Supporting Information

Cobalt(III)-Catalyzed Direct *ortho*-Alkenylation of Arylpyrazoles: A Comparative Study on Decarboxylation and Desilylation

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ejoc201900270-sup-0001-SupMat.pdf

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General experimental

General Information. All reactions were carried out using distilled solvents. Reactions were monitored by using precoated silica TLC plates. Mass spectra were recorded on EI, and ESI (TOF) modes. NMR spectra were recorded in at 400 MHz spectrometers in CDCl₃, DMSO-d₆, tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard for ¹H NMR. The corresponding residual non-deuterated solvent signal (CDCl₃; δ = 77.00 ppm and DMSO-d₆; δ = 39.52 ppm) was used as internal standard for ¹³C NMR. Column chromatography was carried out on silica gel 230-400 mesh or 100-200 mesh (Merck) and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from commercial suppliers were used without further purification. All arylpyrazoles derivatives,^[1] arylalkynyl carboxylic acid derivatives^[2], arylalkynyl silane derivatives,^[3] silver phenylacetylide,^[4] and cobalt catalysts^[5] were prepared according to reported literature procedure.

Detailed optimization studies:

Table S1. Survey of the reaction parameters with MnBr(CO)₅ catalyst. ^[a,b]

Reaction scheme: **1a** + **2a** $\xrightarrow[\text{solvent, T (°C), time (h)}]{[\text{Mn}] \text{ (mol\%)}, \text{additive (equiv)}} \text{3aa}$

Entry	[Mn] (mol%)	Additive (equiv)	Solvent	Time (h)	Temp. (°C)	NMR yield (%)
1	-	NaOAc (0.2)	DCE	12	100	nd
2	10	-	DCE	12	100	nd
3	10	NaOAc (1.0)	DCE	12	100	20
4	5	NaOAc (1.0)	DCE	12	100	18
5	2.5	NaOAc (1.0)	DCE	12	100	trace
6	10	NaOAc (0.2)	DCE	12	100	23
7	10	NaOAc (0.2)	DCE	12	80	trace
8	10	NaOAc (0.2)	TFE	16	100	nd
9	10	NaOAc (0.2)	dioxane	16	100	trace
10	10	NaOAc (0.2)	acetone	16	100	12
11	10	NaOAc (0.2)	Et ₂ O	16	100	nd
12	10	NaOAc (0.2)	THF	16	100	10
13	10	NaOAc (0.2)	DCM	16	100	18
14	10	NaOAc (0.2)	toluene	16	100	34
15	10	NaOAc (0.2)	DMF	16	100	nd
16	10	NaOAc (0.2)	ACN	16	100	trace
17	10	NaOAc (0.2)	H ₂ O	16	100	trace
18	10	KOAc (0.2)	toluene	16	100	trace
19	10	AdCO ₂ H (0.4)	toluene	16	100	nd
20	10	NaOPiv.H ₂ O (0.2)	toluene	16	100	15
21	10	CsOPiv (0.2)	toluene	16	100	trace
22	10	CsOAc (0.2)	toluene	16	100	19
23	10	LiOAc (0.2)	toluene	16	100	nd
24	10	CF ₃ CO ₂ Na (0.2)	toluene	16	100	nd
25	10	Cy ₂ NH (0.2)	toluene	16	100	nd
26	10	Et ₃ N (0.2)	toluene	16	100	nd
27	10	DIPEA (0.2)	toluene	16	100	nd

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [Mn] = bromopentacarbonylmanganese(I)-catalyst MnBr(CO)₅ (mol%), additive (equiv), solvent (2 mL) at temperature (°C) for given time. [b] ¹H NMR yield (using terephthalaldehyde as an internal standard). AdCO₂H = 1-adamantane carboxylic acid. nd = not detected.

Table S2. Survey of the reaction parameters with Cp*Co(CO)I₂ catalyst.^[a,b]

$\text{1a} + \text{Ph}-\text{C}\equiv\text{C}-\text{SiMe}_3 \xrightarrow[\text{solvent, T(}^\circ\text{C), time (h)}]{[\text{Co}] (5 \text{ mol\%}), \text{AgSbF}_6 (20 \text{ mol\%}), \text{additive (equiv)}} \text{3aa}$

Entry	[Co] (5 mol%)	Additive (equiv)	Solvent	Time (h)	Temp. (°C)	NMR yield (%)
1	5	AdCO ₂ H (1.0)	DCE	2	100	75
2	5	NaOAc (0.2)	DCE	2	100	36
3	5	CH ₃ CO ₂ H (1.0)	TFE	2	100	75
4	5	CH ₃ CO ₂ H (1.0)	TFE	3	100	82
5	5	CH ₃ CO ₂ H (2.0)/ CsF (1.0)	TFE	3	100	83
6	5	PTSA (1.0)	TFE	3	100	10
7	5	CH ₂ (COOH) ₂ (1.0)	TFE	3	100	82
8	5	(CH ₃) ₃ CCO ₂ H (2.0)	TFE	3	100	77
9	5	Cl ₃ CCO ₂ H (2.0)	TFE	3	100	83
10	5	Cl₃CCO₂H (1.0)	TFE	3	100	86 (83)^c
11	5	Cl ₃ CCO ₂ H (0.2)	TFE	3	100	47
12	5	F ₃ CCO ₂ H (1.0)	TFE	3	100	82
13 ^d	5 [Ru]	Cl ₃ CCO ₂ H (1.0)	TFE	3	100	44
14 ^e	5 [Rh]	Cl ₃ CCO ₂ H (1.0)	TFE	3	100	51
15 ^f	10 [Mn]	Cl ₃ CCO ₂ H (1.0)	TFE	3	100	nd

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), cobalt catalyst [Co] = Cp*Co(CO)I₂ (5 mol%), AgSbF₆ (20 mol%), additive (equiv), solvent (2 mL) at 100 °C for given time (h). [b] ¹H NMR yield (using terephthalaldehyde as an internal standard). [c] Isolated yield. [d] 5 mol% of [Ru(*p*-cymene)Cl₂]₂ was used as a catalyst. [e] 5 mol% of [RhCp*Cl₂]₂ was used as a catalyst. [f] 10 mol % of MnBr(CO)₅ was used as a catalyst.

Table S3. Survey of the reaction parameters.^[a,b]

$\text{1a} + \text{H}-\text{C}\equiv\text{C}-\text{CO}_2\text{H} \xrightarrow[\text{solvent, T(}^\circ\text{C), time(h)}]{[\text{Co}] (5 \text{ mol\%}), \text{AgSbF}_6 (20 \text{ mol\%}), \text{additive (X equiv)}} \text{6aa}$

Entry	[Co] (mol %)	Additive (equiv)	Solvent	Time (h)	Temp. (°C)	NMR yield (%)
1	5	NaOAc (0.2)	TFE	3	100	25
2 ^c	5	NaOAc (0.2)	TFE	3	100	18
3	5	NaOAc (0.2)	TFE	3	120	25
4	5	NaOAc (1.0)	DCE	3	100	20
5	5	NaOH (1.0)	TFE	3	100	15

[a] Reaction conditions: **1a** (0.3 mmol), **5a** (0.36 mmol), cobalt catalyst [Co] = [Cp*Co(CO)I₂] (5 mol%), AgSbF₆ (20 mol%), additive (equiv), solvent (3 mL) for 3 h at given temperature. [b] ¹H NMR yield (using terephthalaldehyde as an internal standard). [c] 0.6 mmol of **5** was used.

Table S4. Survey of the reaction parameters.^[a,b]

$\text{1a} + \text{H}-\text{C}\equiv\text{C}-\text{SiMe}_3 \xrightarrow[\text{Solvent, T(}^\circ\text{C), Time(h)}]{\begin{matrix} [\text{Co}] (5 \text{ mol}\%) \\ \text{AgSbF}_6 (20 \text{ mol}\%) \\ \text{Additive (X equiv)} \end{matrix}} \text{6aa}$

Entry	[Co] (mol%)	Additive (equiv)	Solvent	Time (h)	Temp. (°C)	NMR yield (%)
1	5	CH ₃ CO ₂ H (3.0)	TFE	3	100	50
2	5	CH ₃ CO ₂ H (10.0)	TFE	3	100	50
3	5	Cl ₃ CCO ₂ H (2.0)	TFE	3	100	56
4	5	Cl₃CCO₂H (1.0)	TFE	3	100	58 (51%)^c
5	5	CH ₃ CO ₂ H (2.4)/ CsF (1.2)	TFE	3	100	27
6	5	CCl ₃ CO ₂ H (2.0)	TFE	6	80	25
7	5	CCl ₃ CO ₂ H (2.0)	TFE	6	120	54
8	5	CCl ₃ CO ₂ H (2.0)	TFE	3	140	44
9	10	Cl ₃ CCO ₂ H (2.0)	TFE	3	100	56
10	5	Cl ₃ CCO ₂ H (2.0)	TFE (degassed)	3	100	56
11	5	Cl ₃ CCO ₂ H (2.0)	TFE (0.5 mL)	3	100	52
12	5	NH ₄ Cl (1.2)	TFE	3	100	nd
13	5	H ₂ O (5.0)	TFE	3	100	nd
14	5	F ₃ CCO ₂ H (2.0)	TFE	3	100	52
15	5	none	TFE	3	100	15
16	5	AdCO ₂ H (2.0)	TFE	3	100	40
17	5	HCO ₂ H (2.0)	TFE	3	100	52
18	5	PhCO ₂ H (2.0)	TFE	3	120	56
19	5	CCl ₃ CO ₂ H (2.0)	THF	6	100	30
20	5	Cl ₃ CCO ₂ H (2.0)	toluene	6	100	35
21	5	Cl ₃ CCO ₂ H (2.0)	Et ₂ O	6	100	30
22	5	Cl ₃ CCO ₂ H (2.0)	DMF	6	100	nd
23	5	Cl ₃ CCO ₂ H (2.0)	DME	3	100	10
24	5	H—C≡C—CO ₂ H (1.0)	TFE	3	100	traces

[a] Reaction conditions: **1a** (0.3 mmol), **5a'** (0.36 mmol), cobalt catalyst [Co] = [Cp*Co(CO)I₂] (5 mol%), AgSbF₆ (20 mol%), Additive (equiv.), solvent (2 mL) at given time (h) and temperature. [b] ¹H NMR yield (using terephthalaldehyde as an internal standard). [c] Isolated yield. nd = not detected. AdCOOH = 1-adamantane carboxylic acid.

Scheme S1: Scope for 1-phenylpyrazole derivatives with trimethylsilylacetylene.^[a,b]

[a] Reaction conditions: **1** (0.3 mmol), **5a'** (0.36 mmol), $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ (5 mol%), AgSbF_6 (20 mol%), $\text{Cl}_3\text{CCO}_2\text{H}$ (1.0 equiv), TFE (3 mL), at 100 °C for 3 h. [b] ^1H NMR yields (measured by using terephthalaldehyde or 1,3,5-trimethoxybenzene as an internal standard).

The *ortho*-alkenylated products, **6ga-6ka**, are inseparable mixture with corresponding 1-phenylpyrazole derivatives in both solvent system (ethyl acetate/petroleum ether or dichloromethane/petroleum ether). Therefore, crude sample of ^1H NMR spectras have been provided for **6ga-6ka** molecules.

1,3,5-Trimethoxybenzene as an internal standard (0.1 mmol)

6fa = 0.31 X 100 = 31%

Scheme S2: Unsuccessful Substrates for *ortho*-alkenylation.^[a]

[a] The desired *ortho*-alkenylated products were not detected.

Mechanistic studies

H/D-Exchange reaction

In a 8-mL screw cap reaction vial, 1-(4-methylphenyl)pyrazole **1c** (160 mg, 10.0 mmol), D₂O (10 equiv), cobalt catalyst Cp*CoCOI₂ (5 mol %), NaOAc (20 mol %), AgSbF₆ (20 mol %) were added followed by the addition of DCE (6 mL). This vial was sealed with a screw cap, placed on a pre-heated metal block at 100 °C for 24 h and cooled to room temperature and the crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1) to yield 81% **deuterio-1c** as a brown liquid (157 mg, 98%). Deuterium incorporation was estimated by ¹H-NMR analysis (See the following ¹H NMR spectra).

Deuterium incorporation reaction

In a 8-mL screw cap reaction vial, 1-(4-methylphenyl)pyrazole **1c** (32 mg, 0.2 mmol), **2a'** (42 mg, 0.24 mmol), cobalt catalyst $\text{Cp}^*\text{CoCOI}_2$ (4.8 mg, 5 mol %), CD_3COOD (12.0 mg, 1.0 mmol), AgSbF_6 (13.4 mg, 20 mol %) were added followed by the addition of DCE (2 mL). This vial was sealed with a screw cap, placed on a pre-heated metal block at 100 °C for 3 h and cooled to room temperature and concentrated to yield the crude product, which was further purified by flash chromatography (EtOAc/petroleum ether, 2:98) to furnish the product. The product was obtained with 10% of deuterium incorporation at the alkene carbon. The deuterium incorporation was calculated by ^1H NMR analysis (See the following ^1H NMR spectra).

Kinetic isotopic effect experiment

In an 8-mL screw cap reaction vial, 1:1 ratio of **1a-d₂** (100% D) [ie. by weighing 0.25 mmol of **deuterio-1c** 81% D, which contains 0.2 mmol of **1a-d₂** (100% D) and 0.05 mmol of **1a**] and **1a** (0.15 mmol) were taken. (Now the reaction vial contains 0.2 mmol of each of **1a** and **1a-d₂** (100% D)). Then **2a** (35 mg, 0.24 mmol), cobalt catalyst $\text{Cp}^*\text{CoCOI}_2$ (4.8 mg, 5 mol%), NaOAc (3.3 mg, 20 mol%), AgSbF_6 (13.4 mg, 20 mol %) were added followed by the addition of DCE (2 mL). This vial was sealed with a screw cap, placed on a pre-heated metal block at $100\text{ }^\circ\text{C}$ for 3 h and cooled to room temperature and concentrated to yield the crude product, which was further purified by flash chromatography (EtOAc /petroleum ether, 2:98) to furnish the product **deuterio-3ca** in 65% yield. The KIE was calculated from ^1H NMR analysis (See the following ^1H NMR spectra).

Competitive experiment with aryl pyrazoles

In a 8-mL screw cap reaction vial, **3h** (34.8 mg, 0.2 mmol), **3j** (37.2 mg, 0.2 mmol), **2a** (35.0 mg, 0.24 mmol), cobalt catalyst $\text{Cp}^*\text{CoCOI}_2$ (4.8 mg, 5 mol %), CD_3COOD (12.0 mg, 1.0 equiv), AgSbF_6 (13.4 mg, 20 mol %) were added followed by the addition of TFE (2 mL). This vial was sealed with a screw cap, placed on a pre-heated metal block at 100 °C for 3 h, cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuum. The crude products were submitted directly for ^1H NMR analysis for calculating the NMR yields (terephthalaldehyde (0.1 mmol, 13.4 mg) has been used as an internal standard, see the following ^1H NMR spectra). Aromatic protons were not assigned to individual products due to the intrinsic complexity of the spectrum.

In a 8-mL screw cap reaction vial, **3h** (34.8 mg, 0.2 mmol), **3j** (37.2 mg, 0.2 mmol), **2a** (35.0 mg, 0.24 mmol), cobalt catalyst $\text{Cp}^*\text{CoCOI}_2$ (4.8 mg, 5 mol %), NaOAc (3.3 mg, 0.2 mmol), AgSbF_6 (13.4 mg, 20 mol %) were added followed by the addition of TFE (2 mL). This vial was sealed with a screw cap, placed on a pre-heated metal block at 100 °C for 3 h and cooled to room temperature filtered through a silica pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuum. The crude products were submitted directly for ^1H NMR analysis for calculating the NMR yields (terephthalaldehyde (0.1 mmol, 13.4 mg) has been used as an internal standard, see the following ^1H NMR spectra). Aromatic protons were not assigned to individual products due to the intrinsic complexity of the spectrum.

Characterization data for products

(E)-1-(2-Styrylphenyl)-1H-pyrazole (3aa). Colorless oil; Yield - (42.0 mg, 85%); R_f (10% EtOAc/Petroleum Ether) 0.50; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3140, 3055, 3029, 2955, 2924, 2361, 2336, 1598, 1493, 1458, 1392, 1328, 1218; **^1H NMR** (400 MHz, CDCl_3): δ 6.55 (t, $J = 2.02$ Hz, 1 H) 7.02 (d, $J = 16.28$ Hz, 1 H) 7.13 (d, $J = 16.28$ Hz, 1 H) 7.31 - 7.43 (m, 3 H) 7.45 - 7.54 (m, 5 H) 7.74 (d, $J = 1.77$ Hz, 1 H) 7.84 - 7.86 (m, 2 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 106.6, 123.9, 126.3, 126.5, 126.7, 127.9, 128.1, 128.4, 128.6, 131.2, 133.0, 137.0, 138.7, 140.7; **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{14}\text{N}_2$ ($M + \text{Na}$): 269.1055, found ($M + \text{Na}$): 269.1058.

(E)-1-(2-Methyl-6-styrylphenyl)-1H-pyrazole (3ba). Colorless oil; Yield - (38.0 mg, 73%); R_f (10% EtOAc/Petroleum Ether) 0.50; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3052, 3030, 2956, 2923, 2853, 2361, 1594, 1511, 1470, 1390, 963; **^1H NMR** (400 MHz, CDCl_3) δ 2.05 (s, 3H) 6.43 (d, $J = 16.32$ Hz, 1 H) 6.48 - 6.49 (m, 1 H) 6.97 (d, $J = 16.32$ Hz, 1 H) 7.21 - 7.23 (m, 2 H) 7.26 - 7.31 (m, 4 H) 7.36 (t, $J = 7.64$ Hz, 1 H) 7.50 (d, $J = 2.02$ Hz, 1 H) 7.62 (d, $J = 7.58$ Hz, 1 H) 7.79 - 7.80 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 17.4, 106.2, 123.3, 126.6, 127.9, 128.6, 129.2, 129.7, 131.2, 131.8, 135.8, 136.7, 137.0, 138.0, 140.4; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2$ ($M + \text{Na}$): 283.1211, found ($M + \text{Na}$): 283.1215.

(E)-1-(4-Methyl-6-styrylphenyl)-1H-pyrazole (3ca). Colorless oil; Yield - (48.0 mg, 92%); R_f (20% EtOAc/Petroleum Ether) 0.60; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3107, 3052, 3028, 2955, 2923, 2855, 2361, 2336, 1724, 1514, 1393, 963; **^1H NMR** (400 MHz, CDCl_3) δ 2.45 (s, 3H) 6.45 (t, $J = 1.92$ Hz, 1H) 6.89 (d, $J = 16.28$ Hz, 1 H) 7.03 (d, $J = 16.28$ Hz, 1 H) 7.17 (d, $J = 8.0$ Hz 1 H) 7.22 - 7.25 (m, 1 H) 7.29-7.33 (m, 3 H) 7.38 (d, $J = 7.32$ Hz, 2 H) 7.57 (s, 1H) 7.62 (d, $J = 2.16$ Hz, 1 H) 7.76 - 7.77 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 21.2, 106.4, 123.9, 126.2, 126.6, 126.8, 127.8, 128.6, 128.9, 130.9, 131.6, 132.7, 136.5, 137.1, 138.3, 140.5; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2$ ($M + \text{Na}$): 283.1211, found ($M + \text{Na}$): 283.1209.

(E)-1-(5-Chloro-2-styrylphenyl)-1H-pyrazole (3da). Dark yellow oil; Yield - (40.0 mg, 71%); R_f (20% EtOAc/Petroleum Ether) 0.45; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3057, 3027, 2923, 2851, 2362, 2336, 1594, 1514, 1493, 1399; **^1H NMR** (400 MHz, CDCl_3) δ 6.48 (t, $J = 2.15$ Hz, 1 H) 6.91 (d, $J = 16.28$ Hz, 1 H) 7.03 (d, $J = 16.28$ Hz, 1 H) 7.22 - 7.27 (m, 1 H) 7.32 (t, $J = 7.33$ Hz, 2 H) 7.37 - 7.40 (m, 3 H) 7.49 (d, $J = 2.27$ Hz, 1 H) 7.66 - 7.70 (m, 2 H) 7.78 (d, $J = 1.77$ Hz, 1 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 107.0, 122.9, 126.3, 126.7, 127.7, 128.2, 128.5, 128.7, 131.3, 131.5, 131.7, 133.4, 136.7, 139.3, 141.2; **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{Cl}$ ($M + \text{Na}$): 303.0665, found ($M + \text{Na}$): 303.0669.

(E)-1-(2-Fluoro-6-styrylphenyl)-1H-pyrazole (3ea). Light yellow solid; Yield - (43.5 mg, 82%); *mp*: 114-116 °C; *R_f* (10% EtOAc/Petroleum Ether) 0.4; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3053, 3028, 2923, 2852, 2361, 1608, 1578, 1476, 1390, 1237; **¹H NMR** (400 MHz, CDCl_3) δ 6.51 (s, 1 H) 6.68 (d, J = 16.36 Hz, 1 H) 7.03 (d, J = 16.36 Hz, 1 H) 7.12 (t, J = 8.72 Hz, 1 H) 7.22 - 7.25 (m, 1 H) 7.28 - 7.35 (m, 4 H) 7.37 - 7.42 (m, 1 H) 7.56 - 7.61 (m, 2 H) 7.83 (s, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 106.7, 114.8 ($J_{\text{C-F}}$ = 20.4 Hz), 121.3 ($J_{\text{C-F}}$ = 3.4 Hz), 122.3 ($J_{\text{C-F}}$ = 3.2 Hz), 126.7, 126.8, 128.2, 128.6, 129.8 ($J_{\text{C-F}}$ = 8.6 Hz), 132.5 ($J_{\text{C-F}}$ = 14.4 Hz), 136.6, 137.5, 141.1, 157.9 ($J_{\text{C-F}}$ = 249.5 Hz); **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{F}$ ($M + \text{Na}$): 287.0960, found ($M + \text{Na}$): 287.0960.

(E)-1-(4-Fluoro-2-styrylphenyl)-1H-pyrazole (3fa). Light brown solid; Yield - (46.5 mg, 88%); *mp*: 66-68 °C; *R_f* (10% EtOAc/Petroleum Ether) 0.5; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3058, 2921, 2851, 2361, 2357, 1636, 1610, 1585, 1496, 1394, 1268, 966; **¹H NMR** (400 MHz, CDCl_3) δ 6.48 (t, J = 2.15 Hz, 1 H) 6.82 (dd, J = 16.04, 1.26 Hz, 1 H) 7.02 - 7.08 (m, 2 H) 7.25 - 7.42 (m, 6 H) 7.45 (dd, J = 9.85, 2.78 Hz, 1 H) 7.61 (d, J = 2.02 Hz, 1 H) 7.77 (d, J = 1.52 Hz, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 106.7, 112.6 ($J_{\text{C-F}}$ = 23.2 Hz), 114.9 ($J_{\text{C-F}}$ = 23.1 Hz), 122.7, 126.8, 128.3 ($J_{\text{C-F}}$ = 4.3 Hz), 128.4 ($J_{\text{C-F}}$ = 4.6 Hz), 128.7, 131.7, 132.4, 134.9, 135.5 ($J_{\text{C-F}}$ = 8.3 Hz), 136.5, 140.8, 162.3 ($J_{\text{C-F}}$ = 246 Hz); **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{F}$ ($M + \text{Na}$): 287.0960, found ($M + \text{Na}$): 287.0961.

(E)-1-(5-Methoxy-2-styrylphenyl)-1H-pyrazole (3ga). Light yellow oil; Yield - (26.0 mg, 47%); *R_f* (20% EtOAc/Petroleum Ether) 0.45; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3055, 2928, 2841, 2361, 2336, 1604, 1513, 1289, 1044; **¹H NMR** (400 MHz, CDCl_3) δ 3.84 (s, 3 H) 6.47 (s, 1 H) 6.85 - 6.70 (m, 4 H) 7.19 - 7.24 (m, 1 H) 7.28 (t, J = 7.45 Hz, 2 H) 7.36 - 7.38 (m, 2 H) 7.66 - 7.68 (m, 2 H) 7.78 (s, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 55.6, 106.6, 110.7, 115.3, 123.6, 125.2, 126.4, 127.6, 127.7, 128.6, 129.3, 131.7, 137.3, 139.5, 140.7, 159.5; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$ ($M + \text{Na}$): 299.1160, found ($M + \text{Na}$): 299.1157.

(E)-1-(4-Methoxy-2-styrylphenyl)-1H-pyrazole (3ha). White solid; Yield - (42.5 mg, 77%); *mp*: 73-75 °C; *R_f* (10% EtOAc/Petroleum Ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3055, 3025, 2957, 2928, 2841, 2361, 2336, 1604, 1576, 1513, 1288, 1220, 1044, 963; **¹H NMR** (400 MHz, CDCl_3) δ 3.90 (s, 3 H) 6.44 (t, J = 2.02 Hz, 1 H) 6.82 (d, J = 16.28 Hz, 1 H) 6.90 (dd, J = 8.59, 2.78 Hz, 1 H) 7.01 (d, J = 16.28 Hz, 1 H) 7.22 - 7.25 (m, 2 H) 7.29 - 7.38 (m, 5 H) 7.58 (d, J = 2.27 Hz, 1 H) 7.75 (d, J = 1.52 Hz, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 55.6, 106.3, 110.8, 113.7, 123.6, 126.7, 127.8, 128.0, 128.6, 131.4, 131.7, 132.4, 134.6, 136.8, 140.4, 159.4; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$ ($M + \text{Na}$): 299.1160, found ($M + \text{Na}$): 299.1163.

(E)-4-(1H-Pyrazol-1-yl)-3-styrylbenzonitrile (3ia). Off-white solid; Yield - (41.0 mg, 76%); *mp*: 129-131 °C; *R_f* (20% EtOAc/Petroleum Ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3059, 3025, 2923, 2852, 2230, 1601, 1518, 1494, 1394, 1334; **¹H NMR** (400 MHz, CDCl_3) δ 6.53 (t, $J = 2.15$ Hz, 1 H) 7.02 (d, $J = 16.32$ Hz, 1 H) 7.12 (d, $J = 16.32$ Hz, 1 H) 7.26 - 7.38 (m, 3 H) 7.43 - 7.44 (m, 2 H) 7.60 - 7.66 (m, 2 H) 7.73 (d, $J = 2.27$ Hz, 1 H) 7.82 (d, $J = 1.26$ Hz, 1 H) 8.03 - 8.04 (m, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 107.8, 111.9, 118.1, 122.3, 126.6, 126.9, 128.7, 128.8, 131.2, 131.4, 133.4, 133.5, 136.1, 141.5, 141.9; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{13}\text{N}_3$ ($M + \text{Na}$): 294.1007, found ($M + \text{Na}$): 294.1008.

(E)-1-(4-(1H-Pyrazol-1-yl)-3-styrylphenyl)ethan-1-one (3ja). Colorless Oil; Yield - (36.3 mg, 63%); *R_f* (30% EtOAc/Petroleum Ether) 0.4; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3057, 3022, 2923, 2853, 1684, 1599, 1495, 1395, 1283; **¹H NMR** (400 MHz, CDCl_3) δ 2.69 (s, 3 H) 6.51 (t, $J = 1.84$ Hz, 1 H) 7.07 (d, $J = 16.28$ Hz, 1 H) 7.18 (d, $J = 16.28$ Hz, 1 H) 7.29 (d, $J = 7.07$ Hz, 1 H) 7.35 (t, $J = 7.45$ Hz, 2 H) 7.44 (d, $J = 7.33$ Hz, 2 H) 7.59 (d, $J = 8.08$ Hz, 1 H) 7.74 (d, $J = 2.27$ Hz, 1 H) 7.81 - 7.82 (m, 1 H) 7.94 (dd, $J = 8.34, 1.77$ Hz, 1 H) 8.35 - 8.36 (m, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 26.8, 107.3, 123.4, 126.0, 126.8, 127.2, 128.0, 128.3, 128.7, 131.4, 132.4, 132.5, 136.3, 136.6, 141.5, 141.9, 197.2; **HRESI-MS** (m/z): Calculated for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}$ ($M + \text{Na}$): 311.1160, found ($M + \text{Na}$): 311.1162.

(E)-1-(4-Nitro-2-styrylphenyl)-1H-pyrazole (3ka). Yellow solid; Yield - (20.4 mg, 35%); *mp*: 141-143 °C; *R_f* (20% EtOAc/Petroleum Ether) 0.50; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3084, 3028, 2923, 2855, 2362, 2337, 1610, 1576, 1523, 1319, 1344, 1338; **¹H NMR** (400 MHz, CDCl_3) δ 6.55 (t, $J = 2.02$ Hz, 1 H) 7.09 (d, $J = 16.24$ Hz, 1 H) 7.20 - 7.26 (m, 1 H) 7.29 - 7.39 (m, 3 H) 7.45 - 7.47 (m, 2 H) 7.67 (d, $J = 8.59$ Hz, 1 H) 7.77 (d, $J = 2.53$ Hz, 1 H) 7.84 (d, $J = 1.52$ Hz, 1 H) 8.20 (dd, $J = 8.84, 2.53$ Hz, 1 H) 8.62 (d, $J = 2.53$ Hz, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 107.9, 122.3, 122.4, 122.7, 126.6, 127.0, 128.8, 131.5, 133.3, 133.9, 136.0, 142.1, 142.8, 146.9; **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2$ ($M + \text{Na}$): 314.0905, found ($M + \text{Na}$): 314.0903.

(E)-2-(2-Styrylphenyl)pyridine (3la). Yellow Oil; Yield - (19.1 mg, 37%); *R_f* (10% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (b). **IR** (Neat, cm^{-1}): 2362, 2335, 1647; **¹H NMR** (400 MHz, CDCl_3) δ 7.05 (d, $J = 16.2$ Hz, 1 H), 7.20 - 7.32 (m, 5 H), 7.36 - 7.46 (m, 5 H), 7.54 - 7.56 (m, 1 H), 7.71 - 7.77 (m, 2 H), 8.75 (d, $J = 4.58$ Hz, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 121.8, 125.0, 126.2, 126.6, 127.5, 128.6, 128.7, 130.1, 130.2, 135.7, 136.0, 137.5, 139.5, 149.5, 158.8; **HRESI-MS** (m/z): Calculated for $\text{C}_{19}\text{H}_{15}\text{N}$ ($M + \text{H}$): 258.1283, found ($M + \text{H}$): 258.1281.

(E)-1-(2-(4-Methylstyryl)phenyl)-1H-pyrazole (4aa). Light yellow oil; Yield - (35.0 mg, 67%); R_f (10% EtOAc/Petroleum Ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3025, 2920, 2852, 1597, 1514, 1488, 1392; **^1H NMR** (400 MHz, CDCl_3) δ 2.33 (s, 3 H) 6.46 (s, 1 H) 6.88 (d, $J = 16.28$ Hz, 1 H) 7.02 (d, $J = 16.28$ Hz, 1 H) 7.12 (d, $J = 7.84$ Hz, 2 H) 7.29 (d, $J = 7.92$ Hz, 2 H) 7.33 - 7.45 (m, 3 H) 7.64 - 7.65 (m, 1 H) 7.74 - 7.77 (m, 2 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 21.2, 106.5, 122.8, 126.3, 126.4, 126.6, 127.9, 128.3, 129.3, 131.2, 131.5, 133.1, 134.2, 137.9, 138.6, 140.7; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2$ ($M + \text{Na}$): 283.1211, found ($M + \text{Na}$): 283.1212.

(E)-1-(2-(4-Methoxystyryl)phenyl)-1H-pyrazole (4ab). Light yellow semi-solid; Yield - (40.0 mg, 72%); R_f (10% EtOAc/Petroleum Ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3055, 2928, 2841, 2361, 2336, 1604, 1513, 1289, 1044; **^1H NMR** (400 MHz, CDCl_3) δ 3.80 (s, 3 H) 6.46 (s, 1 H) 6.79 (d, $J = 16.24$ Hz, 1 H) 6.85 (d, $J = 8.60$ Hz, 2 H) 7.00 (d, $J = 16.24$ Hz, 1 H) 7.32 - 7.35 (m, 3 H) 7.38 - 7.44 (m, 2 H) 7.65 (s, 1 H) 7.74 - 7.77 (m, 2 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 55.3, 106.5, 114.1, 121.6, 126.3, 126.4, 127.7, 127.9, 128.4, 129.8, 130.7, 131.5, 133.3, 128.5, 140.6, 159.5; **HRESI-MS** (m/z): Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$ ($M + \text{Na}$): 299.1160, found ($M + \text{Na}$): 299.1161.

(E)-1-(2-(4-Fluorostyryl)phenyl)-1H-pyrazole (4ac). Light yellow oil; Yield - (46.0 mg, 87%); R_f (10% EtOAc/Petroleum Ether) 0.50; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3064, 3041, 2925, 2388, 2285, 1598, 1510, 1393, 1230; **^1H NMR** (400 MHz, CDCl_3) δ 6.47 - 6.48 (m, 1 H) 6.85 (d, $J = 16.24$ Hz, 1 H) 6.98 - 7.02 (m, 3 H) 7.34 - 7.44 (m, 5 H) 7.65 (s, 1 H) 7.74 - 7.78 (m, 2 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 106.6, 115.6 ($J_{\text{C-F}} = 21.5$ Hz), 123.6 ($J_{\text{C-F}} = 2.2$ Hz), 126.4 ($J_{\text{C-F}} = 9.3$ Hz), 128.13, 128.15, 128.2, 128.4, 129.9, 131.5, 132.9, 133.2 ($J_{\text{C-F}} = 3.4$ Hz), 138.7, 140.7, 162.4 ($J_{\text{C-F}} = 246.2$ Hz); **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{F}$ ($M + \text{Na}$): 287.0960, found ($M + \text{Na}$): 287.0957.

(E)-1-(2-(4-Bromostyryl)phenyl)-1H-pyrazole (4ad). Off-white solid; Yield - (54.0 mg, 83%); **mp**: 83-85 $^{\circ}\text{C}$; R_f (20% EtOAc/Petroleum Ether) 0.5; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3138, 3052, 2921, 2851, 1514, 1490, 1393, 1327; **^1H NMR** (400 MHz, CDCl_3) δ 6.48 (t, $J = 2.02$ Hz, 1 H) 6.95 (d, $J = 4.29$ Hz, 2 H) 7.23 - 7.25 (m, 2 H) 7.37 - 7.44 (m, 5 H) 7.65 (d, $J = 2.27$ Hz, 1 H) 7.74 - 7.78 (m, 2 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 106.7, 121.7, 124.6, 126.3, 126.5, 128.1, 128.4, 128.5, 129.8, 131.46, 131.74, 132.66, 135.93, 138.73, 140.83; **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{Br}$ ($M + \text{Na}$): 347.0160, found ($M + \text{Na}$): 347.0161.

(E)-1-(2-(3-Chlorostyryl)phenyl)-1H-pyrazole (4ae). Light yellow oil; Yield - (47.0 mg, 84%); R_f (10% EtOAc/Petroleum Ether) 0.4; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3298, 2924, 2852, 2342, 2285, 1592, 1515, 1489, 1392; **^1H NMR** (400 MHz, CDCl_3) δ 6.49 (s, 1 H) 6.96 (s, 2 H) 7.22 - 7.25 (m, 3 H) 7.35 - 7.46 (m, 5 H) 7.65 - 7.66 (m, 1 H) 7.73 - 7.79 (m, 2 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 106.7, 124.7, 125.4, 126.3, 126.6, 126.7,

127.8, 128.4, 128.5, 129.7, 129.8, 131.4, 132.5, 134.6, 138.8, 138.9, 140.9; **HRESI-MS** (*mz*): Calculated for C₁₇H₁₃N₂Cl (M + Na): 303.0665, found (M + Na): 303.0667.

(E)-1-(2-(2-Methylstyryl)phenyl)-1H-pyrazole (4af). Light yellow oil; Yield - (28.0 mg, 54%); R_f (20% EtOAc/Petroleum Ether) 0.60; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm⁻¹): 3052, 3030, 2956, 2923, 2853, 2361, 1511, 1470, 1390; **¹H NMR** (400 MHz, CDCl₃) δ 2.06 (s, 3 H) 6.43 (d, *J* = 16.48 Hz, 1 H) 6.49 (t, *J* = 1.98 Hz, 1 H) 6.97 (d, *J* = 16.48 Hz, 1 H) 7.21 - 7.23 (m, 2 H) 7.28 - 7.31 (m, 4 H) 7.36 (t, *J* = 7.63 Hz, 1 H) 7.50 (d, *J* = 2.14 Hz, 1 H) 7.62 (d, *J* = 7.93 Hz, 1 H) 7.80 (d, *J* = 1.83 Hz, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 19.9, 106.6, 125.1, 125.5, 126.2, 126.4, 126.8, 127.8, 128.1, 128.4, 129.0, 130.4, 131.5, 133.3, 135.9, 136.0, 138.7, 140.7; **HRESI-MS** (*mz*): Calculated for C₁₈H₁₆N₂ (M + Na): 283.1211, found (M + Na): 283.1212.

(E)-1-(2-(4-(tert-Butyl)styryl)phenyl)-1H-pyrazole (4ag). Yellow semi-solid; Yield - (41.0 mg, 68%); R_f (20% EtOAc/Petroleum Ether) 0.60; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm⁻¹): 3060, 3033, 2960, 2925, 2862, 1514, 1461, 1392; **¹H NMR** (400 MHz, CDCl₃) δ 1.31 (s, 9 H) 6.46 (t, *J* = 2.02 Hz, 1 H) 6.90 (d, *J* = 16.28 Hz, 1 H) 7.03 (d, *J* = 16.28 Hz, 1 H) 7.32 - 7.37 (m, 5 H) 7.38 - 7.46 (m, 2 H) 7.65 (d, *J* = 2.27 Hz, 1 H) 7.75 - 7.78 (m, 2 H); **¹³C NMR** (100 MHz, CDCl₃) δ 31.2, 34.6, 106.5, 123.1, 125.6, 126.3, 126.4, 126.5, 127.9, 128.4, 131.1, 131.6, 133.2, 134.2, 138.6, 140.7, 151.2; **HRESI-MS** (*mz*): Calculated for C₂₁H₂₂N₂ (M + Na): 325.1681, found (M + Na): 325.1683.

(E)-4-(2-(1H-Pyrazol-1-yl)styryl)benzonitrile (4ah). Light yellow solid; Yield - (49.5 mg, 91%); *mp*: 97-99 °C; R_f (20% EtOAc/Petroleum Ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm⁻¹): 3118, 3062, 2955, 2942, 2224, 1601, 1512, 1415, 1393, 1330; **¹H NMR** (400 MHz, CDCl₃) δ 6.50 (t, *J* = 2.15 Hz, 1 H) 7.02 (d, *J* = 16.32 Hz, 1 H) 7.09 (d, *J* = 16.32 Hz, 1 H) 7.40 - 7.48 (m, 5 H) 7.59 (d, *J* = 8.34 Hz, 2 H) 7.66 (d, *J* = 2.27 Hz, 1 H) 7.78 - 7.80 (m, 2 H); **¹³C NMR** (100 MHz, CDCl₃) δ 106.9, 110.8, 118.9, 126.3, 126.7, 127.0, 127.7, 128.5, 129.0, 129.0, 131.4, 132.1, 132.4, 139.0, 140.9, 141.5; **HRESI-MS** (*mz*): Calculated for C₁₈H₁₃N₃ (M + Na): 294.1007, found (M + Na): 294.1013.

(E)-1-(2-(4-Nitrostyryl)phenyl)-1H-pyrazole (4ai). Yellow solid; Yield - (45.0 mg, 77%); *mp*: 109-111 °C; R_f (20% EtOAc/Petroleum Ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm⁻¹): 3069, 2926, 2852, 1593, 1514, 1393, 1340; **¹H NMR** (400 MHz, CDCl₃) δ 6.52 (t, *J* = 2.15 Hz, 1 H) 7.08 (d, *J* = 16.32 Hz, 1 H) 7.16 (d, *J* = 16.32 Hz, 1 H) 7.44 - 7.53 (m, 5 H) 7.68 (d, *J* = 2.27 Hz, 1 H) 7.79 - 7.81 (m, 2 H) 8.17 - 8.20 (m, 2 H); **¹³C NMR** (100 MHz, CDCl₃) δ 106.9, 124.1, 126.3, 126.8, 127.1, 128.5, 128.6, 128.6, 129.2, 131.4, 132.0, 139.1, 141.1, 143.5, 146.9; **HRESI-MS** (*mz*): Calculated for C₁₇H₁₃N₃O₂ (M + Na): 314.0905, found (M + Na): 314.0907.

(E)-1-(4-(2-(1H-Pyrazol-1-yl)styryl)phenyl)ethan-1-one (4aj). Light yellow solid; Yield - (34.5 mg, 60%); *mp*: 121-123 °C; *R_f* (20% EtOAc/Petroleum Ether) 0.25; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3116, 3061, 3006, 2923, 2854, 1678, 1599, 1515, 1394, 1267; **¹H NMR** (400 MHz, CDCl_3) δ 2.58 (s, 3 H) 6.50 (t, $J = 2.02$ Hz, 1 H) 7.07 (s, 2 H) 7.38 - 7.47 (m, 5 H) 7.66 (d, $J = 2.53$ Hz, 1 H) 7.77 - 7.80 (m, 2 H) 7.89 - 7.91 (m, 2 H); **¹³C NMR** (100 MHz, CDCl_3) δ 26.6, 106.8, 126.3, 126.7, 126.7, 128.5, 128.7, 128.8, 129.8, 131.4, 132.4, 136.1, 139.0, 140.9, 141.6, 197.4; **HRESI-MS** (m/z): Calculated for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}$ ($M + \text{Na}$): 311.1160, found ($M + \text{Na}$): 311.1158.

Ethyl (E)-4-(2-(1H-pyrazol-1-yl)styryl)benzoate (4ak). Brown solid; Yield - (60.2 mg, 92%); *mp*: 75-77 °C; *R_f* (20% EtOAc/Petroleum Ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3060, 2980, 2929, 2361, 1712, 1604, 1515, 1393, 1276; **¹H NMR** (400 MHz, CDCl_3) δ 1.39 (t, $J = 7.07$ Hz, 3 H) 4.36 (q, $J = 7.24$ Hz, 2 H) 6.48 - 6.50 (m, 1 H) 7.06 (s, 2 H) 7.39 - 7.46 (m, 5 H) 7.66 (d, $J = 2.27$ Hz, 1 H) 7.77 - 7.79 (m, 2 H) 7.99 (d, $J = 8.34$ Hz, 2 H); **¹³C NMR** (100 MHz, CDCl_3) δ 14.3, 60.9, 106.8, 126.3, 126.4, 126.5, 126.6, 128.5, 129.5, 129.9, 130.0, 131.4, 132.5, 138.9, 140.9, 141.3, 166.3; **HRESI-MS** (m/z): Calculated for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2$ ($M + \text{Na}$): 341.1266, found ($M + \text{Na}$): 341.1268.

(E)-1-(2-(2-(Thiophen-2-yl)vinyl)phenyl)-1H-pyrazole (4al). Orange oil; Yield - (30.5 mg, 62%); *R_f* (10% EtOAc/Petroleum Ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3104, 3068, 2921, 2805, 2382, 2284, 1623, 1597, 1515, 1392, 949; **¹H NMR** (400 MHz, CDCl_3) δ 6.47 - 6.48 (m, 1 H) 6.75 (d, $J = 16.08$ Hz, 1 H) 6.96 - 6.98 (m, 1 H) 7.03 (d, $J = 3.28$ Hz, 1 H) 7.12 - 7.18 (m, 2 H) 7.33 - 7.44 (m, 3 H) 7.65 (d, $J = 2.02$ Hz, 1 H) 7.71 (d, $J = 7.58$ Hz, 1 H) 7.78 (s, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 106.6, 123.4, 124.2, 124.9, 126.3, 126.4, 126.5, 127.6, 128.1, 131.5, 132.6, 138.5, 140.8, 142.5; **HRESI-MS** (m/z): Calculated for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{S}$ ($M + \text{Na}$): 257.0619, found ($M + \text{Na}$): 257.0616.

(E)-1-(2-(Prop-1-en-1-yl)phenyl)-1H-pyrazole (4am). Colorless oil; Yield - (24.0 mg, 65%); *R_f* (20% EtOAc/Petroleum Ether) 0.65; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3111, 3037, 2963, 2914, 2852, 2437, 2361, 2336, 1692, 1652, 1599, 1515, 1492, 1393, 1328; **¹H NMR** (400 MHz, CDCl_3) δ 1.82 - 1.83 (m, 3 H) 6.19 - 6.22 (m, 2 H) 6.43 - 6.45 (m, 1 H) 7.26 - 7.37 (m, 3 H) 7.57 - 7.62 (m, 2 H) 7.73 (d, $J = 1.77$ Hz, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 18.8, 106.2, 126.1, 126.3, 126.5, 127.3, 128.3, 128.7, 131.3, 133.5, 137.9, 140.4; **HRESI-MS** (m/z): Calculated for $\text{C}_{12}\text{H}_{12}\text{N}_2$ ($M + \text{Na}$): 207.0898, found ($M + \text{Na}$): 207.0895.

(E)-1-(2-(Pent-1-en-1-yl)phenyl)-1H-pyrazolepyrazole (4an). Yellow oil; Yield - (25.0 mg, 29%); *R_f* (20% EtOAc/Petroleum Ether) 0.80; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3107, 3068, 3039, 2959, 2867, 2334, 1694, 1648, 1600, 1515, 1491, 1491, 1459, 1393; **¹H NMR** (400 MHz, CDCl_3) δ 0.91 (t, $J = 7.36$ Hz, 3 H) 1.41 - 1.47 (m, 2 H) 2.12 (dtd, $J = 7.29, 5.01, 2.40$ Hz, 2 H) 6.17 - 6.19 (m, 2 H) 6.43 - 6.44 (m, 1 H) 7.26 - 7.39 (m, 3 H) 7.58 - 7.62 (m, 2 H) 7.73 (s, 1 H); **¹³C NMR** (100 MHz, CDCl_3) δ 13.7, 22.3, 35.2,

106.2, 125.1, 126.26, 126.6, 127.3, 128.2, 131.3, 133.5, 133.9, 138.0, 140.4; **HRESI-MS** (*m/z*): Calculated for C₁₄H₁₆N₂ (M + Na): 235.1211, found (M + Na): 235.1214.

(1-(2,6-di((E)-Pent-1-en-1-yl)phenyl)-1H-pyrazole (4an'). Light yellow oil; Yield - (16.0 mg, 14%); R_f (20% EtOAc/Petroleum Ether) 0.70; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm⁻¹): 3061, 2959, 2927, 2867, 2362, 1647, 1583, 1513, 1461, 1390, 966; **¹H NMR** (400 MHz, CDCl₃) δ 0.86 (t, *J* = 7.33 Hz, 6 H) 1.37 (sxt, *J* = 7.33 Hz, 4 H) 2.00 - 2.06 (m, 4 H) 5.72 (d, *J* = 15.84 Hz, 2 H) 6.14 (t, *J* = 6.95 Hz, 1 H) 6.10 (t, *J* = 6.95 Hz, 1 H) 6.45 (t, *J* = 2.15 Hz, 1 H) 7.33 (t, *J* = 7.71 Hz, 1 H) 7.45 (d, *J* = 8.08 Hz, 3 H) 7.75 (d, *J* = 1.52 Hz, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 13.6, 22.2, 35.8, 105.9, 124.0, 124.5, 129.0, 132.3, 133.9, 135.3, 136.5, 140.1; **HRESI-MS** (*m/z*): Calculated for C₁₉H₂₄N₂ (M + Na): 303.1837, found (M + Na): 303.1837.

1-(2-Vinylphenyl)-1H-pyrazole (6aa). Light Yellow Oil; Yield - (26.0 mg, 51%); R_f (10% EtOAc/Petroleum Ether) 0.55; Prepared as shown in general experimental procedure (b). **IR** (KBr, cm⁻¹): 2923, 2852, 2361, 2361, 2085, 1840, 1630, 1605, 1514, 1489, 1392; **¹H NMR** (400 MHz, CDCl₃) δ 5.30 (d, *J* = 11.12 Hz, 1 H) 5.73 (d, *J* = 17.48 Hz, 1 H) 6.44 - 6.45 (m, 1 H) 6.57 (dd, *J* = 17.48, 11.12 Hz, 1 H) 7.36 - 7.42 (m, 3 H) 7.63 - 7.67 (m, 2 H) 7.74 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 106.4, 116.6, 126.1, 126.6, 128.3, 128.4, 131.4, 132.3, 133.2, 138.5, 140.6; **HRESI-MS** (*m/z*): Calculated for C₁₁H₉N₂Cl (M + Na): 193.0742, found (M + Na): 193.0745.

1-(2-Fluoro-6-vinylphenyl)-1H-pyrazole (6da). Brown Oil; Yield - (28.0 mg, 44%); R_f (10% EtOAc/Petroleum Ether) 0.35; Prepared as shown in general experimental procedure (b). **IR** (KBr, cm⁻¹): 2920, 2851, 2362, 2337, 1610, 1577, 1520, 1475, 1389, 1264; **¹H NMR** (400 MHz, CDCl₃) δ 5.31 (d, *J* = 11.04 Hz, 1 H) 5.73 (d, *J* = 17.52 Hz, 1 H) 6.33 (dd, *J* = 17.52, 11.04 Hz, 1 H) 6.49 (t, *J* = 2.02 Hz, 1 H) 7.11 - 7.16 (m, 1 H) 7.39 (td, *J* = 8.02, 5.43 Hz, 1 H) 7.45 - 7.49 (m, 1 H) 7.59 (s, 1 H) 7.79 - 7.80 (m, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 106.6, 115.2 (*J*_{C-F} = 20.1 Hz), 117.9, 121.3 (*J*_{C-F} = 3.5 Hz), 126.7 (*J*_{C-F} = 12.6 Hz), 129.8 (*J*_{C-F} = 8.7 Hz), 130.9 (*J*_{C-F} = 3.2 Hz), 132.4, 137.6, 141.0, 157.7 (*J*_{C-F} = 249.5 Hz); **HRESI-MS** (*m/z*): Calculated for C₁₁H₉N₂F (M + Na): 211.0647, found (M + Na): 211.0645.

1-(4-Fluoro-2-vinylphenyl)-1H-pyrazole (6ea). Brown Oil; Yield - (31.0 mg, 48%); R_f (10% EtOAc/Petroleum Ether) 0.55; Prepared as shown in general experimental procedure (b). **IR** (KBr, cm⁻¹): 2924, 2854, 2362, 2140, 1652, 1615, 1584, 1516, 1421, 1330, 1268, 1023; **¹H NMR** (400 MHz, CDCl₃) δ 5.35 (d, *J* = 10.96 Hz, 1 H) 5.74 (d, *J* = 17.48 Hz, 1 H) 6.43 - 6.50 (m, 2 H) 7.06 (td, *J* = 8.21, 2.84 Hz, 1 H) 7.26 - 7.38 (m, 2 H) 7.58 (d, *J* = 2.24 Hz, 1 H) 7.72 - 7.73 (m, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 106.6, 112.8 (*J*_{C-F} = 23.3 Hz), 115.3 (*J*_{C-F} = 23.0 Hz), 117.8, 128.2 (*J*_{C-F} = 9.0 Hz), 131.4 (*J*_{C-F} = 1.9 Hz), 131.5, 134.7, 135.6 (*J*_{C-F} = 8.3 Hz), 140.8, 162.3 (*J*_{C-F} = 246.2 Hz); **HRESI-MS** (*m/z*): Calculated for C₁₁H₉N₂Cl (M +): 188.0750, found (M +): 188.0752.

1-(5-Chloro-2-vinylphenyl)-1H-pyrazole (6fa). Light Brown Oil; Yield - (34.5 mg, 56%); R_f (10% EtOAc/Petroleum Ether) 0.60; Prepared as shown in general experimental procedure (b). **IR** (KBr, cm^{-1}): 2958, 2922, 2851, 2362, 1724, 1595, 1516, 1487, 1401, 1034; **^1H NMR** (400 MHz, CDCl_3) δ 5.33 (dd, $J = 10.96, 0.76$ Hz, 1 H) 5.72 (dd, $J = 17.52, 0.76$ Hz, 1 H) 6.46 (s, 1 H) 6.55 (dd, $J = 17.52, 10.96$ Hz, 1 H) 7.36 (dd, $J = 8.32, 1.92$ Hz, 1 H) 7.45 (d, $J = 2.12$ Hz, 1 H) 7.58 (d, $J = 8.32$ Hz, 1 H) 7.64 (d, $J = 1.88$ Hz, 1 H) 7.74 - 7.75 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 106.9, 117.1, 126.1, 127.8, 128.4, 131.3, 131.4, 131.6, 133.7, 139.1, 141.1; **HRESI-MS** (m/z): Calculated for $\text{C}_{11}\text{H}_9\text{N}_2\text{Cl}$ ($M + \text{Na}$): 227.0352, found ($M + \text{Na}$): 227.0363.

2-(1H-Pyrazol-1-yl)benzaldehyde (7). White Solid; Yield - (33.6 mg, 98%); R_f (10% EtOAc/Petroleum Ether) 0.40; Prepared as shown in general experimental procedure (d). **IR** (KBr, cm^{-1}): 2954, 2924, 2853, 1690, 1600, 1519, 1493, 1458; **^1H NMR** (400 MHz, CDCl_3) δ 6.55 (s, 1 H) 7.51 (t, $J = 7.80$ Hz, 2 H) 7.68 (t, $J = 7.72$ Hz, 2 H) 7.83 (d, $J = 15.32$ Hz, 2 H) 8.02 (d, $J = 7.83$ Hz, 1 H) 10.02 (s, 1 H); **^{13}C NMR** (100 MHz, CDCl_3) δ 108.0, 124.4, 128.0, 128.7, 130.2, 130.7, 134.2, 141.9, 142.2, 190.1; **HRESI-MS** (m/z): Calculated for $\text{C}_{11}\text{H}_9\text{N}_2\text{Cl}$ ($M + \text{Na}$): 195.0534, found ($M + \text{Na}$): 195.0535.

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