Supporting Information

Irradiation-Induced Palladium-Catalyzed Decarboxylative Heck Reaction of Aliphatic N-(Acyloxy)phthalimides at Room

Temperature

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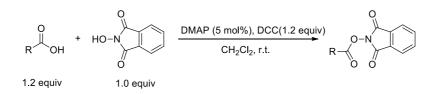
1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.99%) unless otherwise mentioned. Commercial reagents were purchased from Adamas, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

¹H-NMR, ¹⁹F-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ¹H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ¹³C- NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. UV-Vis spectrum was measured by UV-3600.

2. Preparation of Substrates

2.1 Preparation of redox active esters

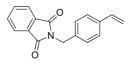


The corresponding alkyl carboxylic acids or N-protected amino acids (12 mmol, 1.2 equiv), N-hydroxyphthalimide (1.63 g, 10 mmol, 1.0 equiv), and 4-dimethylaminopyridine (61mg, 0.5 mmol, 5 mol%) were mixed in a flask with a magnetic stirring bar, 30 mL CH_2Cl_2 was added. Then a solution of N,N'-dicyclohexylcarbodiimide (2.06 g, 12 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) was added slowly at room temperature. The reaction mixture was maintained at room temperature with stirring for 0.5 - 3h. When the N-hydroxyphthalimide was

completely converted, the white precipitate was filtered off and the solution was concentrated on a rotary evaporator. The residue was purified by flash column chromatography to give corresponding redox active esters.

2.2 Preparation of vinyl arenes and vinyl heteroarenes

General Procedure for preparation of vinyl arenes and vinyl heteroarenes: Ph_3PMeBr (4.29 g, 12.0 mmol) was added to an oven-dried transparent Schlenk tube (100 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Anhydrous tetrahydrofuran (THF) (40.0 mL) was added to the tube under argon, and then n-BuLi (2.5 M, 4.8 mL, 12.0 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred at 0 °C for 15 min, then a THF solution of aldehyde (10 mmol) was added at 0 °C. The reaction mixture was stirred at r.t. for 48 h. The resulting solution was quenched with aqeous solution of NH₄Cl and the mixture was extracted with ethyl acetate (3 x 40 mL). The combined organic phases were dried over MgSO₄, concentrated under vacuo. The residue was purified by column chromatography on silica gel.

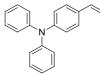


2-(4-vinylbenzyl)isoindoline-1,3-dione (S-1): 1-(chloromethyl)-4-vinylbenzene (10 mmol) was added to a solution of phthalimide (10 mmol) and K_2CO_3 (1.2 equiv) in DMF (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was diluted with Et₂O, washed with water, saturated NaHCO₃, and brine, dried over Na₂SO₄, and concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20 : 1). White solid. (2.31g, 88%)

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 4.0 Hz, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.37 (dd, *J* = 18.3, 8.0 Hz, 4H), 6.67 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 11.1 Hz, 1H), 4.83 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 168.0, 137.2, 136.3, 135.8, 134.0, 132.1, 128.9, 126.5, 123.4, 114.2, 41.3.

HRMS (ESI) Calcd for $C_{17}H_{14}NO_2^+$ [M+H]⁺: 264.1019, found: 264.1011.

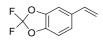


N,N-diphenyl-4-vinylaniline (S-2): The styrene was prepared according to General Procedure from the corresponding aldehyde, *4-(diphenylamino)benzaldehyde*. The product was purified by flash column chromatography on silica gel (petroleum ether). White solid. (2.47g, 91%)

¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.26 (m, 6H), 7.15 – 6.97 (m, 8H), 6.66 (dd, J = 17.6, 11.0 Hz, 1H), 5.64 (d, J = 17.6 Hz, 1H), 5.15 (d, J = 10.9 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 147.5, 136.2, 131.9, 129.3, 127.1, 124.4, 123.6, 122.9, 112.2.

HRMS (ESI) Calcd for $C_{20}H_{18}N^+$ [M+H]⁺: 272.1434, found: 272.1424.



2,2-difluoro-5-vinylbenzo[d][1,3]dioxole (S-3): The styrene was prepared according to General Procedure from the corresponding aldehyde, *2,2-difluorobenzo[d][1,3]dioxole-5-carbaldehyde*. The product was purified by flash column chromatography on silica gel (petroleum ether). White solid. (85%, 1.58g) ¹H NMR (400 MHz, CDCl₃) δ 7.04 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.55 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.55 (d, *J* = 17.5 Hz, 1H), 5.15 (d, *J* = 10.9

Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 144.2, 143.3, 135.6, 134.2, 129.74 (t, *J* = 254.6 Hz), 122.4, 114.2, 109.3, 106.5.

HRMS (EI) Calcd for $C_9H_6F_2O_2^+[M]^+$: 184.0336, found: 184.0332.

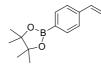


2-(4-vinylphenyl)thiophene (S-4): The styrene was prepared according to General Procedure from the corresponding aldehyde, *4-(thiophen-2-yl)benzaldehyde*. The product was purified by flash column chromatography on silica gel (petroleum ether). White solid. (81%,1.51g)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 6.9 Hz, 2H), 7.34 – 7.25 (m, 2H), 7.08 (s, 1H), 6.72 (dd, *J* = 19.3, 10.8 Hz, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 144.1, 136.7, 136.3, 133.8, 128.1, 126.7, 126.0, 124.8, 123.0, 113.9.

HRMS (EI) Calcd for $C_{12}H_{10}S^+$ [M]⁺: 186.0503, found: 186.0506.



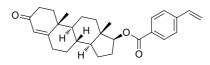
4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane

(S-5):

(4-vinylphenyl)boronic acid (20 mmol) was added to a solution of 2,3-dimethylbutane-2,3-diol (20 mmol) in Et₂O (0.2 M) with anhydrous MgSO₄ (20 mmol) at room temperature and then stirred overnight. Next, the reaction mixture was filted, concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20 : 1). White solid. (Ref: *Macromolecules*, **2005**, *38*, 8987). (4.37g, 95%)

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.72 (m, 2H), 7.41 (t, J = 6.8 Hz, 2H), 6.82 – 6.65 (m, 1H), 5.81 (dd, J = 17.6, 4.9 Hz, 1H), 5.28 (dd, J = 10.8, 4.1 Hz, 1H), 1.34 (s, 12H).

 13 C NMR (101 MHz, CDCl₃) δ 140.2, 136.9, 135.0, 125.5, 114.9, 83.7, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



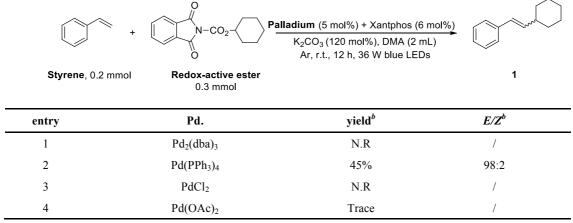
(8R.9S.10R.13S.14S.17S)-10.13-dimethyl-3-oxo-2.3.6.7.8.9.10.11.12.13.14.15.16.17 -tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl (S-6): 4-vinylbenzoic acid (20)mmol), added solution of Testosterone was to а (8R,9S,10R,13S,14S,17S)-17-hydroxy-10,13-dimethyl-6,7,8,9,10,11,12,13,14,15,16,1 7-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (20 mmol), DMAP (20 mmol), DCC (20 mmol), in CH₂Cl₂ (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was filtered, concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20 : 1). White solid. (42%, 1.75g)

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.74 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 5.73 (s, 1H), 5.37 (d, J = 10.9 Hz, 1H), 4.83 (t, J = 8.3 Hz, 1H), 2.47 – 2.22 (m, 5H), 2.01 (d, J = 12.7 Hz, 1H), 1.86 (d, J = 12.7 Hz, 2H), 1.72 – 1.56 (m, 5H), 1.49 – 1.35 (m, 2H), 1.29 – 0.99 (m, 7H), 0.97 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 199.4, 170.9, 166.1, 141.7, 135.9, 129.7, 129.6, 126.0, 123.9, 116.4, 82.8, 53.6, 50.2, 42.8, 38.5, 36.6, 35.6, 35.3, 33.8, 32.7, 31.4, 27.6, 23.5, 20.5, 17.3, 12.2.

HRMS (ESI) Calcd for $C_{28}H_{35}O_3^+$ [M+H]⁺: 419.2581, found: 419.2566.

3. Investigation of the Key Reaction Parameter



3.1 Screening of palladium salts ^a

5	Pd(PPh ₃) ₂ Cl ₂	69%	99:1
6	Pd(PhCN) ₂ Cl ₂	N.R	/

^{*a*}Reaction condition: styrene (0.2 mmol), redox-active ester (0.3 mmol), **palladium salt** (5 mol%), Xantphos (6 mol%) K₂CO₃ (120 mol%) in DMA (2 mL), irradiation by 36W blue LEDs at room temperature for 12 h under argon atmosphere. ^{*b*}GC yield using biphenyl as an internal standard.

3.2 Screening of solvents ^{*a*}

+	N-CO ₂ -	(PPh ₃) ₂ Cl ₂ (5 mol%) + Xantphos (6 mol%) K ₂ CO ₃ (120 mol%), Solvent (2 mL) Ar, r.t., 12 h, 36 W blue LEDs	
Styrene, 0.2 mmol	Redox-active ester 0.3 mmol		1
entry	Solvent	yield ^b	E/Z^b
1	Toluene	Trace	/
2	DCE	N.R	/
3	CH ₃ CN	Trace	/
4	DMA	71%	99:1
5	DMF	55%	98:2
6	THF	16%	/
7	Dioxane	Trace	/

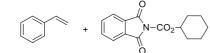
^{*a*}Reaction condition: styrene (0.2 mmol), redox-active ester (0.3 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), Xantphos (6 mol%), K₂CO₃ (120 mol%) in **solvent** (2 mL), irradiation by 36W blue LEDs at room temperature for 12 h under argon atmosphere. ^{*b*}GC yield using biphenyl as an internal standard.

3.3 Screening of bases^{*a*}

+		d (PPh ₃) ₂ Cl ₂ (5 mol%) + Xantphos (6 mo Base (120 mol%), DMA (2 mL) Ar, r.t., 12 h, 36 W blue LEDs	1%)
Styrene, 0.2 mmol	Redox-active ester 0.3 mmol		1
entry	Base	yield ^b	E/Z^b
1	KOAc	30%	/
2	Na ₂ CO ₃	48%	/
3	K ₂ CO ₃	70%	99:1
4	Cs ₂ CO ₃	65%	99:1
5	NaHCO ₃	16%	/
6	K ₂ HPO ₄	42%	/

^{*a*}Reaction condition: styrene (0.2 mmol), redox-active ester (0.3 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), Xantphos (6 mol%), **base** (120 mol%) in DMA (2 mL), irradiation by 36W blue LEDs at room temperature for 12 h under argon atmosphere. ^{*b*}GC yield using biphenyl as an internal standard.

3.4 Optimization of the ratio of reactant ^a



Pd(PPh₃)₂Cl₂ (a mol%) + Xantphos (b mol%) K_2CO_3 (c mol%), DMA (2 mL) Ar, r.t., 24 h, 36 W blue LEDs

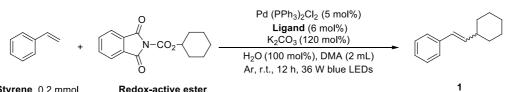


Styrene, 0.2 mmol Redox-ester, x mmol

entry	a	b	с	X	yield ^b
1	5	6	120	0.30	88%
2	3	3.6	120	0.30	65%
3	2	2.4	120	0.30	38%
4	5	6	100	0.30	62%
5	5	6	150	0.30	88%
6	5	10	120	0.30	72%
7	5	6	120	0.24	78%
8°	5	6	120	0.30	96%

^aReaction condition: styrene (0.2 mmol), redox-active ester (x mmol), Pd(PPh₃)₂Cl₂ (a mol%), Xantphos (b mol%), K₂CO₃ (c mol%) in DMA (2 mL), irradiation by 36W blue LEDs at room temperature for 24 h under argon atmosphere. ^bGC yield using biphenyl as an internal standard. ^cwith 1 equiv H₂O

3.5 Screening of ligands ^a



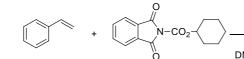
Styrene, 0.2 mmol

Redox-active ester 0.3 mmol

entry	Ligand	yield ^b	E/Z^b
1	Xantphos	96%	99:1
2	Ni-xant-phos	72%	98:2
3	DPE-phos	81%	98:2
4	BINAP	18 %	/
5	Tri-phos	Trace	/
6	Dtbpy	13%	/
7	Dppbz	11%	/
8	Dppen	Trace	/
9	DPPP	Trace	/
10	Dppf	N.R	/
11	X-phos (12 mol%)	12%	/

^aReaction condition: styrene (0.2 mmol), redox-active ester (0.3 mmol), Pd(PPh₃)₂Cl₂ (5 mol%), ligand (6 mol%), K₂CO₃ (120 mol%), H₂O (100 mol%) in DMA (2 mL), irradiation by 36W blue LEDs at room temperature for 24 h under argon atmosphere. ^bGC yield using biphenyl as an internal standard.

3.6 Investigation of effect of monophosphine ligands ^{*a*}



PdCl₂ (5 mol%) + Xantphos (6 mol%) **Monophosphine ligand (10 mol%)** K₂CO₃ (120 mol%), H₂O (100 mol%) DMA (2 mL), Ar, r.t., 24 h, 36 W blue LEDs



1

Styrene, 0.2 mmol

Redox-active ester 0.3 mmol

entry	monophosphine ligand	yield ^b	E/Z^b
1	PPh ₃	96%	99:1
2	P(3-OMe-Ph) ₃	66%	98:2
3	P(4-OMe-Ph) ₃	85%	98:2
4	P(2,4-Me-C6H4)3	72%	98:2
5	P(4-F-Ph)3	83%	98:2
6	P(perfluorophenyl)3	48%	/
7	P(furan)3	Trace	/
8	РСуз	33%	/
9	PPh ₃ (20 mol%)	95%	99:1
10	PPh ₃ (5 mol%)	55%	98:2

^{*a*}Reaction condition: styrene (0.2 mmol), redox-active ester (0.3 mmol), PdCl₂ (5 mol%), **monophosphine ligand** (10 mol%), Xantphos (6 mol%), K₂CO₃ (120 mol%), H₂O (100 mol%) in DMA (2 mL), irradiation by 36W blue LEDs at room temperature for 24 h under argon atmosphere. ^{*b*}GC yield using biphenyl as an internal standard.

3.7 Control experiments investigating the necessity of dual ligands^a

$\begin{array}{c} \begin{array}{c} & & \\ & \\ & \\ 0.2 \text{ mmol} \end{array} \end{array} + \begin{array}{c} & \begin{array}{c} & \\ & \\ & \\ & \\ & \\ \end{array} \end{array} \\ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $				
entry	Pd. cat. (5 mol%)	L_1	L_2	yield ^a
1	Pd(PPh ₃) ₂ Cl ₂	/	Xantphos (6 mol%)	96%
2	PdCl ₂	/	Xantphos (6 mol%)	Trace
3	$Pd(PPh_3)_2Cl_2$	/	/	15%
4	PdCl ₂	PPh3 (20 mol%)	/	33%
5	PdCl ₂	/	Xantphos (10 mol%)	16%
6	Pd(Xantphos)Cl ₂	/	/	Trace
7	$Pd(PPh_3)_4$	/	/	21%
8	/	PPh ₃ (20 mol%)	/	N.R
9	/	/	Xantphos (10 mol%)	N.R

^{*a*}GC yields using biphenyl as an internal standard.

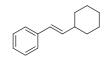
4. General Procedure and Spectral Data

4.1 General procedure A

Vinyl arene (1.0 equiv, 0.2 mmol) (if solid), redox active ester (1.5 equiv, 0.3 mmol) (if solid), Pd(PPh₃)₂Cl₂ (5 mol%, 7 mg) and Xantphos (6 mol%, 6.9 mg), K_2CO_3 (0.24 mmol, 33 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, vinyl arene (1.0 equiv, 0.2 mmol) (if liquid), redox active ester (1.5 equiv, 0.3 mmol) (if liquid), anhydrous DMA (2.0 mL), and H₂O (1 equiv) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h. After completion of the reaction, the mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel with petroleum ether or a mixture of petroleum ether and ethyl acetate as eluent.

4.2 General procedure B

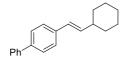
Vinyl arene (1.0 equiv, 0.2 mmol) (if solid), Redox active ester (2 equiv, 0.4 mmol) (if solid), Pd(PPh₃)₂Cl₂ (5 mol%, 7 mg) and Xantphos (6 mol%, 6.9 mg), K_2CO_3 (0.24 mmol, 33 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, vinyl arene (1.0 equiv, 0.2 mmol) (if liquid), redox active ester (1.5 equiv, 0.3 mmol) (if liquid), anhydrous DMA (2.0 mL), and H₂O (1 equiv) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 36 h. The mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel with petroleum ether or a mixture of petroleum ether and ethyl acetate as eluent.



(*E*)-(2-cyclohexylvinyl) benzene (1): Following the general procedure A, obtained in 95% yield as a colorless liquid (35.4 mg, eluent: petroleum ether). (Ref: *Angew. Chem. Int. Ed.* 2014, *53*, 5974)

¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 7.9 Hz, 2H), 7.27 (t, J = 12.5 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 6.9 Hz, 1H), 2.19 – 2.04 (m, 1H), 1.83 – 1.65 (m, 5H), 1.36 – 1.12 (m, 5H).

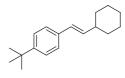
¹³C NMR (101 MHz, CDCl₃) δ 138.0, 136.8, 128.4, 127.2, 126.7, 125.9, 41.2, 32.9, 26.2, 26.1.



(*E*)-4-(2-cyclohexylvinyl)-1,1'-biphenyl (2): Following the general procedure A, obtained in 96% yield as a white solid (50.4 mg, eluent: petroleum ether). (Ref: *Org. Lett.*, 2016, 18, 1)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.43 - 7.40 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 15.9, 6.9 Hz, 1H), 2.23 - 2.09 (m, 1H), 1.87 - 1.60 (m, 5H), 1.38 - 1.14 (m, 5H).

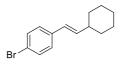
¹³C NMR (101 MHz, CDCl₃) δ 140.9, 139.4, 137.1, 137.0, 128.7, 127.1, 127.0, 126.8 126.7, 126.3, 41.2, 32.9, 26.1, 26.0.



(*E*)-1-(tert-butyl)-4-(2-cyclohexylvinyl)benzene (3): Following the general procedure A, obtained in 94% yield as a colorless liquid (45.5 mg, eluent: petroleum ether). (Ref: *Org. Biomol. Chem.*, 2015, *13*, 6170)

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.27 (m, 4H), 6.32 (d, J = 15.9 Hz, 1H), 6.13 (dd, J = 16.0, 7.0 Hz, 1H), 2.19 – 2.05 (m, 1H), 1.80 – 1.65 (m, 5H), 1.36 – 1.13 (m, 14H).

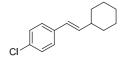
¹³C NMR (101 MHz, CDCl₃) δ 149.7, 136.1, 135.3, 126.9, 125.6, 125.3, 41.2, 34.4, 33.0, 31.3, 26.2, 26.1.



(*E*)-1-bromo-4-(2-cyclohexylvinyl)benzene (4): Following the general procedure A, obtained in 55% yield as a colorless liquid (29.0 mg, eluent: petroleum ether). (Ref: *J. Org. Chem.* 2013, *9*, 1718)

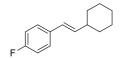
¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 6.27 (d, J = 16.0 Hz, 1H), 6.16 (dd, J = 16.0, 6.7 Hz, 1H), 2.20 – 2.04 (m, 1H), 1.82 – 1.64 (m, 5H), 1.34 – 1.14 (m, 5H).

¹³C NMR (101 MHz, CDCl3) δ 137.7, 137.0, 131.5, 127.5, 126.1, 120.3, 41.1, 32.8, 26.1, 26.0.



(*E*)-1-chloro-4-(2-cyclohexylvinyl)benzene (5): Following the general procedure A, obtained in 85% yield as a colorless liquid (37.4 mg, eluent: petroleum ether). (Ref: *J. Org. Chem.* 2013, *9*, 1718)

¹H NMR (400 MHz, CDCl₃) δ 7.27 –7.22 (m, 4H), 6.28 (d, J = 16.0 Hz, 1H), 6.14 (dd, J = 16.0, 6.8 Hz, 1H), 2.15 – 2.08 (m, 1H), 1.84 – 1.65 (m, 5H), 1.35 – 1.13 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 137.5, 136.5, 132.2, 128.5, 127.1, 126.1, 41.1, 32.8, 26.1, 26.0.

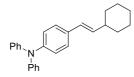


(*E*)-1-(2-cyclohexylvinyl)-4-fluorobenzene (6): Following the general procedure A, obtained in 78% yield as a colorless liquid (31.8 mg, eluent: petroleum ether). (Ref: *Org. Biomol. Chem.*, 2015, *13*, 6170)

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 2H), 6.97 (t, J = 8.7 Hz, 2H), 6.30 (d, J = 16.0 Hz, 1H), 6.08 (dd, J = 16.0, 7.0 Hz, 1H), 2.17 – 2.04 (m, 1H), 1.85 – 1.64 (m, 5H), 1.35 – 1.14 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 161.82 (d, J = 245.4 Hz), 136.6, 134.2, 127.30 (d, J = 7.8 Hz), 126.0, 115.26 (d, J = 21.5 Hz), 41.1, 32.9, 26.1, 26.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -116.1.

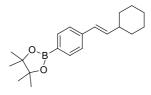


(*E*)-4-(2-cyclohexylvinyl)-N, N-diphenylaniline (7): Following the general procedure A, obtained in 85% yield as a white solid (60.0 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, J = 11.2, 4.6 Hz, 6H), 7.07 (d, J = 8.2 Hz, 4H), 7.00 (dd, J = 7.7, 5.3 Hz, 4H), 6.29 (d, J = 16.0 Hz, 1H), 6.08 (dd, J = 16.0, 7.0 Hz, 1H), 2.14 – 2.07 (m, 1H), 1.80 – 1.65 (m, 5H), 1.35 – 1.14 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 146.5, 135.6, 132.7, 129.2, 126.8, 126.6, 124.3, 124.0, 122.6, 41.2, 33.1, 26.2, 26.1.

HRMS (ESI) Calcd for C₂₆H₂₈NO⁺ [M+H]⁺: 354.2216, found: 354.2211.

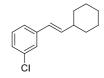


(E)-2-(4-(2-cyclohexylvinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(8):

Following the general procedure A, obtained in 96% yield as a colorless liquid (60.0 mg, eluent: petroleum ether:ethyl acetate = 20:1). (Ref: *Tetrahedron Lett.*, **2013**, *54*, 1211)

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.27 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 6.7 Hz, 1H), 2.01 – 2.08 (m, 1H), 1.74 – 1.58 (m, 5H), 1.26 (s, 12H), 1.23 – 0.97 (m, 5H).

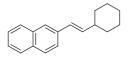
 13 C NMR (101 MHz, CDCl₃) δ 140.8, 137.9, 135.0, 127.2, 125.2, 83.6, 41.2, 32.8, 26.1, 26.0, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



(*E*)-1-chloro-3-(2-cyclohexylvinyl) benzene (9): Following the general procedure A, obtained in 81% yield as a colorless liquid (35.6 mg, eluent: petroleum ether). (Ref: *Chem. Commun.*, 2015, *51*, 7546)

¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.20 – 7.14 (m, 3H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 6.6 Hz, 1H), 2.15 – 2.08 (m, 1H), 1.80 – 1.66 (m, 5H), 1.36 – 1.16 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 139.9, 138.4, 134.4, 129.6, 126.6, 126.0, 125.8, 124.2, 41.1, 32.8, 26.1, 26.0.

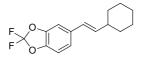


(*E*)-2-(2-cyclohexylvinyl)naphthalene(10) : Following the general procedure A, obtained in 85% yield as a white solid (40.1 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.78 –7.74 (m, 3H), 7.67 (s, 1H), 7.58 (dd, J = 8.5, 1.6 Hz, 1H), 7.47 – 7.36 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.30 (dd, J = 16.0, 6.9 Hz, 1H), 2.21 – 2.14 (m, 1H), 1.89 – 1.66 (m, 5H), 1.36 – 1.17 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 137.4, 135.5, 133.7, 132.6, 128.0, 127.9, 127.7, 127.3, 126.1, 125.5, 125.4, 123.6, 41.3, 33.0, 26.2, 26.1.

HRMS (EI) Calcd for $C_{18}H_{20}^+$ [M]⁺: 236.1565, found: 236.1552.



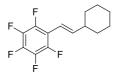
(E)-5-(2-cyclohexylvinyl)-2,2-difluorobenzo[d][1,3]dioxole (11): Following the general procedure A, obtained in 55% yield as a colorless liquid (29.3 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, J = 1.5 Hz, 1H), 6.97 (dt, J = 14.3, 4.9 Hz, 2H), 6.28 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 15.9, 6.9 Hz, 1H), 2.17 – 2.07 (m, 1H), 1.83 – 1.66 (m, 5H), 1.36 – 1.13 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 144.2, 142.5, 137.3, 134.7, 131.63 (t, J = 254.6 Hz),126.0, 121.7, 109.2, 106.3, 41.1, 32.9, 26.1, 26.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -50.3.

HRMS (EI) Calcd for $C_{15}H_{16}F_2O_2^+$ [M]⁺: 266.1118, found: 266.1105



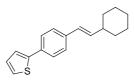
*(E)***-1-(2-cyclohexylvinyl)-2,3,4,5,6-pentafluorobenzene (12):** Following the general procedure A, obtained in 75% yield as a colorless liquid (41.4 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 6.50 (dd, J = 16.4, 7.2 Hz, 1H), 6.22 (dd, J = 16.4, 1.1 Hz, 1H), 2.22 – 2.11 (m, 1H), 1.85 – 1.66 (m, 5H), 1.38 – 1.16 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 146.58 (td, J = 7.4, 2.3 Hz), 144.8 (dm, J = 249.0 Hz), 139.3 (dm, J = 256.5 Hz), 137.7 (dm, J = 251.3 Hz), 112.80 (td, J = 14.0, 3.8 Hz), 111.8, 42.5, 32.5, 26.0, 25.9.

¹⁹F NMR (376 MHz, CDCl3) δ -143.8 (dd, J = 21.8, 7.8 Hz), -158.2 (t, J = 20.9 Hz), -163.2 - -164.1 (m).

HRMS (ESI) Calcd for $C_{14}H_{14}F_5^+$ [M+H]⁺: 277.1010, found: 277.1016.



(*E*)-2-(4-(2-cyclohexylvinyl)phenyl)thiophene (13): Following the general procedure A, obtained in 90% yield as a white solid (49.8 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.28 (dd, J = 3.6, 1.1 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.06 (dd, J = 5.1, 3.6 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 6.19 (dd, J = 16.0, 6.9 Hz, 1H), 2.17 – 2.09 (m, 1H), 1.84 – 1.66 (m, 5H), 1.36 – 1.13 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 144.4, 137.3, 137.1, 132.8, 128.0, 126.7, 126.4, 125.9, 124.5, 122.7, 41.2, 32.9, 26.2, 26.1.

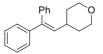
HRMS (EI) Calcd for $C_{18}H_{20}S^+$ [M]⁺: 268.1286, found: 268.1274.



(E)-2-(2-cyclohexylvinyl)pyridine (14): Following the general procedure A, obtained in 85% yield as a colorless liquid (31.8 mg, eluent: petroleum ether:ethyl acetate = 20:1). (Ref: *Angew. Chem. Int. Ed.* 2014, *53*, 5974)

¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, J = 4.2 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.70 (dd, J = 15.9, 6.9 Hz, 1H), 6.45 (d, J = 16.9 Hz, 1H), 2.23 – 2.15 (m, 1H), 1.87 – 1.65 (m, 5H), 1.36 – 1.16 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 156.3, 149.3, 141.5, 136.4, 127.3, 121.5, 121.1, 41.0,

32.6, 26.1, 26.0.

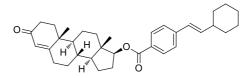


4-(2,2-diphenylvinyl)tetrahydro-2H-pyran (15): Following the general procedure A, obtained in 61% yield as a white solid (32.2 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.30 (m, 3H), 7.27 – 7.10 (m, 7H), 5.89 (d, *J* = 9.8 Hz, 1H), 3.91 (d, *J* = 11.3 Hz, 2H), 3.29 (td, *J* = 11.2, 4.0 Hz, 2H), 2.49 – 2.27 (m, 1H), 1.63 – 1.47 (m, 4H).

13C NMR (101 MHz, CDCl3) δ 137.5, 134.6, 128.5, 128.2, 127.1, 126.0, 67.7, 38.4, 32.6.

HRMS (ESI) Calcd for C₁₉H₂₁O⁺ [M+H]⁺: 265.1587, found: 265.1581.



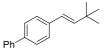
(8R, 9S, 10R, 13S, 14S, 17S)-10, 13-dimethyl-3-oxo-2, 3, 6,7,8,9,10,11,12,13,14,15, 16, 17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-(*(E)*-2-cyclohexyl

vinyl) benzoate (16): Following the general procedure A, obtained in 82% yield as a white solid (82.0 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.33 (dt, J = 16.0, 11.3 Hz, 2H), 5.74 (s, 1H), 4.84 (t, J = 8.3 Hz, 1H), 2.49 – 2.25 (m, 5H), 1.91 – 1.58 (m, 12H), 1.49 – 0.95 (m, 19H).

¹³C NMR (101 MHz, CDCl₃) δ 199.5, 171.0, 166.4, 142.6, 139.7, 129.8, 128.7, 126.6, 125.8, 124.0, 82.8, 53.7, 50.3, 42.9, 41.3, 38.6, 36.7, 35.7, 35.5, 33.9, 32.8, 31.5, 29.7, 27.7, 26.1, 26.0, 23.6, 20.6, 17.4, 12.3.

HRMS (ESI) Calcd for $C_{33}H_{45}O_3^+$ [M+H]⁺:501.3363, found: 501.3359.

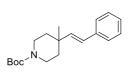


(E)-4-(3,3-dimethylbut-1-en-1-yl)-1,1'-biphenyl (17): Following the general procedure A, obtained in 94% yield as a white solid (44.4 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.44 –7.41 (m, 4H), 7.32 (t, J = 7.2 Hz, 1H), 6.38 – 6.26 (m, 2H), 1.14 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 142.0, 140.9, 139.5, 137.1, 128.7, 127.2, 127.1, 126.9, 126.4, 124.1, 33.4, 29.6.

HRMS (EI) Calcd for $C_{18}H_{20}^+$ [M]⁺: 236.1565, found: 236.1560.

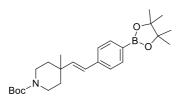


(*E*)-tert-butyl 4-methyl-4-styrylpiperidine-1-carboxylate (18): Following the general procedure A, obtained in 95% yield as a colorless liquid (57.2 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.15 (m, 5H), 6.35 (d, *J* = 16.4 Hz, 1H), 6.17 (d, *J* = 16.4 Hz, 1H), 3.58 – 3.30 (m, 4H), 1.68 (d, *J* = 4.2 Hz, 2H), 1.46 (s, 11H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.0, 138.5, 137.6, 128.5, 127.3, 127.3, 126.0, 79.3, 40.4, 36.9, 34.8, 28.5, 26.8.

HRMS (ESI) Calcd for $C_{19}H_{28}NO_2^+$ [M+H]⁺: 302.2115, found: 302.2109.



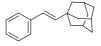
(E)-2-(4-(3,3-dimethylbut-1-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborol

ane (19): 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (1.0 equiv, 5 mmol), redox active ester (1.5 equiv, 7.5 mmol), Pd(PPh₃)₂Cl₂ (5 mol%, 175 mg) and Xant-phos (6 mol%, 258 mg), K₂CO₃ (6 mmol, 828 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, anhydrous DMA (50 mL) and H₂O (1 equiv) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W blue LEDs (distance app. 3.0 cm from the irradiation source) at room temperature for 48 h. The product was obtained in 78% yield as a white solid (1.67g, eluent: petroleum ether: ethyl acetate = 20:1). (Ref: *Macromolecules*, **2005**, *38*, 8987)

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.7 Hz, 2H), 7.35 (d, J = 7.7 Hz, 2H), 6.35 (d, J = 16.4 Hz, 1H), 6.22 (d, J = 16.4 Hz, 1H), 3.41 (dt, J = 13.2, 11.4 Hz, 4H), 1.74 – 1.64 (m, 2H), 1.50 – 1.42 (m, 11H), 1.33 (s, 12H), 1.12 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.9, 140.4, 139.7, 135.1 127.4, 125.3, 83.7, 79.3, 40.4, 36.9, 34.9, 28.5, 26.7 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

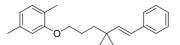
HRMS (ESI) Calcd for C₂₅H₃₈BNO₄Na⁺ [M+Na]⁺: 450.2786, found: 450.2782



(3r,5r,7r)-1-((*E*)-styryl)adamantane (20): Following the general procedure A, obtained in 85% yield as a colorless liquid (40.5mg, eluent: petroleum ether). (Ref: *RSC Adv.*, 2013, *3*, 19264)

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 7.7 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.1 Hz, 1H), 6.24 (d, J = 16.3 Hz, 1H), 6.11 (d, J = 22.5 Hz, 1H), 2.02 (s, 3H), 1.78 – 1.66 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 142.1, 138.2, 128.4, 126.7, 125.9, 124.5, 42.2, 36.9, 35.1, 28.5.

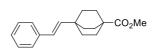


(E)-2-((4,4-dimethyl-6-phenylhex-5-en-1-yl)oxy)-1,4-dimethylbenzene (21):
Following the general procedure A, obtained in 91% yield as a colorless liquid (56.1mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.16 (m, 4H), 7.14 – 7.06 (m, 1H), 6.91 (d, J = 7.0 Hz, 1H), 6.61 – 6.46 (m, 2H), 6.24 (d, J = 16.3 Hz, 1H), 6.11 (dd, J = 16.6, 6.5 Hz, 1H), 3.82 (t, J = 6.1 Hz, 2H), 2.20 (s, 3H), 2.10 (s, 3H), 1.74 – 1.61 (m, 2H), 1.53 – 1.43 (m, 2H), 1.06 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 156.0, 139.2, 136.9, 135.4, 129.2, 127.4, 125.8, 125.1, 125.0, 122.5, 119.5, 110.9, 67.3, 38.3, 35.1, 26.2, 23.9, 20.4, 14.8.

HRMS (ESI) Calcd for C₂₂H₂₈ONa⁺ [M+Na]⁺: 331.2032, found: 331.2025.

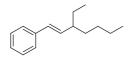


(E)-methyl 4-styrylbicyclo[2.2.2]octane-1-carboxylate (22): Following the general procedure A, obtained in 75% yield as a white solid (40.5 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, J = 7.6 Hz, 2H), 7.21 (t, J = 8.9 Hz, 2H), 7.11 (t, J = 7.1 Hz, 1H), 6.17 (d, J = 16.3 Hz, 1H), 6.05 (d, J = 16.3 Hz, 1H), 3.58 (s, 3H), 1.83 – 1.73 (m, 6H), 1.60 – 1.51 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 177.4, 138.1, 136.8, 127.5, 125.9, 124.9, 124.8, 50.7, 38.1, 32.3, 29.7, 27.3.

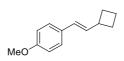
HRMS (ESI) Calcd for C₁₈H₂₂NaO₂⁺ [M+Na]⁺: 293.1512, found: 293.1508.



(*E*)-(3-ethylhept-1-en-1-yl)benzene (23): Following the general procedure A, obtained in 72% yield as a colorless liquid (29.1 mg, eluent: petroleum ether). (Ref: *RSC Adv.*, 2013, *3*, 19264)

¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.08 – 1.95 (m, 1H), 1.54 – 1.43 (m, 2H), 1.37 – 1.21 (m, 6H), 0.90 – 0.82 (m, *J* = 7.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 138.0, 135.6, 129.6, 128.4, 126.7, 125.9, 45.2, 34.9, 29.6, 28.2, 22.9, 14.1, 11.9.

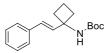


(*E*)-4-(2-cyclobutylvinyl)-1,1'-biphenyl (24): Following the general procedure A, obtained in 78% yield as a colorless liquid (29.3 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 6.3 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 6.23 – 6.05 (m, 2H), 3.72 (s, 3H), 3.08 – 2.94 (m, 1H), 2.14 – 2.03 (m, 2H), 1.92 – 1.72 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 158.6, 133.2, 130.6, 127.0, 126.9, 113.9, 55.2, 38.8, 28.9, 18.5.

HRMS (ESI) Calcd for C₁₃H₁₇O⁺ [M+H]⁺: 189.1274, found: 189.1279.

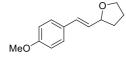


(*E*)-tert-butyl (1-styrylcyclobutyl)carbamate (25): Following the general procedure B, obtained in 55% yield as a white solid (30.0 mg, eluent: petroleum ether:ethyl acetate = 10:1).

¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.53 – 6.41 (m, 2H), 4.83 (s, 1H), 2.45 – 2.21 (m, 4H), 2.03 – 1.83 (m, 2H), 1.44 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.5, 137.1, 133.5, 128.5, 127.3, 126.8, 126.4, 79.4, 57.1, 33.5, 28.4, 15.0,

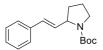
HRMS (ESI) Calcd for C₁₇H₂₃NNaO₂⁺ [M+Na]⁺: 296.1621, found: 296.1618.



(*E*)-2-(4-methoxystyryl)tetrahydrofuran (26): Following the general procedure B, obtained in 61% yield as a colorless liquid (24.9 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.7, 6.9 Hz, 1H), 4.44 (q, J = 6.7 Hz, 1H), 3.96 (dd, J = 14.7, 7.4 Hz, 1H), 3.87 – 3.77 (m, 4H), 2.15 – 1.89 (m, 3H), 1.76 – 1.67 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 130.2, 129.6, 128.2, 127.6, 113.9, 79.9, 68.1, 55.3, 32.4, 26.0.

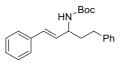
HRMS (ESI) Calcd for $C_{13}H_{17}O_2^+$ [M+H]⁺: 205.1223, found: 205.1226.



(E)-tert-butyl 2-styrylpyrrolidine-1-carboxylate (27): Following the general procedure B, obtained in 75% yield as a white solid (41.5 mg, eluent: petroleum ether:ethyl acetate = 20:1). (Ref: J. Am. Chem. Soc., 2014, 136, 11602)

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.27 (m, 4H), 7.21 (t, *J* = 7.1 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.09 (dd, *J* = 15.7, 6.4 Hz, 1H), 4.43 (s, 1H), 3.52 – 3.38 (m, 2H), 2.13 – 2.08 (m, 1H), 1.96 – 1.76 (m, 3H), 1.43 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 154.7, 137.0, 130.7, 127.4, 128.1, 127.3, 126.2, 79.2, 59.0, 46.2, 32.5, 28.5, 23.0.

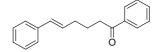


(*E*)-tert-butyl (1,5-diphenylpent-1-en-3-yl)carbamate (28): Following the general procedure B, obtained in 51% yield as a white solid (34.4 mg, eluent: petroleum ether:ethyl acetate = 10:1).

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.09 (m, 10H), 6.44 (d, J = 15.7 Hz, 1H), 6.03 (dd, J = 15.7, 6.1 Hz, 1H), 4.54 (s, 1H), 4.25 (s, 1H), 2.65 (t, J = 7.7 Hz, 2H), 1.86 (d, J = 7.1 Hz, 2H), 1.39 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.4, 141.6, 136.8, 130.3, 128.6, 128.5, 128.4, 127.5, 126.4, 125.9, 79.5, 52.3, 37.3, 32.3, 28.4.

HRMS (ESI) Calcd for $C_{22}H_{27}NNaO_2^+$ [M+Na]⁺: 360.1934, found: 360.1933.

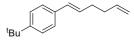


*(E)***-1,6-diphenylhex-5-en-1-one (29):** Following the general procedure B, obtained in 54% yield as a colorless liquid (27 mg, eluent: petroleum ether:ethyl acetate = 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (t, *J* = 10.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.24 (m, 4H), 7.19 (t, *J* = 7.1 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.02 (t, *J* = 7.3 Hz, 2H), 2.32 (q, *J* = 7.7 Hz, 2H), 1.99 – 1.87 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 200.2, 137.6, 137.0, 132.9, 130.7, 129.9, 128.5, 128.4, 128.0, 126.9, 125.9, 37.7, 32.4, 23.7.

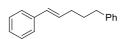
HRMS (ESI) Calcd for C₁₈H₁₈ONa⁺ [M+Na]⁺: 273.1250, found: 273.1249.



(*E*)-1-(tert-butyl)-4-(hexa-1,5-dien-1-yl)benzene (30): Following the general procedure B, obtained in 61% yield as a colorless liquid (26.1 mg, eluent: petroleum ether). (Ref: *Chem. Commun.* 2012, *48*, 8709)

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.24 (m, 4H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.12 (m, 1H), 5.91 – 5.81 (m, 1H), 5.02 (dd, *J* = 27.3, 13.6 Hz, 2H), 2.33 – 2.16 (m, 4H), 1.31 (s, 9H).

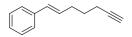
¹³C NMR (101 MHz, CDCl₃) δ 149.9, 138.2, 135.0, 129.9, 129.4, 125.7, 125.4, 115.0, 34.5, 33.7, 32.5, 31.3.



(*E*)-pent-1-ene-1,5-diyldibenzene (31): Following the general procedure B, obtained in 65% yield as a colorless liquid (28.9 mg, eluent: petroleum ether). (Ref: *Org. Lett.*, 2014, *16*, 1904)

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.12 (m, 10H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.74 – 2.56 (m, 2H), 2.27 – 2.22(m, 2H), 1.88 – 1.72 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 142.3, 137.8, 130.5, 130.2, 128.5, 128.3, 126.8, 125.9, 125.7, 35.4, 32.5, 31.0. (one carbon signal is overlapped)

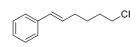


(E)-hept-1-en-6-yn-1-ylbenzene (32): Following the general procedure B, obtained in 55% yield as a colorless liquid (18.7 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.1 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.25 – 6.13 (m, 1H), 2.34 (q, J = 7.2 Hz, 2H), 2.25 (t, J = 7.1 Hz, 2H), 1.98 (s, 1H), 1.72 (p, J = 7.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 137.7, 130.7, 129.6, 128.5, 127.0, 126.0, 84.3, 68.5, 31.9, 28.1, 17.9.

HRMS (EI) Calcd for $C_{13}H_{14}^+$ [M]⁺: 170.1096, found: 170.1092.



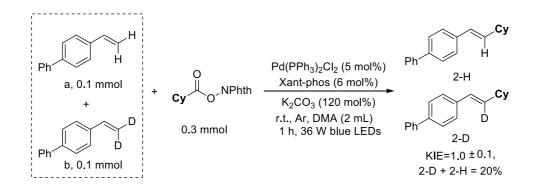
(E)-(6-chlorohex-1-en-1-yl)benzene (33): Following the general procedure B, obtained in 68% yield as a colorless liquid (26.4 mg, eluent: petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 4H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.40 (d, J = 15.7 Hz, 1H), 6.26 – 6.15 (m, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.67 – 1.61 (m, 2H).

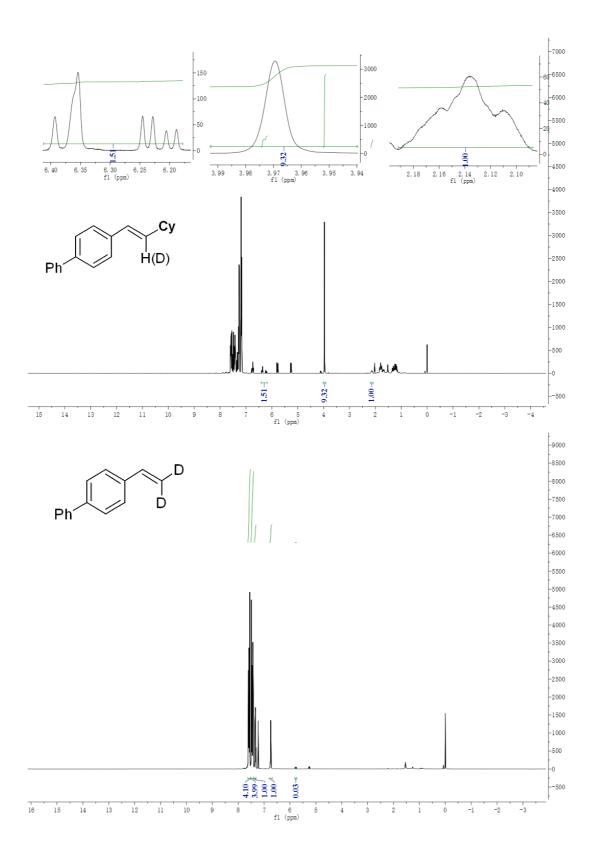
¹³C NMR (101 MHz, CDCl₃) δ 137.6, 130.4, 130.1, 128.5, 127.0, 126.0, 45.0, 32.2, 32.0, 26.6.

HRMS (ESI) Calcd for $C_{12}H_{16}Cl^+ [M+H]^+$: 195.0935, found: 195.0941.

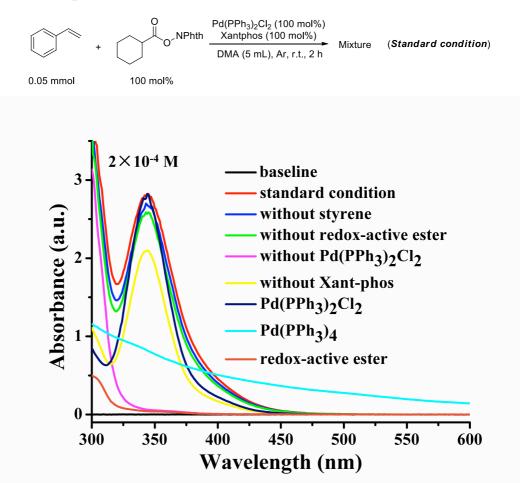
5. Intermolecular kinetic isotope experiment



a (1.0 equiv, 0.1 mmol), **b** (1.0 equiv, 0.1 mmol), redox active ester (3 equiv, 0.3 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%, 3.5 mg), Xantphos (6 mol%, 3.5 mg), and K₂CO₃ (0.24 mmol, 16.5mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, anhydrous DMA (2.0 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation of 36 W blue LEDs (distance app. 3.0 cm from the LEDs) at room temperature for 1 h. The mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. Yield and ratio of products were determined by ¹H-NMR using diphenylmethane as internal standard.



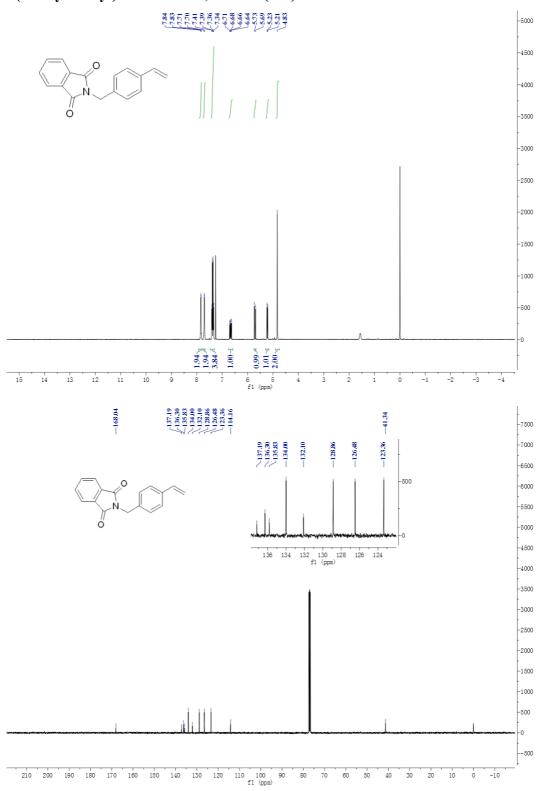
6. UV-Vis. Spectrum

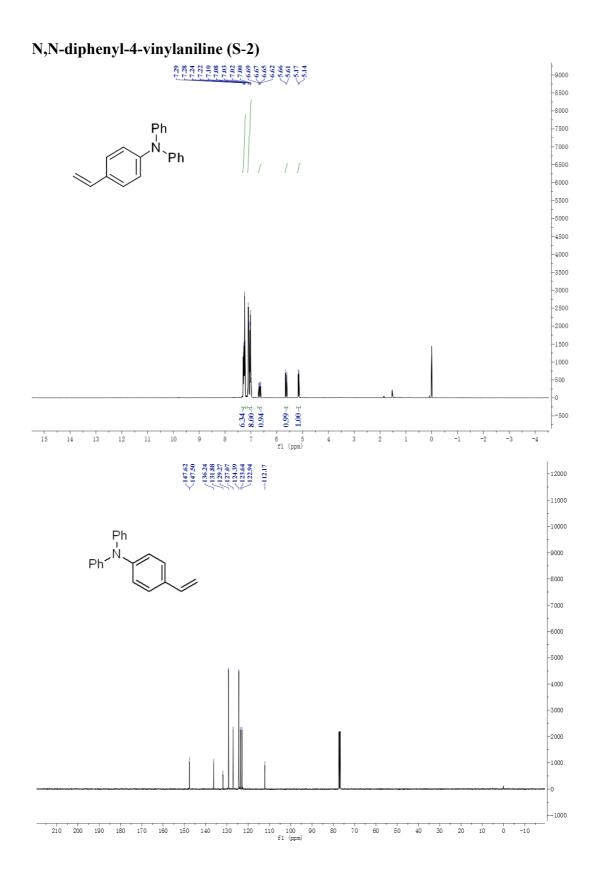


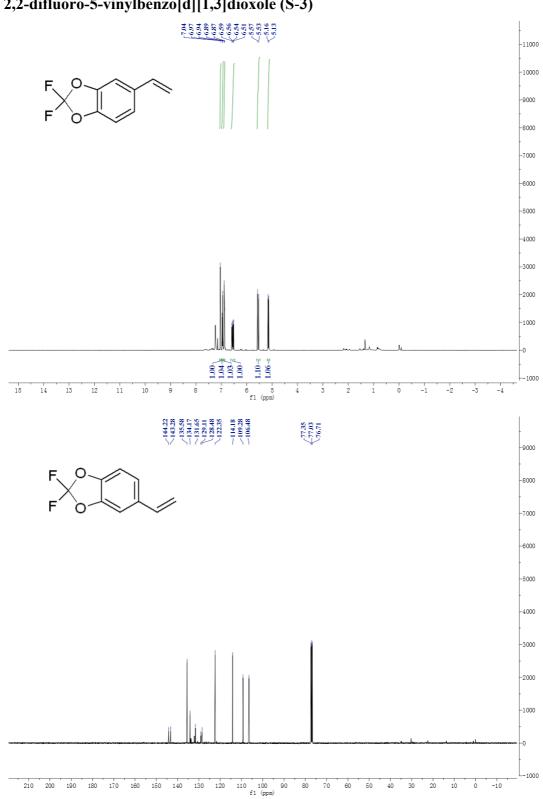
UV/Vis absorption measurements were conducted using a mixture of stoichiometric amount of palladium salt and ligand. UV-Vis absorption onset around 450 nm was observed when measuring the mixture of stoichiometric reaction, suggesting that the palladium complex is excited by the irradiation of blue-LEDs. The absorption is affected by the absence of Xantphos, but not affected by the absence of substrates. N-(acyloxy)phthalimide itself has no absorption in the wavelength range of blue LED irradiation.

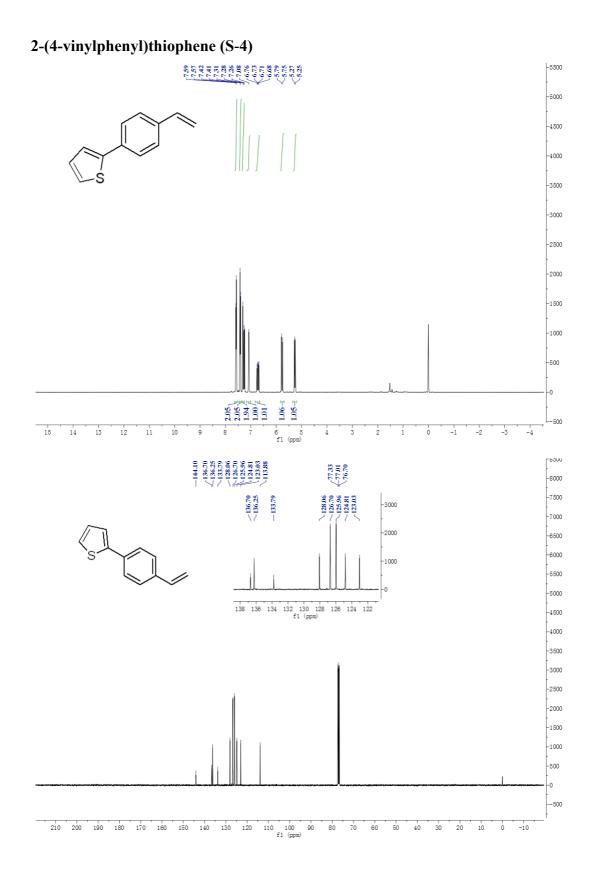
7. NMR Spectra

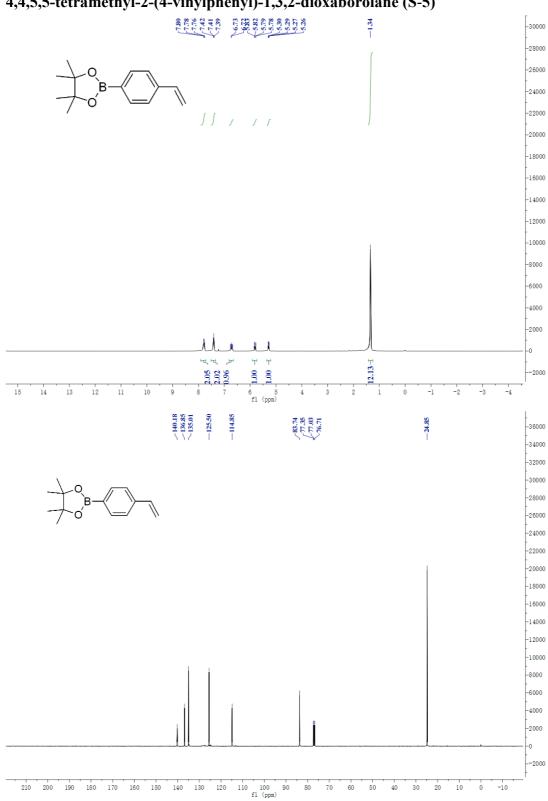
2-(4-vinylbenzyl)isoindoline-1,3-dione (S-1)



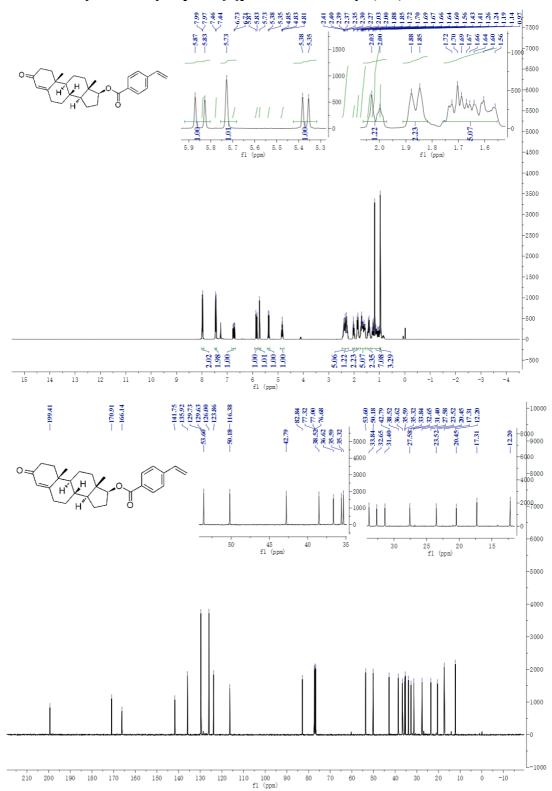




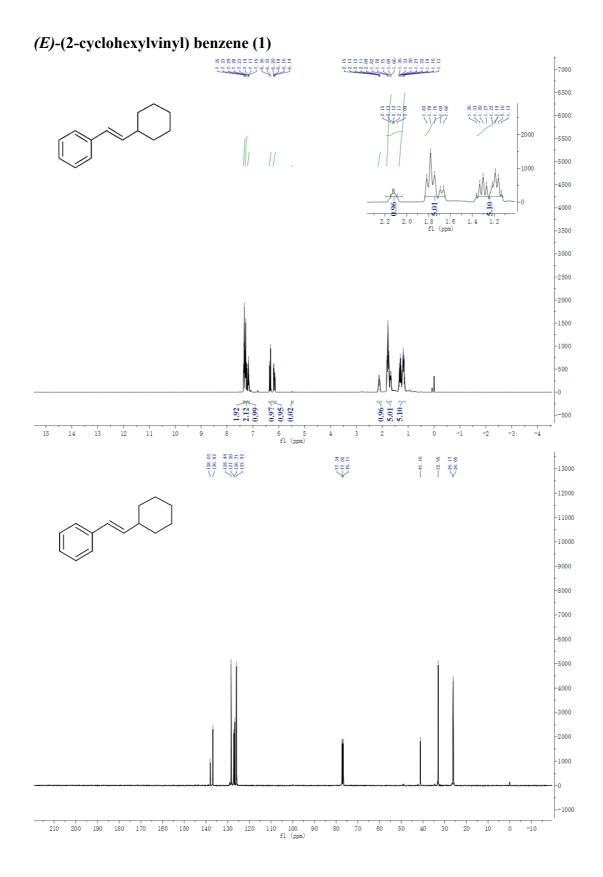


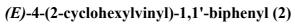


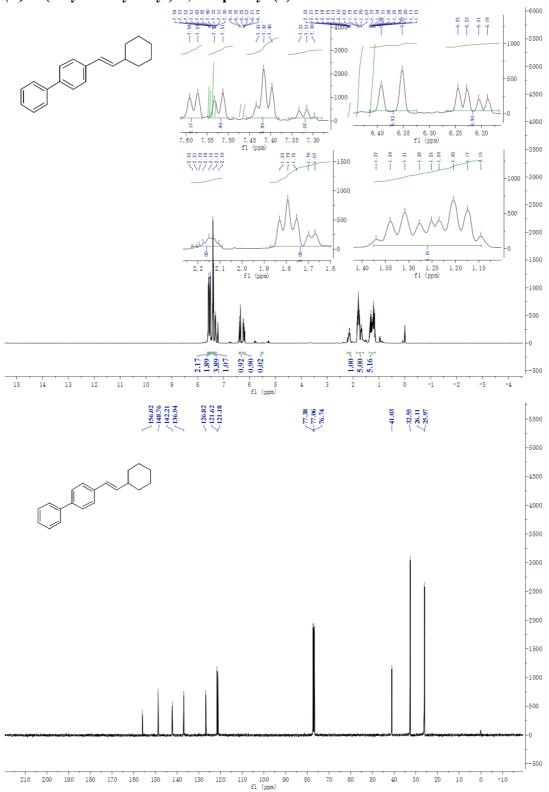
4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (8-5)

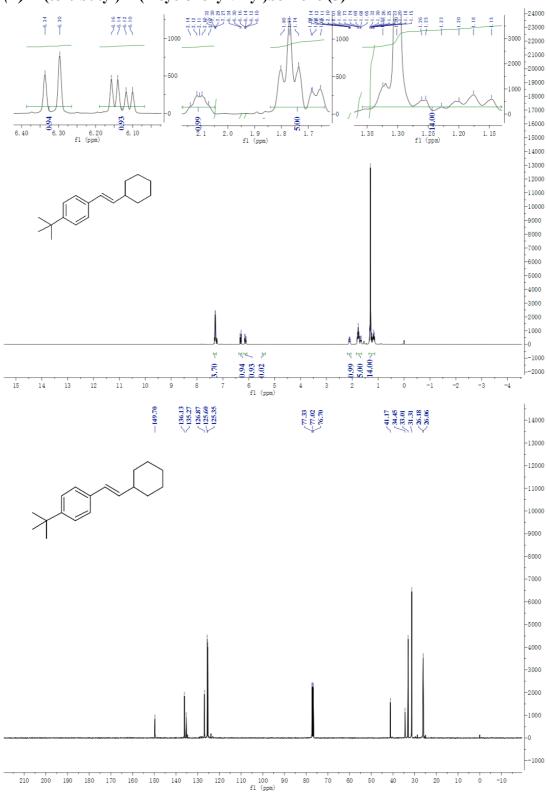


(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17 -tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl (S-6)

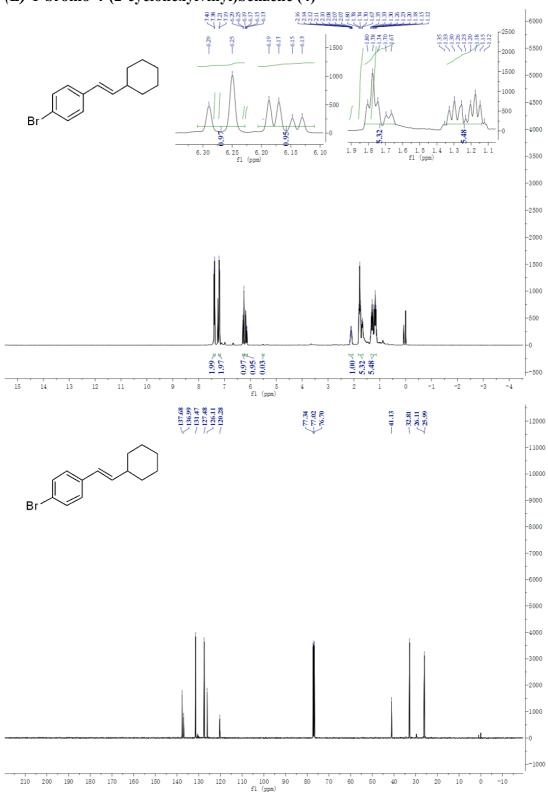




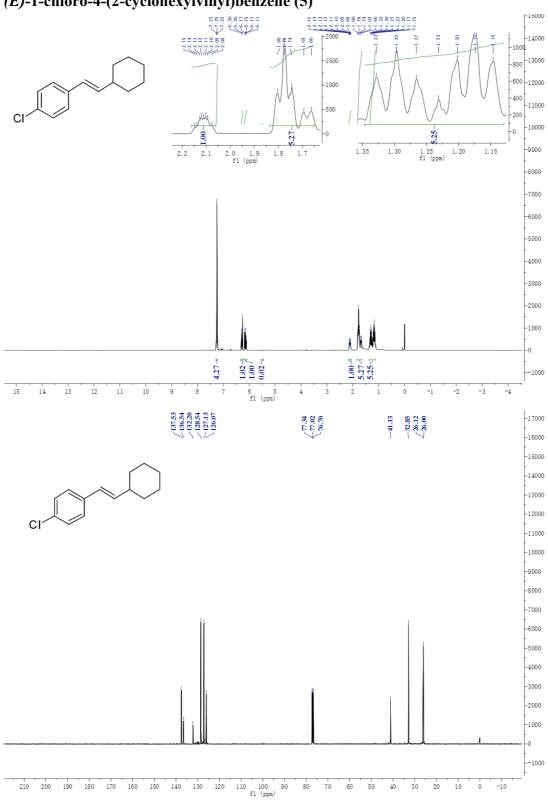




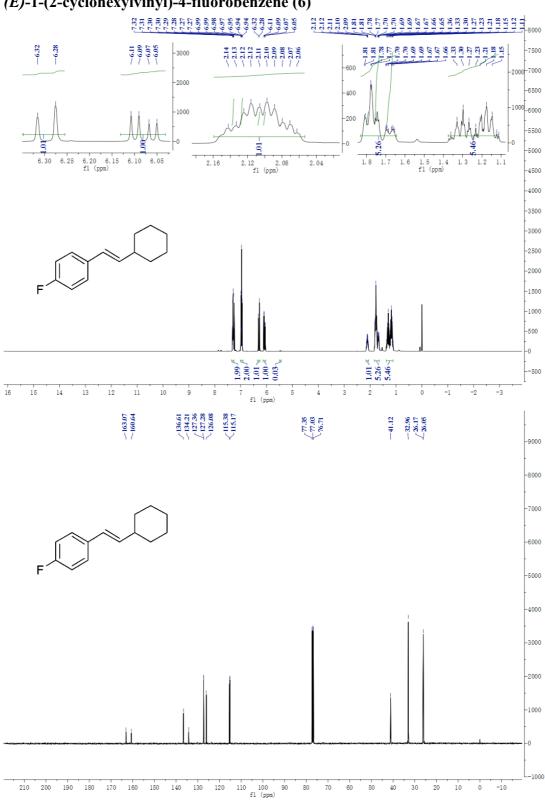
(E)-1-(tert-butyl)-4-(2-cyclohexylvinyl)benzene (3)



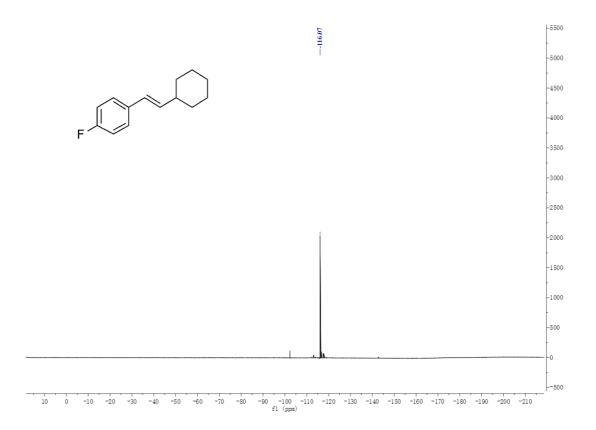
(E)-1-bromo-4-(2-cyclohexylvinyl)benzene (4)

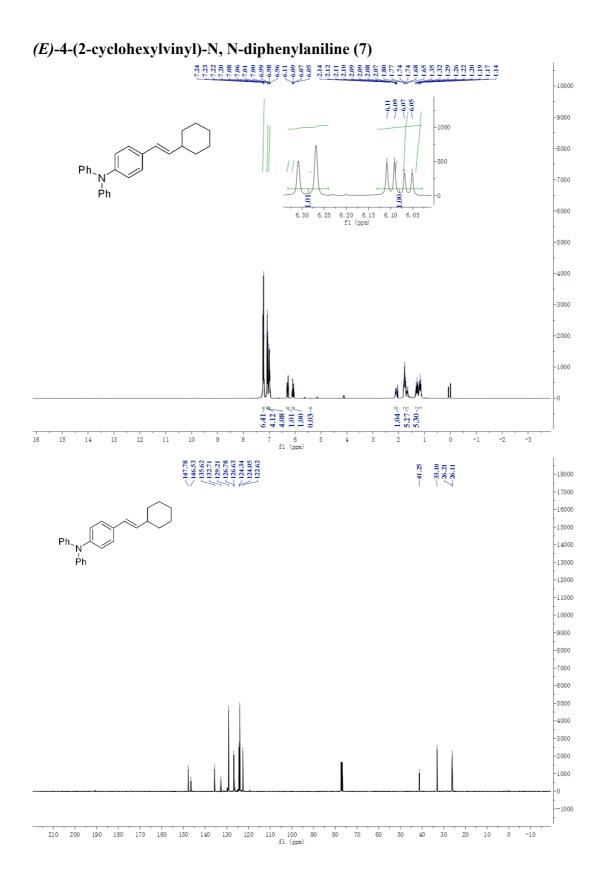


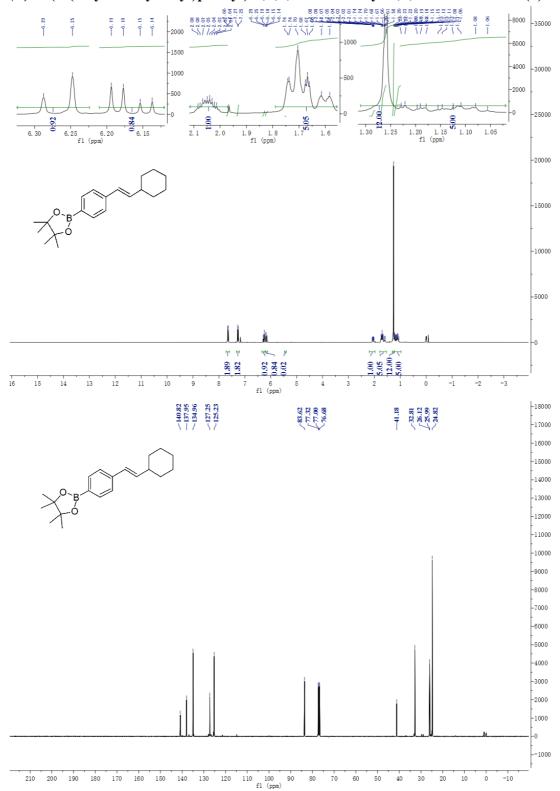
(E)-1-chloro-4-(2-cyclohexylvinyl)benzene (5)



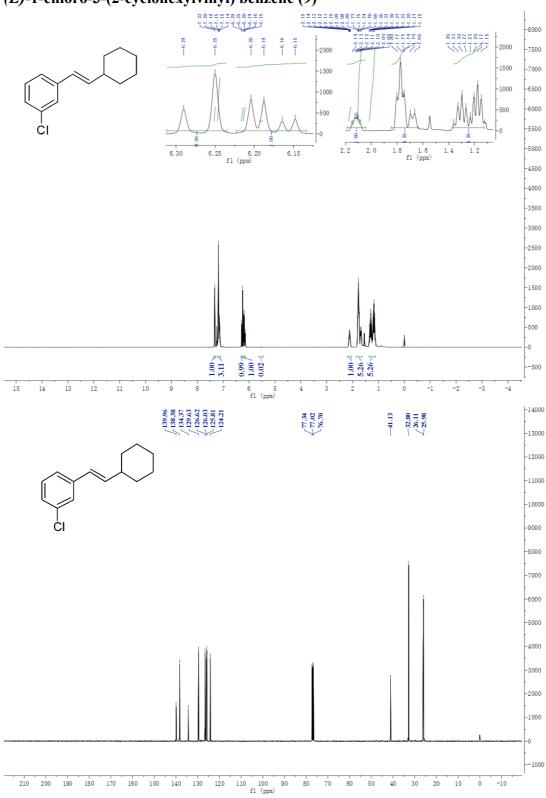
(E)-1-(2-cyclohexylvinyl)-4-fluorobenzene (6)



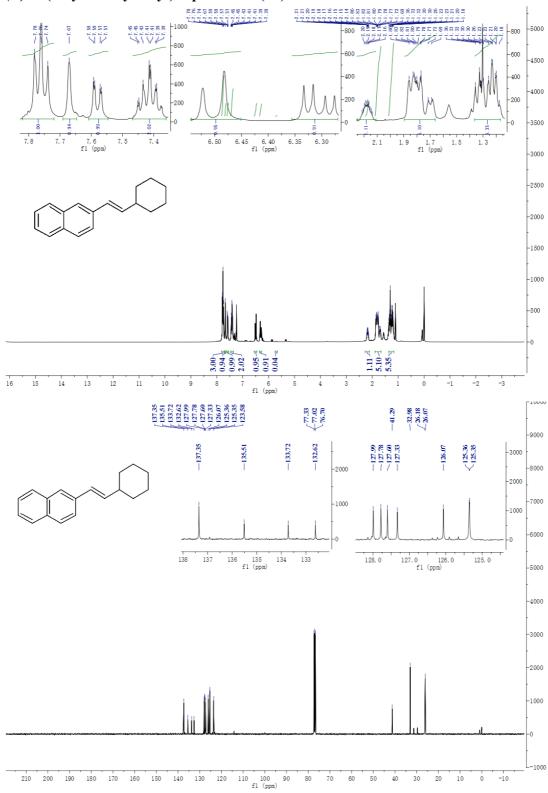




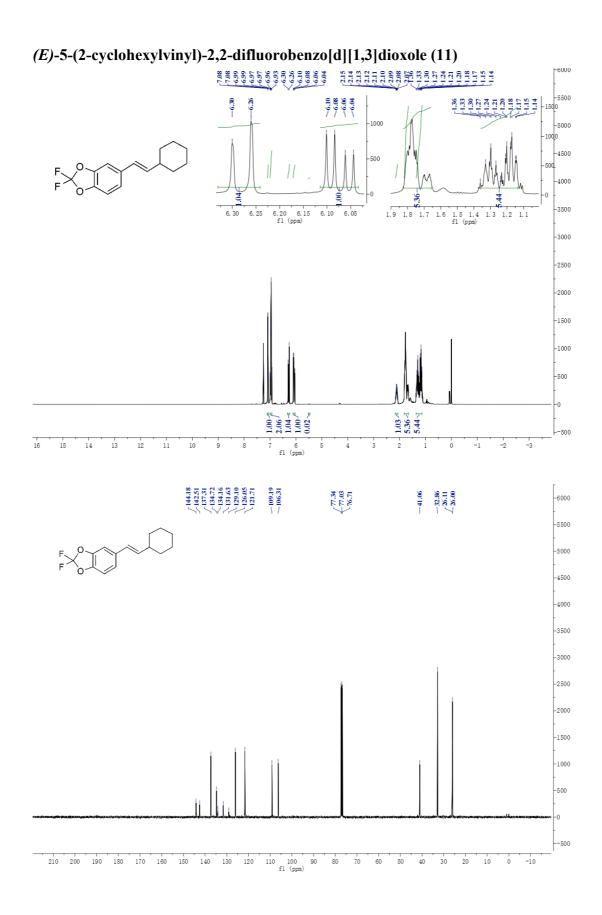
(E)-2-(4-(2-cyclohexylvinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(8)

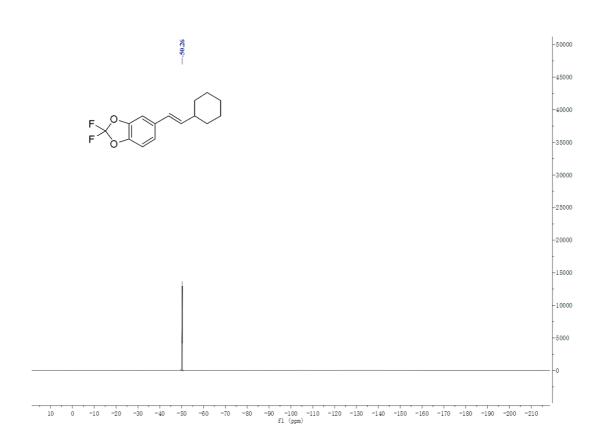


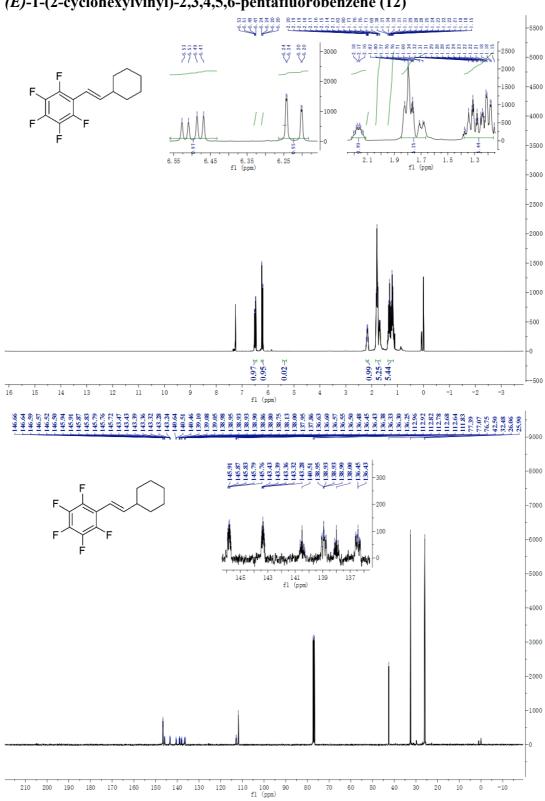
(E)-1-chloro-3-(2-cyclohexylvinyl) benzene (9)



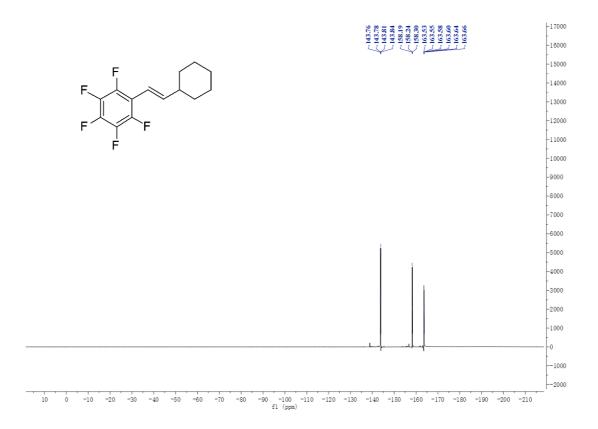
(E)-2-(2-cyclohexylvinyl)naphthalene(10)

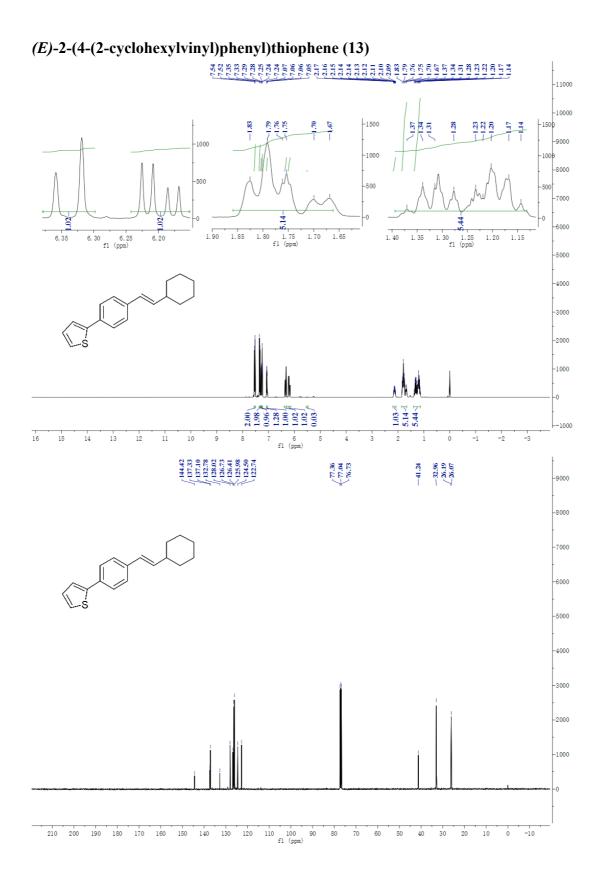


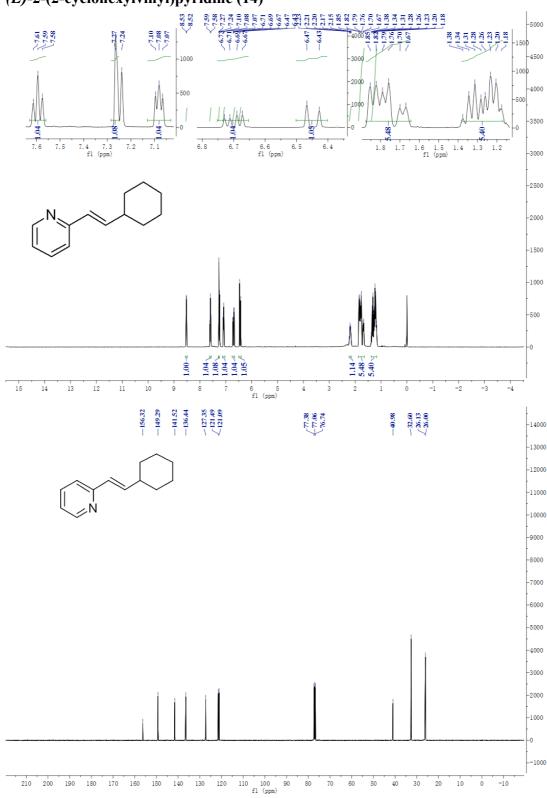




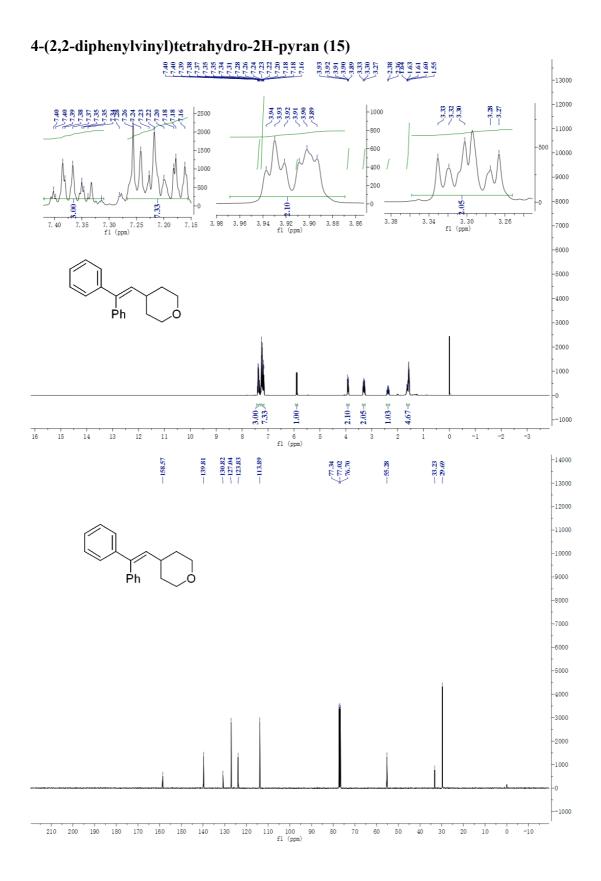
(E)-1-(2-cyclohexylvinyl)-2,3,4,5,6-pentafluorobenzene (12)



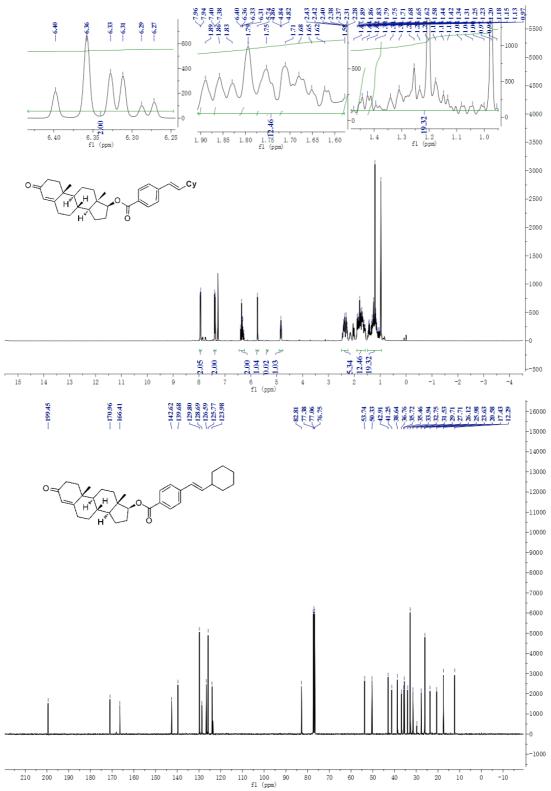


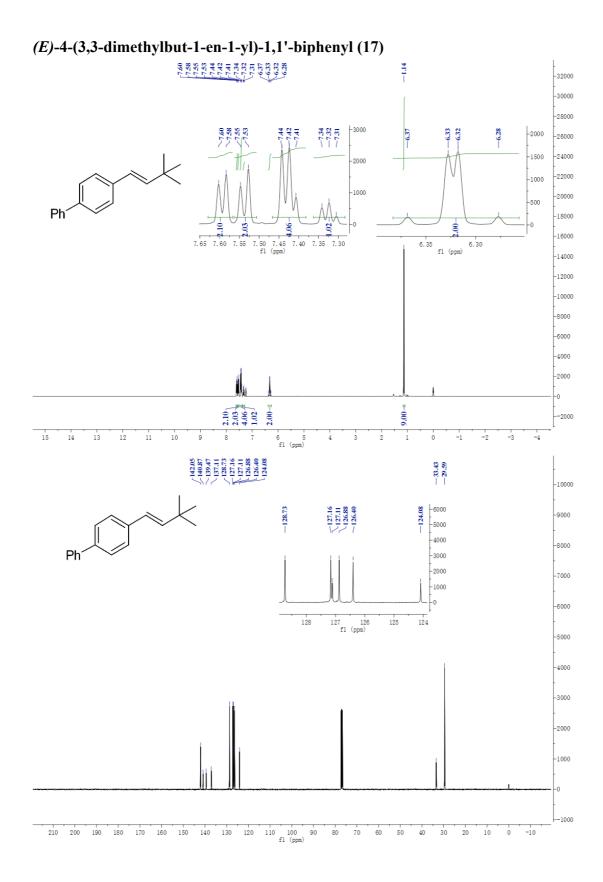


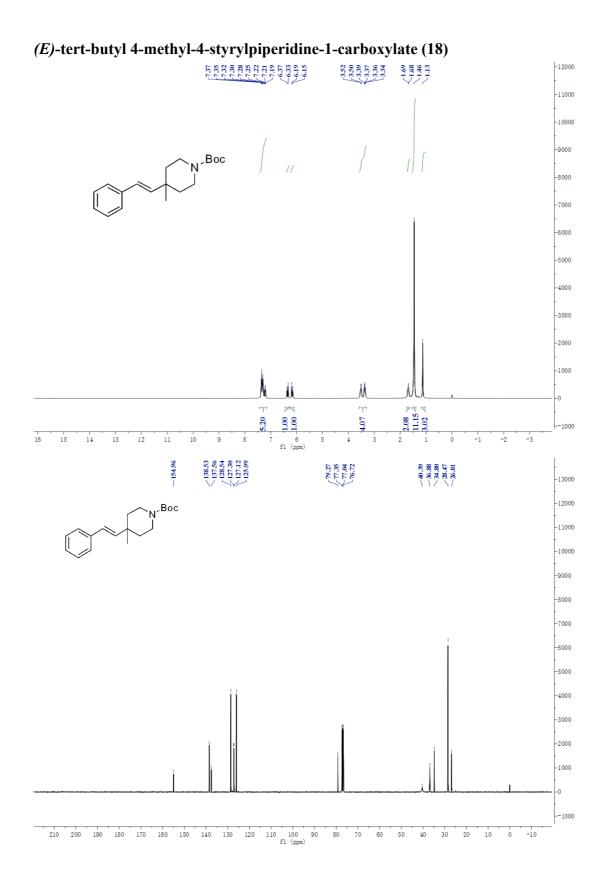
(E)-2-(2-cyclohexylvinyl)pyridine (14)

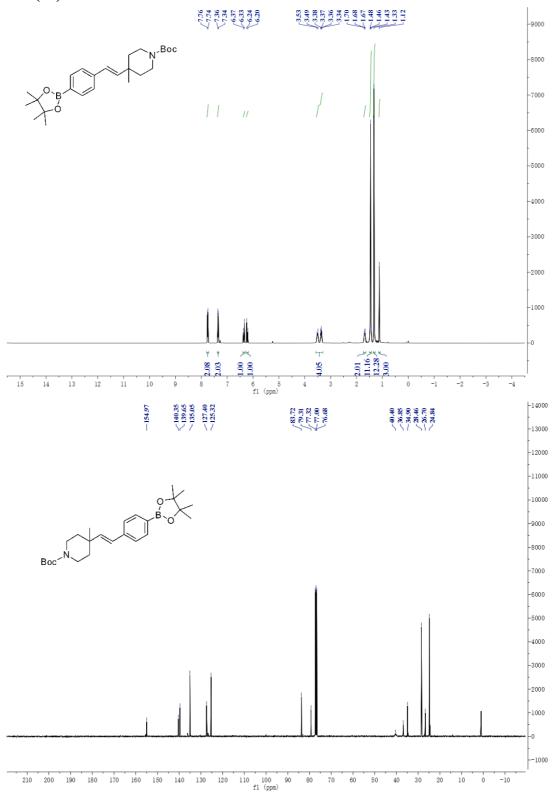


(8R, 9S, 10R, 13S, 14S, 17S)-10, 13-dimethyl-3-oxo-2, 3, 6,7,8,9,10,11,12,13,14,15, 16, 17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-(*(E)*-2-cyclohexyl vinyl) benzoate (16)

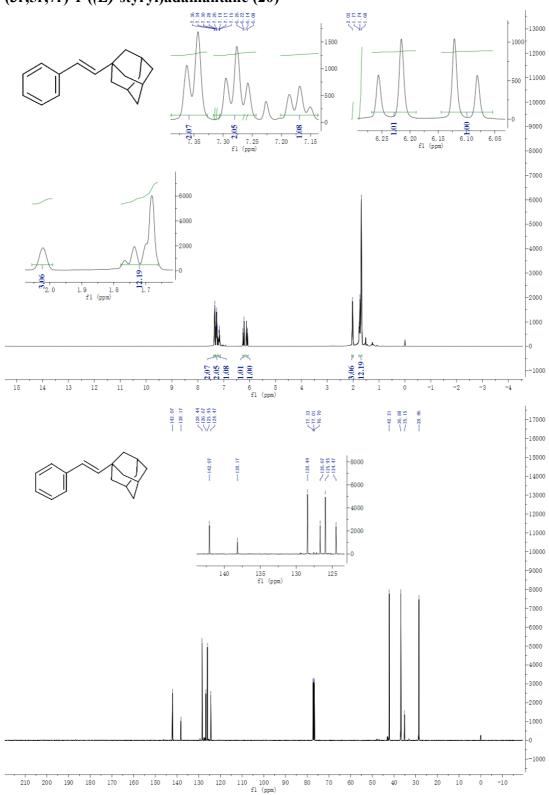




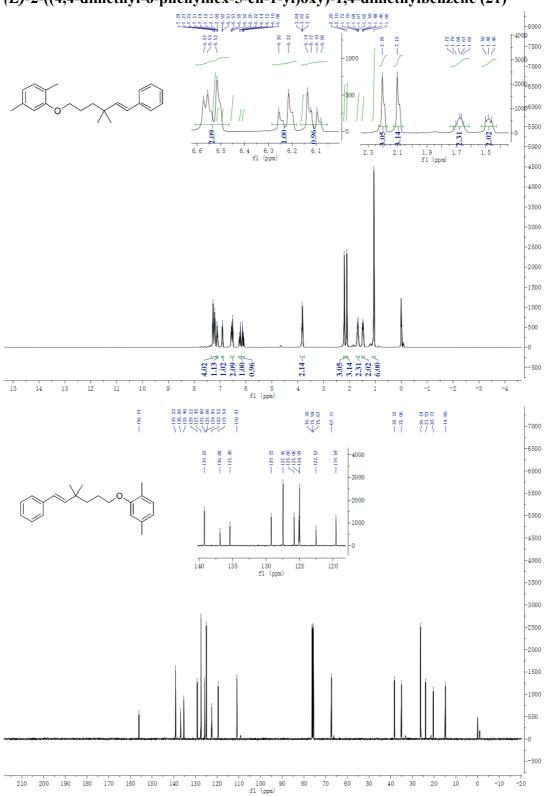




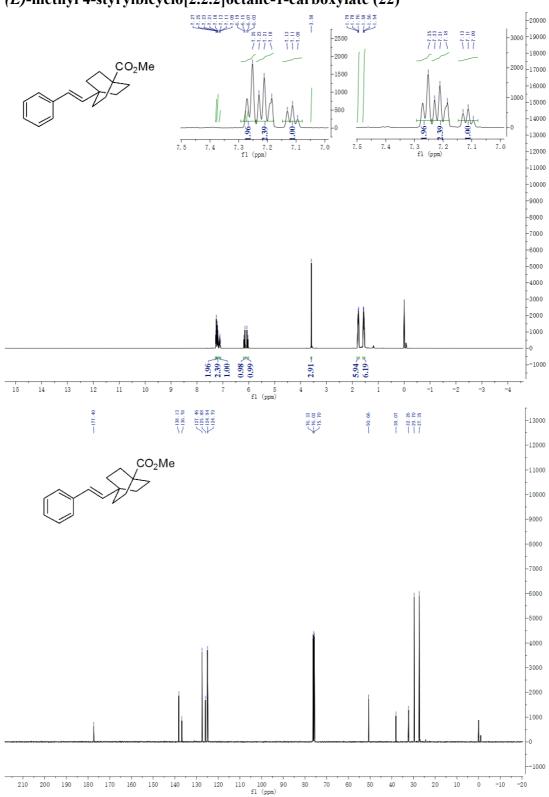
(E)-2-(4-(3,3-dimethylbut-1-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborol ane (19)



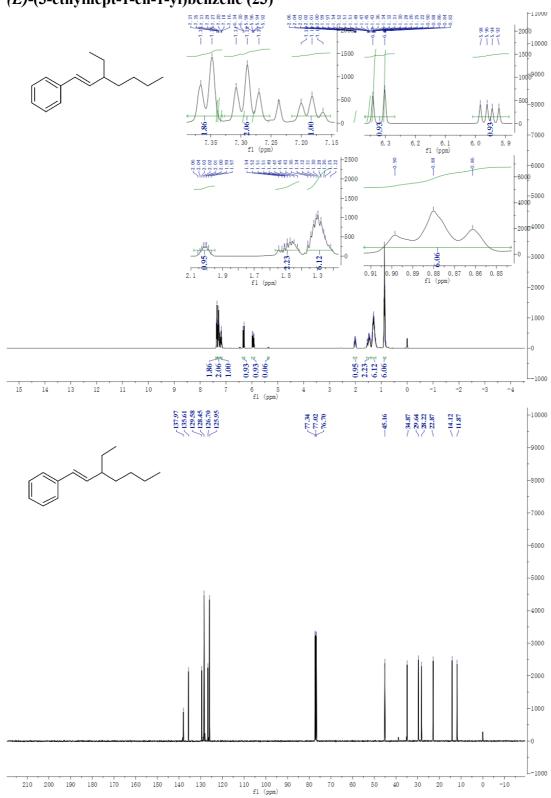
(3r,5r,7r)-1-((E)-styryl)adamantane (20)



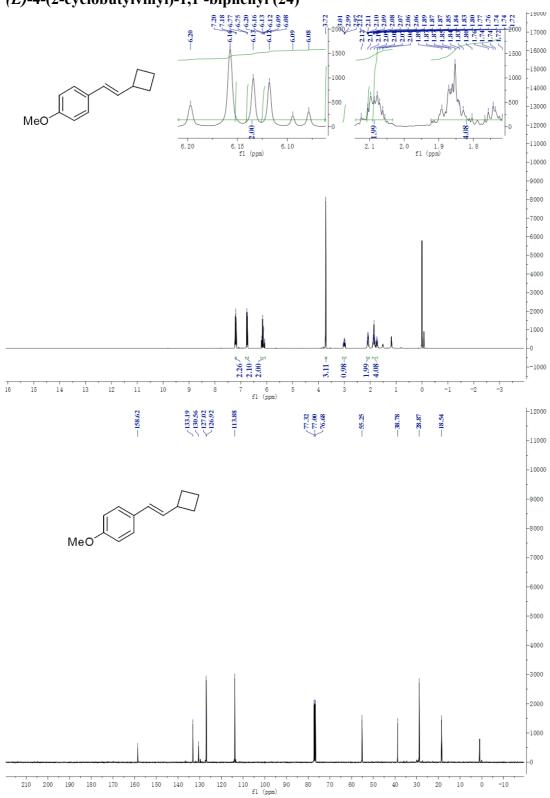
(E)-2-((4,4-dimethyl-6-phenylhex-5-en-1-yl)oxy)-1,4-dimethylbenzene (21)



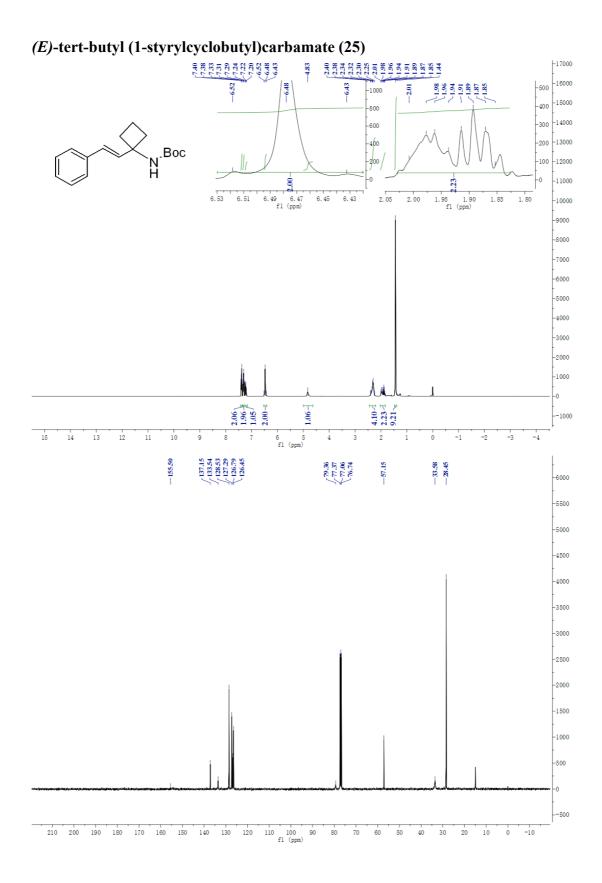
(E)-methyl 4-styrylbicyclo[2.2.2]octane-1-carboxylate (22)

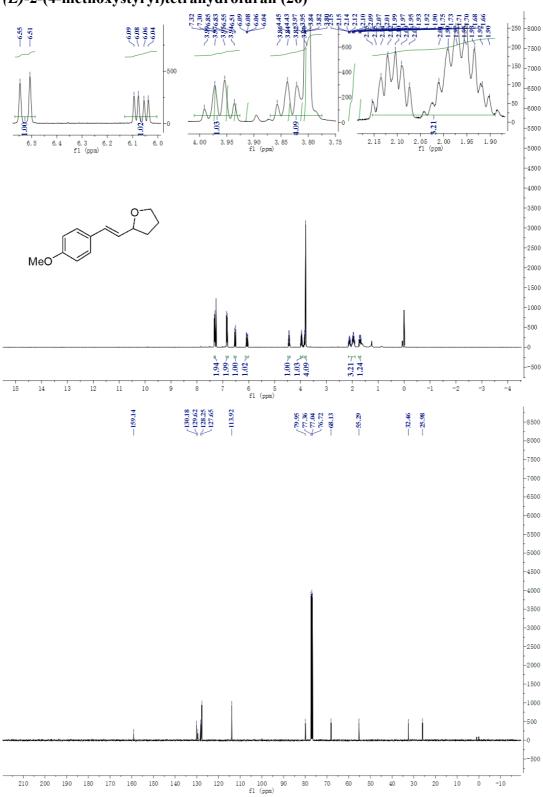


(E)-(3-ethylhept-1-en-1-yl)benzene (23)

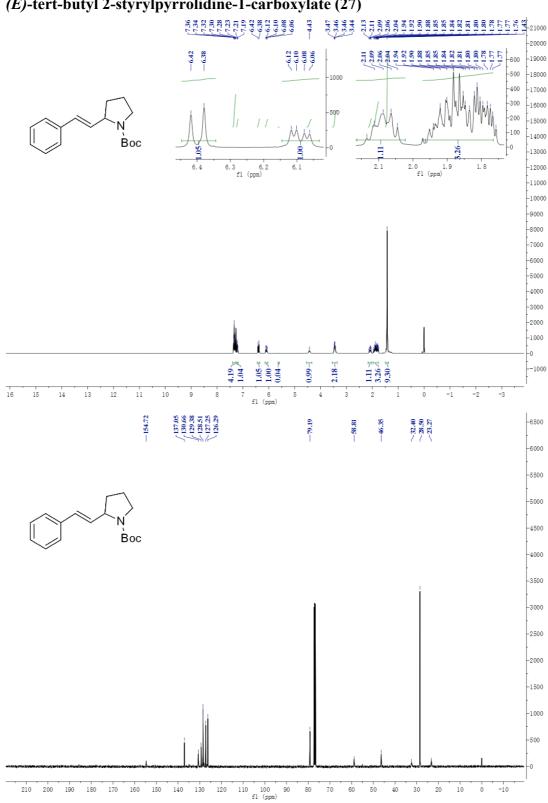


(E)-4-(2-cyclobutylvinyl)-1,1'-biphenyl (24)

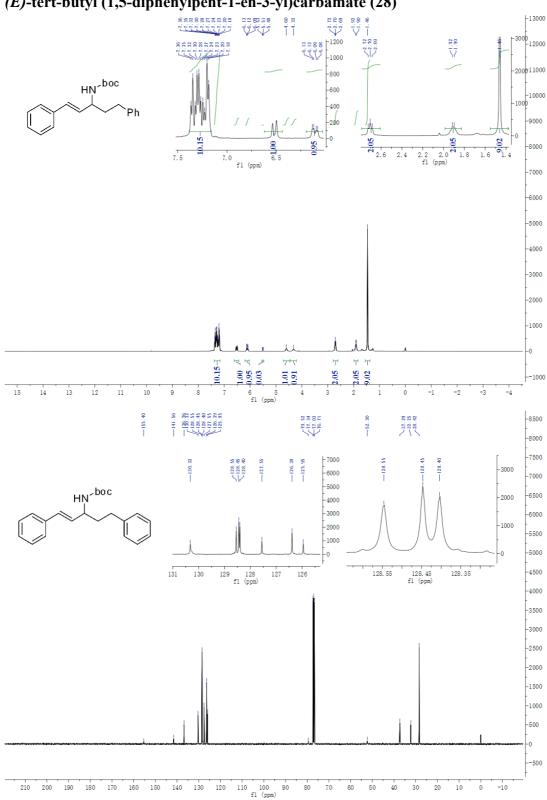




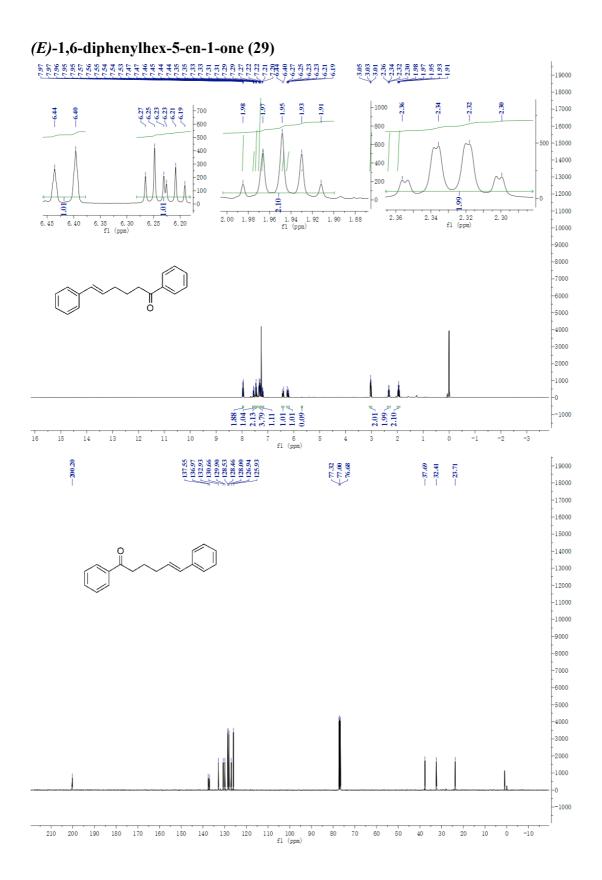
(E)-2-(4-methoxystyryl)tetrahydrofuran (26)

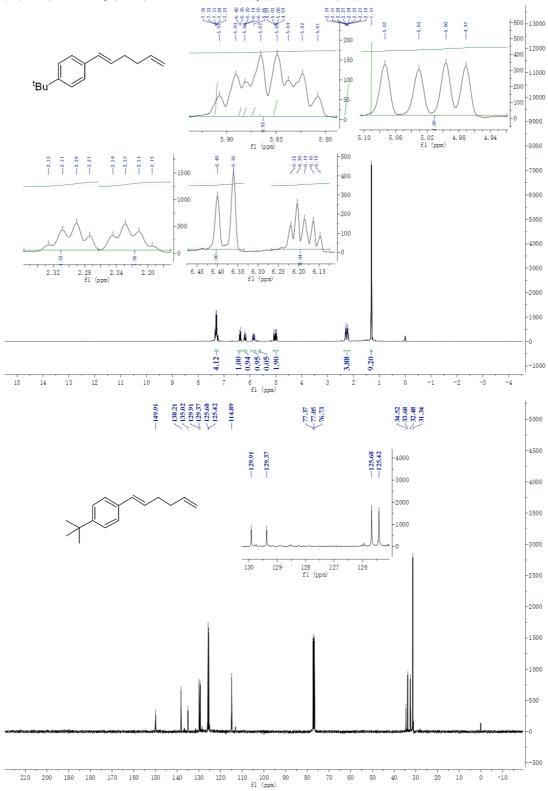


(E)-tert-butyl 2-styrylpyrrolidine-1-carboxylate (27)

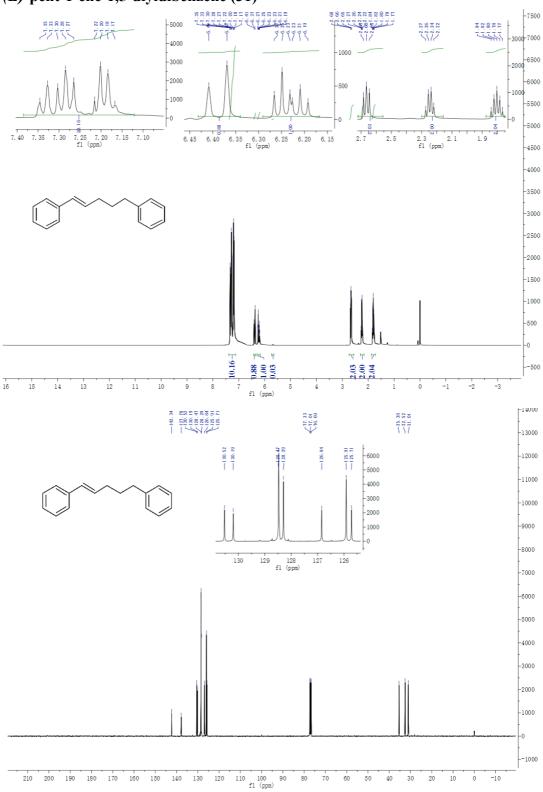


(E)-tert-butyl (1,5-diphenylpent-1-en-3-yl)carbamate (28)





(E)-1-(tert-butyl)-4-(hexa-1,5-dien-1-yl)benzene (30)



(E)-pent-1-ene-1,5-diyldibenzene (31)

(E)-hept-1-en-6-yn-1-ylbenzene (32)

