Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Sustainable C-H functionalization of indoles, pyrroles and furans in blue LED with iodonium ylides

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1. General experimental procedure:

All blue light reactions were carried out under air as specified. Photochemical Reactor Aldrich® Micro Photochemical Reactor, blue LED lights (ALDKIT001-1EA). LED light is IP68 double density 12V DC water proof blue light with spectral range of 435-445 nm with wall plug power supply 500mA with 5-6 watts. The irradiation vessel material is borosilicate glass. The distance of irradiation vessel from light source is 2 cm. Reactions were monitored through TLC by visualising in UV detector. All purifications were done in silica gel (60-120 mesh size) column chromatography. Compound **11a** (CAS# 15741-71-6) and **11b** (CAS# 55747-66-5) were purchased commercially from Sigma Aldrich. Compounds **4c** was synthesized from the literature procedure.[S1a] All ^{1}H and ^{13}C NMR spectra were recorded taking tetramethylsilane (TMS) as an internal standard at ambient temperature unless otherwise indicated with Bruker 400 MHz instruments at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR spectroscopy. Splitting patterns are designated as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), quintet (quin) doublet of doublets (dd) and triplet of doublets (td). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). MS analyses were performed using an Agilent 6540 accurate–mass Q-TOF LC/MS (Agilent Technologies, U.S.A.). under the following operation parameters: dry gas temperature 350°C, dry gas (N_2) flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000 and fragmentor voltage 110 V. Mass spectra were acquired in the positive ion mode by scanning from 100 to 1500 in the mass to charge ratio (m/z). The mobile phase composition used for UHPLC–QTOF MS comprised of H_2O (A) and ACN (B), with optimized linear gradient elution. The injection volume was 5 µL. The flow rate was set at 0.3 mL/min. Accurate mass analysis calibration was carried out by ESI-low concentration tuning mix solution provided by Agilent technologies, U.S.A. The accuracy error threshold was set at 5 ppm. High-performance liquid chromatography (HPLC) experiments were carried out on a Waters Alliance System (Milford, MA) consisting of e2695 separation module and a 2998 photodiode-array detector. The HPLC system was controlled with EMPOWER software (Waters Corporation, Milford, MA).

1.1 Synthetic Procedure:

1.1.1. Representative synthesis and characterization of iodonium ylide (**4a** and **4b**):

The synthesis of Bis(methoxycarbonyl)(phenyliodinio)methanide, **4a** was carried out by following the previously reported procedure. Briefly, in a 50 mL round bottom flask Potassium hydroxide (KOH) (2.00 gm, 36.0 mmol, 6 eq.) were added in acetonitrile (ACN, 20 mL) under argon atmosphere. Then, dimethyl malonate (693 µL, 6.00 mmol, 1 eq.) was also added into the reaction mixture. Now, the heterogeneous mixture was cooled at 0°C and was stirred vigorously for 5 mins to produce a milky white suspension. Now, into that suspension phenyliodonium diacetate, PIDA [$PhI(OAc)_2$] (2.13 gm, 6.60 mmol, 1.1 eq.) was added in one portion and the reaction mixture was stirred vigorously for 2.0 h at 0°C. After that, the reaction mixture gradually became a thick creamy mixture. Into the that 10 mL of water was added and the mixture was stirred for another 5 mins. The beige/yellow biphasic solution containing a fluffy white suspension was filtered filter off and the solid was washed with water (2 x 5 mL). It is important that the solvent be completely removed between each wash. The solid was finally washed with Et_2O (10 mL) and dried under high vacuum.[S1]

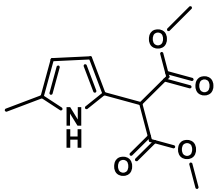
Following the above mention procedure, the desired compound **4a** was prepared in 81% yield as off white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.74-7.72 (dd, J = 8 Hz, 2H), 7.54-7.50 (m, 1H), 7.42-7.38 (m, 2H), 3.73 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 166.46, 131.74, 131.70, 131.47, 114.48, 52.51; HRMS (ESI) m/z calcd for $C_{11}H_{11}IO_4$ $[M+H]^+$ 334.9775, found 334.9765; FTIR (Neat) ν_{max} (cm^{-1}) = 3079, 2985, 2945, 2890, 1672, 1581, 1576, 1559, 1438, 1431, 1311, 1067, 991.The spectral data were consistent with that previously reported results.[S1]
Following the above-mentioned procedure, the desired compound **4b** was prepared in 37% yield as off white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.33 (m, 2H), 4.16-4.11 (q, J = 7 Hz, 4H), 1.19-1.16 (t, J = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.51, 91.67, 61.05, 13.87; HRMS (ESI) m/z calcd for $C_{13}H_{15}IO_4$ $[M + H]^+$ 363.0088, found 363.0085; FTIR (Neat) ν_{max} (cm^{-1}) = 3583, 3512, 3037, 2986, 1603, 1567, 1368, 1323, 1291, 1224, 1169, 1073, 1035, 993. The spectral data were consistent with that previously reported. The product partially degraded during the preparation of the NMR sample.[S1]

1.1.2. General procedure for synthesis of (5a-k, 6a-m):

C2/C3–H functionalization of pyrroles (**1a-i**), indoles (**2a-l**) and furans (**3a-b**) have been achieved by using the following synthetic procedure. Briefly, into a dry 15 ml borosilicate glass vial iodonium ylide (**4a/b**) (1 equiv.) was dissolved in 5 mL of methanol (MeOH), and stirred at r.t. for 5 mins, which was

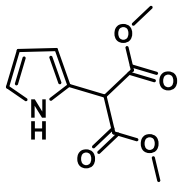
eventually give rise to either a clear solution or a slurry. Now, into that reaction mixture pyrroles/Indoles/furans (2 equiv.) were added, and the reaction mixtures were stirred for 5 mins in dark. After these, the blue LED was turned on in the photoreactor and the reaction mixture was stirred under the blue LED irradiation for another 6-7 hours. The completion of the reaction was confirmed by performing TLC. The solvent was removed from the reaction mixture under reduced pressure. Finally, C2/C3 functionalized heterocycles were purified by column chromatography in silica gel (60-120 mesh size).

1.1.3. Characterization Data:



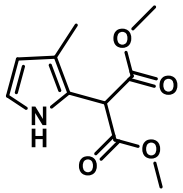
5a

Dimethyl 2-(5-methyl-1H-pyrrol-2-yl)malonate, **5a:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5a** was prepared with an yield of 42.98 mg, 68% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.67 (s, 1H), 6.01-6.00 (t, J = 4 Hz, 1H), 5.81 (m, 1H), 4.73 (s, 1H), 3.76 (s, 6H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.41, 129.22, 119.66, 109.24, 106.12, 53.12, 50.88; HRMS (ESI) m/z calcd for $C_{10}H_{13}NO_4$ $[M + H]^+$ 212.0917, found 212.0921; FTIR (Neat) ν_{max} (cm^{-1}) = 3407.88, 2924.04, 1723.99, 1588.51, 1435.91, 1306.80, 1142.21, 1011.14, 902.34, 754.62, 662.47, 578.17.



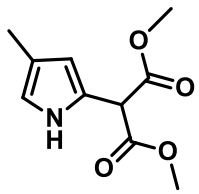
5b

Dimethyl 2-(1H-pyrrol-2-yl)malonate, **5b**: By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5b** was prepared with an yield of 37.77 mg, 64% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.05 (s, 1H), 6.82 (m, 1H), 6.17 (m, 2H), 4.79 (s, 1H), 3.76 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.23, 121.30, 119.10, 109.01, 108.40, 53.20, 50.77; FTIR (Neat) ν_{max} (cm^{-1}) = 3317.89, 2920.85, 1688.50, 1587.48, 1430.95, 1358.07, 1191.21, 1017.03, 934.81, 798.19, 605.29.



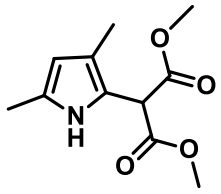
5c

Dimethyl 2-(3-methyl-1H-pyrrol-2-yl)malonate, **5c**: By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5c** was prepared with an yield of 24.49 mg, 37% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.90 (s, 1H), 6.73-6.72 (t, J = 4 Hz, 1H), 6.02-6.01 (t, J = 4 Hz, 1H), 4.79 (s, 1H), 3.76 (s, 6H), 2.08 (s, 3H); 13C NMR ($CDCl_3$, 100 MHz) δ_C 168.35, 117.95, 117.65, 117.59, 110.00, 53.11, 48.57, 10.86; HRMS (ESI) m/z calcd for $C_{10}H_{13}NO_4$ $[M + H]^+$ 212.0917, found 212.0926; FTIR (Neat) ν_{max} (cm^{-1}) = 3407.52, 2947.39, 2353.53, 1729.67, 1439.68, 1265.33, 1204.52, 1137.50, 1012.64, 901.75, 729.38, 641.43, 565.08.



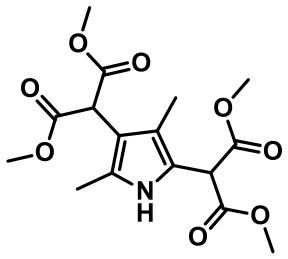
5d

Dimethyl 2-(4-methyl-1H-pyrrol-2-yl)malonate, **5d**: By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5d** was prepared with an yield of 20.52 mg, 31% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.70 (s, 1H), 6.57 (s, 1H), 5.98 (s, 1H), 4.73 (s, 1H), 3.76 (s, 6H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.25, 121.14, 118.97, 116.96, 110.49, 53.18, 50.83, 11.91; HRMS (ESI) m/z calcd for $C_{10}H_{13}NO_4$ $[M + H]^+$ 212.0917, found 212.0926; FTIR (Neat) ν_{max} (cm^{-1}) = 3399.36, 2950.10, 1728.28, 1437.81, 1143.30, 1018.66, 756.68, 668.50, 568.92.



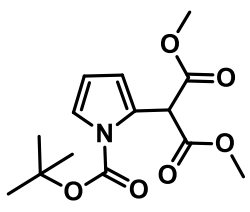
5e

Dimethyl 2-(3,5-dimethyl-1H-pyrrol-2-yl)malonate, **5e:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5e** was prepared with an yield of 39.10 mg, 58% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.49 (s, 1H), 5.69-5.68 (d, J = 4 Hz, 1H), 4.74 (s, 1H), 3.76 (s, 6H), 2.22 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.56, 128.09, 117.97, 115.78, 108.07, 53.06, 48.57, 13.15, 10.81; HRMS (ESI) m/z calcd for $C_{11}H_{15}NO_4$ $[M + H]^+$ 226.1074, found 226.1068; FTIR (Neat) ν_{max} (cm^{-1}) = 3394.47, 2922.11, 1720.62, 1435.03, 1314.67, 1263.11, 1139.44, 102.10, 791.66, 644.12, 564.05.



5f

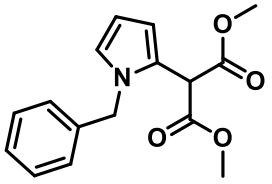
Tetramethyl 2,2'-(3,5-dimethyl-1H-pyrrole-2,4-diyl)dimalonate, **5f:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5f** was prepared with an yield of 27.65 mg, 26% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.68 (s, 1H), 5.71-5.70 (d, J = 4 Hz, 1H), 4.27 (s, 1H), 3.86 (s, 6H), 3.84 (s, 6H), 2.21 (s, 3H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 170.33, 162.72, 126.98, 118.61, 118.53, 110.24, 53.97, 53.89, 13.04, 11.78; HRMS (ESI) m/z calcd for $C_{16}H_{21}NO_8$ $[M + H]^+$ 356.1340, found 356.1337; FTIR (Neat) ν_{max} (cm^{-1}) = 3412.97, 2923.02, 2857.28, 1740.46, 1439.92, 1250.89, 1050.66, 921.53, 794.62, 716.14, 574.03.



5h

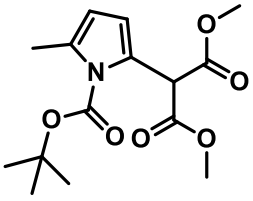
Dimethyl 2-(1-(tert-butoxycarbonyl)-1H-pyrrol-2-yl)malonate, **5h:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5h** was prepared with an yield of 69.41

mg, 78% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.27 (d, *J* = 1.92 Hz, 1H), 6.16 (d, *J* = 2.64 Hz, 2H), 5.37 (s, 1H), 3.79 (s, 6H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.21, 149.31, 125.99, 122.47, 113.90, 110.36, 84.56, 52.99, 52.23, 28.03; HRMS (ESI) m/z calcd for $C_{14}H_{19}NO_6$ $[M + H]^+$ 298.1285, found 298.1291; FTIR (Neat) ν_{max} (cm^{-1}) = 2963.42, 1733.99, 1425.77, 1319.41, 1245.89, 1149.48, 1021.19, 840.59, 734.04, 593.31.



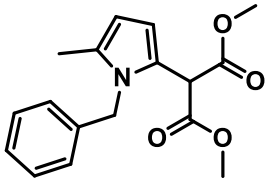
5i

Dimethyl 2-(1-benzyl-1H-pyrrol-2-yl)malonate, **5i**: By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5i** was prepared with an yield of 61.91 mg, 72% yield as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.36-7.28 (m, 3H), 7.04-7.02 (d, *J* = 8 Hz, 2H), 6.72-6.71 (q, *J* = 4 Hz, 1H), 6.33-6.32 (q, *J* = 4 Hz, 1H), 6.23-6.22 (t, *J* = 4 Hz, 1H), 5.14 (s, 2H), 4.69 (s, 1H), 3.65 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.85, 137.66, 128.81, 127.67, 126.61, 123.55, 123.35, 110.54, 108.08, 52.93, 50.95, 50.27; HRMS (ESI) m/z calcd for $C_{16}H_{17}NO_4$ $[M + H]^+$ 288.1230, found 288.1236; FTIR (Neat) ν_{max} (cm^{-1}) = 2922.61, 2855.27, 1733.41, 1441.56, 1258.42, 1139.83, 1078.34, 1017.72, 796.96, 710.12, 458.26.



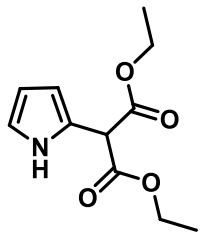
5j

Dimethyl 2-(1-(tert-butoxycarbonyl)-5-methyl-1H-pyrrol-2-yl)malonate, **5j**: By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5j** was prepared with an yield of 65.23 mg, 70% as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent.^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.00-5.99 (d, *J* = 4 Hz, 1H), 5.89-5.88 (d, *J* = 4 Hz, 2H), 5.26 (s, 1H), 3.78 (s, 6H), 2.38 (s, 3H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.51, 150.27, 133.08, 125.84, 112.40, 110.93, 84.63, 53.06, 52.93, 28.11, 16.98; HRMS (ESI) m/z calcd for $C_{15}H_{21}NO_6$ $[M + H]^+$ 312.1442, found 312.1449; FTIR (Neat) ν_{max} (cm^{-1}) = 2955.96, 1733.02, 1442.39, 1313.93, 1255.43, 1097.76, 1016.38, 787.05.



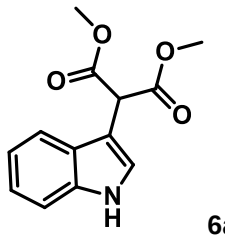
5k

Dimethyl 2-(1-benzyl-5-methyl-1H-pyrrol-2-yl)malonate, **5k:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5k** was prepared with an yield of 67.64 mg, 75% yield as brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.30-7.27 (m, 2H), 7.24-7.20 (m, 1H), 6.86-6.84 (d, *J* = 8 Hz, 2H), 6.21 (d, *J* = 4 Hz, 1H), 5.98-5.97 (d, *J* = 4 Hz, 1H), 5.10 (s, 2H), 4.63 (s, 1H), 3.57 (s, 6H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.06, 137.80, 130.73, 128.81, 127.30, 125.70, 122.66, 109.36, 107.00, 52.85, 50.77, 47.30, 12.64; HRMS (ESI) m/z calcd for $C_{17}H_{19}NO_4$ $[M + H]^+$ 302.1387, found 302.1391; FTIR (Neat) ν_{max} (cm^{-1}) = 2944.48, 1733.76, 1434.76, 1220.87, 1143.51, 1021.13, 730.06, 582.80.

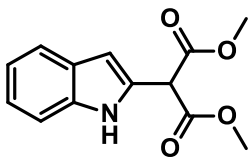


5l

Diethyl 2-(1H-pyrrol-2-yl)malonate, **5l**: By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **5l** was prepared with an yield of 44.15 mg, 71% yield as brown oil. Purification was done by column chromatography using EtOAc/n-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.01 (s, 1H), 6.80-6.79 (q, *J* = 4 Hz, 1H), 6.36-6.35 (m, 1H), 6.20-6.18 (q, *J* = 4 Hz, 1H), 4.35 (s, 1H), 4.34-4.24 (m, 4H), 1.32-1.29 (t, *J* = 4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 169.19, 125.47, 118.45, 108.74, 108.02, 76.55, 63.24, 14.04; HRMS (ESI) m/z calcd for $C_{11}H_{15}NO_4$ [M + H]$^+$ 226.1074, found 226.1071; FTIR (Neat) ν_{max} (cm^{-1}) = 3411.58, 2922.37, 1728.85, 1454.88, 1372.85, 1210.15, 1087.58, 1021.25, 794.34, 726.06, 576.47.

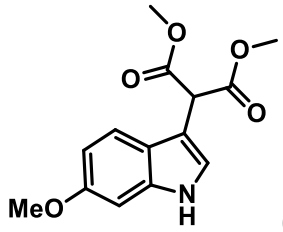


6a

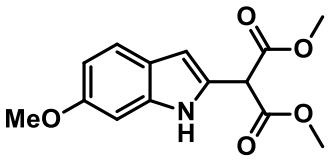


6a'

Dimethyl 2-(1H-indol-3-yl)malonate, **6a**/ *Dimethyl 2-(1H-indol-2-yl)malonate*, **6a':** By following the general synthetic procedure for the C2/C3 functionalization, the inseparable mixture of **6a**/**6a'** was prepared with an yield of 43.66 mg, 43:16% as a brown oil. Purification was done by column chromatography using EtOAc/n-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 11.51 (s, 0.44H), 8.96 (s, 1H), 7.59-7.57 (d, *J* = 8 Hz, 1H), 7.40-7.36 (t, *J* = 8 Hz, 1.51H), 7.24-7.18 (m, 1.30H), 7.12-7.01 (m, 2.04H), 6.50-6.49 (d, *J* = 4 Hz, 1H), 4.96 (s, 1H), 4.36 (s, 0.89H), 3.84-3.82 (d, *J* = 8 Hz, 2.21H), 3.80 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.72, 136.64, 128.34, 128.01, 127.71, 124.36, 123.16, 122.62, 120.69, 120.16, 111.36, 110.70, 103.58, 53.42, 51.77, 51.42; HRMS (ESI) m/z calcd for $C_{13}H_{13}NO_4$ [M + H]$^+$ 248.0917, found 248.0926. FTIR (Neat) ν_{max} (cm^{-1}) = 3362.86, 2945.52, 1723.77, 1617.17, 1533.54, 1435.15, 1218.52, 1152.36, 1083.46, 1021.89, 796.11, 737.07, 655.65, 557.83.

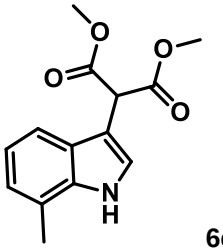


6b

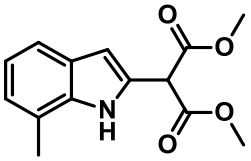


6b'

Dimethyl 2-(6-methoxy-1H-indol-3-yl)malonate, **6b**/ *Dimethyl 2-(6-methoxy-1H-indol-2-yl)malonate*, **6b':** By following the general synthetic procedure for the C2/C3 functionalization, the inseparable mixture of **6b**/**6b'** was prepared with an yield of 45.64 mg, 31:22 % yield as a brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 11.44 (s, 0.75H), 8.82 (s, 1H), 7.44-7.42 (d, *J* = 8 Hz, 1.14H), 7.24-7.22 (d, *J* = 8 Hz, 0.69H), 6.87 (d, *J* = 2 Hz, 1.14H), 6.78-6.75 (dd, *J* = 8 Hz, 1.12H), 6.61-6.59 (m, 1.30H), 6.41-6.40 (d, *J* = 4 Hz, 1.04H), 4.90 (s, 0.98H), 4.27 (s, 1.17H), 3.84-3.83 (d, *J* = 4 Hz, 5.48H), 3.81 (d, *J* = 2 Hz, 4.24H), 3.79 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.84, 160.16, 156.88, 137.45, 127.00, 124.69, 121.94, 121.30, 120.51, 110.41, 108.23, 103.45, 97.68, 94.63, 55.78, 53.37, 51.77, 51.42, 39.93; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_5$ [M + H]$^+$ 278.1023, found 278.1032. FTIR (Neat) ν_{max} (cm^{-1}) = 3288.95, 2941.86, 1736.60, 1623.31, 1541.21, 1494.29, 1434.59, 1351.15, 1215.97, 1022.08, 789.83, 733.39, 623.39, 544.39.

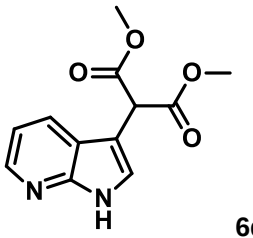


6c



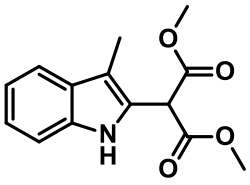
6c'

Dimethyl 2-(7-methyl-1H-indol-3-yl)malonate, **6c**/ *Dimethyl 2-(7-methyl-1H-indol-2-yl)malonate*, **6c':** By following the general synthetic procedure for the C2/C3 functionalization, the inseparable mixture of **6c**/**6c'** was prepared with an yield of 46.92 mg, 51:9 % yield as a brown oil. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent.^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 11.60 (s, 0.34H), 8.84 (s, 1H), 7.43-7.42 (d, *J* = 4 Hz, 0.88H), 7.22-7.20 (d, *J* = 8 Hz, 0.31H), 7.07-6.99 (m, 2.95H), 6.50 (d, *J* = 2 Hz, 0.88H), 4.96 (s, 0.87H), 4.37 (s, 0.54H), 3.85 (s, 1.15H), 3.82-3.80 (d, *J* = 8 Hz, 6.09H), 2.51 (s, 3H), 2.37 (s, 0.79H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.84, 133.81, 129.16, 128.05, 127.26, 123.15, 120.39, 118.37, 104.16, 53.41, 51.40, 16.88; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_4$ $[M + H]^+$ 262.1074, found 262.1069. FTIR (Neat) ν_{max} (cm^{-1}) = 3410.40, 2920.53, 2856.14, 1729.47, 1450.42, 1194.56, 1076.81, 1012.01, 800.30.



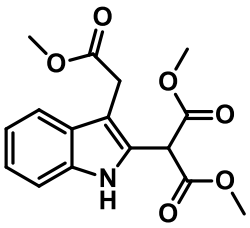
6d

Dimethyl 2-(1H-pyrrolo[2,3-b]pyridin-3-yl)malonate, **6d:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6d** was prepared with an yield of 45.32 mg, 61% as a red solid. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent.^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.11 (s, 1H), 8.34-8.33 (t, *J* = 4 Hz, 1H), 8.05-8.02 (dd, *J* = 4 Hz, 1H), 7.50 (s, 1H), 7.15-7.12 (q, *J* = 4 Hz, 1H), 4.92 (s, 1H), 3.77 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.78, 148.64, 143.46, 128.57, 124.82, 119.32, 116.43, 106.17, 53.05, 49.85; HRMS (ESI) m/z calcd for $C_{12}H_{12}N_2O_4$ $[M + H]^+$ 249.0870, found 249.0865; FTIR (Neat) ν_{max} (cm^{-1}) = 3136.44, 2921.65, 1733.19, 1583.33, 1428.37, 1255.96, 1089.65, 1016.12, 787.50, 592.93, 480.57.



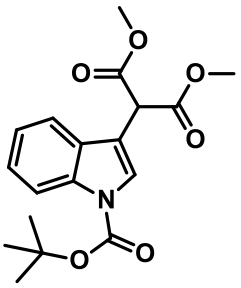
6e

Dimethyl 2-(3-methyl-1H-indol-2-yl)malonate, **6e:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6e** was prepared with an yield of 51.61 mg, 66% as a yellow solid. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.83 (s, 1H), 7.55-7.53 (d, *J* = 8 Hz, 1H), 7.36-7.34 (d, *J* = 8 Hz, 1H), 7.23-7.18 (m, 1H), 7.13-7.09 (t, *J* = 8 Hz, 1H), 5.01 (s, 1H), 3.78 (s, 6H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.89, 136.03, 128.37, 124.33, 122.68, 119.48, 118.98, 111.23, 110.92, 53.30, 49.09, 8.60; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_4$ $[M + H]^+$ 262.1074, found 262.1079; FTIR (Neat) ν_{max} (cm^{-1}) = 3403.29, 2921.60, 1728.91, 1439.89, 1254.80, 1199.04, 1147.54, 1086.06, 1017.62, 903.49, 798.38, 738.46, 655.31, 598.29, 535.20.



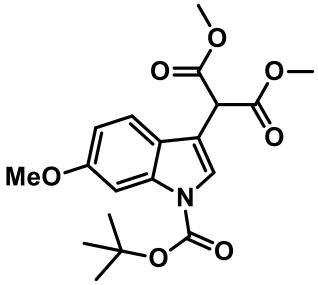
6f

Dimethyl 2-(3-(2-methoxy-2-oxoethyl)-1H-indol-2-yl)malonate, **6f:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6f** was prepared with an yield of 60.21 mg, 63% as an off white solid. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.08 (s, 1H), 7.60-7.58 (d, J = 8 Hz, 1H), 7.38-7.36 (d, J = 8 Hz, 1H), 7.23-7.20 (t, J = 4 Hz, 1H), 7.15-7.11 (t, J = 8 Hz, 1H), 5.16 (s, 1H), 3.86 (s, 2H), 3.79-3.77 (d, J = 8 Hz, 6H), 3.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 171.79, 167.61, 135.79, 127.55, 126.16, 122.96, 120.12, 118.93, 111.46, 107.75, 53.95, 53.42, 52.16, 49.15, 30.06; HRMS (ESI) m/z calcd for $C_{16}H_{17}NO_6$ $[M + H]^+$ 320.1129, found 320.1125; FTIR (Neat) ν_{max} (cm^{-1}) = 3409.36, 2924.10, 2130.95, 1728.92, 1444.27, 1364.71, 1252.30, 1150.29, 1024.95, 749.10, 631.87.



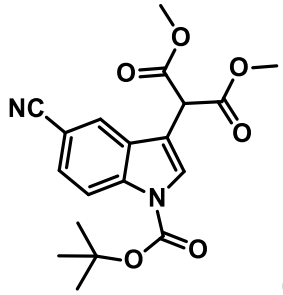
6g

Dimethyl 2-(1-(tert-butoxycarbonyl)-1H-indol-3-yl)malonate, **6g:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6g** was prepared with an yield of 63.4 mg, 61% yield as an orange solid. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.17-8.15 (d, J = 8 Hz, 1H), 7.77 (s, 1H), 7.57-7.56 (d, J = 4 Hz, 1H), 7.35-7.32 (m, 1H), 7.30-7.28 (m, 1H), 4.90 (s, 1H), 3.82-3.78 (d, J = 16 Hz, 6H), 1.66 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.32, 125.63, 124.87, 122.98, 120.90, 119.39, 115.50, 84.14, 53.15, 49.31, 29.85, 28.32, 28.27; HRMS (ESI) m/z calcd for $C_{18}H_{21}NO_6$ $[M + H]^+$ 348.1442, found 348.1436; FTIR (Neat) ν_{max} (cm^{-1}) = 2925.51, 1727.90, 1446.67, 1367.06, 1323.00, 1257.65, 1146.88, 1084.58, 1022.02, 747.12, 585.82.



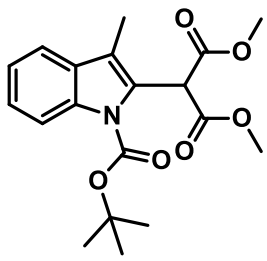
6h

Dimethyl 2-(1-(tert-butoxycarbonyl)-6-methoxy-1H-indol-3-yl)malonate, **6h:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6h** was prepared with an yield of 68.90 mg, 61% yield as a pink oil. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.65 (d, J = 1.6 Hz, 1H), 7.38-7.36 (d, J = 8 Hz, 1H), 6.88-6.85 (dd, J = 4 Hz, 1H), 6.46 (s, 1H), 5.46 (s, 1H), 3.86 (s, 3H), 3.81(s, 6H), 1.66 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.05, 157.98, 150.57, 137.46, 130.66, 122.45, 121.27, 112.31, 109.94, 100.47, 84.86, 55.69, 53.46, 53.09, 28.26; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_7$ $[M + H]^+$ 378.1547, found 378.1541; FTIR (Neat) ν_{max} (cm^{-1}) = 2947.68, 1728.78, 1616.71, 1442.56, 1372.46, 1323.48, 1206.55, 1149.00, 1023.64, 917.59, 834.73, 747.71, 618.55.



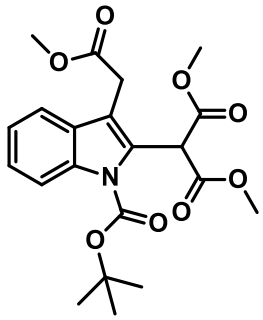
6i

2-(1-(tert-butoxycarbonyl)-5-cyano-1H-indol-3-yl)malonate, **6i:** Following the general procedure the desired compound was prepared with an yield of 71.33 mg, 83% as an off white oil. The eluent was EtOAc/*n*-hexane (25:75). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.05-8.03 (d, J = 8 Hz, 1H), 7.76 (s, 1H), 7.70 (d, J = 1.6 Hz, 1H), 7.44-7.41 (dd, J = 4 Hz, 1H), 4.83 (s, 1H), 3.79 (s, 6H), 1.66 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.04, 134.26, 127.81, 126.79, 122.23, 116.95, 116.48, 111.41, 84.66, 53.26, 49.12, 28.28; HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2O_6$ $[M + H]^+$ 373.1394, found 266.1185; FTIR (Neat) ν_{max} (cm^{-1}) = 2925.39, 2231.69, 1727.61, 1445.97, 1366.85, 1322.79, 1257.61, 1146.59, 1084.68, 1021.89, 747.31, 582.79.



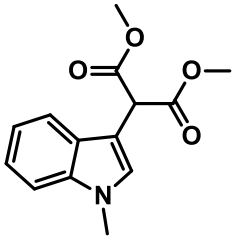
6j

Dimethyl 2-(1-(tert-butoxycarbonyl)-3-methyl-1H-indol-2-yl)malonate, **6j:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6j** was prepared with an yield of 73.55 mg, 68% as an off white oil. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.02-8.00 (d, J = 8 Hz, 1H), 7.51-7.49 (d, J = 8 Hz, 1H), 7.33-7.29 (t, J = 8 Hz, 1H), 7.25-7.23 (d, J = 8 Hz, 1H), 5.51 (s, 1H), 3.76 (s, 6H), 2.21 (s, 3H), 1.66 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.58, 150.83, 135.64, 130.33, 127.44, 124.85, 122.69, 118.90, 118.55, 115.86, 84.57, 52.88, 50.22, 28.36, 8.94; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_6$ $[M + H]^+$ 362.1598, found 362.1591; FTIR (Neat) ν_{max} (cm^{-1}) = 2923.59, 1727.91, 1435.89, 1254.75, 1198.95, 1147.48, 1085.93, 1017.69, 903.10, 798.25, 738.67, 654.90, 598.11, 530.79.



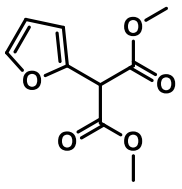
6k

Dimethyl 2-(1-(tert-butoxycarbonyl)-3-(2-methoxy-2-oxoethyl)-1H-indol-2-yl)malonate, **6k:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6k** was prepared with an yield of 57.36 mg, 60% as a yellowish solid. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.03-8.01 (d, J = 8 Hz, 1H), 7.55-7.53 (d, J = 8 Hz, 1H), 7.34-7.28 (m, 2H), 5.55 (s, 1H), 3.86 (s, 2H), 3.75-3.74 (d, J = 4 Hz, 6H), 3.64 (s, 3H), 1.66 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 170.80, 167.07, 150.67, 135.67, 130.26, 129.41, 129.18, 125.12, 123.03, 119.03, 116.01, 115.69, 84.99, 53.95, 52.96, 52.26, 49.93, 30.23, 28.31; HRMS (ESI) m/z calcd for $C_{21}H_{25}NO_8$ $[M + H]^+$ 420.1653, found 420.1641; FTIR (Neat) ν_{max} (cm^{-1}) = 2924.23, 2131.25, 1729.91, 1443.27, 1364.91, 1252.00, 1153.15, 1025.15, 748.40, 631.14.



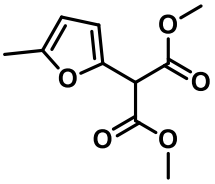
6l

Dimethyl 2-(1-methyl-1H-indol-3-yl)malonate, **6l:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **6l** was prepared with an yield of 53.96 mg, 69% as an off white oil. Purification was done by column chromatography using EtOAc/*n*-hexane (15:85) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.60-7.58 (d, *J* = 8 Hz, 1H), 7.33-7.31 (d, *J* = 8 Hz, 1H), 7.24-7.22 (m, 1H), 7.13-7.09 (t, *J* = 8 Hz, 1H), 6.59 (s, 1H), 4.98 (s, 1H), 3.81 (s, 6H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.52, 138.07, 130.68, 127.32, 122.25, 120.95, 119.95, 109.47, 103.26, 53.30, 51.01, 30.41, 29.84 ; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_4$ $[M + H]^+$ 262.1074, found 262.1069; FTIR (Neat) ν_{max} (cm^{-1}) = 2920.55, 2855.97, 1729.57, 1450.11, 1193.96, 1076.49, 1012.95, 800.21.



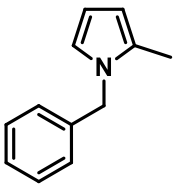
7a

Dimethyl 2-(furan-2-yl)malonate, **7a:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **7a** was prepared with an yield of 36.18 mg, 61% as a yellow oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.71-9.69 (d, *J* = 8 Hz, 1H), 7.50-7.43 (m, 2H), 6.51-6.42 (m, 1H), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 192.88, 164.49, 163.85, 143.06, 140.53, 139.62, 132.40, 53.54, 53.07, 53.00; HRMS (ESI) m/z calcd for $C_9H_{10}O_5$ $[M + H]^+$ 199.0601, found 199.0591; FTIR (Neat) ν_{max} (cm^{-1}) = 2947.87, 2852.72, 1718.17, 1438.62, 1363.69, 1220.43, 1092.23, 1058.25, 976.50, 837.01, 759.33, 566.85.



7b

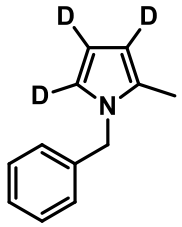
Dimethyl 2-(5-methylfuran-2-yl)malonate, **7b:** By following the general synthetic procedure for the C2/C3 functionalization, the desired compound **7b** was prepared with an yield of 38.74 mg, 61% as a yellow oil. Purification was done by column chromatography using EtOAc/*n*-hexane (25:75) as an eluent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.43-7.35 (m, 2H), 6.49-6.46 (m, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 197.68, 164.70, 164.10, 141.69, 139.28, 135.38, 131.80, 53.52, 52.93, 52.87, 27.91; HRMS (ESI) m/z calcd for $C_{10}H_{12}O_5$ $[M + H]^+$ 213.0757, found 213.0746; FTIR (Neat) ν_{max} (cm^{-1}) = 2953.71, 2855.11, 1717.90, 1589.96, 1436.80, 1362.75, 1222.97, 1057.18, 985.58, 797.62, 514.29.



1i

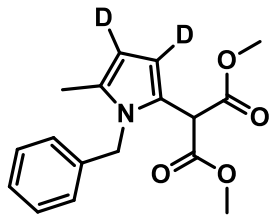
1-benzyl-2-methyl-1H-pyrrole, **1i:** Following the general procedure descried by the desired compound was prepared in 78 % yield as a yellow oil.[S2] The eluent was EtOAc/*n*-hexane (25:75). ^{1}H NMR (CD_3OD, 400 MHz) δ_H 7.31-7.20 (m, 3H), 7.00-6.98 (d, *J* = 8 Hz, 2H), 6.65-6.64 (t, *J* = 4 Hz, 1H), 6.01-5.99 (t, *J*

= 4 Hz, 1H), 5.85 (bs, 1H), 5.06 (s, 2H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 140.43, 129.55, 128.12, 127.38, 121.85, 107.97, 107.72, 51.07, 11.97; HRMS (ESI) m/z calcd for $C_{12}H_{13}N$ $[M + H]^+$ 172.1121, found 172.1129; FTIR (Neat) ν_{max} (cm^{-1}) = 2921.33, 1491.58, 1484.09, 1355.97, 1295.23, 1073.68, 1024.79, 892.26, 699.43.



1i-D

1-benzyl-2-methyl-1H-pyrrole-3,4,5-d$_3$, **1i-D:** Following the procedure described by Fischer *et al.* the desired compound **1i-D** was prepared with an yield of 54.95 mg, 54% yield as yellow oil.[S3] The eluent was EtOAc/*n*-hexane (25:75). ^{1}H NMR (CD_3OD, 400 MHz) δ_H 7.29-7.23 (m, 3H), 6.99-6.97 (d, J = 8 Hz, 2H), 4.95 (s, 2H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 140.83, 130.59, 130.53, 130.06, 129.50, 128.95, 128.68, 128.38, 127.98, 127.35, 126.61, 50.91, 12.06; HRMS (ESI) m/z calcd for $C_{12}H_{10}D_3N$ $[M + H]^+$ 175.1309, found 175.1312 and ; FTIR (Neat) ν_{max} (cm^{-1}) = 2918.37, 1490.98, 1433.87, 1355.89, 1295.38, 1073.67, 1023.97, 892.12, 699.49.

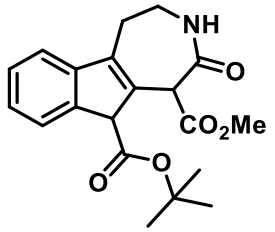


5i-D

Dimethyl 2-(1-benzyl-5-methyl-1H-pyrrol-2-yl-3,4-d$_2$)malonate, **5i-D:** Following the general procedure for C2-H functionalization reaction the desired compound **5i-D** was prepared in 44.49 mg, with an yield of 49% as a yellow oil in which we observed ~67% deuteriation in the final compound. The eluent was EtOAc/*n*-hexane (25:75). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.30-7.28 (m, 2H), 7.23-7.20 (m, 1H), 6.86-6.84 (d, J = 8 Hz, 2H), 5.10 (s, 2H), 4.63 (s, 1H), 3.57 (s, 6H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 167.93, 137.65, 128.67, 127.16, 125.56, 106.75, 52.75, 50.61, 47.15, 29.71, 12.49; HRMS (ESI) m/z calcd for $C_{17}H_{17}D_2NO_4$ $[M + H]^+$ 302.1387, found mixture of 302.1356 and 304.1510; FTIR (Neat) ν_{max} (cm^{-1}) = 2923.91, 1735.60, 1434.54, 1259.68, 1141.83, 1022.50, 799.65, 724.79, 561.90.

1.1.4. General procedure for synthesis of azepino[4, 5-b]indoles (12a and b):

Synthesis of *10-(tert-butyl) 1-methyl 2-oxo-1,2,3,4,5,10-hexahydroindeno[1,2-d]azepine-1,10-dicarboxylate* **(12a):**

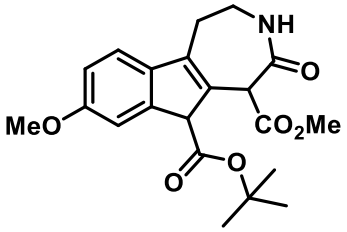


12a

A solution of **11a** (1.02 g, 3.538 mmol), Boc anhydride (1.16 g, 5.31 mmol), triethyl amine (0.152 mL, 1.062 mmol) and DMAP (86 mg, 0.7 mmol) in dry MeOH (10 mL) was stirred from 0 °C to r. t. over 3 h. Once TLC indicates complete consumption of the starting material iodonium ylide **4a** (1.769 mmol) stirred at r. t. for 10 minutes, after which, the blue LED was turned on in the photoreactor. After 8 hours the TLC confirmed the completion of the reaction. Next, hydrazine monohydrate (3.538 mmol) was further added to the reaction mixture which was then stirred for 2h at 35 °C. The progress of the reaction was monitored by TLC and until product formation. After completion of reaction, reaction mixture was

cooled at ambient temperature, then solvent was removed under reduced pressure and the crude was purified by column chromatography (*n*-Hexane: EtOAc = 50:50, R_f = 0.14) to afford pure product with an yield of 347.8 mg, 27% as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.06-8.04 (d, *J* = 8 Hz, 1H), 7.42-7.40 (d, *J* = 8 Hz, 1H), 7.34–7.30 (m, 1H), 7.24-7.22 (d, *J* = 8 Hz, 1H), 6.64-6.61 (t, *J* = 8 Hz, 1H), 5.87 (s, 1H), 3.83 (s, 3H), 3.80-3.71 (m, 1H), 3.44-3.36 (m, 1H), 2.99 – 2.95 (m, 2H), 1.66 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.43, 168.91, 150.39, 135.95, 129.45, 125.40, 125.24, 122.93, 119.85, 118.23, 115.94, 84.80, 54.37, 53.23, 38.84, 28.34, 26.68. HRMS (ESI) m/z calcd for $C_{19}H_{22}N_2O_5$ [M + H]$^+$ 359.1601, found 359.1599; FTIR (Neat) ν_{max} (cm^{-1}) = 3371.67, 3302.93, 3180.30, 3051.37, 2922.37, 1724.29, 1645.73, 1456.67, 1356.54, 1314.14, 1135.72, 1010.87, 842.88, 734.71, 588.72, 495.47.

Synthesis of *10-(tert-butyl) 1-methyl 8-methoxy-2-oxo-1,2,3,4,5,10-hexahydroindeno[1,2-d]azepine-1,10-dicarboxylate* **(12b):**



12b

A solution of **11b** (0.5g, 1.561 mmol), Boc anhydride (0.51g, 2.342 mmol), triethyl amine (0.066 mL, 0.47 mmol) and DMAP (37.87 mg, 0.31 mmol) in dry MeOH (10 mL) was stirred from 0 °C to r.t. over 3 h. Once TLC indicates complete consumption of the starting material iodonium ylide **4a** (0.212 mg, 0.636 mmol) was added and after stirring for 10 min, the blue LED was turned on in the photoreactor. After 8 hours the TLC indicated completion of the reaction and hydrazine monohydrate (0.141g, 2.83 mmol) was charged followed by heating for 2h at 35 °C. The progress of the reaction was monitored by TLC and until product formation. After completion of reaction, reaction mixture was cooled at ambient temperature, then solvent was removed under reduced pressure and purification was done by column chromatography (Hexane:EtOAc = 50:50, R_f = 0.14) to afford pure product as white solid in a yield of 188 mg, 31%.^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.95-7.93 (d, *J* = 8 Hz, 1H), 6.94-6.91 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.84-6.83 (d, *J* = 2.5 Hz, 1H), 6.36-6.32 (t, *J* = 6.5 Hz, 1H), 5.87 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.79-3.71 (m, 1H), 3.42 – 3.35 (m, 1H), 2.94-2.91 (m, 2H), 1.64 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.25, 168.92, 156.11, 150.31, 147.52, 130.63, 130.24, 126.05, 119.59, 116.86, 113.62, 101.05, 84.63, 55.90, 54.38, 53.23, 38.84, 28.35, 26.78. HRMS (ESI) m/z calcd for $C_{20}H_{24}N_2O_6$ [M + H]$^+$ 389.1707, found 389.1718; FTIR (Neat) ν_{max} (cm^{-1}) = 3202.31, 3089.37, 2929.40, 1718.71, 1664.08, 1612.68, 1463.22, 1322.65, 1243.75, 1118.62, 1012.07, 796.86, 585.19, 441.53.

1.1.5. Experimental procedure for Scheme 4(b) and 4(c):

Into a dry 15 ml borosilicate glass vial iodonium ylide (**4a**) (1 equiv., 10 mg) was dissolved in 5 mL of methanol (MeOH), and stirred at r.t. for 5 mins, which was eventually give rise to either a clear solution or a slurry. Now, into that reaction mixture 1-benzyl-2-methyl-1H-pyrrole, **1i** (2 equiv., 10.24 mg) and N-tertbutyl a-phenylnitrone (PBN) (1.5 equiv., 8.72 mg) **[Scheme 4(b)]** or 2,2,6,6-tetramethylpiperidine (TEMPO) (1.5 equiv., 7.01 mg) **[Scheme 4(c)]** were added, and the reaction mixtures were stirred for 5 mins in dark. After these, the blue LED was turned on in the photoreactor and the reaction mixture was stirred under the blue LED irradiation for another 6-7 hours. The completion of the reaction was confirmed by performing TLC. Further the generated products were checked by HRMS from the reaction mixtures.

2. Kinetic isotope effect study:

Initial rate of formation of products of Blue LED mediated C-H activation reaction between (**1i**) with iodonium ylide (**4a**) has been calculated by HPLC based kinetic study, in which initial 0%-15% formation of product (**5i**) was considered as the initial rate of formation of product.

Two simultaneous reactions were carried out taking **1i** (2 equiv.) and **4a** (1 equiv.) in MeOH in one vial, and **1i-D** (2 equiv.) and **4a** (1 equiv.) in MeOH in another vial using same general procedure of synthesis of blue LED mediated C-H activation reaction. Fractions of crude reaction mixtures were collected every 10 minutes interval during first two hours of reaction. HPLC analysis was done to measure the initial rate of formation of product in which initial 0%-10% formation of products (**5i** and **5i-D**) was considered as the initial rate of formation of product.

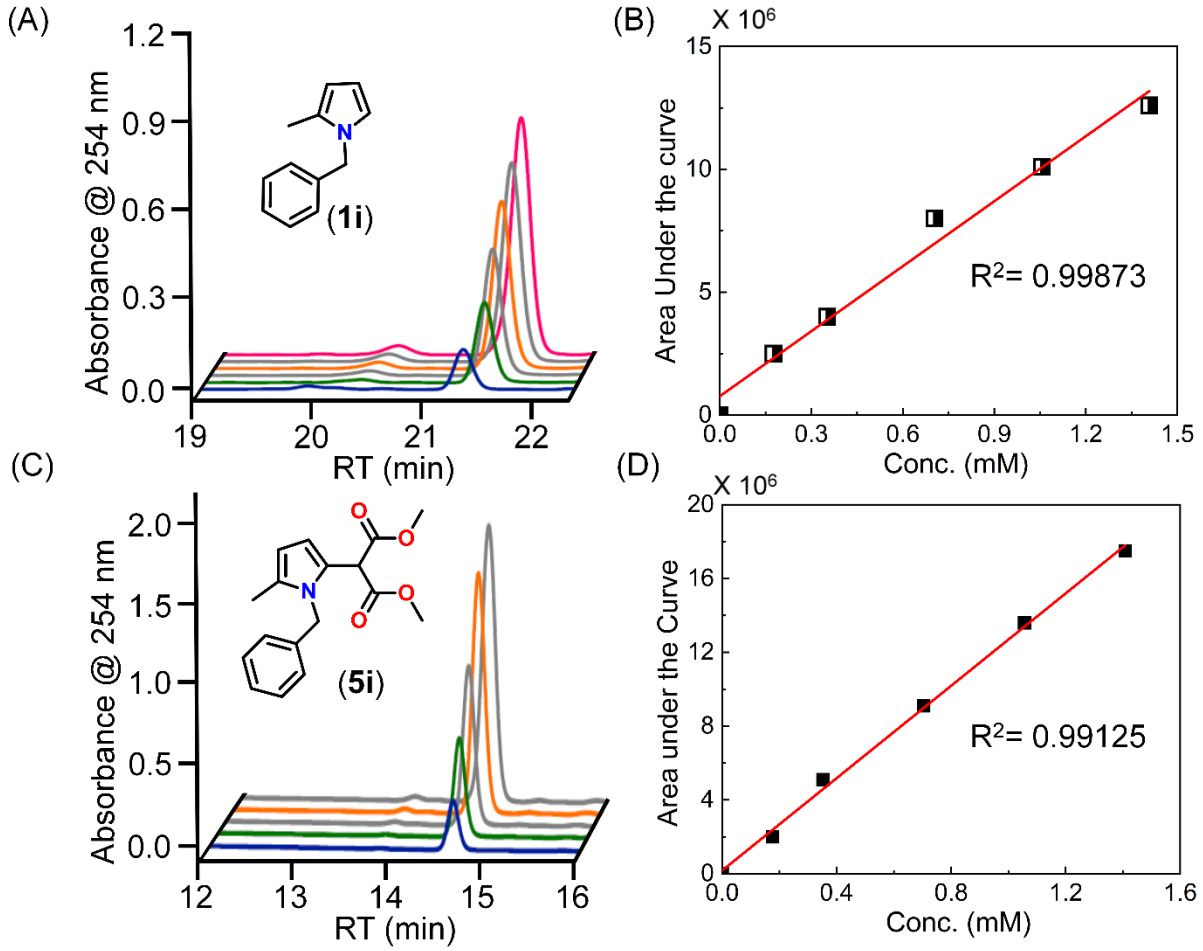


Figure S1: HPLC stack chromatogram of **1i** with various concentrations at 254 nm (A) and the corresponding standard calibration curve generated from the same (B) (using area under the curve)**;** HPLC stack chromatogram of **5i** with various concentrations at 254 nm (C) and the corresponding standard calibration curve generated from the same (D) (using area under the curve).

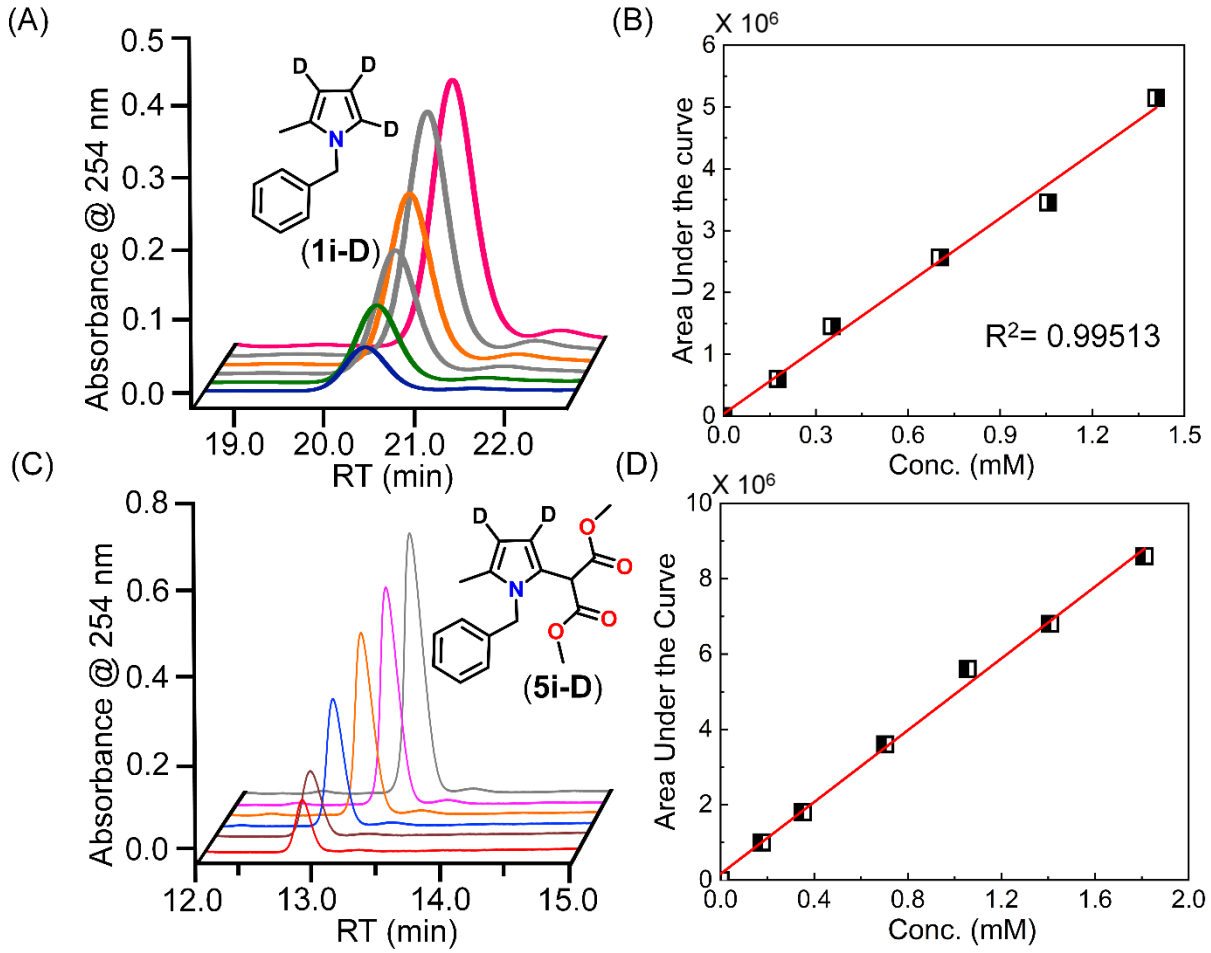


Figure S2: HPLC stack chromatogram of **1i-D** with various concentrations at 254 nm (A) and the corresponding standard calibration curve generated from the same (B) (using area under the curve)**;** HPLC stack chromatogram of **5i-D** with various concentrations at 254 nm (C) and the corresponding standard calibration curve generated from the same (D) (using area under the curve).

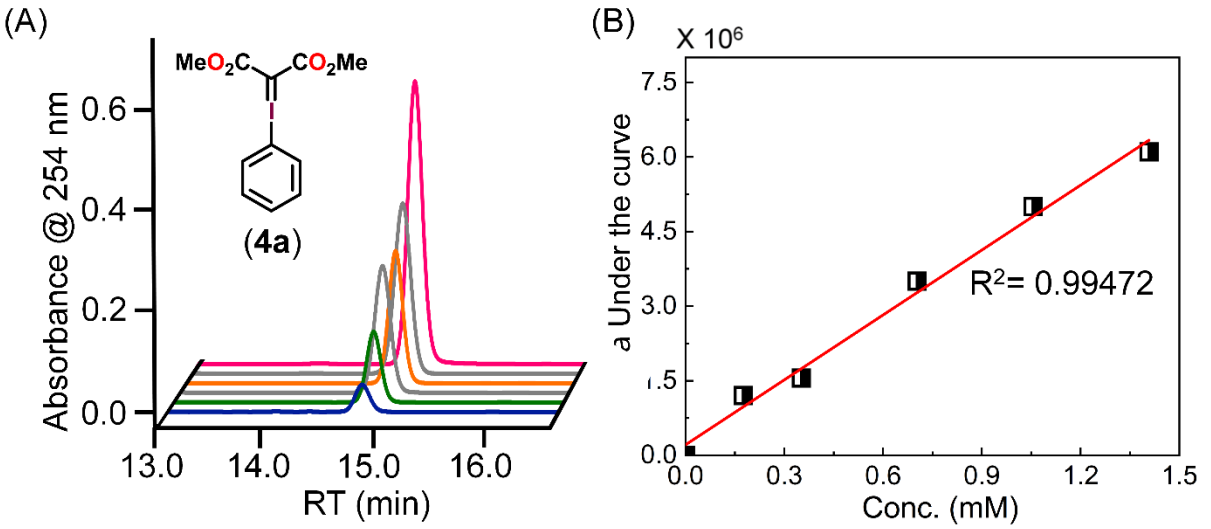


Figure S3: HPLC stack chromatogram of **1i-D** with various concentrations at 254 nm (A) and the corresponding standard calibration curve generated from the same (B) (using area under the curve)

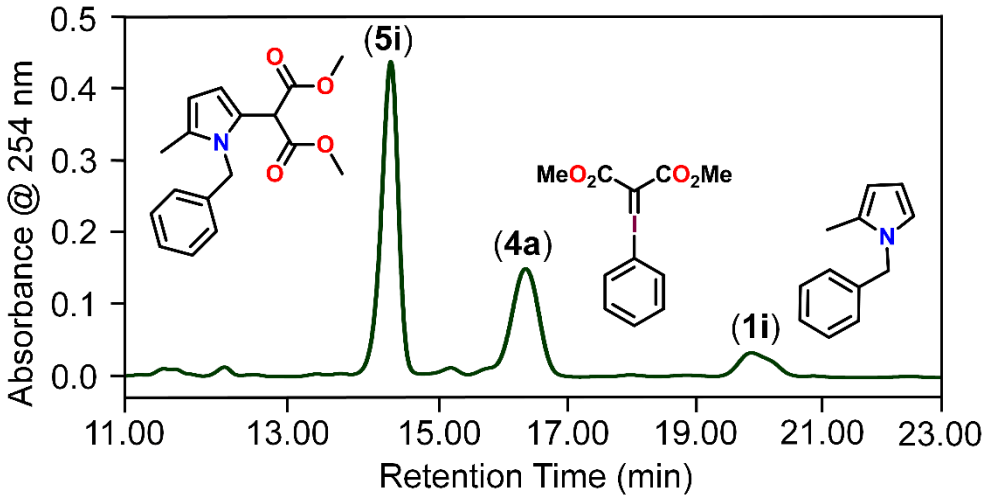
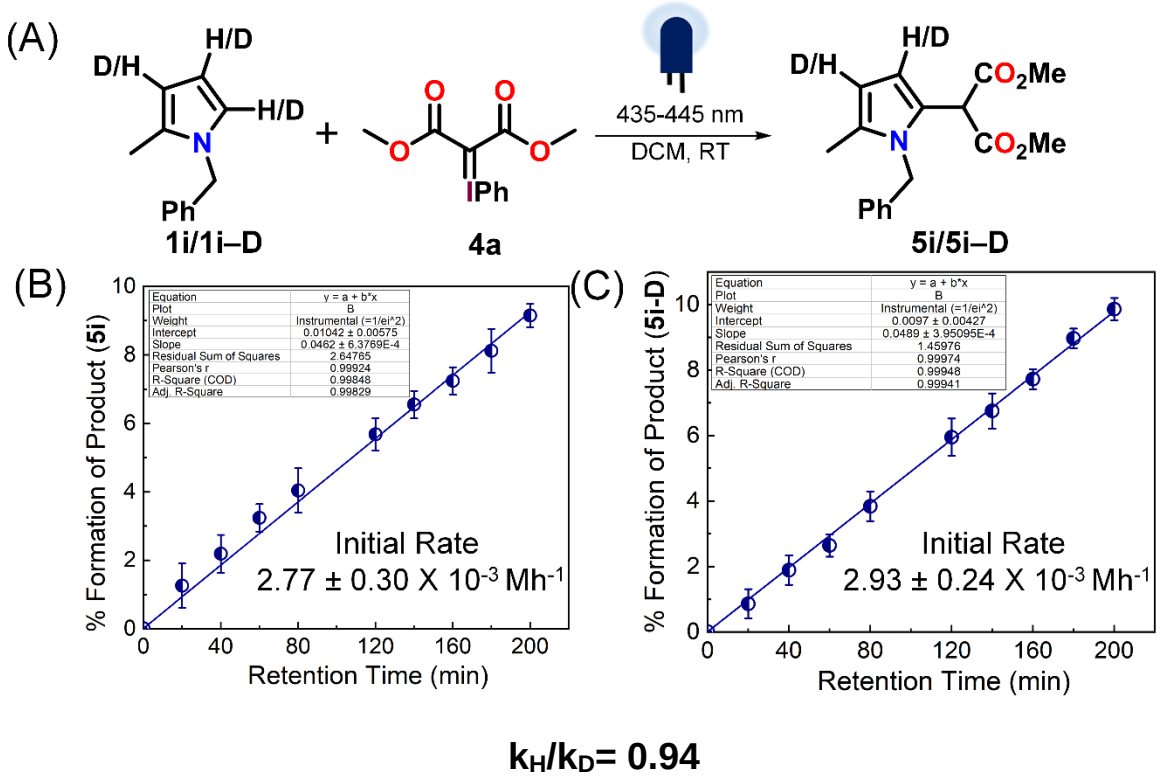


Figure S4: HPLC chromatogram of the blue light mediated C2-H functionalization reaction of **1i** with iodonium ylide **4a** after 6 h.



$$k_H/k_D = 0.94$$

Figure S5: (A) Blue LED mediated C2-H functionalization of **1i/1i-D** with dimethylmalonate derived iodonium ylide **4a** in MeOH for ~3.5 h and the production of desired product **5i/5i-D**.; (B) and (C) Showing the calculation of initial rate of formation of product **5i** and **5i-D** in Mh^{-1}.

3. Spin trapping and spin scavenging experimental details:

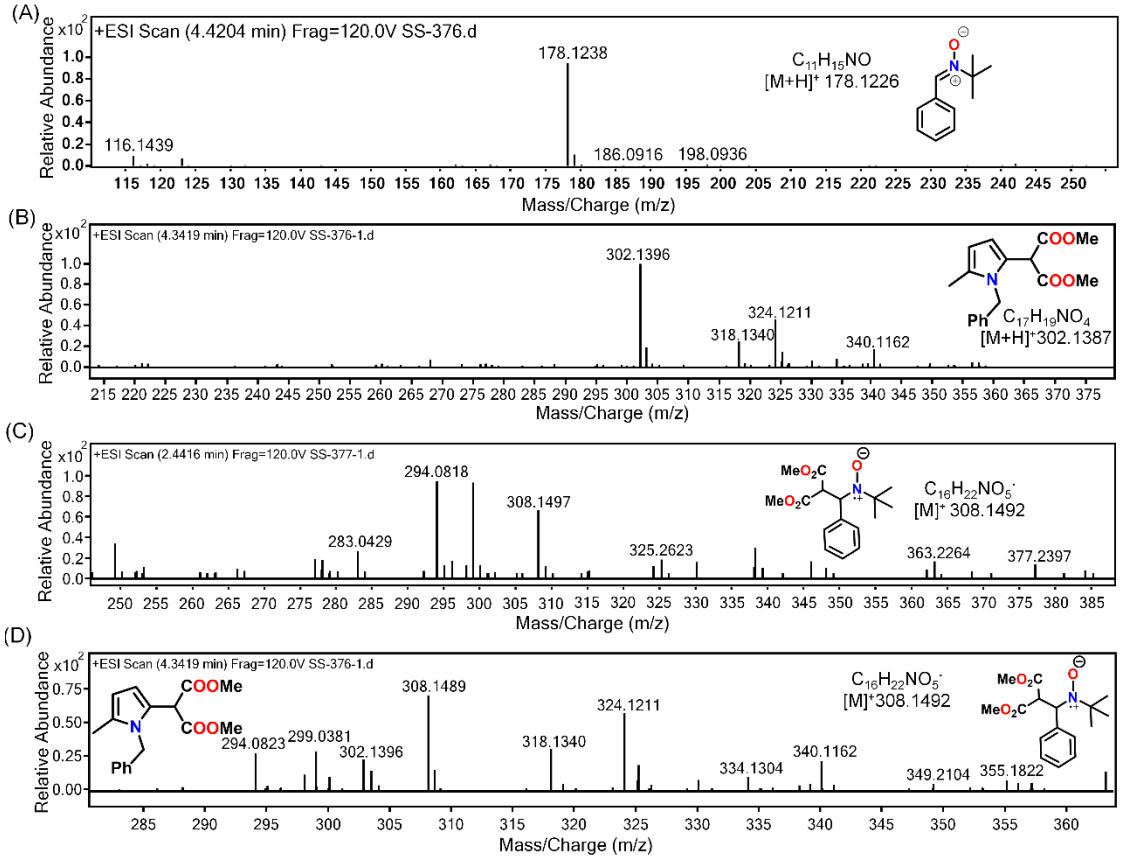


Figure S6: EIC/ESI-HRMS chromatogram of the **PBN, 5e**, and **9** obtained from the reaction mixture when **1i** treated with **4a** in presence of PBN and Finally irradiate with blue LED.

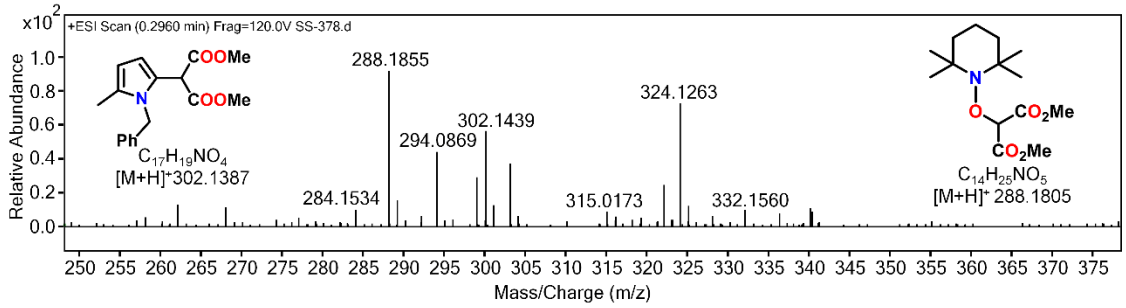


Figure S7: EIC/ESI-HRMS chromatogram of the **5e**, and **10** obtained from the reaction mixture when **1i** treated with **4a** in presence of TEMPO and Finally irradiate with blue LED.

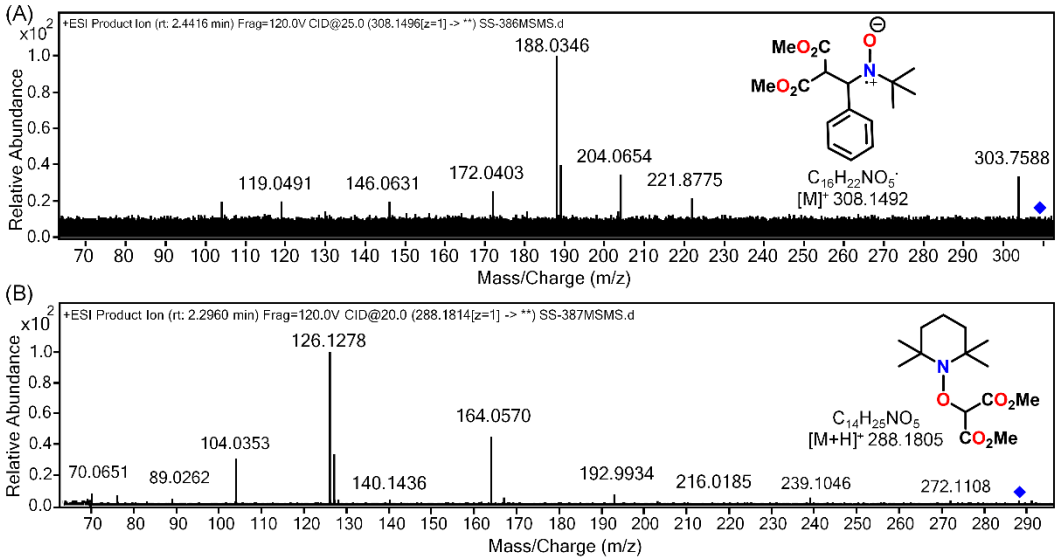


Figure S8: ESI/HR-LCMS/MS fragmentation pattern of (A) **9** and **10**

6. References:

S1. (a) T. Chidley, I. Jameel, S. Rizwan, P. A. Peixoto, L. Pouységu, S. Quideau, W. S. Hopkins, G. K. Murphy, *Angew Chem. Int. Ed*. 2019, **58**, 16959. (b) S. R. Goudreau, D. Marcoux, A. B. Charette, *J. Org. Chem.* 2009, **74**, 470.
S2. S. Liu, S., C. C. Tzschucke, *Eur. J. Org. Chem.* 2016, *21*, 3509.
S3. O. Fischer, A. Hubert, A., M. R. Heinrich, *J. Org. Chem.* 2020, **85**, 11856.