Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Copper-Catalyzed Tandem Annulation of 2-Alkynoyl-2'-iodo-1,1'-biphenyls with Isocyanoacetates: A Rapid Access to Pyrrole-Fused Tetracyclic Skeletons

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Supporting Information

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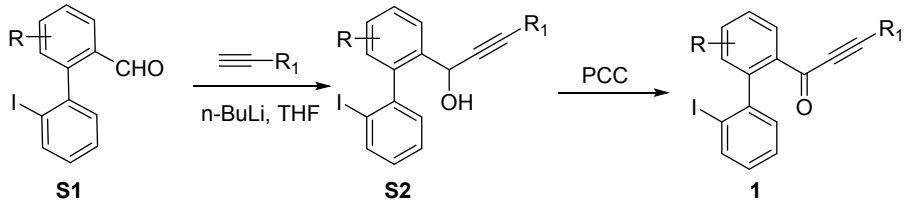
I. General Remarks

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 or 600 MHz spectrometer. Chemical shifts (δ) are given in relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$. Coupling constants, *J*, were reported in hertz unit (Hz). High resolution mass spectra (HRMS) were obtained on a Q-STAR Elite ESI-LC-MS/MS Spectrometer. Chemical names were generated using Cambridge Soft. ChemDraw Ultra 16.0. Commercially obtained reagents were used without further purification.

II. Synthesis of Substrates

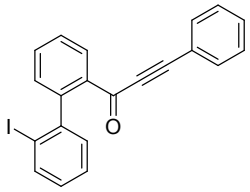
General Procedure for the synthesis of 1:



S1 **S2** **1**

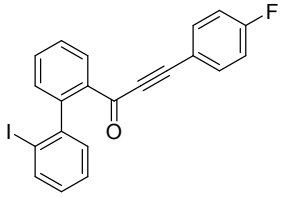
n-BuLi (2 mL, 2.5 M in hexane) was added dropwise to a solution of the terminal alkynes (5 mmol) in 5 mL of THF under argon at -78℃. The mixture was stirred for 30 minutes, then compound **S1**[1](4 mmol) was added. The mixture is slowly warmed to room temperature for 4 h and then quenched with NH_4Cl aqueous solution. The mixture was extracted with dichloromethane (10 mL × 3). The organic layer was combined, dried over Na_2SO_4, concentrated in vacumm to afford the crude product **S2**, which was dissolved in 20 mL DCM and PCC (1.72 g) with SiO_2 was added. The mixture was stirred overnight. After the reaction was completed, the mixture was filtered and the filtrate was concentrated and loaded on silica column to afford the title compound **1** and about 50%-80% yield.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (1a)



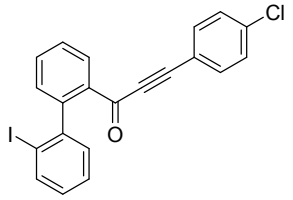
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.18 (m, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.64-7.57 (m, 1H), 7.56-7.48 (m, 1H), 7.50-7.45 (m, 2H), 7.44-7.32 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.02-6.98 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 178.6, 145.6, 144.7, 138.9, 136.4, 133.0, 132.5, 131.5, 130.8, 130.51, 129.9, 129.1, 128.4, 128.2, 128.0, 120.2, 99.3, 93.3, 88.3; ESI-MS *m/z* 409.0 $(M + H)^+$; HRMS calcd for $C_{21}H_{14}IO^+$ $(M + H)^+$ 409.0084, found 409.0087.

3-(4-fluorophenyl)-1-(2'-iodo-[1,1'-biphenyl]-2-yl)prop-2-yn-1-one (1b)



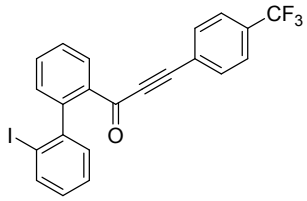
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.50-7.47 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.08-7.01 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.5, 163.8 (d, *J* = 252.0 Hz), 145.5, 144.7, 139.0, 136.4, 135.3 (d, *J* = 9.0 Hz), 132.6, 131.6, 130.7, 130.0, 129.2, 128.3, 128.1, 116.3 (d, *J* = 3.5 Hz), 116.0 (d, *J* = 22.2 Hz), 99.4, 92.3, 88.2; ESI-MS *m/z* 427.0 $(M + H)^+$; HRMS calcd for $C_{21}H_{13}FIO^+$ $(M + H)^+$ 426.9990, found 426.9993.

3-(4-chlorophenyl)-1-(2'-iodo-[1,1'-biphenyl]-2-yl)prop-2-yn-1-one (1c)



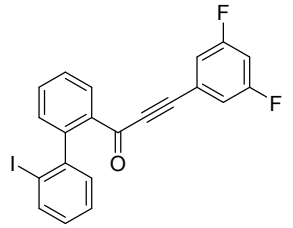
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20-8.18 (m, 1H), 7.91-7.89 (m, 1H), 7.67-7.64 (m, 1H), 7.60-7.57 (m, 1H), 7.43-7.38 (m, 3H), 7.36-7.32 (m, 2H), 7.31-7.26 (m, 2H), 7.04-7.01 (m, 1H); ^{13}C NMR (150 MHz, CDCl3) δ 178.4, 145.5, 144.7, 139.0, 136.8, 136.3, 134.2, 132.7, 131.6, 130.7, 130.0, 129.2, 128.9, 128.3, 128.1, 118.6, 99.4, 91.9, 89.0; ESI-MS *m/z* 443.0 $(M + H)^+$; HRMS calcd for $C_{21}H_{13}ClIO^+$ $(M + H)^+$ 442.9694, found 442.9690.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (1d)



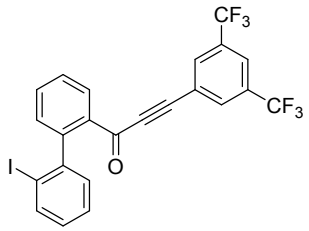
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 1H), 7.89-7.87 (m, 1H), 7.68-7.63 (m, 1H), 7.61-7.53 (m, 5H), 7.40-7.36 (m, 1H), 7.30-7.26 (m, 2H), 7.02-6.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 145.4, 144.8, 139.0, 136.1, 133.0, 132.8, 131.9 (q, *J* = 33.0 Hz), 131.6, 130.7, 130.1, 129.3, 128.3, 128.1, 125.4 (q, *J* = 4.0 Hz), 124.1, 123.6 (q, *J* = 271.0 Hz), 99.4, 90.8, 89.4; ESI-MS *m/z* 427.0 $(M + H)^+$; HRMS calcd for $C_{22}H_{13}F_3IO^+$ $(M + H)^+$ 476.9958, found 476.9953.

3-(3,5-difluorophenyl)-1-(2'-iodo-[1,1'-biphenyl]-2-yl)prop-2-yn-1-one (1e)



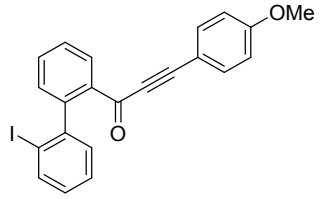
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.59-7.55 (m, 1H), 7.42-7.37 (m, 1H), 7.29-7.25 (m, 2H), 7.05-7.00 (m, 1H), 6.97-6.92 (m, 2H), 6.91-6.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 162.5 (dd, *J* = 248.8 Hz, 12.8 Hz), 145.1 (d, *J* = 52.4 Hz), 139.0, 136.0, 132.9, 131.7, 130.6, 130.1, 129.4, 128.4, 128.1, 122.9 (t, *J* = 11.0 Hz), 115.7 (d, *J* = 27.2 Hz), 115.6 (d, *J* = 11.5 Hz), 106.6 (t, *J* = 25.0 Hz), 99.4, 89.7, 88.9; ESI-MS *m/z* 445.0 $(M + H)^+$; HRMS calcd for $C_{21}H_{12}F_2IO^+$ $(M + H)^+$ 444.9895, found 444.9899.

3-(3,5-bis(trifluoromethyl)phenyl)-1-(2'-iodo-[1,1'-biphenyl]-2-yl)prop-2-yn-1-one (1f)



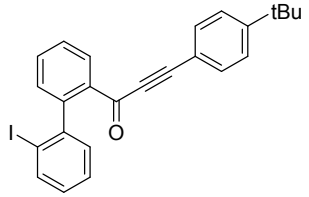
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.12 (m, 1H), 7.92-7.88 (m, 2H), 7.83 (s, 2H), 7.69-7.64 (m, 1H), 7.60-7.55 (m, 1H), 7.44-7.39 (m, 1H), 7.33-7.28 (m, 2H), 7.05-7.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 145.4, 144.9, 139.1, 135.9, 133.1, 132.6 (m), 132.1 (q, J = 34.0 Hz), 131.8, 130.4, 130.3, 129.5, 128.5, 128.2, 123.6 (q, J = 4.0 Hz), 122.7, 123.5 (m), 122.6 (q, J = 270.9 Hz), 99.6, 89.9, 88.6; ESI-MS *m/z* 545.0 $(M + H)^+$; HRMS calcd for $C_{23}H_{12}F_6IO^+$ $(M + H)^+$ 544.9832, found 544.9830.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1g)



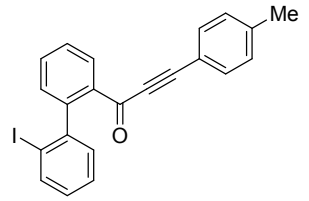
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 1H), 7.90-7.87 (m, 1H), 7.64-7.59 (m, 1H), 7.57-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.38-7.35 (m, 1H), 7.28-7.25 (m, 2H), 7.02-6.98 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.6, 161.5, 145.7, 144.5, 138.9, 136.7, 135.1, 132.3, 131.5, 130.7, 129.9, 129.0, 128.2, 128.0, 114.2, 112.0, 99.3, 94.5, 88.4, 55.4; ESI-MS *m/z* 439.0 $(M + H)^+$; HRMS calcd for $C_{22}H_{16}IO_2^+$ $(M + H)^+$ 439.0189, found 439.0193.

3-(4-(tert-butyl)phenyl)-1-(2'-iodo-[1,1'-biphenyl]-2-yl)prop-2-yn-1-one (1h)



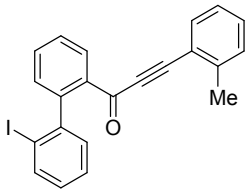
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (m, 1H), 7.91-7.89 (m, 1H), 7.65-7.60 (m, 1H), 7.58-7.53 (m, 1H), 7.44-7.35 (m, 5H), 7.29-7.25 (m, 2H), 7.04-6.99 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl3) δ 178.6, 154.3, 145.6, 144.6, 138.9, 136.6, 133.0, 132.4, 131.5, 130.8, 129.9, 129.1, 128.2, 128.0, 125.5, 117.1, 99.3, 94.0, 88.2, 35.1, 31.1; ESI-MS *m/z* 465.1 $(M + H)^+$; HRMS calcd for $C_{25}H_{22}IO^+$ $(M + H)^+$ 465.0710, found 465.0714.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(p-tolyl)prop-2-yn-1-one (1i)



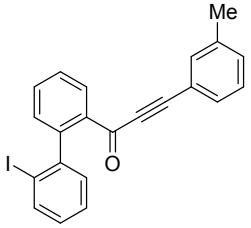
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.20 (m, 1H), 7.93-7.90 (m, 1H), 7.67-7.63 (m, 1H), 7.60-7.56 (m, 1H), 7.44-7.38 (m, 3H), 7.32-7.27 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05-7.00 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.6, 145.7, 144.6, 141.2, 138.9, 136.6, 133.1, 132.4, 131.5, 130.8, 129.9, 129.3, 129.1, 128.2, 128.0, 117.1, 99.3, 94.0, 88.2, 21.8; ESI-MS *m/z* 423.0 $(M + H)^+$; HRMS calcd for $C_{22}H_{16}IO^+$ $(M + H)^+$ 423.0240, found 423.0240.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(o-tolyl)prop-2-yn-1-one (1j)



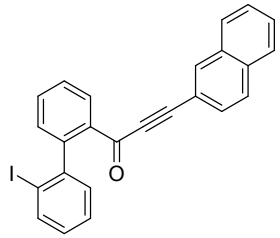
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.26 (m, 1H), 7.89-7.87 (m, 1H), 7.66-7.62 (m, 1H), 7.60-7.55 (m, 1H), 7.47-7.40 (m, 1H), 7.39-7.34 (m, 1H), 7.33-7.27 (m, 1H), 7.28-7.22 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.03-6.98 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.4, 145.8, 144.8, 142.2, 138.8, 136.3, 133.3, 132.5, 131.5, 131.2, 130.6, 129.8, 129.6, 128.9, 128.2, 128.0, 125.8, 120.1, 99.1, 92.2, 92.0, 20.8; ESI-MS *m/z* 423.0 $(M + H)^+$; HRMS calcd for $C_{22}H_{16}IO^+$ $(M + H)^+$ 423.0240, found 423.0243.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(m-tolyl)prop-2-yn-1-one (1k)



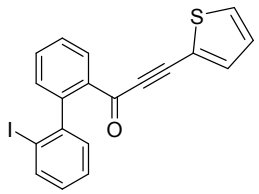
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.19 (m, 1H), 7.90-7.88 (m, 1H), 7.65-7.61 (m, 1H), 7.59-7.54 (m, 1H), 7.41-7.36 (m, 1H), 7.32-7.20 (m, 6H), 7.03-6.99 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.6, 145.7, 144.7, 138.9, 138.2, 136.5, 133.6, 132.5, 131.5, 131.5, 130.9, 130.2, 129.9, 129.1, 128.4, 128.2, 128.0, 120.0, 99.3, 93.7, 88.1, 21.2; ESI-MS *m/z* 423.0 $(M + H)^+$; HRMS calcd for $C_{22}H_{16}IO^+$ $(M + H)^+$ 423.0240, found 423.0244.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(naphthalen-2-yl)prop-2-yn-1-one (1l)



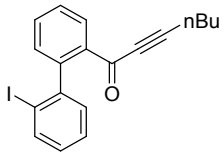
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.23 (m, 1H), 8.04 (s, 1H), 7.92-7.89 (m, 1H), 7.85-7.78 (m, 3H), 7.68-7.51 (m, 4H), 7.48-7.43 (m, 1H), 7.40-7.38 (m, 1H), 7.32-7.28 (m, 2H), 7.03-6.97 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 178.6, 145.6, 144.7, 139.0, 136.6, 134.3, 133.8, 132.6, 132.5, 131.6, 130.8, 130.0, 129.2, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.0, 117.4, 99.4, 93.9, 88.6; ESI-MS *m/z* 459.0 $(M + H)^+$; HRMS calcd for $C_{25}H_{16}IO^+$ $(M + H)^+$ 459.0240, found 459.0241.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)-3-(thiophen-2-yl)prop-2-yn-1-one (1m)



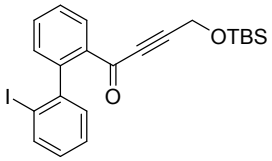
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 1H), 7.93-7.90 (m, 1H), 7.65-7.60 (m, 1H), 7.57-7.53 (m, 1H), 7.45-7.39 (m, 1H), 7.42-7.36 (m, 2H), 7.28-7.26 (m, 2H), 7.06-6.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 178.2, 145.4, 144.7, 139.1, 137.0, 136.4, 132.5, 131.6, 131.5, 130.4, 130.1, 129.3, 128.3, 128.1, 127.6, 119.9, 99.4, 93.1, 87.5; ESI-MS *m/z* 415.0 $(M + H)^+$; HRMS calcd for $C_{19}H_{12}IOS^+$ $(M + H)^+$ 414.9648, found 414.9651.

1-(2'-iodo-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1n)



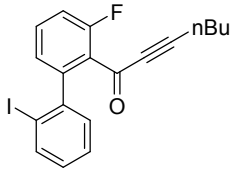
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.08 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.61-7.57 (m, 1H), 7.54-7.49 (m, 1H), 7.40-7.36 (m, 1H), 7.22-7.20 (m, 2H), 7.06-7.01 (m, 1H), 2.22 (t, *J* = 6.8 Hz, 2H), 1.48-1.42 (m 2H), 1.39-1.33 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.7, 145.9, 144.6, 138.7, 136.5, 132.2, 131.4, 130.7, 129.8, 128.9, 128.1, 127.9, 99.3, 97.5, 81.0, 29.7, 22.0, 19.0, 13.5; ESI-MS *m/z* 389.0 $(M + H)^+$; HRMS calcd for $C_{19}H_{18}IO^+$ $(M + H)^+$ 389.0397, found 389.0401.

4-((tert-butyldimethylsilyl)oxy)-1-(2'-iodo-[1,1'-biphenyl]-2-yl)but-2-yn-1-one (1o)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.16 (m, 1H), 7.91-7.88 (m, 1H), 7.63-7.59 (m, 1H), 7.55-7.50 (m, 1H), 7.41-7.36 (m, 1H), 7.23-7.20 (m, 2H), 7.07-7.02 (m, 1H), 4.44-4.31 (m, 2H), 0.93 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 177.6, 145.8, 144.8, 138.7, 135.7, 132.8, 131.4, 131.3, 129.6, 129.0, 128.2, 128.0, 99.2, 92.9, 83.8, 51.7, 25.8, 18.3, -5.0, -5.1; ESI-MS *m/z* 477.1 $(M + H)^+$; HRMS calcd for $C_{22}H_{26}IO_2Si^+$ $(M + H)^+$ 477.0741, found 477.0746.

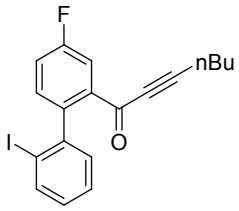
1-(3-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1p)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 1H), 7.49-7.43 (m, 1H), 7.37-7.33 (m, 1H), 7.20-7.14 (m, 2H), 7.06-7.02 (m, 2H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.44-1.38 (m, 2H), 1.35-1.25 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 159.8 (d, *J* = 254.0 Hz), 144.6, 143.5, 143.4,

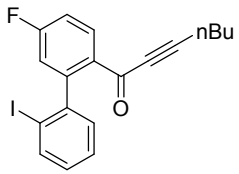
139.1, 131.6 (d, J = 9.2 Hz), 130.7, 129.5, 128.0, 127.7 (d, J = 13.0 Hz), 126.8 (d, J = 4.0 Hz), 115.9 (d, J = 22.0 Hz), 99.1, 98.4, 82.0, 29.5, 22.0, 19.1, 13.5; ESI-MS *m/z* 407.0 $(M + H)^+$; HRMS calcd for $C_{19}H_{17}FIO^+$ $(M + H)^+$ 407.0303, found 407.0304.

1-(4-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1q)



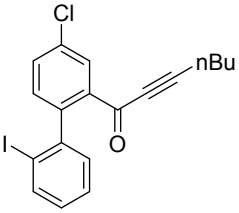
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 1H), 7.79-7.75 (m, 1H), 7.40-7.36 (m, 1H), 7.31-7.26 (m, 1H), 7.21-7.18 (m, 2H), 7.07-7.02 (m, 1H), 2.21 (t, J = 7.2 Hz, 2H), 1.50-1.42 (m, 2H), 1.40-1.32 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 162.0 (d, J = 247.0 Hz), 144.8, 140.6 (d, J = 4.0 Hz), 138.8, 138.1 (d, J = 6.0 Hz), 133.0 (d, J = 8.0 Hz), 130.1, 129.2, 128.0, 119.2 (d, J = 21.0 Hz), 117.2 (d, J = 23.0 Hz), 99.7, 98.4, 80.6, 29.6, 22.1, 19.0, 13.5; ESI-MS *m/z* 407.0 $(M + H)^+$; HRMS calcd for $C_{19}H_{17}FIO^+$ $(M + H)^+$ 407.0303, found 407.0304.

1-(5-fluoro-2'-iodo-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1r)



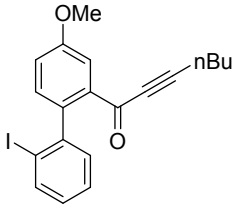
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.13 (m, 1H), 7.91-7.88 (m, 1H), 7.41-7.36 (m, 1H), 7.22-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.92-6.89 (m, 1H), 2.22 (t, J = 7.2 Hz, 2H), 1.50-1.42 (m, 2H), 1.41-1.30 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 164.5 (d, J = 255.0 Hz), 147.5 (d, J = 9.0 Hz), 144.8, 138.8, 133.7 (d, J = 9.0 Hz), 132.8 (d, J = 3.0 Hz), 129.5, 129.3, 128.0, 118.5 (d, J = 22.0 Hz), 115.2 (d, J = 21.0 Hz), 98.7, 97.6, 80.8, 29.7, 22.1, 19.0, 13.6; ESI-MS *m/z* 407.0 $(M + H)^+$; HRMS calcd for $C_{19}H_{17}FIO^+$ $(M + H)^+$ 407.0303, found 407.0305.

1-(4-chloro-2'-iodo-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1s)



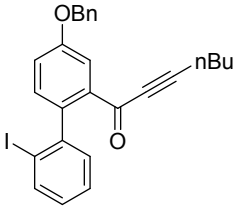
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 2.4 Hz, 1H), 7.92-7.89 (m, 1H), 7.56-7.53 (m, 1H), 7.40-7.36 (m, 1H), 7.19-7.15 (m, 2H), 7.07-7.03 (m, 1H), 2.23 (t, J = 6.8 Hz, 2H), 1.50-1.42 (m, 2H), 1.40-1.31 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 177.2, 144.7, 142.9, 138.8, 137.8, 134.2, 132.8, 132.1, 130.5, 129.9, 129.2, 128.0, 99.2, 98.5, 80.6, 29.6, 22.0, 19.0, 13.5; ESI-MS *m/z* 423.0 $(M + H)^+$; HRMS calcd for $C_{19}H_{17}ClIO^+$ $(M + H)^+$ 423.0007, found 423.0008.

1-(2'-iodo-4-methoxy-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1t)



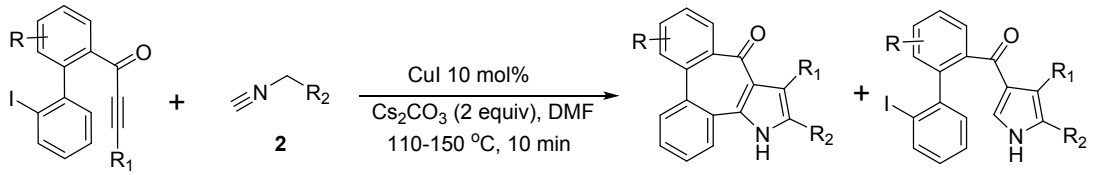
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 1H), 7.59-7.58 (m, 1H), 7.38-7.34 (m, 1H), 7.22-7.19 (m, 1H), 7.13-7.12 (m, 2H), 7.04-6.99 (m, 1H), 3.91 (s, 3H), 2.18 (t, *J* = 7.2 Hz, 2H), 1.47-1.39 (m, 2H), 1.37-1.29 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.5, 159.1, 145.6, 138.7, 137.5, 137.4, 132.6, 130.4, 128.8, 127.8, 118.4, 114.8, 100.4, 97.8, 81.0, 55.6, 29.6, 22.0, 19.0, 13.5; ESI-MS *m/z* 419.1 $(M + H)^+$; HRMS calcd for $C_{20}H_{20}IO_2^+$ $(M + H)^+$ 419.0502, found 419.0505.

1-(4-(benzyloxy)-2'-iodo-[1,1'-biphenyl]-2-yl)hept-2-yn-1-one (1u)



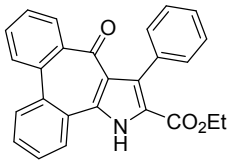
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 1H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.51-7.46 (m, 2H), 7.46-7.40 (m, 2H), 7.39-7.34 (m, 2H), 7.23-7.18 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.05-7.00 (m, 1H), 5.16 (s, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 1.47-1.40 (m, 2H), 1.37-1.30 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 178.5, 158.3, 145.6, 138.7, 137.6, 137.5, 136.4, 132.6, 130.3, 128.8, 128.7, 128.3, 127.9, 127.7, 119.0, 115.9, 100.3, 97.8, 80.9, 70.4, 29.6, 22.1, 19.0, 13.5; ESI-MS *m/z* 495.1 $(M + H)^+$; HRMS calcd for $C_{26}H_{24}IO_2^+$ $(M + H)^+$ 495.0815, found 495.0818.

Ⅲ. Copper-Catalyzed Tandem Reactions



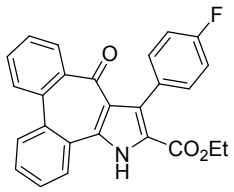
Isocyanoacetate derivative **2** (1.2 mmol) was added to a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.), copper iodide (10 mg, 0.05 mmol, 10% equiv.), **1** (0.5 mmol, 1.0 equiv.) in DMF (3 mL) at appointed temperature. The mixture was stirred under argon for 10 minutes. Monitoring with TLC showed that the reaction was complete. Water (5 mL) was added and the aqueous phase was extracted with ethyl acetate (5 mL×3). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was loaded on silica column and purified by column chromatography (ethyl acetate/petroleum ether, 1:3) to afford product **3** and the corresponding [3 + 2] side products **4.**

ethyl 7-phenyl-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3aa)



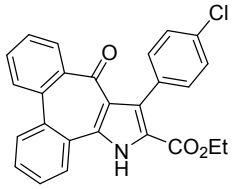
133 mg, 68% yield, white solid.[1]H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.86-7.75 (m, 4H), 7.63-7.59 (m, 1H), 7.56-7.46 (m, 3H), 7.42-7.30 (m, 5H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); [13]C NMR (100 MHz, CDCl3) δ 189.6, 161.4, 142.9, 136.5, 135.7, 135.0, 132.9, 132.1, 131.2, 130.6, 130.4, 130.1, 128.8, 128.5, 128.4, 128.3, 127.9, 127.4, 127.3, 126.5, 121.3, 60.9, 13.9; ESI-MS *m/z* 394.1 $(M + H)^+$; HRMS calcd for $C_{26}H_{20}NO_3^+$ $(M + H)^+$ 394.1438, found 394.1441.

ethyl 7-(4-fluorophenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ba)



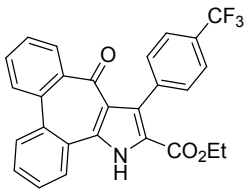
137 mg, 67% yield, white solid.[1]H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.87-7.79 (m, 3H), 7.79-7.74 (m, 1H), 7.64-7.60 (m, 1H), 7.58-7.51 (m, 3H), 7.37-7.33 (m, 2H), 7.11-7.06 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 189.4, 162.3 (d, *J* = 241.0 Hz), 142.7, 136.5, 135.7, 134.9, 132.2, 131.9 (d, *J* = 8.0 Hz), 130.6 (d, *J* = 27.0 Hz), 130.1, 128.9, 128.5, 128.2, 127.9, 127.3, 126.2, 121.4, 114.4 (d, *J* = 21.0 Hz), 61.0, 13.9; ESI-MS *m/z* 412.1 $(M + H)^+$; HRMS calcd for $C_{26}H_{19}FNO_3^+$ $(M + H)^+$ 412.1343, found 412.1345.

ethyl 7-(4-chlorophenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ca)



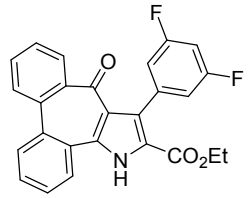
147 mg, 69% yield, white solid. [1]H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.86-7.79 (m, 3H), 7.79-7.75 (m, 1H), 7.66-7.59 (m, 1H), 7.56-7.52 (m, 3H), 7.39-7.29 (m, 4H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2, Hz, 3H); [13]C NMR (100 MHz, CDCl3) δ 189.4, 161.1, 142.6, 136.5, 135.8, 135.0, 133.3, 132.2, 131.6, 131.4, 130.8, 130.5, 129.8, 129.0, 128.5, 128.5, 128.1, 127.9, 127.6, 127.2, 126.3, 121.3, 61.1, 14.0; ESI-MS *m/z* 428.1 $(M + H)^+$; HRMS calcd for $C_{26}H_{19}ClNO_3^+$ $(M + H)^+$ 428.1048, found 428.1049.

ethyl 7-(4-(trifluoromethyl)phenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3da)



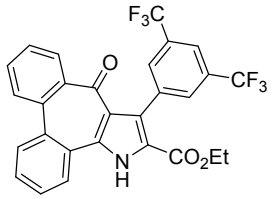
157 mg, 68% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.87-7.76 (m, 4H), 7.68-7.61 (m, 3H), 7.57-7.53 (m, 3H), 7.52-7.48 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 161.0, 142.5, 137.0, 136.6, 135.8, 135.2, 132.3, 130.9, 130.6, 129.6, 129.1, 128.6, 128.5, 128.1, 127.9, 127.1, 126.3, 124.4 (q, *J* = 270.0 Hz), 124.3 (q, *J* = 4.0 Hz), 121.5, 61.2, 13.8; ESI-MS *m/z* 462.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{19}F_3NO_3^+$ $(M + H)^+$ 462.1312, found 462.1314.

ethyl 7-(3,5-difluorophenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ea)



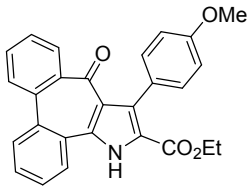
144 mg, 67% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.89-7.77 (m, 4H), 7.65-7.61 (m, 1H), 7.59-7.46 (m, 3H), 6.91-6.84 (m, 2H), 6.81-6.76 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 162.1 (dd, *J* = 245.0 Hz, 13.0 Hz), 161.1, 142.4, 136.5, 136.4 (t, *J* = 5.0 Hz), 132.2, 130.9, 130.6, 129.0, 128.6, 128.4, 128.0, 127.9, 127.1, 126.6, 121.5, 113.4 (d, *J* = 25.0 Hz), 113.3 (d, *J* = 12.0 Hz), 102.7 (t, *J* = 25.0 Hz), 61.2, 13.8; ESI-MS *m/z* 430.1 $(M + H)^+$; HRMS calcd for $C_{26}H_{18}F_2NO_3^+$ $(M + H)^+$ 430.1249, found 430.1251.

ethyl 7-(3,5-bis(trifluoromethyl)phenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3fa)



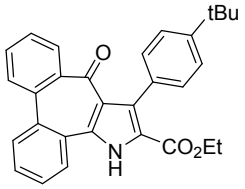
180 mg, 68% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.88-7.84 (m, 5H), 7.83-7.76 (m, 2H), 7.68-7.63 (m, 1H), 7.60-7.55 (m, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 160.9, 142.2, 136.6, 135.9, 135.5, 135.2, 132.4, 131.1, 130.8, 130.7, 130.4, 129.3, 128.8, 128.6, 128.0, 127.9, 127.4, 126.8, 126.3, 123.6 (q, *J* = 271.0 Hz), 121.7, 121.1 (m), 61.5, 13.6; ESI-MS *m/z* 530.1 $(M + H)^+$; HRMS calcd for $C_{28}H_{18}F_6NO_3^+$ $(M + H)^+$ 530.1185, found 530.1188.

ethyl 7-(4-methoxyphenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ga)



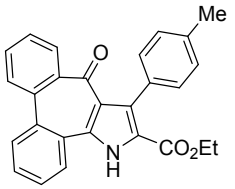
137 mg, 65% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.85-7.76 (m, 4H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.56-7.48 (m, 3H), 7.34-7.29 (m, 2H), 6.95-6.92 (m, 2H), 4.18 (q, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 1.14 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.8, 161.3, 158.9, 143.0, 136.5, 135.7, 134.9, 132.1, 131.4, 131.0, 130.6, 130.4, 128.8, 128.4, 128.4, 128.2, 127.8, 127.5, 126.4, 124.9, 121.2, 112.9, 60.9, 55.2, 14.0; ESI-MS *m/z* 424.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{22}NO_4^+$ $(M + H)^+$ 424.1543, found 424.1546.

ethyl 7-(4-(tert-butyl)phenyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ha)



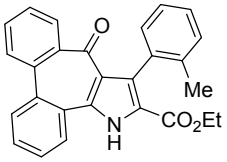
143 mg, 64% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.85-7.80 (m, 3H), 7.78-7.75 (m, 1H), 7.63-7.58 (m, 1H), 7.56-7.48 (m, 3H), 7.42-7.39 (m, 2H), 7.33-7.30 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.37 (s, 9H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.7, 161.4, 150.0, 143.0, 136.5, 135.7, 134.9, 132.1, 131.3, 130.6, 130.4, 129.8, 129.7, 128.7, 128.4, 128.2, 127.8, 127.5, 126.4, 124.3, 121.3, 60.9, 34.6, 31.4, 13.8; ESI-MS *m/z* 450.1 $(M + H)^+$; HRMS calcd for $C_{30}H_{28}NO_3^+$ $(M + H)^+$ 450.2064, found 450.2067.

ethyl 7-(p-tolyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ia)



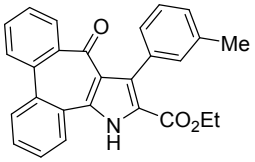
134 mg, 66% yield, white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.86-7.84 (m, 1H), 7.83-7.77 (m, 3H), 7.63-7.59 (m, 1H), 7.56-7.52 (m, 1H), 7.52-7.45 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl3) δ 189.9, 161.4, 142.9, 136.9, 136.4, 135.7, 135.1, 132.0, 131.3, 130.6, 130.4, 130.0, 129.8, 128.7, 128.4, 128.3, 128.27, 128.2, 127.8, 127.5, 126.6, 121.2, 60.9, 21.5, 14.0; ESI-MS *m/z* 408.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{22}NO_3^+$ $(M + H)^+$ 408.1594, found 408.1598.

ethyl 7-(o-tolyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ja)



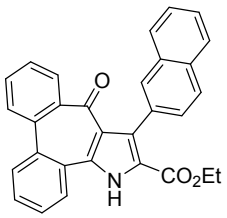
142 mg, 70% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.86-7.78 (m, 4H), 7.63-7.58 (m, 1H), 7.57-7.52 (m, 2H), 7.51-7.47 (m, 1H), 7.28-7.24 (m, 2H), 7.21-7.16 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 188.6, 161.4, 142.2, 136.8, 136.6, 135.9, 135.0, 133.5, 132.3, 130.7, 130.7, 130.6, 129.7, 129.1, 128.7, 128.4, 128.4, 128.3, 128.2, 127.6, 127.5, 126.3, 124.8, 121.5, 60.7, 20.3, 13.7; ESI-MS *m/z* 408.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{22}NO_3^+$ $(M + H)^+$ 408.1594, found 408.1597.

ethyl 7-(m-tolyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ka)



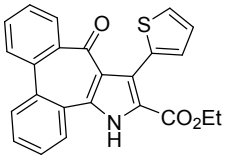
134 mg, 66% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.86-7.80 (m, 3H), 7.78-7.76 (m, 1H), 7.64-7.59 (m, 1H), 7.57-7.49 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.22-7.13 (m, 3H), 4.20-4.16 (m, 2H), 2.39 (s, 3H), 1.13-1.08 (m, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.7, 161.4, 143.0, 136.6, 136.5, 135.7, 134.9, 132.7, 132.1, 131.0, 130.6, 130.4, 128.8, 128.5, 128.4, 128.3, 128.1, 127.8, 127.4, 127.3, 127.1, 126.4, 121.3, 60.87, 21.5, 13.9; ESI-MS *m/z* 408.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{22}NO_3^+$ $(M + H)^+$ 408.1594, found 408.1598.

ethyl 7-(naphthalen-2-yl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3la)



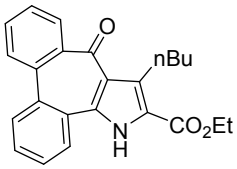
157 mg, 71% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.90-7.77 (m, 8H), 7.66-7.60 (m, 1H), 7.58-7.44 (m, 6H), 4.11 (q, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.7, 161.4, 142.9, 136.5, 135.8, 135.1, 133.0, 132.8, 132.1, 131.0, 130.7, 130.5, 130.4, 129.3, 128.8, 128.5, 128.4, 128.4, 128.1, 127.8, 127.7, 127.4, 126.7, 126.5, 125.8, 125.7, 121.6, 60.9, 13.9; ESI-MS *m/z* 444.1 $(M + H)^+$; HRMS calcd for $C_{30}H_{22}NO_3^+$ $(M + H)^+$ 444.1594, found 444.1599.

ethyl 7-(thiophen-2-yl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ma)



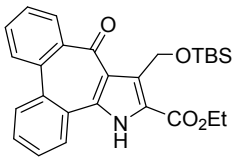
123 mg, 62% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.86-7.79 (m, 3H), 7.77-7.74 (m, 1H), 7.63-7.58 (m, 1H), 7.55-7.50 (m, 3H), 7.40-7.38 (m, 1H), 7.16-7.15 (m, 1H), 7.10-7.07 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.4, 161.0, 142.9, 136.6, 135.6, 134.8, 132.8, 132.2, 130.7, 130.4, 128.9, 128.8, 128.8, 128.5, 128.4, 127.9, 127.2, 126.4, 126.3, 126.0, 122.7, 122.4, 61.1, 13.9; ESI-MS *m/z* 400.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{18}NO_3S^+$ $(M + H)^+$ 400.1002, found 400.1009.

ethyl 7-butyl-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3na)



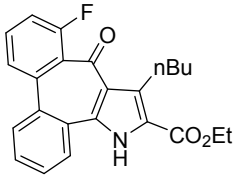
138 mg, 74% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.97-7.94 (m, 1H), 7.82-7.76 (m, 2H), 7.73-7.70 (m, 1H), 7.61-7.56 (m, 1H), 7.55-7.46 (m, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.12-3.04 (m, 2H), 1.66-1.56 (m, 2H), 1.50-1.34 (m, 5H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 190.3, 161.9, 142.4, 136.4, 135.8, 135.3, 133.8, 132.0, 130.6, 130.5, 128.6, 128.3, 128.3, 128.2, 128.2, 127.7, 126.3, 121.0, 60.9, 33.7, 24.6, 22.9, 14.4, 14.1; ESI-MS *m/z* 374.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{24}NO_3^+$ $(M + H)^+$ 374.1751, found 374.1751.

ethyl 7-(((tert-butyldimethylsilyl)oxy)methyl)-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta [1,2-b]pyrrole-6-carboxylate (3oa)



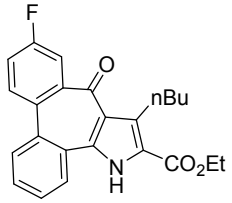
159 mg, 69% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.96-7.93 (m, 1H), 7.83-7.75 (m, 2H), 7.73-7.70 (m, 1H), 7.60-7.55 (m, 1H), 7.54-7.46 (m, 3H), 5.20 (s, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.91 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 190.3, 161.7, 142.4, 136.5, 135.7, 135.3, 132.1, 130.6, 130.4, 129.7, 128.6, 128.3, 128.2, 127.9, 127.5, 126.2, 121.9, 61.2, 54.7, 26.1, 18.6, 14.4, -5.2; ESI-MS *m/z* 462.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{32}NO_4Si^+$ $(M + H)^+$ 462.2095, found 462.2089.

ethyl 7-butyl-9-fluoro-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3pa)



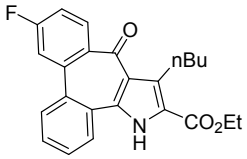
133 mg, 68% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.81-7.76 (m, 1H), 7.70-7.65 (m, 1H), 7.51-7.43 (m, 4H), 7.24-7.18 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.11-2.99 (m, 2H), 1.66-1.58 (m, 2H), 1.47-1.33 (m, 5H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 162.0, 158.7 (d, *J* = 253.0 Hz), 137.6, 135.5 (d, *J* = 3.0 Hz), 142.7, 134.1, 132.9, 130.7 (d, *J* = 9.0 Hz), 130.6 (d, *J* = 9.0 Hz), 128.7, 128.4, 127.9, 126.5, 126.4 (d, *J* = 5.0 Hz), 121.0, 115.7 (d, *J* = 22.0 Hz), 61.0, 33.8, 24.4, 22.8, 14.4, 14.0; ESI-MS *m/z* 392.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{23}FNO_3^+$ $(M + H)^+$ 392.1656, found 392.1652.

ethyl 7-butyl-10-fluoro-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3qa)



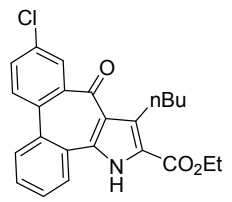
139 mg, 71% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.80-7.70 (m, 3H), 7.68-7.64 (m, 1H), 7.49-7.46 (m, 2H), 7.30-7.24 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.11-3.01 (m, 2H), 1.64-1.56 (m, 6.3 Hz, 2H), 1.46-1.36 (m, 5H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 162.5 (d, *J* = 248.0 Hz), 161.9, 144.1 (d, *J* = 7.0 Hz), 135.5 (d, *J* = 9.0 Hz), 134.0, 132.8 (d, *J* = 8.0 Hz), 132.1 (d, *J* = 3.0 Hz), 131.9, 128.7, 128.3, 127.5, 127.4, 126.5, 121.2, 117.9 (d, *J* = 19.0 Hz), 114.6 (d, *J* = 23.0 Hz), 61.00, 33.7, 24.6, 22.9, 14.4, 14.1; ESI-MS *m/z* 392.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{23}FNO_3^+$ $(M + H)^+$ 392.1656, found 392.1665.

ethyl 7-butyl-11-fluoro-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ra)



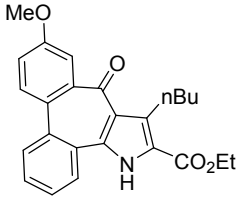
137 mg, 70% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.00-7.97 (m, 1H), 7.81-7.75 (m, 1H), 7.73-7.66 (m, 1H), 7.56-7.46 (m, 3H), 7.25-7.20 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.12-3.02 (m, 2H), 1.63-1.56 (m, 2H), 1.45-1.37 (m, 5H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 163.7 (d, *J* = 250.0 Hz), 161.8, 139.0 (d, *J* = 2.0 Hz), 138.3 (d, *J* = 9.0 Hz), 135.2, 134.9, 133.9, 132.0, 131.2 (d, *J* = 9.0 Hz), 129.0, 128.8, 127.8 (d, *J* = 8.0 Hz), 126.3, 121.1, 116.8 (d, *J* = 23.0 Hz), 115.5 (d, *J* = 21.0 Hz), 60.9, 33.6, 24.5, 22.9, 14.4, 14.1; ESI-MS *m/z* 392.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{23}FNO_3^+$ $(M + H)^+$ 392.1656, found 392.1652.

ethyl 7-butyl-10-chloro-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3sa)



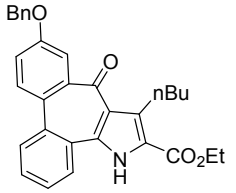
148 mg, 73% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.78-7.69 (m, 3H), 7.56-7.49 (m, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.10-3.01 (m, 2H), 1.63-1.56 (m, 2H), 1.47-1.37 (m, 5H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 188.5, 161.8, 143.3, 135.3, 135.2, 134.7, 134.2, 134.0, 132.1, 131.8, 130.6, 128.7, 128.7, 128.0, 127.7, 127.6, 126.3, 121.2, 61.0, 33.6, 24.6, 22.9, 14.4, 14.0; ESI-MS *m/z* 408.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{23}ClNO_3^+$ $(M + H)^+$ 408.1361, found 408.1367.

ethyl 7-butyl-10-methoxy-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ta)



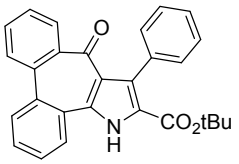
151 mg, 75% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.79-7.67 (m, 3H), 7.50-7.43 (m, 3H), 7.17-7.13 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 3.14-3.05 (m, 2H), 1.64-1.58 (m, 2H), 1.47-1.38 (m, 5H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.8, 161.8, 159.6, 143.5, 136.2, 135.4, 133.9, 132.2, 131.6, 128.8, 128.6, 127.7, 127.7, 127.1, 126.1, 120.9, 118.2, 111.1, 60.8, 55.6, 33.7, 24.6, 22.9, 14.4, 14.1; ESI-MS *m/z* 404.1 $(M + H)^+$; HRMS calcd for $C_{25}H_{26}NO_4^+$ $(M + H)^+$ 404.1856, found 404.1857.

ethyl 10-(benzyloxy)-7-butyl-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ua)



177 mg, 74% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.80-7.77 (m, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.69-7.65 (m, 1H), 7.59 (d, *J* = 2.8 Hz, 1H), 7.51-7.44 (m, 4H), 7.43-7.38 (m, 2H), 7.36-7.32 (m, 1H), 7.24-7.20 (m, 1H), 5.19 (s, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.13-3.04 (m, 2H), 1.61-1.56 (m, 2H), 1.47-1.38 (m, 5H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 189.7, 161.7, 158.7, 143.5, 136.5, 136.2, 135.3, 133.9, 132.3, 131.7, 129.0, 128.7, 128.6, 128.7, 127.8, 127.6, 127.1, 126.0, 120.8, 118.8, 112.3, 70.3, 60.8, 33.6, 24.6, 22.9, 14.4, 14.1; ESI-MS *m/z* 480.1 $(M + H)^+$; HRMS calcd for $C_{31}H_{30}NO_4^+$ $(M + H)^+$ 480.2169, found 480.2169.

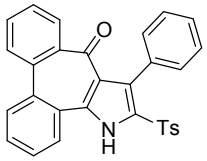
tert-butyl 7-phenyl-8-oxo-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (3ab)



151 mg, 72% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.86-7.73 (m, 4H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54-7.45 (m, 3H), 7.42-7.31 (m, 5H), 1.27 (s, 9H); ^{13}C NMR (100 MHz,

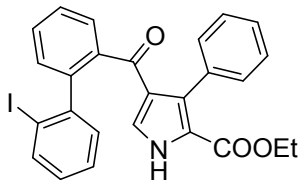
CDCl3) δ 189.6, 161.0, 142.9, 136.4, 135.8, 134.6, 133.6, 132.0, 130.6, 130.4, 130.3, 130.1, 128.6, 128.4, 128.4, 128.3, 127.9, 127.6, 127.4, 127.1, 126.6, 123.0, 81.9, 28.0; ESI-MS *m/z* 422.1 (M + H)$^+$; HRMS calcd for $C_{28}H_{24}NO_3^+$ (M + H)$^+$ 422.1751, found 422.1755.

7-phenyl-6-tosyldibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrol-8(5H)-one (3ac)



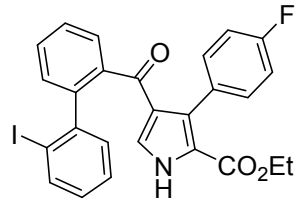
154 mg, 65% yield, white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.86-7.74 (m, 4H), 7.62-7.57 (m, 1H), 7.51-7.45 (m, 3H), 7.41-7.34 (m, 3H), 7.32-7.29 (m, 2H), 7.26-7.21 (m, 2H), 7.06-7.01 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 188.9, 144.4, 142.5, 137.9, 136.4, 135.9, 134.6, 132.1, 130.9, 130.8, 130.5, 130.3, 129.6, 129.4, 129.1, 128.6, 128.4, 128.2, 128.0, 127.9, 127.7, 127.3, 126.8, 126.7, 21.6; ESI-MS *m/z* 476.1 (M + H)$^+$; HRMS calcd for $C_{30}H_{22}NO_3S^+$ (M + H)$^+$ 476.1315, found 476.1319.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-phenyl-1H-pyrrole-2-carboxylate (4aa)



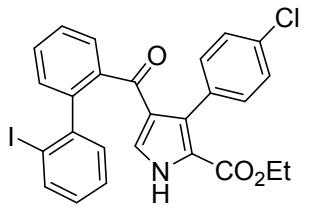
78 mg, 30% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.84-7.79 (m, 1H), 7.53-7.46 (m, 2H), 7.43-7.38 (m, 1H), 7.35-7.27 (m, 2H), 7.26-7.24 (m, 3H), 7.22-7.19 (m, 1H), 7.18-7.12 (m, 3H), 6.96-6.91 (m, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 161.1, 144.4, 141.8, 140.4, 139.3, 133.2, 131.5, 131.3, 131.1, 130.1, 129.7, 129.4, 128.9, 128.5, 127.8, 127.6, 127.1, 127.1, 125.7, 121.2, 99.3, 60.7, 13.8; ESI-MS *m/z* 522.1 (M + H)$^+$; HRMS calcd for $C_{26}H_{21}INO_3^+$ (M + H)$^+$ 522.0561, found 522.0555.

ethyl 3-(4-fluorophenyl)-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4ba)



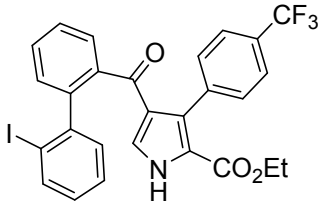
78 mg, 29% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.52-7.47 (m, 2H), 7.45-7.38 (m, 1H), 7.34-7.31 (m, 1H), 7.28-7.24 (m, 1H), 7.21-7.08 (m, 4H), 6.98-6.90 (m, 3H), 4.16-4.06 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 162.2 (d, *J* = 244.0 Hz), 161.0, 144.3, 141.8, 140.4, 139.3, 131.9 (d, *J* = 8.0 Hz), 131.2 (d, *J* = 23.1 Hz), 130.4, 129.9, 129.5, 129.1 (d, *J* = 3.0 Hz), 129.0, 128.4, 127.7 (d, *J* = 7.3 Hz), 125.6, 121.3, 114.0 (d, *J* = 21.3 Hz), 99.2, 60.8, 13.9; ESI-MS *m/z* 540.0 (M + H)$^+$; HRMS calcd for $C_{26}H_{20}FINO_3^+$ (M + H)$^+$ 540.0466, found 504.0465.

ethyl 3-(4-chlorophenyl)-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4ca)



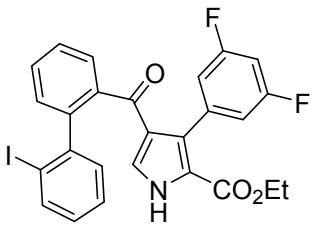
80 mg, 29% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.84-7.78 (m, 1H), 7.53-7.48 (m, 2H), 7.46-7.40 (m, 1H), 7.35-7.32 (m, 1H), 7.29-7.22 (m, 3H), 7.21-7.15 (m, 2H), 7.10-7.06 (m, 2H), 6.96-6.91 (m, 1H), 4.14-4.09 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 160.8, 144.3, 141.8, 140.4, 139.3, 133.1, 131.7, 131.6, 131.4, 131.2, 130.1, 129.8, 129.5, 129.0, 128.3, 127.7, 127.7, 127.3, 125.6, 121.3, 99.2, 60.8, 13.9; ESI-MS *m/z* 556.0 $(M + H)^+$; HRMS calcd for $C_{26}H_{20}ClINO_3^+$ $(M + H)^+$ 556.0171, found 556.0165.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(4-(trifluoromethyl)phenyl)-1H-pyrrole-2-carboxylate (4da)



82 mg, 28% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.48 (m, 4H), 7.46-7.42 (m, 1H), 7.37-7.33 (m, 1H), 7.30-7.25 (m, 3H), 7.21-7.18 (m, 2H), 6.98-6.92 (m, 1H), 4.12-4.05 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 160.8, 144.2, 141.8, 140.3, 139.4, 137.4, 131.4, 131.2, 130.5, 129.9, 129.8, 129.5, 129.1 (q, *J* = 32.0 Hz), 129.0, 128.3, 127.8, 127.7, 125.5, 124.4 (q, *J* = 270.0 Hz), 124.0 (q, *J* = 3.7 Hz), 121.5, 99.2, 60.9, 13.4; ESI-MS *m/z* 590.0 $(M + H)^+$; HRMS calcd for $C_{27}H_{20}F_3INO_3^+$ $(M + H)^+$ 590.0434, found 590.0432.

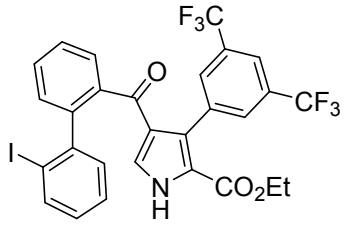
ethyl 3-(3,5-difluorophenyl)-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4ea)



75 mg, 27% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.41 (m, 3H), 7.37-7.29 (m, 2H), 7.22-7.16 (m, 2H), 6.99-6.94 (m, 1H), 6.74-6.68 (m, 1H), 6.65-6.61 (m, 2H), 4.17-4.05 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 162.0 (dd, *J* = 245.0 Hz, 13.1 Hz), 160.7, 144.1, 141.7, 140.2, 139.4, 136.7 (t, *J* = 10.7 Hz), 131.3, 131.2, 129.6, 129.5, 129.1, 128.5, 128.1, 127.9, 127.7, 125.7, 121.5, 113.3 (d, *J* =

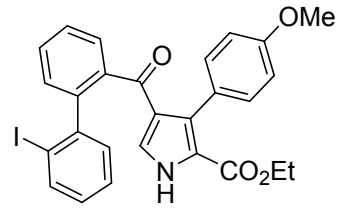
25.0 Hz), 113.3 (d, *J* = 12.0 Hz), 102.5 (t, *J* = 25.0 Hz), 99.1, 61.0, 13.7; ESI-MS *m/z* 558.0 (M + H)$^+$; HRMS calcd for $C_{26}H_{19}F_2INO_3^+$ (M + H)$^+$ 558.0372, found 558.0370.

ethyl 3-(3,5-bis(trifluoromethyl)phenyl)-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4fa)



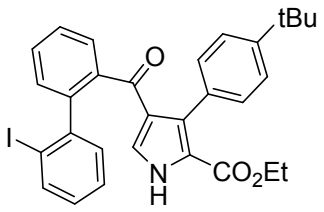
92 mg, 28% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.85-7.79 (m, 2H), 7.62-7.58 (m, 2H), 7.55-7.43 (m, 3H), 7.39-7.36 (m, 1H), 7.31-7.26 (m, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.99-6.94 (m, 1H), 4.11-4.06 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 160.7, 143.9, 141.5, 140.3, 139.6, 135.6, 131.4, 131.2, 130.7 (m), 130.3, 130.0, 129.9, 129.6, 129.2, 127.9, 127.8, 127.4, 125.6, 123.6 (q, *J* = 271.0 Hz), 121.9, 120.9 (m), 119.5, 99.1, 61.2, 13.5; ESI-MS *m/z* 658.0 (M + H)$^+$; HRMS calcd for $C_{28}H_{19}F_6INO_3^+$ (M + H)$^+$ 658.0308, found 658.0305.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (4ga)



77 mg, 28% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.84-7.80 (m, 1H), 7.53-7.45 (m, 2H), 7.43-7.38 (m, 1H), 7.34-7.28 (m, 2H), 7.23-7.17 (m, 2H), 7.12-7.07 (m, 2H), 6.96-6.91 (m, 1H), 6.85-6.80 (m, 2H), 4.15-4.12 (m, 2H), 3.81 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 160.9, 158.8, 144.4, 141.8, 140.6, 139.3, 131.5, 131.3, 131.2, 129.5, 129.3, 128.9, 128.5, 127.7, 127.6, 125.8, 125.1, 121.0, 112.6, 99.2, 60.6, 55.2, 14.0; ESI-MS *m/z* 552.1 (M + H)$^+$; HRMS calcd for $C_{27}H_{23}INO_4^+$ (M + H)$^+$ 552.0666, found 552.0662.

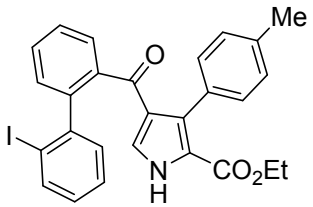
ethyl 3-(4-(tert-butyl)phenyl)-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4ha)



86 mg, 30% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50-7.43 (m, 2H), 7.39-7.34 (m, 1H), 7.33-7.27 (m, 4H), 7.25-7.21 (m, 1H), 7.19 (d, *J* =

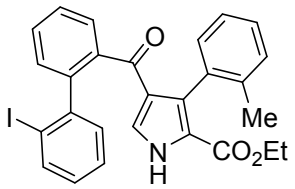
3.6 Hz, 1H), 7.13-7.09 (m, 2H), 6.96-6.90 (m, 1H), 4.14-4.05 (m, 2H), 1.32 (s, 9H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 161.2, 149.8, 144.5, 141.8, 140.4, 139.3, 131.7, 131.2, 131.0, 130.0, 129.9, 129.7, 129.4, 128.9, 128.7, 127.8, 127.6, 125.7, 124.0, 121.1, 99.3, 60.6, 34.5, 31.4, 13.8; ESI-MS *m/z* 578.1 $(M + H)^+$; HRMS calcd for $C_{30}H_{29}INO_3^+$ $(M + H)^+$ 578.1187, found 578.1185.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(p-tolyl)-1H-pyrrole-2-carboxylate (4ia)



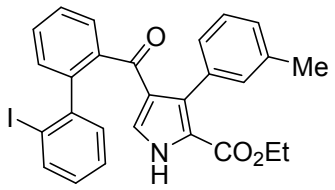
80 mg, 30% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.53-7.46 (m, 2H), 7.43-7.38 (m, 1H), 7.34-7.31 (m, 1H), 7.30-7.26 (m, 1H), 7.24-7.20 (m, 1H), 7.15 (d, J = 3.6 Hz, 1H), 7.10-7.04 (m, 4H), 6.96-6.90 (m, 1H), 4.13-4.10 (m, 2H), 2.33 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 161.0, 144.4, 141.8, 140.6, 139.3, 136.7, 131.7, 131.3, 131.2, 130.0, 129.9, 129.3, 128.9, 128.5, 127.9, 127.7, 127.6, 125.6, 121.0, 99.3, 60.6, 21.4, 14.0; ESI-MS *m/z* 536.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{23}INO_3^+$ $(M + H)^+$ 536.0717, found 536.0715.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(o-tolyl)-1H-pyrrole-2-carboxylate (4ja)



67 mg, 25% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 & 9.77 (two s, 1H), 7.84-7.79 (m, 1H), 7.51-7.47 (m, 2H), 7.45-7.39 (m, 1H), 7.36-7.31 (m, 1H), 7.26-7.01 & 6.73-6.70 (m, 7H), 6.94-6.89 (m, 1H), 4.06-3.99 (m, 2H), 2.05 & 1.75 (two s, 3H), 0.96-0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 190.9, 161.3, 144.28, 144.26, 141.7, 141.5, 140.7, 140.6, 139.4, 139.1, 136.7, 136.5, 133.9, 133.9, 131.5, 131.4, 131.3, 131.1, 131.0, 130.9, 130.8, 129.9, 129.6, 129.3, 129.1, 129.0, 128.9, 128.9, 128.1, 127.9, 127.9, 127.8 127.5, 127.2, 127.1, 125.8, 125.2, 124.6, 124.5, 121.6, 121.4, 99.3, 99.1, 60.5, 20.1, 19.8, 13.7; ESI-MS *m/z* 536.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{23}INO_3^+$ $(M + H)^+$ 536.0717, found 536.0715.

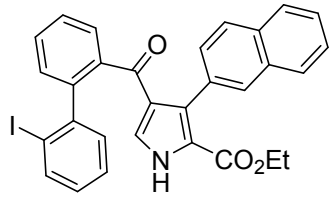
ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(m-tolyl)-1H-pyrrole-2-carboxylate (4ka)



75 mg, 28% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 7.52-7.45 (m, 2H), 7.42-7.37 (m, 1H), 7.34-7.26 (m, 2H), 7.23-7.14 (m, 3H), 7.06 (d, J =

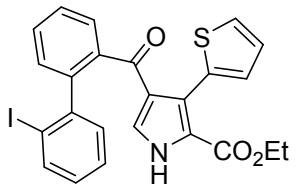
7.6 Hz, 1H), 6.98-6.91 (m, 3H), 4.13-4.09 (m, 2H), 2.32 (s, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 161.1, 144.4, 141.8, 140.5, 139.3, 136.3, 132.9, 131.5, 131.2, 131.1, 130.8, 129.5, 129.3, 128.9, 128.5, 127.9, 127.8, 127.6, 127.2, 127.0, 125.9, 121.1, 99.3, 60.6, 21.4, 13.8; ESI-MS *m/z* 536.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{23}INO_3^+$ $(M + H)^+$ 536.0717, found 536.0715.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(naphthalen-2-yl)-1H-pyrrole-2-carboxylate (4la)



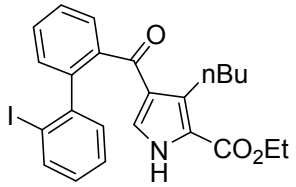
71 mg, 25% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.86-7.73 (m, 4H), 7.63 (s, 1H), 7.54-7.51 (m, 1H), 7.50-7.38 (m, 4H), 7.34-7.26 (m, 3H), 7.24-7.19 (m, 2H), 7.00-6.95 (m, 1H), 4.13-3.99 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 161.1, 144.4, 141.8, 140.5, 139.3, 132.8, 132.7, 131.3, 131.2, 131.2, 130.7, 129.7, 129.4, 129.2, 129.0, 128.6, 128.4, 128.0, 127.8, 127.6, 127.6, 126.3, 125.9, 125.6, 125.5, 121.4, 99.3, 60.7, 13.9; ESI-MS *m/z* 572.1 $(M + H)^+$; HRMS calcd for $C_{30}H_{23}INO_3^+$ $(M + H)^+$ 572.0717, found 572.0713.

ethyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-(thiophen-2-yl)-1H-pyrrole-2-carboxylate (4ma)



79 mg, 30% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.55-7.47 (m, 2H), 7.43-7.38 (m, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.29-7.26 (m, 2H), 7.21-7.14 (m, 2H), 6.98-6.89 (m, 3H), 4.16-4.13 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 160.7, 144.3, 142.1, 140.2, 139.3, 133.1, 131.4, 131.0, 129.6, 129.1, 128.9, 128.8, 128.7, 128.0, 127.6, 126.6, 126.1, 125.9, 123.1, 122.2, 99.1, 60.8, 13.9; ESI-MS *m/z* 528.0 $(M + H)^+$; HRMS calcd for $C_{24}H_{19}INO_3S^+$ $(M + H)^+$ 528.0125, found 528.0122.

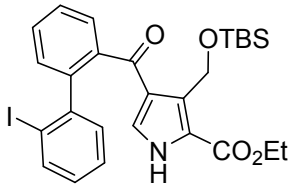
ethyl 3-butyl-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4na)



55 mg, 22% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.53-7.42 (m, 3H), 7.37-7.33 (m, 1H), 7.25-7.22 (m, 2H), 7.09 (d, J = 2.4 Hz, 1H), 6.92-6.87 (m, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.11-2.94 (m, 2H), 1.38-1.22 (m, 7H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 161.6, 144.2, 141.6, 141.1, 139.2, 134.7, 131.3, 131.1, 130.6,

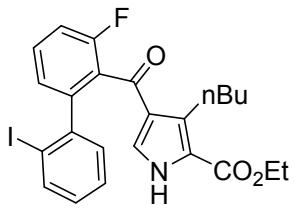
129.0, 128.8, 127.8, 127.7, 127.6, 125.0, 121.0, 99.1, 60.6, 32.9, 24.7, 22.7, 14.3, 14.1; ESI-MS *m/z* 502.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{25}INO_3^+$ $(M + H)^+$ 502.0874, found 502.0872.

ethyl 3-(((tert-butyldimethylsilyl)oxy)methyl)-4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4oa)



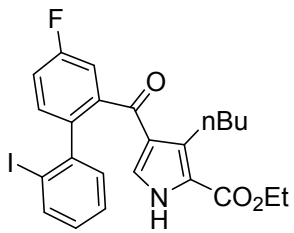
76 mg, 26% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.81-7.76 (m, 1H), 7.53-7.48 (m, 2H), 7.46-7.41 (m, 1H), 7.35-7.31 (m, 1H), 7.27-7.22 (m, 2H), 7.13 (d, *J* = 3.2 Hz, 1H), 6.93-6.87 (m, 1H), 5.02 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 161.4, 144.4, 142.0, 140.5, 139.1, 131.4, 131.1, 130.3, 129.8, 129.3, 128.9, 128.4, 127.7, 127.5, 125.2, 122.3, 99.1, 61.0, 54.9, 26.1, 18.6, 14.4, -5.1; ESI-MS *m/z* 590.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{33}INO_4Si^+$ $(M + H)^+$ 590.1218, found 590.1217.

ethyl 3-butyl-4-(3-fluoro-2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4pa)



73 mg, 28% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.79-7.74 (m, 1H), 7.47-7.40 (m, 1H), 7.28-7.21 (m, 2H), 7.20-7.10 (m, 3H), 6.94-6.89 (m, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.11-2.92 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.29-1.18 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 161.6, 158.8 (d, *J* = 246.0 Hz), 143.1 (d, *J* = 4.0 Hz), 142.5, 139.2, 134.5, 131.2, 130.9, 129.6 (d, *J* = 10.0 Hz), 129.3 (d, *J* = 20.0 Hz), 129.3, 127.6, 127.0 (d, *J* = 3.0 Hz), 125.4, 121.3, 115.1 (d, *J* = 21.0 Hz), 99.0, 60.6, 32.63, 24.7, 22.5, 14.3, 14.1; ESI-MS *m/z* 520.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{24}FINO_3^+$ $(M + H)^+$ 520.0779, found 520.0775.

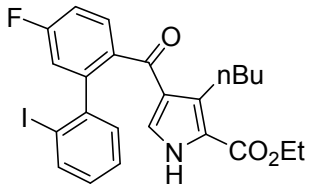
ethyl 3-butyl-4-(4-fluoro-2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4qa)



62 mg, 24% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.35-7.30 (m, 1H), 7.24-7.16 (m, 4H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.92-6.87 (m, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.09-2.93 (m, 2H), 1.38-1.33 (m, 5H), 1.24-1.21 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 161.7 (d, *J* = 248.0 Hz), 161.7, 143.2, 142.8 (d, *J* = 6.0 Hz), 139.3, 137.6 (d, *J* = 3.5 Hz), 134.8, 133.3 (d, *J* = 7.8 Hz), 131.2, 130.8, 129.1, 127.8, 124.4, 121.2,

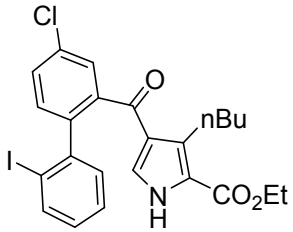
116.1 (d, J = 21.0 Hz), 114.7 (d, J = 23.0 Hz), 99.4, 60.7, 32.8, 24.7, 22.6, 14.3, 14.1; ESI-MS *m/z* 520.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{24}FINO_3^+$ $(M + H)^+$ 520.0779, found 520.0776.

ethyl 3-butyl-4-(5-fluoro-2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4ra)



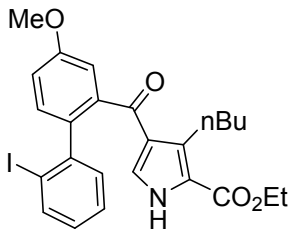
62 mg, 24% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.81-7.75 (m, 1H), 7.52-7.48 (m, 1H), 7.26-7.22 (m, 2H), 7.17-7.11 (m, 1H), 7.10-7.04 (m, 2H), 6.94-6.89 (m, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.05-2.95 (m, 2H), 1.38-1.31 (m, 5H), 1.27-1.24 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 162.4 (d, J = 249.0 Hz), 161.6, 144.2 (d, J = 8.0 Hz), 143.2, 139.3, 137.4 (d, J = 3.2 Hz), 134.7, 130.9, 130.3, 130.2 (d, J = 8.0 Hz), 129.2, 127.8, 125.0, 121.1, 118.4 (d, J = 22.0 Hz), 114.6 (d, J = 21.0 Hz), 98.5, 60.6, 32.9, 24.7, 22.7, 14.3, 14.0; ESI-MS *m/z* 520.1 $(M + H)^+$; HRMS calcd for $C_{24}H_{24}FINO_3^+$ $(M + H)^+$ 520.0779, found 520.0777.

ethyl 3-butyl-4-(4-chloro-2'-iodo-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4sa)



62 mg, 23% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.80-7.76 (m, 1H), 7.50-7.45 (m, 2H), 7.32-7.28 (m, 1H), 7.25-7.20 (m, 2H), 7.12 (d, J = 3.6 Hz, 1H), 6.94-6.89 (m, 1H), 4.31 (q, J = 7.2 Hz, 2H), 3.09-2.93 (m, 2H), 1.37-1.32 (m, 5H), 1.29-1.23 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 161.5, 143.0, 142.5, 139.9, 139.3, 134.7, 133.7, 132.8, 131.1, 130.5, 129.2, 129.1, 127.8, 127.7, 124.5, 121.2, 98.9, 60.7, 32.8, 24.7, 22.6, 14.3, 14.0; ESI-MS *m/z* 536.0 $(M + H)^+$; HRMS calcd for $C_{24}H_{24}ClINO_3^+$ $(M + H)^+$ 536.0484, found 536.0487.

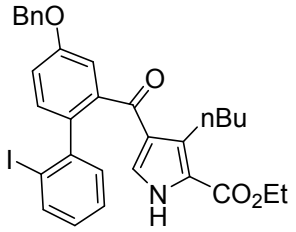
ethyl 3-butyl-4-(2'-iodo-4-methoxy-[1,1'-biphenyl]-2-carbonyl)-1H-pyrrole-2-carboxylate (4ta)



58 mg, 22% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.29-7.26 (m, 1H), 7.22-7.20 (m, 2H), 7.12 (d, J = 3.6 Hz, 1H), 7.05-7.00 (m, 2H), 6.88-6.83 (m, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 3.10-2.94 (m, 2H), 1.39-1.23 (m, 7H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 161.6, 158.8, 143.8, 142.3, 139.2, 134.6, 134.0, 132.6, 131.4, 130.7, 128.6, 127.7, 124.8, 121.0, 114.9, 112.7, 99.8, 60.6, 55.5, 32.8, 24.7, 22.7, 14.3,

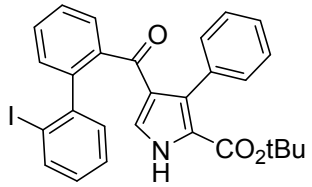
14.1; ESI-MS *m/z* 532.1 $(M + H)^+$; HRMS calcd for $C_{25}H_{27}INO_4^+$ $(M + H)^+$ 532.0979, found 532.0978.

ethyl 4-(4-(benzyloxy)-2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-butyl-1H-pyrrole-2-carboxylate (4ua)



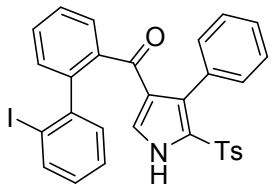
67 mg, 22% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.48-7.34 (m, 5H), 7.30-7.27 (m, 1H), 7.23-7.20 (m, 2H), 7.13-7.07 (m, 3H), 6.89-6.84 (m, 1H), 5.12 (d, *J* = 2.0 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.11-2.94 (m, 2H), 1.37-1.24 (m, 7H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 161.6, 157.9, 143.9, 142.3, 139.2, 136.6, 134.7, 134.4, 132.6, 131.4, 130.7, 128.7, 128.2, 127.7, 127.6, 124.7, 121.0, 115.8, 113.7, 99.8, 70.3, 60.6, 32.9, 24.7, 22.7, 14.4, 14.1; ESI-MS *m/z* 608.1 $(M + H)^+$; HRMS calcd for $C_{31}H_{31}INO_4^+$ $(M + H)^+$ 608.1292, found 608.1286.

tert-butyl 4-(2'-iodo-[1,1'-biphenyl]-2-carbonyl)-3-phenyl-1H-pyrrole-2-carboxylate (4ab)



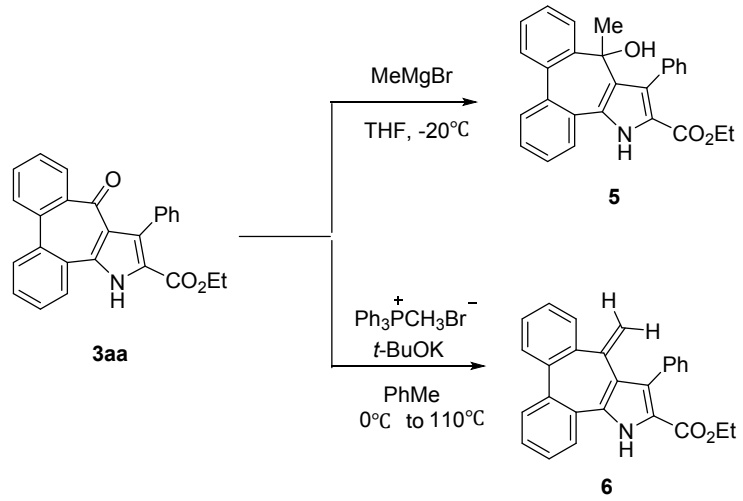
71 mg, 26% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51-7.44 (m, 2H), 7.41-7.36 (m, 1H), 7.33-7.27 (m, 2H), 7.26-7.15 (m, 5H), 7.13-7.10 (m, 2H), 6.97-6.92 (m, 1H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 160.8, 144.4, 141.8, 140.5, 139.3, 133.9, 131.3, 131.1, 130.6, 130.1, 129.2, 129.1, 128.9, 128.5, 127.7, 127.5, 127.1, 126.8, 125.7, 122.6, 99.3, 81.7, 28.0; ESI-MS *m/z* 550.1 $(M + H)^+$; HRMS calcd for $C_{28}H_{25}INO_3^+$ $(M + H)^+$ 550.0874, found 550.0871.

(2'-iodo-[1,1'-biphenyl]-2-yl)(4-phenyl-5-tosyl-1H-pyrrol-3-yl)methanone (4ac)



87 mg, 29% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49-7.44 (m, 2H), 7.40-7.35 (m, 1H), 7.29-7.26 (m, 1H), 7.25-7.12 (m, 7H), 7.10-7.02 (m, 3H), 6.98-6.93 (m, 2H), 6.86-6.80 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 144.4, 144.1, 142.1, 139.9, 139.2, 138.0, 131.2, 130.9, 130.9, 130.4, 129.8, 129.7, 129.3, 128.8, 128.7, 128.5, 127.7, 127.6, 127.6, 127.3, 127.1, 126.2, 99.2, 21.6; ESI-MS *m/z* 604.0 $(M + H)^+$; HRMS calcd for $C_{30}H_{23}INO_3S^+$ $(M + H)^+$ 604.0438, found 604.0434.

IV. Synthetic Transformations



ethyl 7-phenyl-8-hydroxy-8-methyl-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (5) : A solution of compound **3aa** (200 mg, 0.5 mmol) in dry THF (10 ml) was cooled to -20 °C in argon. Methylmagnesium bromide (119 mg, 1 mmol) in THF was added slowly at -20°C and the reaction mixture stirred for 30 minutes under argon. The reaction mixture was quenched with saturated NH_4Cl and extracted with ethyl acetate (5 mL×3). The organic layer was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:4) to afford product **5** as a white solid (155mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.84-7.80 (m, 1H), 7.77-7.72 (m, 1H), 7.66-7.61 (m, 1H), 7.56-7.53 (m, 1H), 7.49-7.44 (m, 3H), 7.44-7.37 (m, 4H), 7.36-7.27 (m, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 1H), 1.32 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 161.3, 149.7, 139.5, 135.7, 134.7, 132.0, 131.7, 130.6, 130.4, 129.9, 129.25, 129.1, 128.0, 127.8, 127.6, 127.5, 127.4, 126.7, 125.6, 122.1, 120.5, 74.3, 60.1, 27.8, 13.8; ESI-MS *m/z* 432.1 $(M + Na)^+$; HRMS calcd for $C_{27}H_{23}NNaO_3^+$ $(M + Na)^+$ 432.1570, found 432.1578.

ethyl 7-phenyl-8-methylene-5,8-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]pyrrole-6-carboxylate (6): A solution of methyl triphenylphosphonium bromide (214 mg, 0.6 mmol) in anhydrous PhMe (5 mL) was cooled to 0°C under argon, followed by addition of *t*-BuOK (67mg, 0.6 mmol). The reaction mixture was stirred at 0°C for 30 minutes, and then a solution of compound **3aa** (200 mg, 0.5 mmol) in anhydrous PhMe (2 mL) was added dropwise. The resulting mixture was warmed gradually to 110°C and kept stirring for 8 h. The reaction mixture was quenched with saturated NaCl and extracted with ethyl acetate (5 mL×3). The organic layer was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure.[2] The residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:5) to afford product **6** as a white solid (173 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.72-7.69 (m, 1H), 7.63-7.57 (m, 2H), 7.50-7.30 (m, 10H), 5.15 (d, *J* = 1.6 Hz, 1H), 4.66 (d, *J* = 1.6 Hz, 1H), 4.30-4.21 (m, 1H), 4.15-4.06 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 161.4, 145.2, 140.8, 138.2, 136.8, 133.8, 131.7, 131.1, 130.7, 130.6, 129.5, 128.4, 128.3, 127.9, 127.8, 127.4, 127.4, 126.8, 125.8, 120.5, 118.7, 115.3, 60.4, 14.0; ESI-MS *m/z* 392.1 $(M + H)^+$; HRMS calcd for $C_{27}H_{22}NO_2^+$ $(M + H)^+$ 392.1645, found 392.1649.

V. References

1. J. P. Knowles, V. E. O'Connor, A. Whiting, *Org. Biomol. Chem*., **2011**, 9, 1876-1886.
2. X. T. Li, Q. S. Gu, X. Y. Dong, X. Meng, X. Y. Liu, *Angew. Chem. Int. Ed*., **2018**, 57, 7668-7672.

VI. NMR Spectra