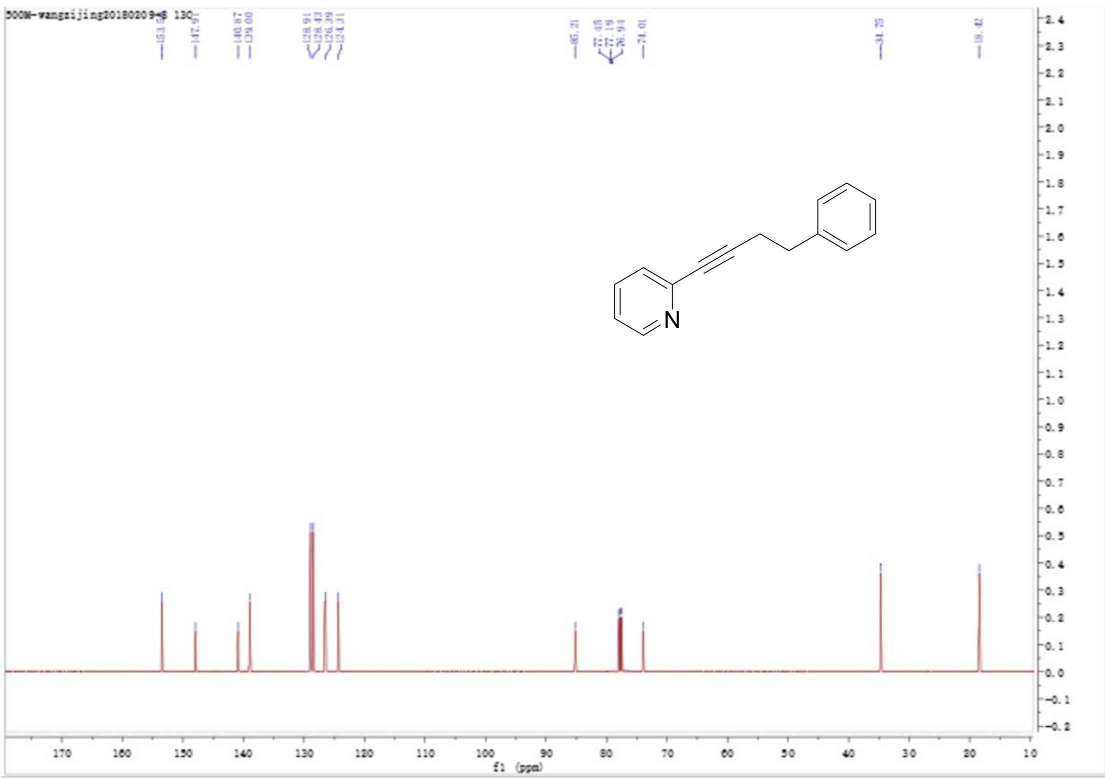


Figure S19. ^{13}C NMR spectrum of 2-(4-phenyl-but-1-ynyl)-pyridine ($CDCl_3$)

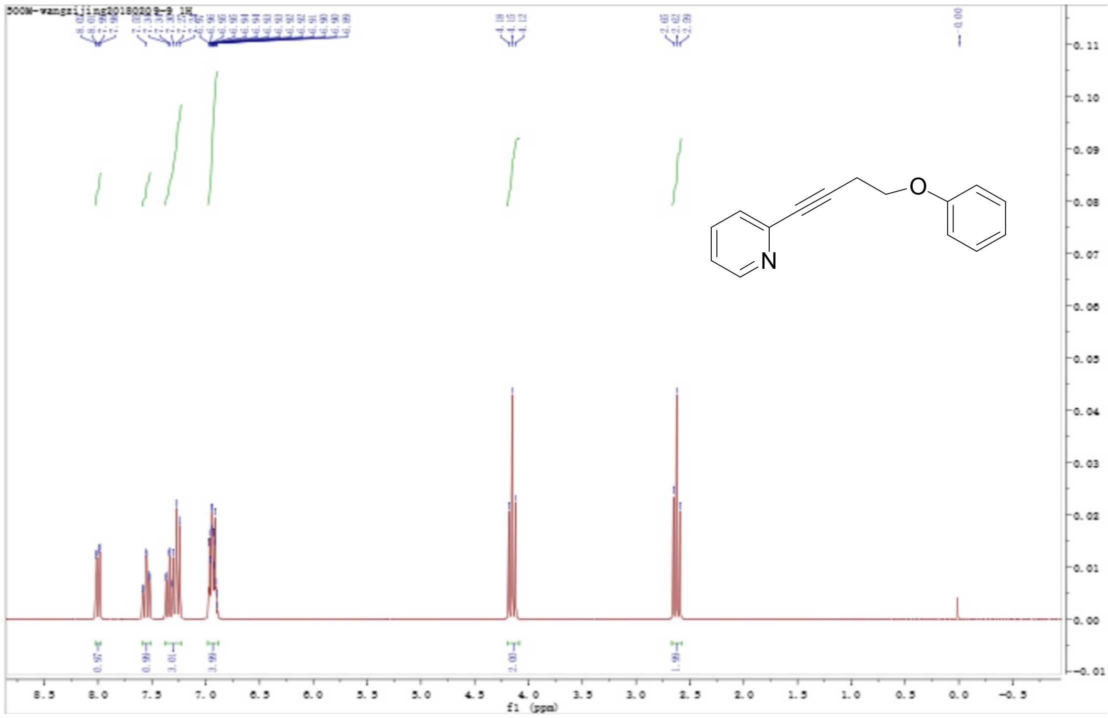


Figure S20. ^{1}H NMR spectrum of 2-(4-phenoxy-but-1-ynyl)-pyridine ($CDCl_3$)

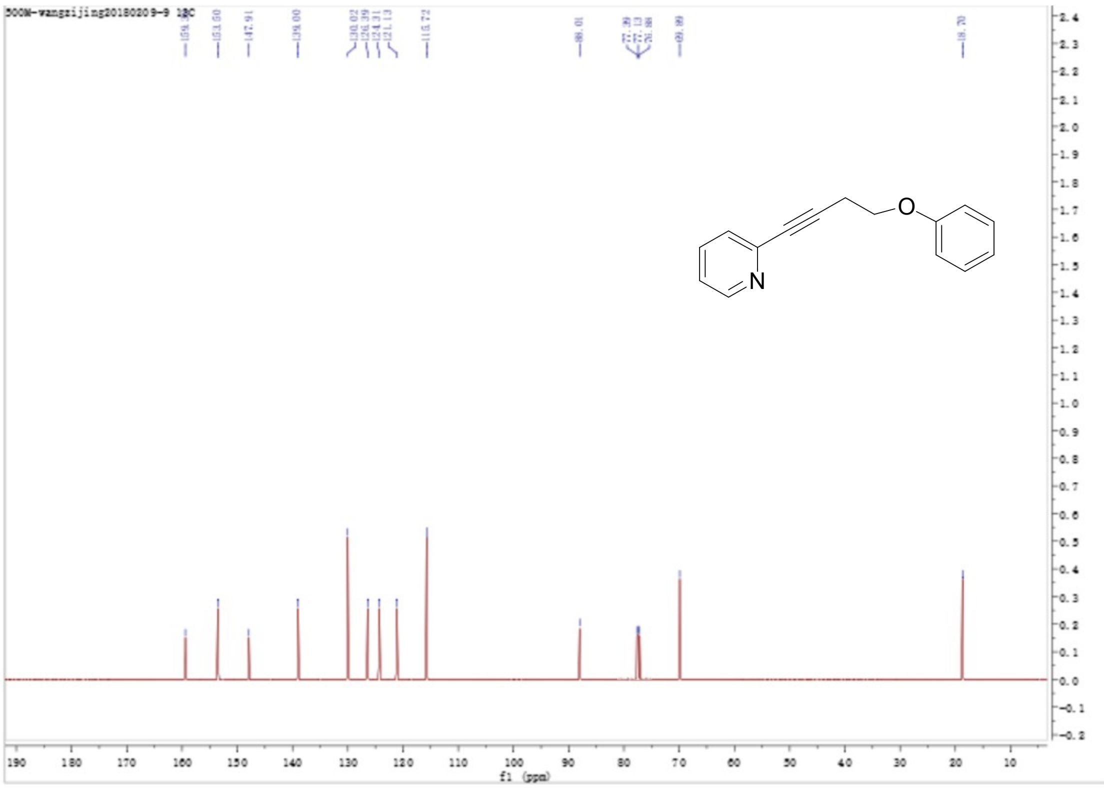


Figure S21. ^{13}C NMR spectrum of 2-(4-phenoxy-but-1-ynyl)-pyridine ($CDCl_3$)

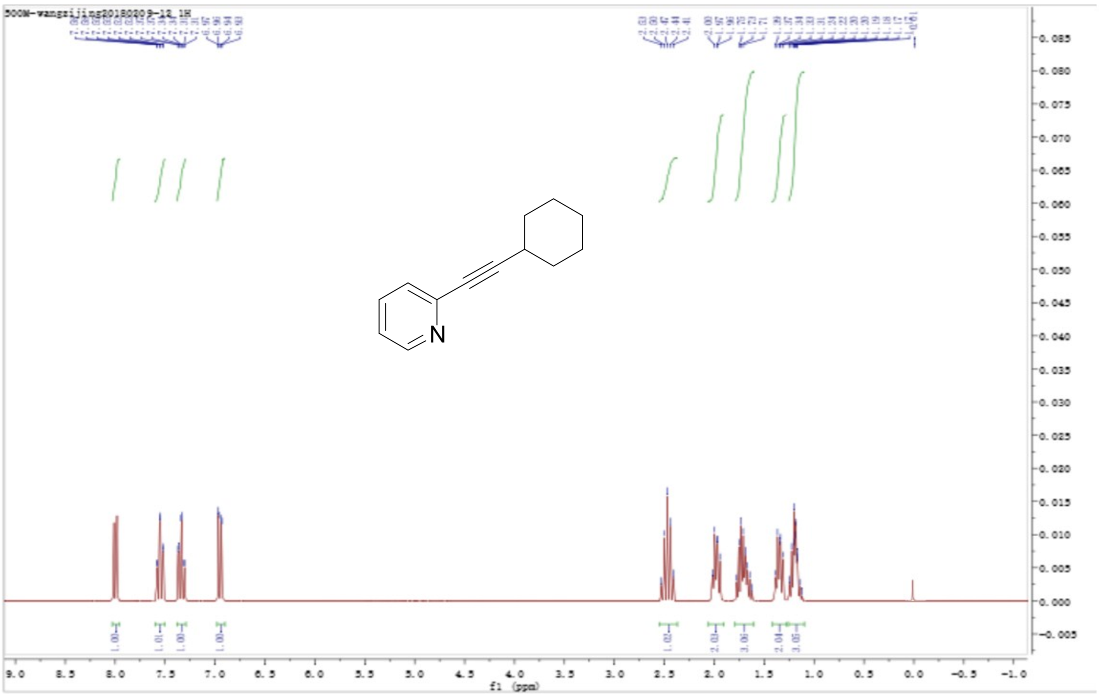


Figure S22. ^{1}H NMR spectrum of 2-cyclohexylethynyl-pyridine ($CDCl_3$)

Figure S23. ^{13}C NMR spectrum of 2-cyclohexylethynyl-pyridine ($CDCl_3$)

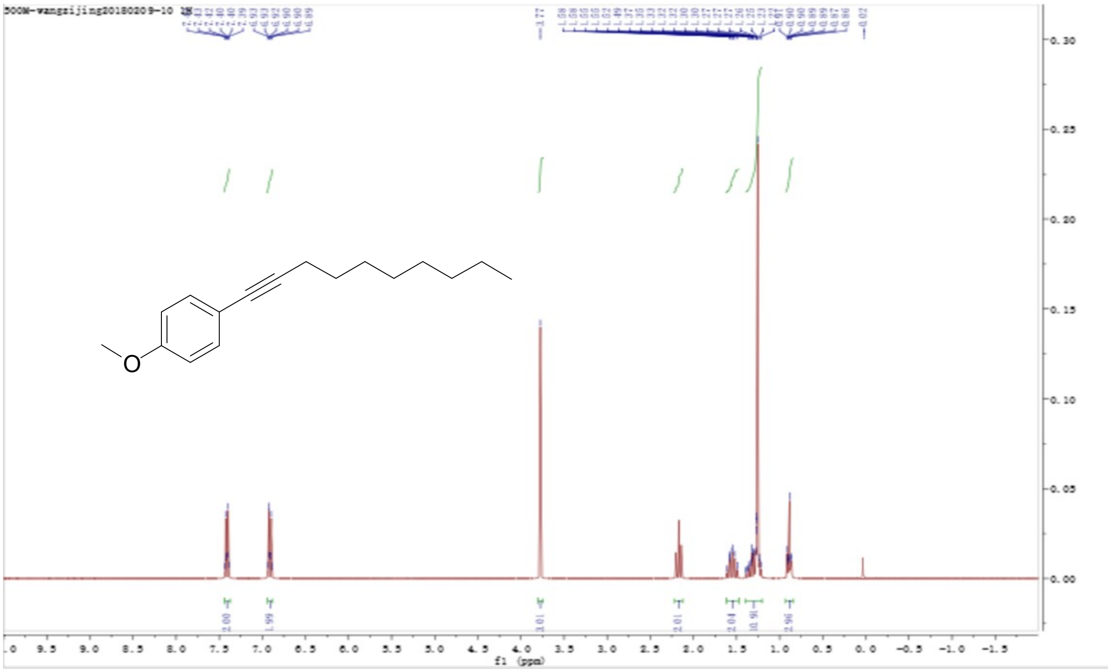


Figure S24. ^{1}H NMR spectrum of 1-dec-1-ynyl-4-methoxy-benzene ($CDCl_3$)

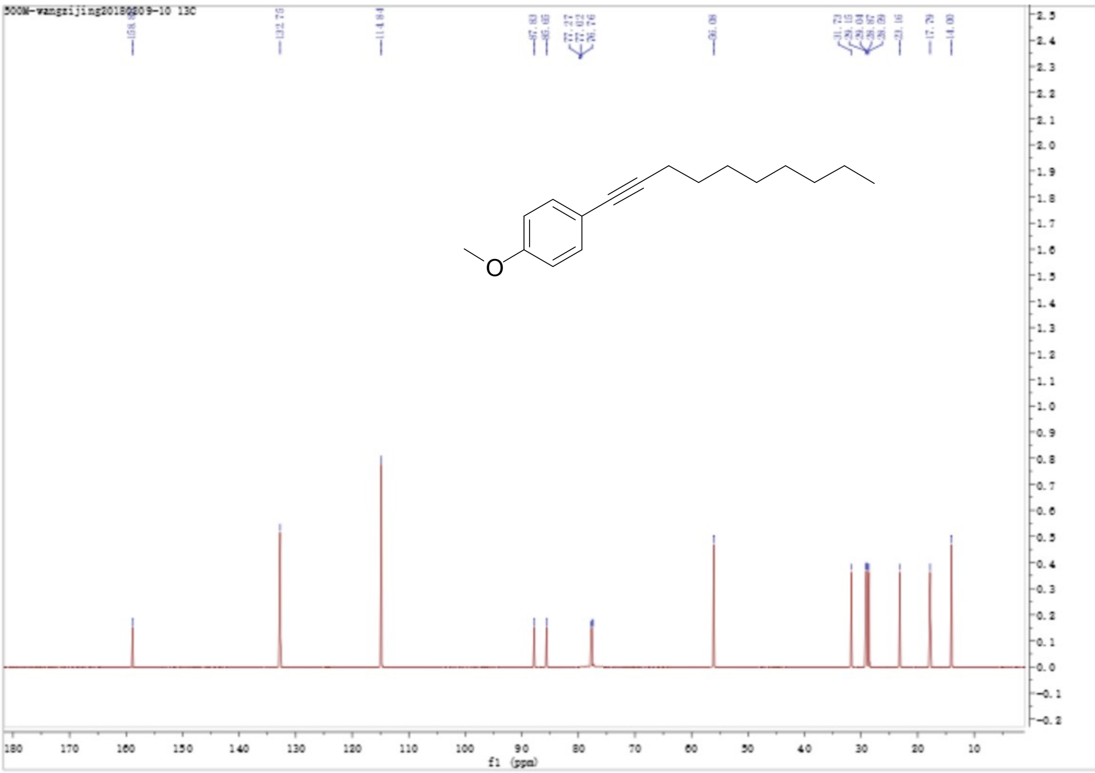


Figure S25. ^{13}C NMR spectrum of 1-dec-1-ynyl-4-methoxy-benzene ($CDCl_3$)

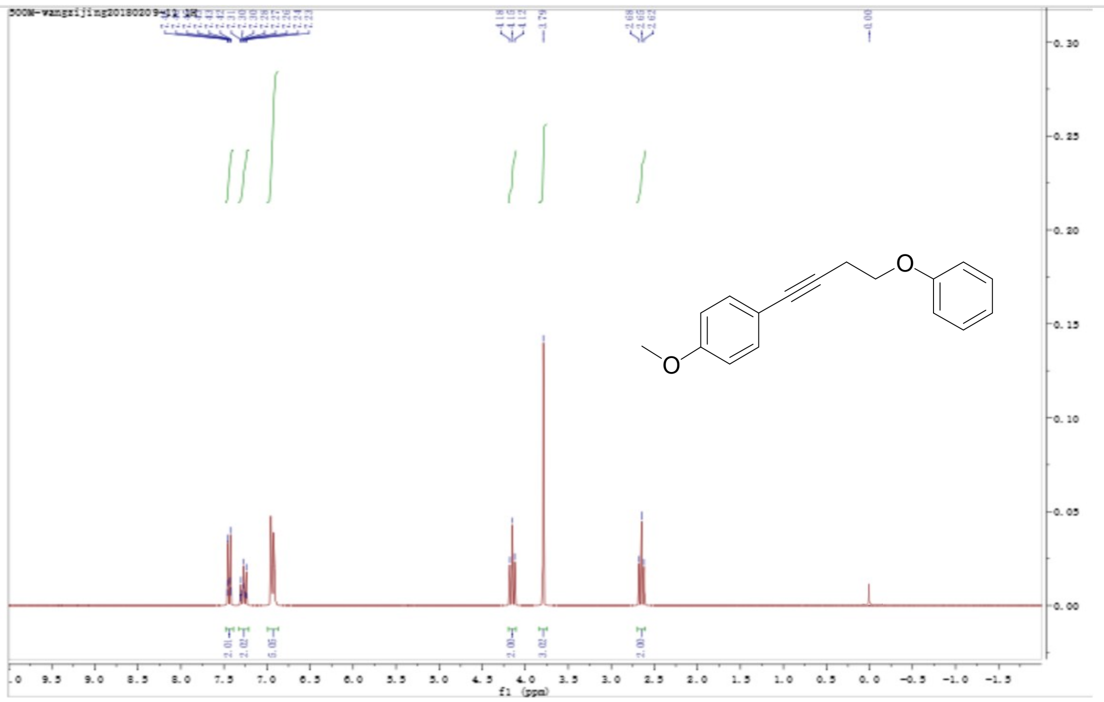


Figure S26. ^{1}H NMR spectrum of 1-methoxy-4-(4-phenoxy-but-1-ynyl)-benzene ($CDCl_3$)

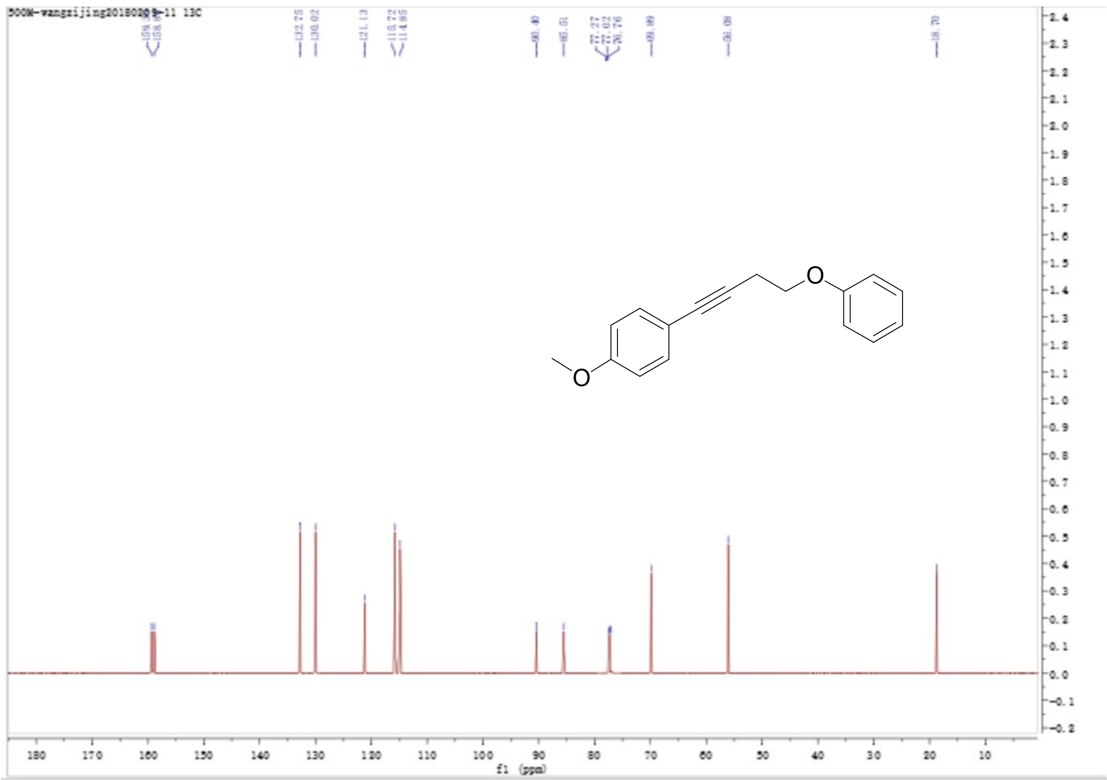


Figure S27. ^{13}C NMR spectrum of 1-methoxy-4-(4-phenoxy-but-1-ynyl)-benzene ($CDCl_3$)

SIV. IR spectrum of phenylethynyl copper

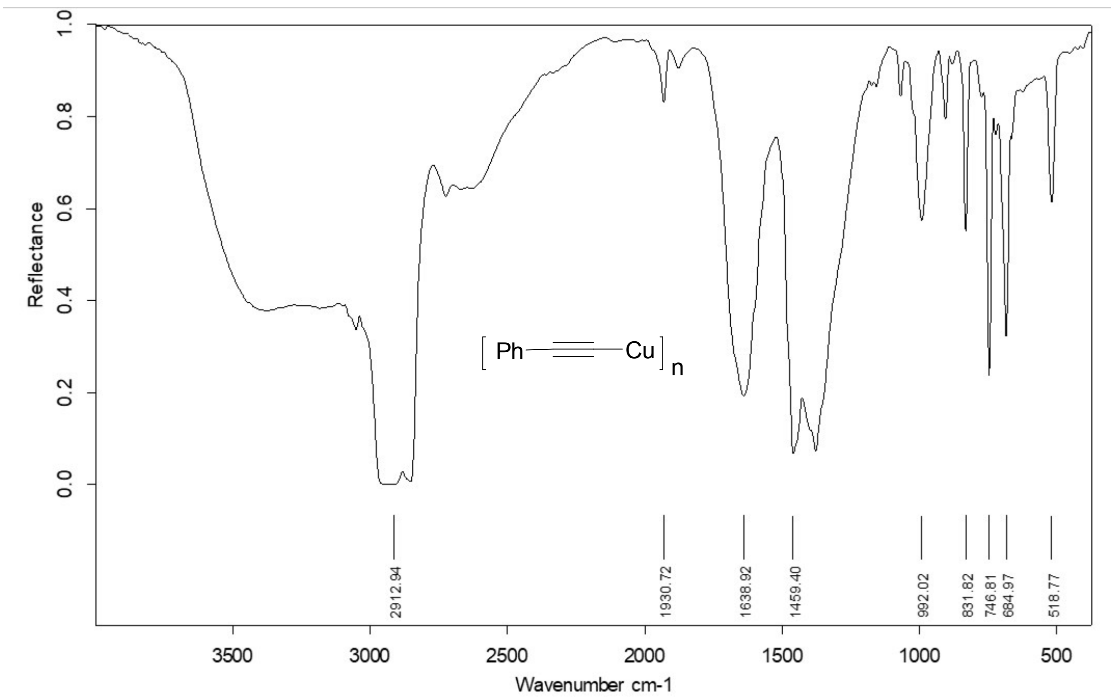
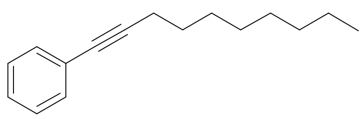
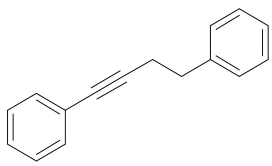


Figure S28. IR spectrum of phenylethynyl copper

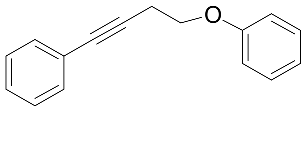
SV. Analytical data of the catalytic products



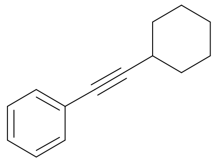
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 2H), 7.23 – 7.13 (m, 3H), 2.31 (t, *J* = 7.0 Hz, 2H), 1.59 – 1.44 (m, 2H), 1.43 – 1.31 (m, 2H), 1.21 (m, 8H), 0.81 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.25, 128.94, 127.75, 124.37, 87.83, 85.65, 31.73, 29.15, 29.04, 28.87, 28.59, 23.16, 17.79, 14.00.



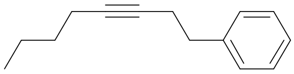
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 15.0, 3.2 Hz, 2H), 7.42 (dd, *J* = 27.8, 2.8 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.26 – 7.15 (m, 5H), 2.83 (t, *J* = 14.0 Hz, 2H), 2.58 (t, *J* = 14.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.87, 131.25, 128.94, 128.91, 128.43, 127.75, 126.57, 124.37, 85.00, 78.71, 34.75, 18.42.



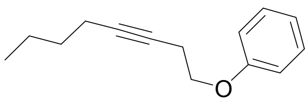
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.29 – 7.16 (m, 5H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 2H), 4.10 (t, *J* = 5.9 Hz, 2H), 3.69 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.17, 132.57, 129.73, 129.30, 128.47, 121.95, 121.36, 114.79, 81.66, 74.04, 68.00, 41.86.



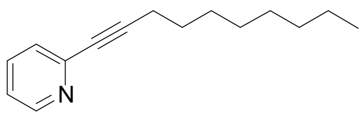
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.31 (m, 1H), 2.47 (p, *J* = 7.8 Hz, 1H), 1.98 (dd, *J* = 13.4, 5.6 Hz, 2H), 1.73 (p, *J* = 5.7 Hz, 2H), 1.67 (p, *J* = 5.8 Hz, 1H), 1.35 (dt, *J* = 7.7, 5.7 Hz, 2H), 1.18 (dp, *J* = 16.8, 5.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.68, 128.91, 128.37, 124.65, 93.83, 87.64, 28.15, 26.59, 25.92, 24.85.



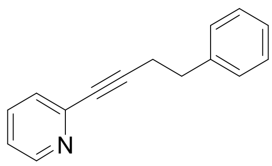
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 5H), 2.81 (t, *J* = 15.2 Hz, 2H), 2.51 – 2.41 (m, 2H), 2.13 (tt, *J* = 14.2, 4.9 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.33 – 1.17 (m, 2H), 0.89 (t, *J* = 13.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.87, 130.91, 130.43, 128.57, 82.11, 80.24, 36.75, 31.83, 23.70, 23.02, 20.04, 16.00.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 16.7, 13.5 Hz, 2H), 6.97 – 6.88 (m, 3H), 4.14 (t, *J* = 14.7 Hz, 2H), 2.56 (tt, *J* = 14.7, 5.0 Hz, 2H), 2.19 – 2.07 (m, 2H), 1.55 (ddd, *J* = 26.8, 15.2, 11.6 Hz, 2H), 1.34 – 1.16 (m, 2H), 0.89 (t, *J* = 13.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.39, 130.02, 121.13, 115.72, 79.28, 69.89, 29.83, 21.76, 18.04, 14.00.

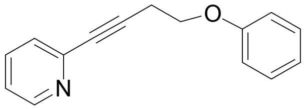


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 14.9, 3.0 Hz, 1H), 7.55 (td, *J* = 15.0, 3.0 Hz, 1H), 7.34 (td, *J* = 14.9, 3.0 Hz, 1H), 6.95 (dd, *J* = 15.0, 3.1 Hz, 1H), 2.18 (t, *J* = 11.9 Hz, 2H), 1.62 – 1.48 (m, 2H), 1.40 – 1.20 (m, 11H), 0.93 – 0.84 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.50, 147.91, 139.00, 126.39, 124.31, 86.89, 83.35, 31.73, 29.15, 29.04, 28.87, 28.59, 23.16, 17.79, 14.00.

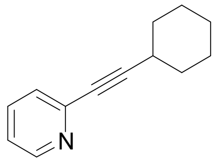


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 14.9, 3.0 Hz, 1H), 7.55 (td, *J* = 15.0, 3.0 Hz, 1H), 7.34 (td, *J* = 14.9, 3.0 Hz, 1H), 7.26 – 7.16 (m, 5H), 6.95 (dd, *J* = 15.0, 3.1 Hz, 1H), 2.83 (td, *J* = 14.7, 1.5

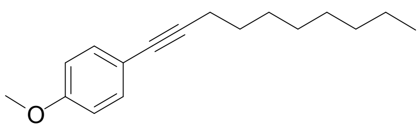
Hz, 2H), 2.54 (td, J = 14.7, 1.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.50, 147.91, 140.87, 139.00, 128.91, 128.43, 126.39, 124.31, 85.21, 74.01, 34.75, 18.42.



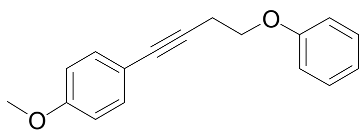
^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 14.9, 3.0 Hz, 1H), 7.55 (td, J = 15.0, 3.0 Hz, 1H), 7.32 (ddd, J = 35.2, 22.7, 8.9 Hz, 3H), 6.93 (dddd, J = 14.5, 9.8, 6.3, 3.2 Hz, 4H), 4.15 (t, J = 15.0 Hz, 2H), 2.62 (t, J = 15.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.39, 153.50, 147.91, 139.00, 130.02, 126.39, 124.31, 121.13, 115.72, 88.01, 69.89, 18.70.



^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 14.9, 3.0 Hz, 1H), 7.55 (td, J = 14.9, 3.0 Hz, 1H), 7.34 (td, J = 14.9, 3.0 Hz, 1H), 6.95 (dd, J = 14.9, 3.1 Hz, 1H), 2.47 (p, J = 15.5 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.79 – 1.60 (m, 3H), 1.41 – 1.28 (m, 2H), 1.26 – 1.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.48, 147.85, 138.55, 126.70, 123.11, 90.40, 89.05, 28.15, 26.59, 25.92, 24.85.



^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 6.94 – 6.88 (m, 2H), 3.77 (s, 3H), 2.17 (t, J = 15.5 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.39 – 1.20 (m, 11H), 0.93 – 0.84 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.86, 132.75, 114.84, 87.83, 85.65, 56.08, 31.73, 29.15, 29.04, 28.87, 28.59, 23.16, 17.79, 14.00.



^1H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.32 – 7.21 (m, 2H), 6.99 – 6.87 (m, 5H), 4.15 (t, J = 14.2 Hz, 2H), 3.79 (s, 3H), 2.65 (t, J = 14.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.39, 158.86, 132.75, 130.02, 121.13, 115.72, 114.85, 90.40, 85.51, 69.89, 56.08, 18.70.

SVI. ESI-MS data of reactions

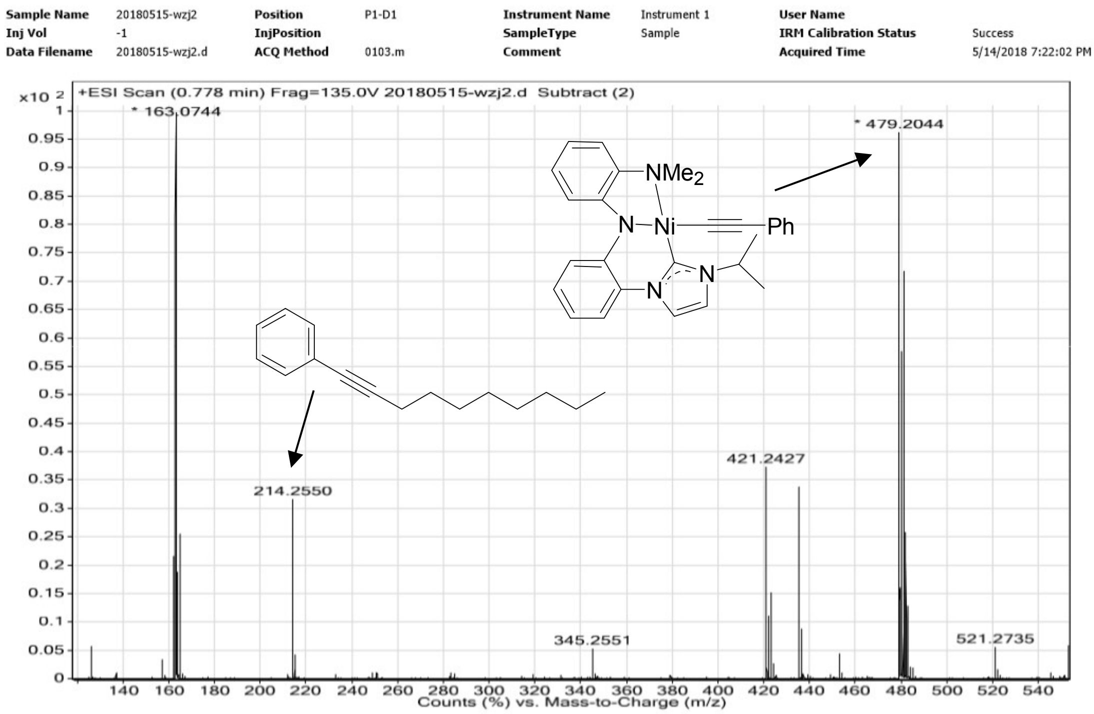


Figure S29. ESI-MS of Eq. (2)

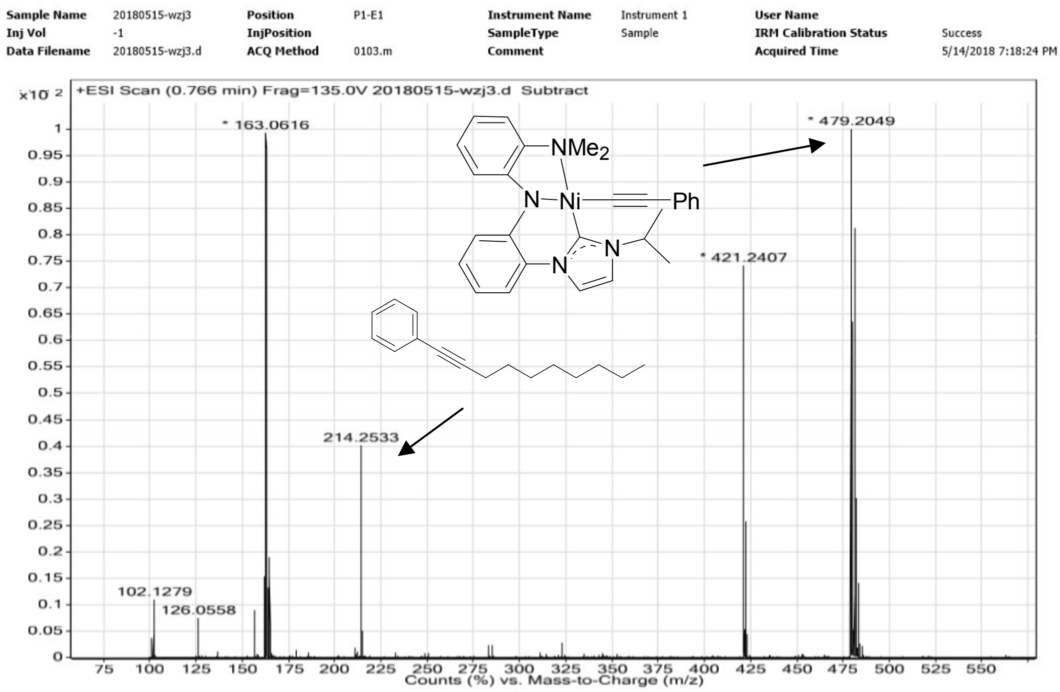


Figure S30. ESI-MS of Eq. (3)

Sample Name	20180515-wzj4	**Position**	P1-C1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	20180515-wzj4.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/14/2018 7:25:41 PM

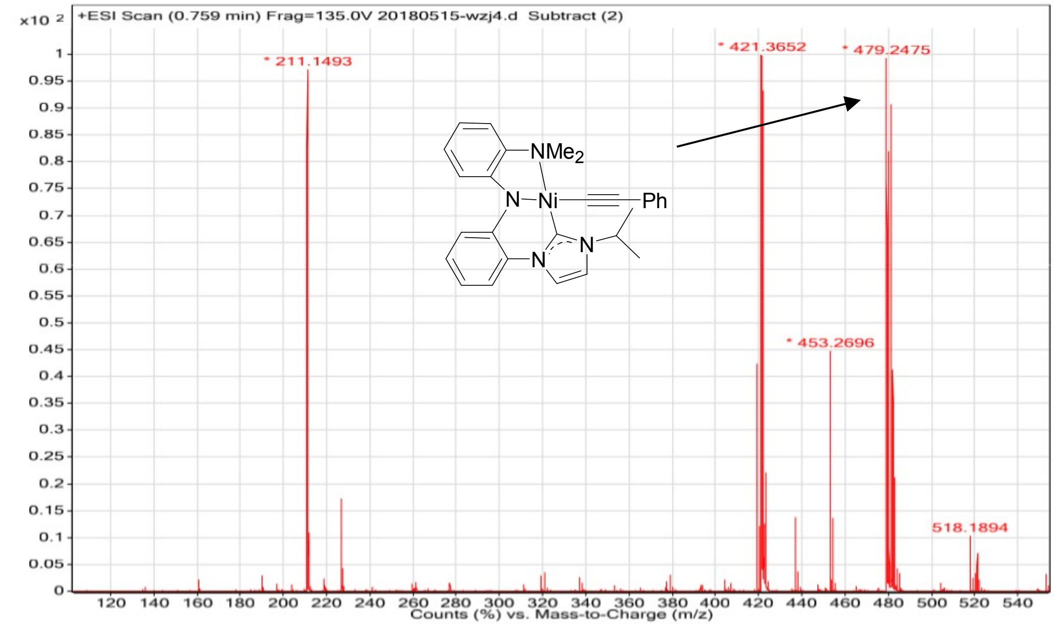
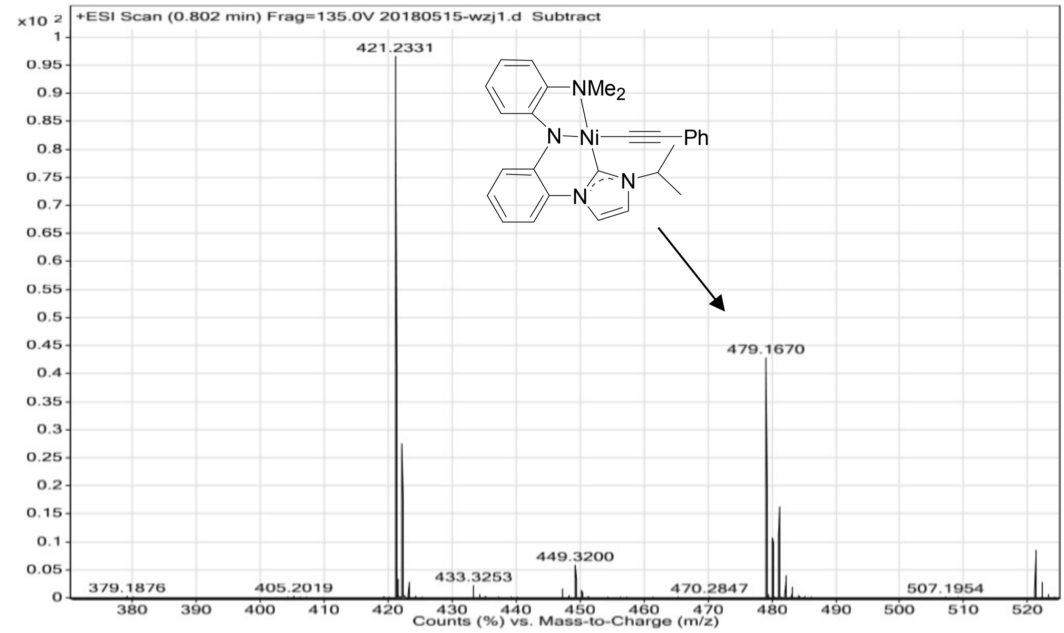


Figure S31. ESI-MS of Eq. (4)

Sample Name	20180515-wzj1	**Position**	P1-F1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	20180515-wzj1.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/14/2018 7:06:34 PM



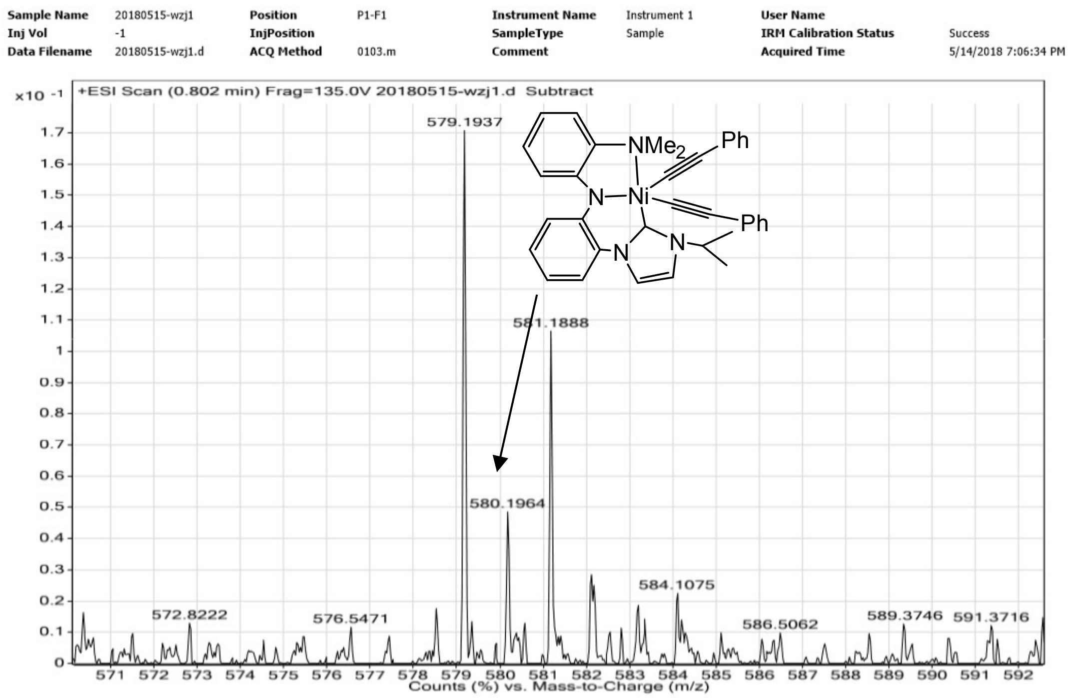
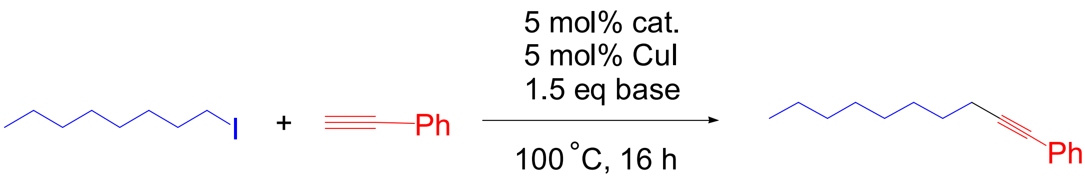


Figure S32. ESI-MS of Eq. (6)

SVII Table S1. Optimization of reaction conditions with 7/8 as catalysts



Entry	Cat.	Base	Solvent	Yield (%)
1	**7/8**	Cs_2CO_3	toluene	20/7
2	**7/8**	Cs_2CO_3	DMSO	86/69
3	**7/8**	Cs_2CO_3	DMF	48/30
4	**7/8**	NaO^{t}Bu	DMSO	0/0
5	**7/8**	K_2CO_3	DMSO	15/32
6	**7/8**	Et_3N	DMSO	88/72