Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Sulphonic Acid Functionalized Porphyrin Anchored with meso-Substituted Triazolium Ionic Liquid Moiety: Heterogeneous Photo-Catalyst for Metal/Base Free C-C Cross-Coupling and C-N/C-H activation using Aryl Chloride under visible light irradiations

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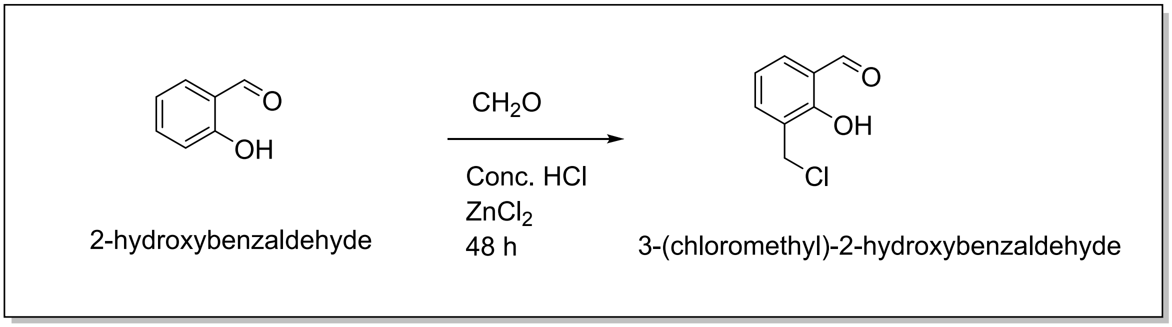
[#]*Equal contribution, Shital contributed for C-N coupling*

Synthesis of SAFPTILM

Synthesis of 3-(chloromethyl)-2-hydroxybenzaldehyde (1a)



Scheme. S1. Synthesis of 1a

The synthesis of 1a was achieved by adapting procedure from the known literature. In a 50 mL round bottom flask (RBF), the mixture of Conc. HCl (30 mL) and formaldehyde (3 mL, 100 mmol) was cooled at 0 ˚C and allowed constant stirring for 30 min. To this mixture, saliacylaldehyde (2.92 mL, 24 mmol) was charged gradually and reaction mixture was kept on magnetic stirring for 48 h at room temperature. The precipitated desired 1a solid (white) was separated and washed with 3 x 10 mL distilled water, followed by acetone and recrystallized from n-hexane. The resulting compound (1a) was dried in hot air oven to give 3.5 g (Yield: 87 %)

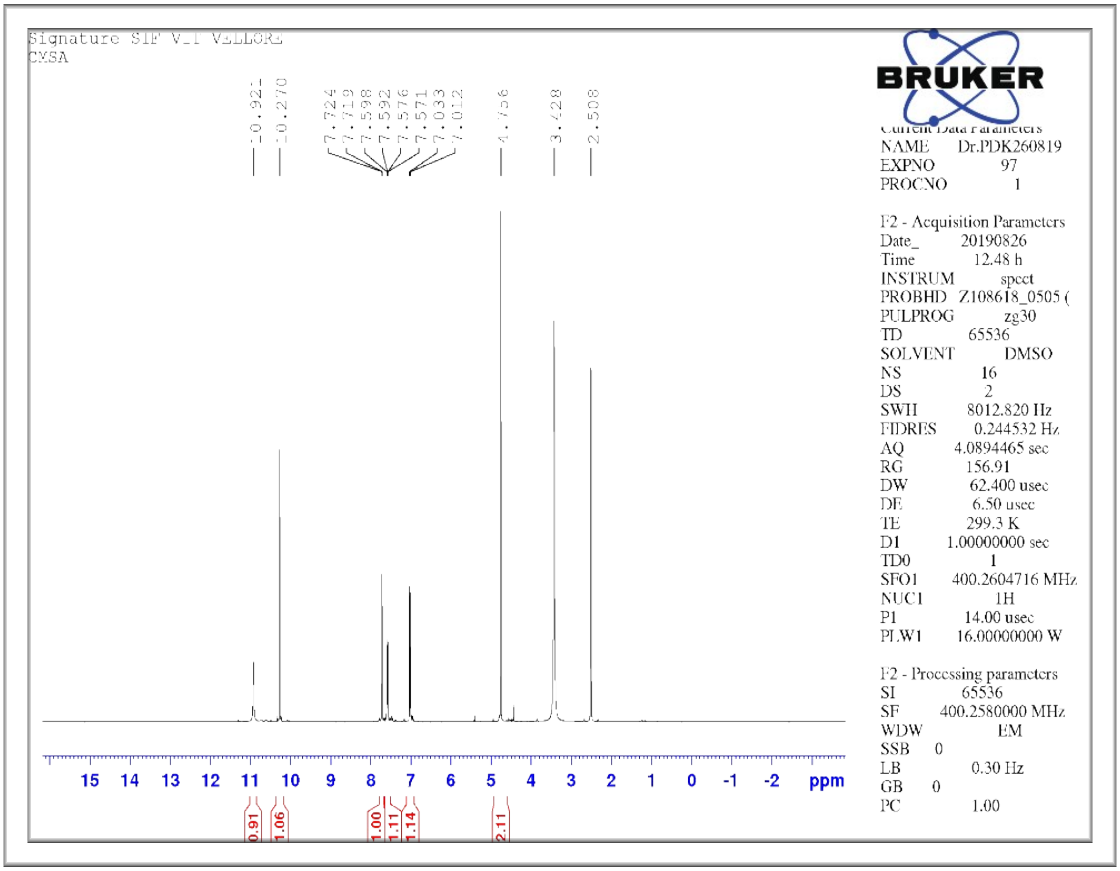
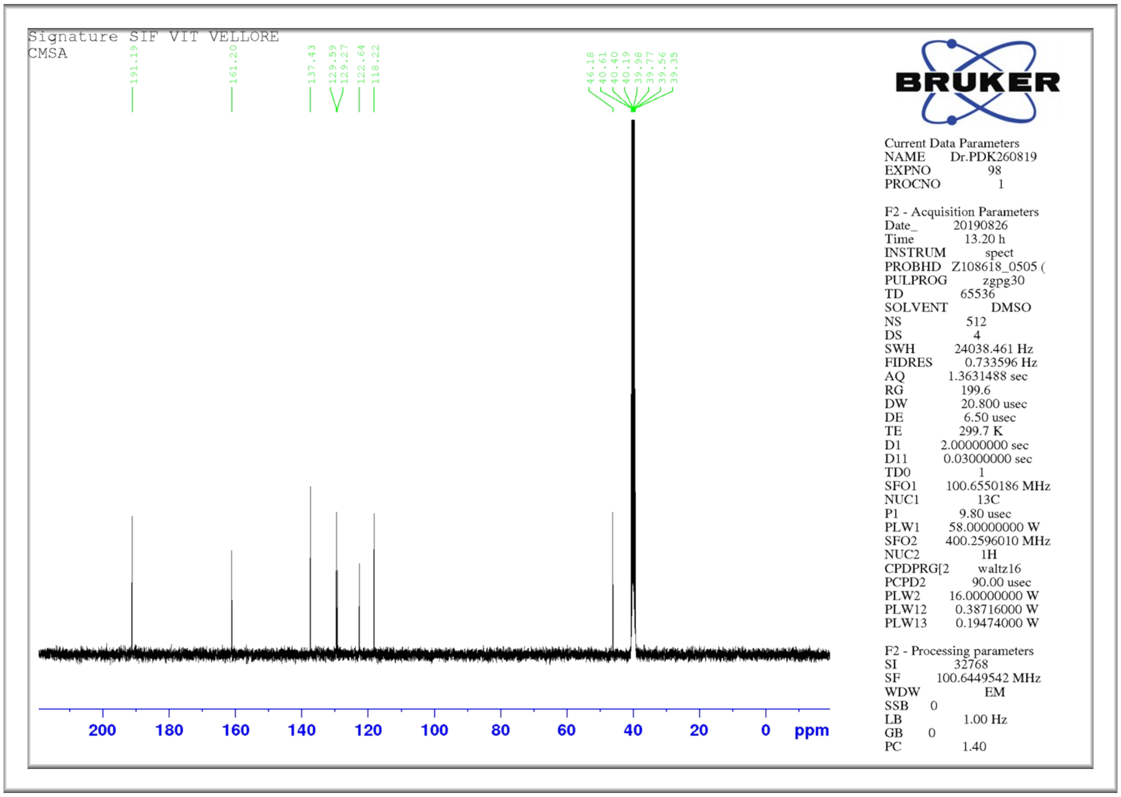


Fig. S1 ^{1}H NMR Spectrum of 3-(chloromethyl)-2-hydroxybenzaldehyde

^{1}H NMR (400 MHz, DMSO-d6) δ: δ 10.92 (s, 1H), 10.27 (s, 1H), 7.72 (d, 1H), 7.58 (q, 1H), 7.02 (d, 1H), 4.75 (s, 2H).



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F2 - Processing parameters
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Fig. S2 ^{13}C NMR Spectrum of 3-(chloromethyl)-2-hydroxybenzaldehyde

^{13}C NMR (100 MHz, DMSO-d6) δ: 191.19, 161.20, 137.43, 129.59, 129.27, 122.44, 118.22, 44.16

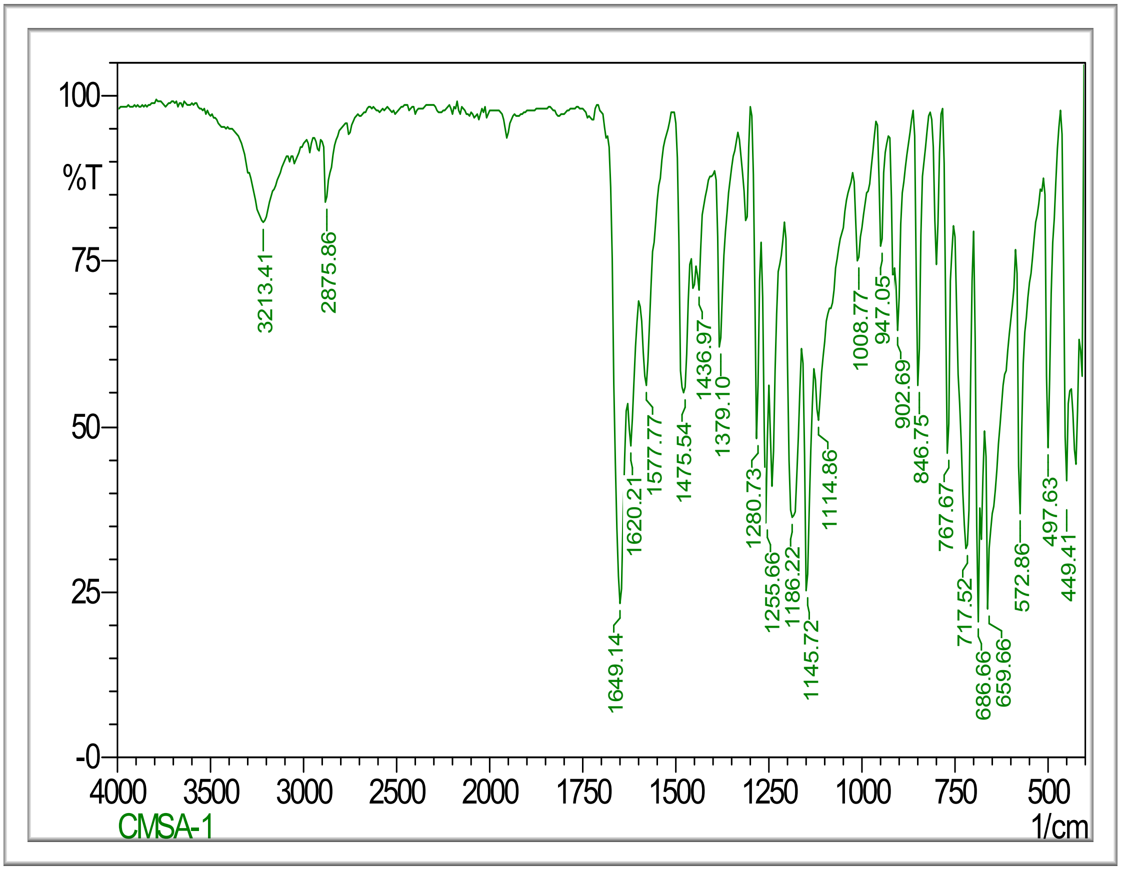
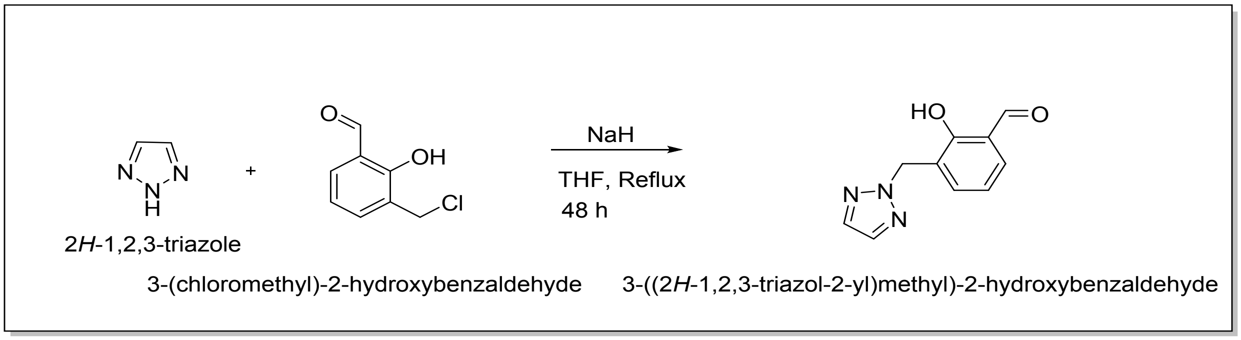


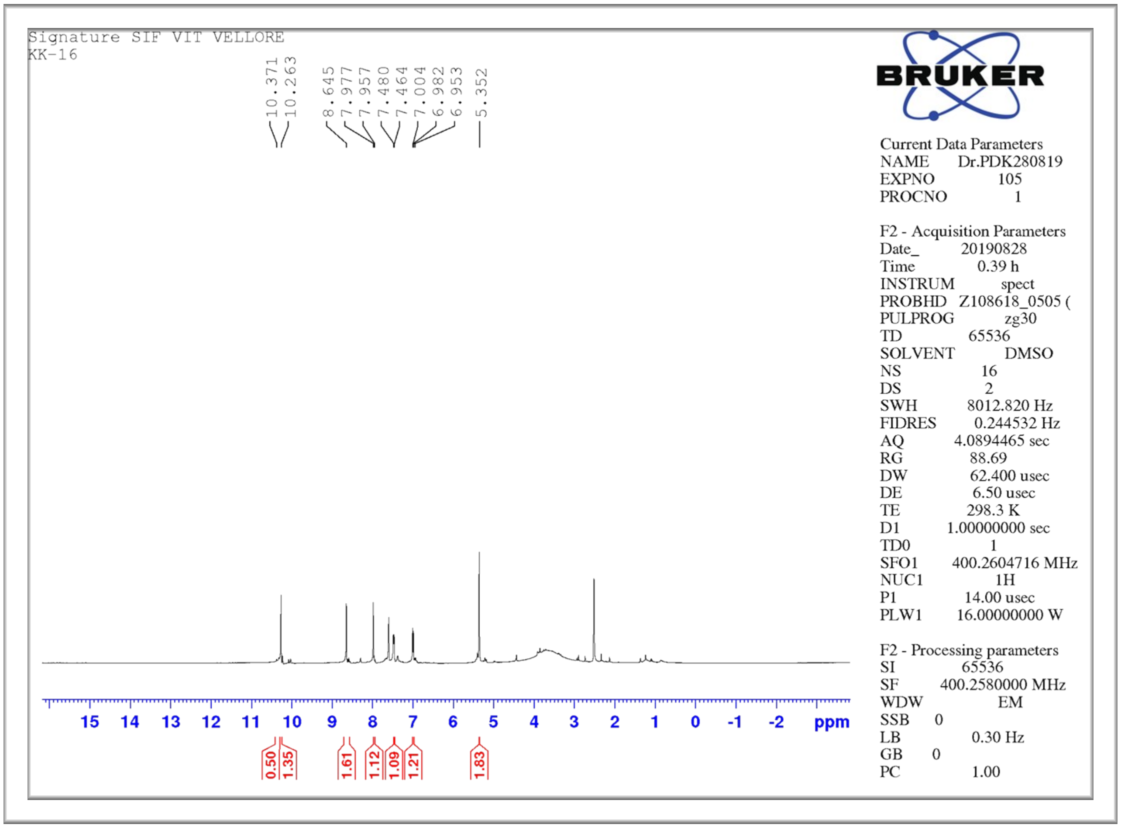
Fig. S3 FT-IR: (KBr, ν/cm^{-1}):– 3213.41, 2875.86, 1649.14, 1620.21, 1577.77, 1475.54, 1436.97, 1379.10, 1280.73, 1255.66, 1186.22, 1145.72, 1114.86, 1008.77, 947.05, 902.69, 846.75, 767.67, 717.52, 686.66, 659.66, 572.86, 497.63, 449.41.

Synthesis of 3-((2H-1,2,3-triazole-2-yl)methyl)-2-hydroxybenzaldehyde (1b)



Scheme. S2 Synthesis of 1b

Into a 100 mL RBF sodium hydride was placed and mixed with 30 mL n-hexane. The reaction mixture was stirred at room temperature (RT) for 40 min., after which time the excess solvent was decanted under vacuum to remove paraffin oil.[28] The flask containing NaH (1.32 g, 55 mmol) was charged with 15 mL tetrahydrofuran (THF), cooled in ice bath to maintain 2 to 3 °C temperature, and solution of triazole (3.45 g, 50 mmol) in THF was added dropwise and stirred for 2 h at cold condition. The reaction mixture was loaded with chloromethylated salicylaldehyde (1a) (8.50 g, 50 mmol) in THF very slowly at the same temperature. The reaction mixture was then reflux for 48 h (60 °C). After cooling, the salt was removed by filtration and the solvent was evaporated under vacuum by rotavapour to get sticky yellowish liquid. The product was charged with the mixture of ethyl acetate and saturated brine solution to remove remaining salt. The organic layer was separated and dried using anhydrous sodium sulphate for overnight. The ethyl acetate layer was concentrated using rotavapour to get sticky yellowish solid. The resulting solid was rinsed by diethyl ether (3 X 10 mL) and dried in hot air oven to afford yellowish fine powder 1b. Yield-84%, 8.5 gram.



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P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
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SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
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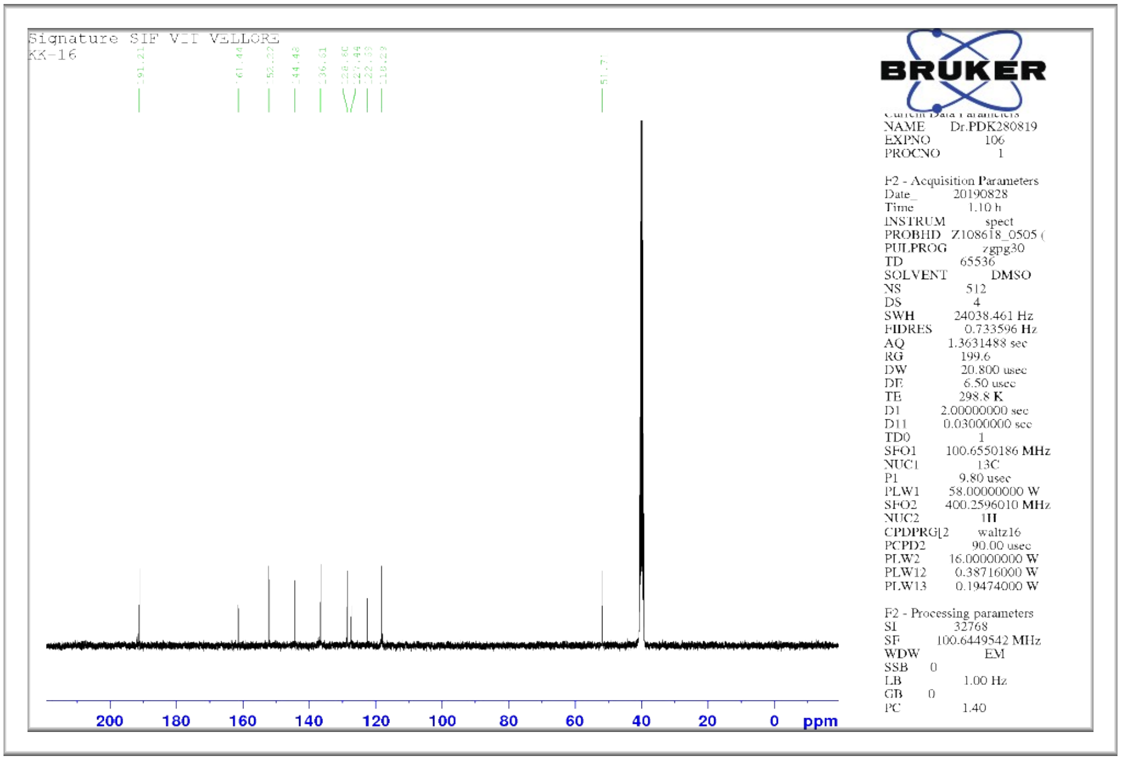
PC 1.00

Fig. S4 ^{1}H NMR Spectrum of 3-((2H-1,2,3-triazole-2-yl)methyl)-2-hydroxybenzaldehyde (1b) ^{1}H NMR (400 MHz, DMSO-d6) δ: δ 10.37 (s, 1H), 10.26 (s, 1H), 8.64 (s, 2H), 7.96 (d, 1H), 7.47 (d, 1H), 6.98 (t, 1H), 5.35 (s, 2H).



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TE 298.8 K
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D11 0.03000000 sec
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SFO1 100.6550186 MHz
NUC1 13C
P1 9.80 usec
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SFO2 400.2596010 MHz
NUC2 1H
CPDPRG[2 waltz16
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F2 - Processing parameters
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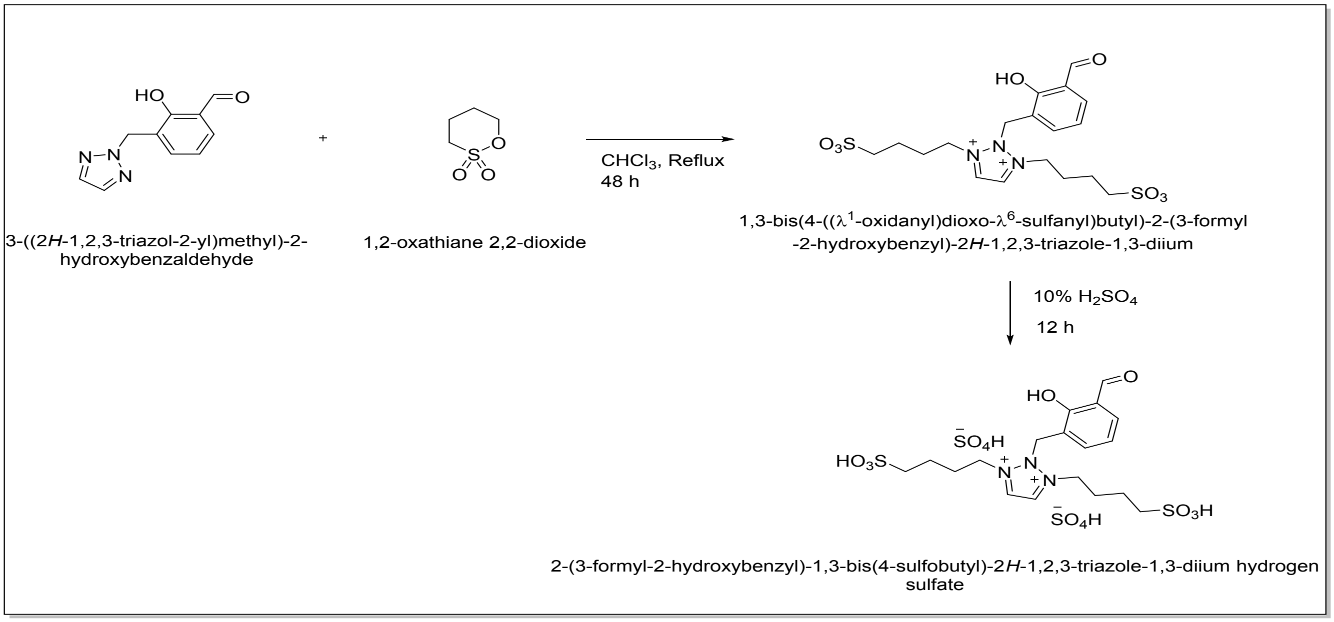
GB 0
PC 1.40

Fig. S5 ^{13}C NMR Spectrum of of 3-((2H-1,2,3-triazole-2-yl)methyl)-2-hydroxybenzaldehyde (1b)

^{13}C NMR (100 MHz, DMSO-d6) δ: 191.20, 161.44, 152.21, 144.48, 136.61, 128.60, 127.43, 122.68, 118.29, 51.71

Synthesis of 2-(3-formyl-2-hydroxybenzyl)1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole1,3-diium hydrogen sulfate (1c)



Scheme. S3 Synthesis of 1c

1, 4-Butylsultone (6.80 g, 50 mmol) was added slowly to a 30 mL solution of triazole salicylaldehyde (5.08 g, 25 mmol) (1b) in acetonitrile into a flask and the mixture was refluxed with constant stirring for 48 h. The solvent was evaporated to dryness by rotavapor and the resulting zwitter ion intermediate was quenched with 10% (1ml of H_2SO_4 in 10 ml of H_2O) aq. H_2SO_4 solution.[29] The reaction mixture was refluxed for 12 h, after which time the excess sulfuric acid was evaporated under vacuum. The solid sticky product was washed with diethyl ether (3 x 10 mL), to achieve pure sticky product (1c) confirm by by ^{1}H NMR and ^{13}C NMR. Yield=89%, 15 g.

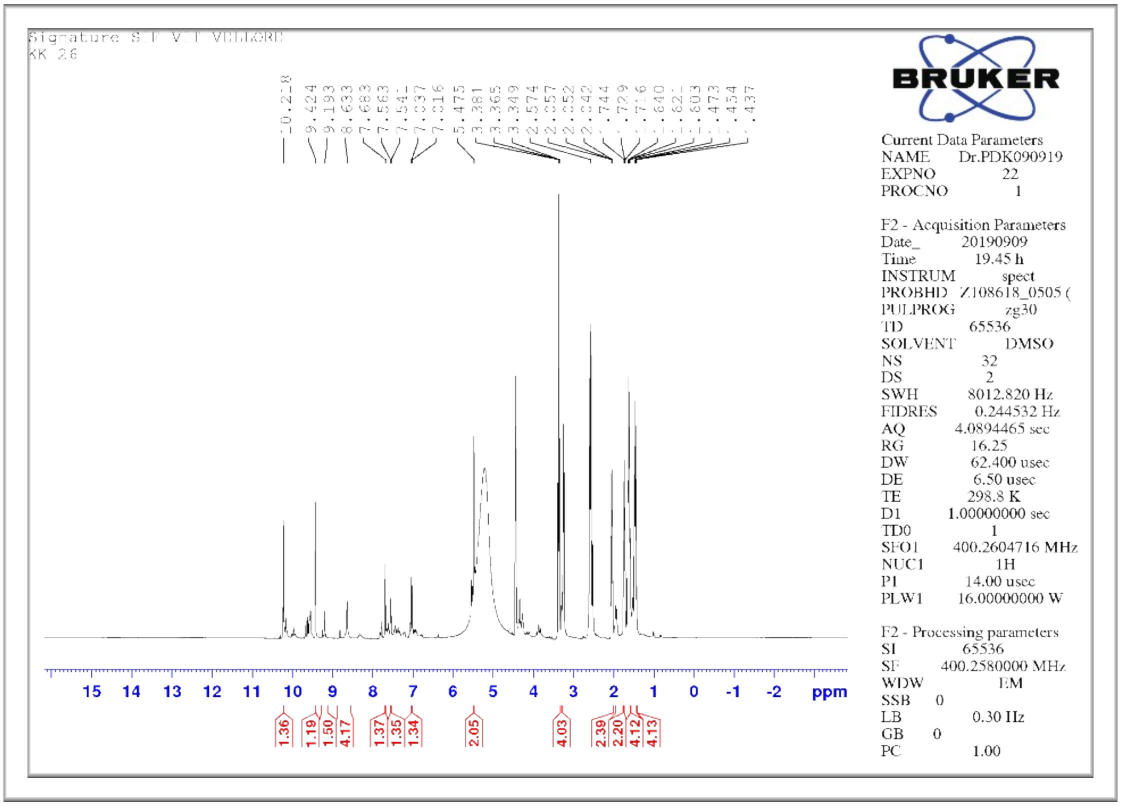
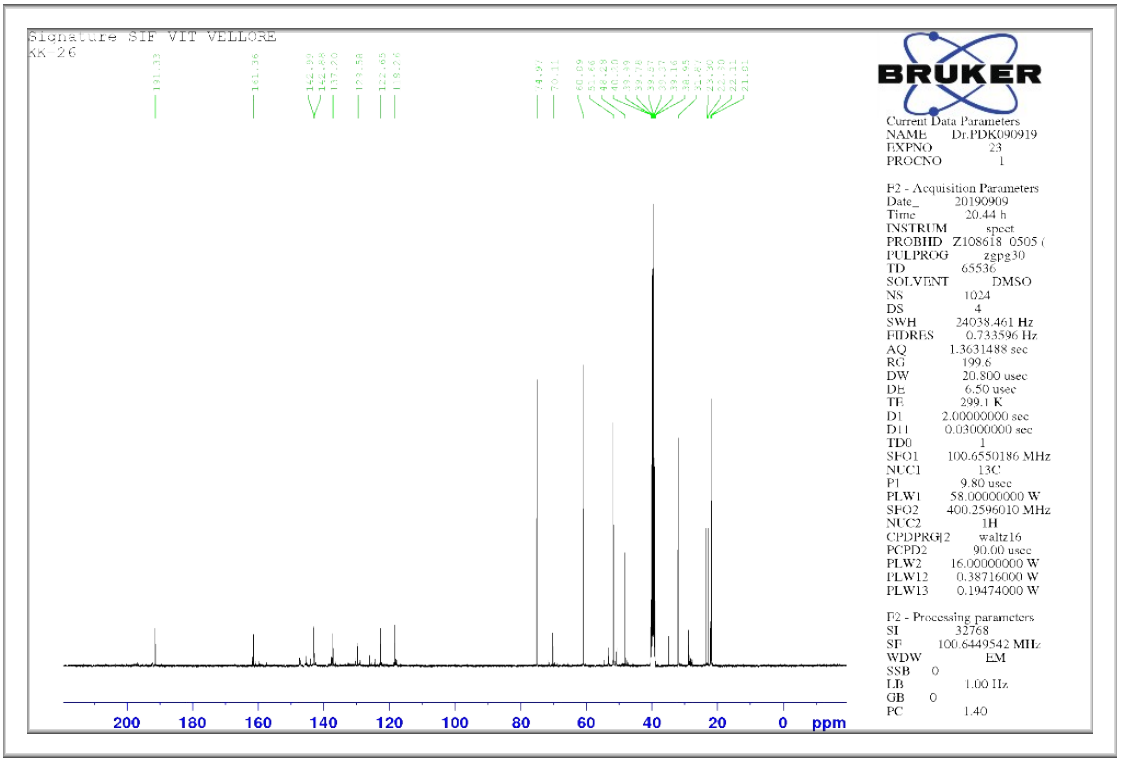


Fig. S6 ^{1}H NMR Spectrum of 2-(3-formyl-2-hydroxybenzyl)1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole1,3-diium hydrogen sulfate (1c)

^{1}H NMR (400 MHz, DMSO-d6) δ: δ 10.21 (s, 1H), 9.42 (s, 1H), 9.19 (s, 1H), 8.63 (s, 4H), 7.68 (s, 1H), 7.55 (d, 1H), 7.02 (d, 1H), 5.47 (s, 2H), 3.36 (t, 4H), 2.05 (t, 2H), 1.72 (t, 2H), 1.62 (t, 4H), 1.45 (t, 4H).



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F2 - Processing parameters
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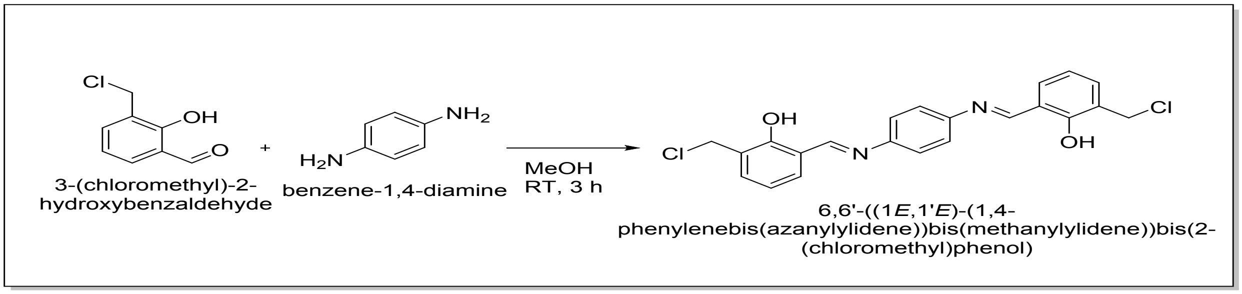
PC 1.40

Fig. S7 ^{13}C NMR Spectrum of 2-(3-formyl-2-hydroxybenzyl)1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole1,3-diium hydrogen sulfate (1c)

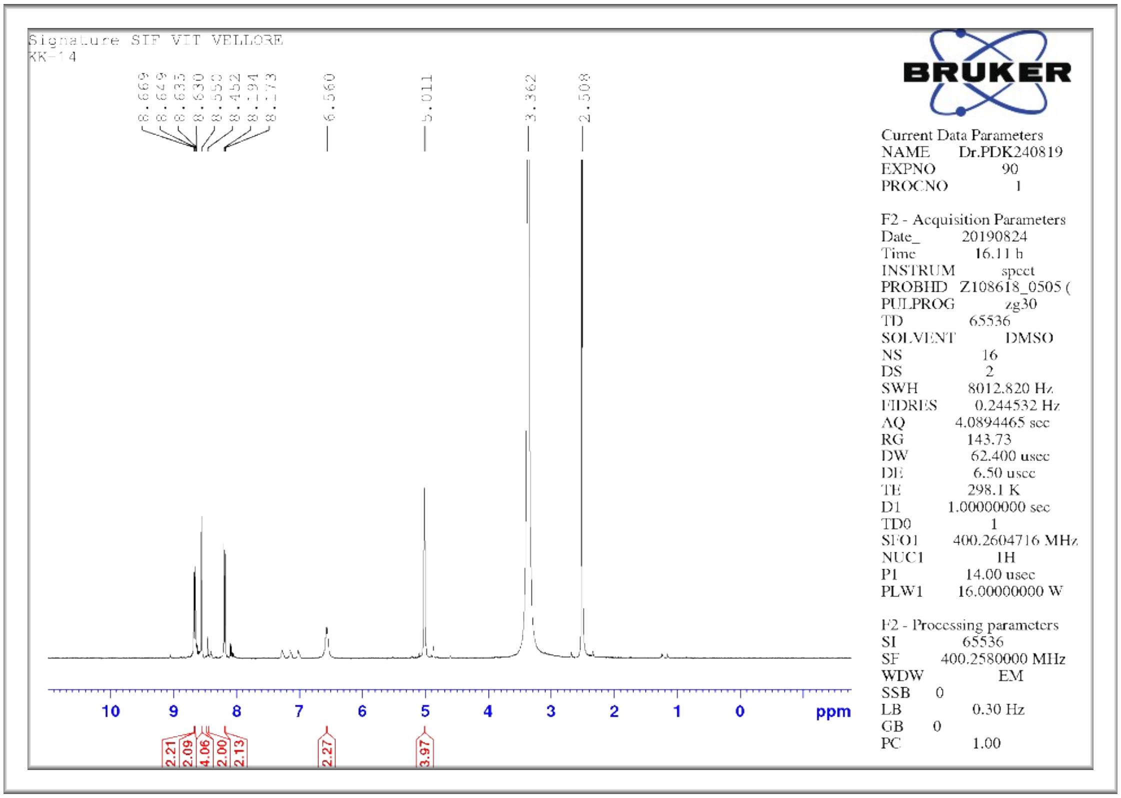
^{13}C NMR (100 MHz, DMSO-d6) δ: 191.32, 161.35, 142.99, 142.87, 137.19, 129.58, 122.64, 118.25, 74.97, 70.10, 60.89, 51.66, 48.27, 31.87, 23.30, 22.90, 22.10, 21.81.

Synthesis of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-(chloromethyl)phenol) (2a)



Scheme. S4 Synthesis of 2a

p-Phenylenediamine (2.16 g, 20 mmol) and chloromethylated salicylaldehyde (1a, 6.80 g, 40 mmol) were weighed and mixed into a 100 mL RBF containing 30 mL methanol and the mixture was refluxed with a magnetic stirring for 3 h.[30] The reaction mixture was cooled to RT affording the product as a red colour solid product in quantitative yield. The resulting product was washed with methanol to acquire red colour solid, obtained by filtering and dried in hot air oven at 80 °C. Yield = 92%, 14.5 g.



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SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
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LB 0.30 Hz
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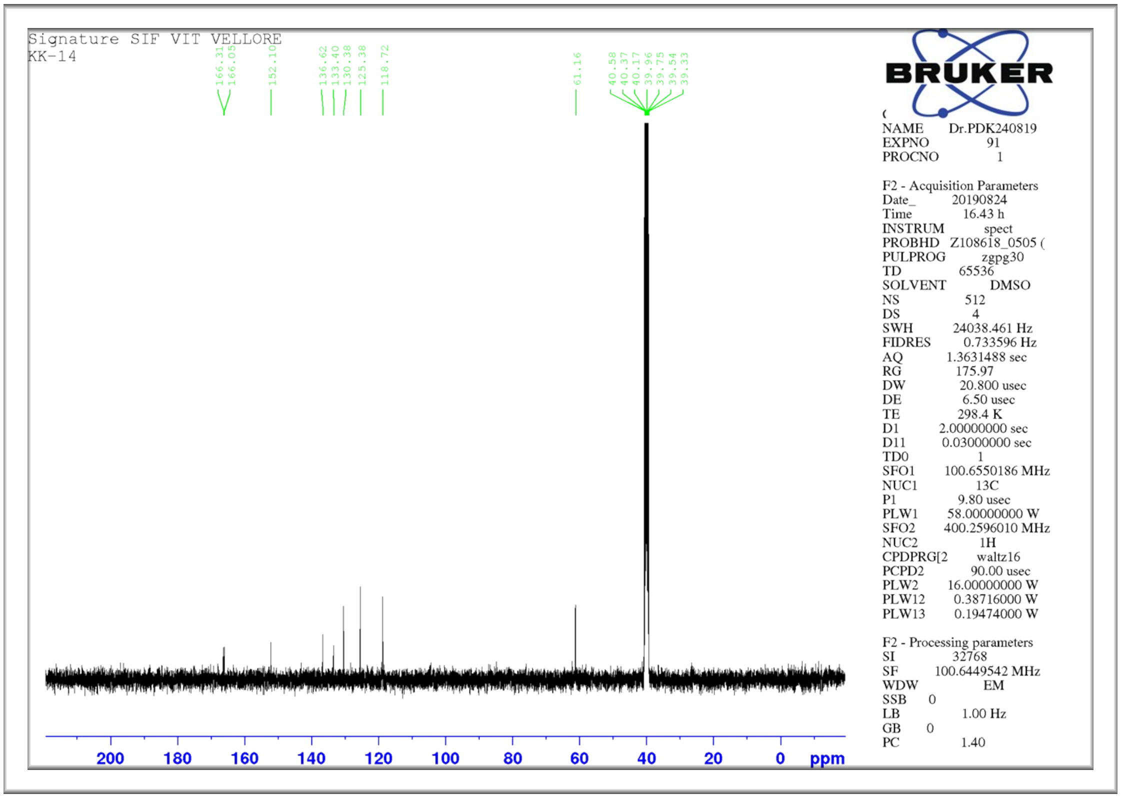
PC 1.00

Fig. S8 ^{1}H NMR Spectrum of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-(chloromethyl)phenol) (2a)

^{1}H NMR (400 MHz, DMSO-d6): δ 8.65 (d, 2H), 8.63 (d, 2H), 8.54 (s, 4H), 8.45 (s, 2H), 8.18 (d, 2H), 6.55 (s, 2H), 5.01 (s, 4H)



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NUC2              1H
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F2 - Processing parameters
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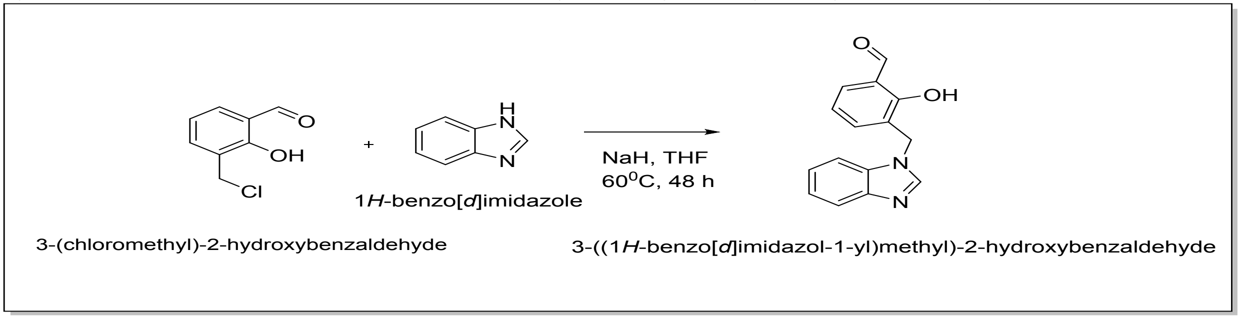
Fig. S9 ^{13}C NMR Spectrum of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-(chloromethyl)phenol) (2a)

^{13}C NMR (100 MHz, DMSO-d6) δ: 166.048, 152.10, 136.61, 133.40, 130.38, 125.37, 118.71, 61.16

Synthesis of 3-((1H-benzo[d]imidazole-1-yl)methyl)-2-hydroxybenzaldehyde(2b)



Scheme. S5 Synthesis of 2b

To a 100 mL RBF sodium hydride was placed and 30 mL n-hexane was added and the reaction mixture was stirred at RT for 40 min., after which time the excess solvent was decanted under vacuum to remove paraffin oil (same ref no as for 1a). The flask containing NaH (0.96g, 40 mmol) was charged with 15 mL tetrahydrofuran (THF), cooled in ice bath to maintain 2 to 3 ^{o}C temperature, and solution of benzimidazole (2.36 g, 20 mmol) in THF was added gradually and stirred for 2 h at cold condition. The reaction mixture was charged with chloromethylated salicylaldehyde (1a) (3.41 g, 20 mmol) in THF steadily at the same temperature. The reaction mixture was then refluxed for 48 h (60 ^{o}C). After cooling, the salt was discarded by filtration and the solvent was concentrated under vacuum by rotavapour to get sticky yellowish liquid. To the product the mixture of ethyl acetate and saturated brine solution was added to remove remaining salt. The organic layer was separated and dried using anhydrous sodium sulphate for 12 h. The ethyl acetate layer was evaporated using rotavapour to get sticky yellowish solid.[31] The resulting solid was washed by diethyl ether (3 X 10 mL) and dried in hot air oven to obtain yellowish fine powder 2b. Yield- 82 %, 8.2 gram.

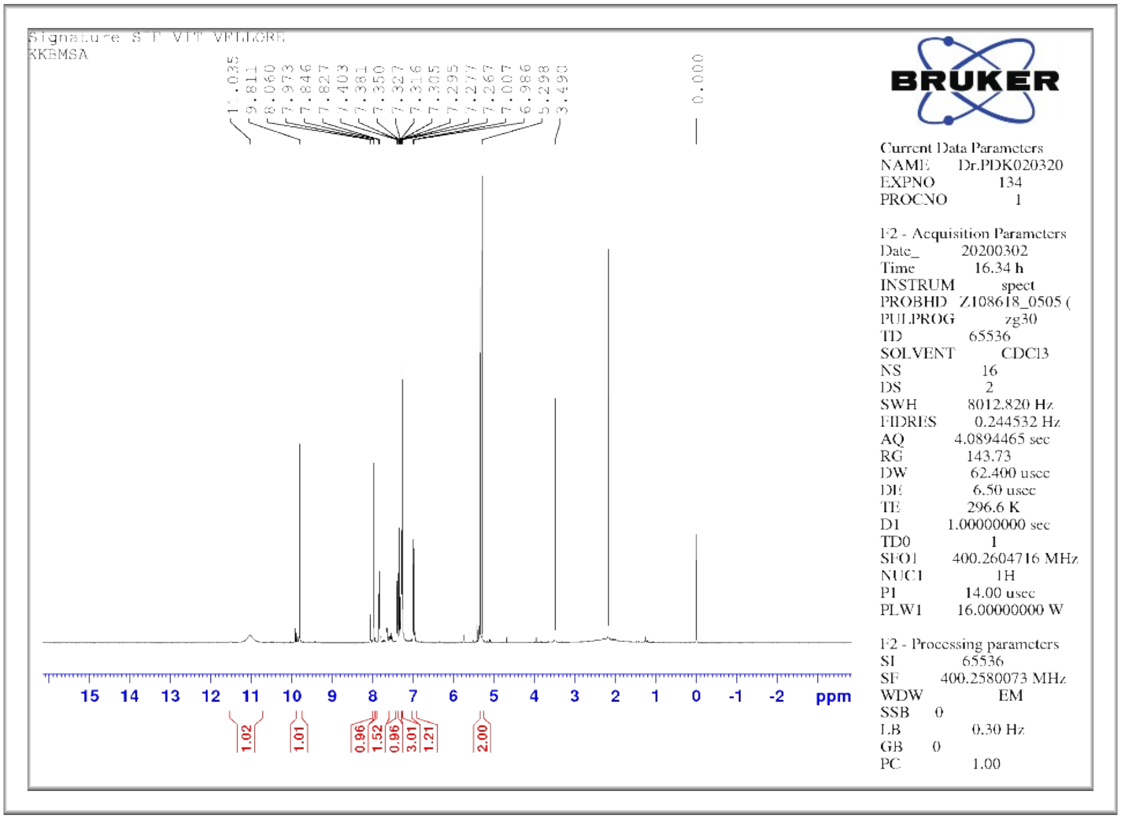
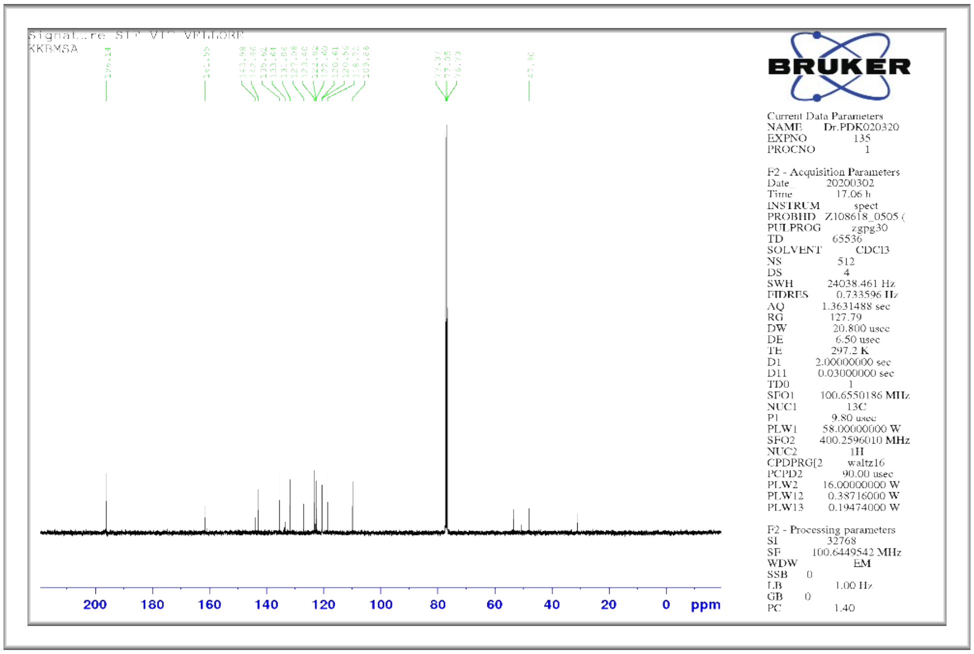


Fig. S10 ^{1}H NMR Spectrum of Synthesis of 3-((1H-benzo[d]imidazole-1-yl)methyl)-2-hydroxybenzaldehyde(2b)

^{1}H NMR, "1H NMR (400MHz, CdCl3-d6) : δ 11.03 (s, 1H), 9.81 (s, 1H), 7.97 (s, 1H), 7.83 (d 2H), 7.39 (d, 1H), 7.26-7.27 (m, 3H), 6.99 (d, 1H), 5.20 (s, 2H).



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F2 - Processing parameters
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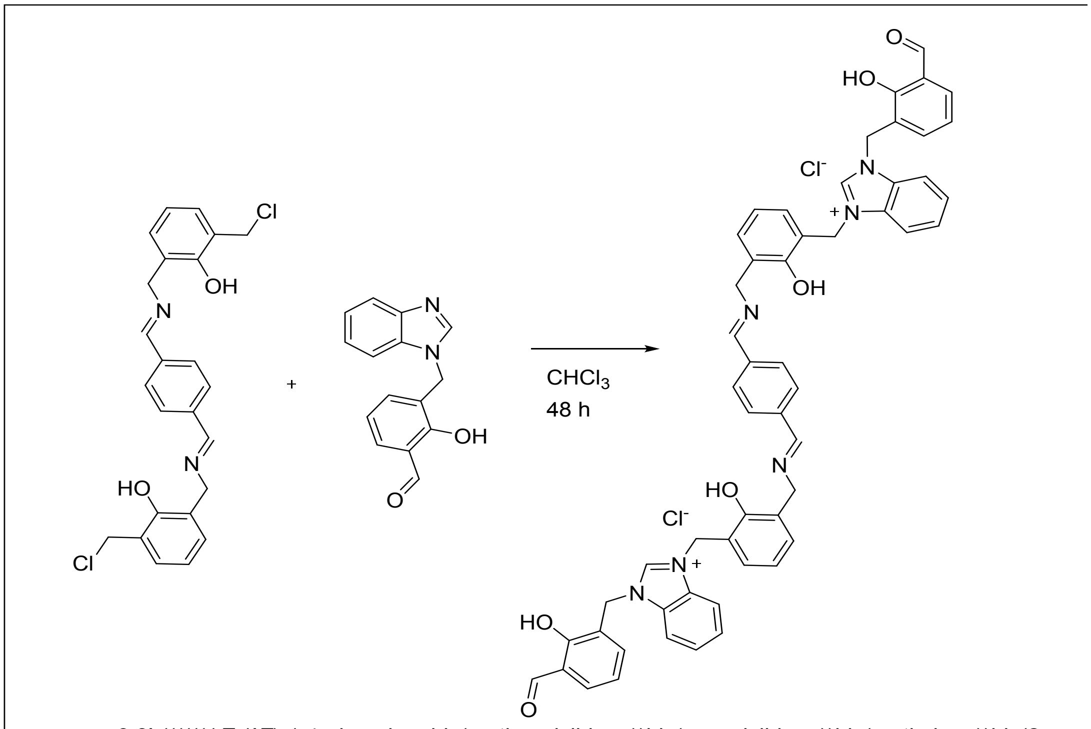
Fig. S11 ^{13}C NMR Spectrum of Synthesis of 3-((1H-benzo[d]imidazole-1-yl)methyl)-2-hydroxybenzaldehyde(2b)

^{13}C NMR (100MHz, $CdCl_3$): δ 196.13, 161.54, 143.97, 142.95, 135.62, 133.63, 131.86, 127.07, 123.40, 122.60, 120.60, 120.55, 118.72, 109.86, 47.89

Synthesis of 1,1’-((((((1E, 1’E)-1,4-phenylenebis(methanylylidene))bis(methylene))bis(2-hydroxy-3,1-phenylene))bis(methylene))bis(3-(3-formyl-2-hydroxybenzyl)-1H-benzo[d]imidazole-3-ium) chloride (2c)



3,3'-((((((1*E*,1'*E*)-1,4-phenylenebis(methanylylidene))bis(azanylylidene))bis(methylene))bis(2-hydroxy-3,1-phenylene))bis(methylene))bis(1-(3-formyl-2-hydroxybenzyl)-1*H*-benzo[*d*]imidazol-3-ium) chloride

Scheme. S6 Synthesis of 2c

In a 50 mL RBF, the mixture of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-(chloromethyl)phenol) 2a (0.412 g 1 mmol**)** and benzamidazole salicylaldehyde 2b (0.504 g, 2 mmol) was suspended in 30 mL chloroform. The mixture was set aside on constant stirring for 48 h.[32] After the completion of reaction, the precipitated NaCl salt was separated by filtration and rinsed with chloroform twice. The resulting filtrate was concentrated under vacuum to acquire precipitate, dried in hot air oven to give 2c.Yield: 74 %, 14.2 g.

In a 50 mL RBF, the mixture of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-(chloromethyl)phenol) 2a (0.412 g 1 mmol**)** and benzamidazole salicylaldehyde 2b (0.504 g, 2 mmol) was suspended in 30 mL chloroform. The mixture was set aside on constant stirring for 48 h.[32] After the completion of reaction, the precipitated NaCl salt was separated by filtration and rinsed with chloroform twice. The resulting filtrate was concentrated under vacuum to acquire precipitate, dried in hot air oven to give 2c.Yield: 74 %, 14.2 g.

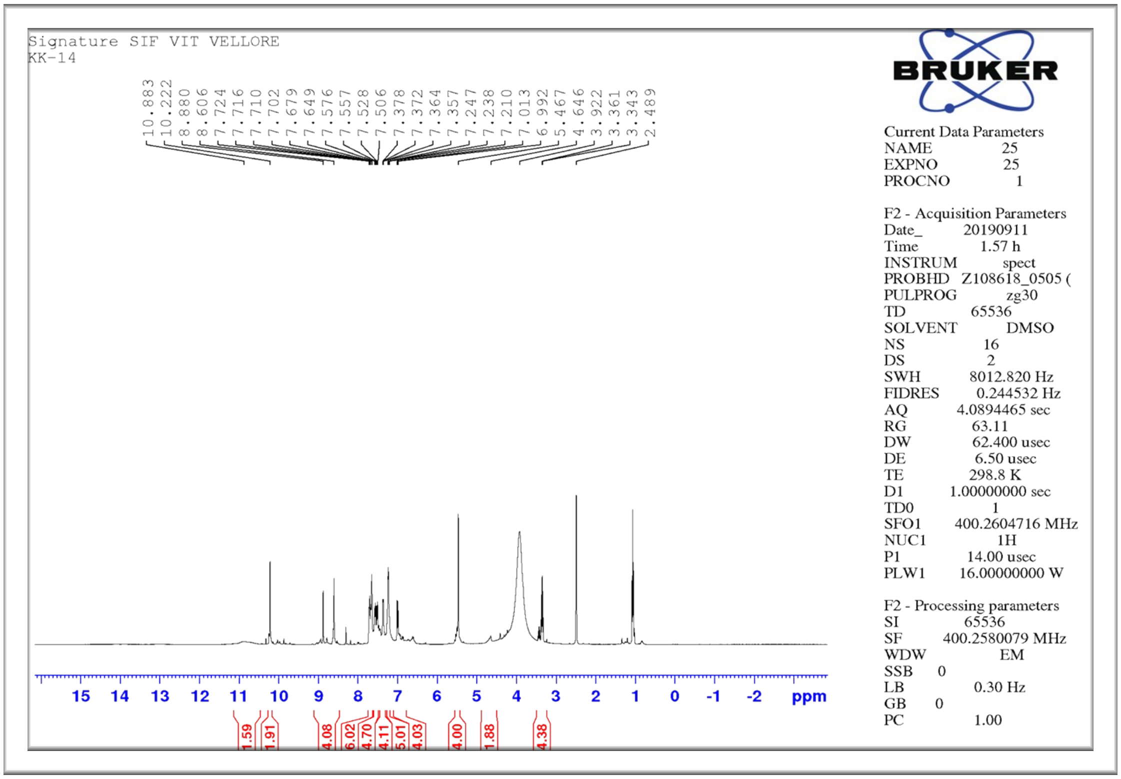


Fig. S12 ^{1}H NMR Spectrum of 1,1'-((((((1E, 1'E)-1,4-phenylenebis(methanylylidene))bis(methylene))bis(2-hydroxy-3,1-phenylene))bis(methylene))bis(3-(3-formyl-2-hydroxybenzyl)-1H-benzo[d]imidazole-3-ium) chloride (2c)

^{1}H NMR (400 MHz, DMSO-d6): δ 10.88 (s, 2H), 10.22 (s, 2H), 8.60 (s, 2H), 8.88 (s, 2H), 7.55-7.57 (m, 6H), 7.51 (d, 5H), 0.00-7.01 (m, 4H), 6.99 (s, 5H), 5.46 (s, 4H), 4.64 (s, 4H), 3.92 (s, 2H), 3.36 (s, 4H)

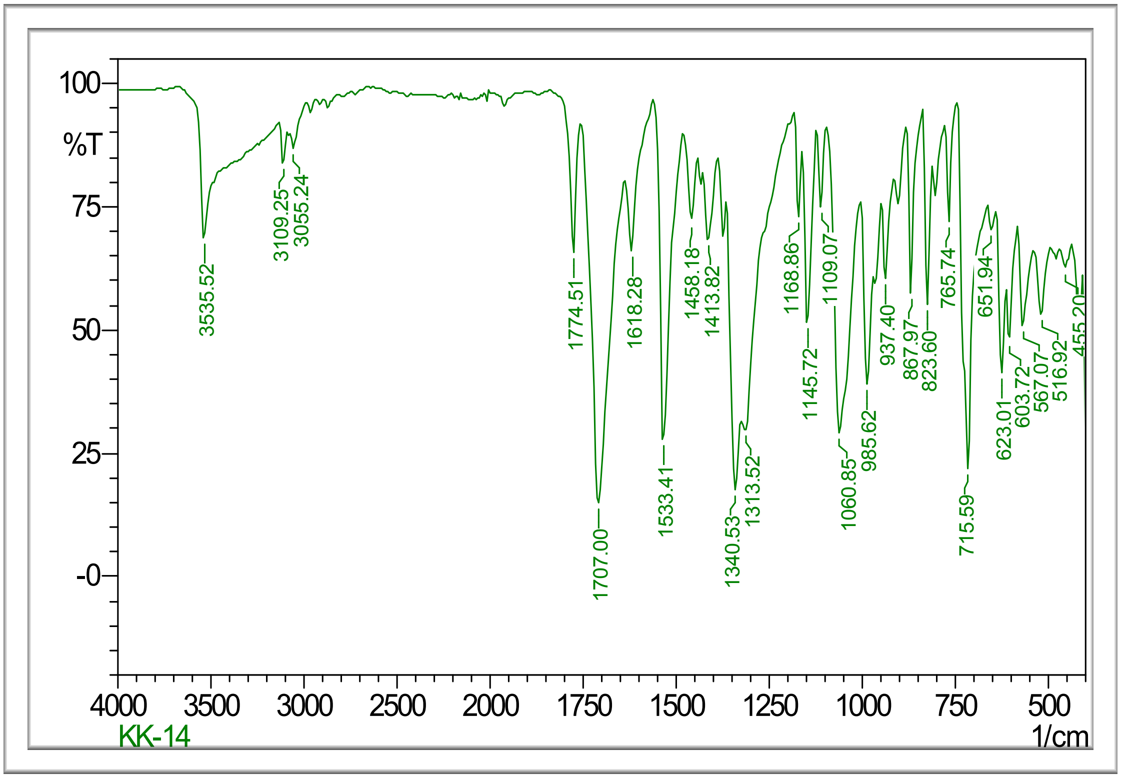
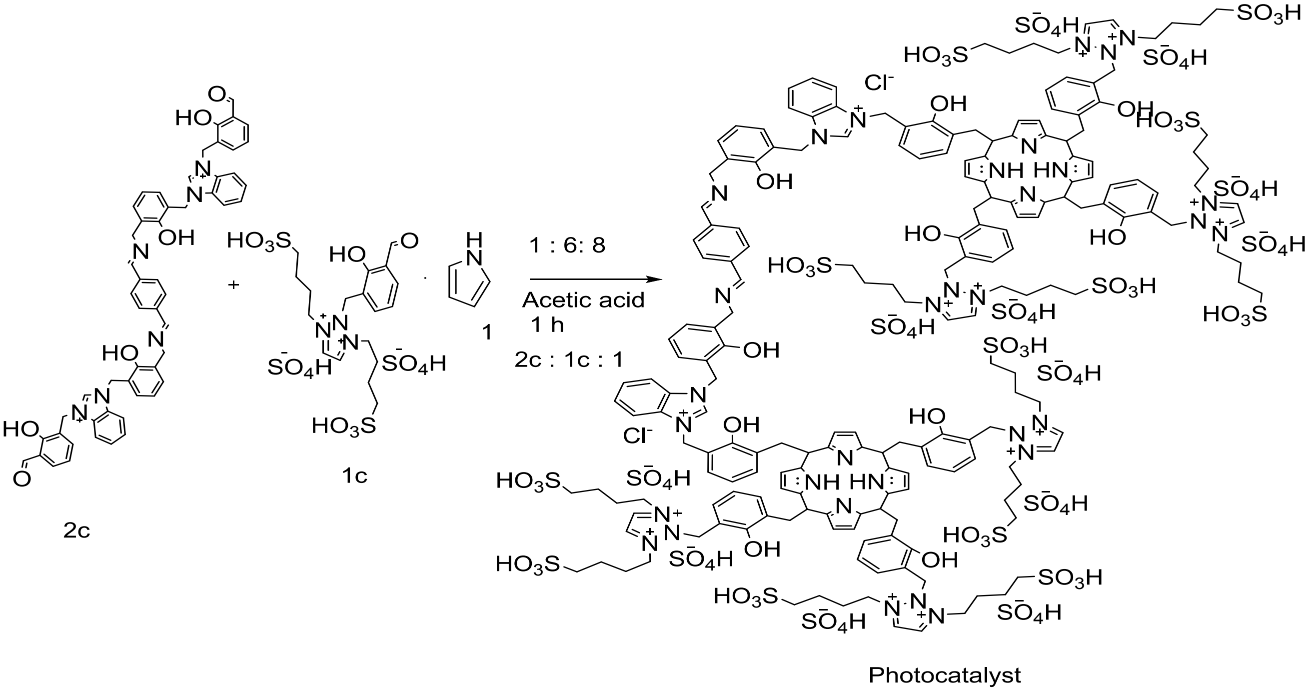


Fig. S13 FT-IR: (KBr, ν/cm^{-1}): 3535.52, 3109.25, 3055.24, 1774.51, 1707, 1618.28, 1533.41, 1458.18, 1413.82, 1340.53, 1313.52, 1168.86, 1145.72, 1109.07, 1060.85, 985.62, 937.40, 867.97, 823.60, 765.74, 715.59, 661.94, 623.01, 603.72, 567.07, 516.92, 465.20

Synthesis of 2-(3-(((9E,16E)-15,20-bis(3-((1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium-2-yl)methyl)-2-hydroxybenzyl)-10-(2-hydroxy-3-((1-(2-hydroxy-3-(((€-2((2-hydroxy-3-((3-(2-hydroxy-3-(((9E,19E)-10, 15, 20-tris(3-((1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium-2-yl)methyl)-2-hydroxybenzyl)-1H,4H,5H,6H,10H,11H,14H,15H,16H,20H-porphyrin-5-yl)methyl)benzyl)-1H-benzo[d]imidazole-3-ium-1-yl)methyl)benzyl)imino)benzylidene)amino)methyl0benzyl)-1H-benzo[d]imidazole-3-ium-3-yl)methyl)benzyl)-1H,4H,5H,6H,10H,11H,14H,15H,19H,20H-porphyrin-5-yl)methyl)-2-hydroxybenzyl)-1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium dichloride dodecakis(hydrogen sulphate)



Scheme. S7. Synthesis of Photocatalyst (SAFPTILM)

In a 100 mL RBF, the precursors (1c) (4.03 g, 6 mmol) and (2c) (0.875 g, 1 mmol) were weighed, mixed with 25 mL acetic acid and stirred for 10 min. To this, pyrrole (0.536 g, 8 mmol) was added and the reaction mixture continued for stirring at room temperature for 1 h. The desired dark brown solid SAFPTILM was separated by vacuum filtration, rinsed with water (5 x 15 mL) to remove traces of acetic acid. Finally the product was frequently washed with acetone and dried in oven at 80^{o}C to furnish the SAFPTILM photocatalyst.[33] Yield: 90 %, 4.52 g.

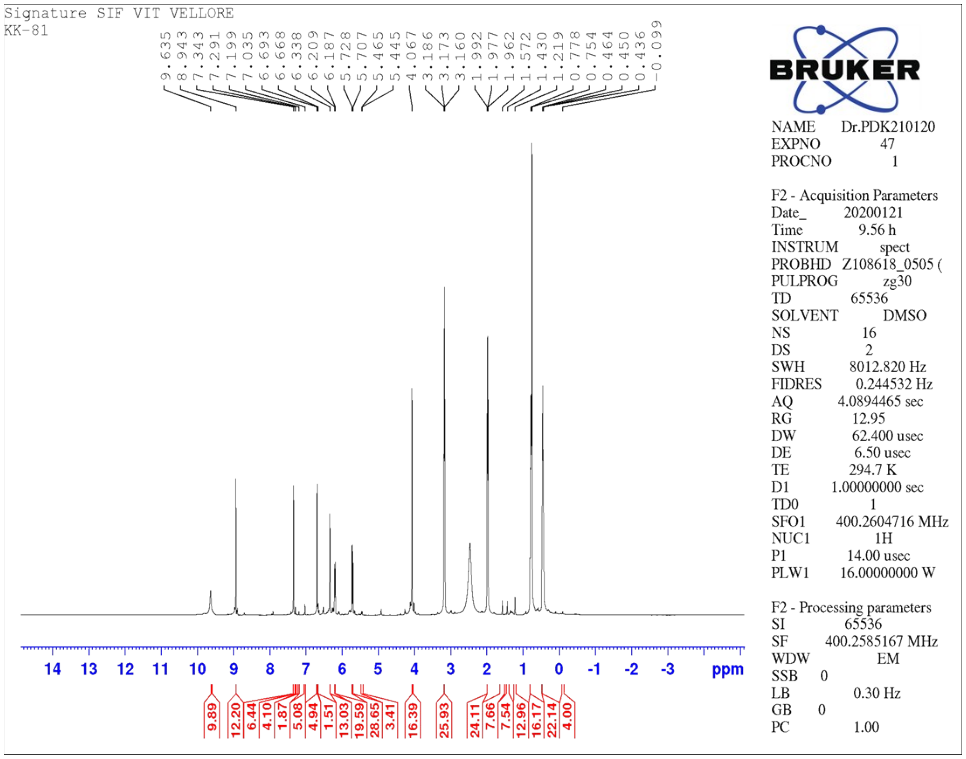


Fig. S14 ^{1}H NMR Spectrum of Synthesis of Synthesis of 2-(3-((15,20-bis(3-((1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium-2-yl)methyl)-2-hydroxybenzyl)-10-(2-hydroxy-3-((1-(2-hydroxy-3-((((E)-4-(E)-((2-hydroxy-3-((3-(2-hydroxy-3-((10,15, 20-tris(3-((1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium-2-yl)methyl)-2-hydroxybenzyl)- porphyrin-5-yl)methyl)benzyl)-1H-benzo[d]imidazole-3-ium-1-yl)methyl)benzyl)imino)benzylidene)amino)methyl)benzyl)-1H-benzo[d]imidazole-3-ium-1-yl)methyl)benzyl)imino)methyl)benzylidene)amino)methyl)benzyl)-1H-benzo[d]imidazol-3-ium-3-yl)methyl)benzyl)Porphyrin-5-yl)methyl)-2-hydroxybenzyl)-1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium dichloride dodecakis (hydrogen sulphate)

^{1}H NMR 400 MHz, DMSO-d6: δ 9.63 (s, 10H), 8.94 (s, 12H), 7.34 (s, 6H), 7.29 (s, 4H), 7.19 (s, 2H), 7.03 (s, 5H), 6.69 (s, 5H), 6.66 (s, 2H), 6.33 (s, 13H), 6.19 (d, 20H), 5.71 (d, 29H), 5.45 (d, 3H), 4.06 (s, 16H), 3.17 (t, 26H), 1.97 (t, 24H), 1.57 (s, 8H), 1.43 (s, 8H), 1.21 (s, 13H), 0.76 (d, 16H), 0.45 (t, 22H), -0.0989 (s, 4H). ^{13}C NMR (100MHz, DMSO) δ 189.80, 158.99, 150.10, 142.38, 134.64, 127.17, 125.65, 120.50, 116.44, 116.08, 72.89, 49.76, 46.26, 21.33, 20.90, -0.50.

Table S1. Optimization of Heck Coupling between 4-chloroaniline and acrylonitrile under Photocatalytic Conditions Catalysed by Photo-catalyst

Entry	Reagent	Catalyst (mg)	Time (h)	Yield (%)
1	R1 +R2	20	24	89
2	R1 +R2	5	24	54
3	R1 +R2	10	24	68
4	R1 +R2	15	24	76
5	R1 +R2	20	24	89
6	R1 +R2	25	24	90
7	R1 +R2	20	6	61
8	R1 +R2	20	12	70
9	R1 +R2	20	18	88
10	R1 +R2	20	24	89
11	R1 +R2	20	15	87[a]
12	R1 +R2	20	13	90[b]
13	R1 +R2	20	18	90[c]
14	R1 +R2	20	18	92[d]
15	R1 +R2	20	18	5[e]

Reaction conditions: 4-chloroaniline (30 mmol, 3.82 gm), acrylonitrile (32 mmol, 1.59 gm), photocatalysts SAFPTILM (20 mg), 5W yellow light, 18 h

a=9W light ; b= 12 W light ; c= 5W Green light;
d= 5W yellow light; e= reaction performed in dark

Effect of photo-catalyst dose

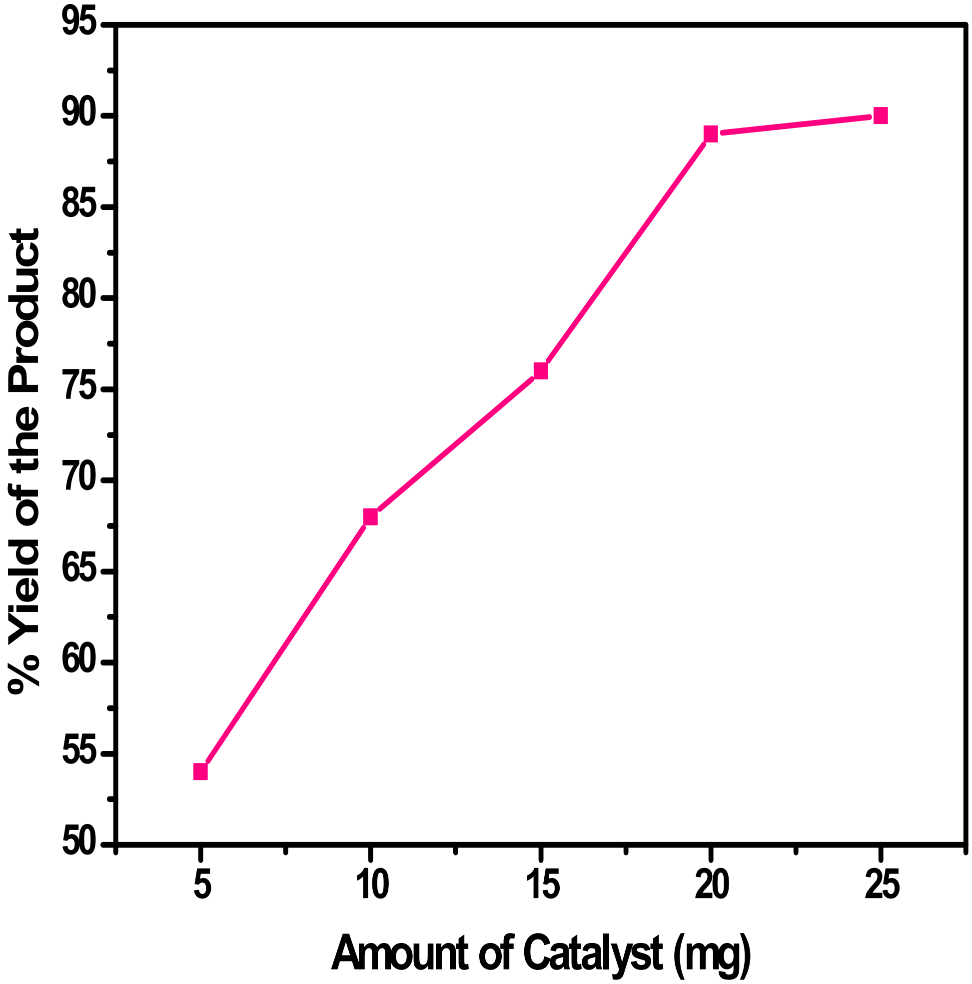


Fig. S15 Photo-catalyst dose

Influence of illumination time

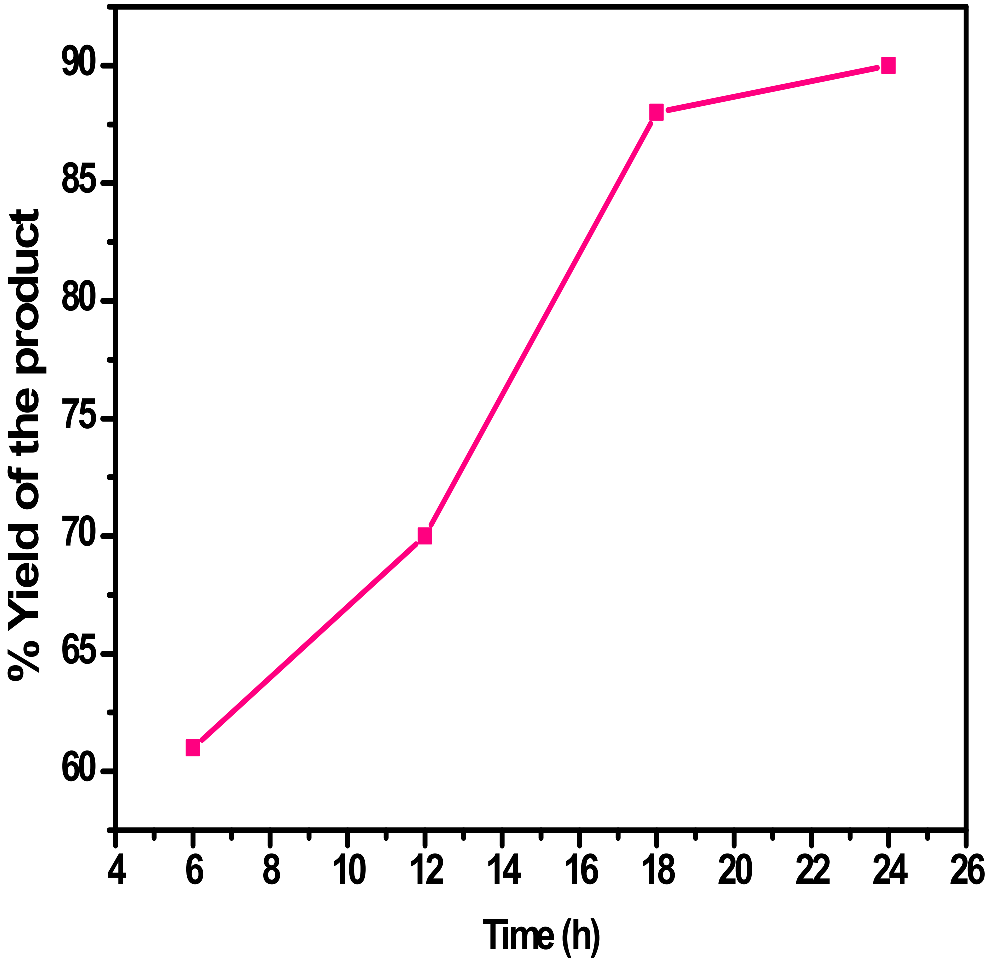


Fig. S16 Influence of illumination time

Effect of light intensity

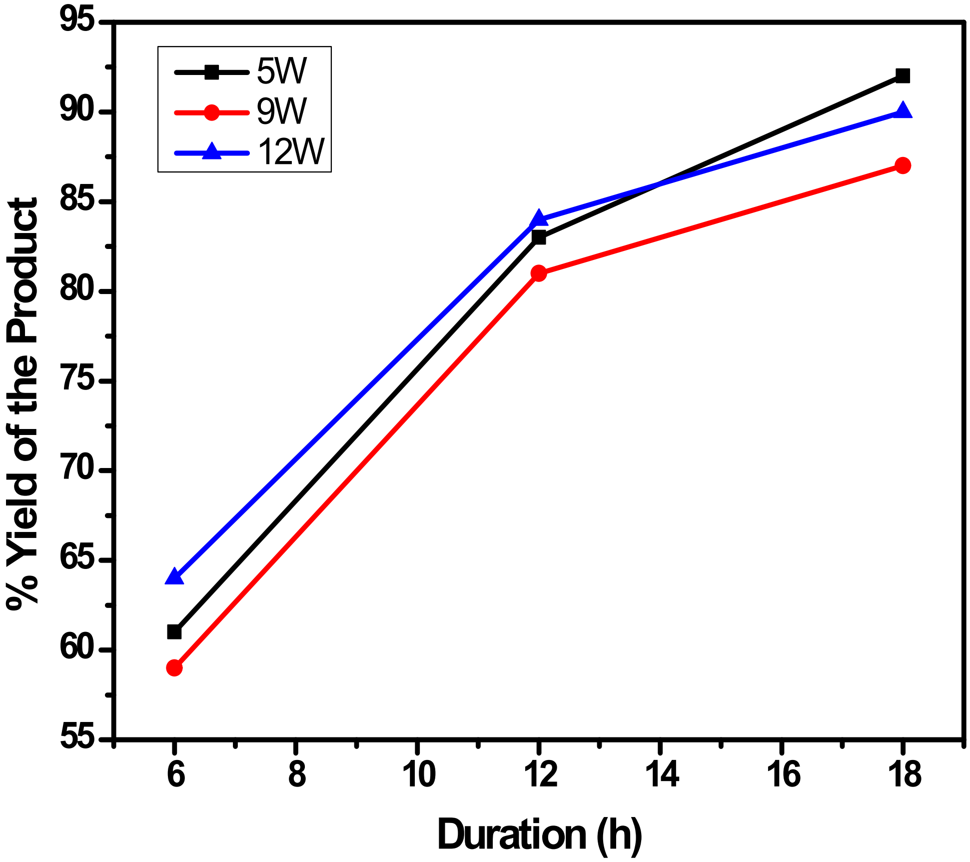


Fig. S17 Effect of light intensity

The effect of wavelength of the irradiation on the C-C coupling

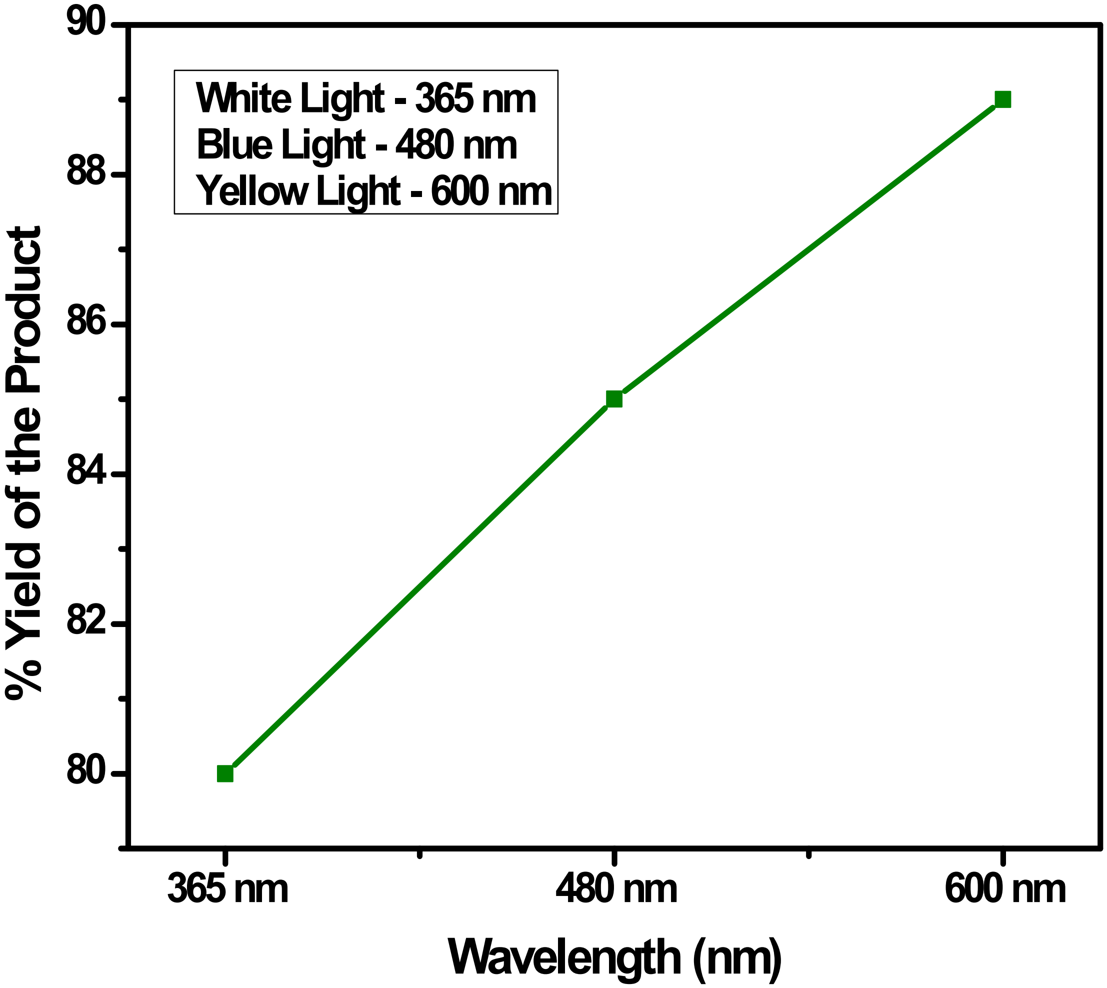


Fig. S18 The effect of wavelength of the irradiation on the C-C Coupling formation

Heck coupling derivatives

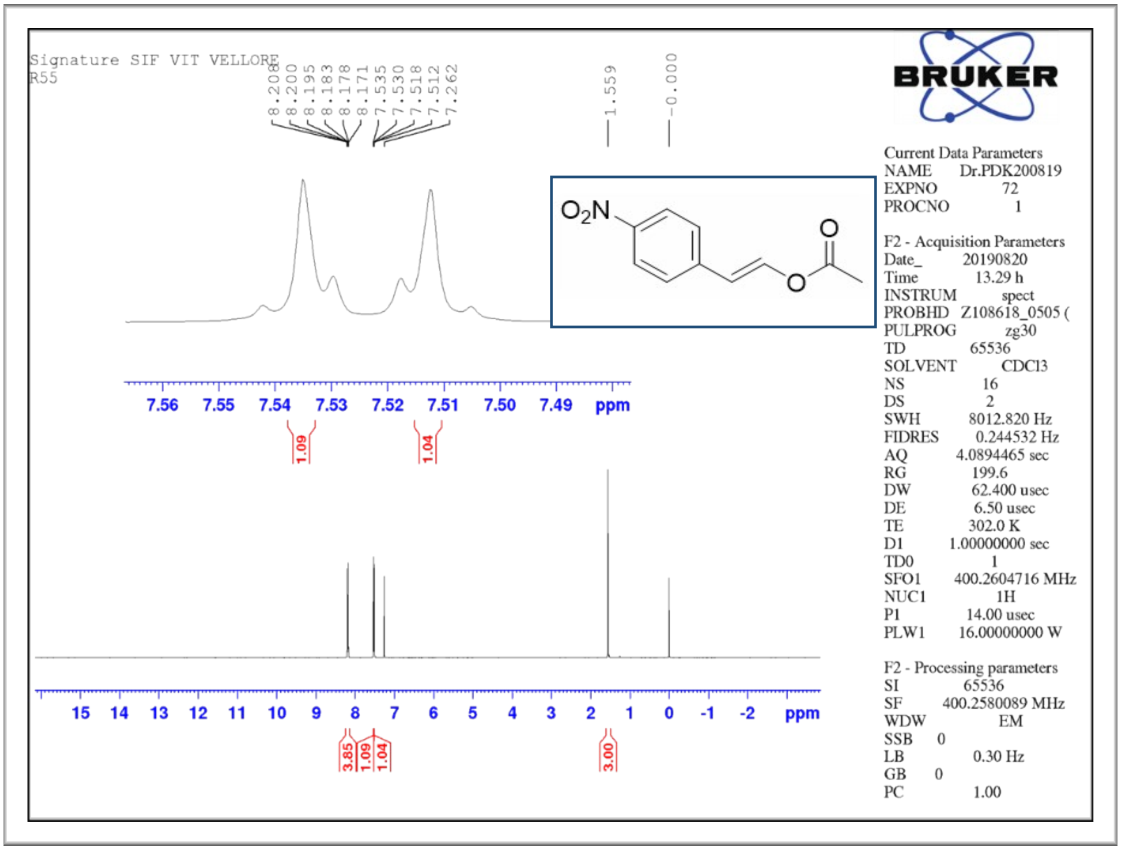


Fig. S19 ^{1}H NMR Spectrum of (Z)-4-nitrostyryl acetate

^{1}H NMR (400 MHz, $CDCl_3$) δ : δ 8.20 (d, 2H), 8.18 (d, 2H), 7.53 (d, 1H), 7.51 (d, 1H), 1.55 (s, 3H)

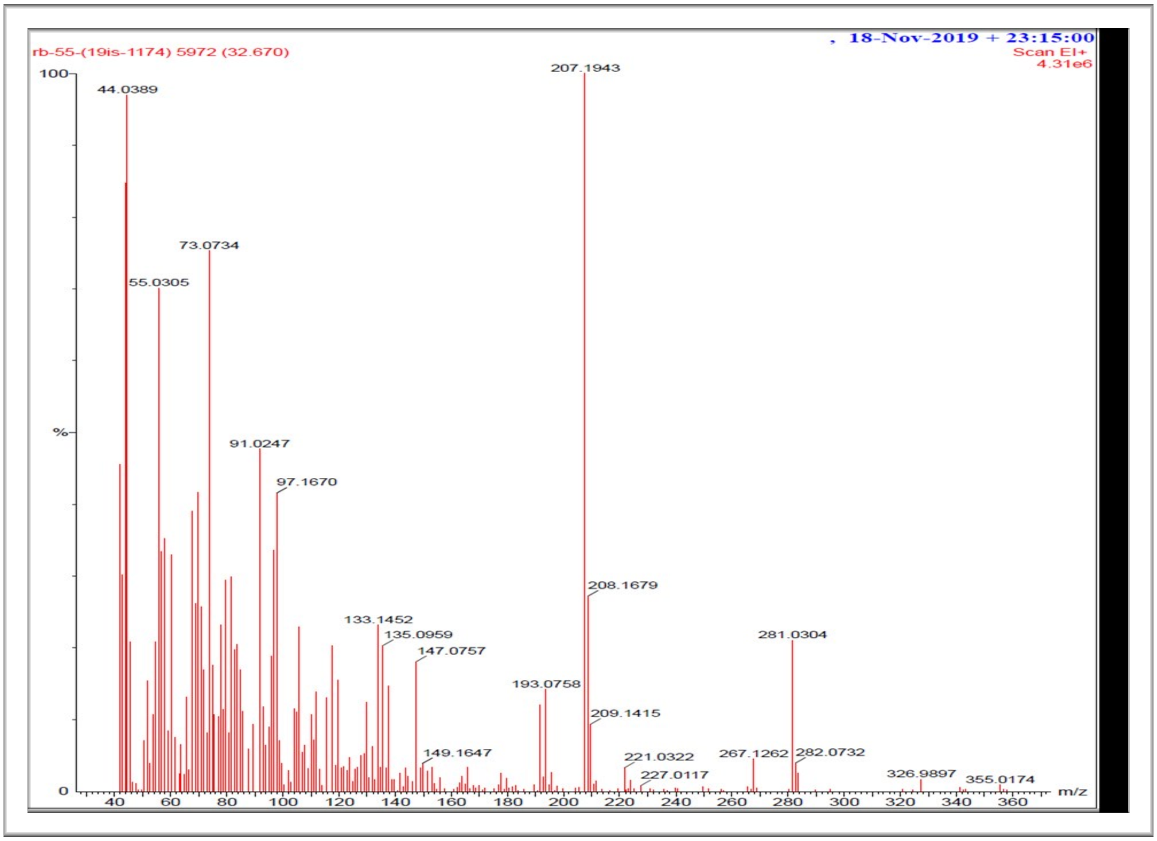
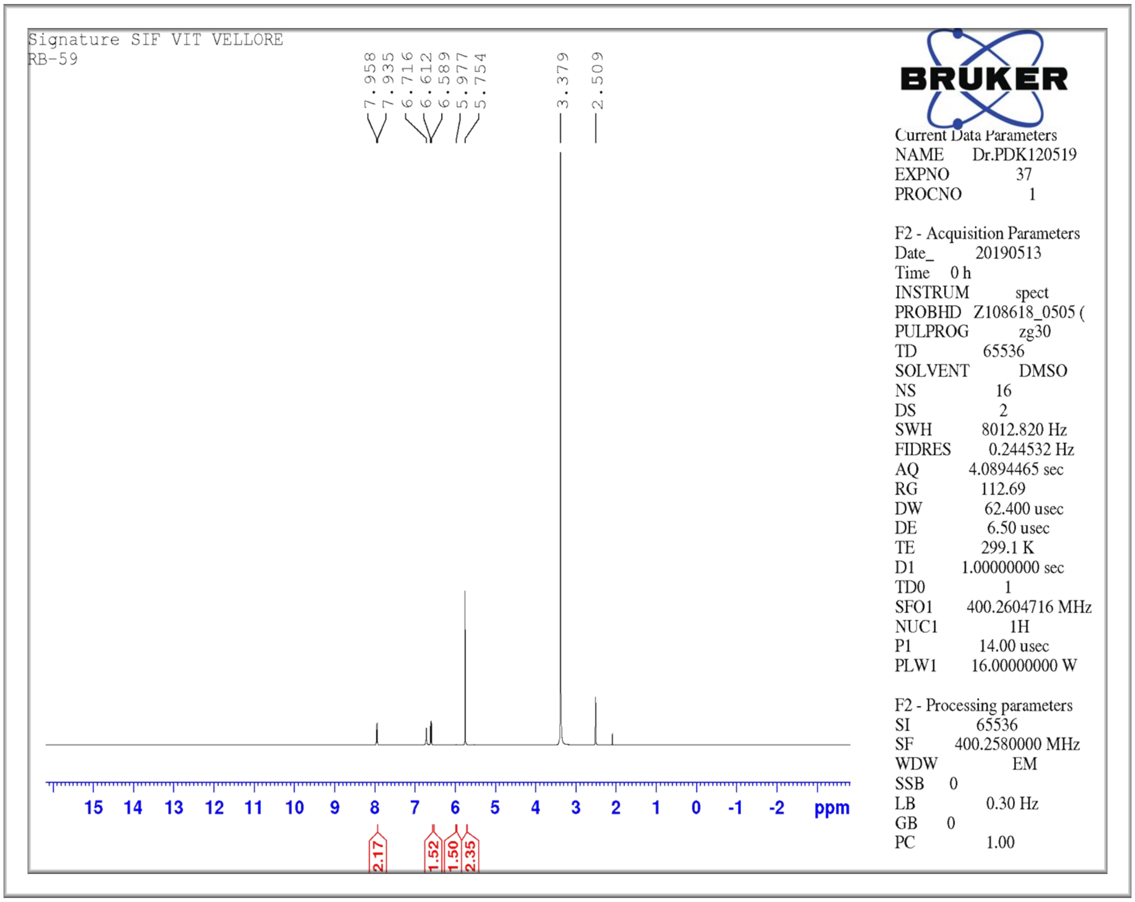


Fig. S20 GC-MS Spectrum of (Z)-4-nitrostyryl acetate GC-MS: 207.19



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EXPNO 37
PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 112.69
DW 62.400 usec
DE 6.50 usec
TE 299.1 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S21 ^{1}H NMR Spectrum of (E)-3-(4-aminophenyl) acrylonitrile

^{1}H NMR (400 MHz, DMSO-d6): δ 7.94 (d, 2H), 6.60 (d, 2H), 5.97 (s, 2H), 5.75 (s, 2H), .

GC-MS: 144.18

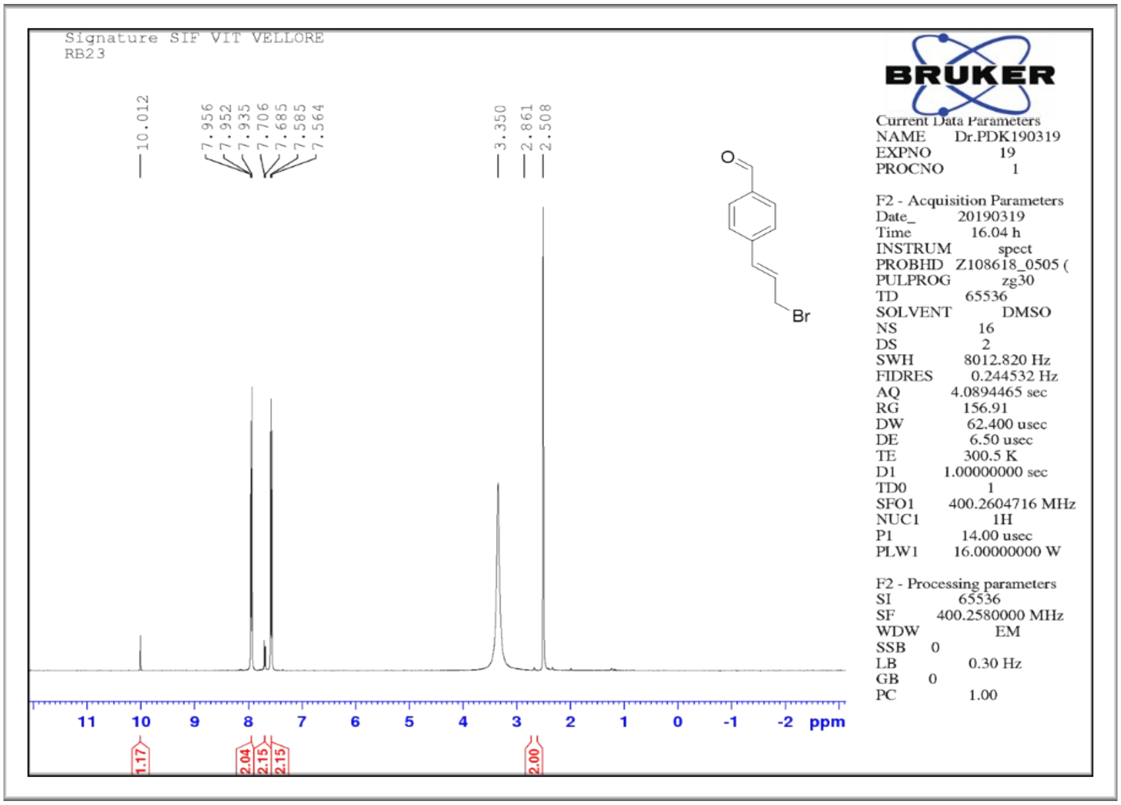
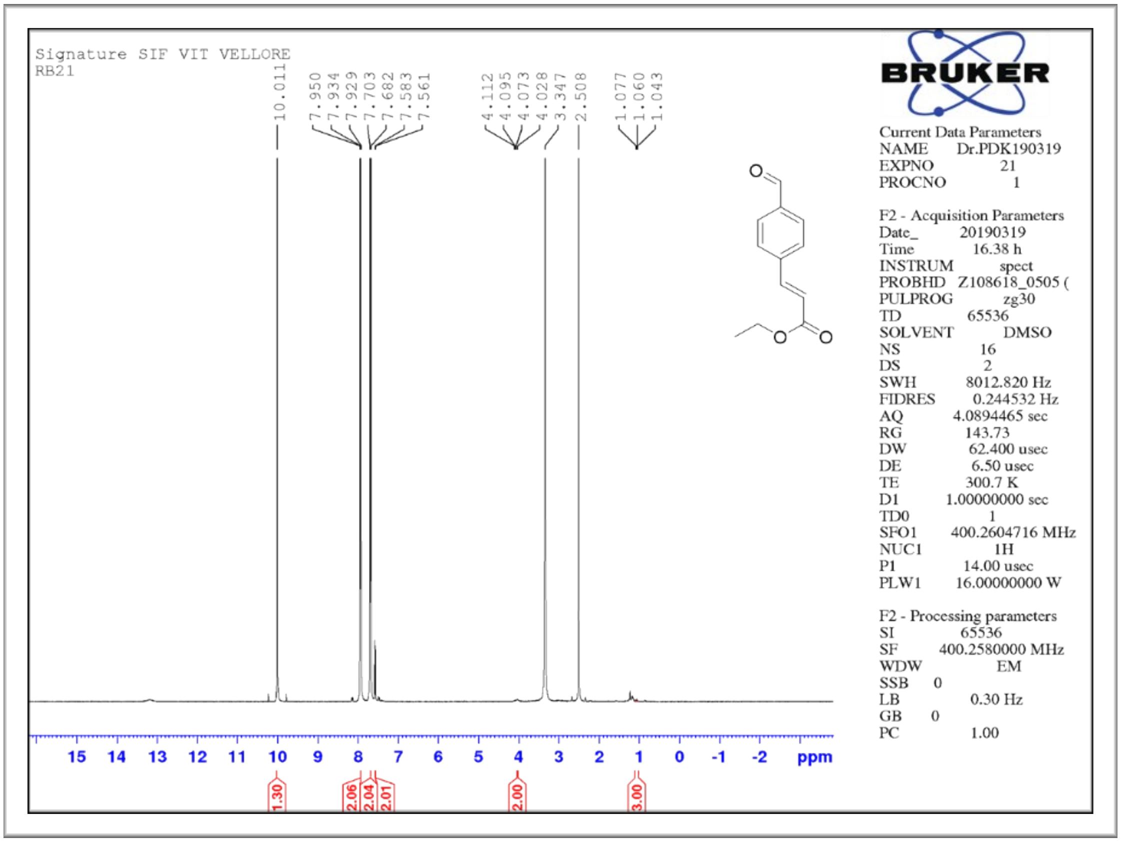


Fig. S22 ^{1}H NMR Spectrum of (E)-4-(3-bromopro-1-en-1yl) benzaldehyde

^{1}H NMR (400 MHz, DMSO-d6): δ 10.01 (s, 1H), 7.95 (t, 2H), 7.70 (d, 2H), 7.57 (d, 2H), 2.86 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d6): δ 166.92, 138.25, 131.65, 131.61, 130.12, 129.85, 129.21, 40.2

GC-MS: 225.09



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EXPNO 21
PROCNO 1

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TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 143.73
DW 62.400 usec
DE 6.50 usec
TE 300.7 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S23 ^{1}H NMR Spectrum of ethyl (E)-3-(4-formylphenyl)acrylate

^{1}H NMR (400 MHz, DMSO-d6): δ 10.01 (s, 1H), 7.93 (t, 2H), 7.69 (d, 2H), 7.57 (d, 2H), 4.07 (q, 2H), 36.36 (t, 3H).

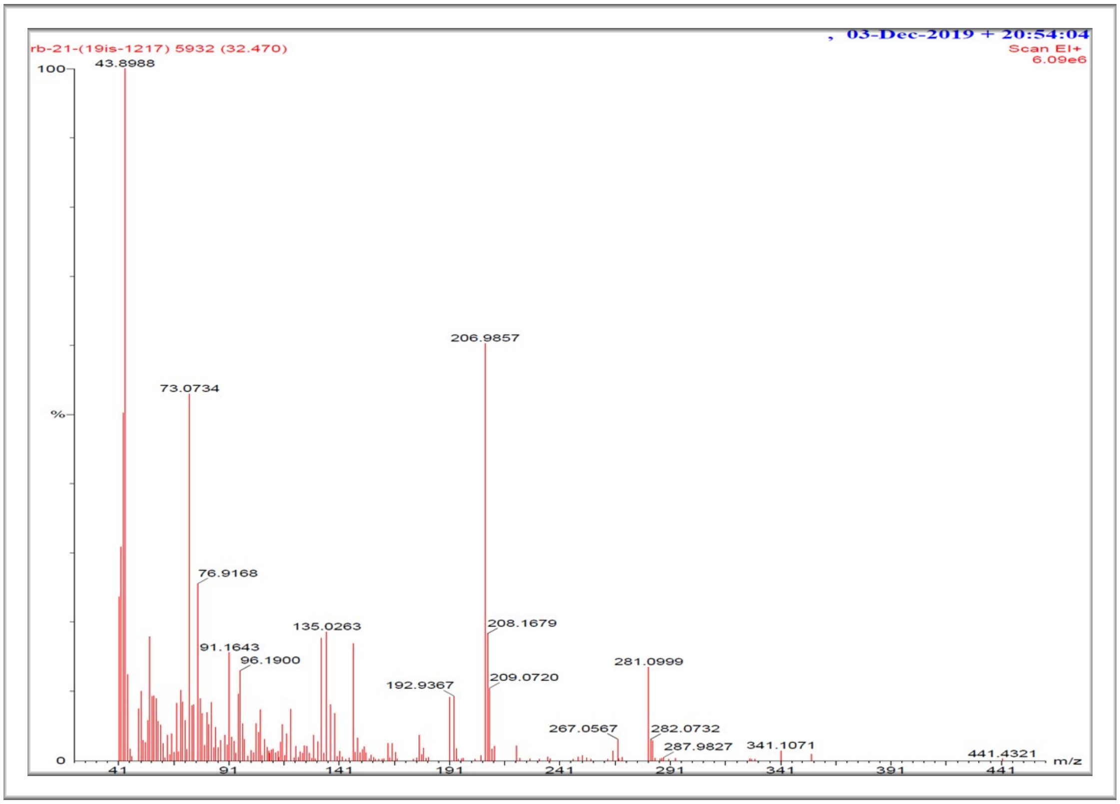
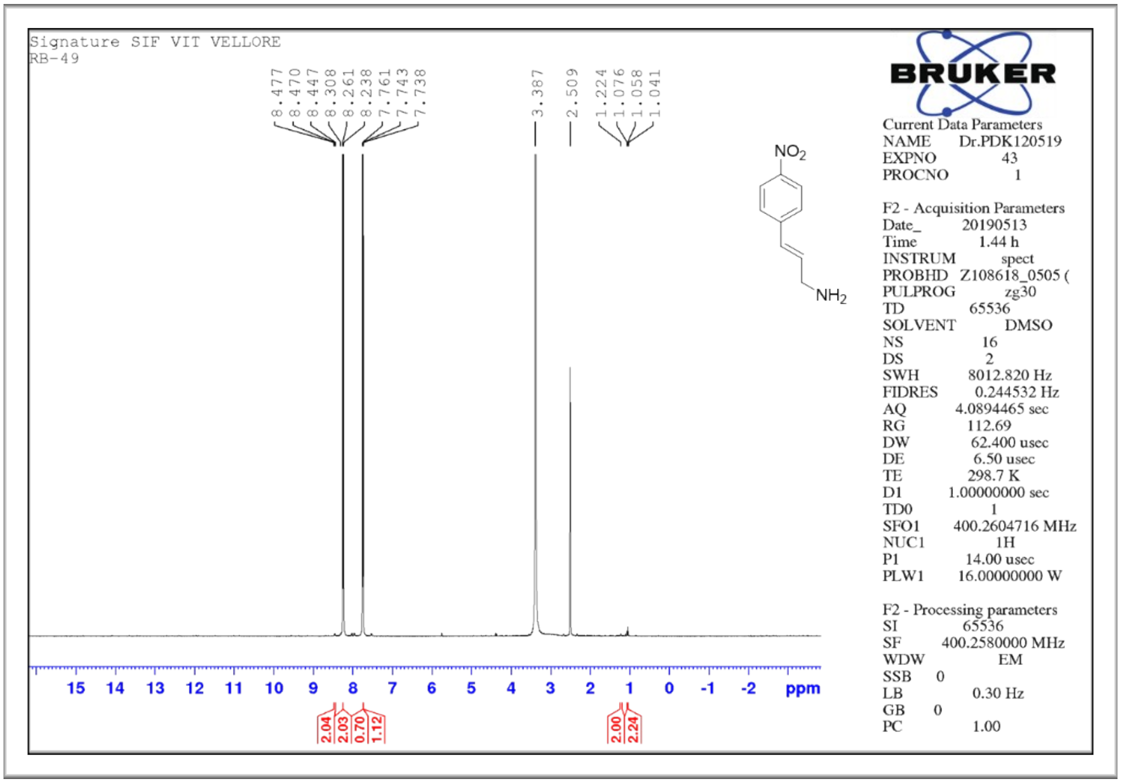


Fig. S24 GC-MS Spectrum of ethyl (E)-3-(4-formylphenyl) acrylate GC-MS: 204.23



Current Data Parameters
NAME Dr.PDK120519
EXPNO 43
PROCNO 1

F2 - Acquisition Parameters
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PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 112.69
DW 62.400 usec
DE 6.50 usec
TE 298.7 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S25 ^{1}H NMR Spectrum of (E)-3-(4-nitrophenyl)prop-2-en-1-amine

^{1}H NMR (400 MHz, DMSO-d6): δ 8.47 (d, 2H), 8.25 (d, 2H), 7.76 (s, 1H), 7.74 (s, 1H), 4.38 (t, 2H), 1.22 (s, 2H)

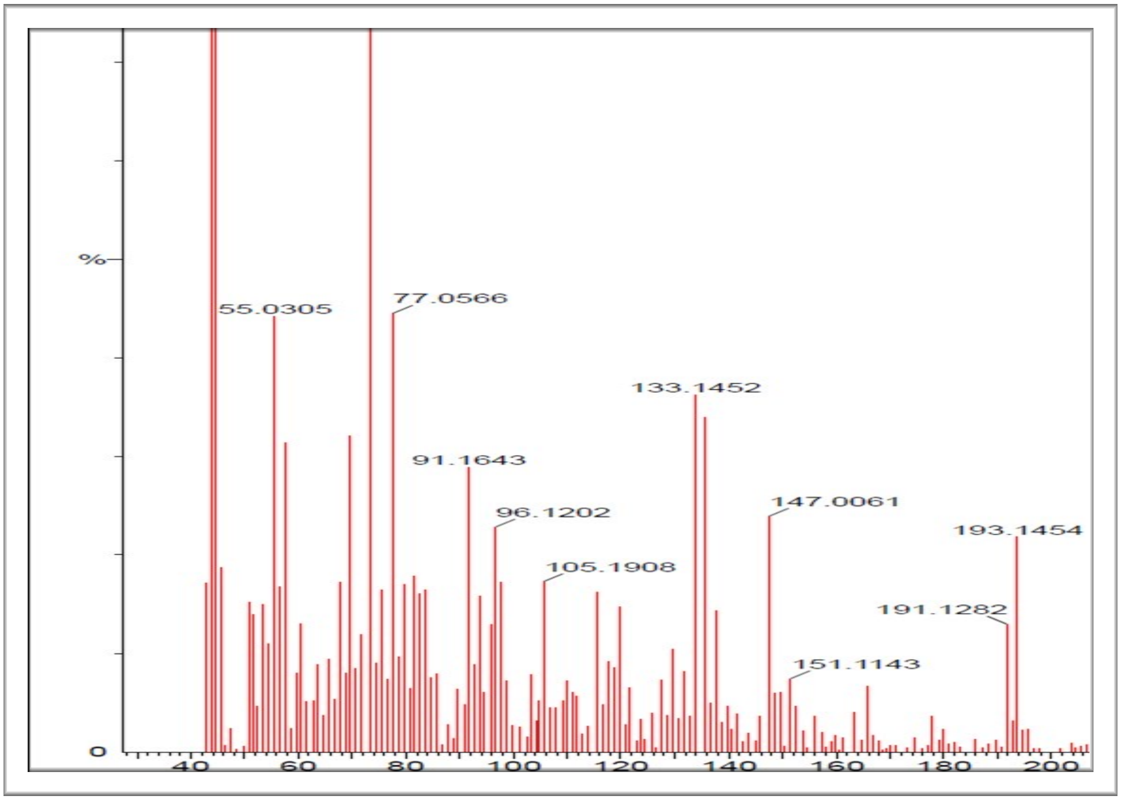


Fig. S26 GC-MS Spectrum of (E)-3-(4-nitrophenyl)prop-2-en-1-amine GC-MS: 178.19

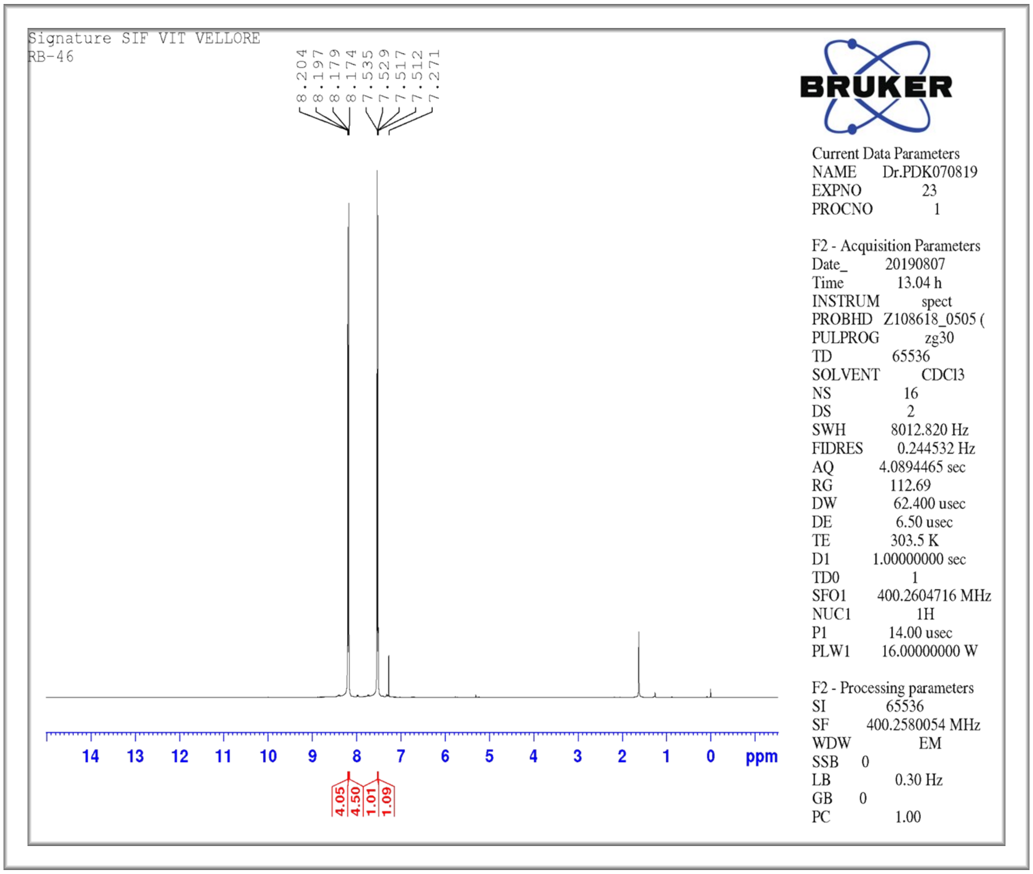
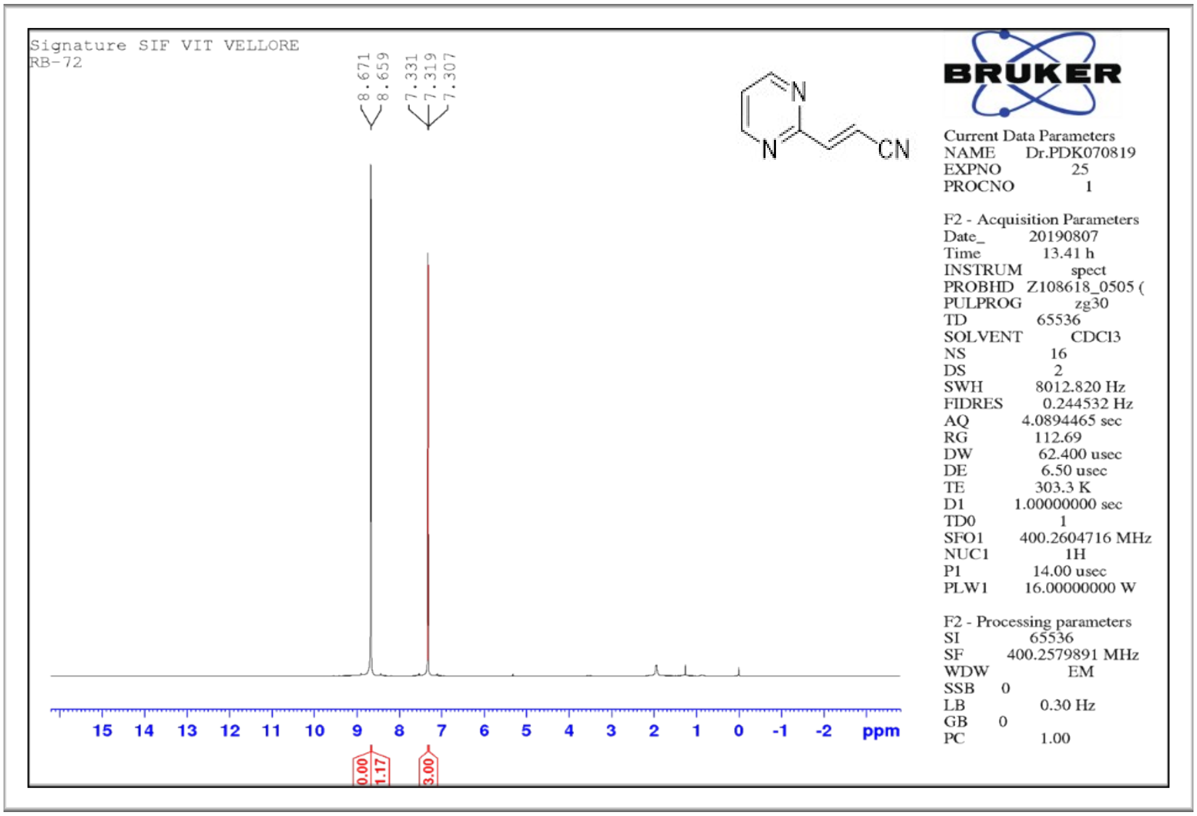


Fig. S27 ^{1}H NMR Spectrum of (E)-1-nitro-4-styrylbenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ : δ 8.19 (d, 4H), 8.18 (d, 4H), 7.53 (d, 1H), 7.51 (d, 1H).

GC-MS: 225.25



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EXPNO 25
PROCNO 1

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TD 65536
SOLVENT CDCl3
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DS 2
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FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 112.69
DW 62.400 usec
DE 6.50 usec
TE 303.3 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2579891 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S28 ^{1}H NMR Spectrum of (E)-3-(pyrimidin-2-yl)acrylonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ : δ 8.66 (d, 2H), 7.53 (d, 1H), 7.31 (t, 1H), 7.11 (d, 1H)

GC-MS: 130.15

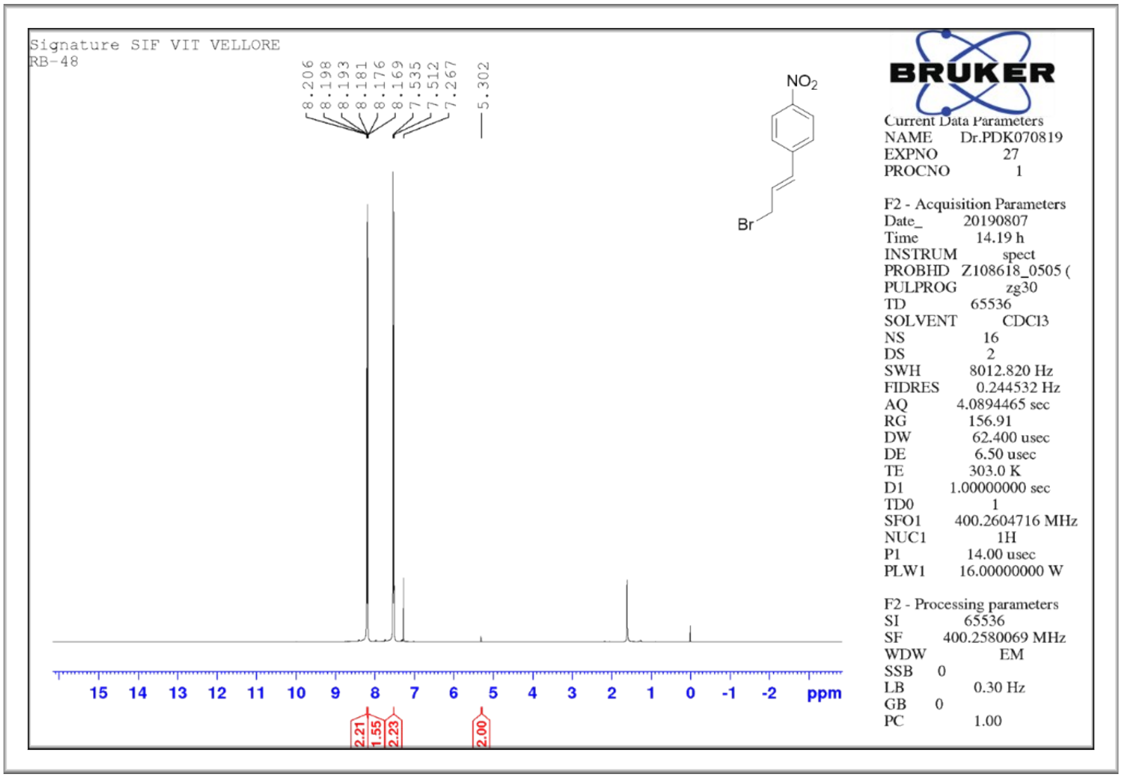


Fig. S29 ^{1}H NMR Spectrum of (E)-1-(3-bromoprop-1-en-1-yl)-4-nitrobenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ :δ 8.19 (d, 2H), 8.18 (d, 2H), 7.53 (d, 1H), 7.51 (t, 1H), 1.59 (s, 1H)

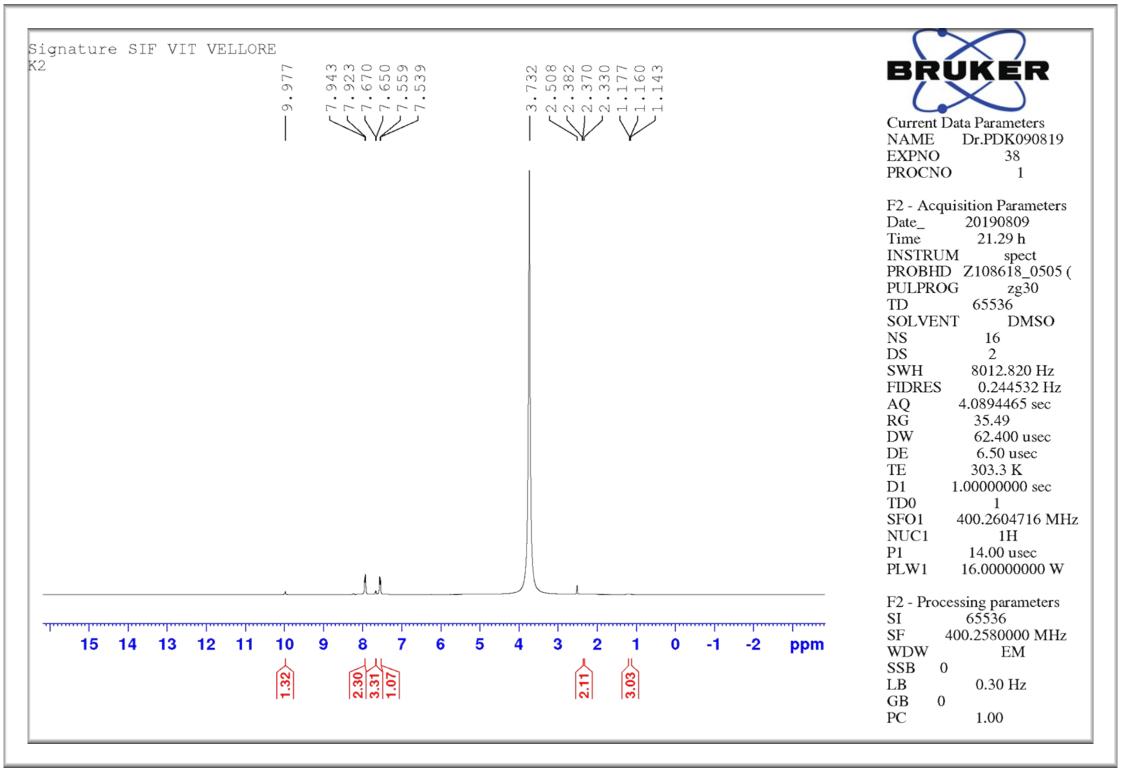
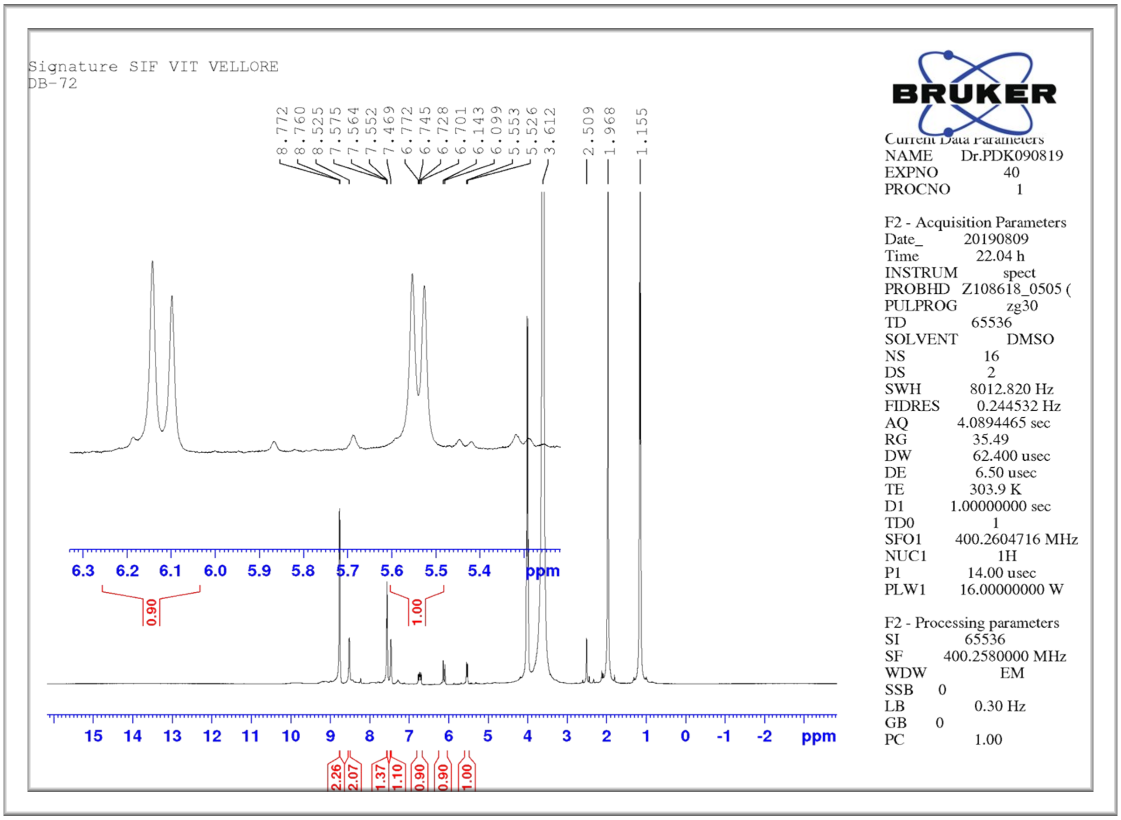


Fig. S30 ^{1}H NMR Spectrum of ethyl(E)-3-(4-formylphenyl)acrylate

^{1}H NMR (400 MHz, DMSO-d6): δ 9.97 (s, 1H), 7.93 (d, 2H), 7.66 (d, 3H), 7.54 (d, 1H), 2.40 (q, 2H), 1.16 (t, 3H).

^{13}C NMR (100 MHz, DMSO-d6): δ 192.69, 167.02, 139.91, 138.32, 138.23, 131.61, 130, 129.62, 129.20, 65.2, 20.4



Current Data Parameters
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PROCNO 1

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SOLVENT DMSO
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FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 35.49
DW 62.400 usec
DE 6.50 usec
TE 303.9 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S31 ^{1}H NMR Spectrum of (E)-(2-(pyridine-4-yl)vinyl)pyrimidine

^{1}H NMR (400 MHz, DMSO-d6): δ 8.77 (d, 2H), 8.52 (s, 2H), 7.56 (t, 1H), 7.46 (s, 1H), 6.74 (t, 1H), 6.12 (d, 1H), 5.54 (d, 1H).

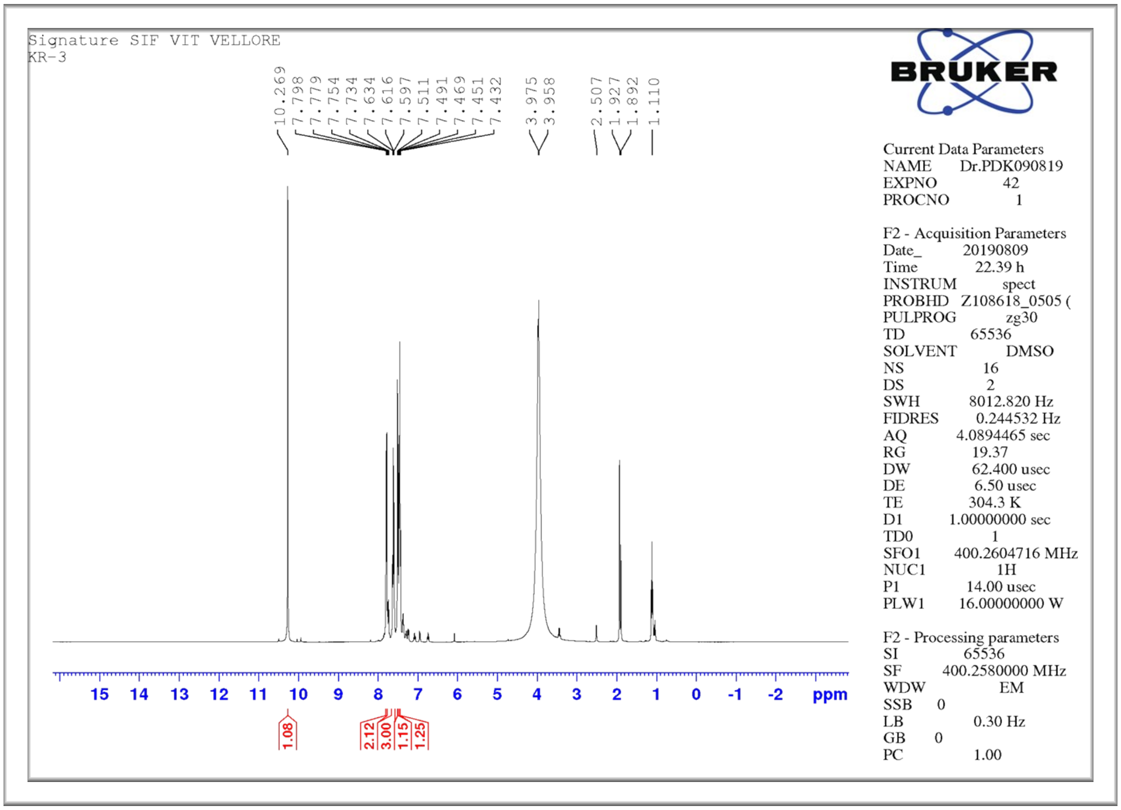


Fig. S32 ^{1}H NMR Spectrum of 2-(thiophen-2-yl)benzaldehyde

^{1}H NMR (400 MHz, DMSO-d6): δ 10.26 (s, 1H), 7.76 (q, 2H), 7.61 (t, 3H), 7.50 (d, 1H), 7.45 (t, 1H).

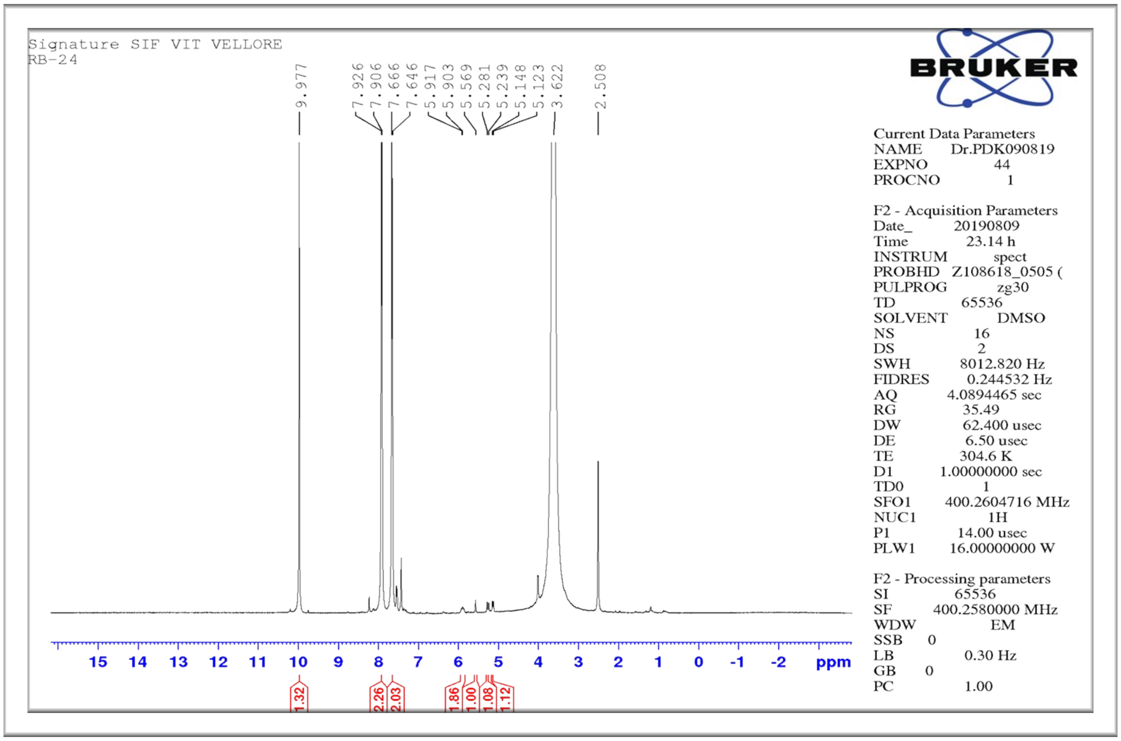


Fig. S33 ^{1}H NMR Spectrum of (Z)-4-(3-hydroxyprop-1-en-yl)benzaldehyde

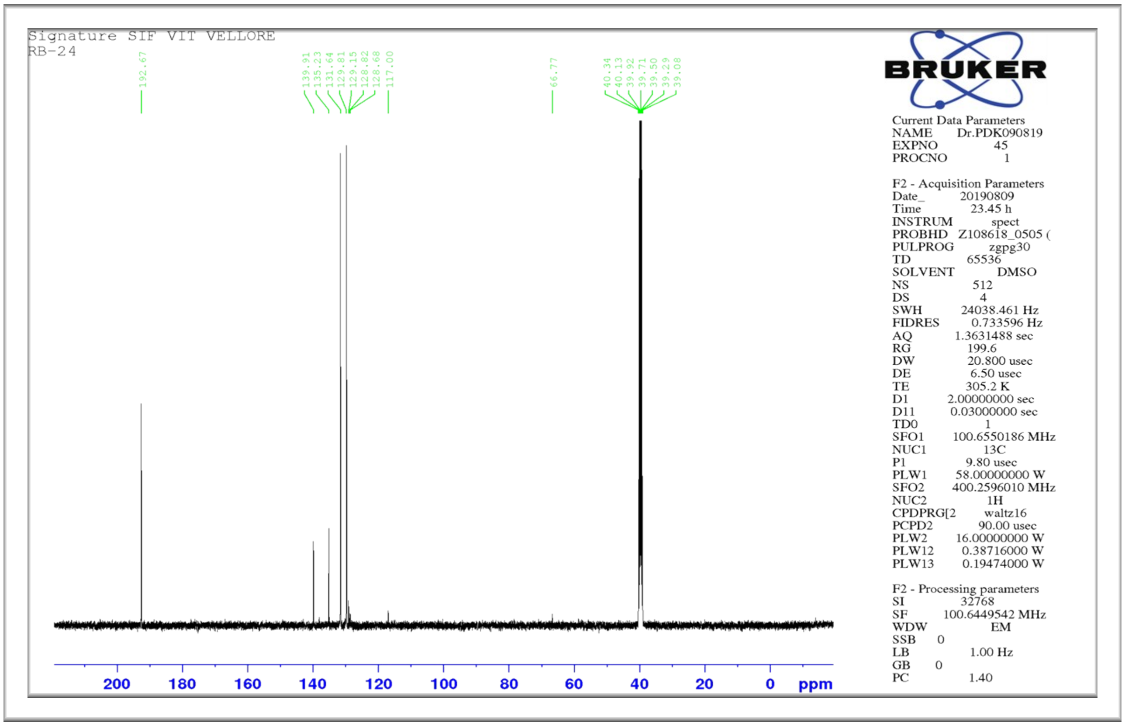


Fig. S34 ^{13}C NMR Spectrum of (Z)-4-(3-hydroxyprop-1-en-yl)benzaldehyde

^{1}H NMR (400 MHz, DMSO-d6): δ 9.97 (s, 1H), 7.91 (d, 2H), 7.65 (d, 2H), 5.91 (d, 2H), 5.56 (s, 1H), 5.26 (d, 1H), 5.13 (d, 1H).

^{13}C NMR (100 MHz, DMSO-d6): δ 192.67, 139.90, 135.23, 131.63, 129.80, 129.14, 128.82, 128.68, 117, 66.74

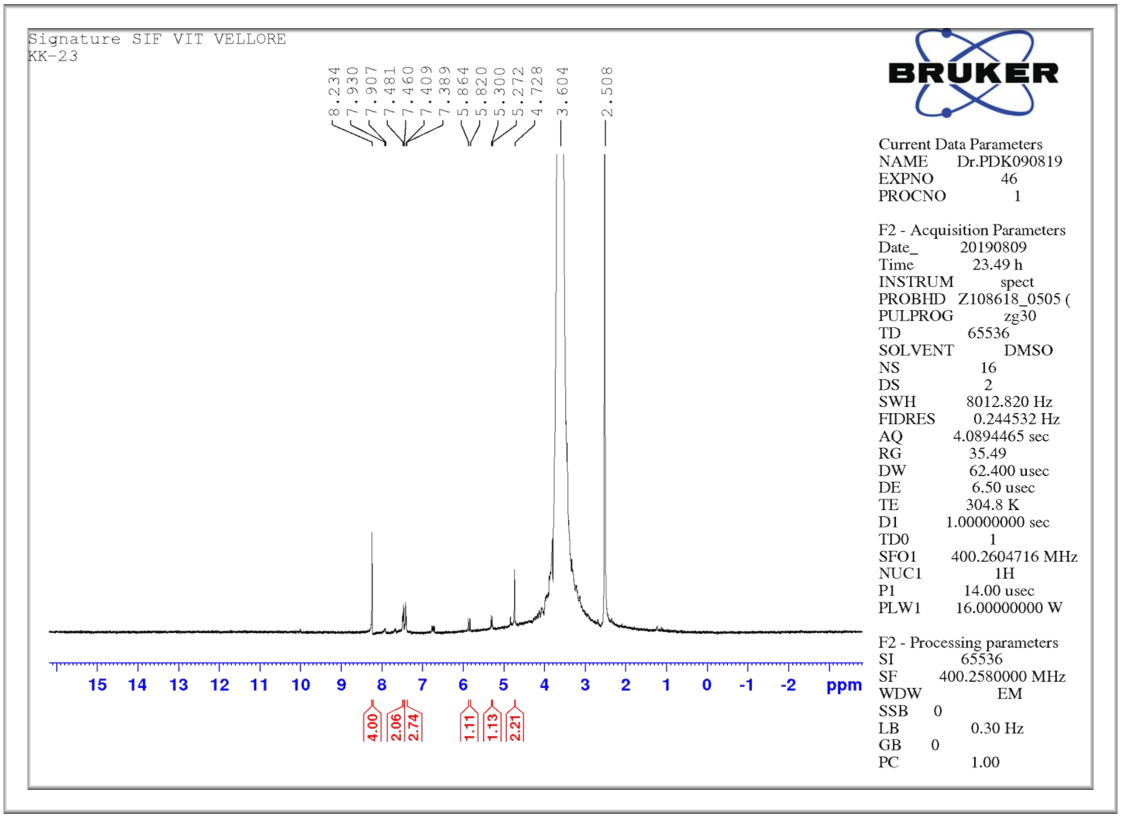


Fig. S35 ^{1}H NMR Spectrum of (Z)-4-(3-bromoprop-1-en-1-yl)benzaldehyde

^{1}H NMR (400 MHz, DMSO-d6): δ 8.23 (s, 4H), 7.47 (d, 2H), 7.39 (d, 3H), 5.84 (d, 1H), 5.29 (d, 1H), 4.72 (s, 2H).

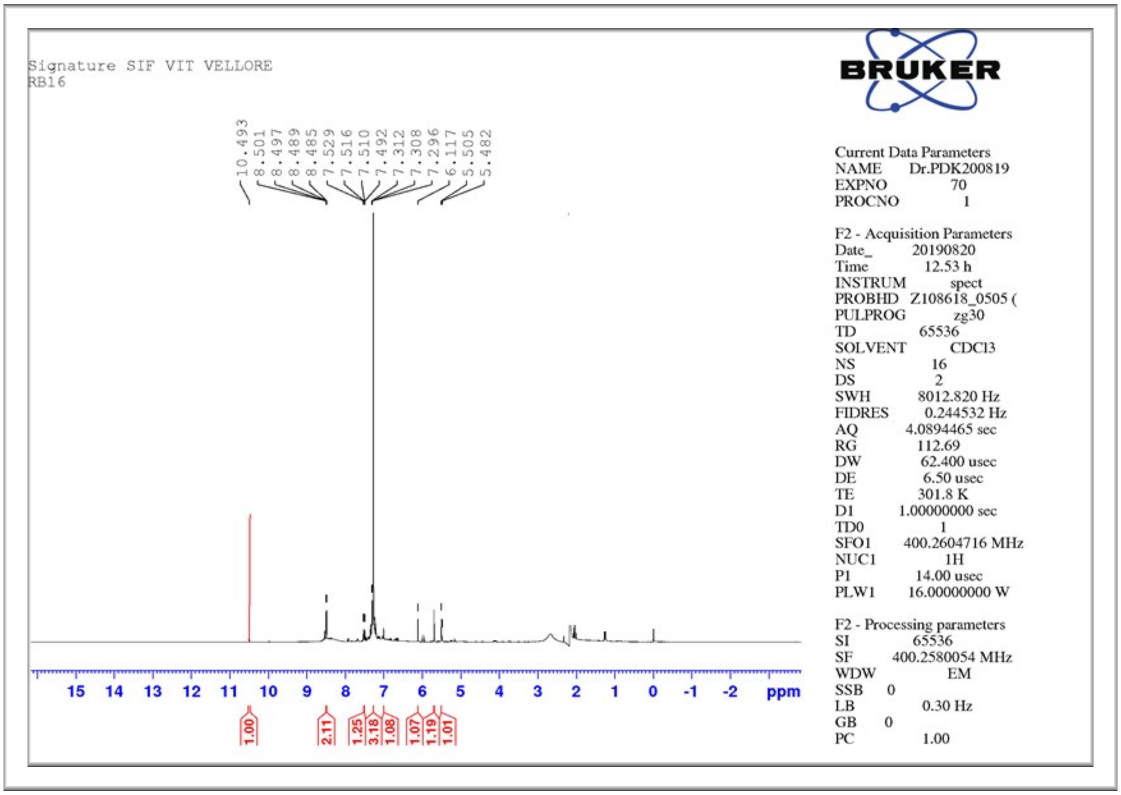
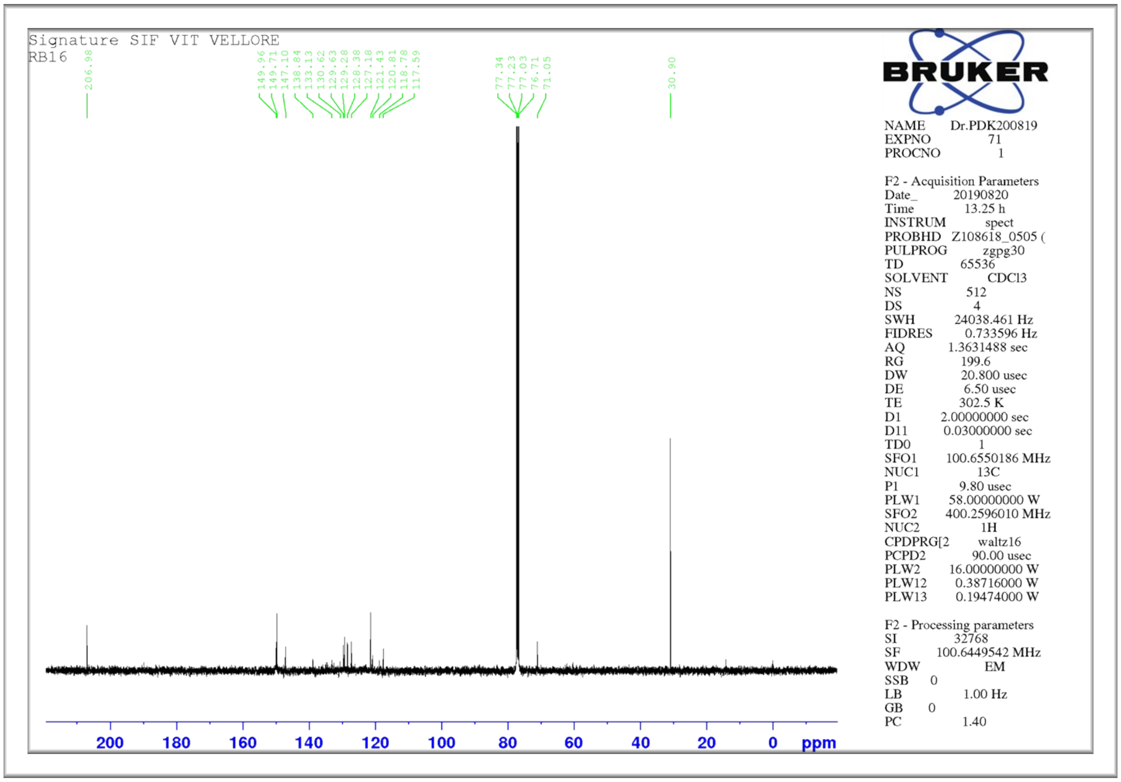


Fig. S36 ^{1}H NMR Spectrum of (E)-2(2-(pyridine-4-yl)vinyl)benzaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) : δ 10.49 (s, 1H), 8.49 (q, 2H), 7.51 (q, 1H), 7.30 (t, 3H), 7.00 (s, 1H), 6.11 (s, 1H), 5.69 (s, 1H), 5.49 (d, 1H).



NAME Dr.PDK200819
EXPNO 71
PROCNO 1

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FIDRES 0.733596 Hz
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RG 199.6
DW 20.800 usec
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TE 302.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6550186 MHz
NUC1 13C
P1 9.80 usec
PLW1 58.00000000 W
SFO2 400.2596010 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.38716000 W
PLW13 0.19474000 W

F2 - Processing parameters
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SF 100.6449542 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Fig. S37 ^{13}C NMR Spectrum of (E)-2(2-(pyridine-4-yl)vinyl)benzaldehyde

^{13}C NMR (100 MHz, $CDCl_3$) : δ 206.97, 149.95, 149.71, 147.10, 138.83, 133.12, 130.62, 129.63, 129.27, 128.37, 127.18, 121.41, 120.80, 118.78, 117.59

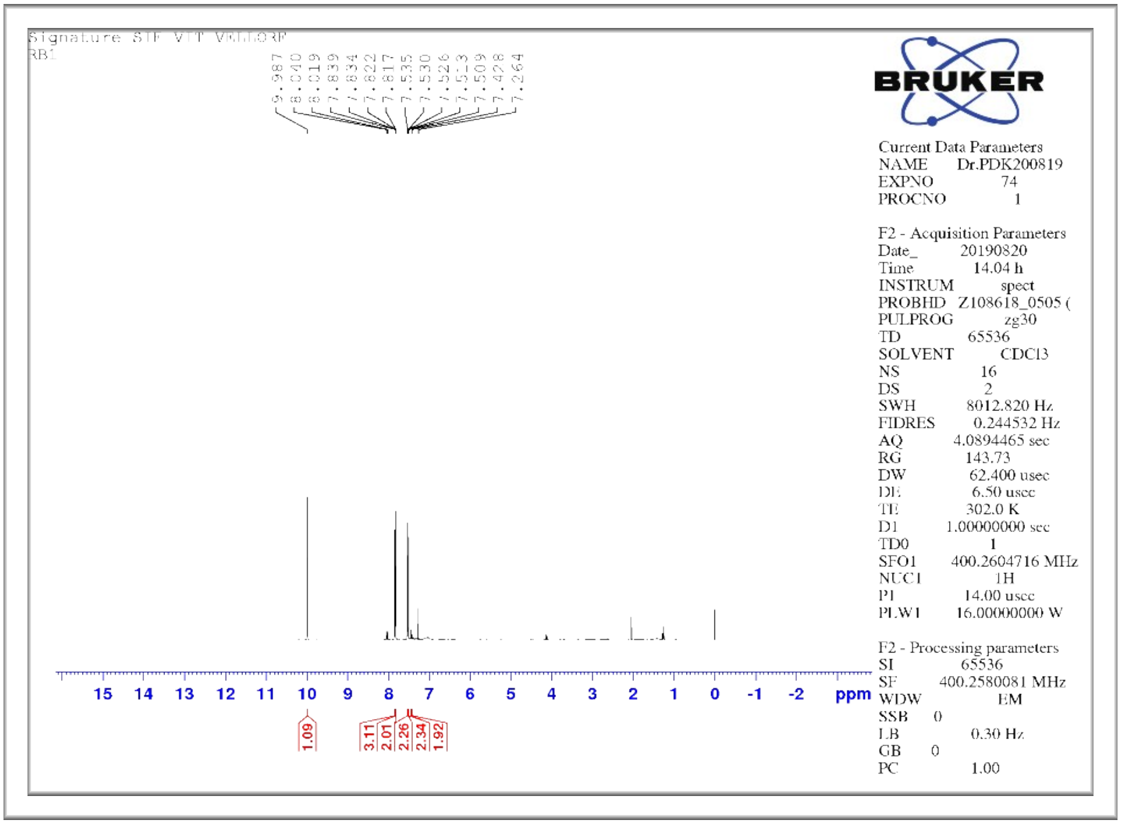
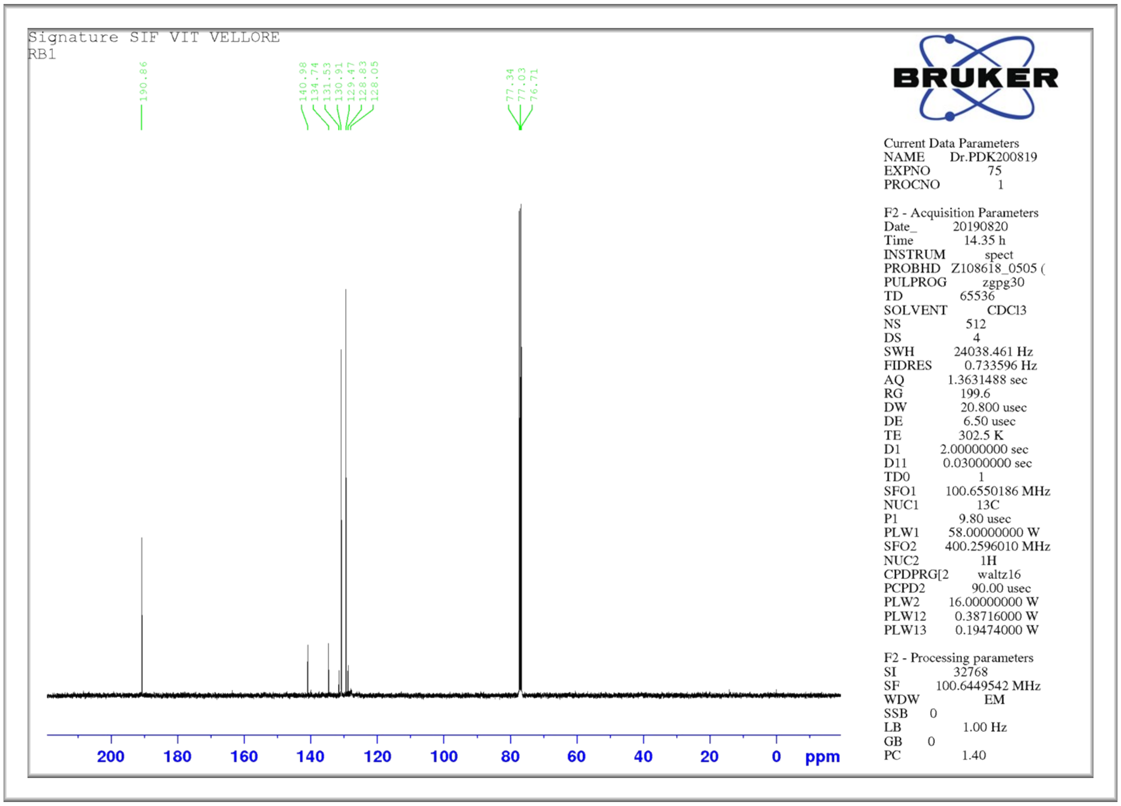


Fig. S38 ^{1}H NMR Spectrum of (Z)-4-styrylbenzaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) : δ 9.98 (s, 1H), 7.83 (d, 3H), 7.82 (d, 2H), 7.52 (t, 2H), 7.51 (d, 2H), 7.42 (s, 2H).



Current Data Parameters
NAME Dr.PDK200819
EXPNO 75
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190820
Time 14.35 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 199.6
DW 20.800 usec
DE 6.50 usec
TE 302.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6550186 MHz
NUC1 13C
P1 9.80 usec
PLW1 58.00000000 W
SFO2 400.2596010 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.38716000 W
PLW13 0.19474000 W

F2 - Processing parameters
SI 32768
SF 100.6449542 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Fig. S39 ^{13}C NMR Spectrum of (Z)-4-styrylbenzaldehyde

^{13}C NMR (100 MHz, $CDCl_3$) : δ 190.86, 140.98, 134.73, 131.52, 130.91, 129.47, 128.83, 128.05.

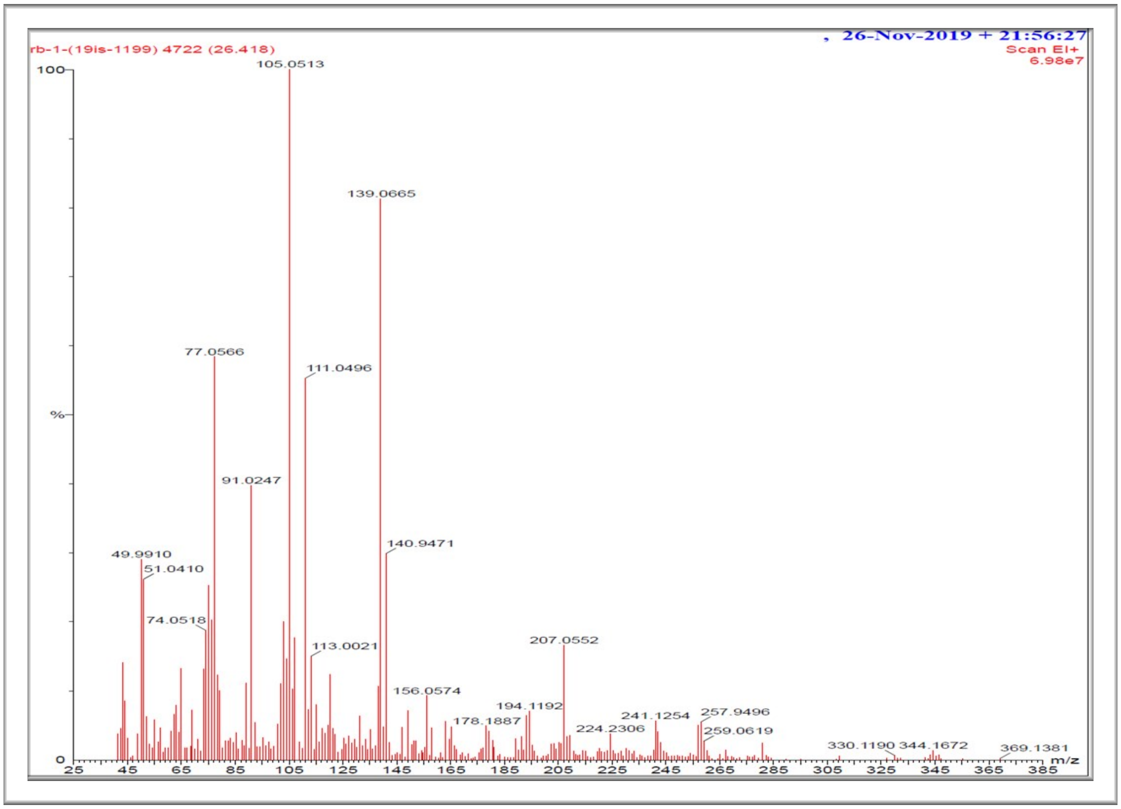


Fig. S40 GC-MS Spectrum of (Z)-4-styrylbenzaldehyde GC-MS: 208.26

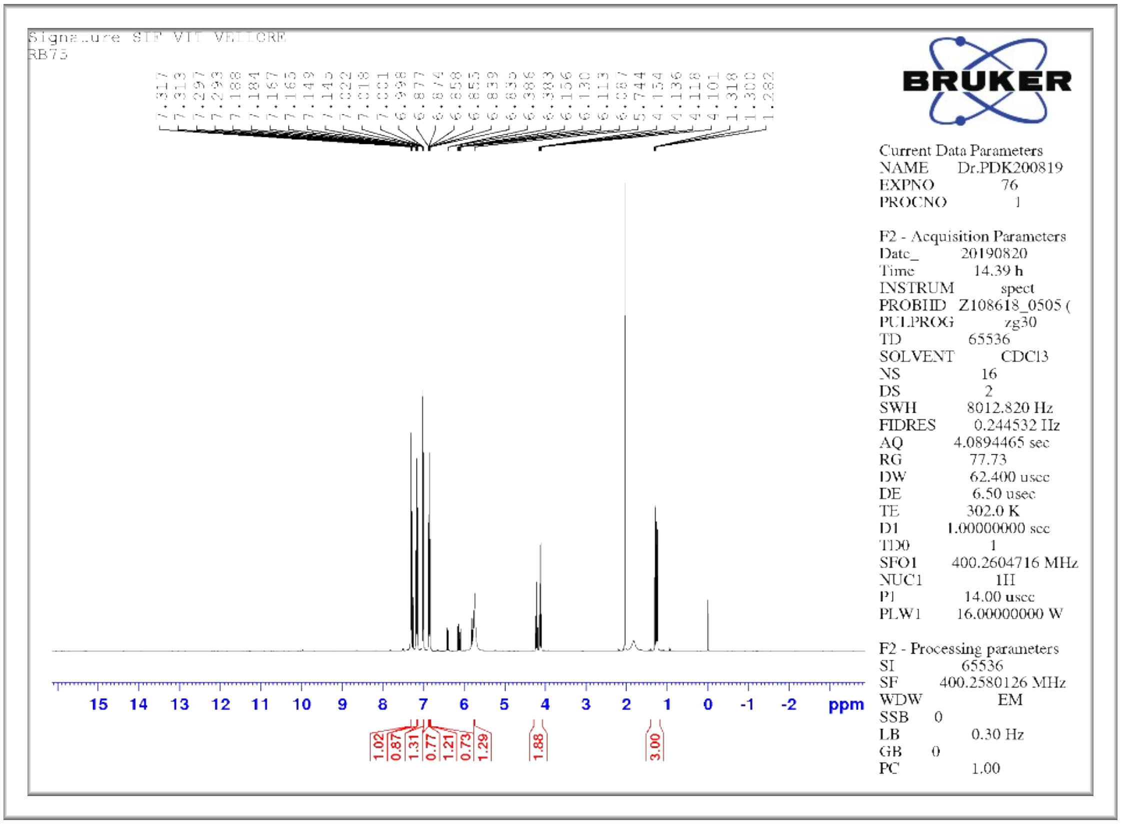


Fig. S41 ^{1}H NMR Spectrum of ethyl(E)-3-(2-hydroxyphenyl)acrylate

^{1}H NMR (400 MHz, CDCl$_3$) : δ 7.30 (d, 1H), 7.14 (d, 1H), 7.35 (d, 1H), 6.87 (d, 1H), 6.85 (d, 1H), 6.83 (d, 1H), 5.74 (s, 1H), 4.12 (q, 2H), 1.29 (t, 3H), .

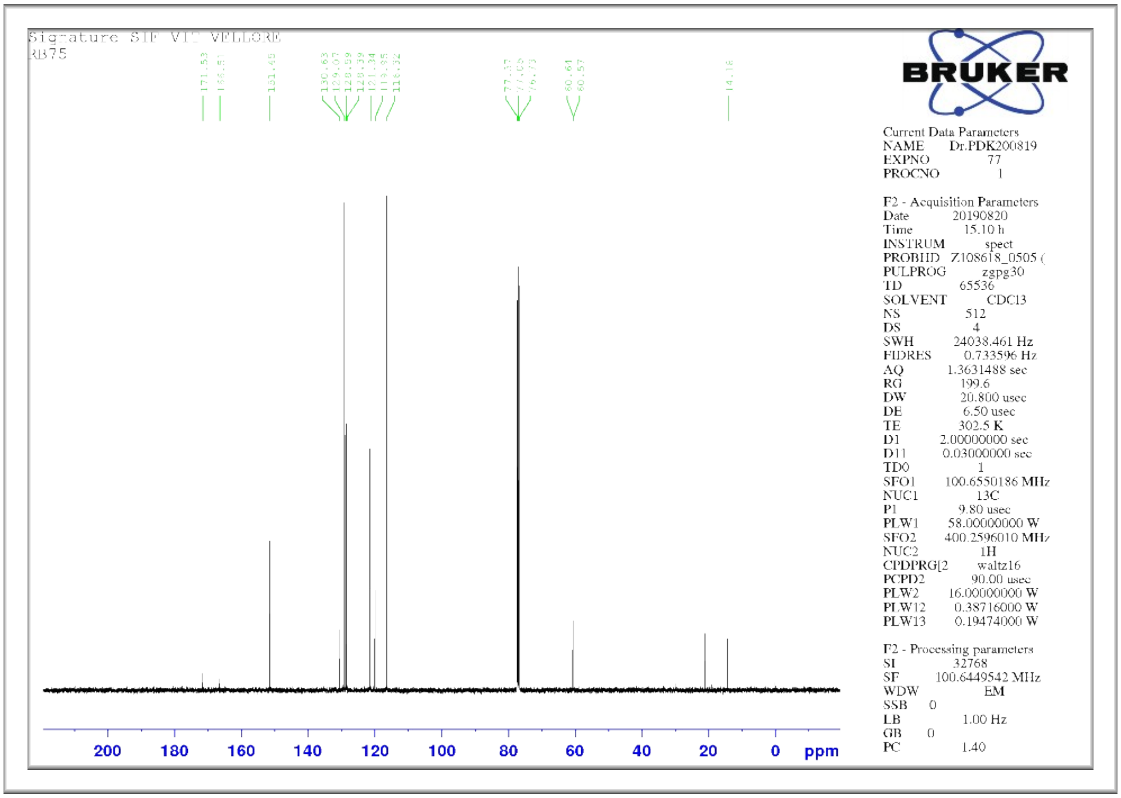


Fig. S42 ^{13}C NMR Spectrum of ethyl(E)-3-(2-hydroxyphenyl)acrylate

^{13}C NMR (100 MHz, $CDCl_3$) : δ 166.51, 151.45, 130.63, 129.07, 128.59, 128.38, 121.33, 119.94, 116.32, 60.64, 14.17

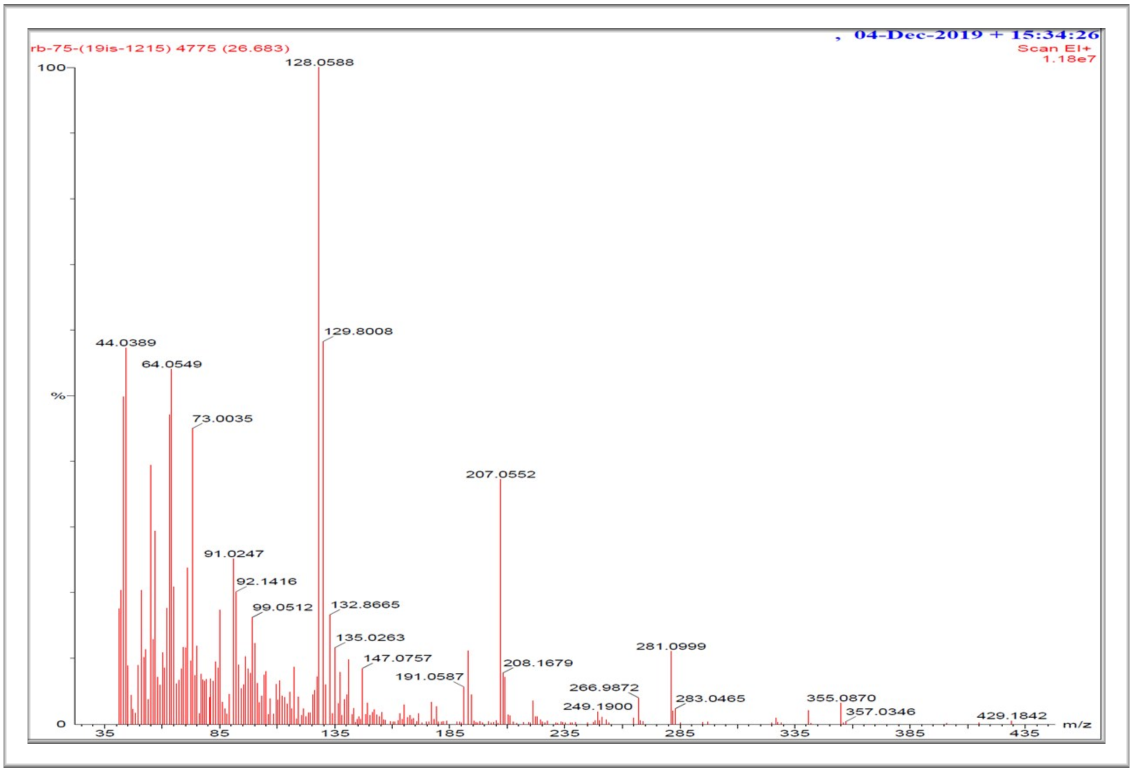
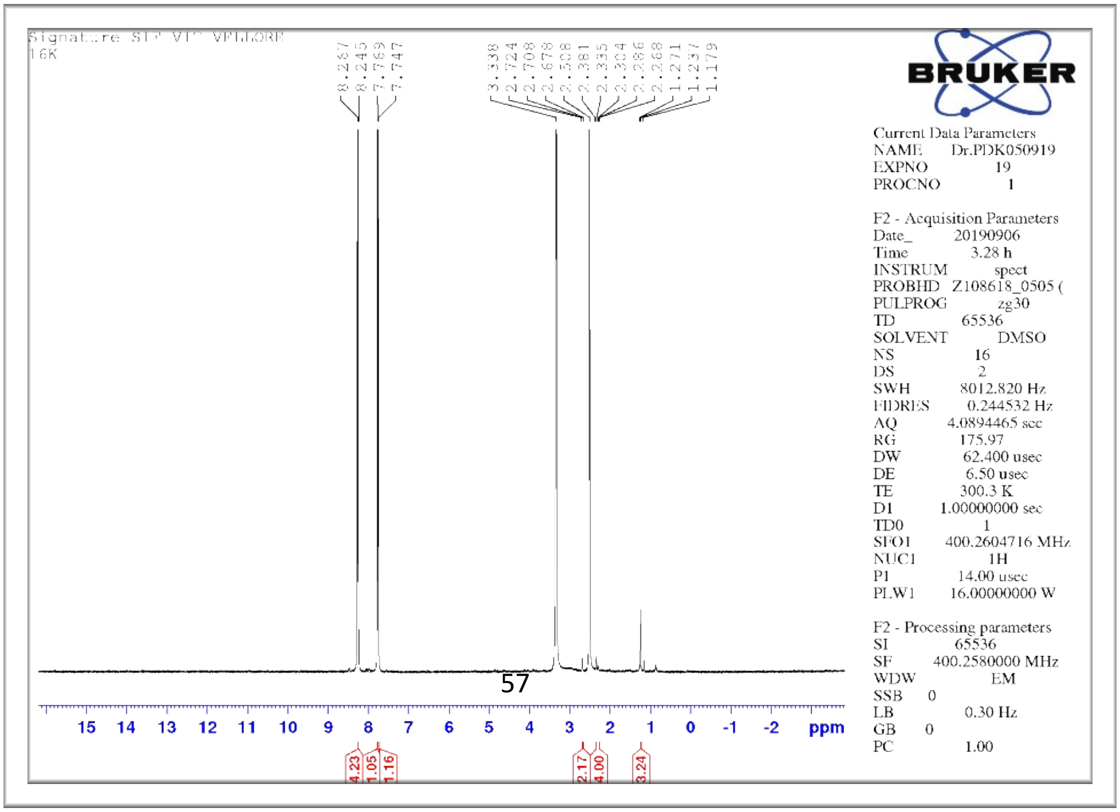


Fig. S43 GC-MS ethyl(E)-3-(2-hydroxyphenyl)acrylate GC-MS : 192.018



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Current Data Parameters
NAME       Dr.PDK050919
EXPNO             19
PROCNO             1

F2 - Acquisition Parameters
Date_         20190906
Time            3.28 h
INSTRUM          spect
PROBHD   Z108618_0505 (
PULPROG           zg30
TD               65536
SOLVENT           DMSO
NS                  16
DS                   2
SWH         8012.820 Hz
FIDRES      0.244532 Hz
AQ        4.0894465 sec
RG              175.97
DW          62.400 usec
DE            6.50 usec
TE             300.3 K
D1       1.00000000 sec
TD0                  1
SFO1    400.2604716 MHz
NUC1                1H
P1           14.00 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI               65536
SF      400.2580000 MHz
WDW                 EM
SSB      0
LB             0.30 Hz
GB       0
PC                1.00
```

Fig. S44 ^{1}H NMR Spectrum of (Z)-1-(4-nitrophenyl)hept-1-en-one

^{1}H NMR (400 MHz, DMSO-d6): δ 8.25 (d, 4H), 7.75 (d, 2H), 2.70 (t, 2H), 2.26-2.28 (m, 4H), 1.22 (t, 3H)

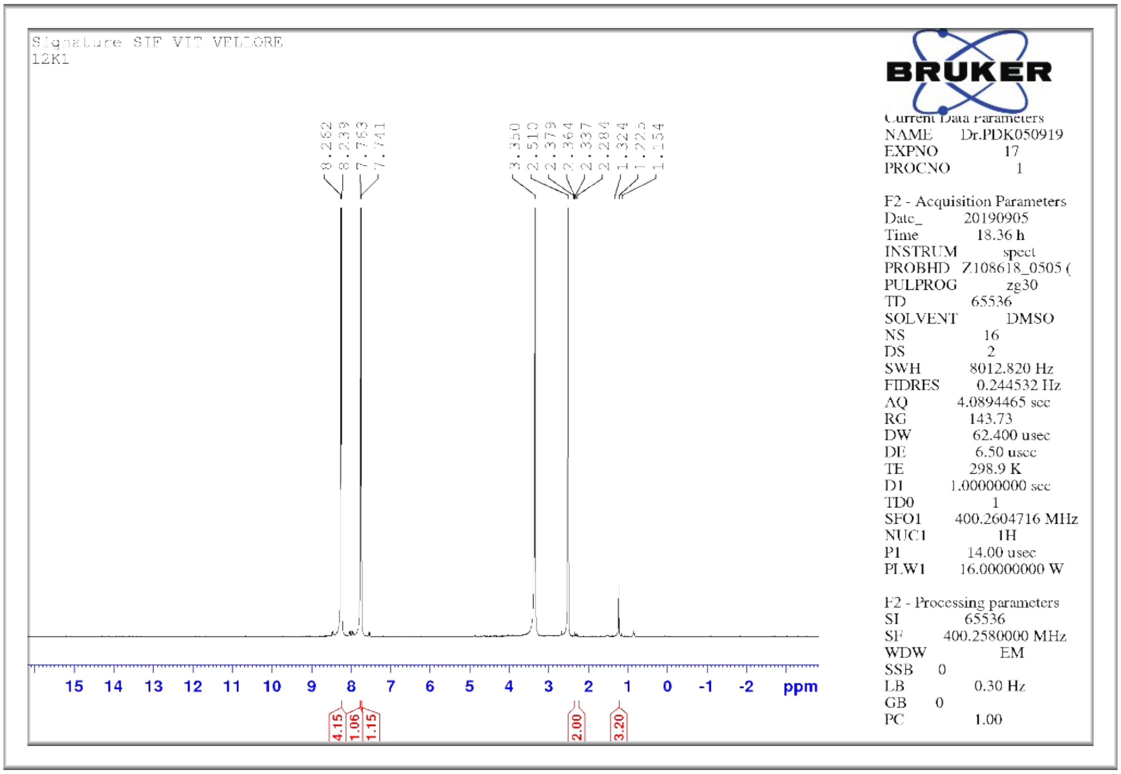
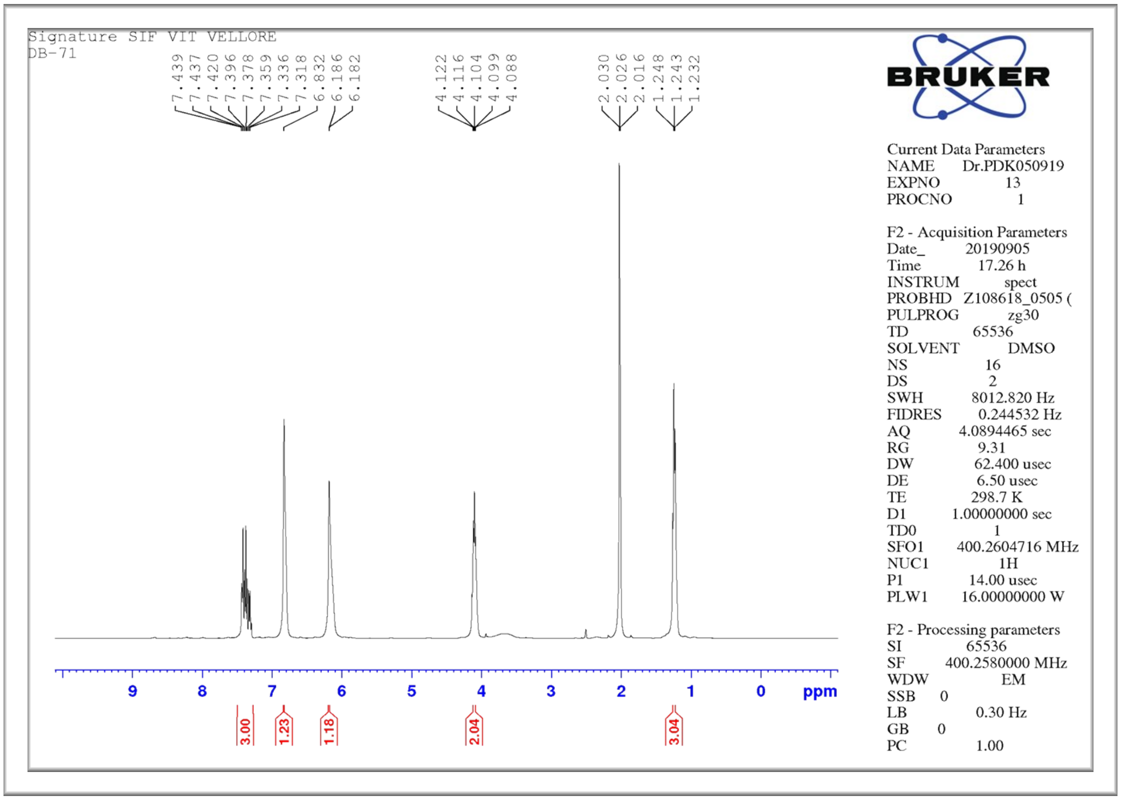


Fig. S45 ^{1}H NMR Spectrum of ethyl(Z)-3(4-nitrophenyl)acrylate

^{1}H NMR (400 MHz, DMSO-d6): δ 8.25 (d, 4H), 7.75 (d, 2H), 2.28-2.33 (m, 2H), 1.23 (t,3H)



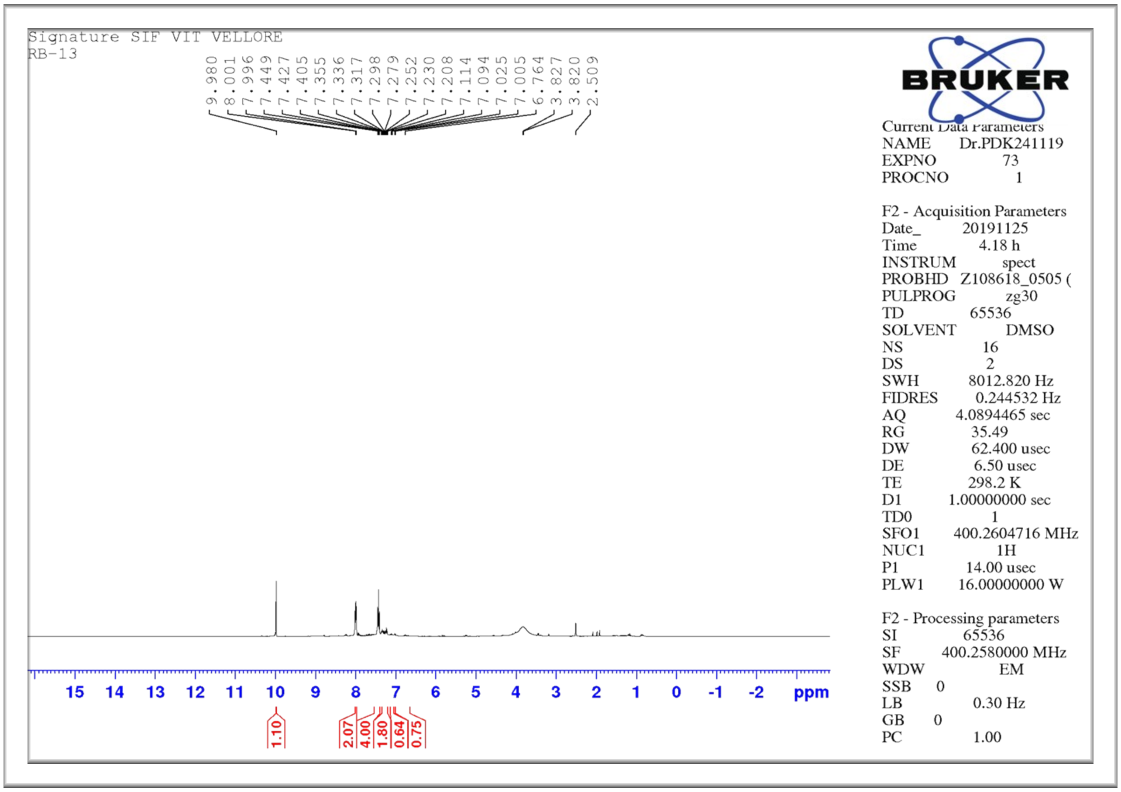
Current Data Parameters
NAME Dr.PDK050919
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190905
Time 17.26 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 9.31
DW 62.400 usec
DE 6.50 usec
TE 298.7 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S46 ^{1}H NMR Spectrum of ethyl(Z)-3-(pyrimidin-2-yl)acrylate

^{1}H NMR (400 MHz, DMSO-d6): δ 7.31-7.33 (m, 3H), 6.83 (s, 1H), 6.18 (d, 1H), 4.09-4.10 (m, 2H), 1.24 (t, 3H)



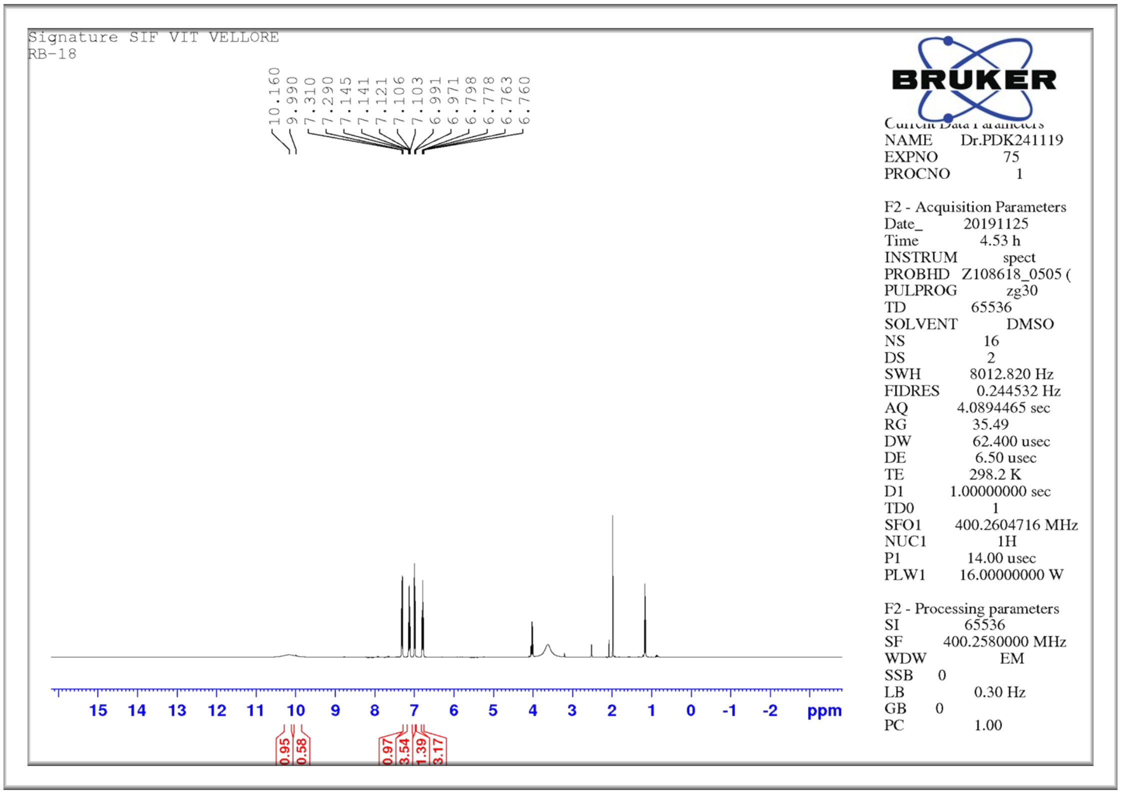
Current Data Parameters
NAME Dr.PDK241119
EXPNO 73
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191125
Time 4.18 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 35.49
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S47 ^{1}H NMR Spectrum of (E)-4-styrylbenzaldehyde

^{1}H NMR (400 MHz, DMSO-d6): δ 9.98 (s, 1H), 8.00 (d, 2H), 7.42 (t, 4H), 7.31 (q, 2H), 7.10 (d, 1H), 6.76 (s, 1H).



Current Data Parameters
NAME Dr.PDK241119
EXPNO 75
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191125
Time 4.53 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 35.49
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S48 ^{1}H NMR Spectrum of (Z)-2-hydroxy-5-(2-(pyridine-4-yl)vinyl)benzaldehyde

^{1}H NMR (400 MHz, DMSO-d6): δ 10.16 (s, 1H), 9.98 (s, 1H), 7.30 (d, 1H), 7.12 (t, 4H), 6.98 (d, 1H), 6.77 (q, 3H).

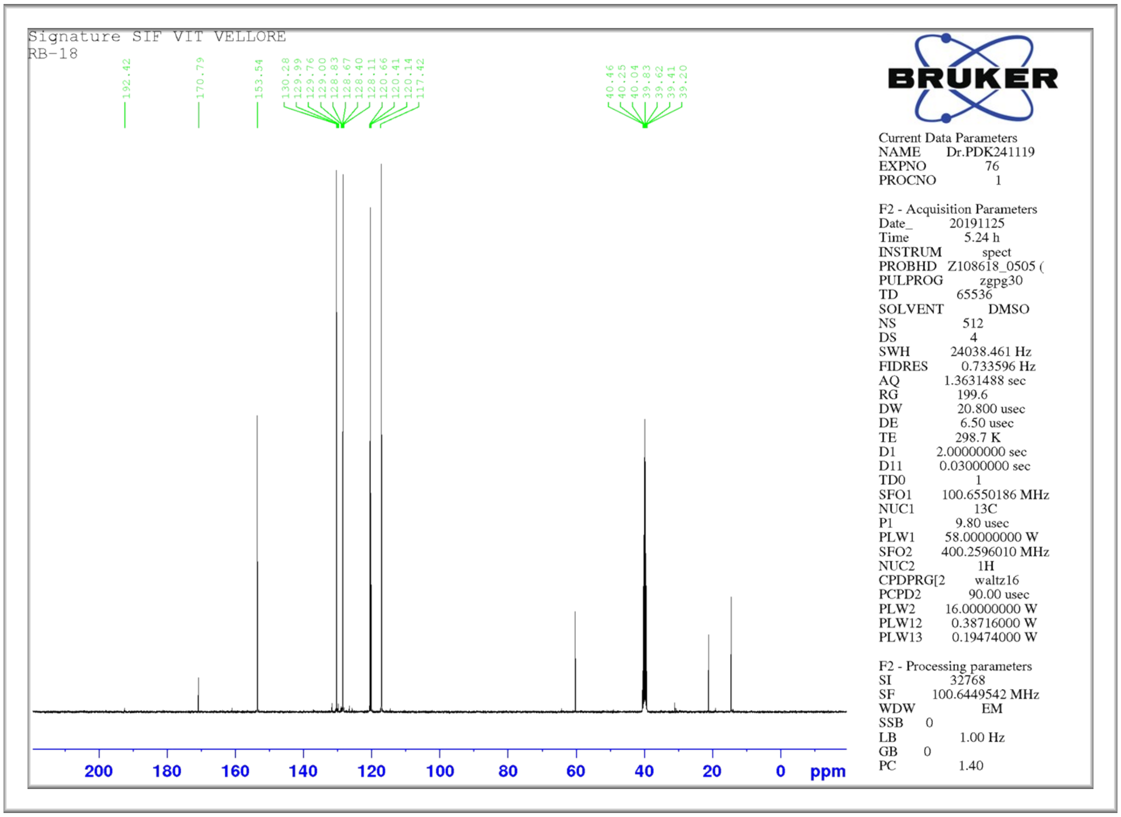


Fig. S49 ^{13}C NMR Spectrum of (Z)-2-hydroxy-5-(2-(pyridine-4-yl)vinyl)benzaldehyde

^{13}C NMR (100 MHz, DMSO-d6): δ 192.42, 170.79, 153.54, 130.28, 129.99, 129.76, 128.99, 128.83, 128.67, 128.40, 128.11, 120.66, 120.41, 120.14, 117.42

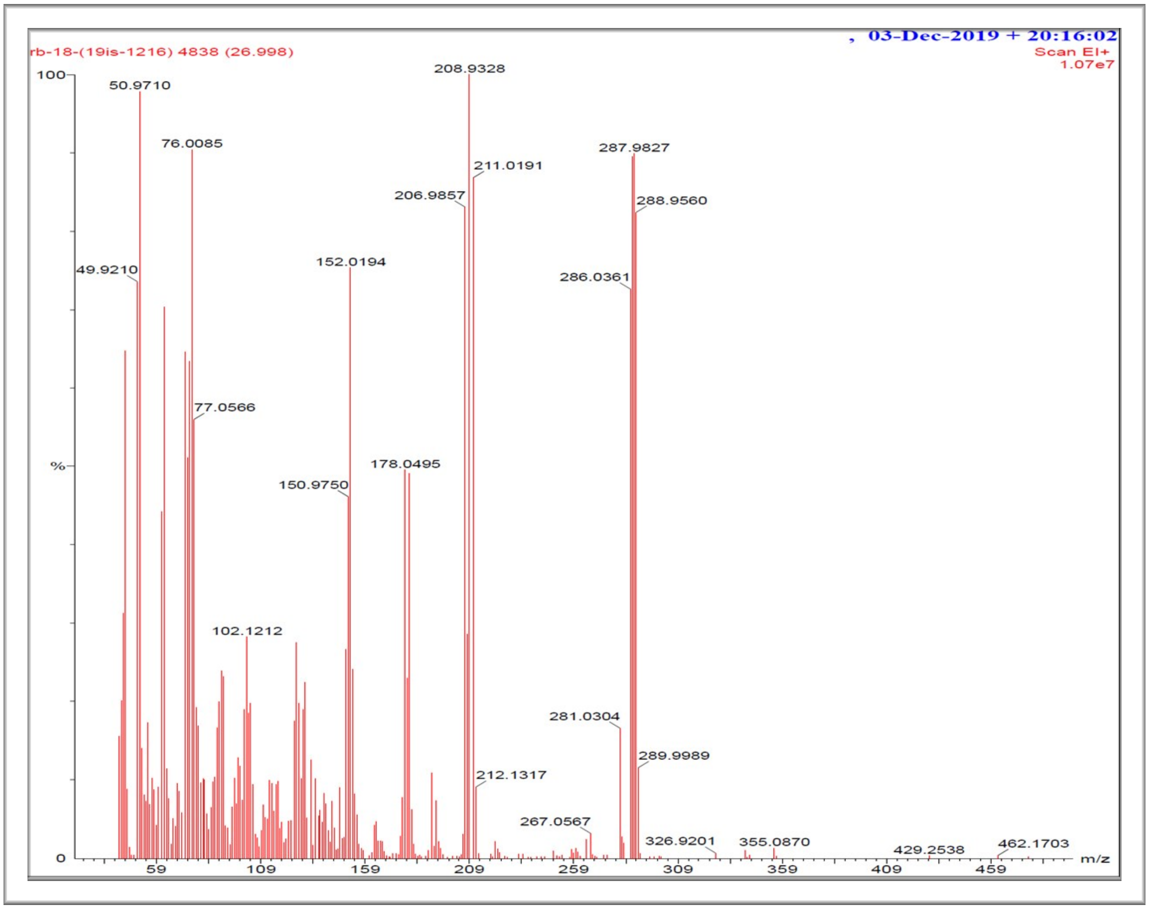


Fig. S50 GC-MS Spectrum of (Z)-2-hydroxy-5-(2-(pyridine-4-yl)vinyl)benzaldehyde
GC-MS: 225.25

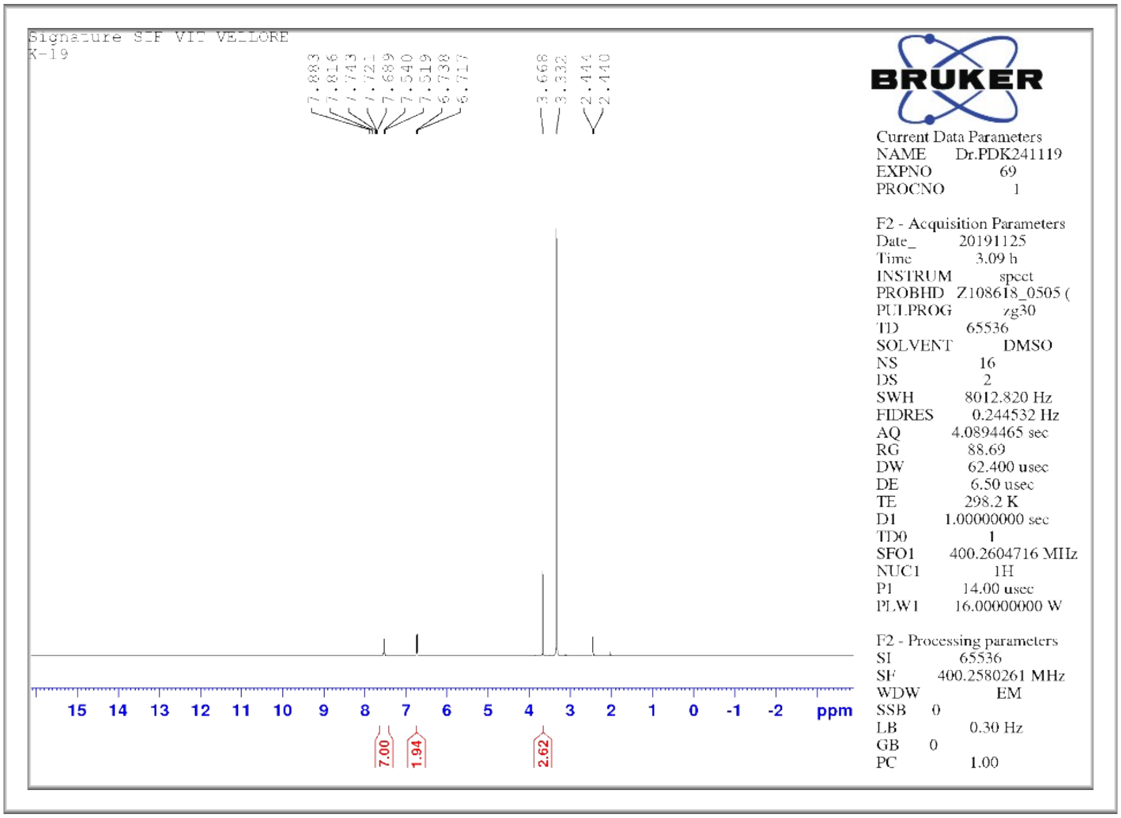
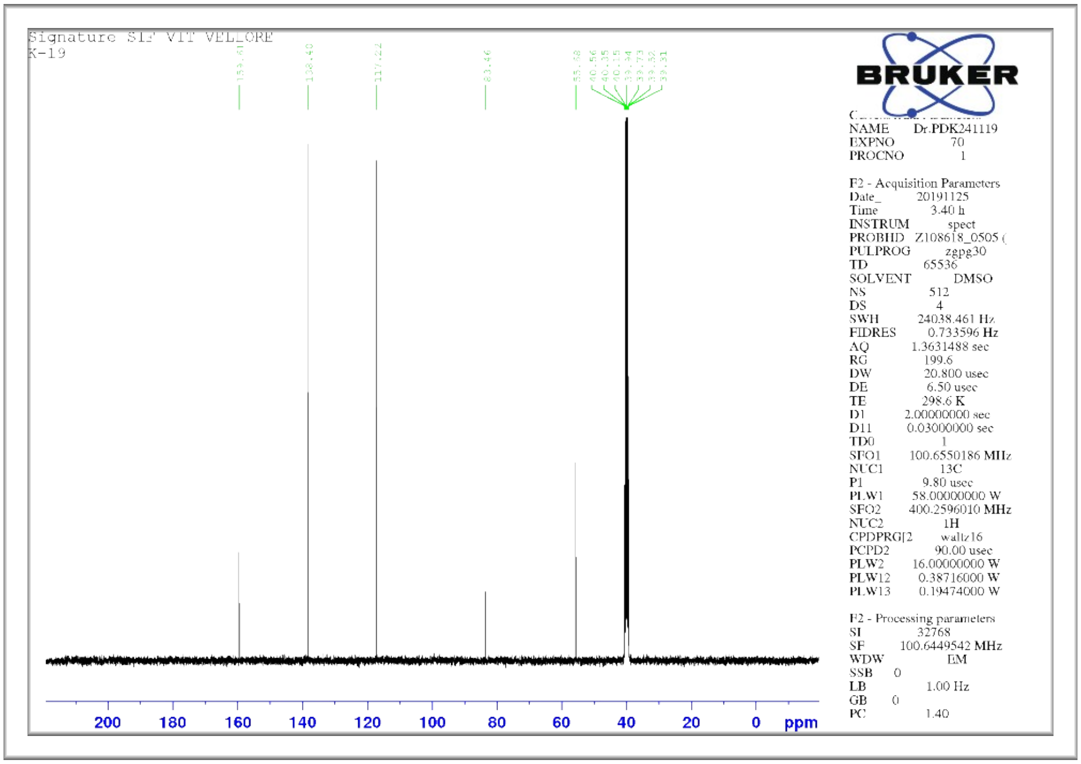


Fig. S51 ^{1}H NMR Spectrum of 4-methoxy-1,1’-biphenyl

^{1}H NMR (400 MHz, DMSO-d6): δ 7.54-7.68 (m, 7H), 6.72 (d, 2H), 3.66 (s, 2H).



NAME Dr.PDK241119
EXPNO 70
PROCNO 1

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INSTRUM spect
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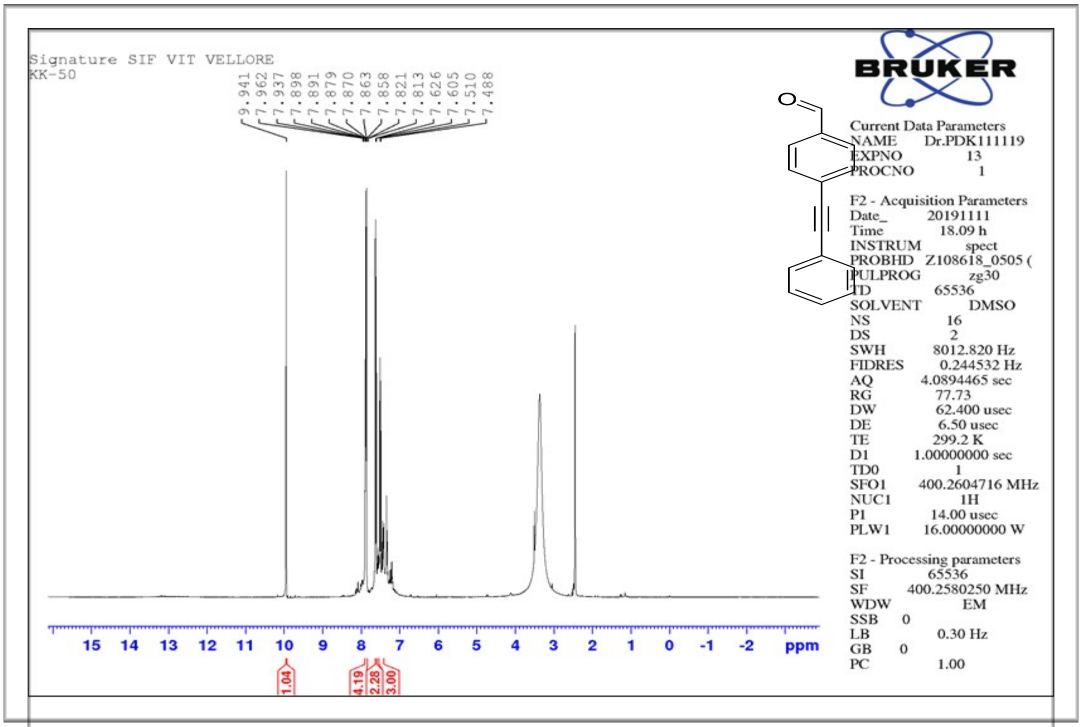
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 199.6
DW 20.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6550186 MHz
NUC1 13C
P1 9.80 usec
PLW1 58.00000000 W
SFO2 400.2596010 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.38716000 W
PLW13 0.19474000 W

F2 - Processing parameters
SI 32768
SF 100.6449542 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Fig. S52 ^{13}C NMR Spectrum of 4-methoxy-1,1'-biphenyl
^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.61, 138.40, 117.21, 83.46, 55.67.

Sonogashira Coupling



Current Data Parameters
NAME Dr.PDK111119
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191111
Time 18.09 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 77.73
DW 62.400 usec
DE 6.50 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580250 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S53 ^{1}H NMR Spectrum of 4-(phenylethyl)benzaldehyde

400 MHz, DMSO-d6: δ 9.94 (s, 1H), 7.82-7.85 (m, 4H), 7.61 (d, 2H), 7.50 (d, 3H).

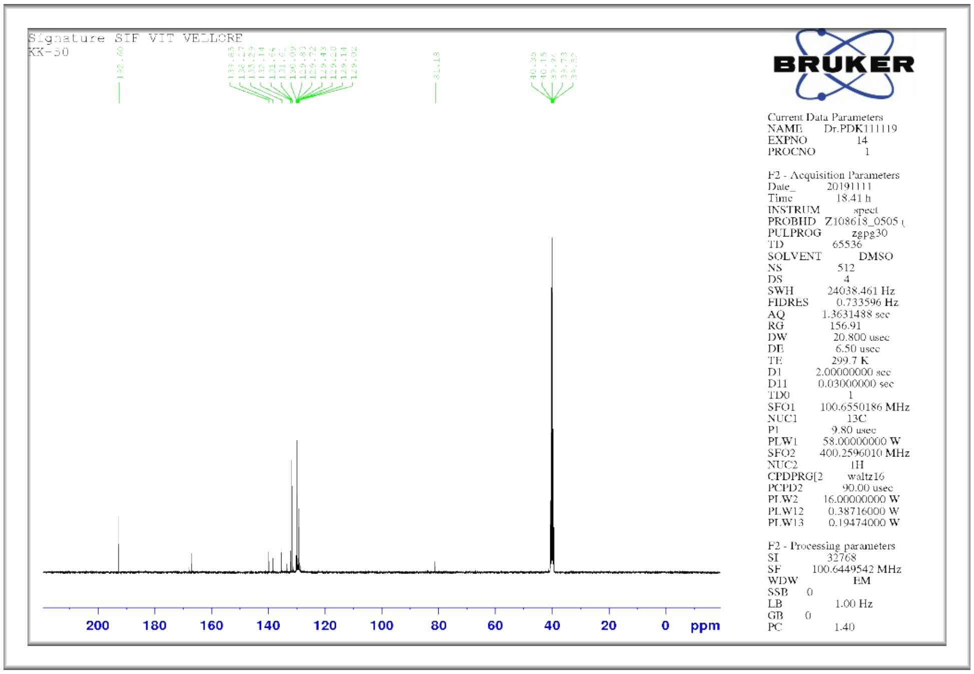


Fig. S54 ^{13}C NMR Spectrum of 4-(phenylethyl)benzaldehyde

^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.60, 137.05, 138.27, 135.74, 132.14, 131.44, 130.09, 129.80, 129.72, 129.43, 129.20, 129.14, 129.02, 81.10

Table S2. ^{1}H and ^{13}C value for Sonogashira coupling between various Ethynylbenzene and Aryl halide under Photocatalytic Conditions.

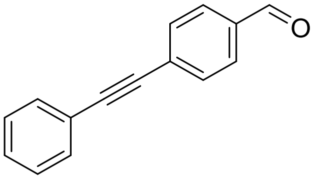
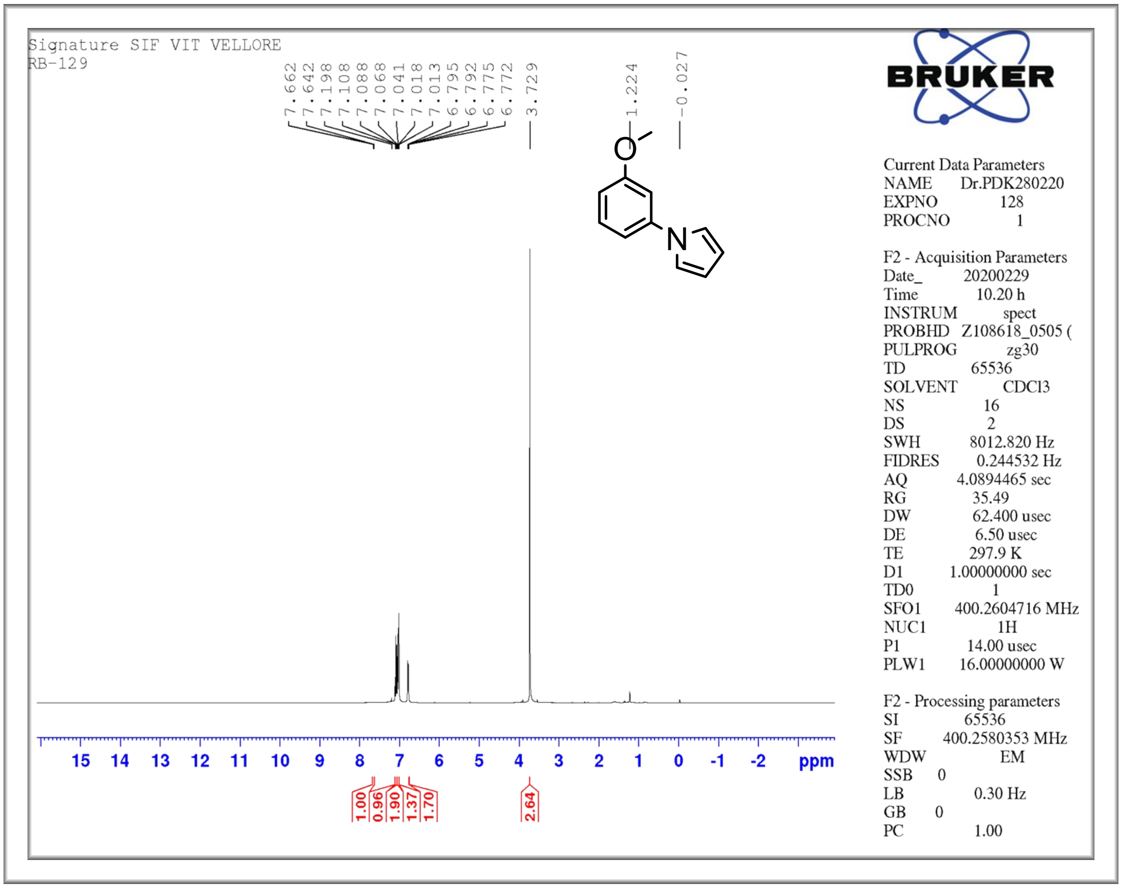
Sonogashira Coupling product	**Conformation Data (NMR data)**
	400 MHz, DMSO-d6: δ 9.94 (s, 1H), 7.82-7.85 (m, 4H), 7.61 (d, 2H), 7.50 (d, 3H). ^{13}C NMR (100 MHz, DMSO) δ: 192.60, 137.05, 138.27, 135.74, 132.14, 131.44, 130.09, 129.80, 129.72, 129.43, 129.20, 129.14, 129.02, 81.10

Table S3. Optimization of Sonogashira between 4-chloroaniline and ethynylbenzene under Photocatalytic Conditions Catalyzed by Photo-catalyst

Entry	Reagent	Catalyst (mg)	Time (h)	Yield (%)
1	R1 + R2	5	24	56
2	R1 + R2	10	24	70
3	R1 +R2	15	24	87
4	R1 + R2	20	24	96
5	R1 + R2	25	24	97
6	R1 + R2	20	6	69
7	R1 + R2	20	12	82
8	R1 + R2	20	18	89
9	R1 + R2	20	24	96

Buchwald-Hartwig Cross Coupling Reaction

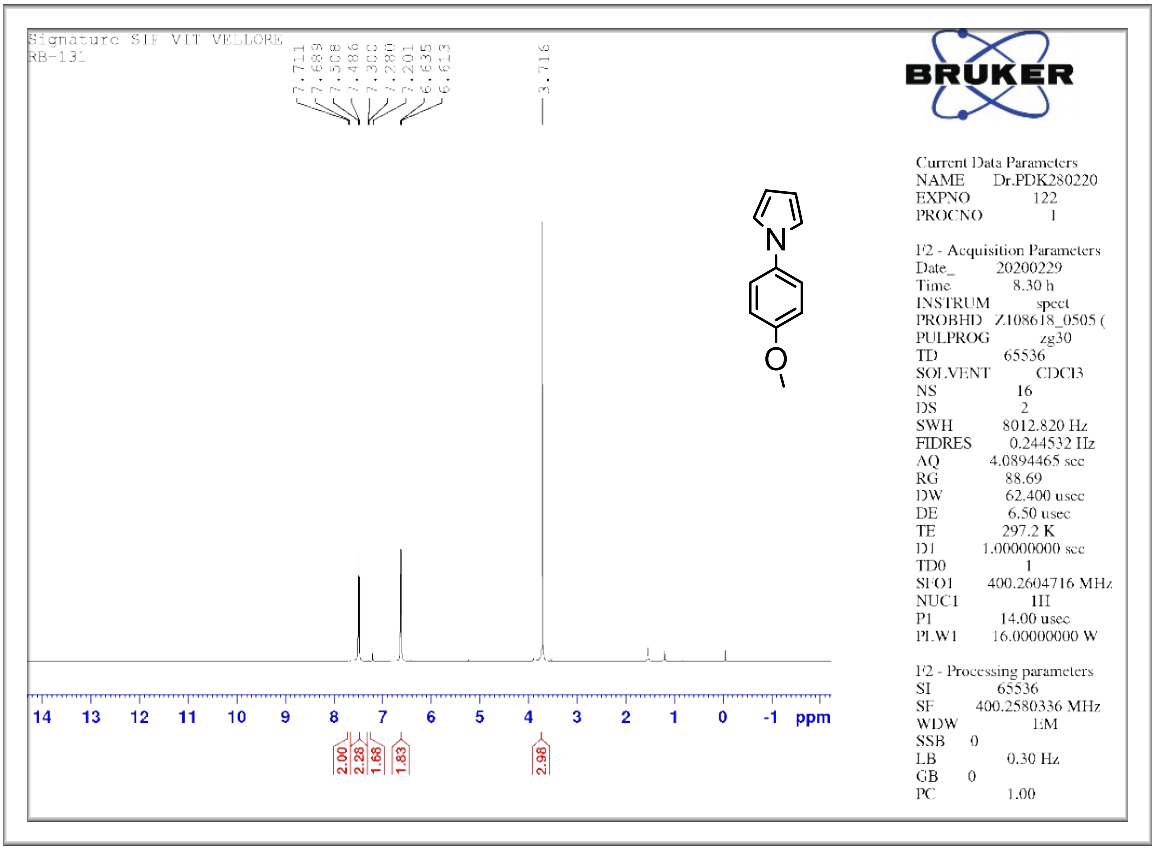


Current Data Parameters
NAME Dr.PDK280220
EXPNO 128
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200229
Time 10.20 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 35.49
DW 62.400 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580353 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S55 ^{1}H NMR Spectrum of 1-(3-methoxyphenyl)-1-H-pyrrole



Current Data Parameters

NAME	Dr.PDK280220
EXPNO	122
PROCNO	1

F2 - Acquisition Parameters

Date_	20200229
Time	8.30 h
INSTRUM	spect
PROBHD	Z108618_0505 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.244532 Hz
AQ	4.0894465 sec
RG	88.69
DW	62.400 usec
DE	6.50 usec
TE	297.2 K
D1	1.00000000 sec
TD0	1
SFO1	400.2604716 MHz
NUC1	1H
P1	14.00 usec
PLW1	16.00000000 W

F2 - Processing parameters

SI	65536
SF	400.2580336 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Fig. S56 ^{1}H NMR Spectrum of 1-(4-methoxyphenyl)-1H-pyrrole

100 MHz, CdCl$_3$-d6: δ 7.70 (d, 2H), 7.49 (d, 2H), 7.29 (d, , 2H), 6.62 (d, 2H), 0.00 (s, 3H).

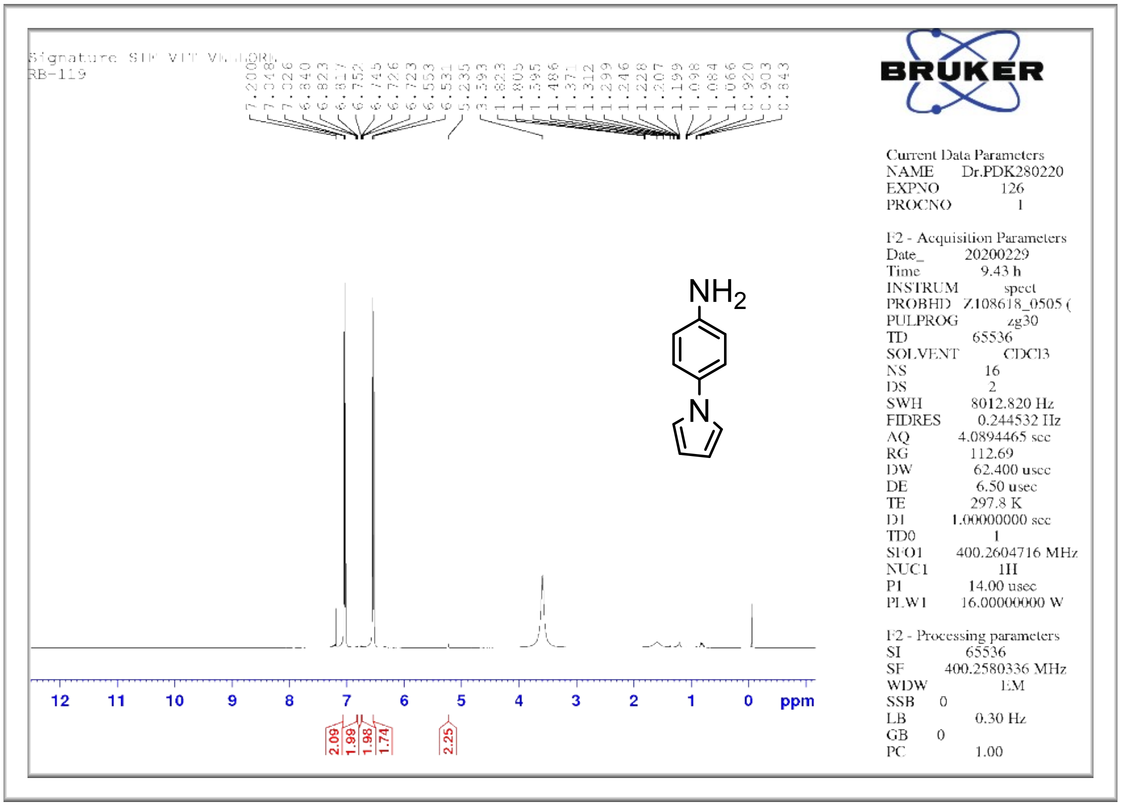


Fig. S57 ^{1}H NMR Spectrum of 4-(1H-pyrrole-1-yl)aniline

400 MHz, DMSO-d6: δ 7.03 (d, 2H), 6.83 (d, 2H), 6.75 (d, 2H), 6.54 (d, 2H), 5.23 (s, 2H).

Table S4. ^{1}H and ^{13}C value for Formation of CN bond between various Aryl halide, Pyrrole and Morpholine under Photocatalytic Conditions.

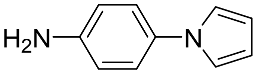
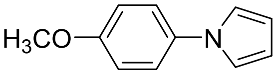
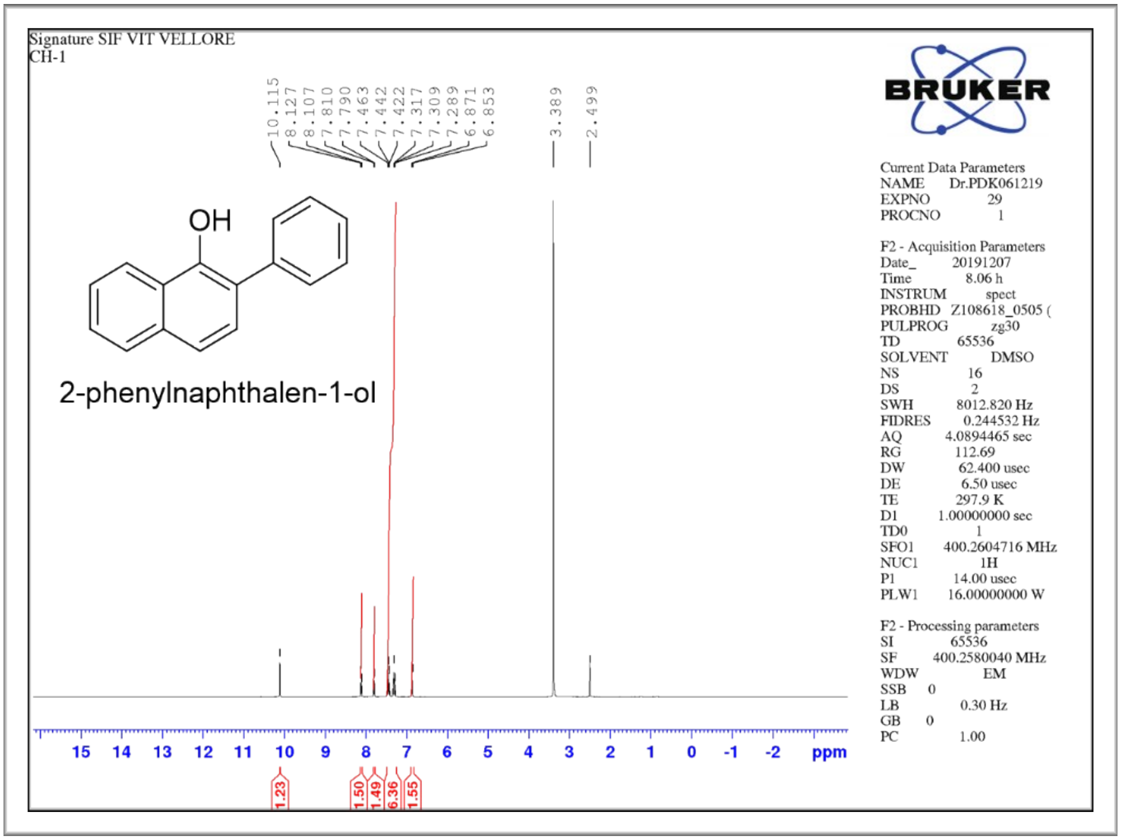
Formation of C-N bond Product	Conformation Data (NMR data)
	400 MHz, DMSO-d6: δ 7.03 (d, 2H), 6.83 (d, 2H), 6.75 (d, 2H), 6.54 (d, 2H), 5.23 (s, 2H).
	400 MHz, CdCl3-d6: δ 7.70 (d, 2H), 7.49 (d, 2H), 7.29 (d, 2H), 6.62 (d, 2H), 0.00 (s, 3H).

Table S5. Optimization of Formation of C-N bond between 4-chloroaniline and 1H-pyrrole under Photocatalytic Conditions Catalyzed by Photo-catalyst

Entry	Reagent	Catalyst (mg)	Time (h)	Yield (%)
1	R1 +R2	20	24	87
2	R1 +R2	5	24	52
3	R1 +R2	10	24	64
4	R1 +R2	15	24	77
5	R1 +R2	20	24	87
6	R1 +R2	25	24	88
7	R1 +R2	20	6	60
8	R1 +R2	20	12	72
9	R1 +R2	20	18	87
10	R1 +R2	20	24	88

C-H Bond Activation



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Current Data Parameters
NAME      Dr.PDK061219
EXPNO           29
PROCNO           1

F2 - Acquisition Parameters
Date_        20191207
Time           8.06 h
INSTRUM        spect
PROBHD  Z108618_0505 (
PULPROG         zg30
TD            65536
SOLVENT         DMSO
NS               16
DS                2
SWH        8012.820 Hz
FIDRES     0.244532 Hz
AQ        4.0894465 sec
RG           112.69
DW           62.400 usec
DE             6.50 usec
TE            297.9 K
D1       1.00000000 sec
TD0               1
SFO1    400.2604716 MHz
NUC1             1H
P1            14.00 usec
PLW1    16.00000000 W

F2 - Processing parameters
SI            65536
SF      400.2580040 MHz
WDW              EM
SSB    0
LB             0.30 Hz
GB     0
PC             1.00
```
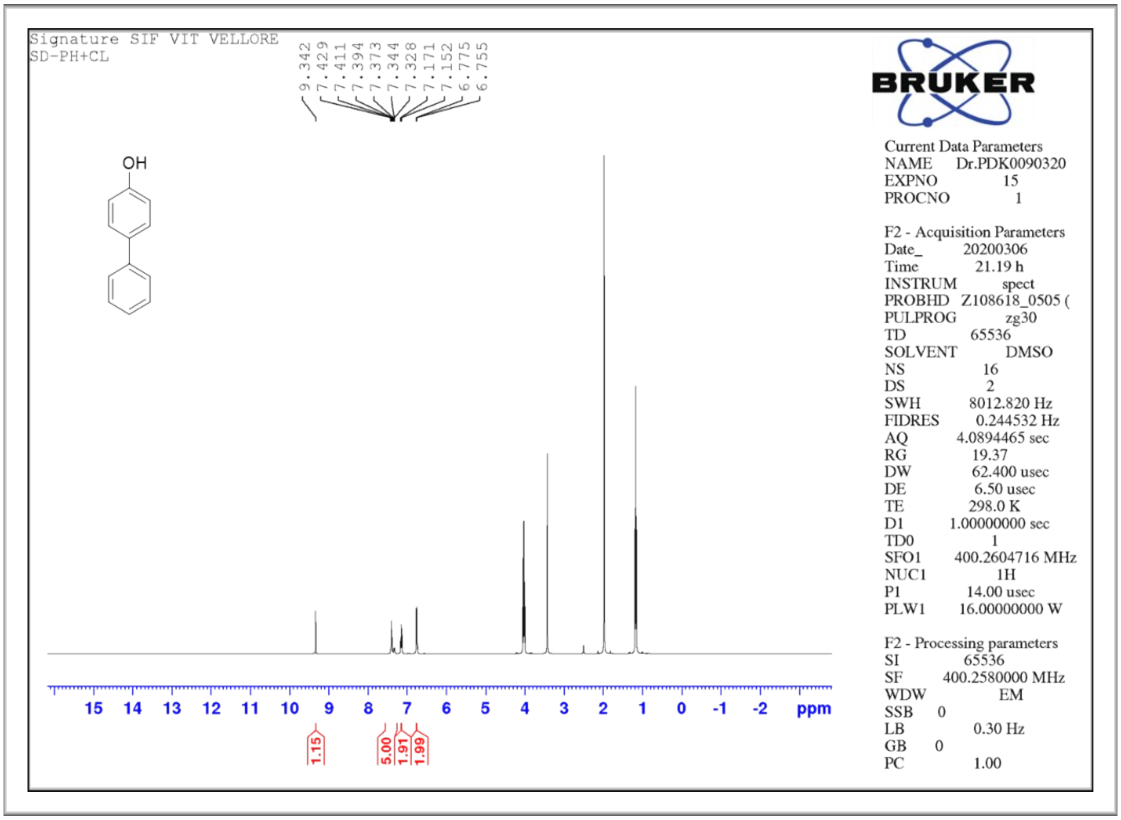

Fig. S58 ^{1}H NMR Spectrum of 2-phenylnapthalen-1-ol



Signature SIF VIT VELLORE
SD-PH+CL

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Current Data Parameters
NAME      Dr.PDK0090320
EXPNO               15
PROCNO               1

F2 - Acquisition Parameters
Date_          20200306
Time             21.19 h
INSTRUM            spect
PROBHD   Z108618_0505 (
PULPROG             zg30
TD                65536
SOLVENT             DMSO
NS                   16
DS                    2
SWH          8012.820 Hz
FIDRES       0.244532 Hz
AQ          4.0894465 sec
RG                19.37
DW           62.400 usec
DE             6.50 usec
TE              298.0 K
D1        1.00000000 sec
TD0                   1
SFO1     400.2604716 MHz
NUC1                 1H
P1            14.00 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI                65536
SF       400.2580000 MHz
WDW                  EM
SSB      0
LB              0.30 Hz
GB       0
PC                 1.00
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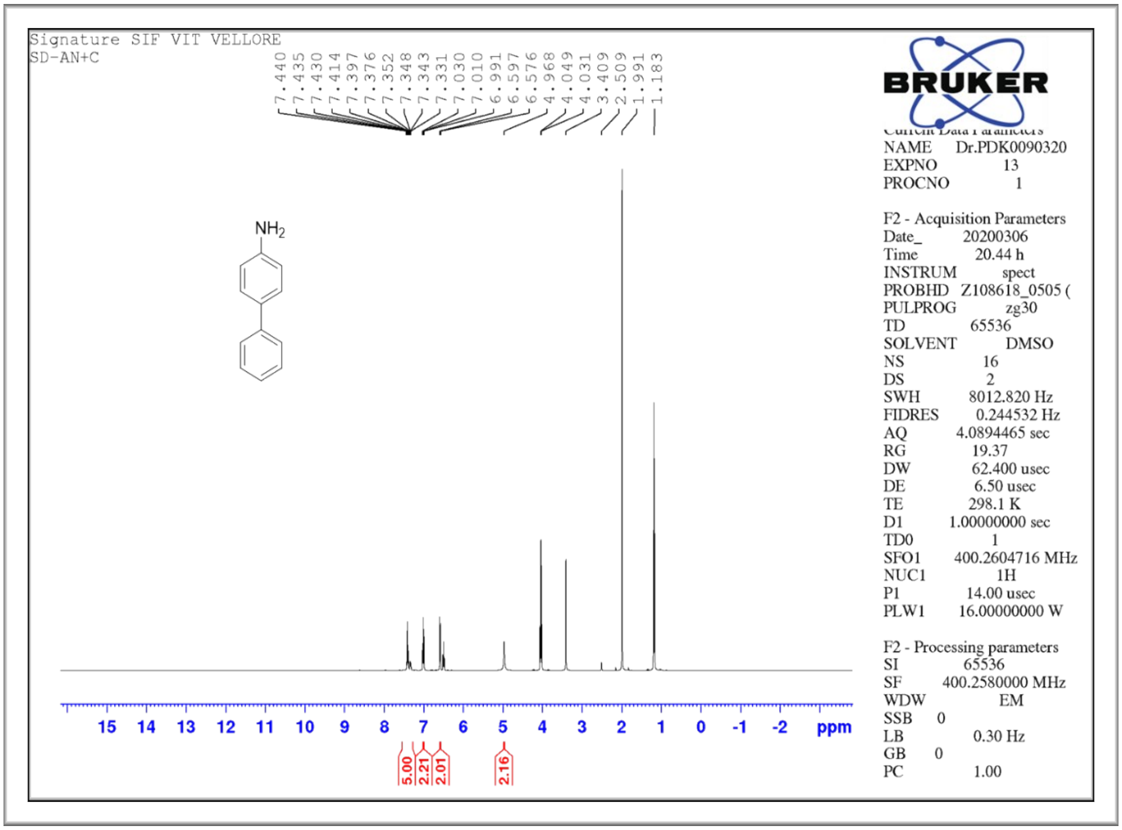
Fig. S59 ^{1}H NMR Spectrum of 1,1’-biphenyl-4-ol



Current Data Parameters
NAME Dr.PDK0090320
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200306
Time 20.44 h
INSTRUM spect
PROBHD Z108618_0505 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 19.37
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SFO1 400.2604716 MHz
NUC1 1H
P1 14.00 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2580000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S60 ^{1}H NMR Spectrum of 1,1'-biphenyl-4-amine

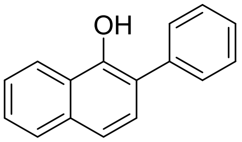
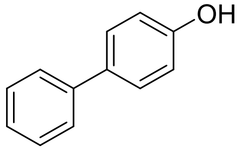
Carbon–hydrogen bond activation Product	Conformation Data (NMR data)
	400 MHz, DMSO-d6: δ 10.11 (s, 1H), 8.11 (d, 2H), 7.80 (d, 1H), 7.44 (t, 6H), 7.30 (t, 2H).
	400 MHz, DMSO-d6: δ 0.00 (s, 1H), 7.32-7.34 (m, 5H), 0.00 (d, 2H), 0.00 (d, 2H).

Table S6. ^{1}H and ^{13}C value CH activation between various Aryl halide and phenolic compound under Photocatalytic Conditions.

Table S7. Optimization of Carbon–hydrogen bond activation between 4-chloroaniline and 1-napthol under Photocatalytic Conditions Catalysed by Photo-catalyst

Entry	Reagent	Catalyst (mg)	Time (h)	Yield (%)
1	R1 +R2	5	25	49
2	R1 +R2	10	25	57
3	R1 +R2	15	25	69
4	R1 +R2	20	25	77
5	R1 +R2	25	25	77
6	R1 +R2	20	5	54
7	R1 +R2	20	10	61
8	R1 +R2	20	15	67
9	R1 +R2	20	20	76
10	R1 +R2	20	25	77

Ullmann Coupling

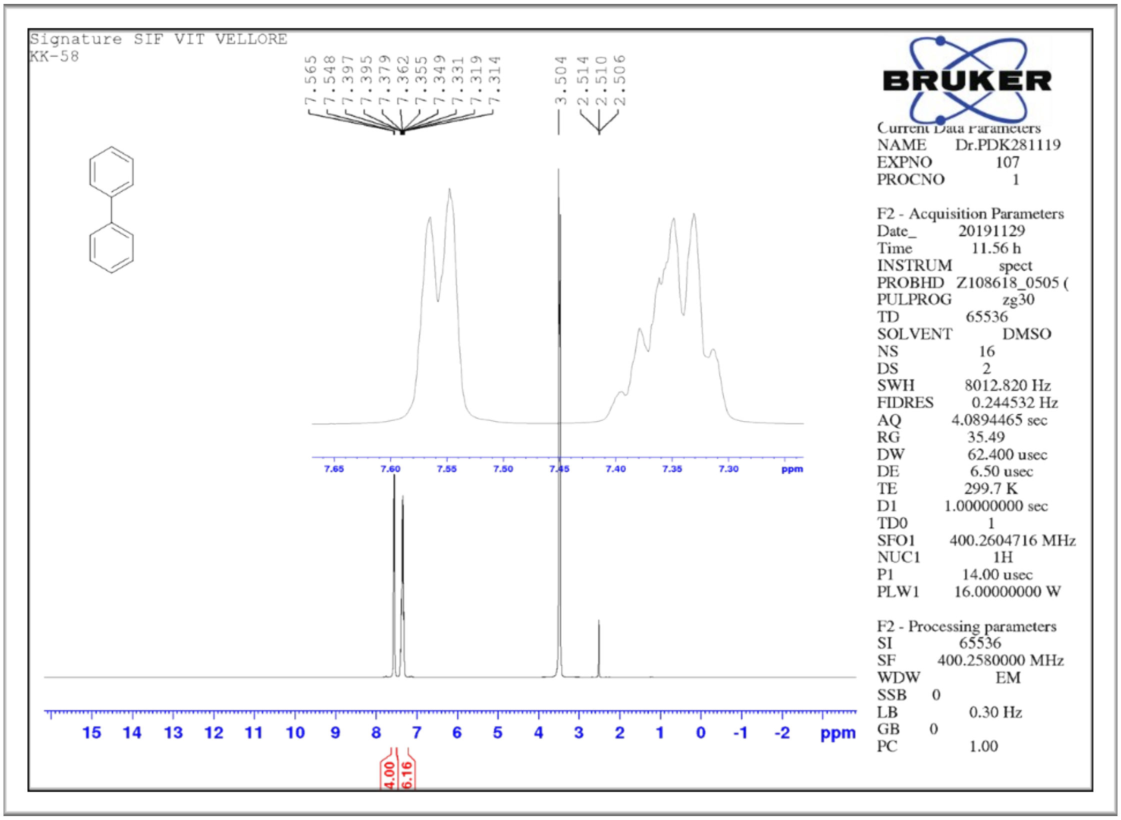


Fig. S61 ^{1}H NMR Spectrum of 1,1-biphenyl

400 MHz, DMSO-d6: δ 7.55 (d, 4H), 7.31-7.33 (m, 6H)

Table S8. ^{1}H and ^{13}C value for Ullmann Coupling

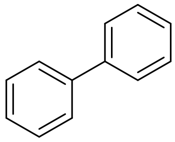
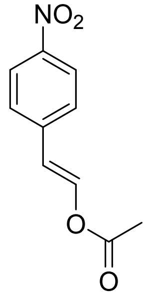
Ullmann Coupling Product	Conformation Data (NMR data)
	400 MHz, DMSO-d6: δ 7.55 (d, *J* = 8.00 Hz, 4H), 7.31-7.33 (m, 6H)

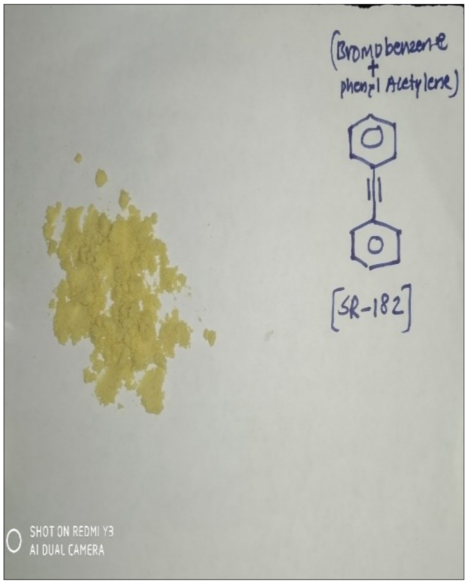
Table 9. Optimization of Ullmann Coupling between 4-chloroaniline under Photocatalytic Conditions Catalysed by Photo-catalyst

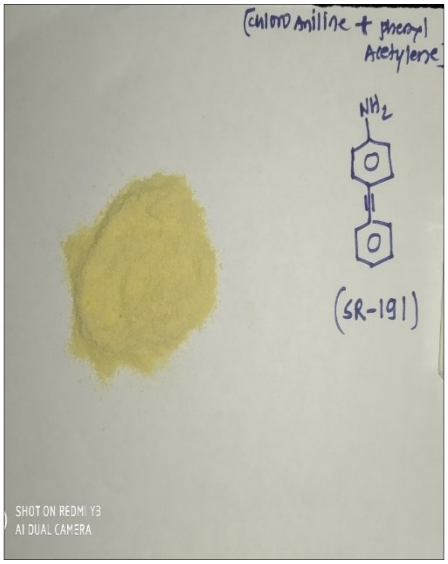
Entry	Reagent	Catalyst (mg)	Time (h)	Yield (%)
1	R1 +R2	5	24	57
3	R1 +R2	10	24	74
4	R1 +R2	15	24	88
5	R1 +R2	20	24	91
6	R1 +R2	25	24	91
7	R1 +R2	20	8	74
8	R1 +R2	20	12	81
9	R1 +R2	20	16	91
10	R1 +R2	20	24	91

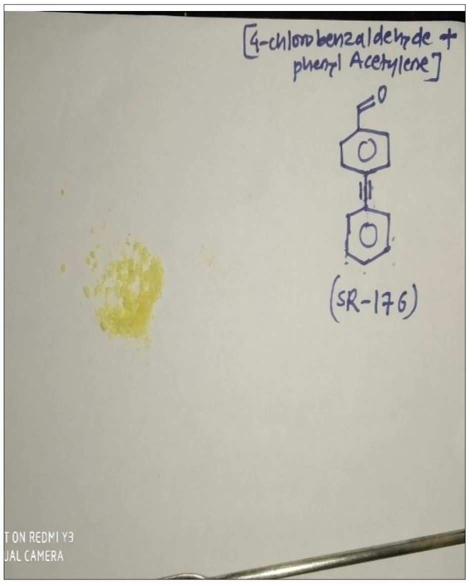


(*E*)-4-nitrostyryl acetate

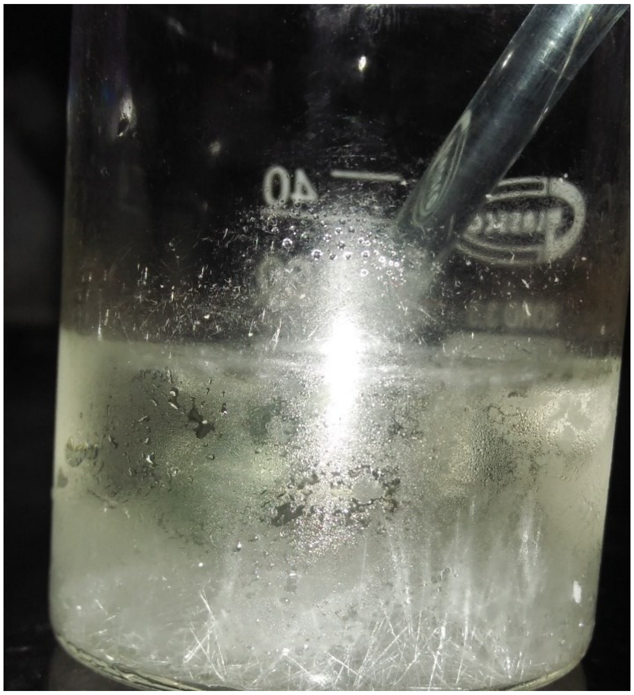
Other derivatives of heck coupling






[4-chlorobenzaldehyde + phenyl Acetylene]
O
(SR-176)
T ON REDMI Y3
JAL CAMERA


[2-chloropyrimidine + phenyl Acetylene]
N
N
(SR-197)
SHOT ON REDMI Y3
AI DUAL CAMERA



During recrystallization of Heck coupling product