Supplementary Information

Palladium-catalyzed regioselective decarboxylative hydroarylation of alkynyl carboxylic acids with arylboronic acids

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1. General information

1.1 Materials

The following chemicals were purchased and used as received:

Palladium chloride (cas: 7647-10-1, Adamas, 5 g), Palladium acetate (cas: 3375-31-3, Adamas, 5 g), other Palladium or Nickel catalyst (Energy or Adamas), Triphenylphosphine (cas: 603-35-0, Energy, 500 g), other Phosphines (Energy or Adamas), Arylboronic acids (Energy or Adamas), Phenylpropiolic acid (cas: 637-44-5, Energy, 10 g), H₂O (ultrapure water, conductivity = 0.055 μ s/cm), Toluene (cas: 108-88-3, Sinopharm, 500 mL), Potassium acetate (cas: 127-08-2, Aladdin, 500 g).

1.2 Analytical methods

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker 400 MHz or Keysight 600 MHz spectrometer at 295 K in deuterated solvents. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration).

GC measurements were conducted on Thermo Fisher. HRMS ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software.

Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (300-400 mesh).

2. Optimization of reaction conditions

Table S1. Optimization of the ligands



Entry	Ligand	Yield (%) ^b
1	PPh ₃	88%
2	PCy ₃	19%
3	1,1'-bis(dicyclohexylphosphino)ferrocene	9%
4	tri-o-tolylphosphine	34%
5	BINAP	N.R.
6	dppb	N.R.
7	XPhos	42%
8	dppf	N.R.
9	XantPhos	40%
10	t-BuXPhos	N.R.
11	DpePhos	N.R.
12	S-Phos	15%

^aReaction conditions: **1** (0.30 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), potassium acetate (0.6 mmol, 2.0 equiv), Pd(OAc)₂ (0.006 mmol, 0.02 equiv), ligand (0.015 mmol, 0.05 equiv), toluene (3.0 mL), H₂O (0.3 mL) under argon for 10 h (oil bath), unless otherwise noted. ^bAll yields were determined by gas chromatography using biphenyl as an internal standard. N.R. = no reaction; BINAP = 1.1'-binaphthyl-2.2'-diphenylphosphine; dppb = 1,4-bis(diphenylphosphino)butane; Xphos = 2-(dicyclohexyl phosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl; dppf = 1,1'-Bis(diphenylphosphino)ferrocene; Xant-Phos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; t-BuXphos = 2-di-tert-butylphosphino-2',4',6'-triisopropyl biphenyl; DpePhos = Bis(2-diphenylphosphinophenyl) ether; Sphos = 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl.

Table S2. Optimization of the reaction solvents



Entry	Solvent	Yield $(\%)^b$
1	PhCl/H ₂ O	80%
2	MeCN/H ₂ O	N.R.
3	acetone/H ₂ O	N.R.
4	1,4-dioxane/H ₂ O	N.R.
5	DMC/H ₂ O	N.R.
6	NMP/H ₂ O	N.R.
7	THF/H ₂ O	N.R.
8	nitrobenzene/H ₂ O	50%
9	DCE/H ₂ O	61%
10	DMSO/H ₂ O	N.R.
11	DMF/H ₂ O	N.R.
12	o-xylene/H ₂ O	31%

^{*a*} Reaction conditions: **1** (0.30 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), Pd(OAc)₂ (0.006 mmol, 0.02 equiv), PPh₃ (0.015 mmol, 0.05 equiv), potassium acetate (0.6 mmol, 2.0 equiv), solvent (3.0 mL), H₂O (0.3 mL) under argon for 10 h (oil bath), unless otherwise noted. ^{*b*} All yields were determined by gas chromatography using biphenyl as an internal standard. N.R. = no reaction; DMC = dimetyl carbonate; NMP = N-methyl-2-pyrrolidone; THF = tetrahydrofuran; DCE = 1,2-dichloroethane; DMSO = dimethyl sulfoxide; DMF = *N*,*N*dimethylformamide.

Table S3. Optimization of the reaction bases

$ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & $	OOH Pd(OAc) ₂ (2 mol%), PPh ₃ (5 mol%) DH base (2.0 equiv) toluene/H ₂ O, N ₂ , 80 °C, 10 h	
Entry	Base	Yield (%) ^b
1	DBU	N.R.
2	DIPEA	37%
3	NEt ₃	56%
4	Na ₂ CO ₃	N.R.
5	TMEDA	N.R.
6	CH ₃ ONa	10%
7	NaHCO ₃	N.R.
8	t-BuONa	N.R.
9	K ₂ CO ₃	N.R.
10	Cs ₂ CO ₃	N.R.

^{*a*}Reaction conditions: **1** (0.30 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), base (0.6 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 0.02 equiv), PPh₃ (0.015 mmol, 0.05 equiv), toluene (3 mL), H₂O (0.3 mL) under argon for 10 h (oil bath), unless otherwise noted. ^{*b*}All yields were determined by gas chromatography using biphenyl as an internal standard. N.R. = no reaction; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DIPEA = N,N-diisopropylethylamine; TMEDA = N,N,N',N'-tetramethyl-ethylenediamine.

Table S4. Optimization of the reaction parameters



Entry	Catalyst	Ligand	Solvent	T/ºC	Yield (%) ^b
1	2 mol%	PPh ₃ (5 mol%)	toluene/H ₂ O	80	88%
2	2 mol%		toluene/H ₂ O	80	N.R.
3	2 mol%	PPh ₃ (2 mol%)	toluene/H ₂ O	80	62%
4	2 mol%	PPh_3 (10 mol%)	toluene/H ₂ O	80	85%
5	2 mol%	PPh ₃ (5 mol%)	toluene	80	N.R.
6	2 mol%	PPh ₃ (5 mol%)	toluene/EtOH	80	N.R.
7	2 mol%	PPh ₃ (5 mol%)	toluene/AcOH	80	N.R.
8	2 mol%	PPh ₃ (5 mol%)	toluene/MeOH	80	45%
9 <i>c</i>	2 mol%	PPh ₃ (5 mol%)	toluene/H ₂ O	80	83%
10	1 mol%	PPh ₃ (5 mol%)	toluene/H ₂ O	80	78%
11		PPh ₃ (5 mol%)	toluene/H ₂ O	80	N.R.
12	2 mol%	PPh ₃ (5 mol%)	toluene/H ₂ O	60	N.R.
13	2 mol%	PPh ₃ (5 mol%)	toluene/H ₂ O	100	84%

^{*a*}Reaction conditions: **1** (0.30 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), potassium acetate (0.6 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 0.02 equiv), PPh_3 (0.015 mmol, 0.05 equiv), toluene (3.0 mL), proton source (0.3 mL) under argon for 10 h (oil bath), unless otherwise noted. ^{*b*}All yields were determined by gas chromatography using biphenyl as an internal standard. ^{*c*}The amount of water in the reaction was increased to 0.5 mL; N.R. = no reaction.

Table S5. Optimization of the palladium catalysts



Entry	Catalyst	Yield (%) ^b
1	$Pd(OAc)_2$ (2 mol%)	N.R.
2	$PdCl_2$ (2 mol%)	N.R.
3	Pd ₂ (dba) ₃ (2 mol%)	N.R.
4	$Pd(acac)_2$ (2 mol%)	N.R.
5	$PdCl_2(2 mol\%) + PPh_3(5 mol\%)$	78%
6	$Pd_2(dba)_3(2 \text{ mol}\%) + PPh_3(5 \text{ mol}\%)$	45%
7	Pd(OAc) ₂ (2 mol%) + PPh ₃ (5 mol%)	88%
8	Pd(PCy ₃) ₂ Cl ₂ (2 mol%)	42%
9	$Pd(PPh_3)_2Cl_2 (2 mol\%)$	66%
10	NiCl ₂ (dppp) (2 mol%)	N.R.
11	Ni(PCy ₃) ₂ Cl ₂ (2 mol%)	N.R.

^{*a*} Reaction conditions: **1** (0.30 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), potassium acetate (0.6 mmol, 2.0 equiv), catalyst (0.006 mmol), toluene (3.0 mL), H₂O (0.3 mL) under argon for 10 h (oil bath), unless otherwise noted. ^{*b*}All yields were determined by gas chromatography using biphenyl as an internal standard. N.R. = no reaction; Dppp = 1,3-Bis(diphenylphosphino)propane.

3. Preparation of non-commercial substrates

 $1a^{1}$, $1b^{1}$, $1c^{1}$, $1d^{1}$, $1f^{1}$, $1g^{1}$, $1h^{1}$, $1i^{1}$, $1e^{2}$, $1j^{3}$, $1k^{4}$, $55^{5,6}$ were prepared according to the reported procedures.



Figure S1 Preparation of non-commercial substrates

4. Time-course reactions under the standard condition.

4.1 Identification of the possible intermediate

To further probe the possible intermediate in the reaction, we conducted a collection of experiments with D_2O under the standard condition by detecting the yields of the possible intermediate 57 and final product 43 at a different time (Figure S2). This experiment showed that the starting substrate 1 was rapidly decarboxylated to intermediate 57, which subsequently underwent a further transformation into the deuterium-labeled alkenes 43.

соон + 	(standard conditions) <i>reaction time(h)</i>	+ 43	<u></u> D 57
entry	Time/h	57/yield%	43 /yield%
1	0	0	0
2	0.25	28	0
3	0.5	42	0
4	0.75	54	2
5	1	60	4
6	1.25	72	10
7	1.5	61	23
8	1.75	45	40
9	2.0	23	65
10	2.5	0	77
11	3.0	0	77
12	3.5	0	77

For experimental details, see the general procedure B. All yields were determined by gas chromatography using biphenyl as an internal standard.



Figure S2 Time-course reactions under the standard condition.

4.2 Control experiment

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To further probe whether alkynes can be converted to the desired product 43 with D_2O under the standard conditions, we conducted a collection of experiments under the standard condition by detecting the yields of the substate and final product at a different time (Figure S3). It is shown that alkyne can only be converted to mono-deuterated product 58 under the standard conditions.

	OH B OH	$\xrightarrow{\text{tions}}_{2(h)} \xrightarrow{H \to D}_{58}$	+
entry	Time/h	58 /yield%	59 /yield%
1	0	0	100
2	0.25	3	78
3	0.5	10	65
4	0.75	23	58
5	1	34	47
6	1.25	47	36
7	1.5	55	28

For experimental details, see the general procedure B. All yields were determined by gas chromatography using biphenyl as an internal standard.

68

68

2.0

2.5

0

0



Figure S3 Time-course reactions under the standard condition.

5. General procedure and characterization of products

5.1 General procedure



Arylpropiolic acid (0.3 mmol, 1.0 equiv), arylboronic acid (0.45 mmol, 1.5 equiv), $Pd(OAc)_2$ (1.35mg, 0.006 mmmol, 0.02 equiv), PPh_3 (4mg, 0.015 mmol, 0.05 equiv) and potassium acetate (60mg, 0.6 mmol, 2.0 equiv) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube kept in vacuum then flushed with argon. This procedure was repeated for 3-4 times. The solvent (toluene = 3.0 mL, $H_2O = 0.3$ mL) was added under argon atmosphere. The reaction mixture was stirred at 80 °C for 10 h (oil bath). Then the reaction mixture was cooled to room temperature, then extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, then concentrated under vacuo. The residue was purified by column chromatography on silica gel to afford the desired product (petroleum ether/ethyl acetate).

procedure B: Preparation of deuterium-labeled alkenes



Arylpropiolic acid (0.3 mmol, 1.0 equiv), arylboronic acid (0.45 mmol, 1.5 equiv), $Pd(OAc)_2$ (1.35mg, 0.006 mmmol, 0.02 equiv), PPh_3 (4mg, 0.015 mmol, 0.05 equiv) and potassium acetate (60mg, 0.6 mmol, 2.0 equiv) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube kept in vacuum then flushed with argon. This procedure was repeated for 3-4 times. Toluene (dried with calcium hydride, distilled, and stored under N₂ atmosphere, 3.0 mL) and D₂O (0.3 mL) was added under argon atmosphere. The reaction mixture was stirred at 80°C for 10 h (oil bath). The reaction mixture was cooled to room temperature, then extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, then concentrated under vacuo. The residue was purified by column chromatography on silica gel to afford the desired deuterated product (petroleum ether/ethyl acetate).

5.2 Characterization data for all products

1-Methyl-4-(1-phenylvinyl)benzene (3)

Following the general procedure A, the product **3** was obtained in 80% yield as a colorless oil after column chromatography (eluent = petroleum ether, 47 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.29 (m, 5H), 7.23 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.43 (s, 1H), 5.40 (s, 1H), 2.36 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.0, 141.8, 138.7, 137.6, 129.0, 128.4, 128.3, 128.2, 127.7, 113.7, 21.3. All data were consistent with that presented in the

1-Methyl-2-(1-phenylvinyl)benzene (4)

Following the general procedure A, the product **4** was obtained in 67% yield as a colorless oil after column chromatography (eluent = petroleum ether, 39 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.24 (m, 5H), 7.24 – 7.20 (m, 3H), 7.18 (d, *J* = 7.0 Hz, 1H), 5.76 (s, 1H), 5.19 (s, 1H), 2.05 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.6, 141.7, 140.7, 136.2, 130.2, 130.1, 128.4, 127.7, 127.6, 126.6, 125.8, 114.9, 20.2. All data were consistent with that presented in the literature^[8].

1-Methyl-3-(1-phenylvinyl)benzene (5)



literature^[7].

Following the general procedure A, the product **5** was obtained in 78% yield as a colorless oil after column chromatography (eluent = petroleum ether, 45 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.24 (m, 5H), 7.23 – 7.16 (m, 1H), 7.15 – 7.07 (m, 3H), 5.41 (s, 2H), 2.31

(s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 150.2, 141.7, 141.5, 137.8, 129.0, 128.5, 128.3, 128.2, 128.1, 127.7, 125.5, 114.2, 21.5. All data were consistent with that presented in the literature^[9].

1-(Tert-butyl)-4-(1-phenylvinyl)benzene (6)



Following the general procedure A, the product **6** was obtained in 75% yield as a colorless oil after column chromatography (eluent = petroleum ether, 53 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 7H), 7.29 – 7.26 (m, 2H), 5.45 (s, 1H), 5.40 (s, 1H), 1.33 (s, 9H). ¹³C{¹H} NMR (101

MHz, CDCl₃) δ 150.8, 149.9, 141.8, 138.5, 128.5, 128.2, 128.0, 127.7, 125.2, 113.8, 34.7, 31.5. All data were consistent with that presented in the literature^[8].

1-Methoxy-3-(1-phenylvinyl)benzene (7)



Following the general procedure A, the product 7 was obtained in 67% yield as a colorless oil after column chromatography (eluent = petroleum ether: ethyl acetate = 50:1, 42 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.19 (m, 5H),

7.18 - 7.12 (m, 1H), 6.92 - 6.66 (m, 3H), 5.36 (s, 2H), 3.68 (s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 159.5, 150.0, 143.1, 141.4, 129.2, 128.3, 128.2, 127.8, 121.0, 114.5, 114.0, 113.3, 55.3. All data were consistent with that presented in the literature^[10].

1,2-Dimethoxy-4-(1-phenylvinyl)benzene (8)



Following the general procedure A, the product **8** was obtained in 75% yield as a colorless oil after column chromatography (eluent = petroleum ether : ethyl acetate = 50:1, 54 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.31 (m, 5H), 6.92 – 6.90 (m, 2H), 6.85 – 6.83 (m,

1H), 5.43 (s, 1H), 5.40 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.8, 148.9, 148.6, 141.6, 134.4, 128.3, 128.1, 127.7, 121.0, 113.2, 111.5, 110.8, 55.9, 55.9. All data were consistent with that presented in the literature^[11].

4-(1-Phenylvinyl)-1,1'-biphenyl (9)



Following the general procedure A, the product **9** was obtained in 83% yield as a white solid after column chromatography (eluent = petroleum ether, 64 mg). ¹H NMR (400 MHz, CDCl₃) 7.58 - 7.48 (m, 4H), 7.41 - 7.25 (m, 10H), 5.46 (s, 1H), 5.41 (s, 1H); ${}^{13}C{}^{1}H$ NMR

 $(101 \text{ MHz}, \text{CDCl}_3) \delta 149.7, 141.6, 140.8, 140.6, 140.5, 128.9, 128.7, 128.4, 128.3, 127.9, 127.4, 127.1, 127.0, 114.4$. All data were consistent with that presented in the literature^[12].

2-(1-Phenylvinyl)naphthalene (10)



Following the general procedure A, the product **10** was obtained in 80% yield as a white solid after column chromatography (eluent = petroleum ether, 55 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.80 (m, 4H), 7.54 – 7.47 (m, 3H), 7.45 – 7.37 (m, 5H), 5.63 (s,

1H), 5.59 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.1, 141.6, 139.0, 133.4, 133.0, 128.5, 128.3, 128.3, 127.9, 127.8, 127.7, 127.4, 126.5, 126.2, 126.1, 114.9. All data were consistent with that presented in the literature^[13].

1-(1-Phenylvinyl)-4-vinylbenzene (11)



Following the general procedure A, the product **11** was obtained in 78% yield as a colorless oil after column chromatography (eluent = petroleum ether, 48 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.46 - 7.30 (m, 9H), 6.82 - 6.71 (m, 1H), 5.80 (d, *J* = 17.6 Hz,

1H), 5.51 (s, 1H), 5.48 (s, 1H), 5.29 (d, J = 10.9 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.8, 141.5, 141.0, 137.1, 136.5, 128.5, 128.4, 128.3, 127.8, 126.1, 114.3, 114.0. All data were consistent with that presented in the literature^[14].

M(4-(1-phenylvinyl)phenyl)sulfane (12)



Following the general procedure A, the product **12** was obtained in 76% yield as a colorless oil after column chromatography (eluent = petroleum ether, 52 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.29 (m, 5H), 7.27 – 7.23 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.43 (s,

1H), 5.40 (s, 1H), 2.48 (s, 3H); ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.6, 141.5, 138.4, 138.1, 128.8, 128.4, 128.3, 127.9, 126.3, 114.0, 15.9. All data were consistent with that presented in the literature^[15].

Methyl(2-(1-phenylvinyl)phenyl)sulfane (13)



Following the general procedure A, the product **13** was obtained in 81% yield as a colorless oil after column chromatography (eluent = petroleum ether, 55 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.23 (m, 6H), 7.22 – 7.14 (m, 3H), 5.82 (s, 1H), 5.27 (s, 1H), 2.30 (s, 3H). ¹³C{¹H} NMR (101

MHz, CDCl₃) δ 148.1, 140.7, 139.9, 137.7, 130.3, 128.3, 128.2, 127.7, 126.6, 125.2, 124.6, 116.2, 15.9. All data were consistent with that presented in the literature^[16].

T(4-(1-phenylvinyl)phenyl)silane (14)



Following the general procedure A, the product **14** was obtained in 76% yield as a colorless oil after column chromatography (eluent = petroleum ether, 58 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 7H), 5.50 (s, 1H), 5.49 (s, 1H), 0.31 (s,

9H); ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 150.2, 141.9, 141.6, 140.0, 133.3, 128.4, 128.3, 127.8, 127.6, 114.5, -1.0. HRMS-ESI m/z Calculated for $C_{17}H_{21}Si^+[(M+H^+)]$ 253.1408, Found 253.1405.

1-(1-Phenylvinyl)-4-(trifluoromethoxy)benzene (15)



Following the general procedure A, the product **15** was obtained in 43% yield as a colorless oil after column chromatography (eluent = petroleum ether, 34 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.30 (m, 7H), 7.19 (d, *J* = 8.3 Hz, 2H), 5.50 (s, 1H), 5.46 (s, 1H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.9, 141.1, 140.3, 129.7, 128.4, 128.3, 128.1, 120.7, 120.6 (q, J = 257.1 Hz), 115.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.7. HRMS-ESI m/z Calculated for C₁₅H₁₂F₃O⁺[(M+H⁺)] 265.0835, Found 265.0830.

1-(1-Penylvinyl)-4-(trifluoromethyl)benzene (16)



Following the general procedure A, the product **16** was obtained in 49% yield as a colorless oil after column chromatography (eluent = petroleum ether, 36 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.29 (m,

5H), 5.57 (s, 1H), 5.52 (s, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.1, 145.2, 140.7, 129.9 (q, J = 32.4 Hz), 128.7, 128.5, 128.3, 128.2, 125.3 (q, J = 3.8 Hz), 124.3 (q, J = 271.9 Hz), 116.0. ¹⁹F NMR (565 MHz, CDCl₃) δ -62.4. All data were consistent with that presented in the literature^[8].

1-Fluoro-4-(1-phenylvinyl)benzene (17)



Following the general procedure A, the product **17** was obtained in 75% yield as a colorless oil after column chromatography (eluent = petroleum ether, 45 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.24 (m, 7H), 7.01 – 6.94 (m, 2H), 5.39 (s, 1H), 5.37 (s, 1H). ¹³C{¹H} NMR

(101 MHz, CDCl₃) 162.6 (d, J = 246.7 Hz), 149.2, 141.4, 137.7 (d, J = 3.3 Hz), 130.0 (d, J = 8.2 Hz), 128.3, 128.3, 128.0, 115.1 (d, J = 21.3 Hz), 114.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.6. All data were consistent with that presented in the literature^[13].

2,4-Difluoro-1-(1-phenylvinyl)benzene (18)



Following the general procedure A, the product **18** was obtained in 70% yield as a colorless oil after column chromatography (eluent = petroleum ether, 45 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.25 (m, 6H), 6.97 – 6.83 (m, 2H), 5.78 (s, 1H), 5.44 (s, 1H). ¹³C{¹H} NMR (101

MHz, CDCl₃) δ 163.9 (d, J = 11.7 Hz), 161.9 – 160.8 (m), 159.1 (d, J = 11.9 Hz), 143.5, 140.5, 132.52 – 131.82 (m), 128.4, 128.0, 126.9, 117.3, 111.38 – 110.91 (m), 104.8 – 103.4 (m). ¹⁹F NMR (565 MHz, CDCl₃) δ -108.7, -110.8. All data were consistent with that presented in the literature^[17].

1-Chloro-2-(1-phenylvinyl)benzene (19)



Following the general procedure A, the product **19** was obtained in 50% yield as a colorless oil after column chromatography (eluent = petroleum ether, 32 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 1H), 7.39 – 7.26 (m, 8H), 5.87 (s, 1H), 5.32 (s, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃)

 δ 147.5, 140.7, 139.8, 133.4, 131.6, 129.8, 128.9, 128.4, 127.8, 126.7, 126.5, 116.3. All data were consistent with that presented in the literature^[18].

1-Chloro-3-(1-phenylvinyl)benzene (20)



Following the general procedure A, the product **20** was obtained in 69% yield as a colorless oil after column chromatography (eluent = petroleum ether, 44 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.28 (m, 6H), 7.28 – 7.17 (m, 3H), 5.48 (s, 1H), 5.45 (s, 1H).

 ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.0, 143.5, 140.9, 134.2, 129.5, 128.4, 128.3, 128.1, 127.9, 126.6, 115.4. All data were consistent with that presented in the literature^[13].

2,4-Dichloro-1-(1-phenylvinyl)benzene (21)



Following the general procedure A, the product **21** was obtained in 67% yield as a colorless oil after column chromatography (eluent = petroleum ether, 50 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 1.8 Hz, 1H), 7.34 – 7.22 (m, 7H), 5.83 (s, 1H), 5.27 (s, 1H). ¹³C{¹H} NMR

 $(101 \text{ MHz}, \text{CDCl}_3) \delta 146.6, 139.5, 139.3, 134.2, 134.1, 132.4, 129.7, 128.5, 128.0, 127.1, 126.5, 116.8.$ All data were consistent with that presented in the literature^[19].

1-Bromo-4-(1-phenylvinyl)benzene (22)



Following the general procedure A, the product **22** was obtained in 71% yield as a colorless oil after column chromatography (eluent = petroleum ether, 55 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.46 (m, 2H), 7.38 – 7.32 (m, 5H), 7.25 – 7.21 (m, 2H), 5.49 (s, 1H), 5.47

(s, 1H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.1, 141.0, 140.5, 131.4, 130.0, 128.4, 128.3, 128.0, 121.9, 114.8. All data were consistent with that presented in the literature^[13].

1-Nitro-3-(1-phenylvinyl)benzene (23)

NO₂

Following the general procedure A, the product 23 was

obtained in 63% yield as an yellow solid after column chromatography (eluent = petroleum ether: ethyl acetate = 20:1, 43 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.25 – 8.15 (m, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.41 – 7.34 (m, 3H), 7.33 – 7.28 (m, 2H), 5.61 (s, 1H), 5.57 (s, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.5, 148.2, 143.4, 140.2, 134.3, 129.2, 128.6, 128.5, 128.2, 123.1, 122.7, 116.6. All data were consistent with that presented in the literature^[20].

Buta-1,3-diene-2,3-diyldibenzene (24)



Following the general procedure A, the product **24** was obtained in 82% yield as a white solid after column chromatography (eluent = petroleum ether, 51 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.42 – 7.38 (m, 4H), 7.29 – 7.22 (m, 6H), 5.55 (d, *J* = 1.6 Hz, 2H), 5.32 (d, *J* = 1.6 Hz, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.8, 140.1, 128.2, 127.5,

127.5, 116.4. All data were consistent with that presented in the literature^[21].

1-Methyl-3-(1-(4-(trifluoromethoxy)phenyl)vinyl)benzene (27)



Following the general procedure A, the product **27** was obtained in 60% yield as a colorless oil after column chromatography (eluent = petroleum ether, 50 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.34 (m, 2H), 7.27 – 7.23 (m,

1H), 7.22 – 7.10 (m, 5H), 5.48 (s, 1H), 5.45 (s, 1H), 2.37 (s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.0, 148.9, 141.1, 140.4, 138.0, 129.7, 129.0, 128.8, 128.3, 125.5, 120.7, 120.6 (q, *J* = 255.4 Hz), 114.9, 21.5. {}^{19}F NMR (565 MHz, CDCl₃) δ -57.7. HRMS-ESI m/z Calculated for C₁₆H₁₄F₃O⁺ [(M+H⁺)] 279.0991, Found 279.0986.

2-(1-(M-tolyl)vinyl)naphthalene (28)



Following the general procedure A, the product **28** was obtained in 74% yield as a white solid after column chromatography (eluent = petroleum ether, 54 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.75 (m, 4H), 7.51 – 7.41 (m, 3H), 7.27 – 7.13 (m, 4H), 5.56 (s, 1H), 5.53 (s, 1H), 2.34 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.2,

141.6, 139.1, 137.9, 133.4, 133.0, 129.2, 128.7, 128.3, 128.2, 127.7, 127.7, 127.3, 126.5, 126.2, 126.1, 125.6, 114.8, 21.5. HRMS-ESI m/z Calculated for $C_{19}H_{17}^+$ [(M+H⁺)] 245.1325, Found 245.1324.

1-Methoxy-4-(1-(p-tolyl)vinyl)benzene (29)



Following the general procedure A, the product **29** was obtained in 75% yield as a colorless oil after column chromatography (eluent = petroleum ether: ethyl acetate = 50:1, 50 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.25 (m,

2H), 7.24 – 7.21 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.87 – 6.83 (m, 2H), 5.33 (s, 1H), 5.32 (s, 1H), 3.80 (s, 3H), 2.35 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.4, 149.5, 139.0, 137.5, 134.3, 129.5, 128.9, 128.3, 113.6, 112.4, 55.4, 21.3. All data were consistent with that presented in the literature^[22].

Trimethyl(4-(1-(p-tolyl)vinyl)phenyl)silane (30)



Following the general procedure A, the product **30** was obtained in 85% yield as a colorless oil after column chromatography (eluent = petroleum ether, 68 mg). ¹H $Si(CH_3)_3$ NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.2 Hz, 2H), 7.33

(d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.44 (s, 1H), 5.43 (s, 1H), 2.37 (s, 3H), 0.29 (s, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.0, 142.1, 139.9, 138.7, 137.6, 133.3, 129.0, 128.3, 127.7, 113.9, 21.3, -1.0. HRMS-ESI m/z Calculated for C₁₈H₂₃Si⁺ [(M+H⁺)] 267.1564, Found 267.1566.

1-Chloro-4-(1-(4-methoxyphenyl)vinyl)benzene (31)



Following the general procedure A, the product **31** was obtained in 64% yield as a colorless oil after column chromatography (eluent = petroleum ether: ethyl acetate = 50:1, 47 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m,

6H), 6.90 – 6.84 (m, 2H), 5.40 (s, 1H), 5.34 (s, 1H), 3.83 (s, 3H). ${}^{13}C{}^{1H}$ NMR (101 MHz, CDCl₃) δ 159.6, 148.5, 140.4, 133.6, 133.6, 129.7, 129.4, 128.4, 113.7, 113.4, 55.4. All data were consistent with that presented in the literature^[23].

3-(1-([1,1'-Biphenyl]-4-yl)vinyl)thiophene (32)



Following the general procedure A, the product **32** was obtained in 42% yield as a white solid after column chromatography (eluent = petroleum ether, 33 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.60 (m, 4H), 7.52 – 7.46 (m, 4H), 7.42 – 7.32 (m, 2H), 7.27 – 7.20 (m, H). ¹³C (¹H) NMR (101 MHz, CDCl₃) δ 144 3, 142 5, 140 8, 140 7

2H), 5.58 (s, 1H), 5.43 (s, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.3, 142.5, 140.8, 140.7, 140.5, 128.9, 128.6, 127.4, 127.4, 127.1, 127.0, 125.6, 123.4, 113.6. All data were consistent with that presented in the literature^[24].

4-(1-(2-Fluorophenyl)vinyl)-1,1'-biphenyl (33)



Following the general procedure A, the product **33** was obtained in 55% yield as a white solid after column chromatography (eluent = petroleum ether, 45 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.57 (m, 4H), 7.51 – 7.42 (m, 4H), 7.42 – 7.31 (m, 3H), 7.23 – 7.10 (m, 2H), 5.86 (s, 1H), 5.49 (s, 1H). ¹³C{¹H} NMR (101 MHz,

CDCl₃) δ 160.2 (d, J = 248.4 Hz), 143.8, 140.7 (d, J = 6.3 Hz), 139.5, 131.6 (d, J = 3.6 Hz), 129.5 (d, J = 8.1 Hz), 129.3 (d, J = 14.3 Hz), 128.9, 127.4, 127.3, 127.1, 127.0, 124.1 (d, J = 3.6 Hz), 117.1, 116.0, 115.8. ¹⁹F NMR (565 MHz, CDCl₃) δ -113.0. HRMS-ESI m/z Calculated for C₂₀H₁₆F⁺[(M+H⁺)] 275.1231, Found 275.1235.

5-(1-([1,1'-Biphenyl]-4-yl)vinyl)benzo[d][1,3]dioxole (34)



Following the general procedure A, the product **34** was obtained in 58% yield as a white solid after column chromatography (petroleum ether: ethyl acetate = 50:1, 52 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.58 (m, 4H), 7.48

-7.42 (m, 4H), 7.40 - 7.35 (m, 1H), 6.90 - 6.87 (m, 2H), 6.83 - 6.80 (m, 1H), 6.00 - 5.98 (m, 2H), 5.44 (s, 1H), 5.42 (s, 1H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.3, 147.6, 147.4, 140.8, 140.7, 140.6, 135.8, 128.9, 128.8, 127.4, 127.1, 127.0, 122.2, 113.5, 108.8, 108.1, 101.2. All data were consistent with that presented in the literature^[25].

4,4'-(Ethene-1,1-diyl)bis(fluorobenzene) (35)



Following the general procedure A, the product **35** was obtained in 74% yield as a colorless oil after column chromatography (eluent = petroleum ether, 48 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 4H), 7.11 – 6.98 (m, 4H),

5.40 (s, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.7 (d, J = 247.1 Hz), 148.2, 137.5 (d, J = 3.3 Hz), 129.9 (d, J = 8.0 Hz), 115.2 (d, J = 21.4 Hz), 114.2. ¹⁹F NMR (565 MHz, CDCl₃) δ -114.3. All data were consistent with that presented in the literature^[13].

1-Fluoro-4-(1-(4-vinylphenyl)vinyl)benzene (36)



Following the general procedure A, the product **36** was obtained in 77% yield as a colorless oil after column chromatography (eluent = petroleum ether, 52 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.37 (m, 2H), 7.36 – 7.25 (m, 4H),

7.13 – 6.96 (m, 2H), 6.83 – 6.69 (m, 1H), 5.79 (d, J = 18.4 Hz, 1H), 5.45 (d, J = 23.3 Hz, 2H), 5.29 (d, J = 10.9 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.6 (d, J = 246.7 Hz), 148.8, 140.8, 137.6 (d, J = 3.3 Hz), 137.3, 136.5, 130.0 (d, J = 7.9 Hz), 128.4, 126.2, 115.1 (d, J = 21.4 Hz), 114.2, 114.2. ¹⁹F NMR (565 MHz, CDCl₃) δ -114.5. HRMS-ESI m/z Calculated for C₁₆H₁₄F⁺ [(M+H⁺)] 225.1075, Found 225.1072.

1-Methyl-2-(1-(4-(trifluoromethyl)phenyl)vinyl)benzene (37)



Following the general procedure A, the product **37** was obtained in 58% yield as a colorless oil after column chromatography (eluent = petroleum ether, 46 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.20 (m, 4H), 5.86 (s,

1H), 5.34 (s, 1H), 2.05 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.5, 144.2, 140.8, 136.1, 130.4, 130.1, 129.8, 129.6 (q, *J* = 32.5 Hz), 126.8, 126.0, 125.4 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 117.1, 20.2. ¹⁹F NMR (565 MHz, CDCl₃) δ -62.4. HRMS-ESI m/z Calculated for C₁₆H₁₄F₃⁺ [(M+H⁺)] 263.1043, Found 263.1044.

1-(4-(1-(4-Chlorophenyl)vinyl)phenyl)ethan-1-one (38)



Following the general procedure A, the product **38** was obtained in 68% yield as a white solid after column chromatography (eluent = petroleum ether: ethyl acetate = 20:1, 52 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.91 (m, 2H), 7.42 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 5.55 (s, 1H), 5.54 (s, 1H), 2.61 (s, 3H).

 $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl₃) δ 197.7, 148.2, 145.7, 139.2, 136.5, 134.0, 129.5, 128.6, 128.5, 128.4, 116.5, 26.7. HRMS-ESI m/z Calculated for $C_{16}H_{14}ClO^{+}$ [(M+H^+)] 257.0728, Found 257.0727.

Methyl 4-(1-(naphthalen-1-yl)vinyl)benzoate (39)



Following the general procedure A, the product **39** was obtained in 62% yield as a white solid after column chromatography (eluent = petroleum ether: ethyl acetate = 20:1, 53 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (m, 4H), 7.70 (d, J = 8.5 Hz, 1H), 7.58 – 7.30 (m, 6H),

6.09 (s, 1H), 5.54 (s, 1H), 3.91 (s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 166.9, 147.6, 145.5, 139.1, 133.7, 131.7, 129.8, 129.2, 128.4, 128.4, 127.4, 126.6, 126.2, 126.1, 125.9, 125.5, 118.4, 52.2. HRMS-ESI m/z Calculated for C₂₀H₁₇O₂+ [(M+H⁺)] 289.1224, Found 289.1220.

4-(1-(4-Nitrophenyl)vinyl)-1,1'-biphenyl (40)



Following the general procedure A, the product **40** was obtained in 58% yield as a white solid after column chromatography (eluent = petroleum ether: ethyl acetate = 50:1, 52 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.27 – 8.18 (m,

2H), 7.65 – 7.59 (m, 4H), 7.57 – 7.52 (m, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.34 (m, 3H), 5.70 (s, 1H), 5.61 (s, 1H). ${}^{13}C{}^{1}H{}$ NMR (101 MHz, CDCl₃) δ 148.1, 148.1, 147.5, 141.3, 140.5, 139.1, 129.2, 129.0, 128.6, 127.7, 127.3, 127.1, 123.7, 117.2. All data were consistent with that presented in the literature^[24].

4-(Oct-1-en-2-yl)-1,1'-biphenyl (41)



Following the general procedure A, the product **41** was obtained in 83% yield as a white solid after column chromatography (eluent = petroleum ether, 66 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.61 (m, 4H), 7.56 – 7.47 (m, 4H),

 $\begin{array}{l} 7.41-7.37\ (m,\ 1H),\ 5.39\ (s,\ 1H),\ 5.14\ (s,\ 1H),\ 2.73-2.44\ (m,\ 2H),\ 1.58-1.52\ (m,\ 2H),\ 1.42-1.31\ (m,\ 6H),\ 0.97-0.91\ (m,\ 3H).\ ^{13}C\{^{1}H\}\ NMR\ (101\ MHz,\ CDCl_3)\ \delta\ 148.3,\ 140.9,\ 140.4,\ 140.1,\ 128.8,\ 127.3,\ 127.0,\ 127.0,\ 126.5,\ 112.1,\ 35.4,\ 31.8,\ 29.1,\ 28.4,\ 22.7,\ 14.2.\ HRMS-ESI\ m/z\ Calculated\ for\ C_{20}H_{25}^{+}[(M+H^+)]\ 265.1951,\ Found\ 265.1950.\end{array}$

4-(1-Cyclopropylvinyl)-1,1'-biphenyl (42)



Following the general procedure A, the product **42** was obtained in 54% yield as a white solid after column chromatography (eluent = petroleum ether, 36 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.58 (m, 4H), 7.50 – 7.42 (m, 2H), 7.40 – 7.32 (m, 1H),

5.37 (s, 1H), 4.99 (s, 1H), 1.80 – 1.63 (m, 1H), 0.95 – 0.82 (m, 2H), 0.71 – 0.57 (m, 2H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 148.9, 140.9, 140.6, 140.4, 128.9, 127.3, 127.1, 127.0, 126.6, 109.2, 15.7, 6.8. All data were consistent with that presented in the literature^[26].

1-Methyl-4-(1-phenylvinyl-2,2-*d*₂)benzene (43)



Following the general procedure B, the product **43** was obtained in 77% yield (91% D) as a colorless oil after column chromatography (eluent = petroleum ether, 45 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.23 (m, 5H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 5.37 (s, 0.09H),

5.34 (s, 0.03H), 2.32 (s, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 149.9, 141.8, 138.7, 137.6, 129.0, 128.4, 128.2, 128.2, 127.7, 21.3. HRMS-ESI m/z Calculated for $C_{15}H_{13}D_{2}^{+}$ [(M+H⁺)] 197.1294, Found 197.1289.

1-Chloro-4-(1-(4-fluorophenyl)vinyl-2,2-d₂)benzene (44)

Following the general procedure B, the product **44** was obtained in 63% yield (94% D) as a colorless oil after column chromatography (eluent = petroleum ether, 44 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.51 – 7.38 (m, 2H), 7.33 – 7.27 (m, 4H), 7.05 – 7.00 (m, 2H), 5.41 (s, 0.10H), 5.30 (s, 0.02H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 162.6 (d, *J* = 247.3 Hz), 147.8, 133.7, 129.8 (d, *J* = 8.0 Hz), 129.5, 129.0, 128.4, 128.2, 115.2 (d, *J* = 21.4 Hz). ¹⁹F NMR (564 MHz, CDCl₃) δ -114.3. HRMS-ESI m/z Calculated for C₁₄H₉D₂ClF⁺[(M+H⁺)] 235.0654, Found 235.0650.

1-(1-(4-Fluorophenyl)vinyl-2,2-*d*₂)naphthalene (45)

Following the general procedure B, the product **45** was obtained in 64% yield (83% D) as a white solid after column chromatography (eluent = petroleum ether, 48 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.91 – 7.84 (m, 2H), 7.37 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 7.01 – 6.90 (m, 2H), 5.91 (s, 0.08H), 5.37 (s, 0.17H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 162.4 (d, *J* = 247.1 Hz), 147.1, 139.5, 137.2 (d, *J* = 3.7 Hz), 133.7, 131.7, 128.3, 128.2, 128.1, 127.2, 126.3, 125.9, 125.7, 125.4, 115.2 (d, *J* = 21.5 Hz). ¹⁹F NMR (564 MHz, CDCl₃) δ -114.7. HRMS-ESI m/z Calculated for C₁₈H₁₂D₂F⁺ [(M+H⁺)] 251.1200, Found 251.1196.

1-Methyl-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d₂)benzene (46)



Following the general procedure B, the product **46** was obtained in 68% yield (93% D) as a colorless oil after column chromatography (eluent = petroleum ether, 54 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.13 (m, 4H), 5.53

(s, 0.07H), 5.45 (s, 0.03H), 2.39 (s, 3H).¹³C {¹H} NMR (151 MHz, CDCl₃) δ 148.7, 145.3, 138.0, 137.7, 129.7 (q, J = 32.4 Hz), 129.1, 128.6, 128.0, 125.1 (q, J = 3.8 Hz), 124.2 (q, J = 271.8 Hz), 21.2. ¹⁹F NMR (564 MHz, CDCl₃) δ -62.5. HRMS-ESI m/z Calculated for C₁₆H₁₂D₂F₃⁺ [(M+H⁺)] 265.1168, Found 265.1167.

1-(Tert-butyl)-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d₂)benzene (47)



Following the general procedure B, the product **47** was obtained in 60% yield (91% D) as a colorless oil after column chromatography (eluent = petroleum ether, 55 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1

Hz, 2H), 7.30 – 7.24 (m, 2H), 7.18 – 7.12 (m, 2H), 5.44 (s, 0.09H), 5.35 (s, 0.03H), 1.25 (s, 9H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 151.3, 148.7, 145.4, 137.7, 129.8 (q, *J* = 32.3 Hz), 128.7, 127.9, 125.4, 125.2 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.7 Hz), 34.7, 31.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3. HRMS-ESI m/z Calculated for C₁₉H₁₈D₂F₃⁺ [(M+H⁺)] 307.1638, Found 307.1630.

1-(4-(1-(3-Methoxyphenyl)vinyl-2,2-d₂)phenyl)ethan-1-one (48)



Following the general procedure B, the product **48** was obtained in 58% yield (86% D) as a white solid after column chromatography (eluent = petroleum ether: ethyl acetate = 15:1, 44 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.94 – 7.91 (m, 2H), 7.46 – 7.40 (m, 2H), 7.28 – 7.25 (m, 1H), 6.91 – 6.87 (m, 2H), 6.86 – 6.82 (m, 1H), 5.55 (s,

0.14H), 5.53 (s, 0.04H), 3.79 (s, 3H), 2.61 (s, 3H). ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃) δ 197.7, 159.5, 148.9, 146.0, 142.1, 136.3, 129.3, 128.4, 128.3, 120.7, 113.9, 113.4, 55.2, 26.6. HRMS-ESI m/z Calculated for C₁₇H₁₅D₂O₂⁺ [(M+H⁺)] 255.1349, Found 255.1344.

1-Methoxy-3-(oct-1-en-2-yl-1,1-*d*₂)benzene (49)



Following the general procedure B, the product **49** was obtained in 62% yield (85% D) as a colorless oil after column chromatography (eluent = petroleum ether, 41 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.28 – 7.22 (m, 1H), 7.04 – 6.99 (m, 1H),

 $6.98 - 6.93 \text{ (m, 1H)}, \ 6.86 - 6.79 \text{ (m, 1H)}, \ 5.26 \text{ (s, 0.15H)}, \ 5.04 \text{ (s, 0.07H)}, \ 3.83 \text{ (s, 3H)}, \ 2.50 - 2.46 \text{ (m, 2H)}, \ 1.48 - 1.43 \text{ (m, 2H)}, \ 1.35 - 1.26 \text{ (m, 6H)}, \ 0.91 - 0.85 \text{ (m, 3H)}. \ ^{13}\text{C}\{^{1}\text{H}\} \text{ NMR (151 MHz, CDCl}_{3}) \ \delta \ 159.5, \ 148.5, \ 143.1, \ 129.1, \ 118.7, \ 112.4, \ 112.1, \ 55.2, \ 35.3, \ 31.7, \ 29.0, \ 28.2, \ 22.6, \ 14.1. \ HRMS-ESI m/z \ Calculated for \ C_{15}H_{21}D_2O^+[(M+H^+)] \ 221.1869, \ Found \ 221.1875.$

2,4-Dichloro-1-(oct-1-en-2-yl-1,1-*d*₂)benzene (50)



Following the general procedure B, the product **50** was obtained in 71% yield (85% D) as a colorless oil after column chromatography (eluent = petroleum ether, 55 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.35 (m, 1H), 7.21 – 7.18 (m, 1H), 7.09 (d,

 $J = 8.2 \text{ Hz}, 1\text{H}, 5.22 \text{ (s, 0.09H)}, 4.95 \text{ (s, 0.15H)}, 2.42 - 2.39 \text{ (m, 2H)}, 1.35 - 1.25 \text{ (m, 8H)}, 0.89 - 0.86 \text{ (m, 3H)}. {}^{13}\text{C} \{^{1}\text{H}\} \text{ NMR (151 MHz, CDCl}_{3}) \delta 147.6, 140.6, 133.1, 132.9, 131.1, 129.3, 126.7, 36.5, 31.7, 28.9, 27.7, 22.6, 14.1. HRMS-ESI m/z Calculated for C_{14}H_{17}D_{2}Cl_{2}^{+} [(M+H^{+})] 259.0984$, Found 259.0980.

(4-(1-Cyclopropylvinyl-2,2-d₂)phenyl)trimethylsilane (51)



Following the general procedure B, the product **51** was obtained in 63% yield (90% D) as a colorless oil after column chromatography (eluent = petroleum ether, 41 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 5.30 (s, 0.22H), 5.30 (s, 0.09H), 1.69 – 1.63 (m,

1H), 0.86 – 0.82 (m, 2H), 0.63 – 0.57 (m, 2H), 0.28 (s, 9H). ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃) δ 149.1, 142.0, 139.5, 133.2, 125.4, 15.4, 6.6, -1.1. HRMS-ESI m/z Calculated for C₁₄H₁₉D₂Si⁺ [(M+H⁺)] 219.1533, Found 219.1529.

4-(Ethynyl-d)-1,1'-biphenyl (53)



To a 15 mL-schlenk tube charged with a stirring bar, was added 3-([1,1'-biphenyl]-4-yl) propiolic acid (67 mg, 0.3 mmol, 1.0 equiv), Pd(OAc)₂ (1.35mg, 0.006 mmmol, 0.02 equiv), PPh₃ (4mg, 0.015 mmol,

0.05 equiv), and KOAc (60 mg, 0.6 mmol, 2.0 equiv). The tube kept in vacuum then flushed with argon. This procedure was repeated for 3-4 times. Then the solvent (toluene = 3 mL, D₂O = 0.3 mL) was added under argon atmosphere. The reaction mixture was stirred at 80°C for 0.5 h (oil bath). The reaction mixture was cooled to room temperature, then extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, then concentrated under vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether) to afford the product **53** (30 mg, 56% yield, 90% D) as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 7.61 – 7.57 (m, 6H), 7.49 – 7.45 (m, 2H), 7.41 – 7.35 (m, 1H), 3.15 (s, 0.10H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 141.6, 140.2, 132.6, 128.9, 127.8, 127.1, 127.0, 121.0, 83.1 (t, *J* = 7.7 Hz), 77.8. All data were consistent with that presented in the literature^[27].

3,3-Diphenylacrylic acid (55)



To an oven-dried Teflon capped vial equipped with a magnetic stirring bar were added sequentially AgOAc (2.59 g, 15.5 mmol) and Pd(OAc)₂ (11.2 mg, 0.05 mmol). The vial kept in vacuum then flushed with argon. This procedure was repeated for 3-4 times. Then AcOH (15 mL), iodobenzene (1.73 mL,

15.5 mmol) and ethyl acrylate (0.54 mL, 5.00 mmol) was added under Ar atmosphere, and the mixture was stirred under an atmosphere of argon at 110 °C for 6 hours. The mixture was cooled to room temperature, diluted with EtOAc (20 mL) and filtered through a pad of Celite. Then the filtrate was concentrated in vacuo, and the crude product ethyl 3,3-diphenylacrylate was purified by flash chromatography on silica column (petroleum ether: ethyl acetate = 15:1, 1.07 g, 85% yield).

To a solution of ethyl 3,3-diphenylacrylate (4.25 mmol) in 25 mL of ethanol was added slowly with stirring an aqueous sodium hydroxide solution (25 mL, 1 N). After 6h, the reaction mixture was diluted with water (50 mL) and was washed with dichloromethane (2 x 25 mL). The aqueous phase was acidified with 20% HCl solution and was extracted with dichloromethane (3 x 50 mL). The combined extracts were dried over MgSO₄ and purified by recrystallization to give 3,3-diphenylacrylic acid (477 mg, 50% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.21 (s, 1H), 7.41 – 7.33 (m, 6H), 7.30 – 7.22 (m, 2H), 7.18 – 7.12 (m, 2H), 6.37 (s, 1H). ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 166.8, 153.7, 140.6, 138.8, 129.2, 129.0, 128.5, 127.9, 118.9. All data were consistent with that presented in the literature^[28].

(Ethynyl-d)benzene (57)



To a 15 mL-schlenk tube charged with a stirring bar, was added phenylpropiolic acid (0.3 mmol, 1.0 equiv, 67 mg), $Pd(OAc)_2$ (1.35mg, 0.006 mmmol, 0.02 equiv), PPh_3 (4mg, 0.015 mmol, 0.05 equiv), and KOAc (60 mg, 0.6 mmol, 2.0 equiv). The tube kept in vacuum then flushed

with argon. This procedure was repeated for 3-4 times. Then the solvent (toluene = 3 mL, $D_2O = 0.3 \text{ mL}$) was added under argon atmosphere. The reaction mixture was stirred at 80°C for 1 h (oil bath). The reaction mixture was cooled to room temperature, then extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, then concentrated under vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether) to afford the product **57** (13 mg, 42% yield, 94% D) as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.53 – 7.49 (m, 2H), 7.37 – 7.31 (m, 3H), 3.09 (s, 0.06H). ¹³C NMR (151 MHz, CDCl₃) δ 132.1, 128.8,

128.3, 122.1, 83.2 (t, J = 7.6 Hz), 76.9 (t, J = 38.6 Hz). All data were consistent with that presented in the literature^[29].

(E)-1-methyl-4-(1-phenylvinyl-2-d)benzene (58)



To a 15 mL-schlenk tube charged with a stirring bar, was added $Pd(OAc)_2$ (1.35 mg, 0.006 mmmol, 0.02 equiv), PPh₃ (4 mg, 0.015 mmol, 0.05 equiv), and KOAc (60 mg, 0.6 mmol, 2.0 equiv). The tube kept in vacuum then flushed with argon. This procedure was repeated

for 3-4 times. Then the solvent (toluene = 3 mL, $D_2O = 0.3$ mL) and phenylacetylene (31mg, 0.3 mmol) was added under argon atmosphere. The reaction mixture was stirred at 80°C for 10 h (oil bath). The reaction mixture was cooled to room temperature, then extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, then concentrated under vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether) to afford the product **58** (40 mg, 68% yield) as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.41 – 7.32 (m, 5H), 7.28 – 7.26 (m, 2H), 7.19 – 7.15 (m, 2H), 5.42 (s, 1H), 2.40 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 149.8, 141.7, 138.6, 137.5, 128.9, 128.3, 128.2, 128.1, 127.7, 113.4 (t, *J* = 24.1 Hz), 21.2. HRMS-ESI m/z Calculated for C₁₅H₁₄D₂⁺[(M+H⁺)] 196.1232, Found 196.1230.

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7. Copies of NMR spectra





1-Methyl-2-(1-phenylvinyl)benzene (4)



)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (f1 (ppm)

1-Methyl-3-(1-phenylvinyl)benzene (5)







1-Methoxy-3-(1-phenylvinyl)benzene (7)





S28







4-(1-Phenylvinyl)-1,1'-biphenyl (9)



)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (f1 (ppm)

S30

2-(1-Phenylvinyl)naphthalene (10)



f1 (ppm)

1-(1-Phenylvinyl)-4-vinylbenzene (11)



)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (f1 (ppm)

Methyl(4-(1-phenylvinyl)phenyl)sulfane (12)








Trimethyl(4-(1-phenylvinyl)phenyl)silane (14)



1-(1-Phenylvinyl)-4-(trifluoromethoxy)benzene (15)



f1 (ppm)





1-Fluoro-4-(1-phenylvinyl)benzene (17)







0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0. fl (ppm)



1-Chloro-2-(1-phenylvinyl)benzene (19)



1-Chloro-3-(1-phenylvinyl)benzene (20)





2,4-Dichloro-1-(1-phenylvinyl)benzene (21)



1-Bromo-4-(1-phenylvinyl)benzene (22)









Buta-1,3-diene-2,3-diyldibenzene (24)









1-Methyl-3-(1-(4-(trifluoromethoxy)phenyl)vinyl)benzene (27)



 1 H NMR (400 MHz, CDCl₃)













- - /











4,4'-(Ethene-1,1-diyl)bis(fluorobenzene) (35)



)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (f1 (ppm)







00 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -1 fl (ppm)































-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -13 fl (ppm)

1-(1-(4-Fluorophenyl)vinyl-2,2-*d*₂)naphthalene (45)



¹H NMR (600 MHz, CDCl₃)



)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)



1-Methyl-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d₂)benzene (46)




-42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 f1 (ppm)







S73













1.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0. f1 (ppm)



3,3-Diphenylacrylic acid (55)



 $^{1}\mathrm{H}\,\mathrm{NMR}\,(400\,\mathrm{MHz},\mathrm{DMSO-}d_{\delta})$











