Supporting information

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

Contents

1. General Information
2. Luminescence Quenching Experiments
3. Picture of Reaction Set-Up
4. Quantum yield
5. General procedure of allylation
6. Characterization of Products
7. NMR spectrum
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 $\delta$ 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 Fluorescence Spectrophotometer for all experiments. All 4CZIPN solutions 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.

Figure 1. 4CZIPN emission quenching by Cp₂TiCl₂.

Stern-Volmer Equation
\[ \frac{F_0}{F} = 1 + K_q \tau_0 [Q] \]

\[ K_q = 1840 \text{ L/mol} \]
\[ \tau_0 = 557 \text{ ns} \]

Figure 2. 4CZIPN emission quenching by allyl bromide.

Stern-Volmer Equation
\[ \frac{F_0}{F} = 1 + K_q \tau_0 [Q] \]

\[ K_q = 324 \text{ L/mol} \]
\[ \tau_0 = 557 \text{ ns} \]
All Ir(ppy)$_2$(dtbby)PF$_6$ solutions 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$_2$TiCl$_2$, HE and BrCF$_2$CO$_2$Et quenched the photoexcited Ir(III)* effectively.

![Stern-Volmer Equation](image1)

$$F_0/F = 1 + K_q \tau_0 [Q]$$

$K_q \tau_0 = 2032$ L/mol

$\tau_0 = 557$ ns

$K_q = 3.65 \times 10^9$ L/(mol·s)

Figure 1, [Ir(ppy)$_2$(dtbby)$_2$]PF$_6$ emission quenching by Cp$_2$TiCl$_2$.

![Stern-Volmer Equation](image2)

$$F_0/F = 1 + K_q \tau_0 [Q]$$

$K_q \tau_0 = 22$ L/mol

$\tau_0 = 557$ ns

$K_q = 3.95 \times 10^7$ L/(mol·s)

Figure 2, [Ir(ppy)$_2$(dtbby)$_2$]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 $\lambda$ is calculated as

$$E_{ph} = \frac{hc}{\lambda} = 4.388 \times 10^{-19} \text{ J}$$

$\lambda$: wavelength ($\lambda = 4.53 \times 10^{-7} \text{ m}$)

h: planck constant ($h = 6.626 \times 10^{-34} \text{ J s}$)

c: velocity of light ($c = 3 \times 10^8 \text{ m/s}$)

The total photon flux $F_{ph}$ is calculated as

$$F_{ph} = \frac{f P}{E_{ph}} = 4.44 \times 10^{18} \text{ S}^{-1}$$

f: $1-10^{-A}$ 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, $E = 0.975 \text{ W/cm}^2$; S: the area irradiated, $S = \pi r^2 = 2.0 \text{ cm}^2$)

Quantum yield was determined as:

$$\phi = \frac{\text{Mole number for the product}}{\text{Mole number photons absorbed}}$$

$$= 0.85 \times 10^{-3} \times 6.02 \times 10^{23} / F_{ph} \times 7200s = 0.016$$

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

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### Spectrogram

![Spectrogram Image]

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### CRI

![CRI Image]

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### Instrument Status

- **Type:** PCS230850  
- **SN:** 0  
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- **Integral Time:** 0.117ms  
- **VPeak:** 54611  
- **VDark:** 2072

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**Remark:** -
**S5 General procedure of allylation**

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

\[
\text{R}_1^1 \text{R}_2^2 + \text{Br} \rightarrow \text{OH} \text{R}_1^1 \text{R}_2^2
\]

1 aldehydes: \( R_1^1 = C, R_2^2 = H \)
3 ketones: \( R_1^1 = C, R_2^2 = C \)

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.), \( \text{C}_2\text{TiCl}_2 \) (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 \(^1\text{H} \) NMR analysis of the crude product was calculated using 1,3,5-Trimethoxybenzene as the internal standard. Yields are shown in manuscripts table 2.

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

\[
\text{R}_1^1 + \text{R}_2^2 \text{Br/Cl} \rightarrow \text{OH} \text{R}_1^1 \text{R}_2^2
\]

Following the standard procedure, a solution of 1 (1.0 mmol, 1.0 eq.), alkyl halide, HE (2.0 mmol, 2.0 eq.), \( \text{C}_2\text{TiCl}_2 \) (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 \(^1\text{H} \) NMR analysis of the crude product was calculated using 1,3,5-Trimethoxybenzene as the internal standard. Yields are shown in manuscripts table 3.
S6 Characterization of Products

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

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

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

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, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 82%, colorless oil, \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 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\(_3\)) \(\delta\) 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.

![2e](image)

2f, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 69%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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.

![2f](image)

2g, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 63%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 141.91, 134.70, 134.31, 130.31, 127.19, 126.21, 125.14, 118.22, 69.12, 41.95. Journal of Organic Chemistry, 78(17), 8712-8721; 2013.

![2g](image)

2h, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 61%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 142.79, 133.90, 131.44, 127.53, 121.22, 118.82, 72.56, 43.77. RSC Advances, 6(28), 23798-23803; 2016.

![2h](image)

2i, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 81%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 134.13, 127.47, 127.39, 118.65, 115.28, 115.07, 72.61, 43.91. Organic Letters, 21(10), 3834-3837; 2019.
2j. Rf=0.4 (PE: EA=3:1), column solvent: PE: EtOAc=20/1. 75%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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. Rf=0.5 (PE: EA=3:1), column solvent: PE: EtOAc=20/1. 65%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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. Rf=0.5 (PE: EA=2:1), column solvent: PE: EtOAc=10/1. 71%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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. Rf=0.5 (PE: EA=3:1), column solvent: PE: EtOAc=20/1. 77%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 147.76, 133.80, 126.61, 124.55, 123.67, 118.82, 69.34, 43.76. Organic Letters, 18(11), 2700-2703; 2016.
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.

![2n](image1)

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.

![2o](image2)

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 (dd, $J$ = 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.

![2q](image3)

2r, 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.

![2r](image4)

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](image5)

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, ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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, ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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, ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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, ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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, ¹H NMR (400 MHz, CDCl₃) 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\(_3\)) \(\delta 132.43, 119.75, 69.29, 47.81, 38.16, 24.15\). HRMS-ESI (m/z) [M+Na] calculated for C\(_8\)H\(_{14}\)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\(_3\)) \(\delta 5.97 – 5.69\) (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\(_3\)) \(\delta 132.49, 119.59, 68.20, 64.12, 64.05, 46.76, 34.54, 30.34\). 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\(_3\)) \(\delta 5.84\) (ddt, \(J = 17.5, 10.3, 7.5\) Hz, 1H), 5.17 – 5.01 (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\(_3\)) \(\delta 133.38, 118.96, 108.70, 69.79, 64.12, 64.05, 46.76, 34.54, 30.34\). 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\(_3\)) \(\delta 5.88\) (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\(_3\)) \(\delta 133.72, 118.62, 70.64, 46.69, 34.78, 33.33, 30.71, 29.59\). 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\(_3\)) \(\delta 5.95 – 5.72\) (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\(_3\)) \(\delta 154.84, 132.56, 119.81, 79.36, 69.13, 47.23, 39.74, 36.62, 28.43\). Journal of the American Chemical Society, 141(6), 2251-2256; 2019.
4j, Rf=0.4 (PE: EA =1:1), column solvent: PE: EtOAc=3:1. 51%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 133.92, 118.66, 71.83, 63.12, 46.63, 38.41, 26.89, 26.58. Organic Letters, 13(2), 332-335; 2011.

4k, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 47%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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, Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10:1. 29%, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 169.32, 168.29, 156.07, 149.89, 141.57, 139.32, 136.19, 134.14, 133.77,

5a, Rf=0.4 (PE: EA =2:1), column solvent: PE: EtOAc=5:1. 72%, white solid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 169.32, 168.29, 156.07, 149.89, 141.57, 139.32, 136.19, 134.14, 133.77,
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$_{29}$H$_{27}$ClNO$_5$, 504.1578, found 504.1571.

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, 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, 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$_3$) $\delta$ 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$_3$) $\delta$ 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, 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$_3$) $\delta$ 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$_3$) $\delta$ 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, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 86%, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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, Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 58%, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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. Rf=0.5 (PE: EA =3:1), column solvent: PE: EtOAc=20/1. 83%, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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. Rf=0.5 (PE: EA =2:1), column solvent: PE: EtOAc=10/1. 72%, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.