

Electronic Supplementary Information

Access to CF₃-benzofulvenes via palladium-catalyzed cascade arylation/Trost-Oppolzer cyclization/double-bond isomerization

Rami Sateesh,^{a,b} Jagaraju Prudviraj,^{a,b} Chiliveru Priyanka,^{a,b} Nagender Punna^{a,b,*}

^a Fluoro-Agro chemicals Division, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India; orcid.org/0000-0003-2761-6078.

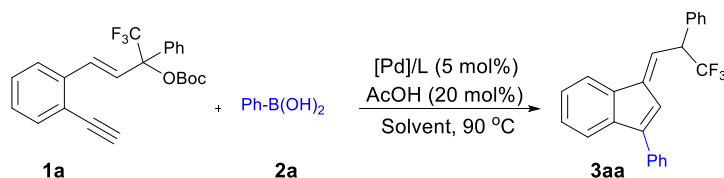
^b Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India.

Email: nagenderpunna@iict.res.in

Table of Contents

1. Table S1 Optimization of the Reaction Conditions.....	S2
2. 2D-NMR analysis of compound 3la	S2
3. Representative examples of bioactive benzofulvenes.....	S3
4. General information	S4
5. Experimental procedures and characterization data of starting materials (S2a-S2t & 1a-1t).....	S5
6. Experimental procedures and characterization data of products (3aa-3oa, 4a-4c & 5)	S29
7. Gram scale reaction.....	S43
8. Synthetic utility of compound 3aa (8,9 &10)	S44
9. Experimental procedure and characterization data of intermediate 7	S46
10. References.....	S48
11. ¹ H NMR, ¹³ C NMR and ¹⁹ F NMR spectral copies of compound.....	S50

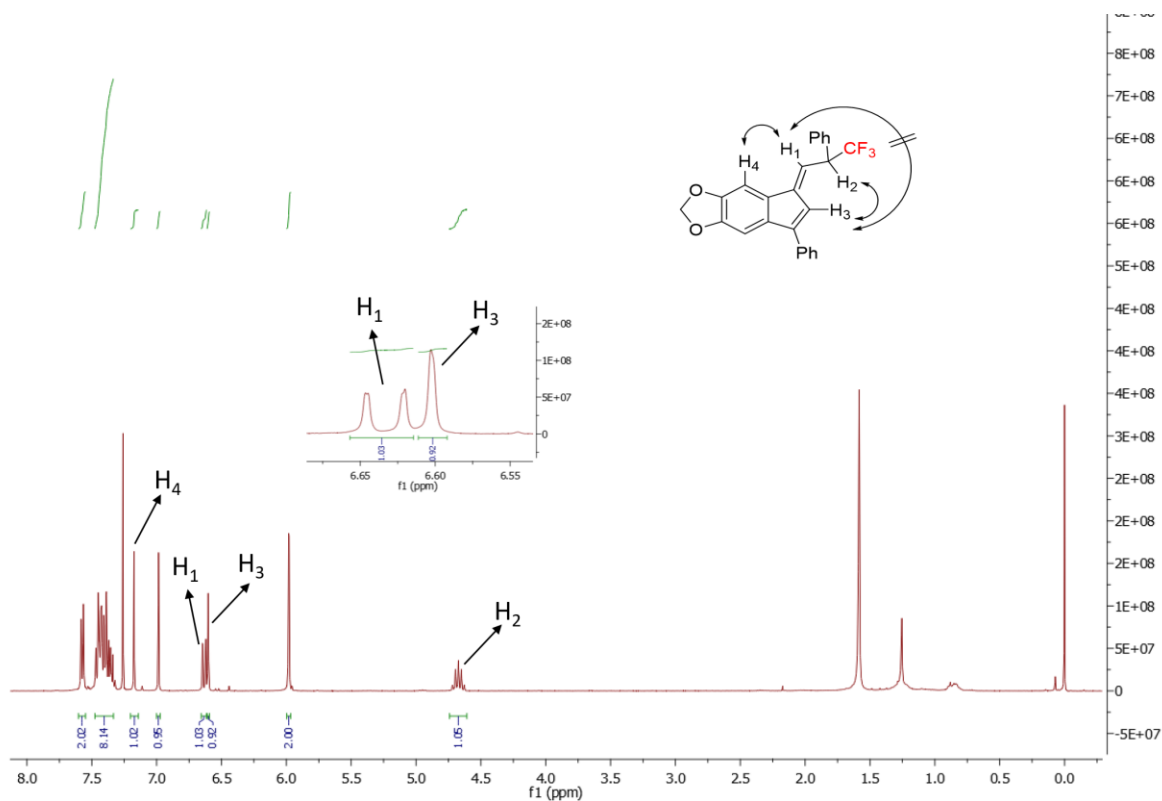
1. Table S1 Optimization of the Reaction Conditions ^a



Entry	[Pd]/L	Solvent	Yield (%)
1	Pd(PPh ₃) ₄	THF	60
2	Pd(PPh ₃) ₄	CH ₃ CN	51
3	Pd(PPh ₃) ₄	DMF	33
4	Pd(PPh ₃) ₄	DMSO	25
5	Pd(PPh ₃) ₄	1,4-dioxane	81
6	Pd(PPh ₃) ₄	CHCl ₃	27
7	Pd(dba) ₃ .CHCl ₃ /PCy ₃	1,4-dioxane	-
8	Pd(dba) ₃ .CHCl ₃ /DPPE	1,4-dioxane	-
9	Pd(dba) ₃ .CHCl ₃ /P(2-furyl) ₃	1,4-dioxane	-
10	PdCl ₂	1,4-dioxane	-
11	Pd(OAc) ₂	1,4-dioxane	32
12 ^b	Pd(PPh ₃) ₄	1,4-dioxane	-
13	-	1,4-dioxane	-

^aExperiment by using **1a** (0.24 mmol), **2a** (0.29 mmol), Pd-source (5 mol%), Ligand (10 mol%), and AcOH (20 mol%) in 3 mL of solvent at 90 °C for 12 h. Isolated yields. ^bReaction at 50 °C.

2. 2D-NMR analysis of compound **3la**



¹H NMR spectrum of **3la** recorded in CDCl₃ at 25 °C

Strong cross-peaks were observed between the indene proton (H3) and the H2 proton, as well as between the alkyldiene proton (H1) and the aromatic proton (H4). Further, we didn't observe any NOE impact between the alkyldiene proton (H1) and the indene proton (H3), indicating that the near proximity requirement for the appearance of cross peaks and NOE was not met. These findings unambiguously demonstrate the formation of an E-conformer over a Z-isomer.

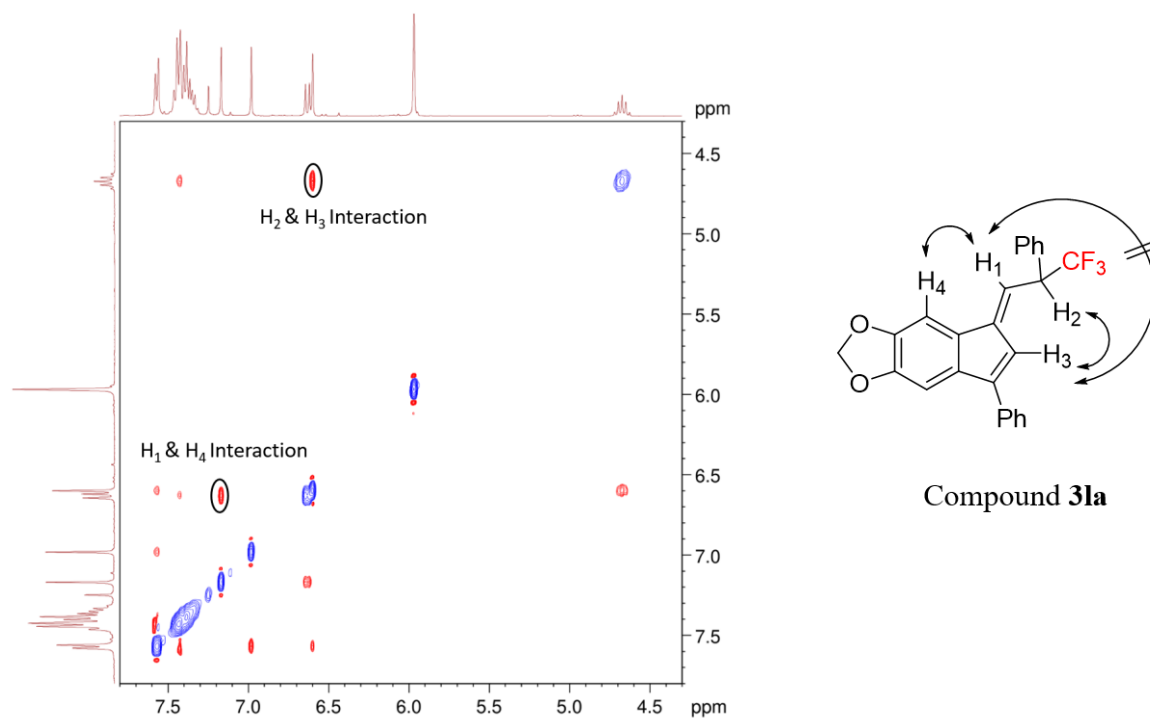
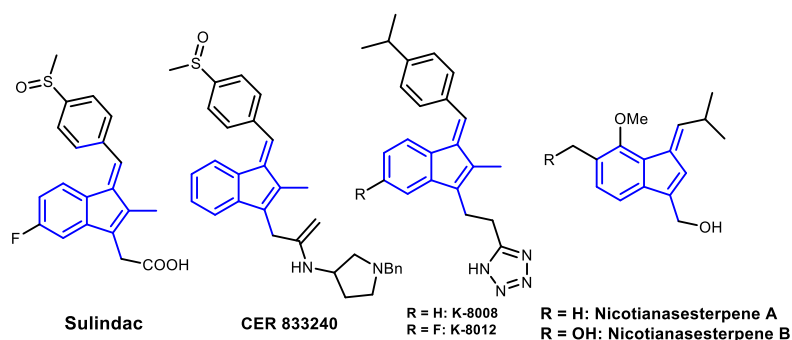


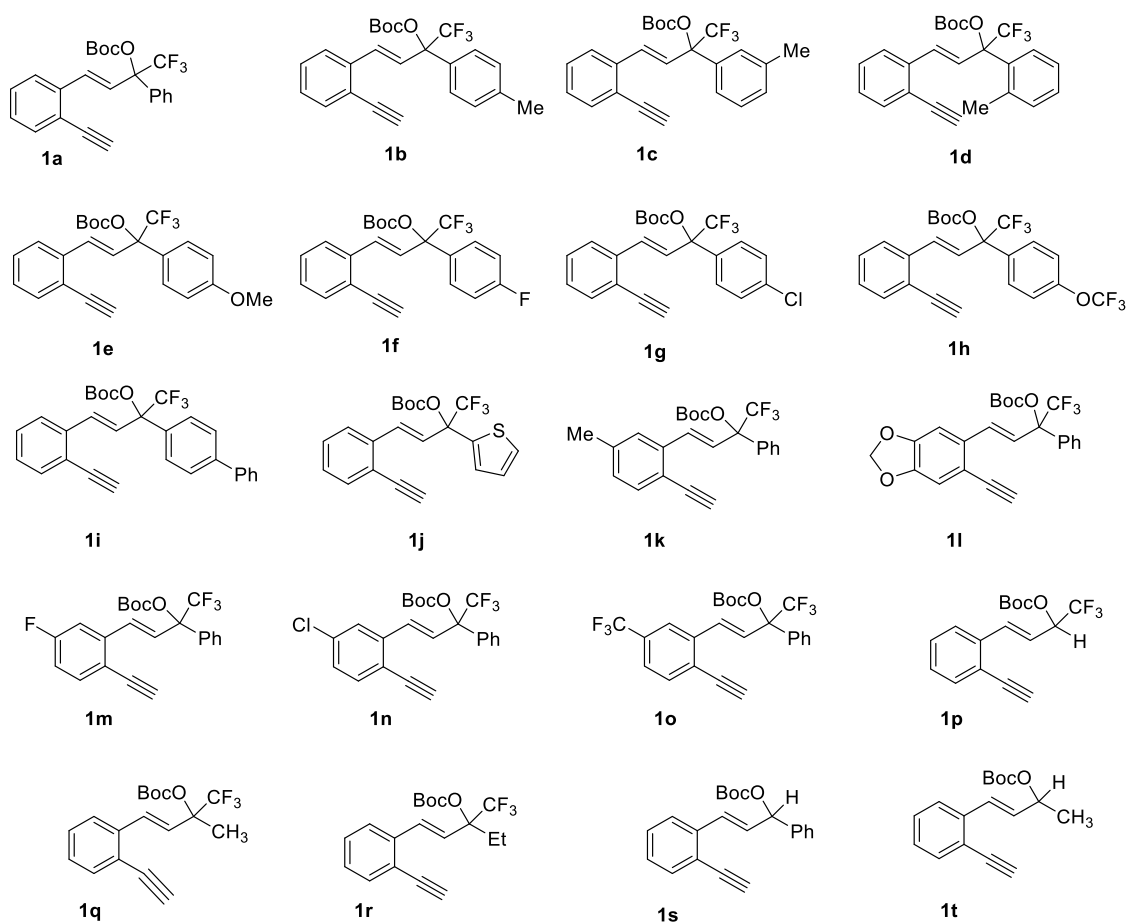
Figure S1. ¹H-¹H 2D-NOESY spectrum of **3la** recorded in CDCl₃ on 400 MHz at 25 °C

3. Fig. S2 Representative examples of bioactive benzofulvenes.



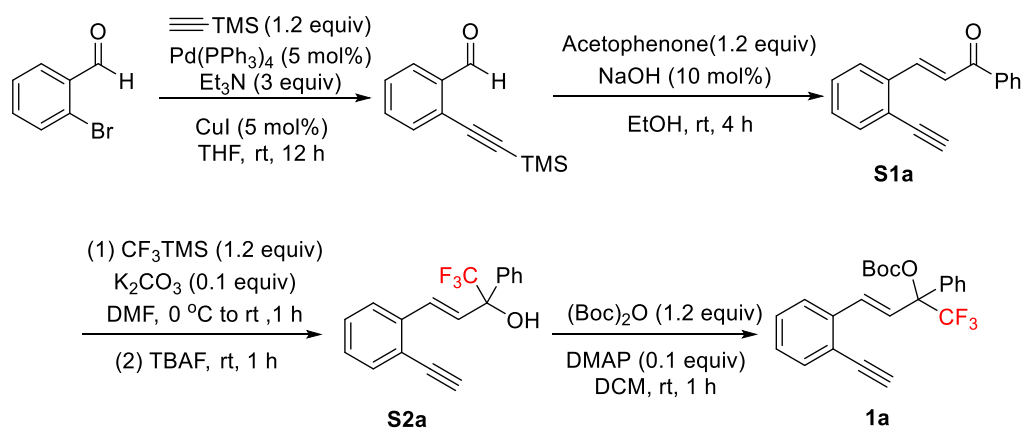
4. General information:

All the reactions were performed in an oven-dried glass apparatus, the air and moisture-sensitive reactions were carried out under an inert atmosphere (nitrogen), using freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography on silica plates using UV light and anisaldehyde for visualization. Column chromatography was performed on silica gel (100-200 mesh) using hexanes and ethyl acetate as eluent. ^1H NMR was recorded in CDCl_3 on 500 and 400 MHz, ^{13}C NMR was recorded on 125 MHz, 100 MHz and 75 MHz. ^{19}F NMR was recorded on 377 MHz. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and J values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. δ 7.26 and δ 1.56 corresponding to CDCl_3 and moisture respectively in ^1H NMR, δ 77.16 is related to CDCl_3 in ^{13}C NMR. FT-IR spectra were recorded on Alpha (Bruker) Infrared Spectrophotometer. High-resolution mass spectra (HRMS) [ESI^+ , ESI^-] were obtained by using either a TOF or a double-focusing spectrometer, reported compounds. Raw materials required for the synthesis of compound **1a-1t** were prepared according to the literature procedure.¹



5. Experimental procedures and characterization data of Starting materials

General reaction:



General procedure A:

Under argon atmosphere, to a solution of 2-bromobenzaldehyde (3.5 g, 18.90 mmol) in THF solvent were added trimethylsilyl acetylene (2.22 g, 22.70 mmol), Et₃N (50 mL), PdCl₂(PPh₃)₂ (0.658 g, 0.94 mmol) and CuI (0.035 g, 1.89 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 h, then filtered through a short pad of silica gel and washed with ethyl acetate. After the removal of solvent, the crude residue was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 100:1, v/v) to afford the desired product 2-((trimethylsilyl)ethynyl)benzaldehyde (3.6 g, 95% yield).

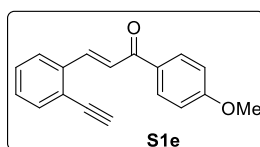
To a solution of 2-((trimethylsilyl)ethynyl)benzaldehyde (2.02 g, 10.0 mmol) in methanol (25 mL) were added acetophenone (1.2 g, 10 mmol) and 10% NaOH aqueous solution (3.6 mL, 11.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then the solution was quenched with water and extracted with EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3x 10 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100:1 to 30:1, v/v) to afford **S1a** (1.9 g, 82%).

According to the literature procedure,² α , β unsaturated ketone **S1a** (10 mmol, 1 equiv) and TMSCF₃ (1.7 mL, 12 mmol, 1.2 equiv) were suspended in anhydrous DMF (20 mL). To this solution, dry K₂CO₃ (13.8 mg, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N₂ atmosphere. Completion of the reaction was monitored by TLC. To this reaction mixture, tetrabutylammonium fluoride (1 M, 3.2 mL, 12 mmol) was added and stirred for 1 h at room temperature. The reaction mixture was diluted with the water, then

extracted with ethyl acetate (3 × 30 mL) and the combined organic layers were finally washed with brine solution, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product **S2a** was further purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 90:10).

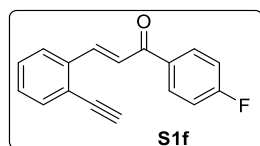
To the stirred solution of alcohol **S2a** (10 mmol, 1 equiv) in DCM (10 mL), were added Boc-anhydride (2.75 mL, 12 mmol, 1.2 equiv) and DMAP (12.2 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred until completion of the starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure, and the obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford the pure CF₃-allyl carbonates (**1**). Most of the compounds were reported in the literature and the data of unknown were summarized below.^{1,2}

(E)-3-(2-Ethynylphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (S1e)



Following general procedure **A**, 2-((trimethylsilyl)ethynyl)benzaldehyde (1g, 4.95 mmol), 4-methoxy acetophenone (0.742 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1e** as a red color oil, yield 82% (1.06 g); ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 15.8 Hz, 1H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.66 (m, 3H), 7.41 (m, 2H), 7.00 (m, 1H), 3.89 (s, 3H), 3.44 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 188.9, 163.6, 141.6, 137.3, 133.8, 131.0, 130.8, 129.7, 129.2, 126.6, 124.2, 123.2, 113.9, 83.6, 81.5, 55.6; IR (neat): ν_{max} = 3296, 1664 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₅O₂ [M+H]⁺: 263.1066, found: 263.1062.

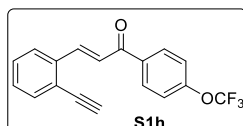
(E)-3-(2-Ethynylphenyl)-1-(4-fluorophenyl)prop-2-en-1-one (S1f)



Following general procedure **A**, 2-((trimethylsilyl)ethynyl)benzaldehyde (1g, 4.95 mmol), 4-fluoro acetophenone (0.683 g, 4.95 mmol), Aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1f** as yellow color solid, mp: 113 – 115 °C yield 75%

(0.928 g); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (d, $J = 15.8$ Hz, 1H), 8.07 (m, 2H), 7.76 (m, 1H), 7.61 (m, 2H), 7.42 (m, 2H), 7.19 (m, 2H), 3.45 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 189.1, 165.7 (d, $J = 254.5$ Hz), 142.6, 136.8, 134.5, 133.8, 131.3 (d, $J = 9.2$ Hz), 130.0, 129.2, 126.6, 123.8, 123.4, 115.8 (d, $J = 21.8$ Hz), 83.7, 81.4; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -105.42 (s, F); **IR (KBr)**: $\nu_{\text{max}} = 3301, 1668$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{17}\text{H}_{12}\text{FO}$ $[\text{M}+\text{H}]^+$: 251.0866, found: 251.0864.

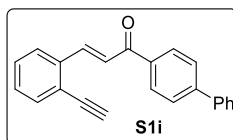
(E)-3-(2-Ethynylphenyl)-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (S1h)



Following general procedure **A**, 2-((trimethylsilyl)ethynyl) benzaldehyde (1g, 4.95 mmol), 4-trifluoromethoxy acetophenone (1 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1h** as a redd colour oil, yield 72% (1.12 g);

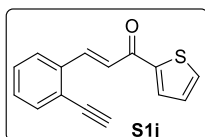
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.27 (d, $J = 15.8$ Hz, 1H), 8.09 (m, 2H), 7.76 (m, 1H), 7.61 (m, 2H), 7.42 (m, 2H), 7.35 (m, 2H), 3.45 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 189.1, 152.5, 143.0, 136.7, 136.4, 133.8, 130.6, 130.4, 130.1, 129.2, 126.6, 123.6, 120.5, 120.4 (q, $J = 258.6$ Hz), 83.8, 81.3; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.60 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3296, 1668$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 317.0783, found: 317.0779.

(E)-1-([1,1'-Biphenyl]-4-yl)-3-(2-ethynylphenyl)prop-2-en-1-one (S1i)



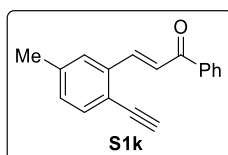
Following general procedure **A**, 2-((trimethylsilyl)ethynyl)benzaldehyde (1g, 4.95 mmol), 1-([1,1'-biphenyl]-4-yl)ethan-1-one (0.970 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1i** as a colourless oil, yield 75% (114.29 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (d, $J = 15.8$ Hz, 1H), 8.09 (d, $J = 8.3$ Hz, 2H), 8.01 (d, $J = 8.3$ Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.71 (d, $J = 8.3$ Hz, 1H), 7.67 (d, $J = 1.5$ Hz, 1H), 7.65 (m, 1H), 7.62 (s, 1H), 7.56 (d, $J = 7.4$ Hz, 1H), 7.47 (m, 2H), 7.40 (m, 3H), 3.44 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.8, 190.0, 145.6, 142.2, 139.9, 137.0, 136.8, 133.8, 129.9, 129.3, 129.2, 129.0, 128.3, 127.3, 126.5, 124.1, 123.3, 83.7, 81.2; **IR (neat)**: $\nu_{\text{max}} = 3292, 1665$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{23}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$: 309.1273, found: 309.1270.

(E)-3-(2-Ethynylphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (S1j)



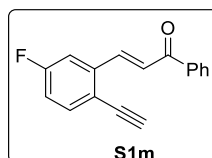
Following general procedure **A**, 2-((trimethylsilyl)ethynyl)benzaldehyde (1g, 4.95 mmol), 2-acetyl thiophene (0.623 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1j** as a light yellow colour oil, yield 70% (0.824 mg); **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (d, J = 15.7 Hz, 1H), 7.77 (d, J = 3.7 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 4.9 Hz, 1H), 7.50 (m, 1H), 7.42 (s, 1H), 7.33 (m, 1H), 7.28 (m, 1H), 7.11 (m, 1H), 3.37 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 182.2, 145.5, 141.6, 136.8, 134.1, 133.8, 132.0, 129.9, 129.1, 128.3, 126.7, 123.9, 123.4, 83.8, 81.4; **IR (neat)**: ν_{\max} = 3295, 1672 cm⁻¹; **HRMS (ESI)**: m/z calcd for C₁₅H₁₁OS [M+H]⁺: 239.0525, found: 239.0522.

(E)-3-(2-Ethynyl-5-methylphenyl)-1-phenylprop-2-en-1-one (S1k)



Following general procedure **A**, 5-methyl-2-((trimethylsilyl)ethynyl)benzaldehyde (1.069 g, 4.95 mmol), acetophenone (0.594 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1k** as a yellow colour solid, mp: 117 – 118 °C, yield 85% (1.03 g); **¹H NMR** (400 MHz, CDCl₃) δ 8.24 (d, J = 15.8 Hz, 1H), 8.05 (m, 2H), 7.63 (m, 3H), 7.53 (m, 3H), 7.16 (d, J = 7.9 Hz, 1H), 3.39 (s, 1H), 2.40 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 190.8, 142.6, 139.4, 138.2, 136.8, 133.7, 132.9, 130.9, 128.7, 128.4, 127.1, 124.0, 120.5, 82.9, 81.5, 21.6; **IR (KBr)**: ν_{\max} = 3290, 1662 cm⁻¹; **HRMS (ESI)**: m/z calcd for C₁₈H₁₅O [M+H]⁺: 247.1117, found: 247.1114.

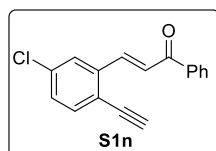
(E)-3-(2-ethynyl-5-fluorophenyl)-1-phenylprop-2-en-1-one (S1m)



Following general procedure **A**, 5-fluoro-2-((trimethylsilyl)ethynyl)benzaldehyde (1.089 g, 4.95 mmol), acetophenone (0.594 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1m** as a yellow colour solid, mp: 123 – 125 °C, yield 75% (0.928 g); **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (dd, J = 15.8, 1.4 Hz, 1H), 8.05 (m, 2H), 7.63 (m, 2H), 7.56 (m, 2H), 7.52 (m, 1H), 7.44 (dd, J = 9.6, 2.6 Hz, 1H), 7.13 (m, 1H), 3.41 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 190.3, 164.0, 161.5, 141.2, 139.4 (d, J = 8.0 Hz),

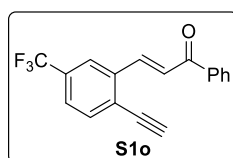
137.9, 135.6 (d, $J = 8.5$ Hz), 133.2, 128.8 (d, $J = 6.9$ Hz), 125.2, 119.5 (d, $J = 2.8$ Hz), 117.4 (d, $J = 22.4$ Hz), 113.1 (d, $J = 22.9$ Hz), 83.4, 80.4; ^{19}F NMR (376 MHz, CDCl_3) δ -104.52 (s, F); IR (KBr): $\nu_{\text{max}} = 3298, 1666$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{12}\text{FO}$ $[\text{M}+\text{H}]^+$: 251.0866, found: 251.0864.

(E)-3-(5-Chloro-2-ethynylphenyl)-1-phenylprop-2-en-1-one (S1n)



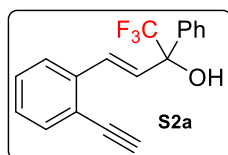
Following general procedure A, 5-chloro-2-((trimethylsilyl)ethynyl)benzaldehyde (1.168 g, 4.95 mmol), acetophenone (0.594 g, 4.95 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1n** as a red colour oil, yield 78% (1.02 g); ^1H NMR (400 MHz, CDCl_3) δ 8.14 (m, 1H), 7.99 (m, 2H), 7.67 (m, 1H), 7.54 (m, 1H), 7.51 (m, 1H), 7.47 (m, 2H), 7.43 (m, 1H), 7.26 (dd, $J = 8.3, 2.1$ Hz, 1H), 3.40 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 189.2, 139.9, 137.7, 136.9, 134.3, 133.9, 132.2, 128.9, 127.8, 127.7, 125.5, 124.1, 120.8, 83.5, 79.4; IR (neat): $\nu_{\text{max}} = 3295, 1663$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{12}\text{ClO}$ $[\text{M}+\text{H}]^+$: 267.0571, found: 267.0569.

(E)-3-(2-Ethynyl-5-(trifluoromethyl)phenyl)-1-phenylprop-2-en-1-one (S1o)



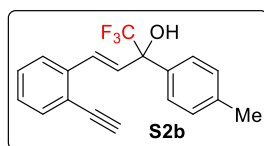
Following general procedure A, 5-(trifluoromethyl)-2-((trimethylsilyl)ethynyl)benzaldehyde (1.336 g, 4.95 mmol), acetophenone (0.594 g, 4.95 mmol), Aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S1o** as a yellow colour solid, mp: 116 – 117 °C, yield 70% (1.03 g); ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 15.8$ Hz, 1H), 8.06 (q, $J = 1.7$ Hz, 1H), 8.04 (t, $J = 1.7$ Hz, 1H), 7.97 (m, 1H), 7.95 (d, $J = 1.4$ Hz, 1H), 7.69 (m, 1H), 7.55 (m, 2H), 7.49 (m, 2H), 3.57 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.1, 140.6, 137.8, 134.3, 133.3, 133.2, 131.2 (q, $J = 32.9$ Hz), 128.8, 128.7, 128.7, 128.4, 125.5, 123.3, 123.2, 86.1, 80.2; ^{19}F NMR (376 MHz, CDCl_3) δ -58.65 (s, 3F); IR (KBr): $\nu_{\text{max}} = 3300, 1670$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 301.0834, found: 301.0831.

(E)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (S2a)



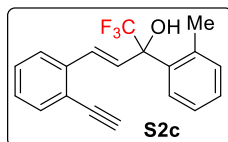
Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-phenylprop-2-en-1-ol **S1a** (69 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.14 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2a** as a colourless oil, yield 82% (74.29 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.68 (m, 2H), 7.55 (m, 1H), 7.49 (m, 1H), 7.43 (m, 4H), 7.29 (m, *J* = 7.6, 1.2 Hz, 1H), 7.22 (m, 1H), 6.80 (d, *J* = 16.1 Hz, 1H), 3.26 (s, 1H), 3.02 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 137.7, 137.4, 133.4, 131.3, 129.2, 128.9, 128.8, 128.5, 128.3, 126.9, 125.6, 122.3 (q, *J* = 286.1 Hz), 121.5, 82.6, 81.7, 77.5 (q, *J* = 28.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.32 (s, 3F); IR (neat): ν_{max} = 3290, 2920, 1450, cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₄F₃O [M+H]⁺: 303.0952, found: 303.1486.

(*E*)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(*p*-tolyl)but-3-en-2-ol (S2b)



Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(*p*-tolyl)prop-2-en-1-ol **S1b** (73 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2b** as a reddish colour oil, yield 85%, (80.60 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.55 (m, 3H), 7.50 (m, 1H), 7.38 (m, 1H), 7.34 (m, 1H), 7.23 (m, 3H), 6.80 (d, *J* = 16.1 Hz, 1H), 3.28 (s, 1H), 2.98 (s, 1H), 2.36 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 138.8, 137.8, 134.5, 133.4, 131.0, 129.2, 129.1, 128.9, 128.2, 126.8, 125.6, 121.5, 125.1 (q, *J* = 275.3 Hz), 82.6, 81.7, 77.4 (q, *J* = 28.9 Hz), 21.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -78.39 (s, 3F); IR (neat): ν_{max} = 3299, 2924, 1491 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₆F₃O [M+H]⁺: 317.1182, found: 317.1185.

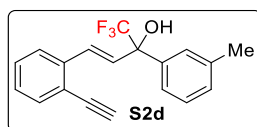
(*E*)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(*o*-tolyl)but-3-en-2-ol (S2c)



Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(*o*-tolyl)prop-2-en-1-ol **S1c** (73 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (41 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2c** as

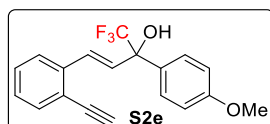
a reddish colour oil, yield 84% (79.65 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.48 (m, 1H), 7.41 (m, 1H), 7.23 (m, 1H), 7.16 (m, 2H), 7.14 (m, 2H), 6.66 (m, 1H), 3.15 (s, 1H), 2.79 (s, 1H), 2.42 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.2, 137.8, 137.3, 133.5, 131.1, 129.7, 129.2, 128.9, 128.4, 128.2, 127.5, 125.6, 125.1 (q, $J = 286.0$ Hz), 124.0, 121.6, 82.6, 81.7, 77.5 (q, $J = 29.0$ Hz), 21.7; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -76.32 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3295, 2920, 1495$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 317.1142, found: 317.1144.

(E)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(*m*-tolyl)but-3-en-2-ol (S2d)



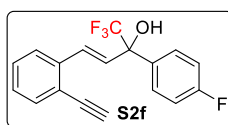
Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(*m*-tolyl)prop-2-en-1-one **S1d** (73 mg, 0.30 mmol), TMSCF_3 (0.05 mL, 0.36 mmol), and K_2CO_3 (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2d** as a reddish colour oil, yield 86% (81.55 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (m, 1H), 7.42 (m, 4H), 7.26 (m, 2H), 7.17 (m, 2H), 6.72 (d, $J = 16.1$ Hz, 1H), 3.20 (s, 1H), 2.9 (s, 1H), 2.29 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.8, 138.3, 138.0, 135.4, 133.3, 133.1, 129.4, 129.2, 128.8, 128.1, 127.9, 125.6 (q, $J = 286.9$ Hz), 125.5, 121.5, 121.3, 82.5, 81.5, 79.1 (q, $J = 28.5$ Hz), 22.7; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -78.28 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3289, 2924, 1490$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 317.1150, found: 317.1152.

(E)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-ol (S2e)



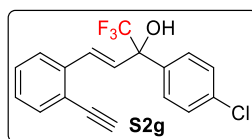
Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one **S1e** (78 mg, 0.30 mmol), TMSCF_3 (0.05 mL, 0.36 mmol), and K_2CO_3 (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2e** as a reddish colour oil, yield 86% (85.68 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.5$ Hz, 3H), 7.50 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.41 (m, 2H), 7.29 (m, 1H), 6.96 (m, 2H), 6.81 (d, $J = 10.0$ Hz, 1H), 3.81 (s, 3H), 3.30 (s, 1H), 2.95 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.9, 137.8, 133.4, 131.1, 129.5, 129.2, 128.9, 128.4, 128.2, 125.6, 125.2 (q, $J = 286.0$ Hz), 121.5, 113.8, 82.6, 81.7, 77.5 (q, $J = 36.4$ Hz), 55.4; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -78.64 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3285, 2925, 1485$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{O}_2$ $[\text{M}-\text{H}]^-$: 331.1296, found: 331.1299.

(E)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(4-fluorophenyl)but-3-en-2-ol (S2f)



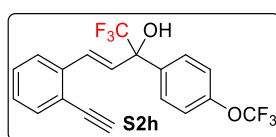
Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(4-fluorophenyl)prop-2-en-1-one **S1f** (75 mg, 0.30 mmol), TMSCF₃ (0.05 mL, 0.36 mmol) and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2f** as a yellow oil, yield 78% (74.89 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 (dd, *J* = 19.1, 7.7 Hz, 2H), 7.27 (m, 4H), 7.09 (m, 1H), 6.65 (m, 1H), 3.19 (s, 1H), 3.01 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 138.7 (d, *J* = 29.0 Hz), 137.7, 135.1 (d, *J* = 115.2 Hz), 133.4, 130.9, 129.1, 129.1, 129.0, 128.8, 128.1, 126.8, 125.8 (q, *J* = 285.3 Hz), 82.5, 81.6, 77.4 (q, *J* = 29.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -78.41 (s, 3F), -80.96 (s, 1F); IR (neat): ν_{max} = 3299, 2924, 1491 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₃F₄O [M+H]⁺: 321.1484, found: 321.1486.

(E)-2-(4-Chlorophenyl)-4-(2-ethynyl phenyl)-1,1,1-trifluoro but-3-en-2-ol (S2g)



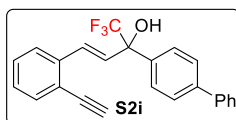
Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(4-chlorophenyl)prop-2-en-1-one **S1g** (79 mg, 0.30 mmol), TMSCF₃ (0.05 mL, 0.36 mmol) and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2g** as a reddish colour oil, yield 80% (80.65 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.39 (m, 4H), 7.24 (m, 1H), 6.78 (s, 1H), 3.29 (s, 1H), 2.95 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 135.8, 135.1, 133.5, 131.9, 129.2, 128.6, 128.6, 128.5, 128.3, 125.6, 124.9 (q, *J* = 286.1 Hz), 121.6, 82.7, 81.6, 77.6 (q, *J* = 28.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -78.63 (s, 3F); IR (neat): ν_{max} = 3285, 2910, 1480 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₃ClF₃O [M+H]⁺: 337.1482, found: 337.1485.

(E)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(4-(trifluoromethoxy)phenyl)but-3-en-2-ol (S2h)



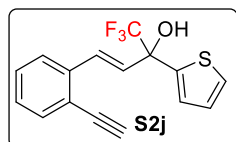
Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(4(trifluoromethoxy)phenyl)prop-2-en-1-one **S1h** (94 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2h** as a reddish colour oil, yield 78% (90.34 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.68 (m, 2H), 7.56 (m, 1H), 7.52 (m, 1H), 7.40 (m, 1H), 7.33 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.28 (m, 1H), 6.81 (d, *J* = 16.2 Hz, 1H), 3.29 (s, 1H), 2.96 (s, *J* = 7.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.2, 137.3, 133.6, 132.3, 131.1 (q, *J* = 32.6 Hz), 129.3, 128.6, 128.1, 127.6, 125.6, 125.4, 125.4, 122.0 (q, *J* = 286.1 Hz), 121.7, 82.7, 81.6, 77.4 (q, *J* = 28.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.25 (s, 3F), -76.35 (s, 3F); IR (neat): ν_{max} = 3275, 2890, 1475 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₃F₆O₂ [M+H]⁺: 387.1275, found: 387.1277.

(*E*)-2-([1,1'-Biphenyl]-4-yl)-4-(2-ethynyl phenyl)-1,1,1-trifluoro but-3-en-2-ol (S2i)



Following general procedure A, (*E*)-1-([1,1'-biphenyl]-4-yl)-3-(2-ethynylphenyl)prop-2-en-1-one **S1i** (92 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added obtain compound **S2i** as a brown colour oil, yield 76% (86.18 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.63 (m, 5H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.44 (m, 3H), 7.37 (m, 2H), 7.28 (m, 1H), 6.87 (d, *J* = 16.1 Hz, 1H), 3.32 (s, 1H), 2.90 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.8, 140.5, 137.7, 136.3, 133.5, 131.4, 129.2, 128.9, 128.7, 128.3, 127.8, 127.4, 127.3, 127.2, 125.6, 125.1 (q, *J* = 286.1 Hz), 121.6, 82.6, 81.7, 77.5 (q, *J* = 29.4 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -78.36 (s, 3F); IR (neat): ν_{max} = 3296, 2890, 1475 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₄H₁₈F₃O [M+H]⁺: 379.1242, found: 379.1245.

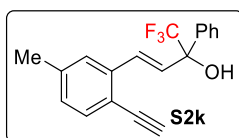
(*E*)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-ol (S2j)



Following general procedure A, (*E*)-3-(2-ethynylphenyl)-1-(thiophen-2-yl)prop-2-en-1-one **S1j** (71 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2j** as a brown colour oil, yield 76% (70.45 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.50 (m, 1H), 7.41 (dd, *J* = 16.5, 8.6 Hz, 2H), 7.29 (m, 2H), 7.19 (m, 2H), 6.96 (dd, *J* = 5.1,

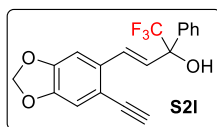
3.7 Hz, 1H), 6.64 (d, $J = 16.0$ Hz, 1H), 3.22 (s, 1H), 3.02 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 140.8, 137.4, 133.4, 131.7, 129.1, 128.3, 127.4, 127.2, 126.9, 126.8, 125.7, 124.5 (q, $J = 286.1$ Hz), 121.6, 82.6, 81.6, 76.5 (q, $J = 30.6$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -79.24 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3296, 2890, 1475$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 309.0891, found: 309.0895.

(E)-4-(2-Ethynyl-5-methylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (S2k)



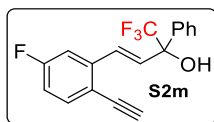
Following general procedure A, (*E*)-3-(2-ethynyl-5-methylphenyl)-1-phenylprop-2-en-1-one **S1k** (73 mg, 0.30 mmol), TMSCF_3 (0.05 mL, 0.36 mmol), and K_2CO_3 (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2k** as a yellow colour oil, yield 85% (80.58 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.69 (m, 2H), 7.45 (m, 6H), 7.06 (dd, $J = 7.9, 0.9$ Hz, 1H), 6.80 (d, $J = 16.2$ Hz, 1H), 3.24 (s, 1H), 2.87 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 139.3, 138.2, 137.5, 137.4, 133.4, 131.4, 129.3, 128.9, 128.5, 126.9, 126.2, 125.1 (q, $J = 286.1$ Hz), 118.7, 81.9, 77.8 (q, $J = 29.1$ Hz), 21.6; ^{19}F NMR (376 MHz, CDCl_3) δ -78.4 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3290, 2885, 1470$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 317.1144, found: 317.1146.

(E)-4-(6-Ethynylbenzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (S2l)



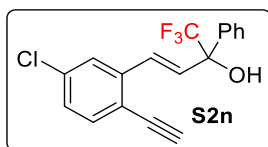
Following general procedure A, (*E*)-3-(6-ethynylbenzo[*d*][1,3]dioxol-5-yl)-1-phenylprop-2-en-1-one **S1l** (82 mg, 0.30 mmol), TMSCF_3 (0.05 mL, 0.36 mmol), and K_2CO_3 (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2l** as a reddish colour oil, yield 82% (85.11 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.4$ Hz, 2H), 7.45 (m, 4H), 7.02 (s, 1H), 6.89 (s, 1H), 6.61 (d, $J = 16.1$ Hz, 1H), 5.97 (m, $J = 0.9$ Hz, 2H), 3.21 (s, 1H), 2.76 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.0, 147.7, 137.4, 133.2, 131.1, 128.9, 128.5, 126.9, 125.1 (q, $J = 286.1$ Hz), 115.5, 112.3, 105.0, 101.9, 81.5, 81.5, 77.5 (q, $J = 29.1$ Hz), 29.8; ^{19}F NMR (376 MHz, CDCl_3) δ -76.41 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 3465, 3280, 1645$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 347.0886, found: 347.0889.

(E)-4-(2-Ethynyl-5-fluorophenyl)-1,1,1-trifluoro-2-phenyl but-3-en-2-ol (S2m)



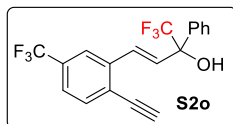
Following general procedure A, (*E*)-3-(2-ethynyl-5-fluorophenyl)-1-phenylprop-2-en-1-one **S1m** (75 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2m** as a reddish colour oil, yield 78% (74.88 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (m, 2H), 7.48 (m, *J* = 7.3, 4.4 Hz, 1H), 7.44 (m, 4H), 7.28 (m, 1H), 6.96 (m, 1H), 6.79 (d, *J* = 16.1 Hz, 1H), 3.27 (s, 1H), 2.82 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 162.9 (d, *J* = 250.2 Hz), 140.1 (d, *J* = 8.1 Hz), 137.1, 135.3 (d, *J* = 8.6 Hz), 130.4, 129.9, 129.1, 128.6, 126.8, 125.0 (q, *J* = 286.1 Hz), 117.7, 115.8 (d, *J* = 22.4 Hz), 112.4 (d, *J* = 23.0 Hz), 82.3, 80.7, 77.5 (q, *J* = 28.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -78.41 (s, 3F), -80.96 (s, 1F); IR (neat): ν_{max} = 3480, 3290, 1600 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₃F₄O [M+H]⁺: 321.0714, found: 321.0716.

(*E*)-4-(5-Chloro-2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (S2n)



Following general procedure A, (*E*)-3-(2-ethynyl-5-chlorophenyl)-1-phenylprop-2-en-1-one **S1n** (79 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. After that TBAF (1 M, 0.09 mL) was added to obtain the compound **S2n** as a reddish colour oil, yield 78% (78.62 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (m, 2H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.41 (m, 3H), 7.37 (m, 2H), 7.24 (m, 1H), 6.81 (m, 1H), 3.31 (s, 1H), 3.14 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 139.4, 137.1, 135.3, 134.6, 130.2, 130.0, 129.1, 128.6, 128.4, 126.8, 124.9 (q, *J* = 256.2 Hz), 125.7, 120.0, 83.5, 80.7, 77.5 (q, *J* = 29.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -78.63 (s, 3F); IR (neat): ν_{max} = 3475, 3290, 1601 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₃ClF₃O [M+H]⁺: 337.1054, found: 337.1055.

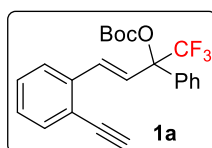
(*E*)-4-(2-Ethynyl-5-(trifluoromethyl)phenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (S2o)



Following general procedure A, (*E*)-3-(2-ethynyl-5-(trifluoromethyl)phenyl)-1-phenylprop-2-en-1-one **S1o** (90 mg, 0.30 mmol), TMSF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol) were taken in 3 mL of DMF. Then TBAF (1 M, 0.09 mL) was added to obtain the

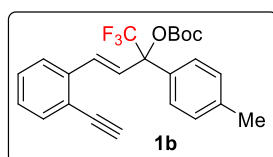
compound **S2o** as a reddish colour oil, yield 72% (79.70 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (s, 1H), 7.68 (m, 2H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.49 (dd, $J = 8.1, 1.1$ Hz, 1H), 7.45 (m, 4H), 6.91 (m, 1H), 3.43 (s, 1H), 2.93 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.18, 137.31, 133.56, 132.28, 131.13 (q, $J = 32.7$ Hz), 129.27, 128.61, 128.10, 127.58, 125.61, 125.44, 125.41, 124.89 (q, $J = 286.1$ Hz), 121.66, 82.74, 81.58, 77.39 (q, $J = 28.9$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.99 (s, 3F), -76.39 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 2965, 1660, 1130$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{19}\text{H}_{13}\text{F}_6\text{O}$ $[\text{M}+\text{H}]^+$: 371.1463, found: 371.1465.

(E)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (1a)



Following general procedure **A**, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **S2a** (120.6 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3mL of DCM to obtain the compound **1a** as a white solid, yield 85% (102.51 mg), mp: 57 – 58 $^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.6$ Hz, 1H), 7.57 (m, $J = 7.3$ Hz, 2H), 7.54 (m, 2H), 7.45 (m, 3H), 7.38 (m, 1H), 7.29 (m, 1H), 6.93 (d, $J = 16.5$ Hz, 1H), 3.33 (s, 1H), 1.47 (s, $J = 3.8$ Hz, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.3, 149.9, 138.1, 134.8, 134.2, 133.4, 129.2, 129.2, 128.4, 127.1, 125.5, 124.1, 123.5 (q, $J = 284.9$ Hz), 121.8, 83.7, 83.3 (q, $J = 29.1$ Hz), 82.6, 81.5, 27.7; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -83.87 (s, 3F); **IR (KBr)**: $\nu_{\text{max}} = 2921, 2853, 1762$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_3$ $[\text{M}-\text{OBoc}]^-$: 285.0885, found: 285.0886.

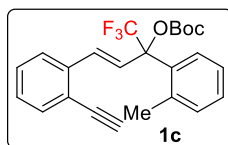
(E)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(p-tolyl)but-3-en-2-yl) carbonate (1b)



Following general procedure **A**, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*p*-tolyl)but-3-en-2-ol **S2b** (124.8 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3mL of DCM to obtain the compound **1b** as a white solid, yield 82% (102.23 mg), mp: 58 – 60 $^\circ\text{C}$; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (d, $J = 7.9$ Hz, 1H), 7.48 (m, 1H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.29 (m, 1H), 7.22 (m, 3H), 7.10 (m, $J = 7.9$ Hz, 1H), 6.83 (d, $J = 16.5$ Hz, 1H), 3.25 (s, 1H), 2.30 (s, 3H), 1.35 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.9,

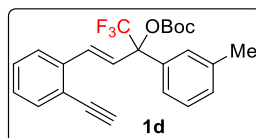
139.2, 138.2, 134.1, 133.4, 131.7, 129.2, 129.2, 128.4, 127.0, 125.6, 124.3, 123.5 (q, $J = 284.8$ Hz), 121.8, 83.6, 83.3 (q, $J = 29.2$ Hz), 82.6, 81.6, 27.8, 21.2; ^{19}F NMR (376 MHz, CDCl_3) δ -76.67 (s, 3F); IR (KBr): $\nu_{\text{max}} = 2921, 2853, 1762 \text{ cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3$ [M-OBoc] $^-$: 299.1042, found: 299.1043.

(E)-Tert-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*o*-tolyl)but-3-en-2-yl)carbonate (1c)



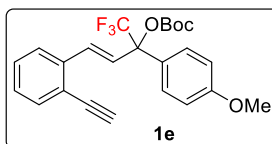
Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*o*-tolyl)but-3-en-2-ol **S2c** (124.8 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (36.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1c** as a white solid, yield 86% (107.32 mg), mp: 58 – 60 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (m, 1H), 7.54 (m, 2H), 7.45 (m, 1H), 7.37 (m, 1H), 7.24 (m, 5H), 6.90 (m, 1H), 3.28 (s, 3H), 2.47 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.1, 138.3, 137.2, 133.3, 133.1, 132.9, 132.0, 129.2, 129.05, 128.5, 128.4, 126.6, 125.8, 125.3, 124.2 (q, $J = 286.2$ Hz), 121.8, 85.1 (q, $J = 29.3$ Hz), 83.6, 82.6, 81.4, 27.7, 21.8; ^{19}F NMR (376 MHz, CDCl_3) δ -76.67 (s, 3F); IR (KBr): $\nu_{\text{max}} = 2920, 2852, 1760 \text{ cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3$ [M-OBoc] $^-$: 299.10421, found: 299.10422.

(E)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*m*-tolyl)but-3-en-2-yl) carbonate (1d)



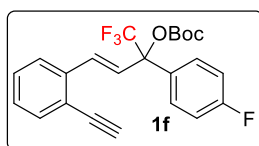
Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*m*-tolyl)but-3-en-2-ol **S2d** (124.8 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1d** as a white solid, yield 84% (104.83 mg), mp: 60 – 62 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 1H), 7.53 (m, 2H), 7.36 (m, 3H), 7.33 (m, 2H), 7.23 (m, 1H), 6.92 (d, $J = 16.6$ Hz, 1H), 3.33 (s, 1H), 2.39 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.9, 138.2, 138.1, 134.7, 134.1, 133.4, 130.0, 129.2, 128.4, 128.4, 127.8, 125.6, 124.3, 124.3, 123.5 (q, $J = 284.9$ Hz), 121.8, 83.7, 83.4 (q, $J = 29.2$ Hz), 82.6, 81.6, 27.8, 21.7; ^{19}F NMR (376 MHz, CDCl_3) δ -76.67 (s, 3F); IR (KBr): $\nu_{\text{max}} = 2919, 2845, 1755 \text{ cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3$ [M-OBoc] $^-$: 299.10421, found: 299.10427.

(E)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-yl) carbonate (1e)



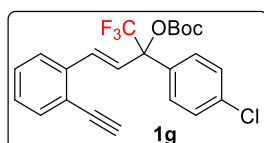
Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-ol **S2e** (129.6 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1e** as a white solid, yield 80% (103.68 mg), mp: 67 – 69 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.36 (m, 1H), 7.31 (m, 1H), 7.23 (m, 2H), 7.12 (m, 2H), 6.84 (m, 2H), 6.57 (m, 1H), 6.34 (d, *J* = 8.8 Hz, 1H), 3.74 (s, 3H), 2.87 (s, 1H), 1.36 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 160.2, 149.9, 138.2, 134.1, 133.4, 131.1, 129.2, 128.6, 128.4, 126.6, 125.6, 124.2, 123.5 (q, *J* = 284.7 Hz), 113.9, 83.6, 83.3 (q, *J* = 29.3 Hz), 82.6, 81.6, 55.4, 27.8; ¹⁹F NMR (376 MHz, CDCl₃) δ –76.67 (s, 3F); IR (KBr): ν_{max} = 2925, 2855, 1758 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₄F₃ [M–OBoc]⁻: 315.0991, found: 315.0992.

(*E*)-Tert-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-fluorophenyl)but-3-en-2-yl) carbonate (1f)



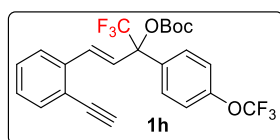
Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-fluorophenyl)but-3-en-2-ol **S2f** (126.6 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1f** as a white solid, yield 78% (98.28 mg), mp: 55 – 57 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.54 (m, 4H), 7.37 (m, *J* = 7.6, 1.2 Hz, 1H), 7.31 (m, 1H), 7.15 (m, 2H), 6.88 (d, 1H), 3.33 (s, 1H), 1.43 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 163.2 (d, *J* = 249.0 Hz), δ 149.9, 137.9, 134.6, 133.4, 130.6 (d, *J* = 3.1 Hz), 129.3, 129.2, 128.6, 125.6, 123.7, 123.4 (q *J* = 285.1 Hz), 121.8, 115.6 (d, *J* = 21.9 Hz), 83.9, 82.6, 81.5, 77.4, 27.8; ¹⁹F NMR (376 MHz, CDCl₃) δ –76.56 (s, 3F), –112.56 (s, 1F); IR (KBr): ν_{max} = 2920, 2850, 1750 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₁F₄O[M–Boc]⁻: 319.0493, found: 319.0494.

(*E*)-Tert-butyl(2-(4-chlorophenyl)-4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate (1g)



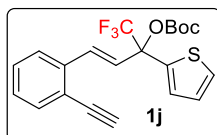
Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-chlorophenyl)but-3-en-2-ol **S2g** (130.80 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1g** as a white solid, yield 82% (107.25 mg), mp: 62 – 64 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.54 (m, 4H), 7.42 (m, 3H), 7.32 (m, 1H), 6.86 (d, *J* = 16.5 Hz, 1H), 3.34 (s, 1H), 1.43 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 137.9, 135.5, 134.7, 133.4, 133.4, 129.2, 128.7, 128.6, 127.1, 126.1 (q, *J* = 284.8 Hz), 125.1, 123.5, 121.9, 84.1, 83.1 (q, *J* = 29.3 Hz), 82.7, 81.5, 27.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -76.67 (s, 3F); IR (KBr): ν_{max} = 2910, 2845, 1750 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₁F₃Cl [M-OBoc]⁻: 319.0580, found: 319.0578

(*E*)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-(trifluoromethoxy)phenyl)but-3-en-2-yl) carbonate (1h)



Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-(trifluoromethoxy)phenyl)but-3-en-2-ol **S2h** (145.8 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1h** as a white solid, yield 76%, (110.80 mg), mp: 74 – 76 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.54 (m, 1H), 7.45 (m, 3H), 7.38 (m, 1H), 7.29 (m, 1H), 6.93 (d, *J* = 16.5 Hz, 1H), 3.33 (s, 1H), 1.47 (d, *J* = 3.8 Hz, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 138.8, 137.8, 135.1, 133.5, 131.5 (q, *J* = 32.8 Hz), 129.3, 128.7, 127.8, 125.6, 125.5, 125.5, 123.9 (q, *J* = 272.3 Hz), 123.4, 121.91, 84.29, 83.0 (q, *J* = 29.6 Hz), 82.7, 81.5, 27.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.59 (s, 3F), -76.24 (s, 3F); IR (KBr): ν_{max} = 2905, 2840, 1740 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₁OF₆ [M-OBoc]⁻: 369.07086, found: 369.07197.

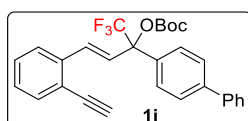
(*E*)-Tert-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl) carbonate (1j)



Following general procedure A, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-ol **S2j** (122.4 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1j** as a yellow colour oil,

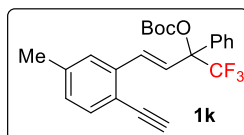
yield 68%, (83.23 mg), mp: 64 – 65 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (dd, $J = 7.7$, 1.0 Hz, 1H), 7.45 (m, 2H), 7.38 (m, 1H), 7.29 (m, 1H), 7.12 (d, $J = 3.1$ Hz, 1H), 7.06 (m, 1H), 6.72 (m, 2H), 3.02 (s, 1H), 1.46 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.0, 140.5, 134.1, 134.0, 133.5, 130.4, 129.5, 128.7, 128.3, 127.3, 126.8, 125.4 (q, $J = 274.4$ Hz), 121.4, 83.1, 82.7, 80.3, 77.6 (q, $J = 44.6$ Hz), 72.9, 27.9; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -79.24 (s, 3F); **IR (KBr)**: $\nu_{\text{max}} = 3296, 2890, 1475 \text{ cm}^{-1}$; **HRMS (ESI)**: m/z calcd for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{S}$ $[\text{M}-\text{OBoc}]^-$: 291.0450, found: 291.0449.

(E)-2-([1,1'-Biphenyl]-4-yl)-4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl tert-butyl carbonate (1i)



Following general procedure **A**, (*E*)-2-([1,1'-biphenyl]-4-yl)-4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-ol **S2i** (143.4 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1i** as a white solid, yield 76%, (108.98 mg), mp: 65 – 67 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 (m, 5H), 7.61 (m, 3H), 7.55 (m, 1H), 7.48 (m, 2H), 7.37 (m, 2H), 7.29 (m, 1H), 6.96 (d, $J = 16.6$ Hz, 1H), 3.34 (s, 1H), 1.53 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.9, 142.1, 140.3, 138.2, 134.3, 133.7, 133.4, 129.2, 128.9, 128.5, 127.8, 127.6, 127.3, 127.2, 125.6, 124.1, 123.5 (q, $J = 284.8$ Hz), 121.8, 83.8, 83.6 (q, $J = 29.2$ Hz), 82.6, 81.6, 27.8; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -76.67 (s, 3F); **IR (KBr)**: $\nu_{\text{max}} = 2965, 1660, 1130 \text{ cm}^{-1}$; **HRMS (ESI)**: m/z calcd for $\text{C}_{24}\text{H}_{16}\text{F}_3$ $[\text{M}-\text{OBoc}]^-$: 361.1745, found: 361.1740.

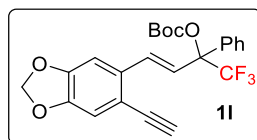
(E)-Tert-butyl (4-(2-ethynyl-5-methylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (1k)



Following general procedure **A**, (*E*)-4-(2-ethynyl-5-methylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **S2k** (124.8 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1k** as a white solid, yield 85% (106.08 mg), mp: 55 – 57 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.0$ Hz, 2H), 7.54 (m, 1H), 7.45 (m, 5H), 7.09 (m, 1H), 6.91 (d, $J = 16.5$ Hz, 1H), 3.28 (s, 1H), 2.38 (s, 3H), 1.42 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.9, 139.4, 137.9, 134.9, 134.3, 133.3, 129.4, 129.2, 128.5, 127.7, 127.2, 126.2, 123.8, 123.5 (q, $J = 284.9$ Hz), 119.0, 83.7, 81.9, 83.4 (q, J

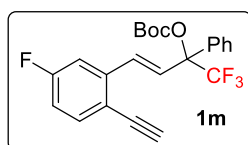
= 29.2 Hz), 27.8, 21.7; ^{19}F NMR (376 MHz, CDCl_3) δ -76.40 (s, 3F); IR (KBr): ν_{max} = 3297, 1757, 1484 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3$ $[\text{M}-\text{OBoc}]^-$: 299.10422, found: 299.10425.

(E)-Tert-butyl (4-(6-ethynylbenzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (11)



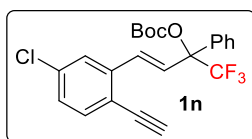
Following general procedure A, (*E*)-4-(6-ethynylbenzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **S2I** (133.8 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **11** as a white solid, yield 78% (104.36 mg); mp: 72 – 74 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.42 (m, 3H), 7.28 (m, 2H), 6.86 (d, J = 31.2 Hz, 2H), 6.58 (d, J = 8.8 Hz, 1H), 6.38 (d, J = 8.8 Hz, 1H), 5.99 (d, J = 1.9 Hz, 2H), 2.75 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.9, 149.3, 147.9, 134.8, 133.9, 133.5, 129.9, 129.2, 128.4, 127.1, 126.3 (q, J = 285.1 Hz), 122.4, 115.8, 112.3, 105.0, 101.9, 83.7, 83.1 (q, J = 31.1 Hz), 81.5, 27.8; ^{19}F NMR (377 MHz, CDCl_3) δ -66.52 (s, 3F); IR (KBr): ν_{max} = 3285, 1746, 1475 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{12}\text{F}_3\text{O}_2$ $[\text{M}-\text{OBoc}]^-$: 329.0786, found: 329.0783.

(E)-Tert-butyl(4-(2-ethynyl-5-fluorophenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (1m)



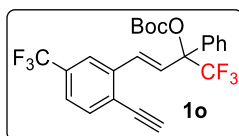
Following general procedure A, (*E*)-4-(2-Ethynyl-5-fluorophenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **S2m** (126.0 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1m** as a white solid, yield 78% (98.28 mg), mp: 55 – 57 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (m, 3H), 7.42 (m, 5H), 7.21 (m, 1H), 6.85 (d, J = 16.6 Hz, 1H), 3.29 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.9 (d, J = 250.2 Hz), 149.89, 140.50 (d, J = 8.1 Hz), 135.27 (d, J = 8.6 Hz), 134.55, 133.31, 129.4, 128.5, 127.1, 125.5, 123.4 (q, J = 284.9 Hz), 117.9 (d, J = 2.8 Hz), 115.9 (d, J = 22.4 Hz), 112.4 (d, J = 23.0 Hz), 83.9, 83.2 (q, J = 29.4 Hz), 82.3, 80.6, 27.8; ^{19}F NMR (376 MHz, CDCl_3) δ -68.54 (s, 3F), -116.49 (s, 1F); IR (KBr): ν_{max} = 3285, 1745, 1476 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{11}\text{F}_4\text{O}$ $[\text{M}-\text{Boc}]^-$: 319.0494, found: 319.0495.

(E)-Tert-butyl (4-(5-chloro-2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (1n)



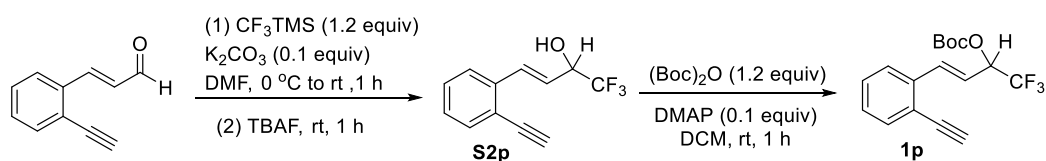
Following general procedure A, (*E*)-4-(2-Ethynyl-5-chlorophenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **S2n** (130.8 mg, 0.30 mmol), (Boc)₂O 0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL DCM to obtain the compound **1n** as a white solid, yield 82% (107.25 mg); mp: 65 – 66 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (m, 2H), 7.50 (m, 1H), 7.47 (m, 4H), 7.33 (m, 1H), 6.98 (m, 1H), 6.92 (d, *J* = 16.5 Hz, 1H), 3.30 (s, 1H), 1.44 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 146.9, 139.7, 135.3, 134.5, 133.1, 129.4, 128.6, 128.5, 127.1, 125.7, 125.6, 123.4 (q, *J* = 284.9 Hz), 120.3, 85.3, 83.9, 83.5, 83.1 (q, *J* = 29.4 Hz), 27.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -76.40 (s, 3F); IR (KBr): ν_{max} = 3285, 1746, 1475 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₁ClF₃ [M-OBoc]⁻: 319.0580, found: 319.0494.

(E)-Tert-butyl (4-(2-ethynyl-5-(trifluoromethyl)phenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate (1o)



Following general procedure A, (*E*)-4-(2-ethynyl-5-(trifluoromethyl)phenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **S2o** (141.0 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1o** as a white solid, yield 75% (105.75 mg), mp: 68 – 70 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.55 (m, 4H), 7.47 (m, 3H), 7.02 (m, 1H), 3.46 (s, 1H), 1.43 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 138.8, 134.4, 133.9, 133.1, 131.2 (q, *J* = 32.9 Hz), 129.4, 128.6, 127.1, 126.2, 124.9, 124.9, 123.8 (q, *J* = 281.7 Hz), 122.5, 122.5, 84.9, 84.0, 83.1 (q, *J* = 29.3 Hz), 80.4, 27.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.99 (s, 3F), -76.39 (s, 3F); IR (KBr): ν_{max} = 3285, 1746, 1475 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₁F₆ [M-OBoc]⁻: 353.0758, found: 353.0759.

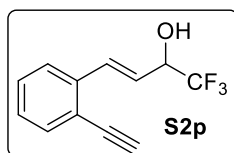
5.1 General procedure for the synthesis of (*E*)-tert-butyl (4-(2-ethynyl phenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate (General procedure B)



According to the literature procedure,² α , β unsaturated aldehyde (10 mmol, 1 equiv) and TMSCF_3 (1.7 mL, 12 mmol, 1.2 equiv) were suspended in anhydrous DMF (20 mL). To this solution, dry K_2CO_3 (13.8 mg, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. Completion of the reaction was monitored by TLC. To this reaction mixture tetrabutylammonium fluoride (1 M, 3.2 mL, 12 mmol) was added and stirred for 1 h at room temperature. The reaction mixture was diluted with the water, then extracted with ethyl acetate (3×30 mL). The combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The crude product was further purified by column chromatography to get the compound **S2p** in 76% yield as a red colour oil.

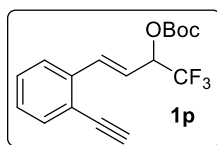
To the stirred solution of alcohol **S2p** (10 mmol, 1 equiv) in DCM (10 mL), was added Boc-anhydride (2.75 mL, 12 mmol, 1.2 equiv) and DMAP (12.2 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred until completion of the starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure, and the obtained residue was purified using column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford the pure CF_3 -allyl carbonate **1p** in 74% yield.

(*E*)-4-(2-Ethynylphenyl)-1,1,1-trifluorobut-3-en-2-ol (**S2p**)



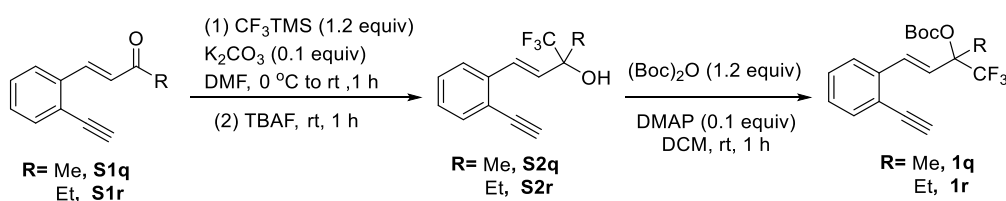
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (m, 2H), 7.34 (m, 2H), 7.26 (m, 1H), 6.29 (dd, $J = 16.0$, 6.5 Hz, 1H), 4.88 (m, 1H), 3.35 (s, 1H), 2.66 (s, 1H); **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 137.5, 134.2, 133.5, 129.2, 128.5, 127.2 (q, $J = 281.4$ Hz), 125.5, 122.9, 121.5, 82.6, 81.6, 71.8 (q, $J = 32.3$ Hz); **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -78.93 (s, 3F); **IR (neat)**: $\nu_{\text{max}} = 2805, 1400, 1045$ cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 227.0639, found: 227.0319.

(E)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate (1p)



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.51 (m, 2H) 7.35 (m, 2H), 7.26 (m, 1H), 6.16 (dd, $J = 16.0$, 7.7 Hz, 1H), 5.64 (m, 1H), 3.28 (s, 1H), 1.45 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.7, 137.0, 136.3, 133.3, 129.1, 128.6, 125.8 (q, $J = 281.4$ Hz), 125.5, 121.7, 119.3, 84.1, 82.6, 81.3, 73.8 (q, $J = 33.5$ Hz), 27.7; $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -63.38 (s, 3F); **IR (KBr)**: $\nu_{\text{max}} = 3125, 1556, 1226 \text{ cm}^{-1}$; **HRMS (ESI)**: m/z calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{O}_3$ $[\text{M}-\text{H}]^-$: 325.1052, found: 325.1845.

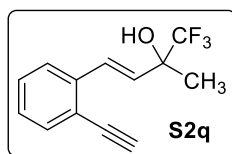
5.2 General procedure for the synthesis of alkyl substituted 2-alkynyl CF_3 -allyl carbonates (1q and 1r) General procedure C:



According to the literature procedure, α , β unsaturated aldehydes (10 mmol, 1 equiv) and TMSCF_3 (1.7 mL, 12 mmol, 1.2 equiv) were suspended in anhydrous DMF (20 mL). To this solution, dry K_2CO_3 (13.8 mg, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. Completion of the reaction was monitored by TLC. To this reaction mixture tetrabutylammonium fluoride (1 M, 3.2 mL, 12 mmol) was added and stirred for 1 h at room temperature. The reaction mixture was diluted with water, then extracted with ethyl acetate (3×30 mL). The combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The crude product **S2q** was further purified by column chromatography.

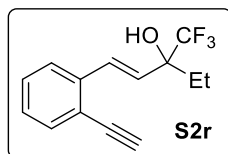
To the stirred solution of alcohol **S2q** (10 mmol, 1 equiv) in DCM (10 mL), was added Boc-anhydride (2.75 mL, 12 mmol, 1.2 equiv) and DMAP (12.2 mg, 0.1 equiv) at 0°C , and the solution was warmed to room temperature and stirred until completion of the starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure, and the obtained residue was purified using column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford the pure CF_3 -allyl carbonates (**1q** and **1r**).

(E)-4-(2-Ethynylphenyl)-1,1,1-trifluoro-2-methylbut-3-en-2-ol (S2q)



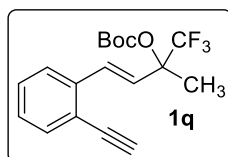
Following general procedure C, (*E*)-4-(2-ethynylphenyl)but-3-en-2-one **S1q** (51 mg, 0.30 mmol), TMSCF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol), were taken in 3 mL of DMF. Then TBAF (1 M, 0.09 mL) was added to obtain the compound **S2q** as a reddish colour oil, yield 78% (56.16 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (m, 2H), 7.36 (d, *J* = 16.2 Hz, 1H), 7.29 (m, 1H), 7.21 (m, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 3.15 (s, 1H), 2.33 (s, 1H), 1.59 (d, *J* = 0.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.6, 132.9, 130.8, 128.9, 128.4, 128.1, 125.7 (q, *J* = 285.1 Hz), 125.5, 122.4, 103.2, 100.2, 74.3 (q, *J* = 29.3 Hz), 22.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.48(s, 3F); IR (neat): ν_{max} = 2850, 1435, 1125 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₃H₁₁F₃O [M+H]⁺: 241.0840, found: 241.1414.

(E)-1-(2-ethynylphenyl)-3-(trifluoromethyl)pent-1-en-3-ol (S2r)



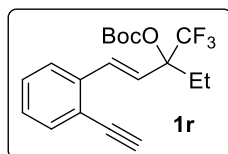
Following general procedure C, (*E*)-1-(2-ethynylphenyl)pent-1-en-3-one **S1r** (55 mg, 0.30 mmol), TMSCF₃ (0.05 mL, 0.36 mmol), and K₂CO₃ (4.1 mg, 0.03 mmol), were taken in 3 mL of DMF. Then TBAF (1 M, 0.09 mL) was added to obtain the compound **S2r** as a reddish colour oil, yield 76% (57.91 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (m, 2H), 7.33 (m, 2H), 7.27 (m, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 3.35 (s, 1H), 2.22 (s, 1H), 1.91 (m, 2H), 0.99 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 138.0, 133.4, 131.0, 129.2, 128.1, 127.2, 125.7 (q, *J* = 274.7 Hz), 125.5, 121.4, 82.4, 81.8, 32.3, 27.2, 6.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -76.55(s, 3F); IR (neat): ν_{max} = 2865, 1445, 1120 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₄H₁₃F₃ONa [M+Na]⁺: 277.0816, found: 277.0860.

(E)-Tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-methylbut-3-en-2-yl) carbonate (1q)



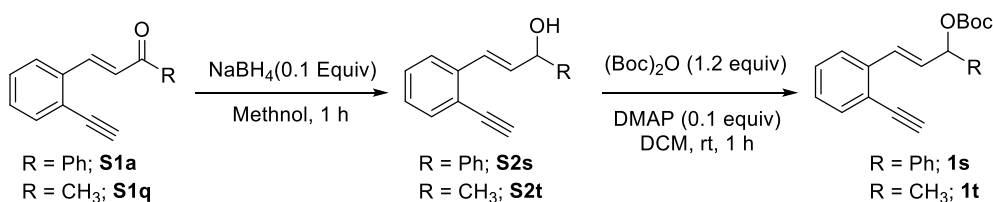
Following general procedure, **C**, (*E*)-4-(2-ethynylphenyl)-1,1,1-trifluoro-2-methylbut-3-en-2-ol **S2q** (72 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1q** as a white colour oil, yield 78% (79.56 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (m, 2H), 7.33 (m, 1H), 7.27 (m, 2H), 6.34 (d, *J* = 16.4 Hz, 1H), 3.33 (s, 1H), 1.92 (m, 3H), 1.48 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 138.5, 133.4, 132.6, 129.1, 128.4, 125.6, 125.5, 123.9 (q, *J* = 261.2 Hz), 121.7, 83.4, 82.4, 81.4, 29.8, 27.9, 17.7; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.05(s, 3F); IR (KBr): ν_{max} = 3135, 1625, 1235 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₃H₁₀F₃ [M-OBoc]⁻: 223.0735, found: 223.0732.

(*E*)-Tert-butyl (1-(2-ethynylphenyl)-3-(trifluoromethyl)pent-1-en-3-yl) carbonate (1r)



Following general procedure, **C**, (*E*)-1-(2-ethynylphenyl)-3-(trifluoromethyl)pent-1-en-3-ol **S2r** (76 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1r** as a white colour oil, yield 76% (80.71 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, *J* = 15.5, 7.7 Hz, 2H), 7.33 (m, 1H), 7.28 (m, 2H), 6.32 (d, *J* = 16.5 Hz, 1H), 3.32 (s, 1H), 2.57 (m, 2H), 1.49 (s, 9H), 1.08 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 137.9, 133.4, 131.8, 129.1, 128.2, 126.1, 125.4, 124.4 (q, *J* = 285.4 Hz), 122.9, 121.6, 83.7, 82.4, 81.7, 27.9, 25.3, 7.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -76.39; IR (KBr): ν_{max} = 3156, 1625, 1246 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₄H₁₂F₃ [M-OBoc]⁻: 237.0891, found: 237.0887.

4.3 General procedure for the synthesis of (*E*)-tert-butyl (3-(2-ethynylphenyl)-1-phenylallyl) carbonate (1s and 1t) (General procedure D)

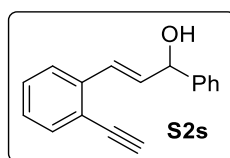


According to the literature procedure,² α, β unsaturated ketone **S1a** (10 mmol, 1 equiv) and sodium borohydride (1.7 mL, 12 mmol, 1.2 equiv) were suspended in methanol (20 mL). The

reaction mixture was stirred vigorously at room temperature under N₂ atmosphere. Completion of the reaction was monitored by TLC. The reaction mixture was diluted with the water, then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were finally washed with brine solution, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel to get the **S2s**.

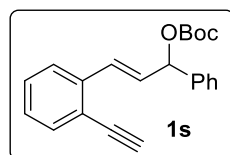
To the stirred solution of alcohol **S2s** (10 mmol, 1 equiv) in DCM (10 mL), was added Boc-anhydride (2.75 mL, 12 mmol, 1.2 equiv) and DMAP (12.2 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred until completion of the starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure, and the obtained residue was purified using column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford the pure allyl carbonate (**1s**).

(E)-3-(2-Ethynylphenyl)-1-phenylprop-2-en-1-ol (S2s)



Following general procedure **D**, (*E*)-3-(2-ethynylphenyl)-1-phenylprop-2-en-1-one **S1s** (116 mg, 0.50 mmol), sodium borohydride (22 mg, 0.6 mmol), were taken in 10 mL of methanol to obtain the compound **S2s** as a red colour oil, yield 78% (91.26 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (m, 2H), 7.43 (m, 2H), 7.38 (m, 2H), 7.30 (m, 3H), 7.19 (m, 1H), 6.46 (m, 1H), 5.39 (d, *J* = 6.6 Hz, 1H), 3.31 (s, 1H), 2.31 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 142.6, 138.7, 133.8, 133.3, 129.0, 128.7, 128.3, 127.9, 127.5, 126.5, 125.2, 121.1, 82.18, 82.1, 75.2; IR (neat): ν_{max} = 2945, 1465 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₇H₁₃ [M-OH]⁻: 217.1017, found: 217.1015

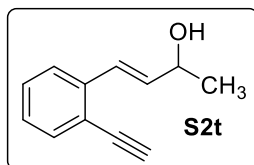
(E)-Tert-butyl (3-(2-ethynylphenyl)-1-phenylallyl) carbonate (1s)



Following general procedure, **C**, (*E*)-3-(2-ethynylphenyl)-1-phenylprop-2-en-1-ol **S2s** (69.6 mg, 0.30 mmol), (Boc)₂O (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1s** as a white colour oil, yield 76% (76.15 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.34 (m, 4H), 7.21 (m, 2H), 7.15 (m, 2H), 7.04 (m, 2H), 6.26 (dd, *J* = 15.9, 7.0 Hz, 1H), 6.06 (d, *J* = 7.1 Hz, 1H), 3.12 (s, 1H), 1.30 (s, 9H); ¹³C NMR (101 MHz,

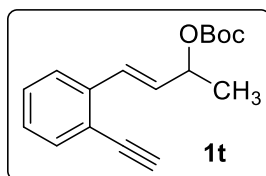
CDCl_3) δ 152.8, 139.1, 138.4, 133.3, 130.4, 129.5, 129.0, 128.7, 128.3, 127.7, 127.1, 125.2, 121.3, 82.6, 82.3, 81.8, 79.3, 27.9; **IR (KBr)**: $\nu_{\text{max}} = 3275, 1425 \text{ cm}^{-1}$; **HRMS (ESI)**: m/z calcd for $\text{C}_{17}\text{H}_{13} [\text{M}-\text{OBoc}]^-$: 217.1017, found: 217.1016

(E)-4-(2-Ethynylphenyl)but-3-en-2-ol (S2t)



Following general procedure **E**, (*E*)-4-(2-ethynylphenyl)but-3-en-2-one **S1q** (51mg, 0,30 mmol), sodium borohydride (13 mg , 0.05 mmol), were taken in 10 mL of methanol to obtain the compound **S2t** as a red colour oil, yield 82% (42.31 mg); **¹H NMR** (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.6 \text{ Hz}$, 1H), 7.46 (m, 1H), 7.29 (m, 1H), 7.17 (m, 1H), 7.05 (d, $J = 16.0 \text{ Hz}$, 1H), 6.36 (dd, $J = 16.0, 6.4 \text{ Hz}$, 1H), 4.52 (m, 1H), 3.33 (s, 1H), 1.66 (s, 1H), 1.41 (m, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 138.6, 135.5, 132.9, 128.8, 127.6, 127.3, 125.1, 121.9, 103.5, 99.5, 69.2, 23.3; **IR (neat)**: $\nu_{\text{max}} = 3165, 1645, 1465 \text{ cm}^{-1}$; **HRMS (ESI)**: m/z calcd for $\text{C}_{12}\text{H}_{11} [\text{M}-\text{OH}]^-$: 155.0867, found: 155.0853.

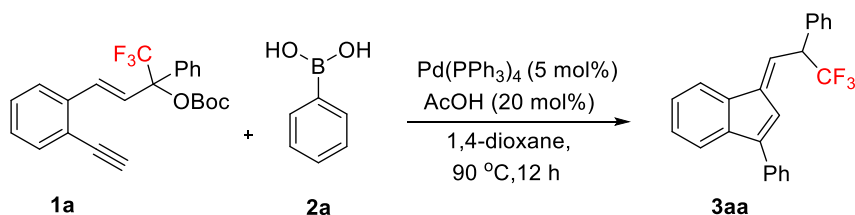
(E)-Tert-butyl (4-(2-ethynylphenyl)but-3-en-2-yl) carbonate (1t)



Following general procedure, **E**, (*E*)-3-(2-ethynylphenyl)-1-phenylprop-2-en-1-ol **S2t** (51.60 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (3.6 mg, 0.03 mmol) were taken in 3 mL of DCM to obtain the compound **1t** as a white colour oil, yield 80% (65.28 mg); **¹H NMR** (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.9 \text{ Hz}$, 1H), 7.47 (dd, $J = 7.7, 1.2 \text{ Hz}$, 1H), 7.30 (m, 1H), 7.20 (m, 1H), 7.15 (m, 1H), 6.33 (m, 1H), 5.36 (m, 1H), 3.32 (s, 1H), 1.50 (s, 9H), 1.47 (m, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 152.9, 138.5, 133.3, 130.8, 129.4, 128.9, 127.6, 125.1, 121.2, 82.2, 82.1, 81.8, 74.1, 27.9, 20.6; **IR (KBr)**: $\nu_{\text{max}} = 3275, 1645, 1425 \text{ cm}^{-1}$; **HRMS (ESI)**: m/z calcd for $\text{C}_{12}\text{H}_{11} [\text{M}-\text{OBoc}]^-$: 155.0861, found: 155.0856

6. Experimental procedure and characterization data of products (3aa-3oa)

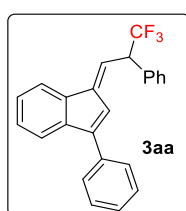
General reaction:



General procedure E:

To a stirred solution of (*E*)-tert-butyl (4-(2-ethynyl aryl)-1,1,1-trifluoro-2-aryl but-3-en-2-yl) carbonate **1a** (0.30 mmol) in 3 mL of 1,4-dioxane was added phenylboronic acid **2a** (0.36 mmol) at room temperature. Then Pd(PPh₃)₄ (5 mol%) and 20 mol% acetic acid were added to the reaction mixture and stirring continued at 90 °C (oil bath temperature) for 10 –12 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was diluted with water and extracted with ethyl acetate (3 X 15 mL). The combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified using flash column chromatography (using 9.5:0.5 hexane/ethyl acetate as eluent) to get the pure product **3aa-3oa**. The characterization data of **3aa-3oa** were summarized below.

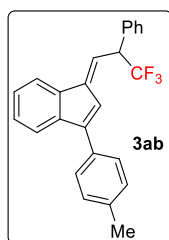
(*E*)-3-Phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1H-indene (**3aa**)



Following general procedure **E**, (*E*)-tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μ L, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3aa** as a yellow colour oil, yield 80% (86.88 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.71 (m, 1H), 7.65 (m, 2H), 7.54 (m, 1H), 7.49 (m, 4H), 7.42 (m, 1H), 7.38 (m, 1H), 7.37 (m, 2H), 7.30 (m, 2H), 6.80 (dd, *J* = 9.8, 0.8 Hz, 1H), 6.73 (s, 1H), 4.81 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 148.2, 143.5, 141.7, 137.5, 135.3, 134.9, 129.2, 129.0, 128.8, 128.6, 128.5, 128.2, 127.8, 126.1, 126.0 (q, *J* = 277.8 Hz), 121.2, 121.1, 120.7,

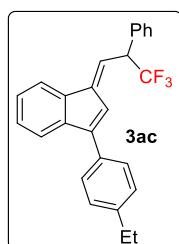
119.9, 50.7 (q, $J = 28.4$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -68.31 (s, 3F); IR (neat): $\nu_{\text{max}} = 2924, 1645 \text{ cm}^{-1}$ HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3[\text{M}+\text{H}]^+$: 363.1506, found: 363.1502.

(E)-3-(*p*-Tolyl)-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene (3ab)



Following general procedure E, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-methyl phenylboronic acid **2b** (48.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ab** as a yellow colour oil, yield 85% (95.91 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.71 (m, 1H), 7.52 (m, 3H), 7.45 (d, $J = 7.4$ Hz, 2H), 7.41 (m, 2H), 7.36 (m, 2H), 7.29 (m, 3H), 6.77 (d, $J = 9.8$ Hz, 1H), 6.70 (s, 1H), 4.71 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 143.5, 141.8, 138.6, 137.6, 135.0, 132.3, 129.5, 129.1, 129.00, 128.5, 128.1, 127.6, 126.1 (q, $J = 280.6$ Hz), 126.0, 120.7, 120.7, 119.9, 77.4, 50.68 (q, $J = 28.5$ Hz), 21.5; ^{19}F NMR (471 MHz, CDCl_3) δ -68.58 (s, 3F); IR (neat): $\nu_{\text{max}} = 2920, 1640 \text{ cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{20}\text{F}_3[\text{M}+\text{H}]^+$: 377.1485, found: 377.1486.

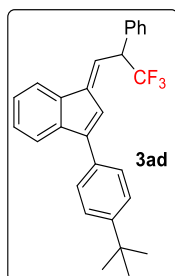
(E)-3-(4-Ethylphenyl)-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene (3ac)



Following general procedure E, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-ethyl phenylboronic acid **2c** (54.0 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ac** as a yellow colour oil, yield 82% (95.97 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.62 (m, 1H), 7.46 (m, 3H), 7.35 (m, 2H), 7.31 (m, 3H), 7.22 (m, 4H), 6.68 (m, 1H), 6.61 (s, 1H), 4.63 (p, $J = 9.2$ Hz, 1H), 2.67 (m, 2H), 1.19 (dd, $J = 9.4, 5.8$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 145.0, 143.5, 141.8, 137.6, 135.0, 132.6, 129.4, 129.1, 129.0, 128.5, 128.4, 128.2, 127.9, 127.7, 126.1 (q, $J = 280.8$ Hz), 126.0, 120.8, 119.9, 50.7 (q, $J = 28.3$ Hz), 28.9, 15.7; ^{19}F NMR (376 MHz, CDCl_3) δ -68.56 (s, 3F); IR (neat):

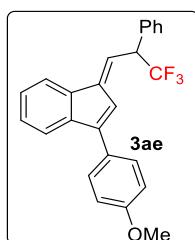
ν_{\max} = 2920, 1640 cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{26}\text{H}_{22}\text{F}_3[\text{M}+\text{H}]^+$: 391.1652, found: 391.1655.

(E)-3-(4-(Tert-butyl)phenyl)-1-(3,3,3-trifluoro-2-phenylpropylidene)-1H-indene (3ad)



Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-*tert*-butyl phenylboronic acid **2d** (64.0 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ad** as a yellow colour oil, yield 78% (97.85 mg); **^1H NMR** (400 MHz, CDCl_3) δ 7.71 (m, 1H), 7.56 (m, 3H), 7.46 (m, 4H), 7.34 (m, 3H), 7.25 (m, 2H), 6.78 (d, J = 9.8 Hz, 1H), 6.70 (s, 1H), 4.71 (p, J = 9.1 Hz, 1H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, CDCl_3) δ 148.1, 145.0, 143.5, 141.8, 137.6, 135.0, 132.6, 129.4, 129.1, 129.0, 128.5, 128.4, 128.2, 127.9, 127.7, 126.1 (q, J = 280.8 Hz), 126.0, 120.8, 119.9, 50.7 (q, J = 28.3 Hz), 28.9, 15.7; **^{19}F NMR** (376 MHz, CDCl_3) δ -68.98 (s, 3F); **IR (neat)**: ν_{\max} = 2925, 1646 cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{28}\text{H}_{26}\text{F}_3[\text{M}+\text{H}]^+$: 419.1980, found: 419.1982.

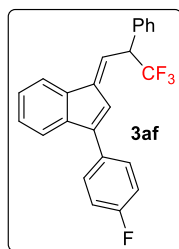
(E)-3-(4-Methoxyphenyl)-1-(3,3,3-trifluoro-2-phenylpropylidene)-1H-indene (3ae)



Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-methoxy phenylboronic acid **2e** (54.7 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ae** as a yellow colour oil, yield 80% (94.11 mg); **^1H NMR** (400 MHz, CDCl_3) δ 7.72 (m, 1H), 7.61 (m, 2H), 7.54 (m, 1H), 7.45 (d, J = 7.3 Hz, 2H), 7.41 (m, 3H), 7.34 (m, 2H), 7.01 (m, 2H), 6.76 (d, J = 10.1 Hz, 1H), 6.66 (s, 1H), 4.71 (m, 1H), 3.87 (s, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 159.7, 148.0, 143.2, 141.7, 137.6, 135.3, 130.1, 128.8, 128.6, 128.2, 127.8, 127.0, 126.1 (q, J = 280.4 Hz), 126.1, 121.4, 121.3, 120.7, 119.9, 114.6, 55.4, 49.9 (q, J = 28.5 Hz); **^{19}F NMR** (376 MHz, CDCl_3) δ -68.98 (s, 3F); **IR**

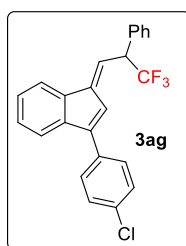
(neat): ν_{\max} = 2950, 1600 cm^{-1} ; **HRMS (ESI):** m/z calcd for $\text{C}_{25}\text{H}_{20}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 393.1440, found: 393.1442.

(E)-3-(4-Fluorophenyl)-1-(3,3,3-trifluoro-2-phenylpropylidene)-1H-indene (3af)



Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-fluoro phenylboronic acid **2f** (50.4 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3af** as a yellow colour oil, yield 75% (85.52 mg); **^1H NMR** (400 MHz, CDCl_3) δ 7.68 (m, 1H), 7.59 (m, 2H), 7.45 (m, 3H), 7.41 (m, 3H), 7.30 (m, 2H), 7.14 (m, 2H), 6.80 (d, J = 9.8 Hz, 1H), 6.68 (s, 1H), 4.82 (p, 1H); **^{13}C NMR (101 MHz, CDCl_3)** δ 162.9 (d, J = 248.1 Hz), 147.1, 143.4, 141.5, 137.5, 134.9, 131.3 (d, J = 2.9 Hz), 129.5, 129.4, 129.2, 128.9, 128.6, 128.3, 126.2, 126.0 (q, J = 280.6 Hz), 121.3, 121.1, 120.3 (d, J = 50.0 Hz), 115.8 (d, J = 21.5 Hz), 50.7 (q, J = 28.3 Hz); **^{19}F NMR (471 MHz, CDCl_3)** δ -68.53 (s, 3F), -112.73 (s, 1F); **IR (neat):** ν_{\max} = 2925, 1650 cm^{-1} ; **HRMS (ESI):** m/z calcd for $\text{C}_{25}\text{H}_{17}\text{F}_4$ $[\text{M}+\text{H}]^+$: 381.1249, found: 381.1250.

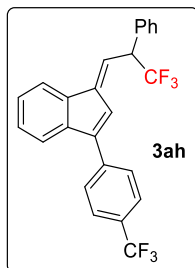
(E)-3-(4-Chlorophenyl)-1-(3,3,3-trifluoro-2-phenylpropylidene)-1H-indene (3ag)



Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-chloro phenylboronic acid **2g** (56.1 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ag** as a yellow colour oil, yield 78% (92.68 mg); **^1H NMR** (400 MHz, CDCl_3) δ 7.65 (m, 1H), 7.51 (m, 2H), 7.37 (m, 3H), 7.35 (m, 2H), 7.31 (m, 2H), 7.24 (m, 2H), 7.20 (m, 1H), 6.75 (m, 1H), 6.64 (s, 1H), 4.64 (p, J = 9.1 Hz, 1H); **^{13}C NMR (101 MHz, CDCl_3)** δ 146.9, 143.2, 141.2, 137.3, 134.7, 134.4, 133.6, 129.1, 128.9, 128.9, 128.9, 128.5, 128.2, 126.2, 125.9 (q, J = 279.9 Hz), 121.5, 121.4, 120.4, 119.9, 50.62 (q, J =

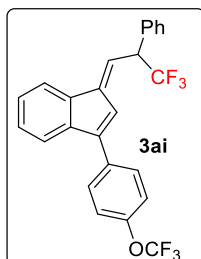
28.3 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -68.57 (s, 3F); **IR (neat)**: ν_{max} = 2930, 1635 cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{24}\text{H}_{17}\text{ClF}_3$ $[\text{M}+\text{H}]^+$: 397.0942, found: 397.0944.

(E)-1-(3,3,3-Trifluoro-2-phenylpropylidene)-3-(4-(trifluoromethyl)phenyl)-1H-indene
(3ah)



Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-trifluoromethyl phenylboronic acid **2h** (68.4 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ah** as a yellow colour oil, yield 65% (83.87 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.74 (m, 5H), 7.45 (m, 3H), 7.40 (m, 2H), 7.35 (m, 1H), 7.32 (m, 2H), 6.87 (d, J = 9.8 Hz, 1H), 6.78 (s, 1H), 4.77 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 143.2, 141.1, 138.8, 137.3, 134.8, 129.2, 129.2, 129.0, 128.7, 128.4, 128.0, 126.5, 125.8, 126.0 (q, J = 280.5 Hz), 125.8, 122.9 (q, J = 264.9 Hz), 122.5, 120.5, 120.2, 50.8 (q, J = 28.4 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.54 (s, 3F), -68.52 (s, 3F); **IR (neat)**: ν_{max} = 2920, 1645 cm^{-1} ; **HRMS (ESI)**: m/z calcd for $\text{C}_{25}\text{H}_{17}\text{F}_6$ $[\text{M}+\text{H}]^+$: 431.1210, found: 431.1212.

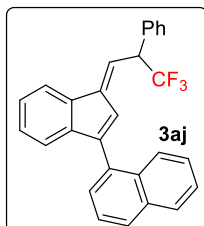
(E)-1-(3,3,3-Trifluoro-2-phenylpropylidene)-3-(4-(trifluoromethoxy)phenyl)-1H-indene
(3ai)



Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 4-trifluoromethoxy phenylboronic acid **2i** (74.1 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ai** as a yellow colour oil, yield 68% (91.00 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 1H), 7.66 (m, 2H), 7.47 (m, 3H), 7.41 (m, 3H),

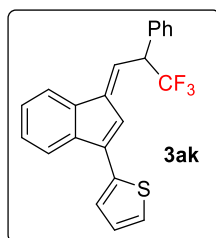
7.33 (m, 4H), 6.85 (d, $J = 9.8, 0.8$ Hz, 1H), 6.73 (s, 1H), 4.73 (p, $J = 9.1$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.3, 144.8, 141.29, 139.3, 135.4, 132.8, 131.9, 129.2 (q, $J = 66.5$ Hz), 127.2, 127.2, 127.0, 126.6, 126.3, 124.3, 124.0 (q, $J = 280.5$ Hz), 119.8, 119.7, 119.3, 118.5, 118.1, 48.7 (q, $J = 28.4$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -57.72 (s, 3F), -68.55 (s, 3F); IR (neat): $\nu_{\text{max}} = 2910, 1650$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{17}\text{F}_6\text{O}[\text{M}+\text{H}]^+$: 447.1149, found: 447.1150.

(E)-1-(1-(3,3,3-Trifluoro-2-phenylpropylidene)-1H-inden-3-yl)naphthalene (3aj)



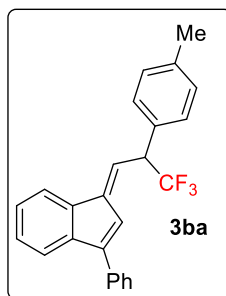
Following general procedure E, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.6 mg, 0.30 mmol), 1-naphthyl phenylboronic acid **2j** (61.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3aj** as a yellow colour oil, yield 70% (86.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83 (m, 3H), 7.62 (m, 1H), 7.46 (m, 3H), 7.36 (m, 2H), 7.32 (m, 4H), 7.16 (m, 1H), 7.13 (m, 1H), 6.94 (d, $J = 7.4$ Hz, 1H), 6.80 (dd, $J = 9.7, 0.7$ Hz, 1H), 6.71 (s, 1H), 4.63 (p, $J = 9.1$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.4, 143.8, 143.4, 136.7, 135.0, 133.9, 133.2, 131.6, 129.2, 129.0, 128.8, 128.6, 128.5, 128.3, 127.5, 126.4, 126.3, 126.2, 126.1, 125.5, 123.8, 123.3 (q, $J = 280.6$ Hz), 121.5, 121.2, 119.8, 50.8 (q, $J = 28.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -68.56 (s, 3F); IR (neat): $\nu_{\text{max}} = 2920, 1650$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{20}\text{F}_3$ $[\text{M}+\text{H}]^+$: 413.1494, found: 413.1496.

(E)-2-(1-(3,3,3-Trifluoro-2-phenylpropylidene)-1H-inden-3-yl)thiophene (3ak)



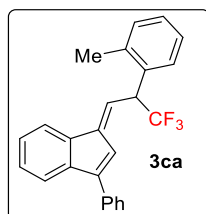
Following general procedure E, (*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1a** (120.60 mg, 0.30 mmol), 2-thiophene boronic acid **2k** (46.0 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ak** as a yellow colour oil, yield 68% (75.08 mg);

¹H NMR (400 MHz, CDCl₃) δ 7.64 (m, 1H), 7.55 (m, 2H), 7.39 (m, 2H), 7.34 (m, 1H), 7.30 (m, 2H), 7.23 (m, 2H), 7.07 (m, 2H), 6.73 (dd, *J* = 9.8, 0.8 Hz, 1H), 6.61 (s, 1H), 4.63 (p, *J* = 9.1 Hz, 1H); **¹³C NMR** (151 MHz, CDCl₃) δ 143.4, 142.3, 141.5, 137.5, 136.1, 134.9, 129.2, 129.0, 128.5, 128.3, 127.4, 126.2, 126.1, 126.0 (q, *J* = 280.5 Hz), 123.1, 120.9, 120.6, 120.4, 119.9, 50.7 (q, *J* = 28.3 Hz); **¹⁹F NMR** (376 MHz, CDCl₃) δ -69.57 (s, 3F); **IR (neat)**: ν_{max} = 2930, 1600 cm⁻¹; **HRMS (ESI)**: *m/z* calcd for C₂₂H₁₆F₃S [M+H]⁺: 369.0934, found: 369.0936.
(*E*)-3-Phenyl-1-(3,3,3-trifluoro-2-(*p*-tolyl)propylidene)-1*H*-indene (3ba)



Following general procedure **E**, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*p*-tolyl)-but-3-en-2-yl) carbonate **1b** (124.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ba** as a yellow colour oil, yield 85% (95.88 mg); **¹H NMR** (400 MHz, CDCl₃) δ 7.61 (m, 1H), 7.55 (m, 2H), 7.44 (m, 1H), 7.38 (m, 2H), 7.31 (m, 1H), 7.23 (m, 2H), 7.21 (m, 2H), 7.11 (m, 2H), 6.72 (d, *J* = 9.9 Hz, 1H), 6.65 (s, 1H), 4.67 (p, 1H), 2.26 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 148.0, 143.3, 141.7, 138.4, 137.6, 135.3, 131.9, 130.3, 129.9, 128.8, 128.6, 128.2, 127.8, 126.1 (q, *J* = 280.5 Hz), 126.0, 121.4, 121.3, 120.7, 119.9, 50.3 (q, *J* = 28.3 Hz), 21.2; **¹⁹F NMR** (376 MHz, CDCl₃) δ -68.67 (s, 3F); **IR (neat)**: ν_{max} = 2950, 1600 cm⁻¹; **HRMS (ESI)**: *m/z* calcd for C₂₅H₂₀F₃ [M+H]⁺: 377.1495, found: 377.1497.

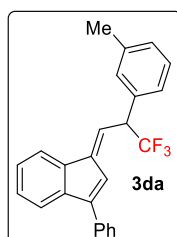
(*E*)-3-Phenyl-1-(3,3,3-trifluoro-2-(*o*-tolyl)propylidene)-1*H*-indene (3ca)



Following general procedure **E**, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*o*-tolyl)-but-3-en-2-yl) carbonate **1c** (124.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ca** as a yellow colour oil, yield 82% (92.49 mg); **¹H**

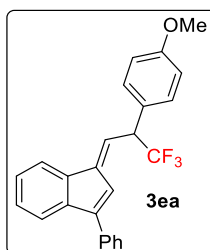
NMR (400 MHz, CDCl₃) δ 7.71 (m, 1H), 7.62 (m, 2H), 7.55 (m, 5H), 7.29 (m, 5H), 6.81 (m, 1H), 6.68 (s, 1H), 5.02 (p, J = 9.1 Hz, 1H), 2.48 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 148.2, 143.3, 141.7, 137.6, 136.5, 135.3, 133.6, 131.2, 129.3, 128.8, 128.6, 128.4, 128.2, 127.8, 126.9, 126.4 (q, J = 280.7 Hz), 126.1, 121.7, 121.2, 120.7, 119.9, 45.9 (q, J = 28.3 Hz), 29.8; **¹⁹F NMR** (471 MHz, CDCl₃) δ -68.11 (s, 3F); **IR (neat):** ν_{\max} = 2900, 1650 cm⁻¹; **HRMS (ESI):** m/z calcd for C₂₅H₂₀F₃ [M+H]⁺: 377.1484, found: 377.1486.

(E)-3-Phenyl-1-(3,3,3-trifluoro-2-(*m*-tolyl)propylidene)-1*H*-indene (3da)



Following general procedure **E**, ((*E*)-*tert*-butyl (4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(*m*-tolyl)but-3-en-2-yl) carbonate **1d** (124.8 mg, 0.30 mmol), phenylboronic acid **2a** (48.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μ L, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3da** as a yellow colour oil, yield 75% (84.60 mg); **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (m, 3H), 7.53 (m, 4H), 7.31 (m, 5H), 7.13 (d, J = 5.7 Hz, 1H), 6.82 (m, 2H), 4.68 (p, J = 9.1 Hz, 1H), 2.46 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 148.1, 143.3, 141.7, 138.9, 137.6, 135.3, 134.8, 129.6, 129.3, 129.0, 128.8, 128.6, 128.4, 128.2, 127.8, 126.1 (q, J = 280.5 Hz), 126.1, 126.0, 121.3, 120.7, 119.9, 50.7 (q, J = 28.3 Hz), 21.60; **¹⁹F NMR** (376 MHz, CDCl₃) δ -68.42 (s, 3F); **IR (neat):** ν_{\max} = 2850, 1600 cm⁻¹; **HRMS (ESI):** m/z calcd for C₂₅H₂₀F₃ [M+H]⁺: 377.1482, found: 377.1483.

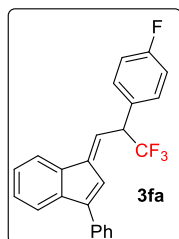
(Z)-3-Phenyl-1-(3,3,3-trifluoro-2-(4-methoxyphenyl)propylidene)-1*H*-indene (3ea)



Following general procedure **E**, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-methoxyphenyl)but-3-en-2-yl)carbonate **1e** (129.6 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μ L, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ea** as a yellow colour oil, yield 78% (91.72 mg); **¹H NMR** (400 MHz, CDCl₃) δ 7.70 (m, 1H), 7.65 (m, 2H), 7.51 (m, 1H), 7.48 (m, 2H), 7.42 (m, 3H), 7.32 (m, 2H), 6.93 (m, 2H), 6.78 (m, 1H), 6.72 (s, 1H), 4.67 (p, J = 9.1 Hz, 1H), 3.78

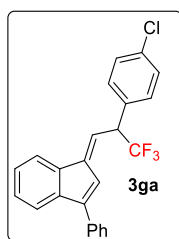
(s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 148.0, 143.2, 141.7, 137.6, 135.3, 130.1, 128.8, 128.6, 128.2, 127.8, 127.0, 126.1 (q, $J = 280.4$ Hz), 126.1, 121.4, 121.3, 120.7, 119.9, 114.6, 55.4, 49.9 (q, $J = 28.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -68.98 (s, 3F); IR (neat): $\nu_{\text{max}} = 2950, 1600 \text{ cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{20}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 393.1440, found: 393.1442.

(E)-3-Phenyl-1-(3,3,3-trifluoro-2-(4-fluorophenyl)propylidene)-1H-indene (3fa)



Following general procedure E, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-fluorophenyl)but-3-en-2-yl) carbonate **1f** (126.0 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3fa** as a yellow colour oil, yield 76% (86.64 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.72 (m, 1H), 7.65 (m, 2H), 7.52 (d, $J = 7.1$ Hz, 1H), 7.49 (m, 5H), 7.29 (m, 2H), 7.12 (m, 2H), 6.75 (d, $J = 9.7$ Hz, 1H), 6.68 (s, 1H), 4.71 (p, $J = 9.0$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.7, 161.8, 148.5, 143.7, 141.7, 137.4, 135.2, 130.7 (d, $J = 8.2$ Hz), 128.9, 128.7, 128.3, 127.7, 126.2, 125.9 (q, $J = 280.5$ Hz), 121.0, 120.8, 120.6, 119.9, 116.2 (d, $J = 21.7$ Hz), 49.9 (q, $J = 28.6$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -68.95 (s, 3F), -113.32 (s, 1F); IR (neat): $\nu_{\text{max}} = 2950, 1650 \text{ cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{17}\text{F}_4$ $[\text{M}+\text{H}]^+$: 381.1450, found: 381.1452.

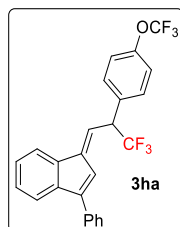
(E)-1-(2-(4-Chlorophenyl)-3,3,3-trifluoropropylidene)-3-phenyl-1H-indene (3ga)



Following general procedure E, (*E*)-*tert*-butyl (2-(4-chlorophenyl)-4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate **1g** (130.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane was taken to furnish compound **3ga** as a yellow colour oil, yield 65% (77.22 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.70 (m, 1H), 7.65 (m, 2H), 7.53 (m, 1H), 7.48 (m, 2H), 7.42 (m, 5H), 7.31 (m, 2H), 6.73 (d, $J = 9.7$ Hz, 1H), 6.67 (s, 1H), 4.70 (p, $J = 9.0$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 143.8, 141.7, 137.4, 135.1, 134.6, 133.5, 130.3, 129.4, 128.9,

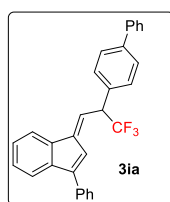
128.7, 128.4, 127.7, 126.2, 125.8 (q, $J = 280.5$ Hz), 121.0, 120.8, 120.2, 120.0, 50.0 (q, $J = 28.6$ Hz); ^{19}F NMR (376 MHz, CDCl_3) $\delta -68.72$ (s, 3F); **IR (neat):** $\nu_{\text{max}} = 2980, 1640$ cm^{-1} ; **HRMS (ESI):** m/z calcd for $\text{C}_{24}\text{H}_{17}\text{ClF}_3$ $[\text{M}+\text{H}]^+$: 397.0955, found: 397.0957.

(*E*)-3-Phenyl-1-(3,3,3-trifluoro-2-(4-(trifluoromethoxy)phenyl)propylidene)-1*H*-indene (3ha)



Following general procedure **E**, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(4-(trifluoromethoxy)phenyl)but-3-en-2-yl) carbonate **1h** (145.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ha** as a yellow colour oil, yield 70% (93.66 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.69 (m, 1H), 7.63 (m, 4H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.52 (m, 1H), 7.49 (m, 2H), 7.43 (m, 1H), 7.32 (m, 2H), 6.75 (m, 1H), 6.67 (s, 1H), 4.79 (p, $J = 8.9$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 144.2, 141.7, 138.9, 137.3, 135.0, 129.5, 128.9 (q, $J = 361.0$ Hz), 128.9, 128.8, 128.5, 127.7, 126.3, 126.2, 126.1, 123.9 (q, $J = 272.2$ Hz), 120.8, 120.8, 120.0, 119.6, 50.5 (q, $J = 28.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) $\delta -62.78$ (s, 3F), -68.46 (s, 3F); **IR (neat):** $\nu_{\text{max}} = 2990, 1650$ cm^{-1} ; **HRMS (ESI):** m/z calcd for $\text{C}_{25}\text{H}_{17}\text{F}_6\text{O}$ $[\text{M}+\text{H}]^+$: 447.1152, found: 447.1154.

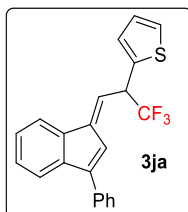
(*E*)-1-(2-([1,1'-Biphenyl]-4-yl)-3,3,3-trifluoropropylidene)-3-phenyl-1*H*-indene (3ia)



Following general procedure **E**, (*E*)-2-([1,1'-biphenyl]-4-yl)-4-(2-ethynylphenyl)-1,1,1-trifluoro-*tert*-butyl carbonate **1i** (143.4 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ia** as a yellow colour oil, yield 68% (89.35 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 1H), 7.66 (m, 2H), 7.60 (m, 3H), 7.54 (m, 3H), 7.49 (m, 5H), 7.39 (m, 1H), 7.31 (m, 2H), 7.27 (m, 1H), 6.83 (m, 1H), 6.76 (s, 1H), 4.77 (p, $J = 9.1$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.30, 143.5, 141.7, 141.5, 140.5, 137.5, 135.3, 133.9, 129.4, 128.9, 128.8, 128.6, 128.2, 127.9, 127.8, 127.7, 127.3, 126.1 (q, $J = 280.4$ Hz),

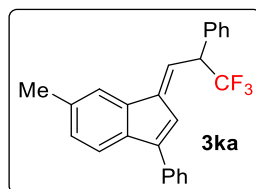
126.0, 121.2, 121.0, 120.8, 120.0, 50.4 (q, $J = 28.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -69.50 (s, 3F); IR (neat): $\nu_{\text{max}} = 2995, 1660, \text{cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{22}\text{F}_3$ $[\text{M}+\text{H}]^+$: 439.1592, found: 439.1596.

(E)-2-(1,1,1-Trifluoro-3-(3-phenyl-1*H*-inden-1-ylidene)propan-2-yl)thiophene (3ja)



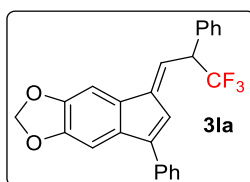
Following general procedure E, (*E*)-*tert*-butyl(4-(2-ethynylphenyl)-1,1,1-trifluoro-2-(thiophen-2-yl)but-3-en-2-yl) carbonate **1j** (122.4 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ja** as a yellow colour oil, yield 60% (66.24 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.72 (m, 1H), 7.67 (m, 2H), 7.53 (m, 1H), 7.50 (m, 2H), 7.41 (m, 1H), 7.34 (m, 3H), 7.16 (d, $J = 3.6$ Hz, 1H), 7.03 (m, 1H), 6.74 (s, 1H), 6.69 (m, 1H), 5.09 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 143.8, 141.8, 137.4, 136.1, 135.2, 128.8, 128.7, 128.4, 127.8, 127.3, 127.3, 126.2, 126.2, 125.3 (q, $J = 280.4$ Hz), 121.0, 120.8, 120.1, 120.0, 46.0 (q, $J = 30.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -69.57 (s, 3F); IR (neat): $\nu_{\text{max}} = 2980, 1640 \text{cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{F}_3\text{S}$ $[\text{M}+\text{H}]^+$: 369.0900, found: 369.0901.

(E)-6-methyl-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene (3ka)



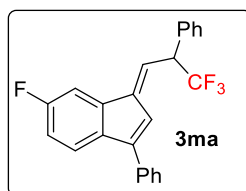
Following general procedure E, (*E*)-*tert*-butyl (4-(2-ethynyl-5-methylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1k** (124.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 5 mol%) and (0.34 μL , 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ka** as a yellow colour oil, yield 85% (95.88 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.64 (m, 2H), 7.51 (s, 1H), 7.44 (m, 4H), 7.41 (m, 5H), 7.10 (d, $J = 7.7$ Hz, 1H), 6.77 (d, $J = 9.8$ Hz, 1H), 6.66 (s, 1H), 4.79 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 143.6, 139.2, 137.9, 136.0, 135.4, 135.1, 129.4, 129.1, 129.0, 128.8, 128.6, 128.5, 127.7, 126.1 (q, $J = 280.5$ Hz), 120.9, 120.6, 120.5, 120.5, 50.7 (q, $J = 28.2$ Hz), 21.7; ^{19}F NMR (376 MHz, CDCl_3) δ -68.59 (s, 3F); IR (neat): $\nu_{\text{max}} = 2990, 1660, \text{cm}^{-1}$; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{20}\text{F}_3$ $[\text{M}+\text{H}]^+$: 377.1492, found: 377.1494.

(*E*)-7-Phenyl-5-(3,3,3-trifluoro-2-phenylpropylidene)-5*H*-indeno[5,6-*d*][1,3]dioxole (3la)



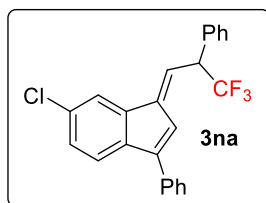
Following general procedure **E**, (*E*)-*tert*-butyl(4-(6-ethynylbenzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)carbonate **11** (133.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3la** as a yellow colour oil, yield 80% (97.44 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (m, 2H), 7.48 (m, 8H), 7.16 (d, *J* = 6.6 Hz, 1H), 6.98 (s, 1H), 6.65 (m, 1H), 6.60 (s, 1H), 6.02 (m, 2H), 4.79 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.0, 147.8, 146.7, 143.2, 136.5, 135.3, 134.9, 131.7, 129.2, 128.9, 128.9, 128.6, 128.5, 127.6, 126.0 (q, *J* = 281.1 Hz), 120.7, 119.8, 102.2, 101.8, 101.5, 50.7 (q, *J* = 28.4 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.41(s, 3F); IR (neat): ν_{max} = 2995, 1670, cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₅H₁₈F₃O₂ [M+H]⁺: 407.1182, found: 407.1185.

(*E*)-6-Fluoro-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene (3ma)



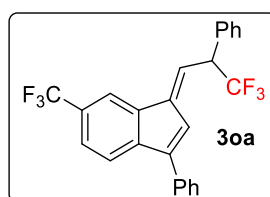
Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynyl-5-fluorophenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1m** (126.0 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3ma** as a yellow colour oil, yield 75% (85.50 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, 1H), 7.59 (m, 2H), 7.49 (m, 4H), 7.42 (m, 4H), 7.29 (m, 2H), 6.79 (m, 1H), 6.72 (s, 1H), 4.70 (p, *J* = 9.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 162.3 (d, *J* = 244.4 Hz), 147.6, 142.6, 137.5, 137.5, 134.9, 134.6, 129.1, 128.9, 128.8, 128.7, 128.5, 127.5, 125.8 (q, *J* = 280.5 Hz), 121.9, 121.4 (d, *J* = 8.6 Hz), 120.9 (d, *J* = 3.4 Hz), 114.5 (d, *J* = 22.8 Hz), 107.8 (d, *J* = 24.2 Hz), 50.6 (q, *J* = 28.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -68.54 (s, 3F), -116.49 (s, F); IR (neat): ν_{max} = 2955, 1680, cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₄H₁₇F₄ [M+H]⁺: 381.1244, found: 381.1246.

(*E*)-6-Chloro-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene (3na)



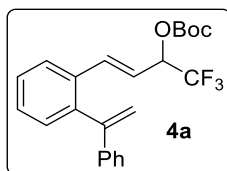
Following general procedure **E**, (*E*)-*tert*-butyl (4-(5-chloro-2-ethynylphenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1n** (130.8 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3na** as a yellow colour oil, yield 78% (92.66 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (m, 2H), 7.49 (m, 10H), 6.98 (m, *J* = 9.1, 8.4, 2.4 Hz, 1H), 6.76 (dd, *J* = 9.8, 0.8 Hz, 1H), 6.69 (s, 1H), 4.70 (p, *J* = 9.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 147.7, 142.6, 140.3, 139.2, 134.8, 134.6, 132.3, 129.3, 128.9, 128.9, 128.9, 128.7, 128.3, 128.0, 127.7, 122.4, 121.6, 121.4, 120.5, 50.7 (q, *J* = 28.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -71.99 (s, 3F); IR (neat): ν_{max} = 2950, 1660, cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₄H₁₇ClF₃ [M+H]⁺: 397.0945, found: 397.0947.

(*E*)-3-Phenyl-1-(3,3,3-Trifluoro-2-phenylpropylidene)-6-(trifluoromethyl)-1H-indene (3oa)



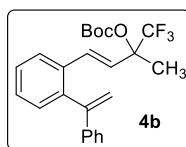
Following general procedure **E**, (*E*)-*tert*-butyl (4-(2-ethynyl-5-(trifluoromethyl)phenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl) carbonate **1o** (141.0 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **3oa** as a yellow colour oil, yield 65% (83.85 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.63 (m, 3H), 7.48 (m, 4H), 7.36 (m, 5H), 6.90 (m, 2H), 4.82 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 144.7, 142.4, 137.8, 134.5, 129.5, 129.3, 129.0, 128.8, 128.4, 127.7, 126.7 (q, *J* = 277.8 Hz), 126.1, 125.9 (q, *J* = 280.0 Hz), 125.3, 123.5, 123.3, 120.7, 116.9, 116.8, 50.8 (q, *J* = 28.5 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.00 (s, 3F), -78.19 (s, 3F); IR (neat): ν_{max} = 2905, 1670, cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₅H₁₇F₆ [M+H]⁺: 431.1213, found: 431.1215.

(*E*)-*Tert*-butyl (1,1,1-trifluoro-4-(2-(1-phenylvinyl)phenyl)but-3-en-2-yl) carbonate (4a)



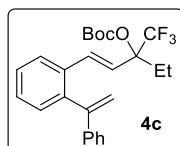
Following general procedure E, (*E*)-tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate **1p** (97.80 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **4a** as a white colour oil, yield 82% (99.38 mg); ¹H NMR (300 MHz, CDCl₃) δ 7.61 (m, 1H), 7.34 (m, 2H), 7.29 (m, 6H), 6.91 (d, *J* = 15.9 Hz, 1H), 5.99 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.85 (d, *J* = 0.9 Hz, 1H), 5.44 (m, 1H), 5.19 (d, *J* = 0.9 Hz, 1H), 1.46 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.7, 147.8, 141.6, 140.7, 137.8, 134.0, 130.6, 128.8, 128.5, 127.9, 126.9, 126.2, 125.9 (q, *J* = 280.4 Hz), 118.1, 116.9, 83.9, 74.7, 29.8, 27.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -78.93; IR (KBr): ν_{max} = 1745, 1642, 1446 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₈H₁₄F₃ [M-OBoc]⁻: 287.1048, found: 287.1038.

(*E*)-Tert-butyl (1,1,1-trifluoro-2-methyl-4-(2-(1-phenylvinyl)phenyl)but-3-en-2-yl) carbonate (4b)



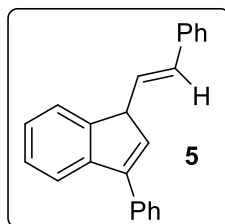
Following general procedure E, (*E*)-tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate **1q** (72 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **4b** as a white colour oil, yield 79% (99.06 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (m, 1H), 7.40 (m, 1H), 7.35 (m, 3H), 7.30 (m, 2H), 7.28 (m, *J* = 2.2 Hz, 4H), 6.77 (m, 1H), 6.25 (d, *J* = 16.3 Hz, 1H), 1.92 (s, 3H), 1.47 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 150.2, 147.9, 141.2, 140.9, 134.6, 132.9, 130.4, 129.1, 128.4, 128.2, 127.8, 127.8, 126.9, 125.9, 124.5, 124.2 (q, *J* = 281.7 Hz), 116.8, 83.7, 27.7, 24.8; ¹⁹F NMR (377 MHz, CDCl₃) δ -63.30; IR (KBr): ν_{max} = 1766, 1645, 1455 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₉H₁₆F₃ [M-OBoc]⁻: 301.1204, found: 301.1259.

(*E*)-Tert-butyl (1-(2-(1-phenylvinyl)phenyl)-3-(trifluoromethyl)pent-1-en-3-yl) carbonate (4c)



Following general procedure **E**, (*E*)-tert-butyl (4-(2-ethynylphenyl)-1,1,1-trifluorobut-3-en-2-yl) carbonate **1r** (76 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **4c** as a white colour oil, yield 78% (101.08 mg); **¹H NMR** (300 MHz, CDCl₃) δ 7.56 (dd, *J* = 8.4, 6.6 Hz, 1H), 7.36 (m, 8H), 6.78 (d, *J* = 16.4 Hz, 1H), 6.06 (dd, *J* = 21.7, 10.4 Hz, 1H), 5.83 (d, *J* = 1.1 Hz, 1H), 5.20 (d, *J* = 1.1 Hz, 1H), 2.29 (m, 2H), 1.43 (s, 9H), 0.88 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 150.3, 148.0, 141.3, 141.0, 134.8, 133.1, 130.5, 128.5, 128.3, 127.9, 127.9, 127.0, 126.1, 124.6, 124.3 (q, *J* = 285.5 Hz), 116.9, 83.6, 77.4, 27.8, 24.9, 7.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -76.53; **IR (KBr)**: ν_{max} = 1756, 1665, 1485 cm⁻¹; **HRMS (ESI)**: *m/z* calcd for C₂₀H₁₈F₃ [M-OBoc]⁻: 315.1361, found: 315.1359.

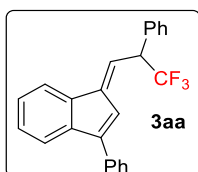
(*E*)-3-Phenyl-1-styryl-1H-indene (**5**)



Following general procedure **E**, (*E*)-tert-butyl (3-(2-ethynylphenyl)-1-phenylallyl) carbonate **1s** (100.2 mg, 0.30 mmol), phenylboronic acid **2a** (43.9 mg, 0.36 mmol), Pd(PPh₃)₄ (17.3 mg, 5 mol%) and (0.34 μL, 20 mol%) acetic acid in 3 mL of 1,4-dioxane were taken to furnish compound **5** as a white colour oil, yield 73% (64.38 mg); **¹H NMR** (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.3 Hz, 1H), 7.39 (m, 5H), 7.32 (m, 4H), 7.23 (m, 1H), 7.20 (m, 4H), 6.81 (d, *J* = 15.7 Hz, 1H), 5.95 (dd, *J* = 15.7, 9.2 Hz, 1H), 4.76 (d, *J* = 9.1 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 145.6, 144.6, 140.4, 137.4, 135.7, 133.3, 129.6, 129.5, 128.8, 128.6, 128.1, 127.6, 127.4, 126.9, 126.4, 125.7, 124.4, 120.6, 55.9; **IR (KBr)**: ν_{max} = 1766, 1645, 1455 cm⁻¹; **HRMS (ESI)**: *m/z* calcd for C₂₃H₁₇ [M-H]⁻: 293.1330, found: 293.1753.

7. Gram scale reaction

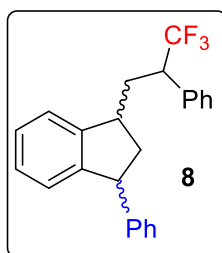
(*E*)-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1H-indene (**3aa**)



To a stirred solution of (*E*)-*tert*-butyl (4-(2-ethynyl phenyl)-1,1,1-trifluoro-2-phenyl but-3-en-2-yl) carbonate **1a** (1g, 2.48 mmol) in 10 mL of 1,4-dioxane was added phenylboronic acid **2a** (364 mg, 2.98 mmol) at room temperature. Then Pd(PPh₃)₄ (143 mg, 0.124 mmol, 5 mol%) and 20 mol% acetic acid were added to the reaction mixture, and stirring continued at 90 °C (oil bath temperature) for 10–12 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was diluted with water and extracted with ethyl acetate (3 X 15 mL). The combined organic layers were dried over sodium sulfate and concentrated on rotary evaporation. The obtained crude product was purified using flash column chromatography (using 9.5:0.5 hexane/ethyl acetate as eluent) to obtain the pure product (*E*)-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene **3aa**, in 78% yield (700.25 mg) as a yellow oil.

8. Synthetic utility of CF₃-benzofulvene (**3aa**)

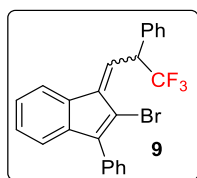
8.1 General procedure for the synthesis of 1-phenyl-3-(3,3,3-trifluoro-2-phenylpropyl)-2,3-dihydro-1*H*-indene (**8**)



To a the stirred solution of (*E*)-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene **3aa** (108.6, 0.30 mmol, 1.0 equiv) in 5 mL of methanol, was suspended palladium carbon (catalytic amount) and hydrogen gas was connected through a balloon. The reaction mixture was stirred vigorously at room temperature for 1h under N₂ atmosphere, completion of the reaction was monitored by TLC. The reaction mixture was diluted with the water, then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were finally washed with brine solution, dried over anhydrous Na₂SO₄, and then the solvent was removed under reduced pressure. The crude product **8** was further purified by column chromatography, pure compound **8** was obtained as a white colour oil; yield 70% (76.86 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.30 (m, *J* = 3.1, 2.6 Hz, 5H), 7.27 (m, 10H), 7.18 (m, 7H), 7.09 (m, 4H), 6.79 (t, *J* = 6.6 Hz, 2H), 4.04 (m, 1.9H, major + minor), 3.53 (m, 1H, major), 3.35 (m, 0.93H, minor), 2.76 (m, 2H, major), 2.62 (m, 0.96H, minor), 2.40 (m, 1H, major), 2.04 (m, 1H, minor), 1.61 (m, 1.96H, minor), 1.50 (m, 2H, major); ¹³C NMR (101 MHz, CDCl₃) δ 146.8, 146.7, 146.7, 146.4, 144.6, 144.5, 135.7, 134.1, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 127.1, 126.8, 126.7, 126.6, 126.2 (q, *J* = 282.3 Hz), 125.1, 125.1 (q, *J* = 275.4 Hz), 124.9, 123.1,

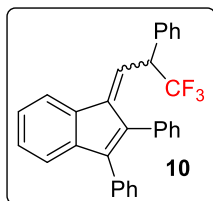
122.7, 50.5, 50.5, 49.4 (q, $J = 26.3$ Hz), 48.4 (q, $J = 26.7$ Hz), 44.95, 43.8, 42.1, 40.1, 35.1, 33.4, 29.8, 22.8, 14.3; ^{19}F NMR (377 MHz, CDCl_3) δ -69.05 (s, 3F), -70.06 (s, 3F); **IR (neat):** $\nu_{\text{max}} = 2974, 2926, 1760, 1489 \text{ cm}^{-1}$; **HRMS (ESI):** m/z calcd for $\text{C}_{24}\text{H}_{20}\text{F}_3$ [M-H]: 366.1572, found: 366.1575.

8.2 General procedure for the synthesis of 2-bromo-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-6-(trifluoromethyl)-1*H*-indene (9)



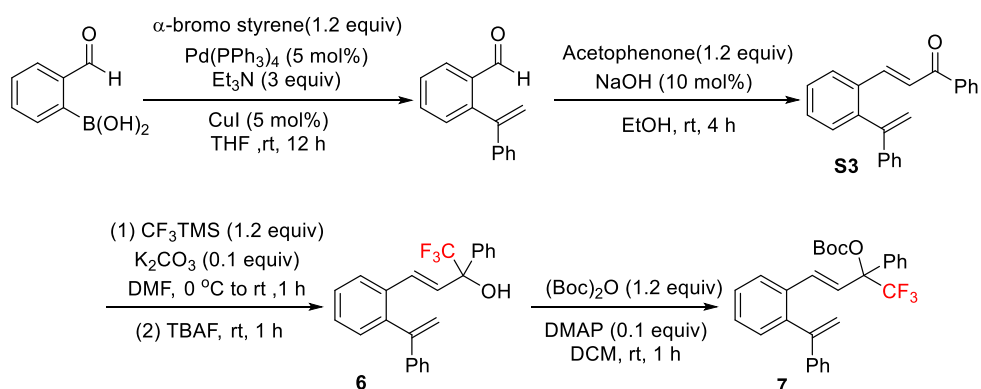
To a stirred solution of (*E*)-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene **3aa** (108 mg, 0.30 mmol, 1.0 equiv) in anhydrous carbon tetrachloride (5 mL) was added *N*-bromosuccinimide (53 mg, 0.30 mmol, 1 equiv) portion wise, the reaction mixture was stirred vigorously at room temperature for 1h under N_2 atmosphere. completion of the reaction was monitored by TLC. The reaction mixture was diluted with the water, then extracted with ethyl acetate (3×30 mL). The combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4 , and then the solvent was removed under reduced pressure. The crude was further purified by column chromatography to obtain the brominated product **9** as yellow colour oil; yield 72% (95.04 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.65 (m, $J = 5.9, 2.5$ Hz, 1H), 7.59 (m, 9H), 7.45 (m, 6H), 7.27 (m, 5H), 7.01 (d, $J = 10.9$ Hz, 1H, major), 6.94 (d, $J = 9.8$ Hz, 0.48H, minor), 6.12 (m, $J = 17.8, 8.9$ Hz, 1H, major), 5.13 (p, $J = 8.7$ Hz, 0.48H, minor); ^{13}C NMR (126 MHz, CDCl_3) δ 148.1 (major), 143.5 (minor), 143.3 (major), 141.3 (minor), 140.7 (major), 138.8 (minor), 136.8 (major), 134.8 (minor), 134.1 (major), 133.3 (minor), 133.1 (major), 133.0 (minor), 129.5, 129.3, 129.1, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.1, 128.1, 126.2, 126.1, 126.1 (d, $J = 280.7$ Hz, major), 125.9 (d, $J = 280.5$ Hz, minor), 124.3, 124.3, 123.3, 120.5, 120.1, 119.8, 118.9, 112.5, 49.4 (q, $J = 28.1$ Hz, minor), 46.2 (q, $J = 28.2$ Hz, major); ^{19}F NMR (377 MHz, CDCl_3) δ -68.76 (s, 3F), -69.56 (s, 3F); **IR (neat):** $\nu_{\text{max}} = 2974, 2926, 1760, 1489 \text{ cm}^{-1}$; **HRMS (ESI):** m/z calcd for $\text{C}_{24}\text{H}_{15}\text{BrF}_3$ [M-H] $^-$: 439.0315, found: 439.0317.

8.3 General procedure for the synthesis of 2,3-diphenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-6-(trifluoromethyl)-1*H*-indene (10)



To a stirred solution of 2-bromo-3-phenyl-1-(3,3,3-trifluoro-2-phenylpropylidene)-1*H*-indene **9** (103.2 mg, 0.24 mmol, 1 equiv) in 3 mL of toluene was added phenylboronic acid (35 mg, 0.28 mmol, 1.2 equiv) at room temperature. Then, Pd(PPh₃)₄ (13 mg, 0.01 mol, 0.05 equiv) and sodium carbonate (50 mg, 0.48 mmol, 2 equiv) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10–12 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was diluted with water and extracted with ethyl acetate (3 X 15 mL). The combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified using flash column chromatography (using 9.5:0.5 hexane/ethyl acetate as a eluent) to get the pure product **10** as a yellow colour oil; yield 75% (98.55 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.77 (m, 1H), 7.46 (m, 5H), 7.30 (m, 3H), 7.26 (m, 4H), 7.22 (m, 4H), 6.96 (m, 3H), 4.33 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 145.7, 142.9, 141.8, 137.4, 136.7, 135.9, 134.6, 134.0, 130.7, 129.3, 129.1, 128.7, 128.5, 128.3, 128.2, 127.8, 127.7, 126.1, 125.8 (q, *J* = 280.7 Hz), 122.9, 122.9, 120.5, 119.2, 47.2 (q, *J* = 28.0 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -68.89 (s, 3F); IR (neat): ν_{max} = 2974, 2926, 1760, cm⁻¹; HRMS (ESI): *m/z* calcd for C₃₀H₂₀F₃ [M-H]⁻: 437.1520, found: 437.1521.

9) General procedure for the synthesis of (*E*)-*tert*-butyl (1,1,1-trifluoro-2-phenyl-4-(2-(1-phenylvinyl)phenyl)but-3-en-2-yl) carbonate (**7**) (General procedure F)

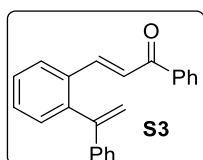


To a solution of (2-formylphenyl) boronic acid (1.5 g, 10 mmol) and α -bromo styrene (2.1 g, 12 mmol) in Et₃N (50 mL) at room temperature were added Pd(PPh₃)₄ (0.577 g, 0.5 mmol) and CuI (0.035 g, 1.89 mmol) under argon. The reaction mixture was stirred at room temperature

for 12 h, then filtered through a short pad of silica gel and washed with ethyl acetate. After the removal of solvent, the crude residue was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 100:1, v/v) to afford the desired product 2-(1-phenylvinyl)benzaldehyde (1.9 g, 95% yield).

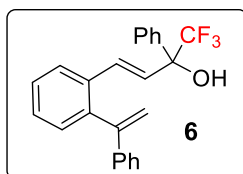
To a solution of 2-(1-phenylvinyl)benzaldehyde (1.04 g, 5 mmol) and acetophenone (0.60 g, 5 mmol) in MeOH (25 mL) at room temperature was added 10% NaOH aqueous solution (1.5 mL, 11.0 mmol). The reaction mixture was stirred at room temperature for 3 h, then the solution was quenched with water and extracted with EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3x 10 mL). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100:1 to 30:1, v/v) to afford **S3** (1.3 g, 85%).

(E)-1-Phenyl-3-(2-(1-phenylvinyl)phenyl)prop-2-en-1-one (S3)



Following general procedure **F**, 2-(1-phenylvinyl)benzaldehyde (104 mg, 0.50 mmol), acetophenone (60 mg, 0.50 mmol), aqueous NaOH solution (10%), were taken in 10 mL of methanol to obtain the compound **S3** as a red colour oil, yield 72% (102 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.82 (m, 4H), 7.44 (m, 5H), 7.30 (m, 7H), 5.89 (d, *J* = 3.2 Hz, 1H), 5.21 (d, *J* = 3.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 191.5, 147.6, 143.9, 143.4, 140.6, 138.2, 133.8, 132.5, 130.9, 130.2, 129.1, 128.6, 128.6, 128.1, 126.9, 126.8, 126.2, 123.9, 117.2; HRMS (ESI): *m/z* calcd for C₂₃H₁₉O [M+H]⁺: 311.1430, found: 311.1426.

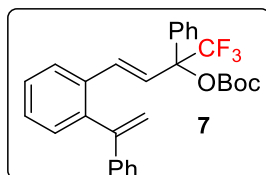
(E)-1,1,1-Trifluoro-2-phenyl-4-(2-(1-phenylvinyl)phenyl)but-3-en-2-ol (6)



Following general procedure **A**, (*E*)-1-Phenyl-3-(2-(1-phenylvinyl)phenyl)prop-2-en-1-one (**S3**) (93 mg, 0.30 mmol), TMSCF₃ (0.5 mL, 0.36 mmol), and K₂CO₃ (41 mg, 0.30 mmol) were taken in 3 mL of DMF. After that TBAF was added to obtain the compound **6** as a reddish colour oil, yield 69% (78.66 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.46 (m, 1H), 7.34 (m, 2H), 7.29 (m, 3H), 7.24 (m, 4H), 7.19 (m, 3H), 7.12 (m, 2H), 6.68 (m, 1H), 6.36 (d, *J* = 16.1 Hz,

1H), 5.67 (d, $J = 1.7$ Hz, 1H), 5.15 (d, $J = 3.6, 1.2$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 141.3, 141.2, 137.3, 134.6, 133.2, 130.7, 128.7, 128.5, 128.5, 128.3, 128.2, 127.9, 127.6, 127.2, 126.9, 126.3, 125.0 (q, $J = 286.1$ Hz), 116.6, 77.2 (q, $J = 29.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -76.39 (s, 3F); IR (neat): $\nu_{\text{max}} = 3285, 2925, 1492$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{O}$ $[\text{M}-\text{H}]^-$: 379.1374, found: 379.1375.

(E)-Tert-butyl(1,1,1-trifluoro-2-phenyl-4-(2-(1-phenylvinyl)phenyl)but-3-en-2-yl) carbonate (7)



Following general procedure A, (*E*)-4-(2-ethynyl-5-(trifluoromethyl)phenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol **6** (114 mg, 0.30 mmol), $(\text{Boc})_2\text{O}$ (0.08 mL, 0.36 mmol), and DMAP (36.6 mg, 0.30 mmol) were taken in 3 mL of DCM to obtain the compound **7** as a white solid, yield 78% (112.32 mg), mp: 65 – 66 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (m, 1H), 7.28 (m, 7H), 7.16 (m, $J = 6.9, 3.3$ Hz, 6H), 6.95 (m, 1H), 6.59 (d, $J = 16.5$ Hz, 1H), 5.75 (d, $J = 1.1$ Hz, 1H), 5.12 (d, $J = 1.1$ Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.9, 147.9, 141.6, 140.8, 135.3, 134.9, 134.7, 130.6, 129.0, 128.5, 128.5, 128.3, 128.0, 127.9, 127.1, 127.0, 126.1, 123.4 (d, $J = 285.0$ Hz), 122.8, 116.8, 83.5 (d, $J = 29.2$ Hz), 83.4, 27.7; ^{19}F NMR (376 MHz, CDCl_3) δ -83.87 (s, 3F); IR (KBr): $\nu_{\text{max}} = 2974, 2926, 1760, 1489$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3$ $[\text{M}-\text{OBoc}]^-$: 363.1355, found: 363.1354.

10. Reference

- (a) Rong, M.G.; Qin, T.Z.; Liu, X.R.; Wang, H.F.; Zi, W. De novo synthesis of phenols and naphthols through oxidative cycloaromatization of dienynes. *Organic letters*. **2018**, 26, 6289-93. (b) Kinoshita, H.; Miyama, C.; Miura, K.; Cyclization of alk-5-ynyl ketones promoted by Tf_2NH and $\text{In}(\text{OTf})_3$: selective synthesis of 5- and 7-membered carbocycles. *Tetrahedron Letters*. **2016**, 57, 5065-9. (c) Yousef, A.L.; Smith, A.G. Multistep Synthesis of a 3 (2 H)-Furanone Featuring a Green Aldol Condensation. *Journal of Chemical Education*. **2022**, 99, 946-51. (d) Wang, J.Y.; Zhang, S.; Tang, Y.; Yan, S.; Li, G. Copper-Catalyzed Annulation–Trifluoromethyl Functionalization of Enynones. *Organic Letters*. **2023**, 25, 2509-14.
- (a) Zhou, M.; Zhang, J.; Zhang, X.G.; Zhang, X. Ni-catalyzed defluorination for the synthesis of gem-difluoro-1, 3-dienes and their [4+ 2] cycloaddition reaction. *Organic letters*. **2019**, 21, 671-4. (b) Ortega, A.; Manzano, R.; Uria, U.; Carrillo, L.; Reyes, E.; Tejero, T.; Merino, P.; Vicario, J.L.; Catalytic Enantioselective Cloke–Wilson Rearrangement. *Angewandte Chemie*.

2018, 130, 8357-61. (c) Priyanka, C.; Subbarao.; Punna, N. Palladium-catalyzed ortho-vinylation of β -naphthols with α -trifluoromethyl allyl carbonates: one-pot access to naphtho [2, 1-*b*] furans. *Organic & Biomolecular Chemistry*. **2021**, 19, 8241-5

11. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectral copies of compounds

