

Supporting Information

Metal-free photoinduced generation and alkynylation of carbamoyl radicals: a facile synthesis of alkynyl amides

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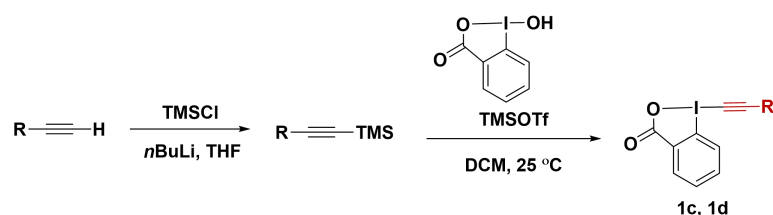
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1. General information

^1H NMR spectra were recorded on JEOLJNM-ECZ400S (400 MHz). Chemical shifts are reported in delta ($\delta(\text{ppm})$) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd=doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR were recorded on JEOLJNM-ECZ400S (100 MHz) with complete proton decoupling spectrophotometers (CDCl_3 : 77.0 ppm). The high-resolution mass spectroscopic (HRMS) data were obtained on a waters UPLC G2-XS Qtof. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. The reactions were monitored by thin-layer chromatography on silica gel coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). Further visualization was achieved by staining with KMnO_4 .

2. Synthetic procedure and spectral data of substrates 1 and 2

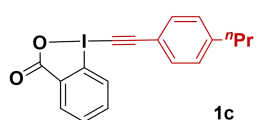
Substrates **1** was prepared through two steps as shown below, in accordance with the known literatures.¹ The NMR data of Substrate **1a**, **1b**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, were reported, except for substrates of **1c**, **1d** shown as the below.



Step 1: To a 250 mL flame-dried round bottom flask was added THF (50 mL) and terminal alkynes (10.0 mmol, 1.0 equiv) under Ar atmosphere. It was cooled to $-78\text{ }^\circ\text{C}$ and $n\text{-BuLi}$ (4.4 mL, 11.0 mmol, 1.1 equiv, 2.5 M in hexane) was added dropwise. The resulting mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h, trimethylsilyl chloride (1.39 mL, 11.0 mmol, 1.1 equiv) was added and continued stirring for 0.5 h and it was

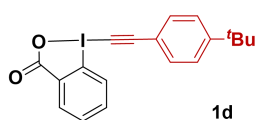
left to slowly warm to room temperature and stirred for 5 h. TLC monitor the completion, and the reaction was quenched by addition of NH₄Cl solution. 100 mL EA was added and the mixture was washed with saturated brine (30 mL). The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The resulting residue was purified by column chromatography to afford the corresponding trimethylsilyl alkynes.

Step 2: To a 100 mL flame-dried flask was added BI-OH and DCM under Ar. Then trimethylsilyl triflate (1.1 equiv) was added dropwise. The resulting yellow mixture was stirred for 1 h, followed by the addition of trimethylsilyl alkyne (1.1 equiv). After stirring for 6 h at room temperature, saturated NaHCO₃ (10 mL) was added and the mixture was stirred vigorously for 30 min. After filtration, the filtrate was washed with saturated NaHCO₃, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The resulting residue was purified by column chromatography (eluted with 0% ~ 10% MeOH in DCM) to afford the target products.



Yellow solid, 84% yield, M.P: 155.8-156.3 °C

¹H NMR (400 MHz, Chloroform-d) δ 8.48 – 8.38 (m, 1H), 8.29 – 8.19 (m, 1H), 7.77 (td, *J* = 6.0, 5.0, 3.1 Hz, 2H), 7.57 – 7.47 (m, 2H), 7.26 (d, *J* = 3.0 Hz, 2H), 2.72 – 2.60 (m, 2H), 1.67 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 146.3, 135.0, 133.0, 132.5, 131.6, 129.0, 126.6, 117.8, 116.4, 107.3, 38.2, 24.4, 13.8. IR (in KBr) 3449, 2953, 2864, 2148, 1604, 1558, 1502, 1435, 1327, 1296, 1004, 826, 747, 687, 641, 564, 530, 472 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₈H₁₆IO₂⁺ ([M+H⁺]) 391.0195, found 391.0917.



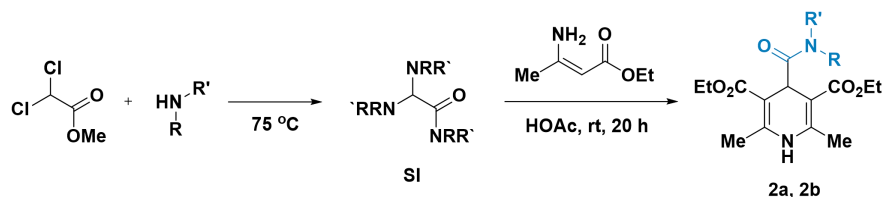
Yellow solid, 62% yield, M.P: 160.8-162.8 °C

¹H NMR (400 MHz, Chloroform-d) δ 8.42 (d, *J* = 7.3 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 2.6 Hz, 2H), 7.70 (s, 4H), 1.35(s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 154.7, 135.0, 132.9, 132.5, 131.6, 126.5, 125.9, 117.6, 116.4, 107.3, 35.2, 31.2. IR (in KBr) 3466, 3066, 2960, 2866, 2148, 1619, 1560, 1502, 1463, 1438, 1396, 1338, 1299, 1266, 1231, 1106, 1011, 964, 834, 807, 741, 690, 642, 564, 523, 472 cm⁻¹. HRMS (ESI) *m/z* calculated for

$C_{19}H_{18}IO_2^+$ ($[M+H]^+$) 405.0351, found 405.0351.

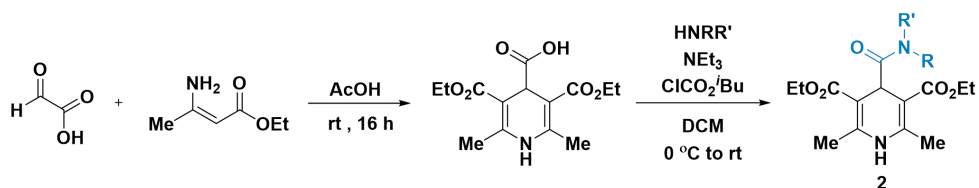
Substrates **2** were prepared through two steps as shown below, in accordance with the known literatures.² The NMR data of substrate **2a**, **2b**, **2c**, **2d**, **2g**, **2h**, **2i**, **2j**, **2l**, **2n**, **2o**, **2q**, **2s**, **2t**, **2z**, were reported, except for substrates of **2e**, **2f**, **2k**, **2m**, **2p**, **2r**, **2u**, **2v**, **2w**, **2x**, **2y** shown as the below.

Method 1:



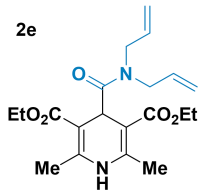
A mixture of methyl dichloroacetate (0.72 g, 5.0 mmol) and amine (25 mmol) was heated at 75 °C for 30 minutes in an oil bath, during which the reaction mixture crystallized. The reaction product was a mixture of SI and amine hydrochloride that was subsequently used without purification. Ethyl 3-aminocrotonate (1.3 g, 10 mmol) and SI (5.0 mmol) were dissolved in glacial acetic acid (10 mL), and the mixture was allowed to stir at room temperature for 20 h. The resultant suspension was diluted with water, the precipitate was removed by filtration, and washed with water to give the corresponding 4-amido-1,4-dihydropyridine **2a** and **2b**.

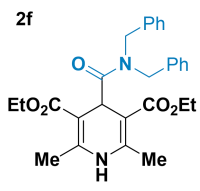
Method 2:

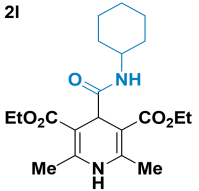


Step 1: A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 3-ethylaminocrotonate (14.9 g, 115 mmol) in glacial acetic acid (5 mL) and the mixture was cooled to 0 °C. A solution of glyoxylic acid (4.6 g, 62 mmol) in glacial acetic acid (20 mL) was then added dropwise to the mixture. The mixture was allowed to warm up to room temperature and stirred overnight. The resulting suspension was then filtered and washed with acetic acid until the yellow color of the washings no longer persisted. The precipitate was collected and 4-carboxyl-4-dihydropyridine was obtained (6.0 g, 40 % yield).

Step 2: A 100 mL round bottom flask equipped with a magnetic stir bar was charged with carboxylic acid (1.0 equiv) and DCM (0.20 M). Triethylamine (1.2 equiv) was added dropwise to the mixture and the yellow solution was cooled to 0 °C. Isobutylchloroformate (1.2 equiv) was then added dropwise. After 10 minutes, the mixture was warmed to room temperature and was stirred for 20 minutes upon which the amine was added, and the mixture was stirred overnight. The mixture was then concentrated under reduced pressure and purified by flash column chromatography.

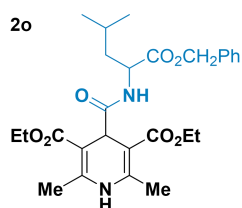
2e  White solid, 76% yield, M.P: 156.3-158.2 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.22 (s, 1H), 5.99 – 5.89 (m, 1H), 5.65 (ddt, *J* = 15.8, 10.4, 5.3 Hz, 1H), 5.22 – 5.15 (m, 3H), 5.08 – 4.99 (m, 2H), 4.37 – 4.35 (m, 2H), 4.28 – 4.09 (m, 4H), 3.93 (d, *J* = 5.2 Hz, 2H), 2.20 (d, *J* = 1.6 Hz, 6H), 1.29 (d, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 168.3, 156.1, 147.8, 131.9, 121.2, 114.1, 97.8, 60.4, 55.6, 42.7, 19.2, 14.5. IR (in KBr) 3292, 3227, 3080, 2981, 2938, 1681, 1648, 1602, 1502, 1448, 1416, 1370, 1325, 1233, 1220, 1203, 1112, 1050, 1023, 920, 861, 757, 709, 655, 628, 577, 470 cm⁻¹. HRMS (ESI) *m/z* calculated for C₂₀H₂₈NaN₂O₅⁺ ([M+Na]⁺) 399.1896, found 399.1904.

2f  Yellow solid, 76% yield, M.P: 156.3-158.2 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.19 (s, 1H), 7.38 – 7.28 (m, 3H), 7.22 (t, *J* = 6.6 Hz, 5H), 7.02 (d, *J* = 6.2 Hz, 2H), 5.38 (s, 1H), 4.96 (s, 2H), 4.47 (s, 2H), 4.22 – 4.10 (m, 2H), 3.85 (dt, *J* = 14.4, 7.2 Hz, 2H), 2.23 (s, 6H), 1.10 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) 176.6, 167.7, 148.4, 137.5, 137.3, 128.6, 128.4, 127.8, 127.7, 127.5, 127.1, 98.3, 60.0, 51.5, 47.3, 37.0, 19.3, 14.4. IR (in KBr) 3461, 3287, 3220, 3093, 2982, 2924, 2853, 1698, 1679, 1618, 1499, 1444, 1387, 1369, 1324, 1280, 1204, 1108, 1050, 1016, 950, 903, 866, 762, 742, 700, 673, 639, 594, 578, 503 cm⁻¹. HRMS (ESI) *m/z* calculated for C₂₈H₃₃N₂O₅⁺ ([M+H]⁺) 477.2389, found 477.2387.

2i  Yellow solid, 84% yield, M.P: 179.8-182.3 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.90 (s, 1H), 6.58 (d, *J* = 8.1

Hz, 1H), 4.52 (s, 1H), 4.18 (q, $J = 7.1$ Hz, 4H), 3.75 – 3.60 (m, 1H), 2.21 (s, 6H), 1.81 (d, $J = 11.4$ Hz, 2H), 1.69 (d, $J = 4.1$ Hz, 3H), 1.34 (d, $J = 11.8$ Hz, 2H), 1.28 (q, $J = 7.1$ Hz, 6H), 1.22 – 1.12 (q, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 168.2, 147.8, 97.7, 60.0, 47.9, 42.1, 33.1, 25.6, 24.7, 18.9, 14.6. IR (in KBr) 3855, 3746, 3672, 3648, 3436, 3274, 3208, 3086, 2983, 2934, 2855, 1702, 1652, 1506, 1448, 1384, 1366, 1308, 1269, 1204, 1147, 1120, 1089, 1051, 1021, 983, 890, 869, 823, 760, 706, 647, 583, 561, 511 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{30}\text{NaN}_2\text{O}_5^+$ ($[\text{M}+\text{Na}]^+$) 401.2052, found 401.2053.

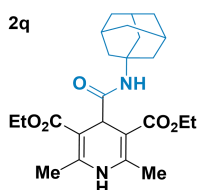
2o



Yellow solid, 70% yield, M.P: 77.6-78.3 °C

^1H NMR (400 MHz, Chloroform- d) δ 7.96 (s, 1H), 7.33 (q, $J = 4.7, 4.2$ Hz, 5H), 7.06 (d, $J = 8.5$ Hz, 1H), 5.12 (d, $J = 4.0$ Hz, 2H), 4.65 (s, 1H), 4.62 – 4.52 (m, 1H), 4.24 – 4.09 (m, 4H), 2.20 (s, 3H), 2.12 (s, 3H), 1.69 – 1.50 (m, 3H), 1.30 – 1.22 (d, 6H), 0.91 (d, $J = 5.9$ Hz, 3H), 0.88 (d, $J = 5.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 172.6, 167.9, 167.8, 147.7, 135.6, 128.6, 128.4, 128.1, 97.65, 97.56, 66.8, 60.3, 60.1, 51.0, 41.6, 24.8, 23.0, 21.9, 18.9, 14.4. IR (in KBr) 3350, 3287, 3214, 3090, 2960, 2869, 1743, 1703, 1653, 1538, 1500, 1372, 1329, 1310, 1266, 1214, 1116, 1093, 1053, 1022, 827, 747, 695, 619, 596, 484 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{36}\text{NaN}_2\text{O}_7^+$ ($[\text{M}+\text{Na}]^+$) 523.2420, found 523.2427.

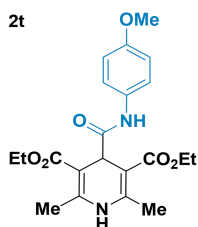
2q



White solid, 90% yield, M.P: 209.9-213.8 °C.

^1H NMR (400 MHz, Chloroform- d) δ 7.96 (s, 1H), 6.36 (s, 1H), 4.43 (s, 1H), 4.18 (m, $J = 7.1, 2.7$ Hz, 4H), 2.22 (s, 6H), 1.96 (d, $J = 2.7$ Hz, 7H), 1.66 (m, 8H), 1.30 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 168.0, 147.5, 98.2, 60.0, 51.5, 42.7, 41.7, 36.5, 29.5, 19.2, 14.6. IR (in KBr) 3452, 3332, 3195, 3082, 2981, 2909, 2851, 1703, 1658, 1548, 1506, 1461, 1384, 1369, 1341, 1311, 1264, 1238, 1214, 1172, 1120, 1098, 1050, 1024, 912, 840, 811, 771, 750, 663, 628, 609, 579, 482 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{35}\text{N}_2\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) 431.2546, found 431.2550.

2t

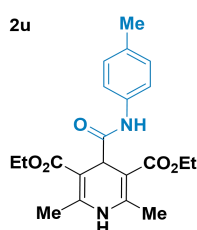


White solid, 76% yield, M.P: 156.3-158.2 °C.

^1H NMR (400 MHz, Chloroform- d) δ 8.74 (s, 1H), 7.96 (s, 1H),

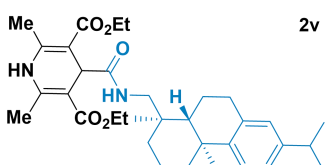
7.45 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 4.70 (s, 1H), 4.18 (q, $J = 7.1$ Hz, 4H), 3.76 (s, 3H), 2.20 (s, 6H), 1.26 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 168.3, 156.1, 147.8, 131.9, 121.2, 114.1, 97.8, 60.4, 55.6, 42.7, 19.2, 14.5. IR (in KBr) 3853, 3747, 3673, 3649, 3295, 3230, 3140, 3089, 2963, 2841, 1871, 1700, 1665, 1649, 1605, 1552, 1512, 1492, 1444, 1414, 1375, 1328, 1305, 1250, 1218, 1196, 1172, 1118, 1100, 1034, 946, 825, 770, 746, 703, 624, 604, 536, 518, 471 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_6^+$ ($[\text{M}+\text{H}]^+$) 403.1869, found 403.1873.

2u



Yellow solid, 84% yield, M.P: 156.7-157.2 $^{\circ}\text{C}$

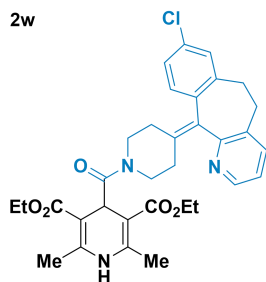
^1H NMR (400 MHz, Chloroform- d) δ 8.78 (s, 1H), 7.69 (s, 1H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 4.72 (s, 1H), 4.20 (q, $J = 7.1$ Hz, 4H), 2.30 (s, 3H), 2.23 (s, 6H), 1.28 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 168.3, 147.9, 136.1, 133.5, 129.5, 119.6, 97.7, 60.4, 42.8, 21.0, 19.1, 14.5. IR (in KBr) 3750, 3294, 3225, 3128, 3090, 3024, 2977, 2929, 1890, 1705, 1670, 1653, 1603, 1544, 1492, 1373, 1321, 1251, 1218, 1189, 1116, 1096, 1044, 877, 838, 813, 769, 748, 691, 625, 603, 507, 470 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{26}\text{NaN}_2\text{O}_5^+$ ($[\text{M}+\text{Na}]^+$) 409.1739, found 409.1743.



2v Yellow solid, 75% yield, M.P: 76.5-78.3 $^{\circ}\text{C}$

^1H NMR (400 MHz, Chloroform- d) δ 7.36 (br, 1H), 7.13 (d, $J = 8.2$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 6.84 (s, 1H), 6.80 (t, $J = 6.2$ Hz, 1H), 4.55 (s, 1H), 4.05 - 3.87 (m, 4H), 3.22 (dd, $J = 13.6, 6.6$ Hz, 1H), 2.95 (dd, $J = 13.6, 6.1$, 1H), 2.87 - 2.71 (m, 3H), 2.27 - 2.22 (m, 2H), 2.19 (s, 3H), 2.11 (s, 3H), 1.84 - 1.79 (m, 1H), 1.76 - 1.60 (m, 4H), 1.39 - 1.34 (m, 2 H), 1.21 - 1.15 (m, 12H), 1.10 (t, $J = 7.1$ Hz, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 168.2, 147.5, 147.4, 147.2, 145.6, 135.0, 126.9, 124.4, 123.8, 98.1, 60.2, 49.9, 45.0, 41.6, 38.6, 37.52, 37.49, 36.2, 33.6, 30.4, 25.4, 24.1, 19.11, 19.06, 18.8, 14.5, 14.4. IR (in KBr) 3298, 3219, 3090, 2959, 2929, 2869, 1706, 1666, 1538, 1498, 1384, 1370, 1326, 1308, 1265, 1215, 1170, 1120, 1097, 1052, 1022, 885, 822, 772, 600 cm^{-1} .

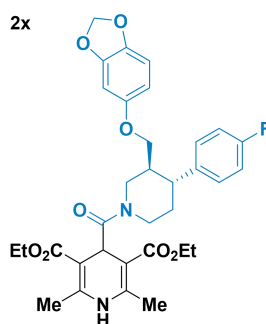
2w



Yellow solid, 77% yield, M.P: 199.7-200.3 °C.

^1H NMR (400 MHz, Chloroform-d) δ 8.40 (t, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 6.2$ Hz, 1H), 7.17 – 7.08 (m, 4H), 6.76 (br, 1H), 5.09 (s, 1H), 4.32 – 4.21 (m, 2H), 4.18 – 4.04 (m, 4H), 3.52 – 3.32 (m, 3H), 3.10 – 3.04 (m, 1H), 2.90 – 2.76 (m, 2H), 2.71 – 2.54 (m, 1H), 2.47 – 2.42 (m, 2H), 2.35 (t, $J = 5.9$ Hz, 1H), 2.27 (dd, $J = 8.4, 4.6$ Hz, 6H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.35 (d, $J = 8.1$ Hz), 167.80, 167.64 (d, $J = 7.1$ Hz), 157.23 (d, $J = 8.9$ Hz), 148.05 (d, $J = 7.6$ Hz), 147.80 (d, $J = 14.3$ Hz), 146.8, 139.6, 138.0, 137.64 (dd, $J = 14.6, 8.5$ Hz), 133.8, 133.5, 132.9, 130.75 (d, $J = 4.1$ Hz), 129.08 (d, $J = 7.5$ Hz), 126.2, 122.4, 98.86 (d, $J = 9.3$ Hz), 98.65 (d, $J = 8.0$ Hz), 59.94 (d, $J = 20.2$ Hz), 47.5, 43.6, 36.6, 34.0, 31.70 (d, $J = 26.2$ Hz), 30.58 (d, $J = 15.3$ Hz), 25.7, 25.0, 19.43 (d, $J = 9.1$ Hz), 14.70 (dd, $J = 7.1, 4.0$ Hz). IR (in KBr) 3462, 2982, 1680, 1630, 1512, 1441, 1367, 1324, 1217, 1121, 1024, 593 cm^{-1} .

2x

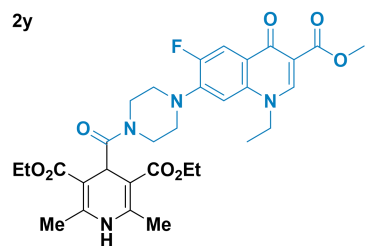


White solid, 57% yield, M.P: 180.3-182.8 °C.

^1H NMR (400 MHz, Chloroform-d) δ 7.41 (s, 1H), 7.15 – 7.12 (m, 1H), 6.97 (t, $J = 8.6$ Hz, 2H), 6.62 (t, $J = 8.0$ Hz, 1H), 6.36 (d, $J = 21.5$ Hz, 1H), 6.15 (dd, $J = 19.9, 8.8$ Hz, 1H), 5.88 (d, $J = 7.7$ Hz, 1H), 5.16 (d, $J = 7.3$ Hz, 1H), 4.92 (d, $J = 13.1$ Hz, 1H), 4.79 (d, $J = 13.0$ Hz, 1H), 4.34 – 4.24 (m, 1H), 4.21 – 4.12 (m, 3H), 3.74 – 3.60 (m, 1H), 3.56 – 3.45 (m, 1H), 3.26 – 3.16 (m, 1H), 2.86 – 2.76 (m, 1H), 2.70 – 2.60 (m, 1H), 2.28 (d, $J = 6.7$ Hz, 6H), 1.98 – 1.84 (m, 2H), 1.74 – 1.64 (m, 1H), 1.31 (t, $J = 7.0$ Hz, 5H), 1.24 (t, $J = 7.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.4, 167.75 (dd, $J = 19.0, 5.5$ Hz), 162.9, 160.4, 154.43 (d, $J = 16.0$ Hz), 148.36 – 147.88 (m), 141.7, 139.76 – 139.18 (m), 128.93 (d, $J = 7.7$ Hz), 115.57 (d, $J = 21.2$ Hz), 107.9, 105.63 (d, $J = 10.7$ Hz), 101.2, 99.0, 98.67 (t, $J = 9.0$ Hz), 98.06 (d, $J = 7.9$ Hz), 68.89 (d, $J = 10.3$ Hz), 60.0, 59.9, 50.4, 47.5, 45.8, 44.0, 43.2, 42.8, 42.0, 36.6, 34.8, 33.7, 19.47 (dd, $J = 27.4, 4.2$ Hz), 14.74 (t, $J = 12.9$ Hz). IR (in KBr) 3451 3094, 2930, 2852, 1695, 1613, 1508, 1489, 1471, 1450, 1384, 1308, 1270, 1223, 1190, 1111, 1094, 1040, 1023, 937, 832, 764,

642, 541 cm⁻¹.

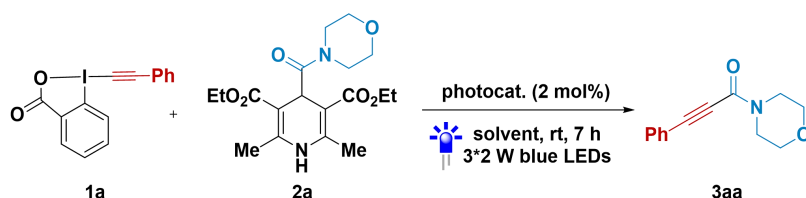
2y



White solid, 57% yield, M.P: 261.7-262.3 °C.

¹H NMR (400 MHz, Chloroform-d) δ 8.46 (s, 1H), 8.11 (d, *J* = 13.1 Hz, 1H), 7.49 (s, 1H), 6.75 (d, *J* = 6.5 Hz, 1H), 5.11 (s, 1H), 4.26 – 4.12 (m, 8H), 3.93 (s, 3H), 3.84 (t, *J* = 5.0 Hz, 2H), 3.37 (t, *J* = 4.8 Hz, 2H), 3.22 (t, *J* = 5.1 Hz, 2H). 2.27 (s, 6H), 1.55 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 174.6, 173.2, 167.6, 166.8, 154.5, 152.1, 148.5, 147.4, 144.8, 136.2, 124.17 (d, *J* = 7.3 Hz), 114.028 (d, *J* = 23.1 Hz), 110.3, 104.0, 99.3, 60.2, 52.3, 50.7, 49.9, 49.1, 46.7, 42.0, 36.7, 19.9, 14.7, 14.6.

3. Condition optimization^a



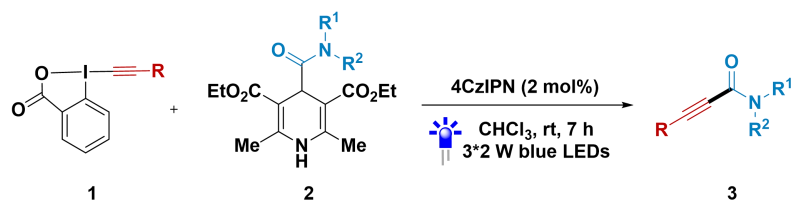
Entry	Photocat.	Solvent	Ratio of 1a to 2a	3aa Yield % ^b
1	Rhodamine B	CHCl ₃	1:1.5	13
2	eosin Y	CHCl ₃	1:1.5	55
3	Rose Bengal	CHCl ₃	1:1.5	61
4	Methylene blue	CHCl ₃	1:1.5	66
5	4CzIPN	CHCl ₃	1:1.5	71
6	4CzIPN	CH ₂ Cl ₂	1:1.5	68
7	4CzIPN	DCE	1:1.5	65
8	4CzIPN	CH ₃ CN	1:1.5	59
9	4CzIPN	THF	1:1.5	66
10	4CzIPN	toluene	1:1.5	39
11	4CzIPN	DMF	1:1.5	34
12	4CzIPN (1%)	CHCl ₃	1:1.5	67
13	4CzIPN	CHCl ₃	1: 1.2	79
14	4CzIPN	CHCl ₃	1.2:1	83

15	4CzIPN	CHCl ₃	1.5:1	91(86)
16 ^c	4CzIPN	CHCl ₃	1.5:1	0
17	-	CHCl ₃	1.5:1	83
18 ^d	4CzIPN	CHCl ₃	1.5:1	85

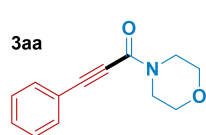
^a Reaction conditions: **1a** (0.2 mmol), **2a** (x equiv), photocat. (2.0 mol%), in 2.0 mL of solvent, at room temperature, 7 h, under irradiation of 3*2 W blue LEDs. ^b Yield was determined by ¹H NMR using (Ph)₃CH as the internal standard. Isolated yield in parentheses. ^c In the dark. ^d Irradiation of 395 - 415 nm light source instead of blue LEDs.

4. Photocatalytic alkylation of carbamoyl radicals

4.1 General procedure and spectral data of the synthesis of amides **3**

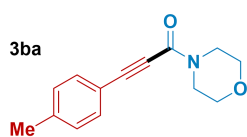


To a dried schlenk tube was treated with **1** (0.30 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), 4CzIPN (0.004 mmol, 2 mol%), and CHCl₃ (2.0 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting mixture was stirred at a distance of ~2 cm under irradiation by 3*2 W blue LEDs at 25 °C for 7 h. After completion, the mixture was concentrated and purified by silica column chromatography using hexane/ethyl acetate or CH₂Cl₂/ MeOH as eluent to afford the desired product **3**.



Yellow solid, 37.0 mg, 86% yield.

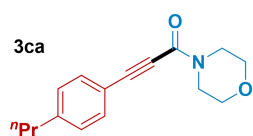
¹H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 3.85 (t, *J* = 4.8 Hz, 2H), 3.76 (t, *J* = 4.8 Hz, 2H), 3.71 (s, 4H).) ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 132.3, 130.1, 128.5, 120.1, 91.1, 80.6, 66.8, 66.4, 47.2, 41.9.



Yellow solid, 43.75 mg, 96% yield, M.P: 85.2-86.5 °C.

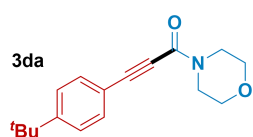
¹H NMR (400 MHz, Chloroform-d) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.88 – 3.81 (m, 2H), 3.80 – 3.73 (m,

2H), 3.71 (s, 4H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 140.9, 132.5, 129.4, 117.2, 91.8, 80.4, 67.0, 66.6, 47.4, 42.0, 21.8. IR (in KBr) 3748, 3552, 3415, 3231, 3035, 2972, 2921, 2858, 2210, 1625, 1511, 1427, 1361, 1299, 1277, 1211, 1197, 1183, 1115, 1068, 1040, 965, 853, 824, 729, 614, 558, 535, 507 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{16}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 230.1181, found 230.1187.



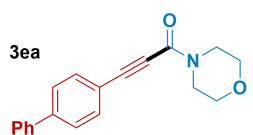
Yellow oil, 47.03 mg, 92% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.46 (d, $J = 8.2$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 3.86 – 3.84 (m, 2H), 3.76 – 3.74 (m, 2H), 3.71 (s, 4H), 2.60 (t, $J = 8.5, 6.8$ Hz, 2H), 1.69 – 1.59 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 145.5, 132.5, 128.8, 117.4, 91.8, 80.4, 67.0, 66.6, 47.4, 42.0, 38.1, 24.3, 13.8. IR (in KBr) 3472, 3030, 2962, 2928, 2859, 2212, 1631, 1508, 1452, 1429, 1363, 1300, 1281, 1211, 1181, 1115, 1069, 1040, 965, 849, 818, 793, 773, 728, 676, 618, 562, 534 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 258.1494, found 258.1499.



Yellow solid, 45.08 mg, 83% yield, M.P: 160.7-162.3 $^\circ\text{C}$.

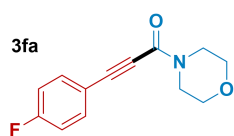
^1H NMR (400 MHz, Chloroform- d) δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 3.88 – 3.82 (m, 2H), 3.80 – 3.73 (m, 2H), 3.71 (s, 4H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 153.5, 132.3, 125.7, 117.2, 91.7, 67.0, 66.6, 47.4, 42.0, 35.1, 31.2. IR (in KBr) 3465, 3053, 2963, 2919, 2858, 2212, 1938, 1622, 1507, 1433, 1399, 1364, 1330, 1299, 1281, 1267, 1225, 1187, 1115, 1070, 1039, 968, 844, 733, 645, 613, 569, 552, 531 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{22}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 272.1651, found 272.1657.



Yellow solid, 57.64 mg, 99% yield, M.P: 123.3-125.4 $^\circ\text{C}$.

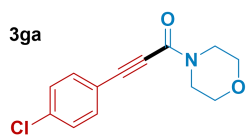
^1H NMR (400 MHz, Chloroform- d) δ 7.60 (d, $J = 11.6$ Hz, 6H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 7.2$ Hz, 1H), 3.87 (t, $J = 5.2$ Hz, 2H), 3.77 (t, $J = 4.8$ Hz, 2H), 3.72 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 143.1, 139.9, 133.0, 129.1, 128.2, 127.2, 119.1, 91.3, 81.4, 67.0, 66.6, 47.4, 42.1. IR (in KBr) 3437, 2961, 2925, 2874, 2212, 1628, 1517, 1486, 1432, 1397, 1362, 1311, 1281, 1216, 1188, 1111, 1072, 1041, 1006, 966, 842, 768, 731, 723, 698, 673, 577, 562, 549, 500 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{18}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 292.1338,

found 292.1346.



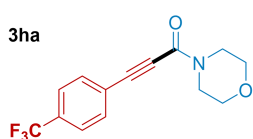
Yellow solid, 39.13 mg, 84% yield, M.P: 91.1-92.3 °C

¹H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.49 (m, 2H), 7.08 (t, J = 8.6 Hz, 2H), 3.85 – 3.83 (m, 2H), 3.77 – 3.75 (m, 2H), 3.71 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 165.0, 162.4, 134.7, 134.6, 116.3, 116.1, 90.3, 80.7, 67.0, 66.6, 47.4, 42.0. IR (in KBr) 3467, 3436, 3058, 2966, 2918, 2852, 2209, 1958, 1618, 1500, 1428, 1383, 1362, 1299, 1275, 1240, 1210, 1177, 1114, 1068, 1040, 1020, 976, 947, 926, 909, 870, 844, 824, 750, 726, 663, 642, 627, 611, 563, 539, 476 cm⁻¹. HRMS (ESI) m/z calculated for C₁₃H₁₃FNO₂⁺ ([M+H]⁺) 234.0930, found 234.0932.



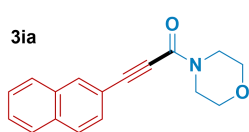
Yellow oil, 49.31 mg, 99% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.48 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 3.864– 3.82 (m, 2H), 3.77 – 3.75 (m, 2H), 3.71 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 153.0, 136.6, 133.7, 129.1, 118.8, 90.0, 81.6, 67.0, 66.5, 47.4, 42.1. IR (in KBr) 3467, 3053, 2965, 2927, 2866, 2220, 1927, 1621, 1598, 1510, 1450, 1428, 1363, 1330, 1299, 1279, 1267, 1226, 1212, 1196, 1159, 1112, 1074, 1039, 969, 921, 842, 824, 766, 725, 667, 616, 563, 536, 527, 506 cm⁻¹. HRMS (ESI) m/z calculated for C₁₃H₁₃ClNO₂⁺ ([M+H]⁺) 250.0635, found 250.0641.



Yellow solid, 52.95 mg, 94% yield, M.P:123.2-124.2 °C.

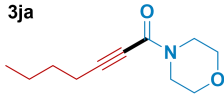
¹H NMR (400 MHz, Chloroform-d) δ 7.65 (s, 4H), 3.85– 3.81 (m, 2H), 3.78 – 3.76 (m, 2H), 3.72 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 132.7, 132.1, 132.0, 131.9, 131.7, 125.6, 124.1, 89.3, 82.6, 66.8 (d, J = 40.5 Hz), 47.4, 42.1. IR (in KBr) 3466, 2966, 2866, 2216, 1624, 1486, 1426, 1282, 1212, 1195, 1114, 1040, 1012, 969, 830, 726, 605, 561, 531 cm⁻¹. HRMS (ESI) m/z calculated for C₁₄H₁₃F₃NO₂⁺ ([M+H]⁺) 217.1341, found 217.1343.

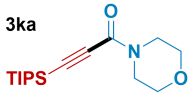


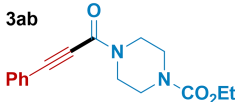
Colorless oil, 67.27 mg, 77% yield.

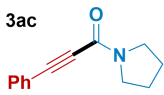
¹H NMR (400 MHz, Chloroform-d) δ 8.09 (s, 1H), 3.84 – 3.80 (m, 3H), 7.56 – 7.51 (m, 3H), 3.89 (t, J = 4.8 Hz, 2H), 3.78 (t, J = 4.5 Hz, 2H), 3.72 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 133.7, 133.5, 133.4,

132.74, 128.5, 128.2, 128.0, 127.8, 127.1, 117.5, 91.7, 81.0, 67.0, 66.6, 47.5, 42.1. IR (in KBr) 3457, 2965, 2934, 2221, 1636, 1613, 1454, 1433, 1405, 1365, 1325, 1304, 1280, 1215, 1164, 1111, 1067, 1038, 1012, 965, 852, 835, 721, 598, 561 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{16}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 266.1181, found 266.1184.

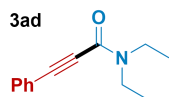
3ja  Yellow oil, 36.02 mg, 92% yield.
 ^1H NMR (400 MHz, Chloroform- d) δ 3.76 – 3.74 (m, 2H), 3.72 – 3.69 (m, 2H), 3.68 – 3.63 (m, 4H), 2.37 (t, $J = 7.1$ Hz, 2H), 1.59 – 1.53 (m, 2H), 1.46 – 1.40 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 94.4, 73.3, 67.0, 66.5, 47.3, 41.9, 29.9, 22.1, 18.7, 13.6. IR (in KBr) 3472, 2961, 2931, 2861, 2238, 1730, 1631, 1453, 1429, 1363, 1300, 1276, 1248, 1115, 1070, 1010, 842, 732, 619, 557 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{18}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 196.1338, found 196.1336.

3ka  Yellow oil, 46.91 mg, 79% yield.
 ^1H NMR (400 MHz, Chloroform- d) δ 3.82 – 3.80 (m, 2H), 3.73 – 3.71 (m, 2H), 3.69 – 3.64 (m, 4H), 1.19 – 1.12 (m, 3H), 1.10 (d, $J = 4.6$ Hz, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 97.4, 95.5, 66.9, 66.6, 47.4, 41.9, 18.6, 11.1. IR (in KBr) 3457, 2220, 1631, 1535, 1444, 1304, 1026, 993, 758, 690, 531 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{30}\text{NO}_2\text{Si}^+$ ($[\text{M}+\text{H}]^+$) 296.2046, found 296.2051.

3ab  Pale yellow oil, 56.69 mg, 99% yield.
 ^1H NMR (400 MHz, Chloroform- d) δ 7.56 (d, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.0$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 2H), 4.18 (q, $J = 6.9$ Hz, 2H), 3.88 – 3.78 (m, 2H), 3.74 – 3.64 (m, 2H), 3.64 – 3.55 (m, 2H), 3.55 – 3.46 (m, 2H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 153.3, 132.5, 130.4, 128.7, 120.2, 91.4, 80.8, 61.9, 46.9, 44.0, 43.4, 41.4, 14.7. IR (in KBr) 3560, 3501, 2985, 2930, 2865, 2210, 1695, 1622, 1490, 1460, 1430, 1386, 1356, 1288, 1253, 1234, 1206, 1175, 1127, 1081, 1035, 989, 941, 760, 726, 692, 601, 571, 534, 492 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3^+$ ($[\text{M}+\text{H}]^+$) 287.1396, found 287.1392.

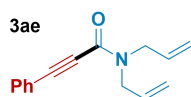
3ac  Pale yellow oil, 33.87 mg, 85% yield.
 ^1H NMR (400 MHz, Chloroform- d) δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.42 (t, $J = 14.5$ Hz, 1H), 7.36 (t, $J = 6.5$ Hz, 2H), 3.74 (t, $J = 5.8$ Hz, 2H), 3.54 (t, $J =$

5.9 Hz, 2H), 2.02 – 1.92 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 132.5, 130.1, 128.6, 120.7, 88.8, 82.7, 48.3, 45.5, 25.5, 24.8. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{14}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 200.1075, found 200.1072.



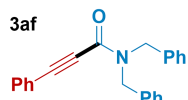
Yellow oil, 36.54 mg, 85% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.56 – 7.53 (m, 2H), 7.44 – 7.43 – 734 (m, 3H), 3.67 (q, $J = 7.1$ Hz, 2H), 3.48 (q, $J = 7.2$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 132.4, 130.0, 128.6, 120.8, 89.1, 82.0, 43.71, 39.4, 14.5, 13.0. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{16}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 202.1232, found 202.1236.



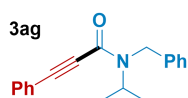
Colorless oil, 39.17 mg, 87% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.43 – 7.38 (m, 1H), 7.35 (t, $J = 7.2$ Hz, 2H), 5.89 – 5.53 (m, 2H), 5.28 – 5.17 (m, 4H), 4.22 (d, $J = 5.7$ Hz, 2H), 4.05 (d, $J = 5.9$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 132.8, 132.5, 132.2, 130.2, 128.6, 120.5, 118.3, 118.1, 81.6, 50.9, 46.5. IR (in KBr) 3472, 3083, 2216, 1629, 1491, 1451, 1412, 1270, 1211, 1135, 992, 927, 758, 734, 690, 615, 531 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{16}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 226.1232, found 226.1237.



White solid, 39.17 mg, 87% yield, M.P: 90.8-92.6 $^\circ\text{C}$.

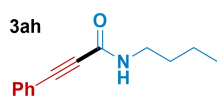
^1H NMR (400 MHz, Chloroform- d) δ 7.51 (d, $J = 7.0$ Hz, 2H), 7.45 – 7.29 (m, 11H), 7.27 (s, 2H), 4.76 (s, 2H), 4.57 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.14, 136.25, 136.17, 132.59, 130.27, 129.02, 128.83, 128.64, 128.60, 128.11, 127.87, 127.79 120.46, 81.72, 51.53, 46.43. HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{20}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 326.1545, found 326.1549.



Colorless oil, 40.38 mg, 58% yield.

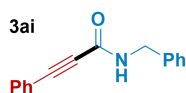
^1H NMR (400 MHz, Chloroform- d) δ 7.58 (d, $J = 6.7$ Hz, 1H), 7.46 – 7.21 (m, 9H), 4.87 – 4.70 (m, 1.5H), 4.70 (q, $J = 6.8$ Hz, 0.5H), 4.64 (s, 1H), 1.22 (d, $J = 6.8$ Hz, 3H), 1.13 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.28 (d, $J = 28.8$ Hz), 138.60 (d, $J = 14.8$ Hz), 132.5, 130.06 (d, $J = 8.8$ Hz), 128.68 (d, $J = 8.7$ Hz), 128.52 (d, $J = 2.2$ Hz), 127.38 (d, $J = 18.3$ Hz), 126.99 (d, $J = 9.2$ Hz), 120.8, 120.6, 90.14 (d, $J = 117.8$ Hz), 82.31 (d, $J = 82.7$ Hz), 50.14 (d, $J = 216.4$ Hz),

45.22 (d, $J = 272.1$ Hz), 21.02 (d, $J = 129.0$ Hz). IR (in KBr) 3457, 3056, 3030, 2970, 2930, 2211, 1621, 1488, 1434, 1414, 1370, 1343, 1308, 1237, 1179, 1160, 1128, 1069, 1029, 995, 938, 770, 735, 725, 694, 633, 586, 560, 535, 457 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{20}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 278.1545, found 278.1548. (Note: the target was obtained as a 1/1 mixture of rotamers).



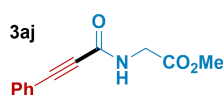
Colorless oil, 37.53 mg, 93% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.53 (d, $J = 8.4$ Hz, 2H), 7.44 – 7.33 (m, 3H), 5.95 (s, 1H), 3.36 (q, $J = 6.5, 6.0$ Hz, 2H), 1.59 – 1.52 (m, 2H), 1.44 – 1.35 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 132.5, 130.1, 128.6, 120.4, 84.5, 83.2, 39.8, 31.5, 20.1, 13.8. IR (in KBr) 3437, 3278, 3059, 2960, 2933, 2872, 2221, 1632, 1543, 1490, 1443, 1304, 1219, 1151, 1071, 1026, 981, 757, 690, 599, 531 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{16}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 202.1232, found 202.1239.



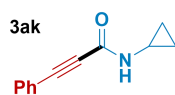
White solid, 40.21 mg, 86% yield, M.P: 99.0-100.1 $^{\circ}\text{C}$

^1H NMR (400 MHz, Chloroform- d) δ 7.53 (d, $J = 8.4$ Hz, 2H), 7.45 – 7.32 (m, 8H), 6.17 (s, 1H), 4.56 (d, $J = 5.7$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 137.3, 132.6, 130.2, 129.0, 128.7, 128.1, 128.0, 120.2, 85.2, 82.9, 44.1. HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{13}\text{NaNO}^+$ ($[\text{M}+\text{Na}]^+$) 258.0895, found 258.0890.



Yellow oil, 38.75 mg, 89% yield.

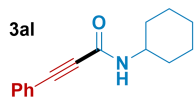
^1H NMR (400 MHz, Chloroform- d) δ 7.56 (d, $J = 7.0$ Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.3$ Hz, 2H), 6.45 (s, 1H), 4.16 (d, $J = 5.2$ Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 153.4, 132.7, 130.4, 128.7, 120.0, 85.9, 82.4, 52.7, 41.5. IR (in KBr) 3456, 3275, 3063, 2951, 2232, 1733, 1626, 1548, 1490, 1446, 1433, 1343, 327, 1284, 1242, 1219, 1039, 1009, 848, 786, 758, 691, 660, 560, 535 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{12}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 218.0817, found 218.0814.



Yellow oil, 38.75 mg, 89% yield.

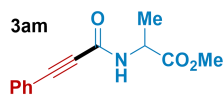
^1H NMR (400 MHz, Chloroform- d) δ 7.59 – 7.50 (m, 2H), 7.47 – 7.34 (m, 3H), 6.03 (s, 1H), 2.83 – 2.76 (m, 1H), 0.91 – 0.83 (m, 2H), 0.66 – 0.58 (m,

2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.8, 132.6, 130.2, 128.6, 120.2, 84.9, 83.0, 23.0, 8.2, 7.0. IR (in KBr) 3435, 3250, 3016, 2220, 1630, 1533, 1490, 1444, 1387, 1360, 1303, 1234, 1201, 1172, 1049, 1026, 992, 911, 840, 757, 690, 603, 532 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{12}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 186.0919, found 186.0915.



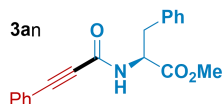
White solid, 37.44 mg, 83% yield, M.P: 110.3-112.1 $^\circ\text{C}$

^1H NMR (400 MHz, Chloroform- d) δ 7.53 (d, $J = 6.9$ Hz, 2H), 7.44 – 7.34 (m, 3H), 5.82 (s, 1H), 3.95 – 3.82 (m, 1H), 1.99 (d, $J = 9.7$ Hz, 2H), 1.74 (d, $J = 13.5$ Hz, 2H), 1.65 – 1.59 (m, 1H), 1.47 – 1.31 (m, 2H), 1.30 – 1.14 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 132.5, 130.1, 128.6, 120.4, 84.3, 83.4, 48.9, 33.0, 25.5, 24.9. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{18}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 228.1388, found 228.1387.



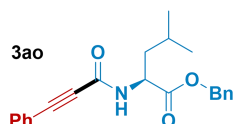
Yellow oil, 40.04 mg, 87% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.55 (d, $J = 8.3$, 1.3 Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.3$ Hz, 2H), 6.52 (d, $J = 6.8$ Hz, 1H), 4.74 – 4.67 (m, 1H), 3.80 (s, 3H), 1.49 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 152.8, 132.7, 130.3, 128.7, 120.1, 85.5, 82.7, 52.8, 48.5, 18.5. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{14}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 232.0974, found 232.0969.



Yellow solid, 60.47 mg, 99% yield, M.P: 94.2-95.3 $^\circ\text{C}$.

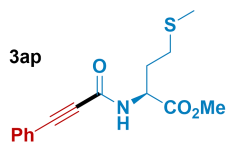
^1H NMR (400 MHz, Chloroform- d) δ 7.58 – 7.51 (m, 2H), 7.45 – 7.27 (m, 6H), 7.17 – 7.11 (m, 2H), 6.40 (d, $J = 7.6$ Hz, 1H), 5.03 – 4.95 (m, 1H), 3.76 (s, 3H), 3.26 – 3.15 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 152.8, 135.5, 132.8, 130.3, 129.4, 128.8, 128.6, 127.4, 120.0, 85.6, 82.5, 53.6, 52.7, 37.8. IR (in KBr) 3466, 3297, 2947, 2217, 1741, 1634, 1531, 1493, 1436, 1320, 1301, 1231, 1212, 1173, 1087, 1044, 1003, 958, 758, 691, 569, 529 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{18}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 308.1287, found 308.1293.



Colorless oil, 30.67 mg, 58% yield.

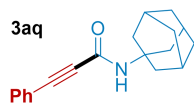
^1H NMR (400 MHz, Chloroform- d) δ 7.55 (d, $J = 7.7$ Hz, 2H), 7.46 – 7.34 (m, 8H), 6.30 (d, $J = 8.5$ Hz, 1H), 5.20 (s, 2H), 4.79 (td, $J = 8.6$, 4.6 Hz, 1H), 1.78 – 1.67 (m, 2H), 1.66 – 1.59 (m, 1H), 0.95 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 153.1, 135.3, 132.7, 130.3, 128.8, 128.6, 128.6, 128.4,

120.1, 85.7, 82.7, 67.4, 51.2, 41.7, 24.9, 22.9, 22.0. IR (in KBr) 3236, 3044, 2959, 2928, 2872, 2218, 1742, 1626, 1537, 1492, 1444, 1384, 1339, 1304, 1271, 1216, 1188, 1150, 1027, 998, 945, 922, 828, 757, 691, 600, 532, 490 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 350.1678, found 350.1677.



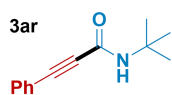
Yellow oil, 34.86 mg, 60% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.56 (d, $J = 6.9$ Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 2H), 6.62 (d, $J = 7.8$ Hz, 1H), 4.85 (q, 1H), 3.80 (s, 3H), 2.64 – 2.50 (m, 2H), 2.29 – 2.21 (m, 1H), 2.12 (s, 3H), 2.11 – 2.02 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 153.1, 132.7, 130.4, 128.7, 120.0, 85.9, 82.5, 52.9, 51.9, 31.7, 29.9, 15.5. IR (in KBr) 3449, 2922, 2215, 1743, 1635, 1536, 1442, 1275, 1210, 759, 691 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{17}\text{NaNO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 314.0827, found 314.0828.



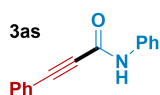
Colorless oil, 46.07 mg, 83% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.52 (d, $J = 6.9$ Hz, 2H), 7.39 (d, $J = 7.1$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 2H), 5.61 (s, 1H), 2.10 (s, 3H), 2.06 (s, 6H), 1.70 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 132.5, 129.9, 128.5, 120.5, 84.2, 53.3, 41.5, 36.3, 29.5. IR (in KBr) 3463, 3322, 3278, 3091, 3046, 2991, 2964, 2958, 2906, 2871, 2848, 2697, 2656, 2295, 2209, 1801, 1627, 1580, 1537, 1496, 1488, 1467, 1444, 1387, 1360, 1352, 1345, 1334, 1303, 1272, 1262, 1236, 1219, 1130, 1090, 1078, 1070, 1036, 1026, 1011, 994, 973, 959, 939, 908, 868, 814, 802, 788, 780, 762, 733, 692, 609, 599, 542, 532, 523, 515 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{22}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 280.1701, found 280.1697.



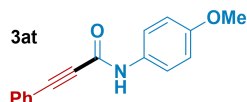
Colorless oil, 34.99 mg, 87% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.42 – 7.33 (m, 3H), 5.72 (s, 1H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 132.5, 130.0, 120.5, 84.1, 82.6, 52.5, 28.7. IR (in KBr) 3547, 3469, 3416, 2966, 2926, 2855, 2218, 1636, 1540, 1456, 1394, 1365, 1308, 1222, 966, 757, 690, 618, 529, 474, 458 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{16}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 202.1232, found 202.1230.



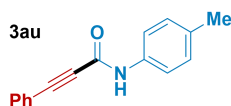
Yellow oil, 31.82 mg, 73% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.50 (m, 4H), 7.46 – 7.33 (m, 5H), 7.14 (t, $J = 7.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.1, 137.4, 132.7, 130.5, 129.3, 128.7, 125.1, 120.0, 85.8, 83.5. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{12}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 222.0919, found 222.0915.



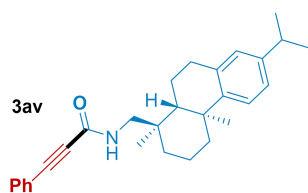
Yellow solid, 43.05 mg, 83% yield, M.P: 121.6-122.8 °C.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, $J = 7.0$ Hz, 2H), 7.49 – 7.37 (m, 6H), 6.89 (d, $J = 8.9$ Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.9, 151.0, 132.7, 130.46, 130.4, 128.7, 121.9, 120.1, 114.3, 85.6, 83.6, 55.5. IR (in KBr) 3450, 3276, 2208, 1630, 1546, 1509, 1488, 1455, 1443, 1412, 1306, 1279, 1248, 1181, 1171, 1035, 829, 796, 764, 724, 695, 639, 604, 574, 519 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{14}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 252.1025, found 252.1023.



White solid, 41.92 mg, 88% yield, M.P: 132.3-134.2 °C.

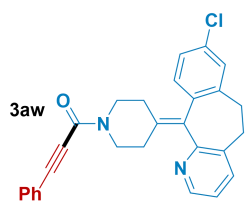
^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, $J = 6.8$ Hz, 2H), 7.52 (br, 1H), 7.49 – 7.31 (m, 5H), 7.16 (d, $J = 7.3$ Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 134.8, 132.7, 130.4, 129.7, 128.7, 120.1, 85.6, 83.5, 21.0. IR (in KBr) 3740, 3283, 2918, 2210, 1637, 1597, 1530, 1441, 1405, 1324, 1300, 1275, 1243, 1172, 1023, 959, 818, 755, 716, 689, 605, 511 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{14}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 236.1075, found 236.1073.



Colorless oil, 55.01 mg, 68% yield.

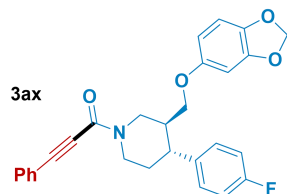
^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, $J = 7.4$ Hz, 2H), 7.40 (d, $J = 6.9$ Hz, 1H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.91 (s, 1H), 5.87 (t, $J = 6.2$ Hz, 1H), 3.36 (dd, $J = 13.8, 6.5$ Hz, 1H), 3.19 (dd, $J = 13.8, 6.8$ Hz, 1H), 2.97 – 2.79 (m, 4H), 2.31 (d, $J = 13.1$ Hz, 1H), 1.93 – 1.88 (m, 1H), 1.83 – 1.65 (m, 4H), 1.51 – 1.40 (m, 2H), 1.23 (s, 6H), 1.21 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.7, 147.1, 145.8, 134.9, 132.6, 130.1, 128.5, 127.1, 124.3, 124.0, 120.3, 85.0, 83.2, 50.1, 45.2, 38.3, 37.7, 37.5, 36.2, 33.5, 30.2, 25.4, 24.1, 19.1, 18.9, 18.7. IR (in KBr) 3269, 3059, 2958, 2927, 2867, 2220, 1631, 1545, 1496, 1443, 1382, 1299, 1215, 1174, 1069, 1026, 992, 911, 821, 756, 731, 689, 531 cm^{-1} . HRMS (ESI)

m/z calculated for C₂₉H₃₆NO⁺ ([M+H]⁺) 414.2797, found 414.2804.



Colorless oil, 67.27 mg, 77% yield.

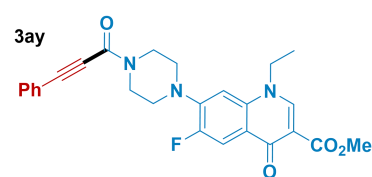
¹H NMR (400 MHz, Chloroform-d) δ 8.42 (t, *J* = 5.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.19 (s, 1H), 7.18 – 7.09 (m, 3H), 4.21 – 4.02 (m, 2H), 3.57 (tt, *J* = 11.9, 4.6 Hz, 1H), 3.46 – 3.23 (m, 3H), 2.85 (td, *J* = 17.1, 16.6, 6.0 Hz, 2H), 2.69 – 2.52 (m, 1H), 2.51 – 2.35 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.15 (d, *J* = 4.0 Hz), 146.9, 146.8, 139.65 (d, *J* = 14.9 Hz), 137.9, 137.7, 137.4, 135.1, 133.52 (d, *J* = 12.7 Hz), 133.3, 133.2, 132.5, 130.55 (d, *J* = 9.1 Hz), 130.1, 129.2, 129.1, 128.6, 126.40 (d, *J* = 9.8 Hz), 122.6, 120.6, 90.7, 81.3, 48.1, 48.1, 42.6, 42.5, 31.65, 31.3, 30.4, 30.2. IR (in KBr) 3417, 3050, 2982, 2908, 2213, 1894, 1764, 1621, 1584, 1488, 1435, 1362, 1322, 1281, 1199, 1175, 1107, 1073, 1027, 995, 920, 889, 870, 833, 792, 758, 728, 691, 640, 594, 564, 531, 484 cm⁻¹. HRMS (ESI) m/z calculated for C₂₈H₂₄ClN₂O⁺ ([M+H]⁺) 439.1577, found 439.1587.



White solid, 63.81 mg, 70% yield, M.P: 158.2-159.9 °C.

¹H NMR (400 MHz, Chloroform-d) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.10 (m, 2H), 7.06 – 6.94 (m, 2H), 6.68 – 6.58 (m, 1H), 6.36 (d, *J* = 17.6 Hz, 1H), 6.15 (t, *J* = 8.8 Hz, 1H), 5.88 (s, 2H), 4.97 – 4.84 (m, 1H), 4.78 (d, *J* = 13.2 Hz, 0.5H), 4.63 (d, *J* = 13.4 Hz, 0.5H), 3.68-3.64 (m, 1H), 3.54 – 3.47 (m, 1H), 3.31 – 3.19 (m, 1H), 2.98 – 2.71 (m, 2H), 2.23 – 2.13 (m, 0.5H), 2.07 – 1.70 (m, 2.5H). ¹³C NMR (100 MHz, CDCl₃) δ 163.0 (d, *J* = 4.9 Hz), 160.6 (d, *J* = 4.9 Hz), 154.2(d, *J* = 22.1 Hz), 153.2 (d, *J* = 2.8 Hz), 148.3 (d, *J* = 10.1 Hz), 141.9 (d, *J* = 5.6 Hz), 138.5 (d, *J* = 13.4 Hz), 132.5 (d, *J* = 8.7 Hz), 130.2 (d, *J* = 7.3 Hz), 128.9 (dd, *J* = 11.7, 7.9 Hz), 128.7, 120.6, 115.8 (dd, *J* = 21.2, 9.2 Hz), 108.0 (d, *J* = 3.4 Hz), 105.7, 105.5, 101.3 (d, *J* = 5.0 Hz), 98.1, 98.0, 90.8 (d, *J* = 5.2 Hz), 81.4 (d, *J* = 5.2 Hz), 68.6, 68.5, 50.7, 47.8, 44.7, 44.4, 43.9, 42.8, 42.1, 42.0, 34.4, 33.6. IR (in KBr) 3461, 2926, 2858, 2214, 1613, 1511, 1488, 1472, 1436, 1389, 1371, 1326, 1283, 1268, 1232, 1179, 1138, 1099, 1073, 1027, 964, 940, 835, 813, 783, 760, 726, 689, 652, 613, 585, 564, 543, 488 cm⁻¹. HRMS (ESI) m/z calculated for C₂₈H₂₅FN₂O⁺

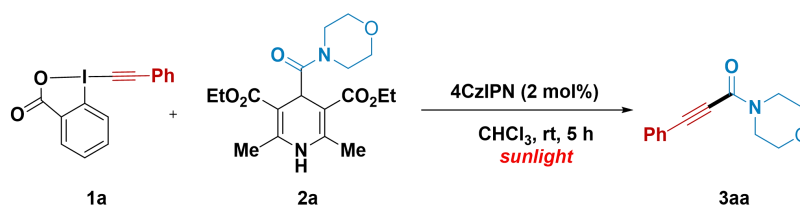
([M+H]⁺) 458.1768, found 458.1766. (Note: the target was obtained as a 1.2/1 mixture of rotamers).



White solid, 63.81 mg, 70% yield, M.P: 158.2-159.9 °C.

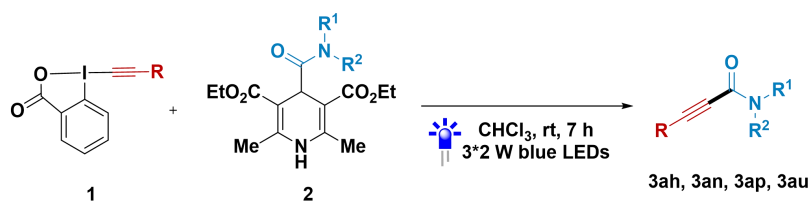
¹H NMR (400 MHz, Chloroform-d) δ 8.43 (s, 1H), 8.07 (d, *J* = 13.0 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.48 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 6.77 (d, *J* = 6.6 Hz, 1H), 4.22 (q, *J* = 6.1, 5.2 Hz, 2H), 4.10 – 4.16 (m, 2H), 3.91 (s, 5H), 3.33 (s, 2H), 3.25 (s, 2H), 1.54 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.0, 166.5, 153.2, 148.4, 144.29 (d, *J* = 11.1 Hz), 136.1, 132.5, 130.4, 128.7, 124.5, 124.5, 120.2, 113.92 (d, *J* = 21.2 Hz), 113.8, 110.3, 104.5, 91.4, 80.8, 52.2, 50.6, 50.63 (d, *J* = 4.0 Hz), 49.70 (d, *J* = 3.0 Hz), 49.1, 46.9, 41.4, 14.5. HRMS (ESI) *m/z* calculated for C₂₆H₂₅N₃O₄F⁺ ([M+H]⁺) 462.1829, found 462.1830.

4.2 Alkynylation of carbamoyl radicals irradiated by sunlight



To a dried Schlenk tube was treated with **1a** (0.30 mmol, 1.5 equiv), **2a** (0.2 mmol, 1.0 equiv), 4CzIPN (0.004 mmol, 2 mol%), and CHCl₃ (2.0 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting mixture was stirred and irradiated by sunlight at 25-32 °C for 5 h. After completion, the mixture was concentrated and purified by silica column chromatography using hexane/ethyl acetate (5:1 to 2:1) as eluent to afford the desired product **3aa** (36.14 mg, 84% yield).

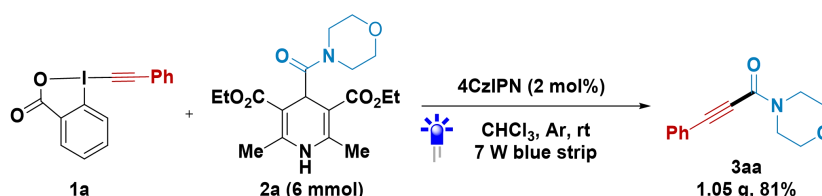
4.3 Alkynylation of carbamoyl radicals without photocatalyst



To a dried schlenk tube was treated with **1** (0.30 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), and CHCl₃ (2.0 mL, bubbled by Ar for 30 min) were added under Ar

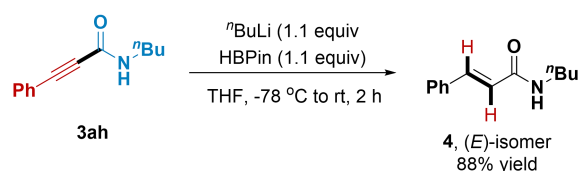
atmosphere. After that, this resulting mixture was stirred at a distance of ~2 cm under irradiation by 3*2 W blue LEDs at 25 °C for 7 h. After completion, the mixture was concentrated and purified by silica column chromatography using hexane/ethyl acetate or CH₂Cl₂/ MeOH as eluent, to afford the corresponding product **3**.

4.4 Gram-scale reaction

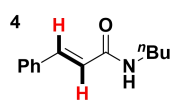


To a dried Schlenk tube was treated with **1a** (9.0 mmol, 1.5 equiv), **2a** (6.0 mmol, 1.0 equiv), 4CzIPN (0.12 mmol, 2 mol%), and CHCl₃ (40 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting mixture was stirred and irradiated by 7 W blue strip for 7 h and cooled by electric fan. After completion, the mixture was concentrated and purified by silica column chromatography using hexane/ethyl acetate (5:1 to 2:1) as eluent to afford the desired product **3aa** (1.05 g, 81% yield).

4.5 Semireduction of alkynyl amide



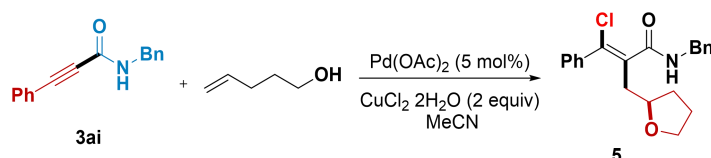
A dried 10 mL Schlenk tube was charged with **3ah** (0.3 mmol) and placed under Ar via Schlenk technique. THF was added (3.3 mL) and the reaction was stirred vigorously. The reaction was cooled to -78 °C over 15 minutes. *n*-BuLi (2.5M in hexanes, 0.33 mmol) was slowly added dropwise (~one drop every 3-4 seconds) then the reaction was equilibrated at -78 °C for 15 minutes. Pinacolborane (47.88 μL, 0.33 mmol) was then slowly added (~1 drop every 3-4 seconds). The reaction was warmed to room temperature by removing the cooling equipment and stirred for 2 h. Silica was added to quench the reaction mixture followed by concentration in vacuo. The crude mixture was then subjected to column chromatography to afford the product **4**.



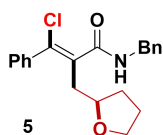
Colorless oil, 53.38 mg, 88% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.63 (d, $J = 15.6$ Hz, 1H), 7.49 – 7.46 (m, 2H), 7.33 – 7.31 (m, 3H), 6.47 (d, $J = 15.6$ Hz, 1H), 6.17 (s, 1H), 3.39 (q, $J = 7.0$ Hz, 2H), 1.60 – 1.52 (m, 2H), 1.43 – 1.33 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 140.6, 134.8, 129.5, 128.7, 127.7, 120.9, 39.5, 31.7, 20.1, 13.7. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{18}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 204.1388, found 204.1389.

4.6 General procedure for synthesis of tetrahydrofuran derivative



A mixture of alkynamide **3ai** (47.02 mg, 0.2 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), olefin (24.9 μL , 0.24 mmol), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (68.19 mg, 0.4 mmol) in CH_3CN (0.3 mL) was stirred at room temperature for 12 h. The mixture was extracted with ethyl acetate (3 \times 10 mL), and organic layer was dried by anhydrous MgSO_4 and concentrated in vacuum. The resulting residue was purified by flash silica gel chromatography to give the desired product **5**.

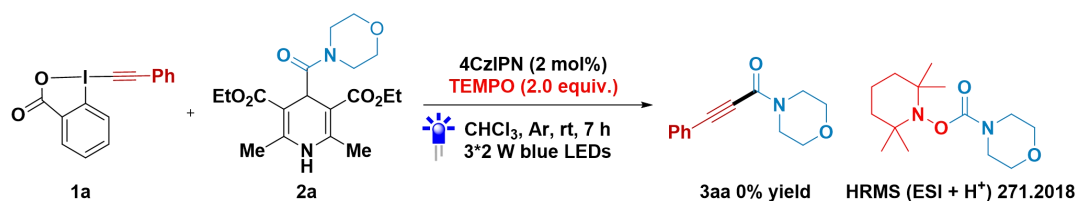


Colorless oil, 56.84 mg, 80% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.29 (m, 10H), 6.66 (s, 1H), 4.65 (dd, $J = 14.8, 5.8$ Hz, 1H), 4.56 (dd, $J = 14.8, 5.6$ Hz, 1H), 3.94 – 3.87 (m, 1H), 3.73 – 3.67 (m, 1H), 3.63 – 3.58 (m, 1H), 2.58 (dd, $J = 14.2, 3.7$ Hz, 1H), 2.38 (dd, $J = 14.2, 10.0$ Hz, 1H), 1.94 – 1.86 (m, 1H), 1.81 – 1.74 (m, 2H), 1.38 – 1.29 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 137.9, 137.3, 134.3, 130.4, 128.9, 128.8, 128.6, 128.4, 128.0, 127.5, 76.9, 67.7, 43.70, 37.9, 31.3, 25.5. The data is in accordance with the known work.³

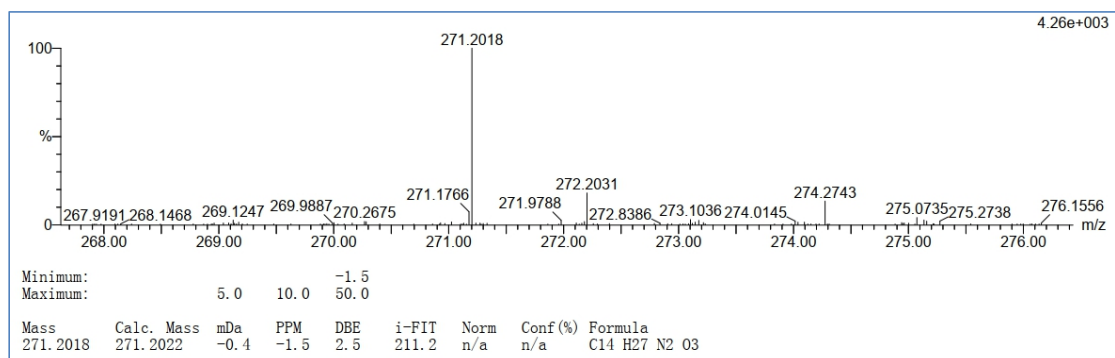
5. Mechanistic studies

5.1 Radical trapping experiment

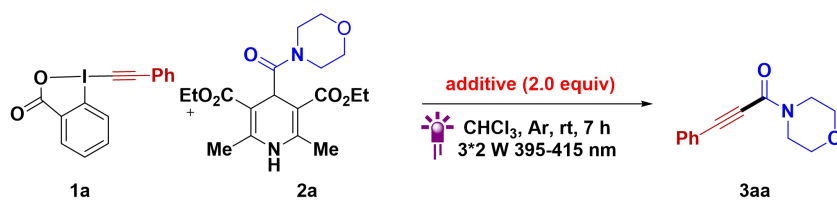


To a dried schlenk tube was treated with **1a** (0.30 mmol, 1.5 equiv), **2a** (0.2 mmol, 1.0 equiv), 4CzIPN (0.004 mmol, 2 mol%), TEMPO (0.4 mmol, 2.0 equiv) and CHCl₃ (2.0 mL, bubbled by Ar for 30 min) were added under Ar atmosphere. After that, this resulting mixture was stirred at a distance of ~2 cm under irradiation by 3*2 W blue LEDs at 25 °C for 7 h. After completion, this mixture was analyzed by ¹H NMR analysis using (Ph)₃CH as external standard.

This result showed no formation of product **3aa**, and indicated that this reaction involved a free radical intermediate. The TEMPO-adduct of carbamoyl radical was found through high-resolution data of the resulting mixture, verifying the generation of carbamoyl radical in this reaction.



5.2 Photoexcited alkylation of carbamoyl radical



Entry	Photocat.	Additive	Light source	Yield % ^b
1	4CzIPN	none	3*2 W blue LEDs	86
2	none	none	3*2 W purple LEDs	80
3	none	BI-OAc	3*2 W purple LEDs	82

^a Reaction conditions: **1a** (0.2 mmol), **2a** (x equiv), photocat. (2.0 mol%), in 2.0 mL of CHCl₃, at room

temperature, 7 h, under irradiation of 3*2 W LEDs. ^b Isolated yield. Note that purple LEDs are 395 - 415 nm light source.

To probe the direct photoexcited process, we used a 395 - 415 nm light source replaced with blue LEDs, and with or without an excess of BI-OAC in this reaction, both slightly decreasing yield of **3aa**, compared to the standard reaction condition to give 86% isolated yield.

5.3 The EDA complex verification experiment

5.3.1 UV/Vis absorption experiments

UV/Vis spectra of **1a**, **2a** and a mixture of **1a** and **2a** in CHCl₃ were performed, no obvious new peak was found.

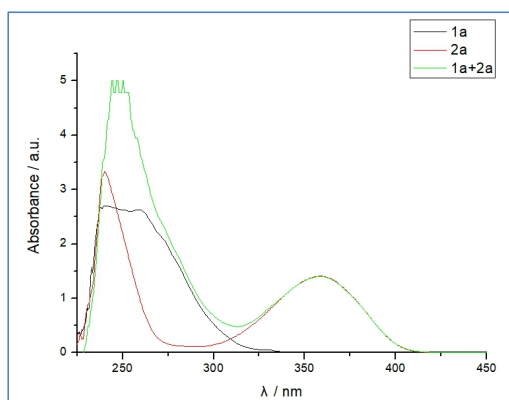
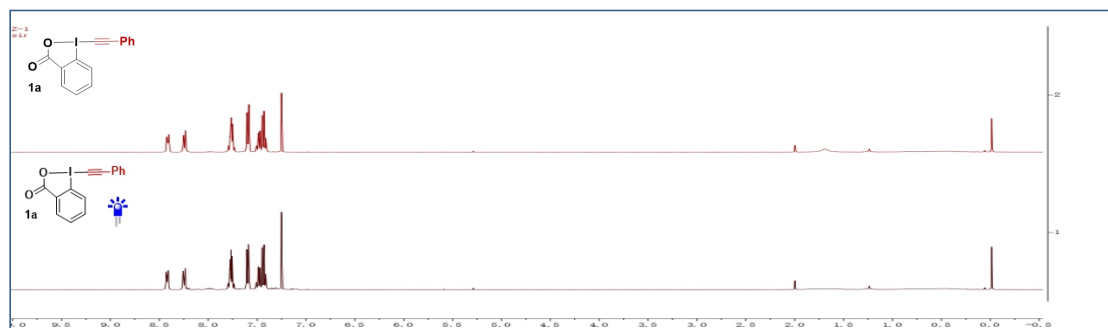


Figure S1. UV/vis absorption spectra of **1a**, **2a** and mixture

5.3.2 ¹H NMR experiments

¹H NMR spectra of **1a**, **2a**, and a mixture of **1a** and **2a** in CDCl₃ were recorded on a JEOLJNM-ECZ400S (400 MHz).



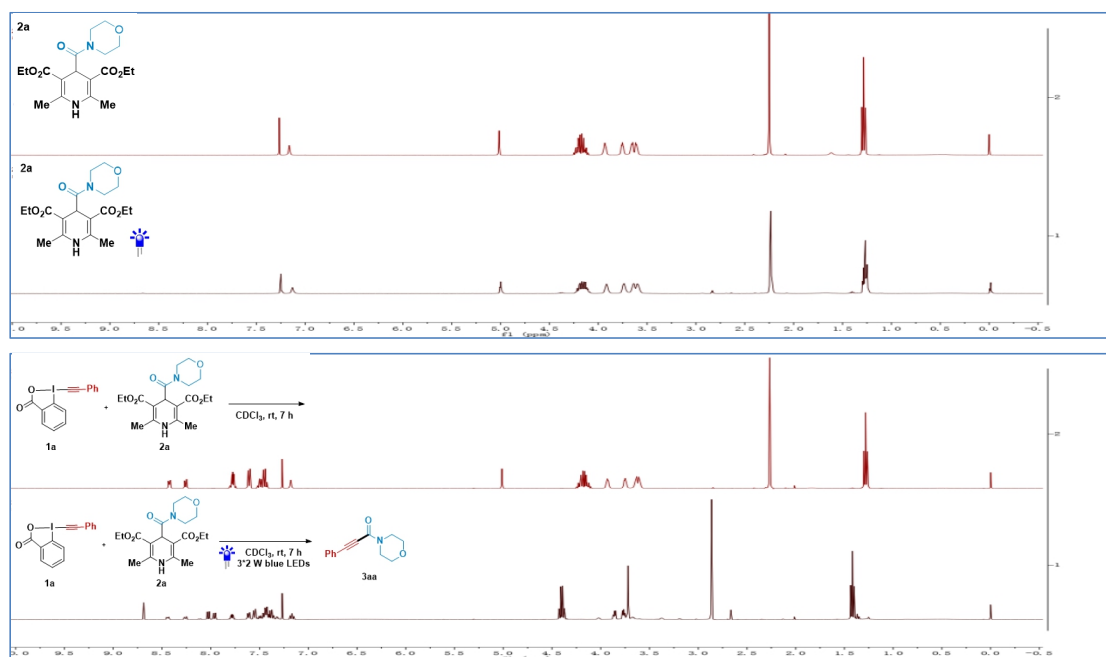


Figure S2. ^1H NMR spectra of **1a**, **2a** and mixture

While with or without irradiation by blue LEDs, ^1H NMR spectrum data of **1a**, **2a**, and a mixture of **1a** and **2a** in CDCl_3 , all were conducted. Whether or not irradiation, almost nothing were changed of **1a** and **2a**. However, while irradiating the mixture, they were completely transformed to **3aa**.

These results are in agreement with control experiments and UV/Vis spectra data, explaining that direct photo-induced this reaction can happen, and the formation of electron-donor-acceptor (EDA) complex between **1a** and **2a** was not observed.

5.4 Fluorescence quenching experiments and Stern-Volmer liner

we performed some fluorescence quenching experiments, including photocatalyst (4CzIPN) respectively quenched with **1a** and **2a**, and **2a** quenched with **1a**. Fluorescence measurements were acquired at room temperature using an MY15090002 Fluorescence Spectrophotometer. Emission quenching of the different samples were done using quartz cuvettes in CHCl_3 .

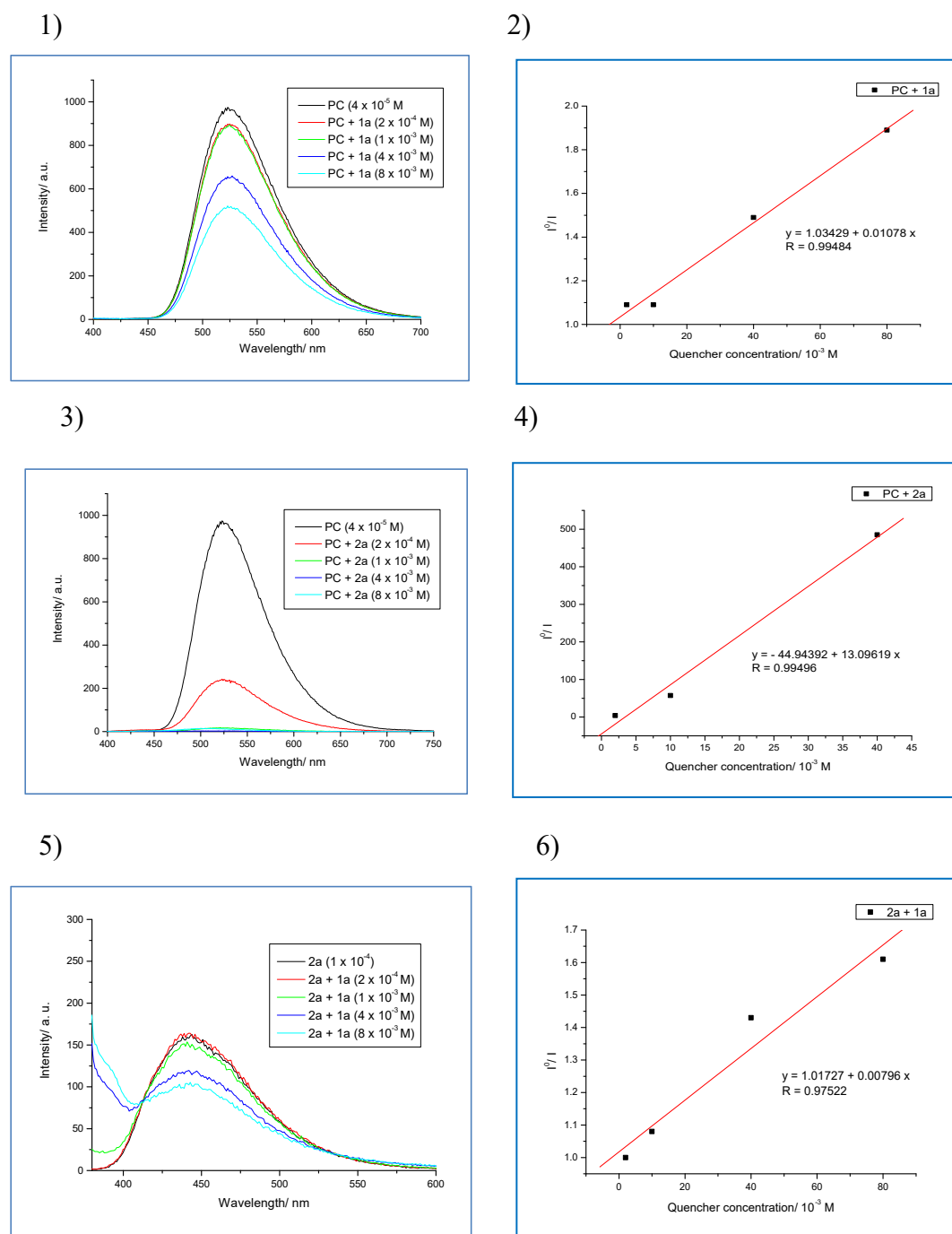


Figure S3. Stern-Volmer quenching studies of three systems. 1) Emission of a 4CzIPN (PC) solution recorded in presence of increasing amounts of **1a** as quencher with a $\lambda_{ex} = 360$ nm. 2) Stern-Volmer plot analysis of 4CzIPN solution quenched by **1a**; 3) Emission of a 4CzIPN (PC) solution recorded in presence of increasing amounts of **2a** as quencher with a $\lambda_{ex} = 360$ nm. 4) Stern-Volmer plot analysis of 4CzIPN solution quenched by **2a**; 5) Emission of **2a** solution recorded in presence of increasing amounts of **1a** as quencher with a $\lambda_{ex} = 365$ nm. 6) Stern-Volmer plot analysis of **2a** solution quenched by **1a**.

Fluorescence quenching experiments showed photocatalyst (4CzIPN) can be respectively quenched with **1a** and **2a**, and **2a** can be quenched with **1a**. But, in terms of the quenching efficiency, photocatalyst quenched with **2a** was more faster and easier.

5.5 Light on/off experiments

Following the general photocatalytic procedure for the reactions between **1a** and **2a** was performed on 0.1 mmol scale. Upon addition of all reagents, the reactions was irradiated alternating intervals of 1.5 h irradiation (light on) with 1.5 h dark (light off), during a total of 6 hours. Once 1.5 h, one reaction was analyzed by ¹H NMR analysis using (Ph)₃CH as external standard to obtain the corresponding yields.

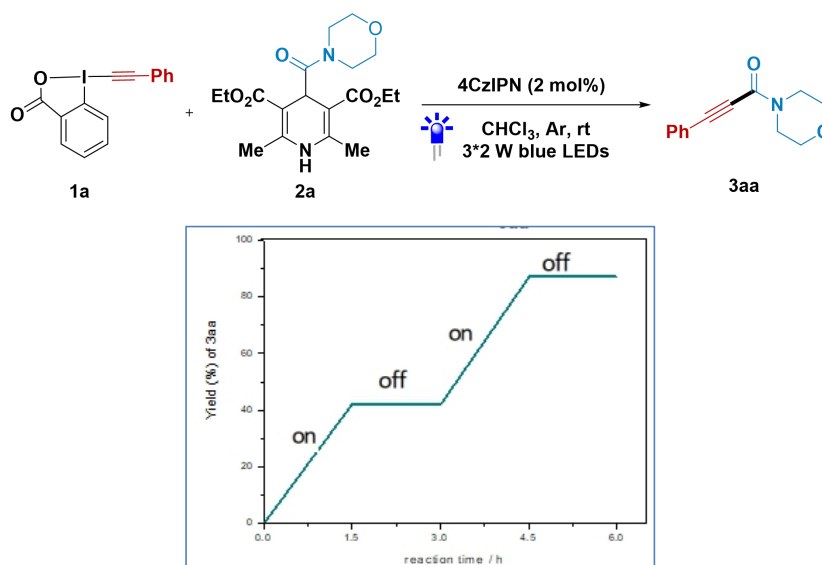


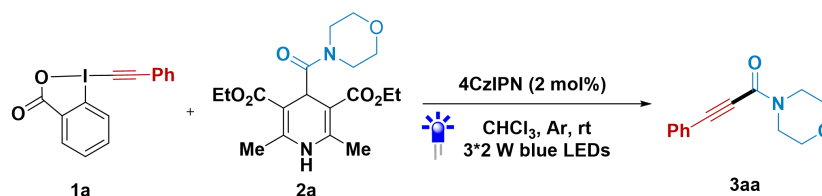
Figure S4. Light on/off experiments

As shown in the figure S4, the reaction proceeds only during the irradiation time, suggesting that this is a photoinduced reaction.

5.6 Measurement of quantum yield

Quantum yield measurement was performed in a standard spectro-cell containing a plastic plug which total volume was 4 mL and path-length was 1 cm. The cuvette was filled with the homogeneous solution which was prepared through the model reaction condition (containing substrate **1a** (0.30 mmol,), **2a** (0.20 mmol), CHCl₃ (2.0 mL) , and photocatalyst (4CzIPN) (0.004 mmol). The quantum efficiency was

measured by the irradiation of 456 nm laser light source, and calculated by using the equation: $\Phi = \text{Mole number for product} / \text{Mole number for absorption of photons}$, where the number of reaction molecular was obtained from ^1H NMR with triphenylmethane as the internal standard and the number of absorbed photons were calculated from the illumination power and absorbance of the reaction solution. The illumination power was measured using a digital photodiode power meter (Optical Power/Energy Meter/Model 842 PE). The amount of absorbed light was determined from reaction solution absorbance (abs) at the illuminated wavelength. Light intensity was measured before the model reaction solution was irradiated by 456 nm laser light, beginning and stopping the photoinduced reaction, which was 1.37 mW cm^{-2} , and irradiate time was set to 10800 s.



$\Phi = \text{Mole number for product} / \text{Mole number for absorption of photons}$

$$\Phi = \frac{n_{3aa} N_A / t}{f P \lambda / h c}$$

n_{3aa} : the mole number of the product **3aa**, $3.77 \times 10^{-5} \text{ mol}$ (18.8% yield); t : reaction time 10800 s; N_A : $6.02 \times 10^{23} \text{ mol}$; f : $1 - 10^{-A}$ (456 nm, $A = 8.4468$); P : $P = E * S$ (E : illumination intensity, $E = 1.37 \text{ mW cm}^{-2}$; S : the irradiated area, $S = 0.15 \text{ cm}^2$); λ : wavelength ($\lambda = 4.56 \times 10^{-7} \text{ m}$); h : planck constant ($h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$); c : velocity of light ($c = 3 \times 10^8 \text{ m/s}$).

we calculated the quantum yield of the model reaction of **1a** with **2a** to be 4.46. This result confirmed the occurrence of radical chain propagation process.

5.7 Possible mechanism

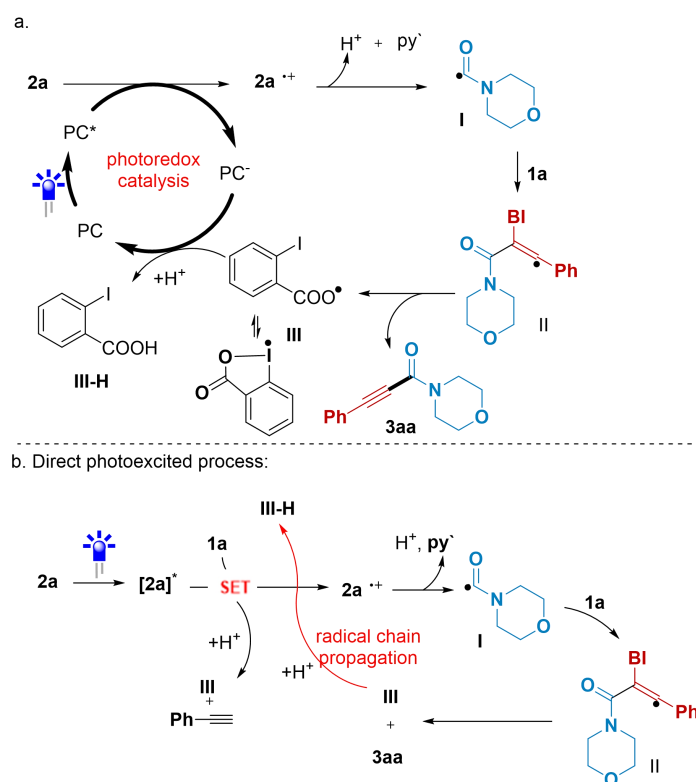


Figure S5. Proposed Mechanism

For the photoredox catalytic cyclic process, under irradiation by visible light, PC was excited to its excited state PC^* ($E_{1/2}(PC^*/PC^-) = +1.43$ V vs. SCE in CH_3CN)^[4]. Then, PC^* was reduced by **2a** ($E_{ox} = +1.17$ V vs. SCE)^[5] via single electron transfer to form PC^- and $2a^{\bullet+}$ species. This radical cation underwent homolytic cleavage of the C-C bond to release pyridine and intermediate **I**. A subsequent radical addition of this key nucleophilic carbamoyl radical to **1a** took place, releasing alkynyl amide **3aa**, along with intermediate **III**. In the end, a SET process between PC^- ($E_{1/2}(PC/PC^-) = -1.24$ V vs. SCE in CH_3CN) and **III** finished the photocatalytic cycle to next.

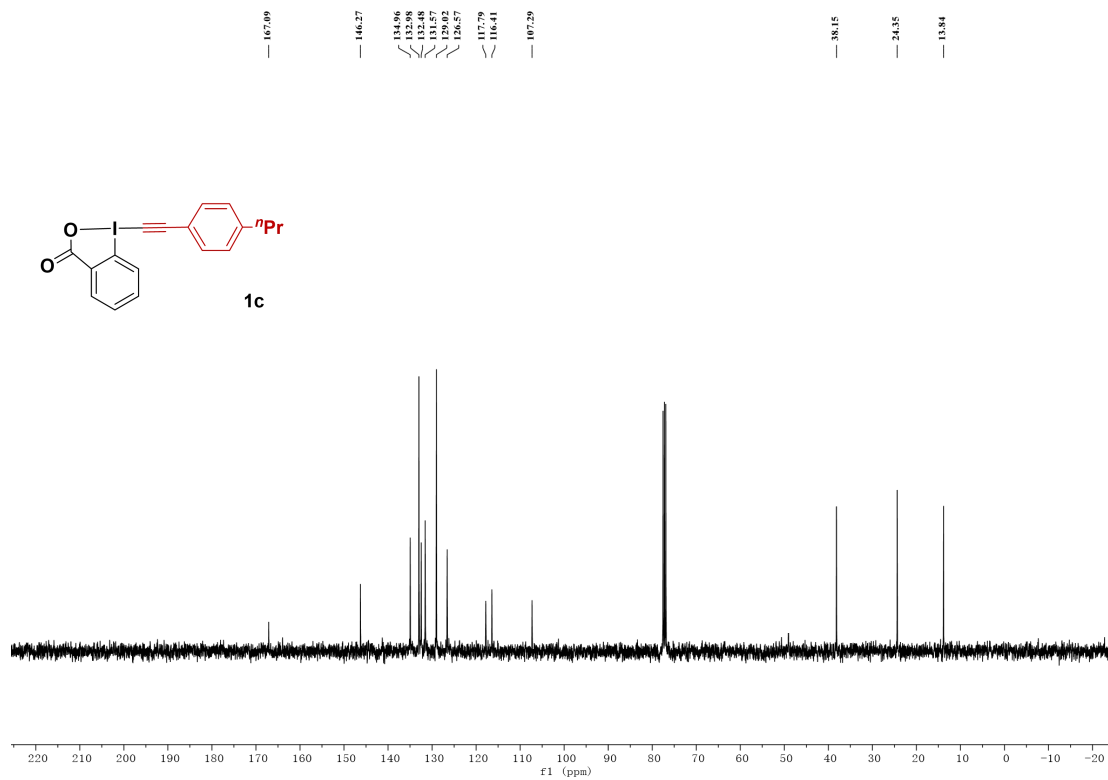
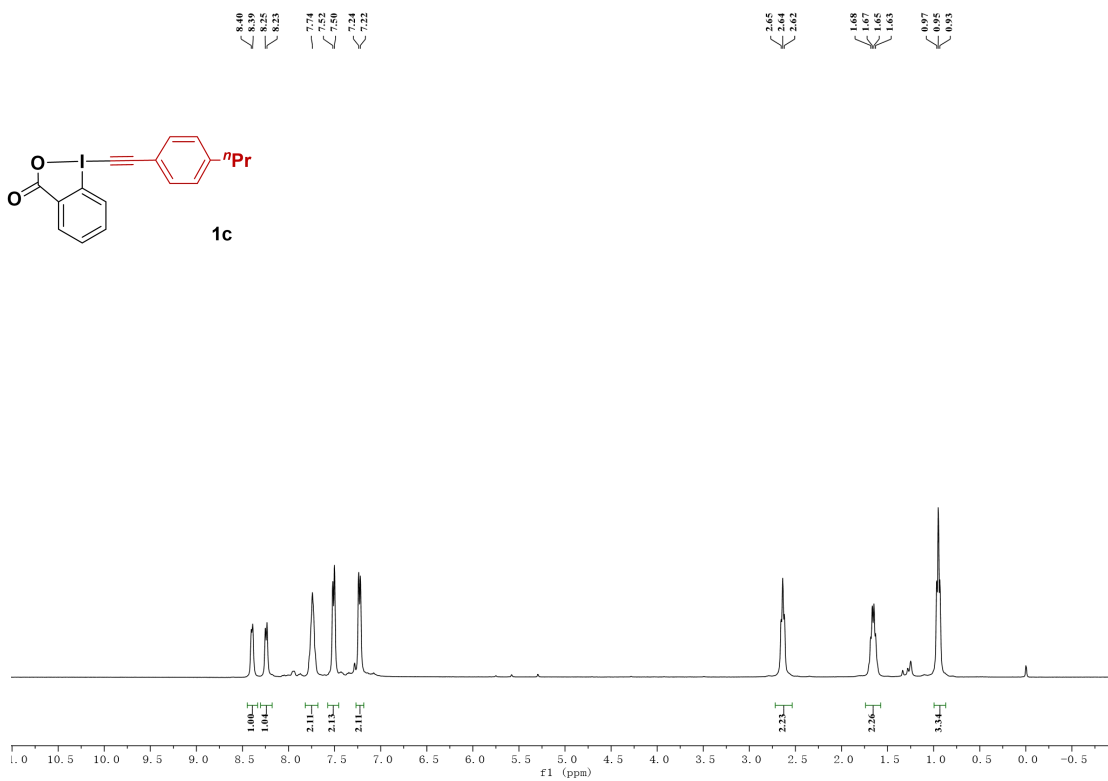
For another direct photoexcited process, upon irradiation by visible light, **2a** was directly excited to its excited state $2a^*$, which is a highly active species ($E_{ox}(2a^{\bullet+}/2a^*) = -1.9$ V vs. SCE)^[5]. A SET process of $2a^*$ with **1a** as oxidant ($E_{1/2}(1a/1a^{\bullet-}) = -0.87$ V vs SCE)^[6], delivering pyridine and intermediate **I**, which is thermodynamically favored.^[7] Then, a radical addition of **I** to **1a**

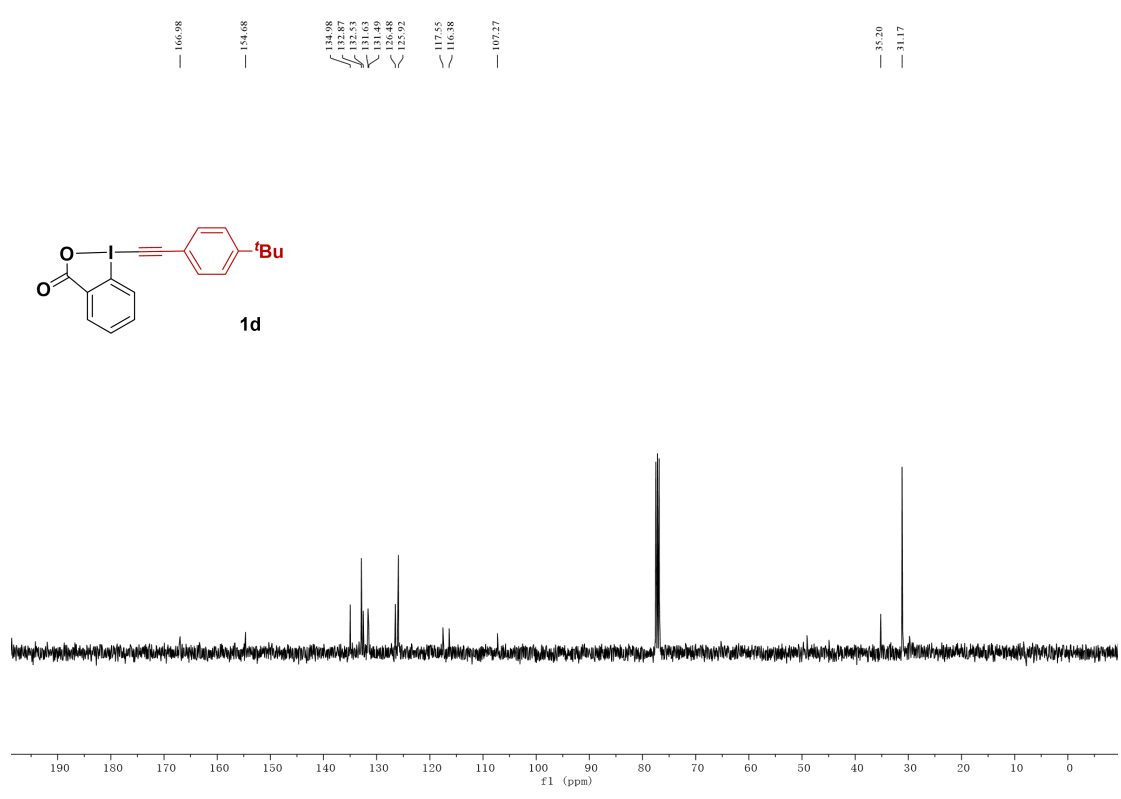
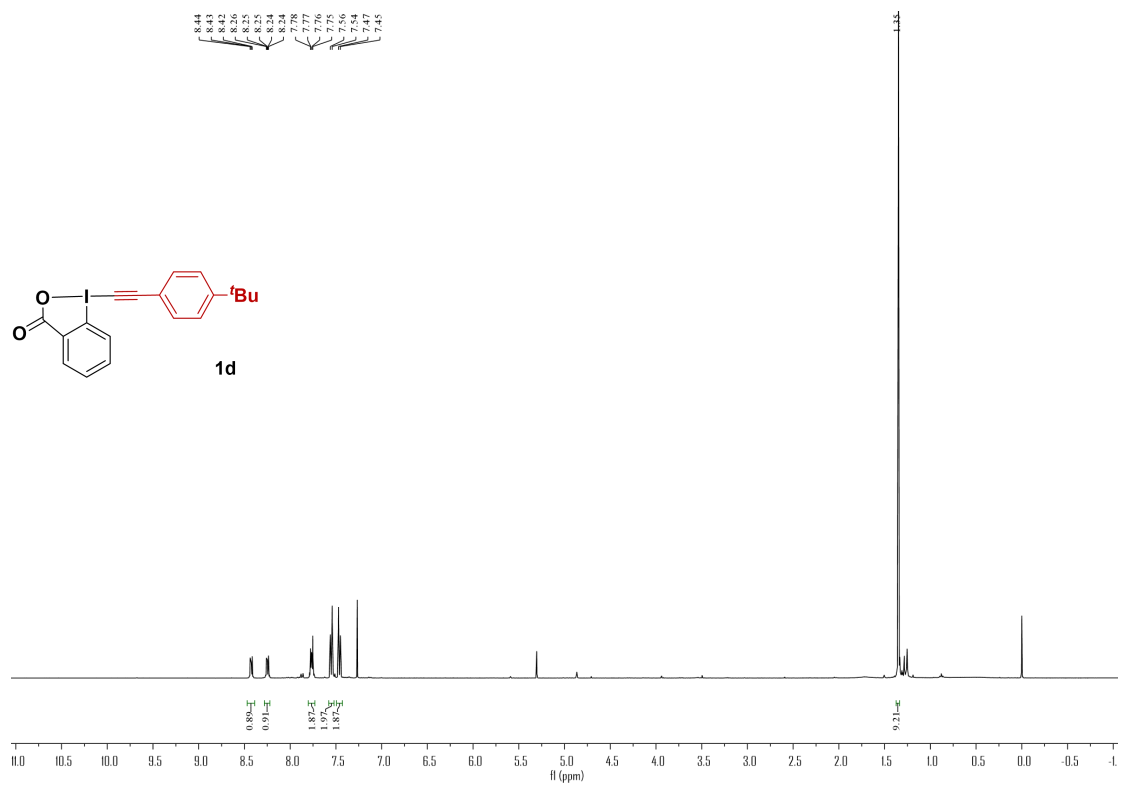
occurred, giving product **3aa** and **III**. Finally, intermediate **III** participates in the radical chain propagation process to promote the **2a*** to form radical **I**.

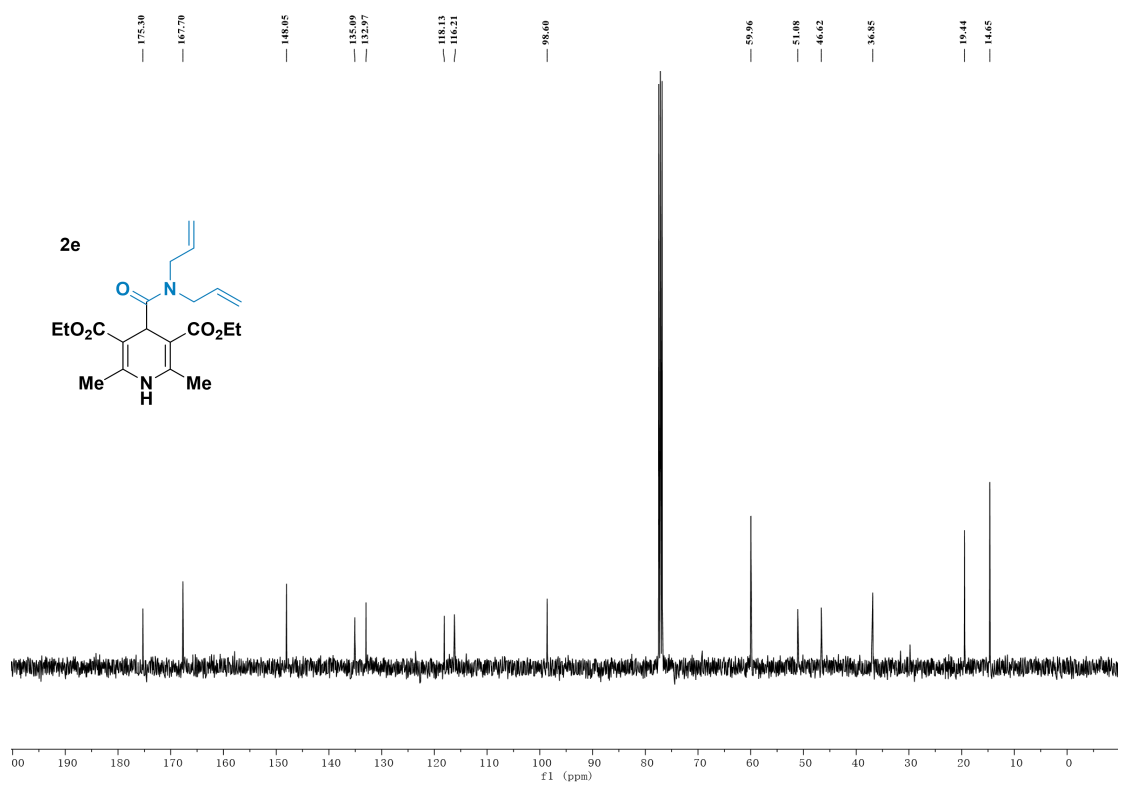
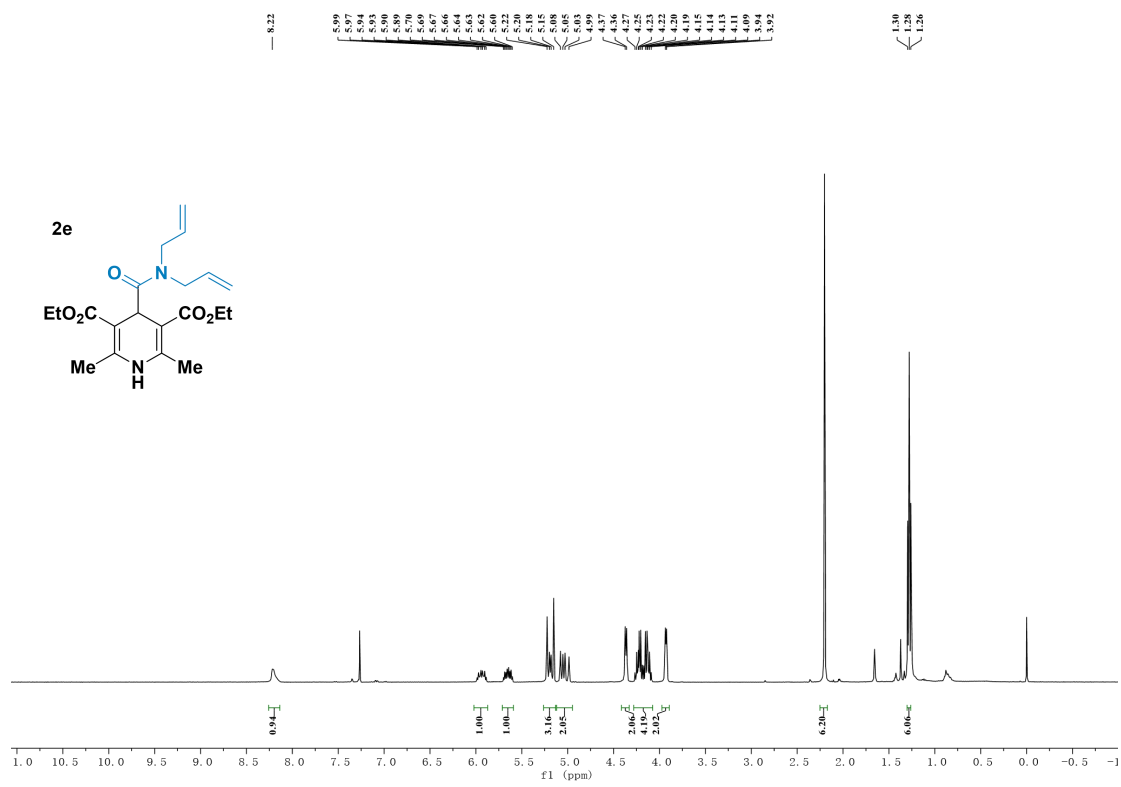
Reference:

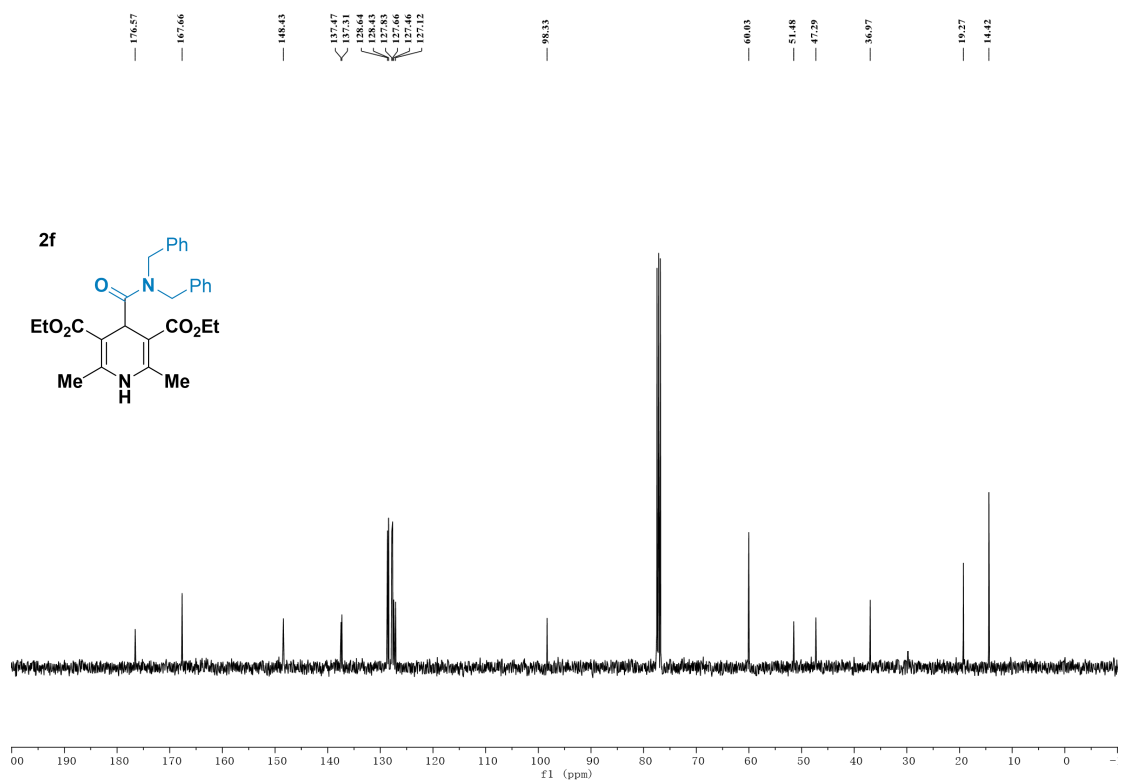
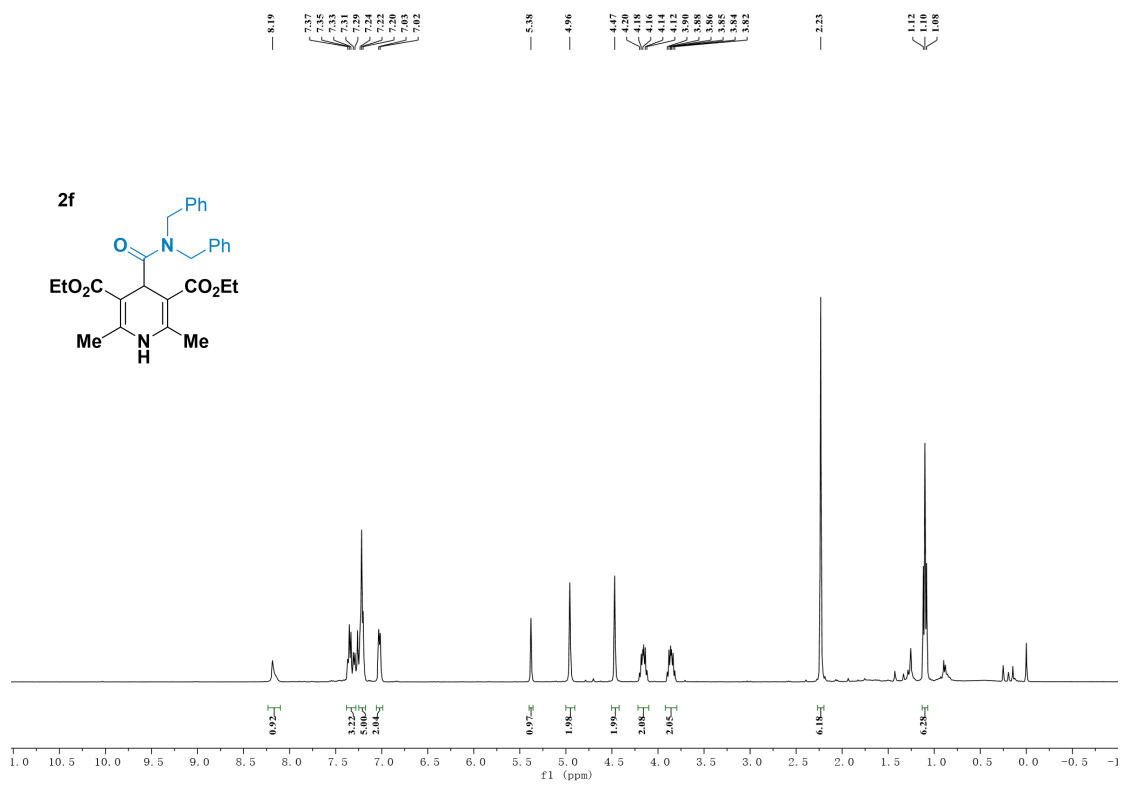
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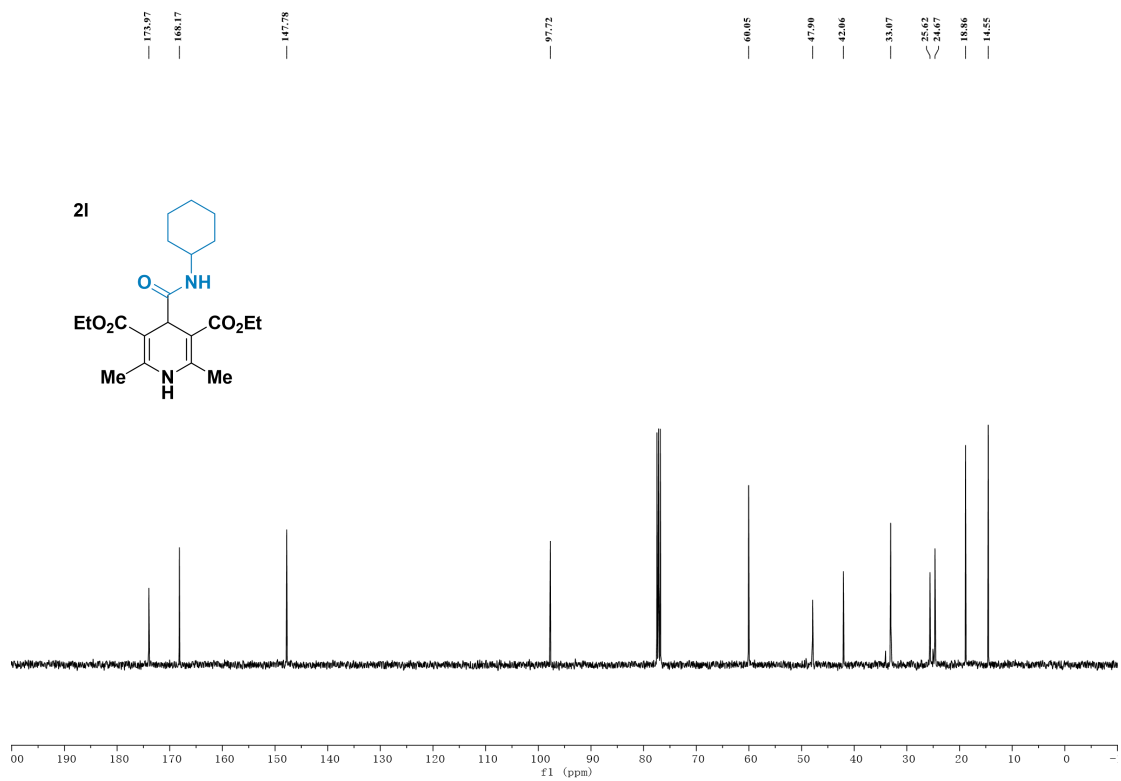
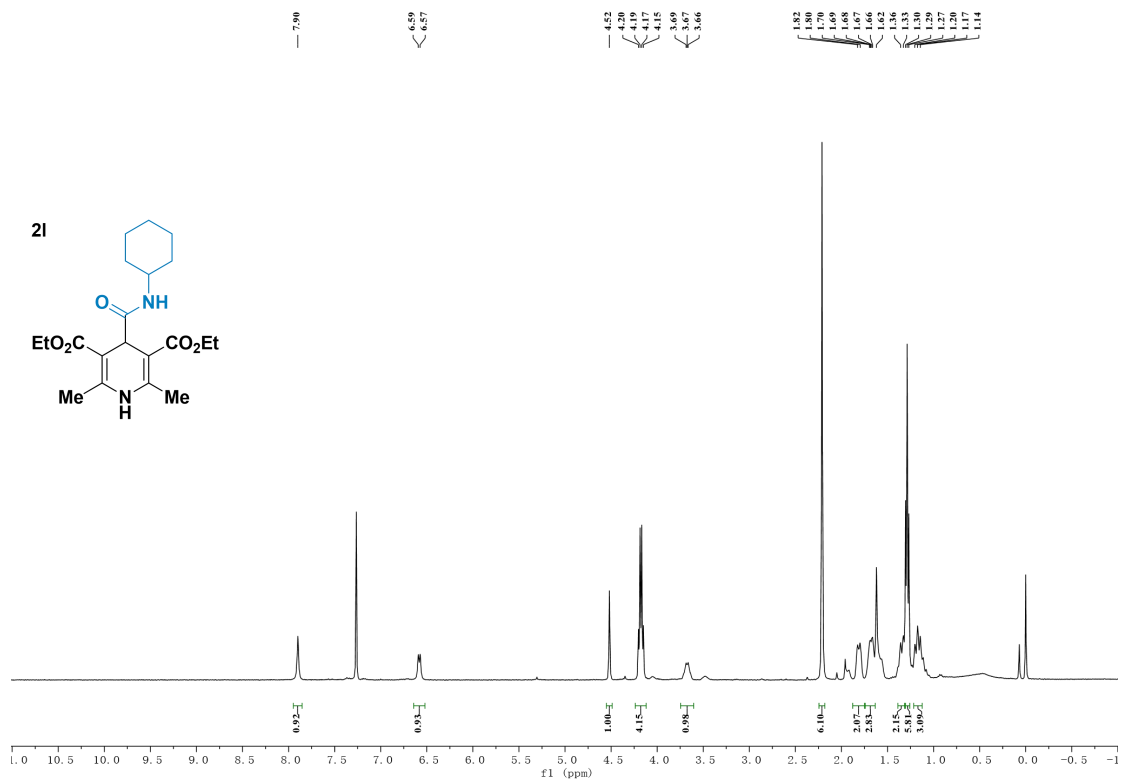
6. ^1H and ^{13}C NMR spectra for all new compounds

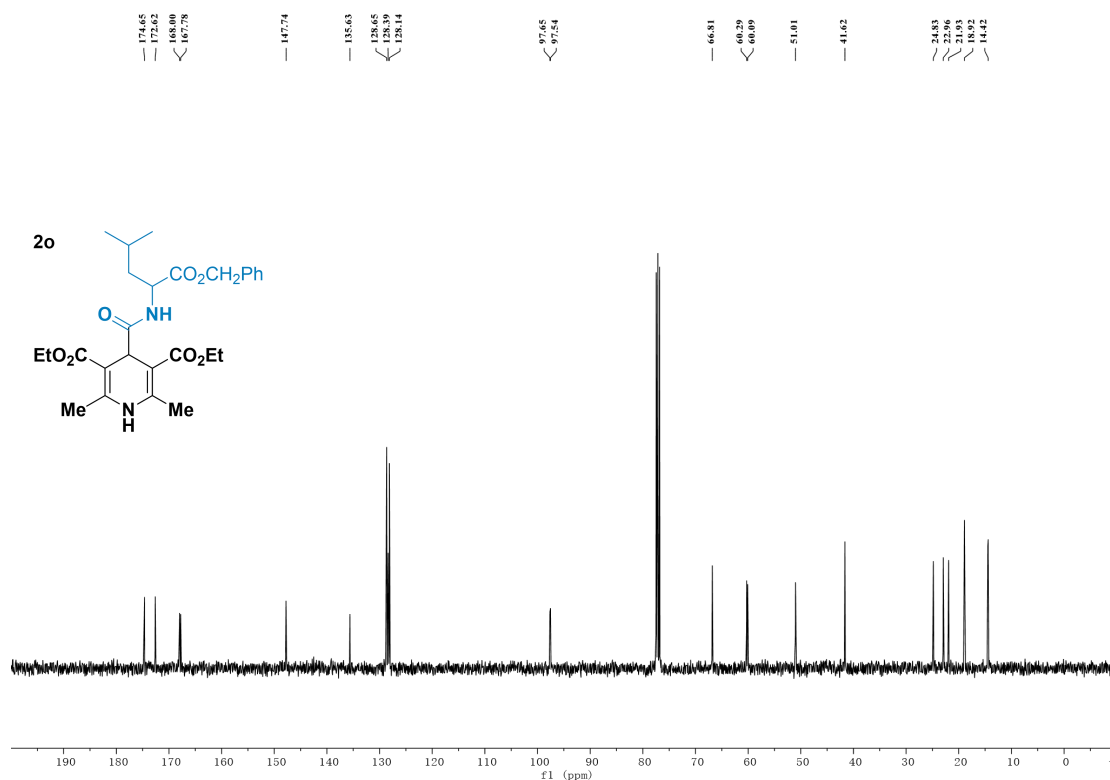
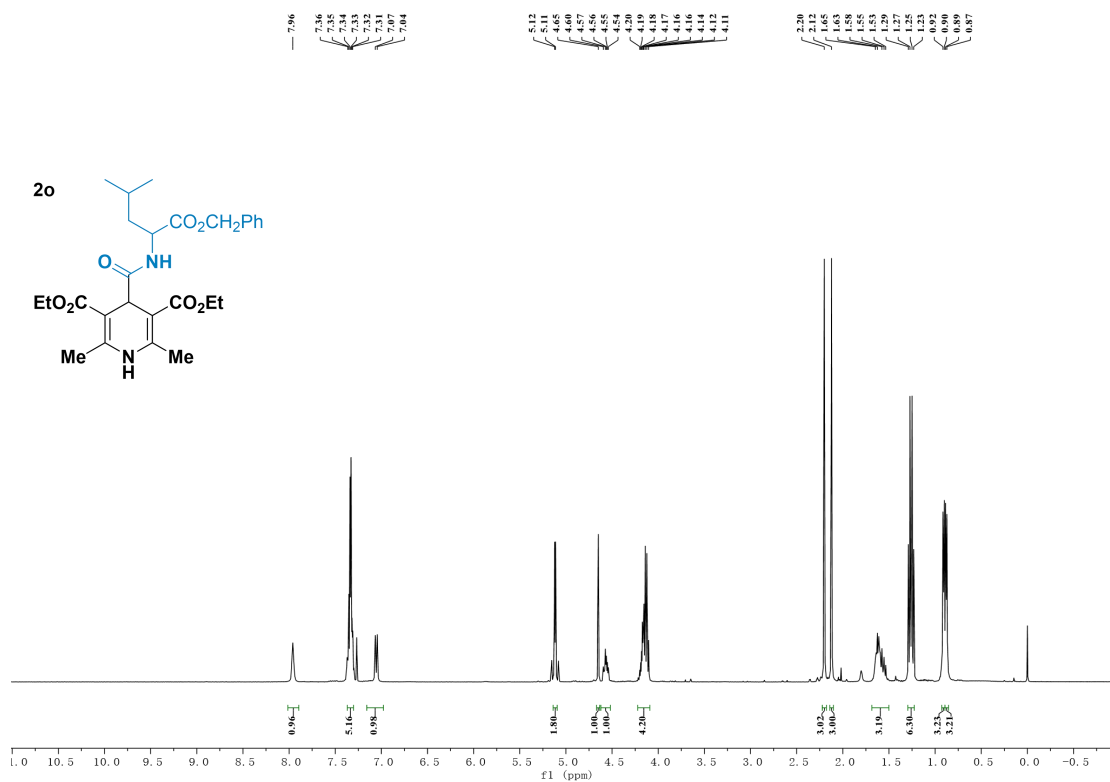


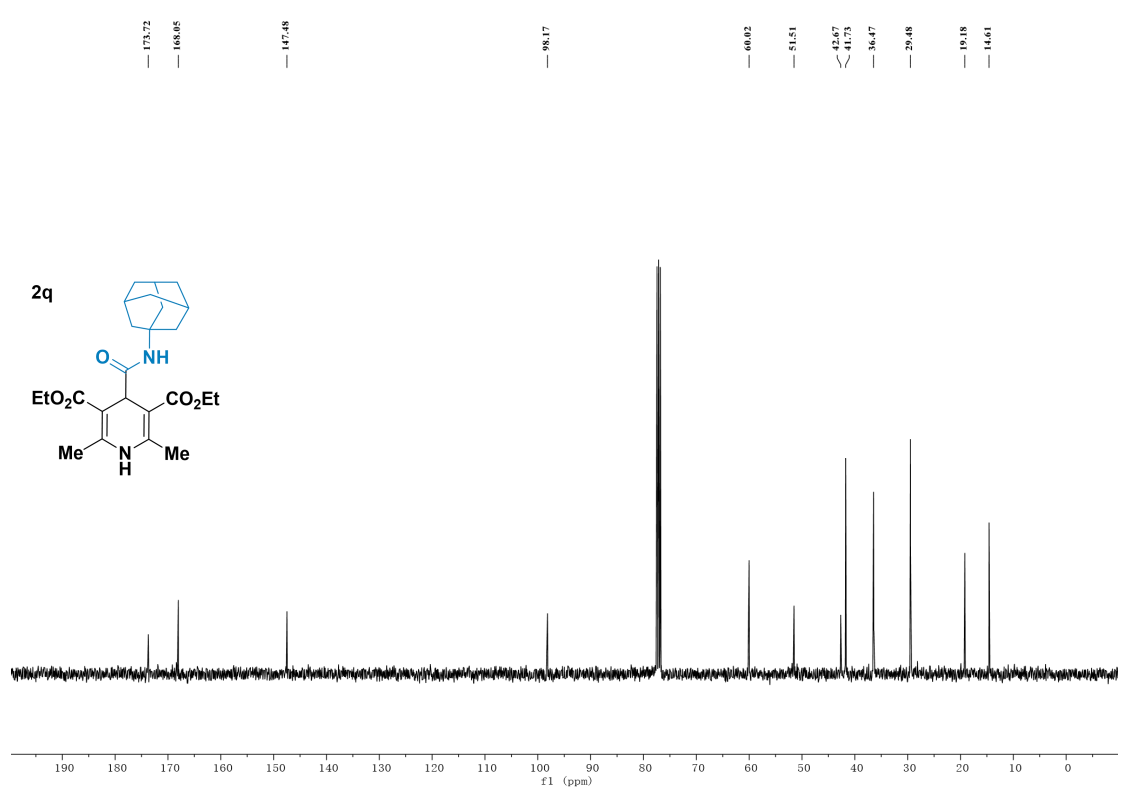
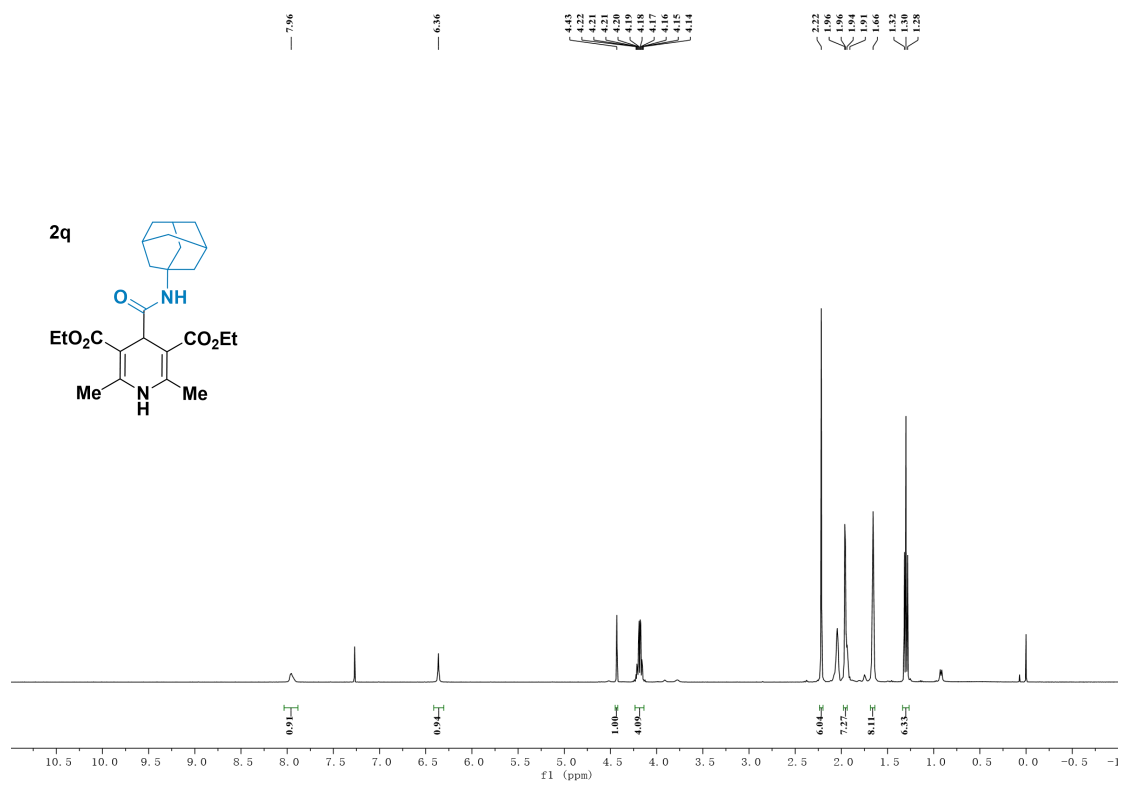


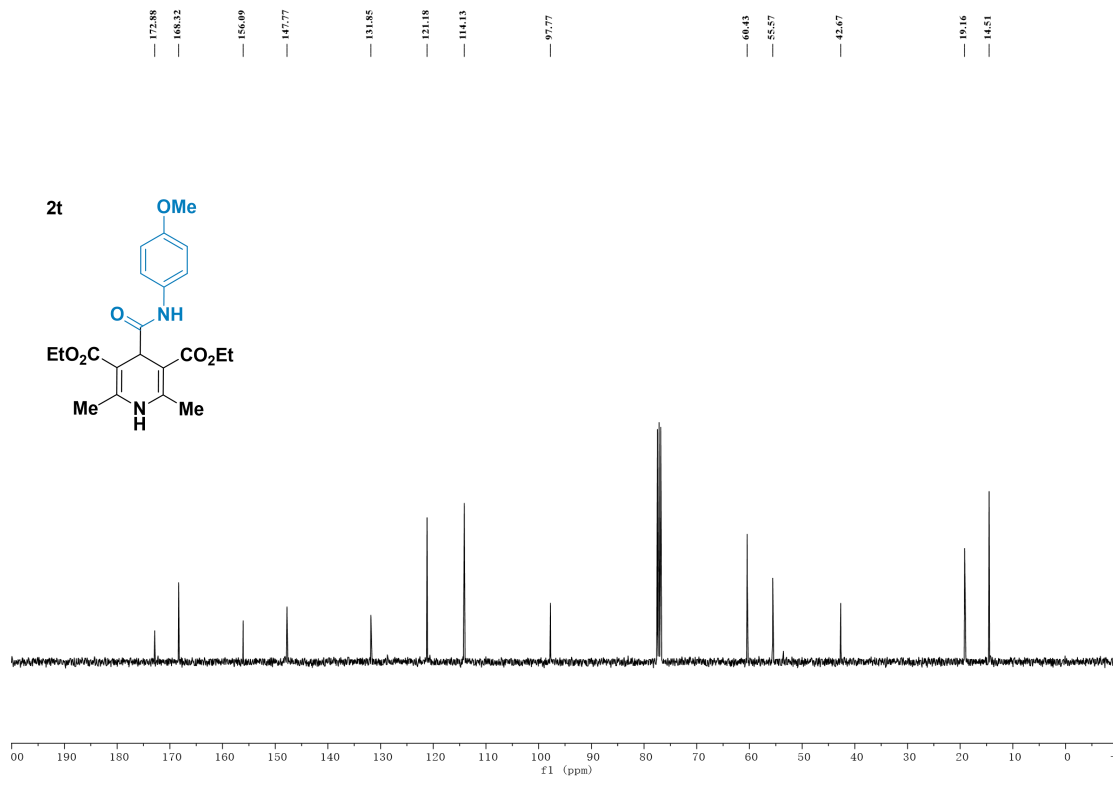
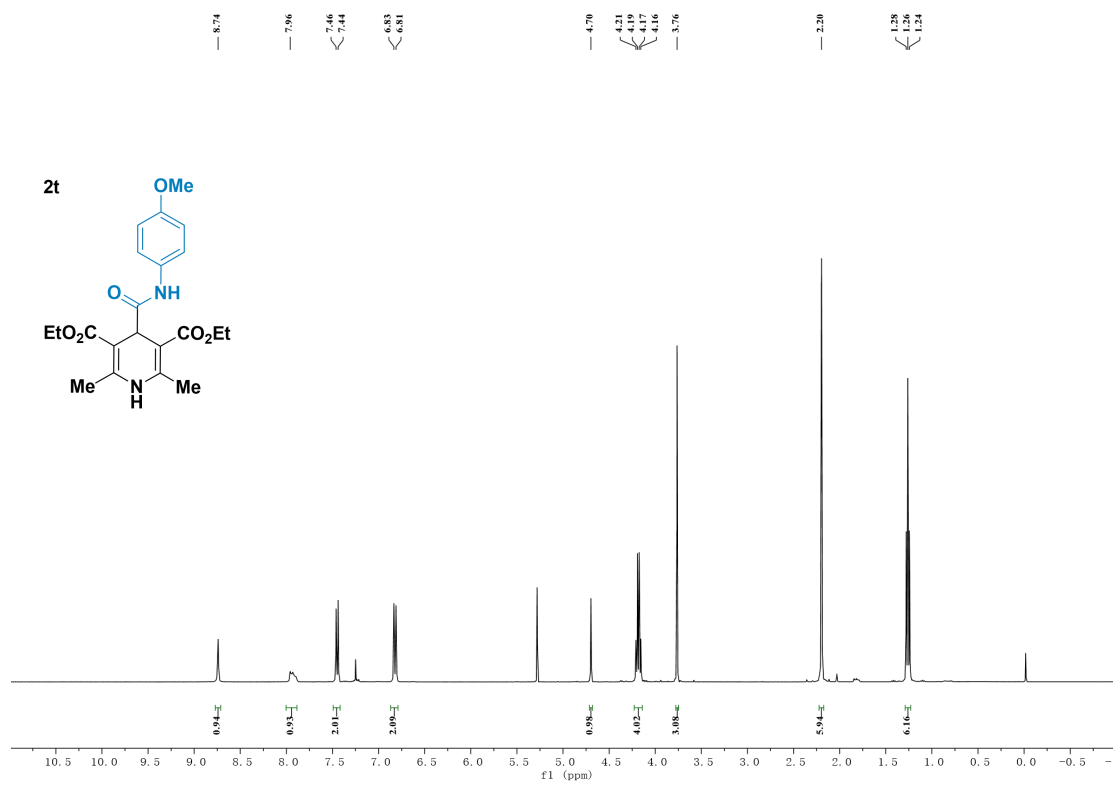


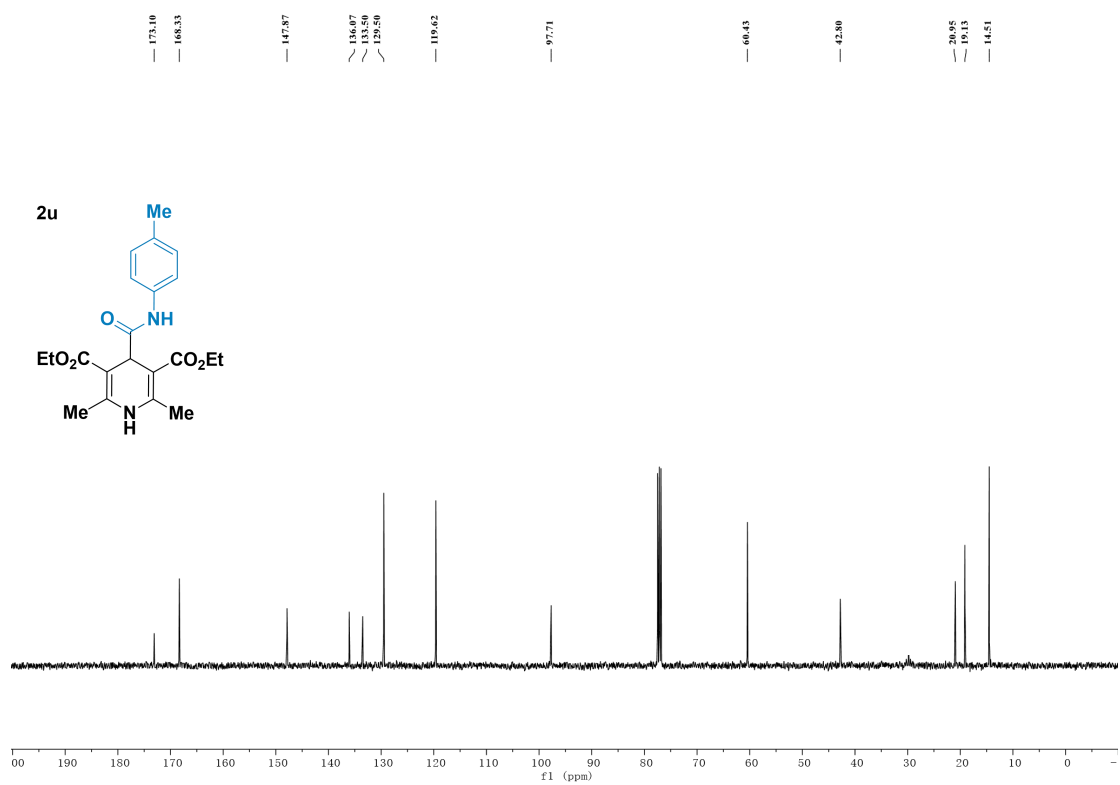
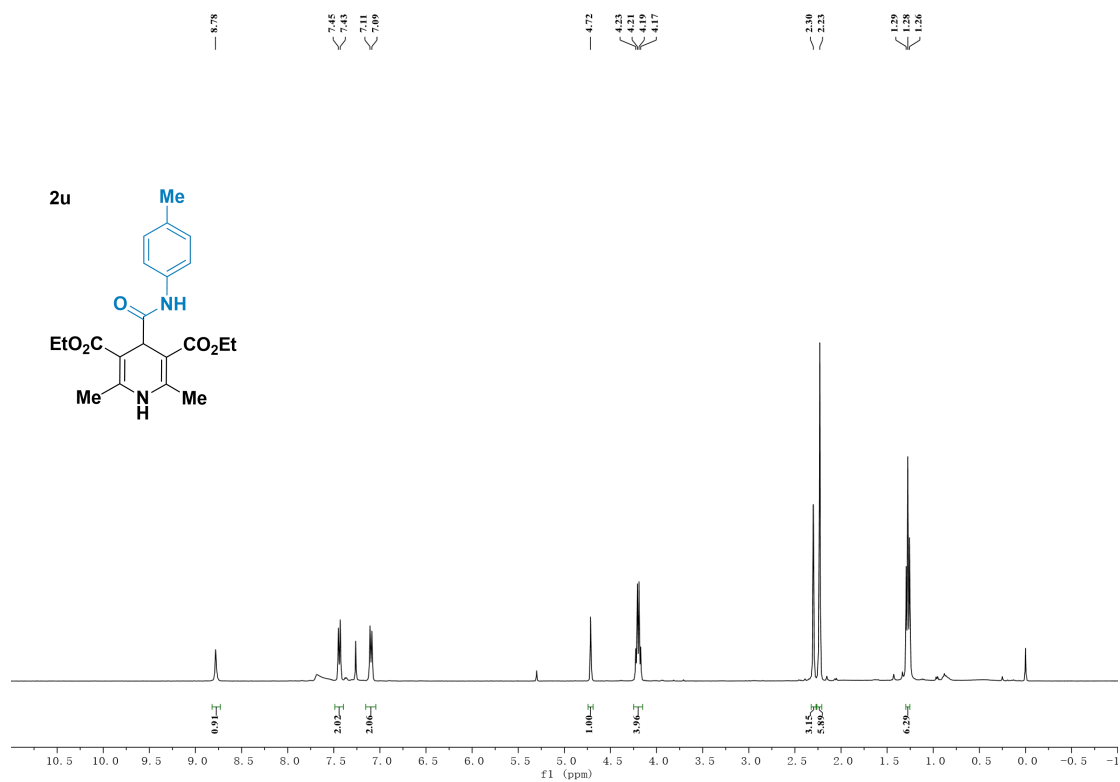




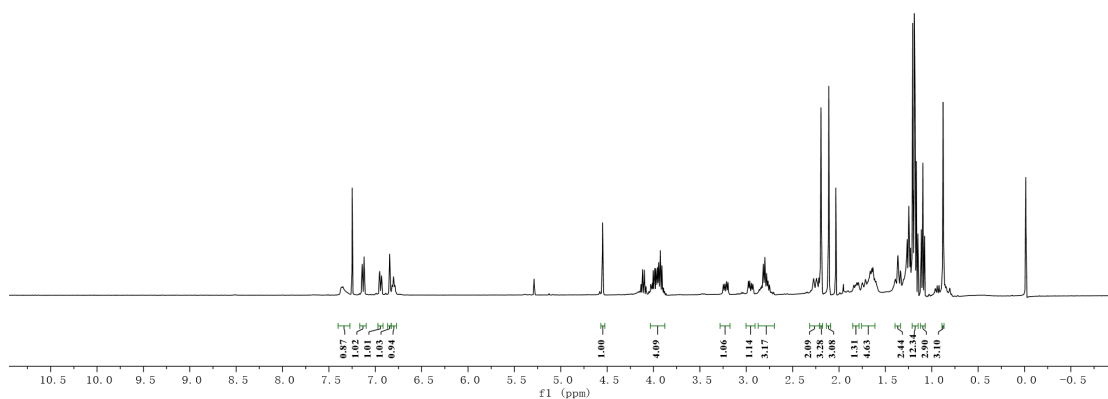
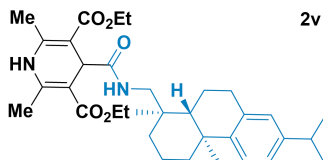








7.57
7.55
7.14
7.12
6.95
6.94
6.84
6.82
6.80
6.79
4.55
4.03
4.02
3.99
3.99
3.97
3.96
3.93
3.93
3.91
3.88
3.88
3.23
3.23
3.21
3.20
3.20
2.96
2.96
2.94
2.93
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2.86
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2.85
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2.78
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2.19
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1.15
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1.11
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1.00
1.00
0.88
0.88



174.82
168.20
147.50
147.44
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145.56
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126.88
125.86
123.80
98.07
60.15
49.94
45.04
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37.49
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30.85
25.43
24.13
19.11
19.06
18.06
14.09
14.00

