Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Visible-light-mediated Barbier allylation of aldehydes and ketones via dual titanium and photoredox catalysis

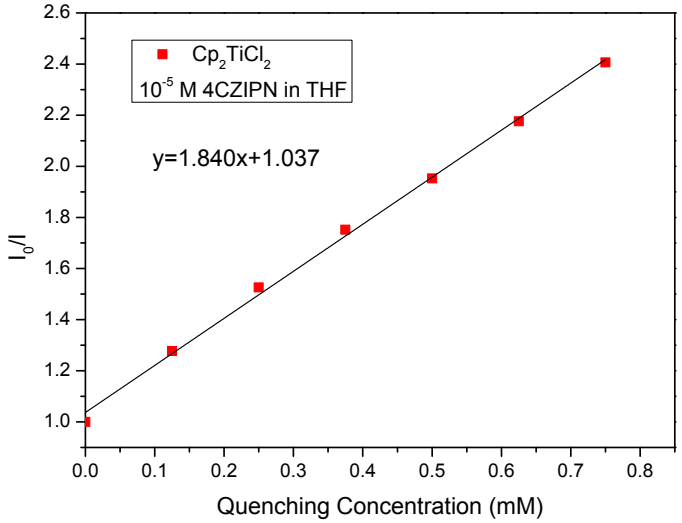
Contents

S1 General Information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L) with 10W LED. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400M spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.26 ppm). Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of $CDCl_3$ (77.00 ppm). ESI mass spectra were obtained from an HPLC-Q-Tof mass spectrometer using acetonitrile as the mobile phase. UV-vis spectra were collected on an HP 8453 spectrometer. The fluorescence emission spectra were collected on an Edinburgh FS920.

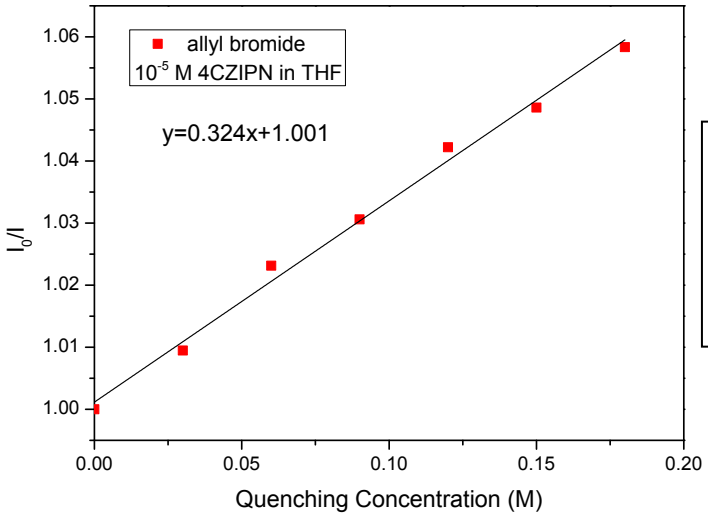
S2 Luminescence Quenching Experiments

Emission intensities were recorded using Edinburgh FS920 Fluorescense Spectrophotometer for all experiments. All 4CZIPN soltions were excited at 450 nm and the emission intensity was collected at 500-800 nm. In a typical experiment, the THF solution of 4CZIPN (10^{-5} M) was added the appropriate amount of quencher in a screw-top 4.5 cm quartz cuvette. After degassing with nitrogen for 15 min, the emission spectra of the samples were collected.



Stern-Volmer Equation
$F_0/F=1+K_q\tau_0[Q]$
$K_q\tau_0$=1840 L/mol
τ_0=557 ns
$K_q=3.30\times10^9$ L/(mol* s)

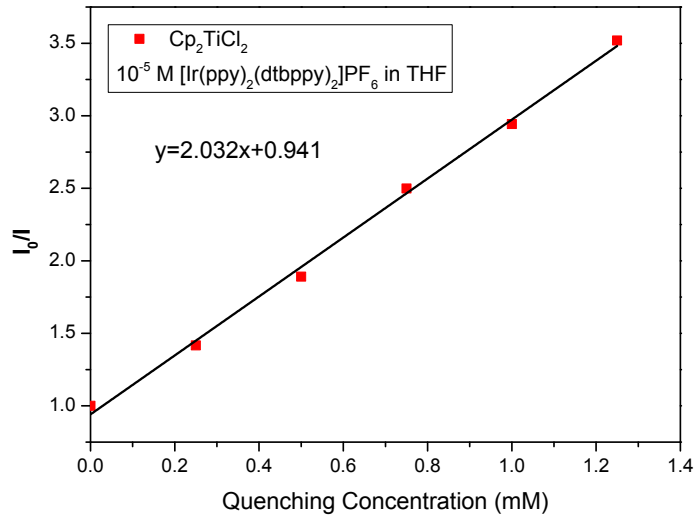
Figure 1. 4CZIPN emission quenching by Cp_2TiCl_2.



Stern-Volmer Equation
$F_0/F=1+K_q\tau_0[Q]$
$K_q\tau_0$=324 L/mol
τ_0=557 ns
$K_q=5.82\times10^8$ L/(mol* s)

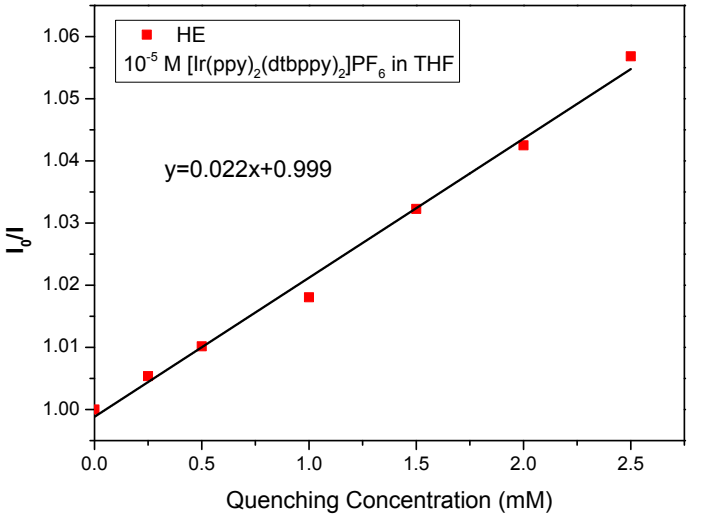
Figure 2. 4CZIPN emission quenching by allyl bromide.

All $Ir(ppy)_2(dtbby)PF_6$ soltions were excited at 468 nm and the emission intensity was collected at 500-800 nm. In a typical experiment, the THF solution of $Ir(ppy)_2(dtbby)PF_6$ (10^{-5} M) was added the appropriate amount of quencher in a screw-top 4.5 cm quartz cuvette. After degassing with nitrogen for 15 min, the emission spectra of the samples were collected. The results showed that Cp_2TiCl_2, HE and $BrCF_2CO_2Et$ quenched the photoexcited Ir(III)* effectively.



Stern-Volmer Equation
$F_0/F=1+K_q\tau_0[Q]$
$K_q\tau_0=2032$ L/mol
$\tau_0=557$ ns
$K_q=3.65\times10^9$ L/(mol* s)

Figure 1, $[Ir(ppy)_2(dtbppy)_2]PF_6$ emission quenching by Cp_2TiCl_2.

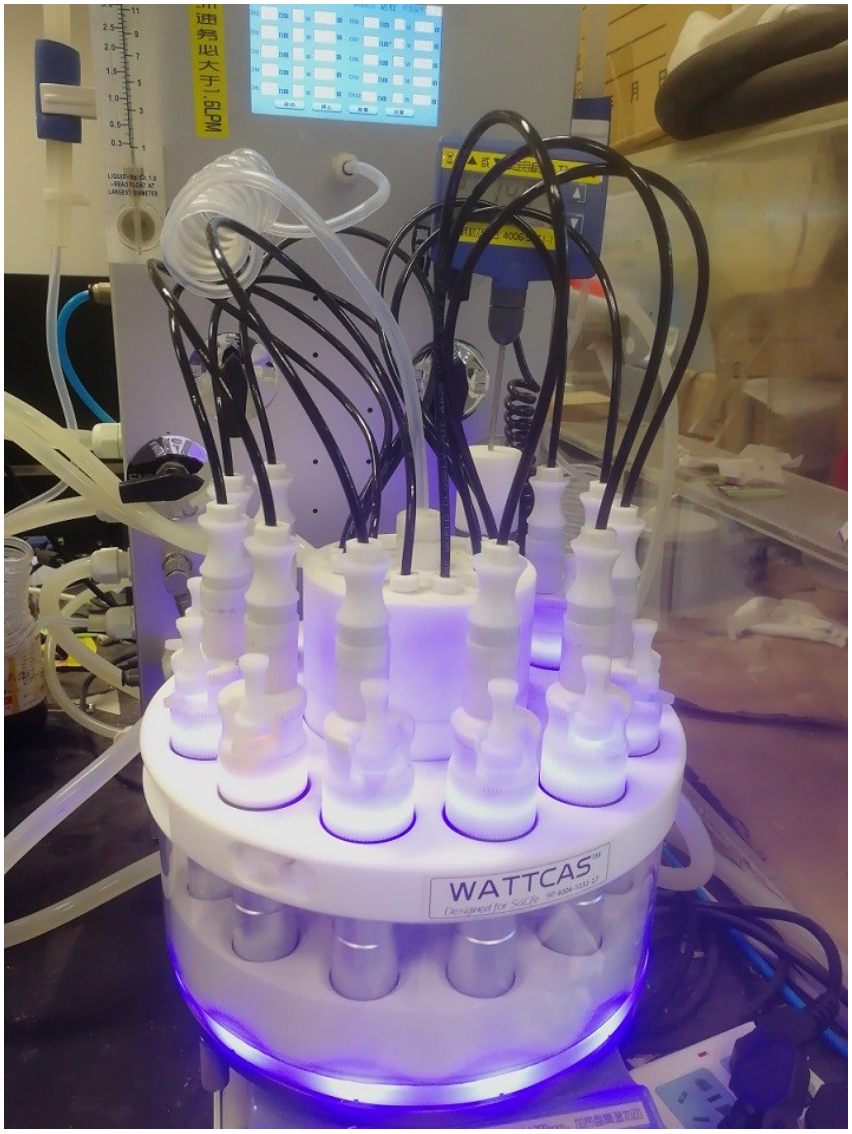


Stern-Volmer Equation
$F_0/F=1+K_q\tau_0[Q]$
$K_q\tau_0=22$ L/mol
$\tau_0=557$ ns
$K_q=3.95\times10^7$ L/(mol* s)

Figure 2, $[Ir(ppy)_2(dtbppy)_2]PF_6$ emission quenching by HE.

S3 Picture of Reaction Set-Up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L).



S4 Quantum yield

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020SL) with blue COB LED 450-455 nm. After irradiation, the yield of alcohol **2a** was determined by ^{1}H NMR based on a 1,3,5-trimethoxybenzene standard and the yield was 85% after 2 hrs. (please see **entry 9, Table 1** in manuscript)

The energy of a photon E_{ph} at a wavelength λ is calculated as
$E_{ph} = hc/\lambda = \underline{4.388 \times 10^{-19}\ J}$
λ: wavelength ($\lambda = 4.53 \times 10^{-7}$ m)
h: planck constant ($h = 6.626 \times 10^{-34}$ J*s)
c:velocity of light ($c = 3 \times 10^{8}$ m/s)

The total photon flux F_{ph} is calculated as
$F_{ph} = f\,P/\,E_{ph} = \underline{4.44 \times 10^{18}\ S^{-1}}$
f: $1\text{-}10^{-A}$ considering that in the reaction condition the number of transmitted photons is negligible in the whole range of emission of the lamp, it can be assumed that all photons are absorbed by the photocatalyst.
P: E*S (E: illumination intensity, E = 0.975 W/cm^2; S: the area irradiated, $S = \pi r^2 = 2.0$ cm^2

Quantum yield was determined as:
ϕ = Mole number for the product/Mole number photons absorbed
$= 0.85 \times 10^{-3} \times 6.02 \times 10^{23} / F_{ph} \times 7200s = 0.016$

This result revealed that the main pathway of this reaction was not a photo-initiated radical chain process, but a photocatalyzed process.

WATTCAS™
华太科思

西安华太科思化学技术有限公司
http://www.wattcas.com
Tel: +4006515117
Fax: +86()

CLED Test Report

Product Mark

Model: 450-455nm 10W
Manufacture:
Temperature: 20°C
Humidity: 35%
Tester: lilu
Test Date: 2020-07-09,11:27:03

Parameter

Name	Value	Name	Value	Name	Value	Name	Value
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FluctuateDepth(%)	36.2	Duv y0,dy	0.0000,0.0000	CIE1931 Z	15369010.000		
BinkPercent(%)	22.1	SDCM	100.00	TLCI-2012	0		
BinkExponent	0.00	Ra	-67.8	Integral Time(ms)	0		
EffectiveLux(lx)	0.0	Ee(mW/cm²)	975.913	Peak Signal	54611		
PeakLux(lx)	0.0	S/P	22.028	Dark Signal	2072		
LuxIntgarl(lx.s)	0.0	Dominant(nm)	458.50	Compensate level	2854		
FlashTime(us)	0	Purity(%)	99.0				
E(lx)	388650.38	HalfWidth(nm)	22.2				
Candle E(fc)	36106.50	Peak(nm)	454.6				
CCT(K)	100000	Center(nm)	454.6				
Duv	-0.06310	Centroid(nm)	455.7				
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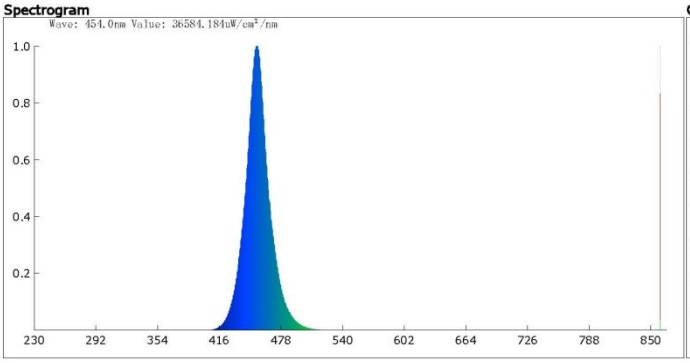
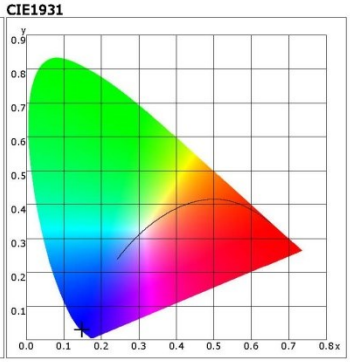
CIE u,v	0.1930,0.0595	CIE1931 X	2769507.500				

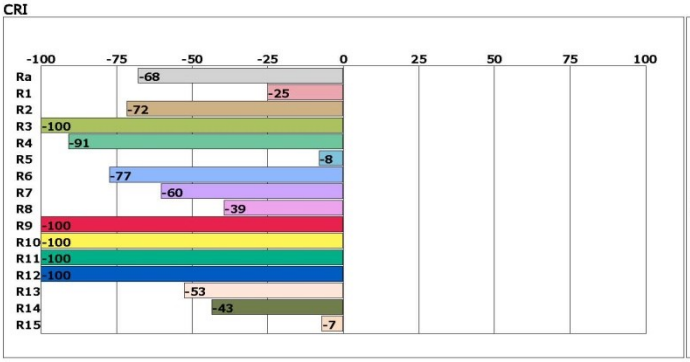
Spectrogram

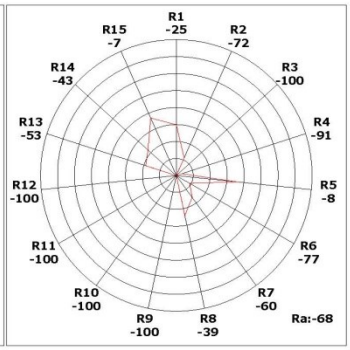


CIE1931



CRI





Instrument Status

Type: PCS230850
SN: 0
Scan Range: 230-850nm
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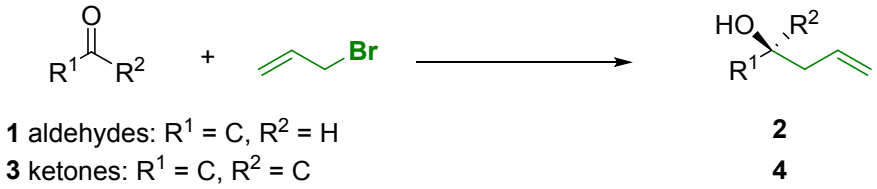
VPeak: 54611
VDark: 2072

Remark:

S5 General procedure of allylation

Procedure 1: General procedure of aldehydes or ketones with allyl bromide, condition A

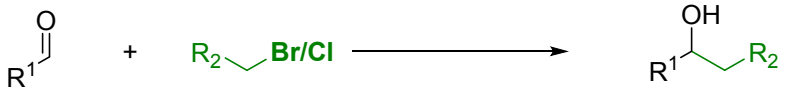


1 aldehydes: R^1 = C, R^2 = H
3 ketones: R^1 = C, R^2 = C

2
4

Following the standard procedure, a solution of **1** or **3** (1.0 mmol, 1.0 eq.), allyl bromide, HE (2.0 mmol, 2.0 eq.), Cp_2TiCl_2 (10.0% mol), and 4CZIPN (1% mol) in THF. The reaction mixture was stirred at room temperature using 10W 450 nm LED for 12 h. The ^{1}H NMR analysis of the crude product was calculated using 1,3,5-Trimethyoxybenzene as the internal standard. Yields are shown in manuscripts table **2**.

Procedure 2: General procedure of aldehydes with alkyl halides, condition B

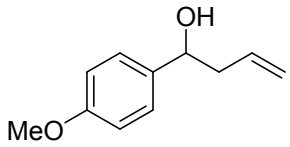


1

6

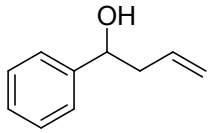
Following the standard procedure, a solution of **1** (1.0 mmol, 1.0 eq.), alkyl halide, HE (2.0 mmol, 2.0 eq.), Cp_2TiCl_2 (10.0% mol), and 4CZIPN (1% mol) in THF. The reaction mixture was stirred at room temperature using 10W 450 nm LED for 12 h. The ^{1}H NMR analysis of the crude product was calculated using 1,3,5-Trimethyoxybenzene as the internal standard. Yields are shown in manuscripts table **3**.

S6 Characterization of Products



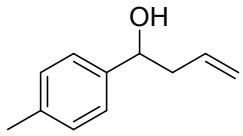
2a

2a, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. Br: 92%, Cl: 84%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.90 – 5.62 (m, 1H), 5.23 – 5.07 (m, 2H), 4.68 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 2.53 – 2.46 (m, 2H), 2.05 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 136.02, 134.58, 127.04, 118.16, 113.75, 72.95, 55.24, 43.71. Organic Letters, 20(18), 5757-5761; 2018.



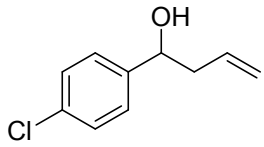
2b

2b, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 73%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H), 5.81 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.22 – 5.09 (m,2H), 4.73 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.15 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.83, 134.42, 128.36, 127.48, 125.77, 118.31, 73.26, 43.75. Organic Letters, 21(10), 3834-3837; 2019.



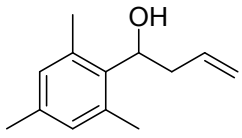
2c

2c, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 76%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 5.81 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.15 (dd, *J* = 12.2, 11.1 Hz, 2H), 4.70 (t, *J* = 6.5 Hz, 1H), 2.57 – 2.42 (m, 2H), 2.35 (s, 3H), 1.95 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.89, 137.16, 134.58, 129.05, 125.74, 118.18, 73.17, 43.71, 21.07. RSC Advances, 6(28), 23798-23803; 2016.



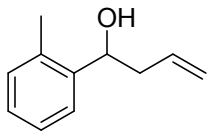
2d

2d, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 73%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.10 (m, 4H), 5.77 – 5.58 (m, 1H), 5.12 – 5.00 (m, 2H), 4.61 (ddd, *J* = 7.7, 5.2, 2.5 Hz, 1H), 2.46 – 2.29 (m, 2H), 2.18 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.25, 133.92, 133.07, 128.46, 127.16, 118.73, 72.51, 43.76. RSC Advances, 6(28), 23798-23803; 2016.



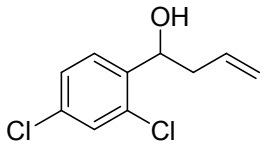
2e

2e, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 82%, colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.85 (s, 2H), 5.99 – 5.78 (m, 1H), 5.29 – 5.10 (m, 3H), 2.84 – 2.65 (m, 2H), 2.43 (s, 6H), 2.28 (s, 3H), 1.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.49, 135.92, 135.24, 130.08, 117.60, 70.65, 40.27, 20.69, 20.66. Organic & Biomolecular Chemistry, 11(48), 8387-8394; 2013.



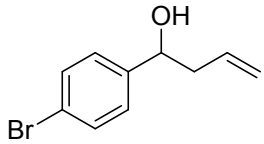
2f

2f, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 69%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.05 (m, 3H), 5.98 – 5.71 (m, 1H), 5.29 – 5.12 (m, 2H), 4.99 (dd, *J* = 8.2, 4.5 Hz, 1H), 2.62 – 2.42 (m, 2H), 2.37 (s, 3H), 2.05 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.91, 134.70, 134.31, 130.31, 127.19, 126.21, 125.14, 118.22, 69.64, 42.58, 19.01. ACS Catalysis, 6(11), 7647-7651; 2016.



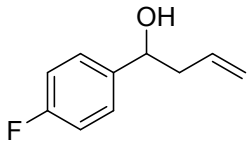
2g

2g, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 63%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.23 – 7.18 (m, 1H), 5.85 – 5.68 (m, 1H), 5.18 – 5.07 (m, 2H), 5.07 – 5.00 (m, 1H), 2.58 – 2.50 (m, 1H), 2.33 – 2.20 (m, 1H), 2.15 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.76, 133.78, 133.41, 132.18, 129.05, 128.08, 127.30, 119.07, 69.12, 41.95. Journal of Organic Chemistry, 78(17), 8712-8721; 2013.



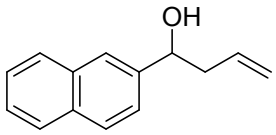
2h

2h, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 61%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.85 – 5.70 (m, 1H), 5.19 – 5.10 (m, 2H), 4.69 (dd, *J* = 7.7, 5.1 Hz, 1H), 2.56 – 2.38 (m, 2H), 2.00 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.79, 133.90, 131.44, 127.53, 121.22, 118.82, 72.56, 43.77. RSC Advances, 6(28), 23798-23803; 2016.



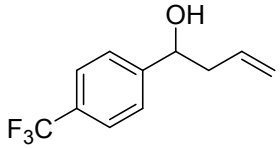
2i

2i, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 81%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.88 – 5.70 (m, 1H), 5.24 – 5.06 (m, 2H), 4.71 (t, *J* = 6.4 Hz, 1H), 2.58 – 2.38 (m, 2H), 2.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.13, 127.47, 127.39, 118.65, 115.28, 115.07, 72.61, 43.91. Organic Letters, 21(10), 3834-3837; 2019.



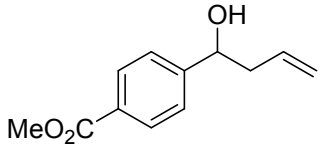
2j

2j, Rf=0.4 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 75%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.75 (m, 4H), 7.57 – 7.43 (m, 3H), 5.95 – 5.76 (m, 1H), 5.27 – 5.09 (m, 2H), 4.90 (t, *J* = 6.3 Hz, 1H), 2.68 – 2.53 (m, 2H), 2.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.21, 134.33, 133.23, 132.92, 128.18, 127.93, 127.65, 126.10, 125.78, 124.48, 123.97, 118.51, 73.36, 43.70. European Journal of Organic Chemistry, 2018(19), 2267-2272; 2018.



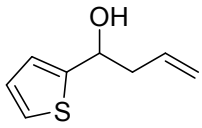
2k

2k, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 65%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 5.89 – 5.62 (m, 1H), 5.23 – 5.09 (m, 2H), 4.86 – 4.66 (m, 1H), 2.62 – 2.38 (m, 2H), 2.24 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.71, 133.66, 129.48 (q, *J* = 31.5 Hz), 126.05, 125.32 (q, *J* = 3.8 Hz), 122.78, 119.18, 72.49, 43.87. Journal of Organic Chemistry, 73(8), 3228–3235; 2008.



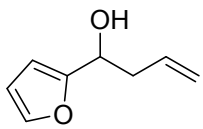
2l

2l, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 71%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 5.85 – 5.66 (m, 1H), 5.20 – 5.06 (m, 2H), 4.84 – 4.69 (m, 1H), 3.89 (s, 3H), 2.60 – 2.38 (m, 2H), 2.27 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.94, 148.99, 133.80, 129.66, 129.19, 125.69, 118.83, 72.74, 52.02, 43.72. Organic Letters, 21(10), 3834-3837; 2019.



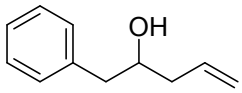
2m

2m, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 77%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 1H), 7.09 – 6.97 (m, 2H), 6.03 – 5.78 (m, 1H), 5.34 – 5.19 (m, 2H), 5.04 (t, *J* = 6.7 Hz, 1H), 2.77 – 2.65 (m, 2H), 2.61 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.76, 133.80, 126.61, 124.55, 123.67, 118.82, 69.34, 43.76. Organic Letters, 18(11), 2700-2703; 2016.



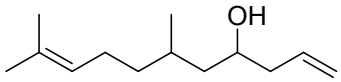
2n

2n, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 81%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 6.32 (s, 1H), 6.24 (d, *J* = 3.5 Hz, 1H), 5.89 – 5.65 (m, 1H), 5.21 – 5.07 (m, 2H), 4.79 – 4.64 (m, 1H), 2.71 – 2.48 (m, 2H), 2.37 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.98, 141.95, 133.66, 118.54, 110.11, 106.07, 66.90, 40.04. Chemistry - A European Journal, 19(41), 13859-13864; 2013.



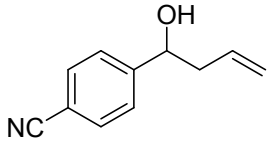
2o

2o, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 71%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.26 (td, *J* = 6.8, 1.8 Hz, 3H), 5.98 – 5.82 (m, 1H), 5.26 – 5.12 (m, 2H), 3.91 (tt, *J* = 7.8, 4.8 Hz, 1H), 2.91 – 2.70 (m, 2H), 2.43 – 2.18 (m, 2H), 1.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.36, 134.67, 129.41, 128.53, 126.47, 118.14, 71.66, 43.27, 41.17. RSC Advances, 6(28), 23798-23803; 2016.



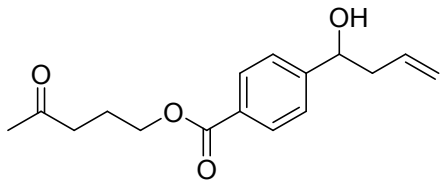
2q

2q, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=15:1. 73%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (dq, *J* = 19.2, 8.0, 7.6 Hz, 1H), 5.04 (t, *J* = 13.0 Hz, 3H), 3.68 (dq, *J* = 8.9, 4.2 Hz, 1H), 2.37 – 2.07 (m, 2H), 2.30 – 1.98 (m, 2H), 1.61 (s, 3H), 1.53 (s, 3H), 1.33 (tt, *J* = 15.2, 7.2 Hz, 3H), 1.09 (dtd, *J* = 25.4, 14.9, 12.9, 7.3 Hz, 2H), 0.86 (dd, *J* = 6.7, 2.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.82, 131.16, 124.73, 118.05, 68.72, 44.28, 42.11, 36.70, 29.25, 25.65, 25.31, 20.18, 17.59. RSC Advances, 6(28), 23798-23803; 2016.



2r

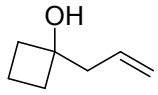
2s, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 43%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.8 Hz, 2H), 7.46 (d, *J* = 6.6 Hz, 2H), 5.84 – 5.64 (m, 1H), 5.21 – 5.03 (m, 2H), 4.83 – 4.64 (m, 1H), 2.49 (s, 1H), 2.47 – 2.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.15, 133.30, 132.13, 126.43, 119.33, 118.79, 110.98, 72.27, 43.73. ACS Catalysis, 10(6), 3857-3863; 2020.



2s

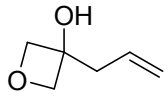
2r, Rf=0.4 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 51%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.81 – 5.52 (m, 1H), 5.12 – 5.00 (m, 2H), 4.70 (t, *J* = 4.7 Hz, 1H), 4.22 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.45 – 2.32 (m, 2H), 2.07 (s, 3H), 1.95 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.75, 166.32, 149.10, 133.78, 129.60,

128.25, 125.70, 118.82, 72.67, 64.02, 43.76, 39.87, 29.96, 22.81. HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{20}NaO_4$, 299.1259, found 299.1253.



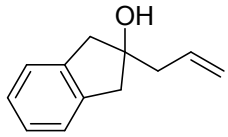
4a

4a, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=10:1. 61%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 – 5.74 (m, 1H), 5.21 – 5.06 (m, 2H), 2.36 (d, J = 7.2 Hz, 2H), 2.05 (dd, J = 6.7, 2.1 Hz, 4H), 2.03 (s, 1H), 1.79 – 1.66 (m, 1H), 1.59 – 1.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.50, 118.90, 73.89, 43.89, 35.36, 11.85. Angewandte Chemie International Edition, 58(25), 8561-8565; 2019.



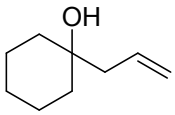
4b

4b, Rf=0.5 (PE: EA =1:1), column solvent: PE: EtOAc=5:1. 71%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 – 5.74 (m, 1H), 5.28 – 5.14 (m, 2H), 4.58 (d, J = 6.6 Hz, 2H), 4.49 (d, J = 6.5 Hz, 2H), 2.59 (d, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.78, 119.76, 83.20, 73.14, 42.21. Organic Chemistry Frontiers, 6(10), 1681-1685; 2019.



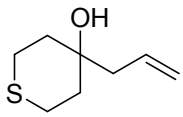
4c

4c, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=10:1. 45%, colorless oil,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 4H), 6.11 – 5.89 (m, 1H), 5.32 – 5.14 (m, 2H), 3.11 (d, J = 16.2 Hz, 2H), 2.96 (d, J = 16.3 Hz, 2H), 2.54 (d, J = 7.3 Hz, 2H), 2.26 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.12, 133.94, 126.57, 124.94, 118.98, 81.43, 46.43, 44.97. European Journal of Organic Chemistry, (6), 1058-1081; 2005.



4d

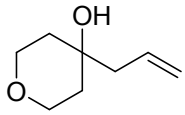
4d, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=10:1. 74%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 – 5.73 (m, 1H), 5.23 – 4.94 (m, 2H), 2.17 (d, J = 7.6 Hz, 2H), 1.71 (s, 1H), 1.65 – 1.19 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.71, 118.67, 70.94, 46.67, 37.37, 25.74, 22.16. RSC Advances, 6(28), 23798-23803; 2016.



4e

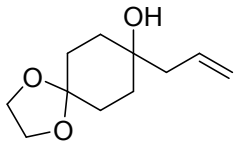
4e, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 77%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dt, J = 17.2, 8.5 Hz, 1H), 5.11 (dd, J = 21.4, 13.6 Hz, 2H), 2.92 (t, J = 12.6 Hz, 2H),

2.49 – 2.27 (m, 2H), 2.16 (d, J = 7.6 Hz, 2H), 1.80 (dd, J = 14.2, 3.6 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.61 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.43, 119.75, 69.29, 47.81, 38.16, 24.15. HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_8H_{14}NaOS$, 181.0663, found 181.0658.



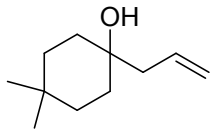
4f

4f, Rf=0.5 (PE: EA =1:1), column solvent: PE: EtOAc=5:1. 80%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.69 (m, 1H), 5.12 (dd, J = 17.9, 14.0 Hz, 2H), 3.72 (d, J = 11.6 Hz, 4H), 2.20 (d, J = 7.6 Hz, 2H), 1.98 (s, 1H), 1.78 – 1.56 (m, 2H), 1.44 (d, J = 13.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.49, 119.59, 68.20, 63.73, 47.45, 37.43. Journal of the American Chemical Society, 141(16), 6489-6493; 2019.



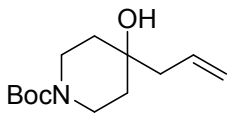
4g

4g, Rf=0.5 (PE: EA =1:1), column solvent: PE: EtOAc=5:1. 84%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddt, J = 17.5, 10.3, 7.5 Hz, 1H), 5.17 – 5.01 (m, 2H), 3.97 – 3.79 (m, 4H), 2.19 (d, J = 7.6 Hz, 2H), 1.93 – 1.76 (m, 2H), 1.70 – 1.44 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.38, 118.96, 108.70, 69.79, 64.12, 64.05, 46.76, 34.54, 30.34. European Journal of Organic Chemistry, (15), 2571-2581; 2008



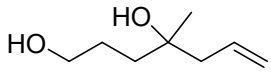
4h

4h, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=10:1. 45%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, J = 16.9, 10.2, 7.5 Hz, 1H), 5.20 – 5.04 (m, 2H), 2.21 (dt, J = 7.5, 1.2 Hz, 2H), 1.55 – 1.42 (m, 6H), 1.39 (s, 1H), 1.26 – 1.14 (m, 2H), 0.93 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.72, 118.62, 70.64, 46.69, 34.78, 33.33, 30.71, 29.59. HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{11}H_{20}NaO$, 191.1412, found 191.1420.



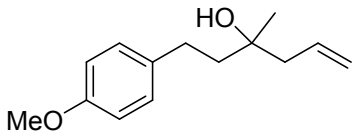
4i

4i, Rf=0.5 (PE: EA =1:1), column solvent: PE: EtOAc=5:1. 50%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 – 5.72 (m, 1H), 5.13 (dd, J = 20.0, 13.7 Hz, 2H), 3.73 (dd, J = 31.7, 9.8 Hz, 2H), 3.14 (dt, J = 14.2, 7.3 Hz, 2H), 2.20 (d, J = 7.6 Hz, 2H), 1.78 (s, 1H), 1.55 – 1.45 (m, 4H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.84, 132.56, 119.81, 79.36, 69.13, 47.23, 39.74, 36.62, 28.43. Journal of the American Chemical Society, 141(6), 2251-2256; 2019.



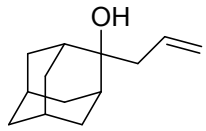
4j

4j, Rf=0.4 (PE: EA =1:1), column solvent: PE: EtOAc=3:1. 51%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 17.6, 10.5, 7.4 Hz, 1H), 5.13 – 4.96 (m, 2H), 3.57 (t, *J* = 5.3 Hz, 2H), 3.41 (s, 1H), 2.20 (d, *J* = 7.4 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.55 – 1.45 (m, 2H), 1.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.92, 118.66, 71.83, 63.12, 46.63, 38.41, 26.89, 26.58. Organic Letters, 13(2), 332-335; 2011.



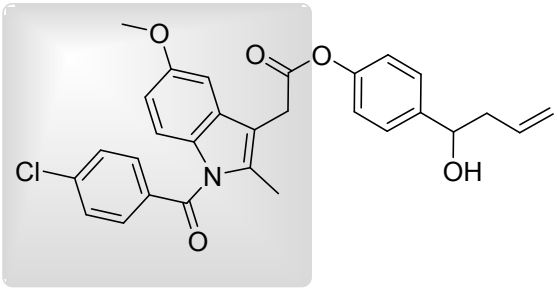
4k

4k, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 47%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.91 (ddt, *J* = 17.9, 10.5, 7.4 Hz, 1H), 5.28 – 5.07 (m, 2H), 3.79 (s, 3H), 2.75 – 2.58 (m, 2H), 2.31 (d, *J* = 7.5 Hz, 2H), 1.89 (s, 1H), 1.81 – 1.69 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 154.58, 134.49, 133.82, 129.15, 118.87, 113.82, 72.02, 55.24, 46.43, 43.91, 29.29, 26.72. European Journal of Organic Chemistry, 2018(43), 5997-6001; 2018.



4l

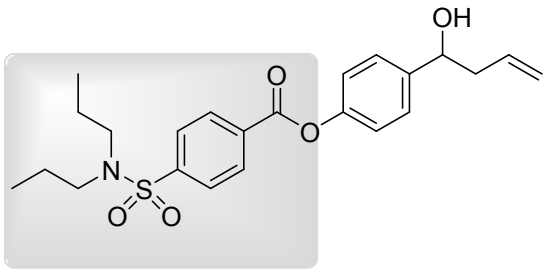
4l, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 29%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.4, 10.2, 7.5 Hz, 1H), 5.20 – 5.02 (m, 2H), 2.42 (d, *J* = 7.5 Hz, 2H), 2.18 (dd, *J* = 12.4, 3.2 Hz, 2H), 1.93 – 1.74 (m, 4H), 1.74 – 1.62 (m, 7H), 1.55 – 1.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.66, 118.73, 74.44, 42.65, 38.31, 37.00, 34.37, 32.89, 29.65, 27.35, 27.25. Journal of Organic Chemistry, 71(10), 3980-3983; 2006.



5a

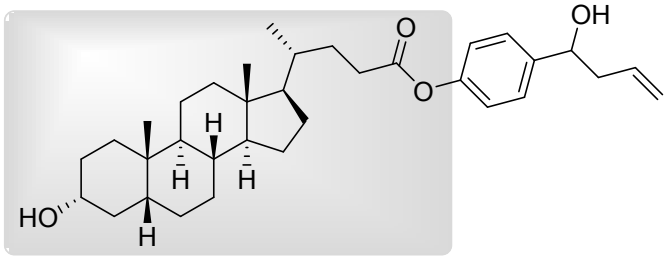
5a, Rf=0.4 (PE: EA =2:1), column solvent: PE: EtOAc=5:1. 72%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.09 – 7.02 (m, 3H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 5.88 – 5.64 (m, 1H), 5.23 – 5.06 (m, 2H), 4.81 – 4.62 (m, 1H), 3.92 – 3.88 (m, 2H), 3.84 (s, 3H), 2.52 – 2.48 (m, 1H), 2.45 (s, 3H), 2.15 – 2.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.32, 168.29, 156.07, 149.89, 141.57, 139.32, 136.19, 134.14, 133.77,

131.17, 130.80, 130.46, 129.12, 126.85, 121.27, 118.66, 115.00, 111.96, 111.77, 101.16, 72.63, 55.70, 43.83, 30.52, 13.42. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{29}H_{27}ClNO_5$, 504.1578, found 504.1571.



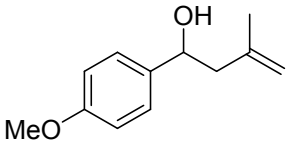
5b

5b, Rf=0.4 (PE: EA =2:1), column solvent: PE: EtOAc=5:1. 87%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 5.91 – 5.74 (m, 1H), 5.23 – 5.10 (m, 2H), 4.78 (ddd, J = 8.0, 4.9, 3.1 Hz, 1H), 3.18 – 3.06 (m, 4H), 2.62 – 2.42 (m, 2H), 2.18 (d, J = 3.2 Hz, 1H), 1.62 – 1.50 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.87, 149.79, 144.85, 141.92, 134.15, 132.74, 130.76, 127.12, 127.04, 121.36, 118.71, 72.63, 49.88, 43.88, 21.89, 11.13. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{23}H_{30}NO_5S$, 432.1845, found 432.1845.



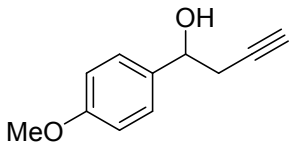
5c

5c, Rf=0.4 (PE: EA =1:1), column solvent: PE: EtOAc=3:1. 84%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 2.7 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 5.89 – 5.71 (m, 1H), 5.21 – 5.07 (m, 2H), 4.78 – 4.65 (m, 1H), 3.68 – 3.54 (m, 1H), 2.67 – 2.40 (m, 4H), 2.02 – 1.58 (m, 10H), 1.56 – 1.02 (m, 18H), 0.98 (d, J = 6.3 Hz, 3H), 0.92 (s, 3H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.79, 150.01, 141.29, 134.27, 126.83, 121.46, 118.54, 72.74, 71.82, 56.48, 55.94, 43.81, 42.74, 42.05, 40.40, 40.15, 36.40, 35.82, 35.35, 35.31, 34.54, 31.35, 30.93, 30.50, 28.22, 27.15, 26.39, 24.18, 23.34, 22.63, 20.80, 18.29, 14.24, 12.04. HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{34}H_{50}NaO_4$, 545.3607, found 545.3604.



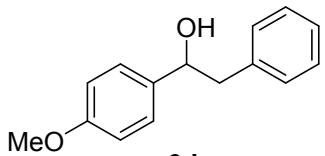
6b

6b, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 52%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 4.88 (d, J = 26.0 Hz, 2H), 4.77 (dd, J = 8.9, 4.8 Hz, 1H), 3.81 (s, 3H), 2.48 – 2.33 (m, 2H), 2.08 (s, 1H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99, 142.50, 136.19, 127.00, 113.93, 113.77, 71.06, 55.26, 48.23, 22.35. Synlett, (12), 1883-1885; 2003.



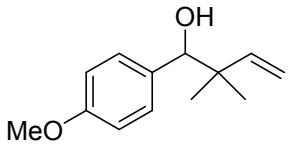
6c

6c, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. Br: 86%, Cl: 47%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.81 (t, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 2.61 (dt, *J* = 6.0, 1.8 Hz, 2H), 2.48 (s, 1H), 2.06 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.27, 134.63, 126.99, 113.80, 80.80, 71.94, 70.82, 55.23, 29.32. Journal of Organic Chemistry, 83(2), 980-992; 2018.



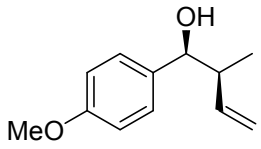
6d

6d, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. Br: 76%, Cl: 50%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 5H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.78 (t, *J* = 6.7 Hz, 1H), 3.75 (s, 3H), 2.95 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.04, 138.13, 135.97, 129.48, 128.45, 127.13, 126.52, 113.75, 74.95, 55.26, 46.00. Organometallics, 37(9), 1425-1427; 2018.



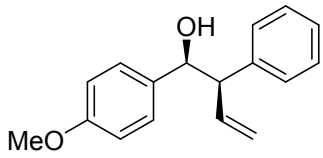
6e

6e, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 86%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.90 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.16 – 4.91 (m, 2H), 4.31 (s, 1H), 3.75 (s, 3H), 2.47 (s, 1H), 0.99 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.91, 145.22, 132.94, 128.82, 113.74, 112.89, 80.28, 55.22, 42.35, 24.52, 20.94. Journal of Organic Chemistry, 78(2), 253-269; 2013.



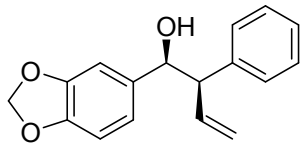
6f

6f, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 58%, colorless oil,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 5.86 – 5.72 (m, 1H), 5.24 – 5.07 (m, 2H), 4.28 (d, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 2.43 (q, *J* = 7.4 Hz, 1H), 2.31 (s, 1H), 0.82 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 140.91, 134.59, 127.89, 116.46, 113.51, 77.40, 55.15, 46.27, 16.49. European Journal of Organic Chemistry, 2018(11), 1333-1341; 2018.



6g

6g, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 83%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.3 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 6.9 Hz, 4H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.32 – 6.19 (m, 1H), 5.32 – 5.13 (m, 2H), 4.81 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.54 (t, *J* = 8.4 Hz, 1H), 2.32 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.81, 140.70, 138.16, 133.97, 128.31, 128.21, 127.81, 126.49, 118.24, 113.29, 76.78, 59.27, 55.13. Organic Letters, 7(12), 2333-2335; 2005.



6h

6g, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10/1. 72%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.24 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 5.92 – 5.84 (m, 2H), 5.32 – 5.15 (m, 2H), 4.76 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.50 (t, *J* = 8.5 Hz, 1H), 2.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.31, 146.68, 140.55, 137.99, 135.79, 128.36, 128.22, 126.58, 120.30, 118.39, 107.59, 106.96, 100.81, 76.97, 59.29. Tetrahedron Letters, 57(31), 3561-3564; 2016.