Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fluorescent Coumarin-Alkynes for Labeling of Amino Acids and Peptides *via* Manganese(I)-Catalyzed C–H Alkenylation

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1. General Remarks

Catalytic reactions were performed under a N_2 atmosphere using pre-dried glassware and standard Schlenk techniques. 1,4-dioxane was dried over CaH_2 and freshly distilled under N_2. Unless stated otherwise, peptides were synthesized under standard solution phase protocols (EDCI/HOBt) according to previously described methods. Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR. **Flash chromatography**: Merck silica gel 60 (40–63 μm). **NMR**: All spectra were recorded at 295 K on a Varian Mercury Vx 300, Varian VNMRS 300, Bruker Avance III HD 400 and Bruker Avance III 400 instrument in the solvent indicated; chemical shifts (δ) are provided in ppm. **IR**: All spectra were recorded on a Bruker FT-IR Alpha device. **MS**: HPLC-MS analysis was recorded on HPLC Agilent 1200 System comprising a Kinetex C18 column (5 μm, 100 Å, 150 x 4.6 mm) and a MS detector configured with an electrospray ionization source (6110 quadrupole LC/MS). ESI-MS was recorded on Bruker Daltonic *micrOTOF.* High resolution mass spectrometry (HR-MS) was recorded on *micrOTOF*, Bruker Daltonic. MALDI analysis was recorded on Bruker UltrafleXtreme MALDI TOF-TOF. **Melting points (Mp.)**: All compounds were measured on StuartTM melting point apparatus SMP3, and the values are uncorrected. **Spectroscopic measurements**: Spectral properties were recorded in a 10 mm quartz cuvette on a JASCO V-770 spectrophotometer. All compounds were measured at room temperature dissolved in a 10 mM solution in MeOH. All E/Z ratios are determined by ^{1}H NMR given by *major E* and *minor Z*.

General Procedure of Manganese-Catalyzed C–H Alkenylation of Amino Acids and Peptides (GP1)

A dry flask was preloaded with the corresponding amino acid or peptide (0.10 mmol, 1.0 equiv.) and alkyne (0.11 mmol, 1.1 equiv.), the catalyst $MnBr(CO)_5$ (2.0 mg, 7.5 mol %) was added and pre-dissolved in a 1,4-dioxane stock solution (2.0 mg/ 1 mL) and added to the solid ingredients. The solution was stirred at 90 °C for 20 h under N_2 atmosphere. After cooling to ambient temperature, the mixture was dissolved in CH_2Cl_2 (3 mL), concentrated in vacuo, and purified by *flash*-column chromatography on silica gel to obtain the desired product.

General Procedures of Alkyne Synthesis (GP2)

Regarding to Taran[1] or Liu[2] the corresponding hydroxy-coumarin or hydroxy-chromone (5.0 – 7.5 mmol, 1.0 equiv.) was dissolved in dry CH_2Cl_2 (0.2 M), dry triethylamine (5.0 equiv.) was added at 0°C, followed by a drop-wise addition of triflic anhydride (1.2 equiv.). After 3 h at 0 °C the reaction mixture was filtered over celite, and the filtrate was concentrated by reduced pressure. The crude product was redissolved in dry MeCN (0.2 M) at room temperature, DIPEA (1.2 equiv.), CuI (10 mol%), tetrakis(triphenylphosphene) palladium (5 mol%) and trimethylsilylacetylene

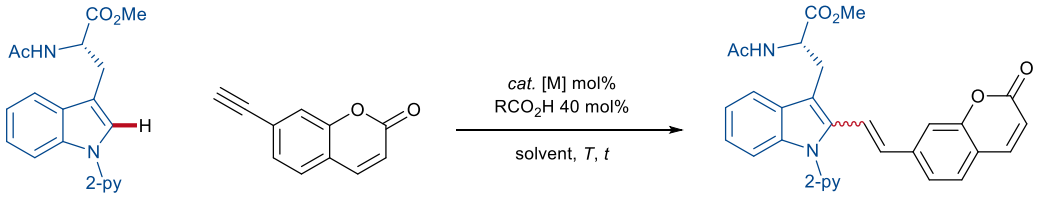
(1.1 equiv.) was added. After 12 h of stirring excess solvent was removed and the crude was dissolved in dry THF (0.2 M) followed by the addition of KF (1.2 equiv.) and were stirred for 1 h at ambient temperature. The crude was product *flash*-column chromatography on silica gel (*n*-hexane/EtOAc, 10:1 to 1:1) to obtain the corresponding desired alkyne.

General Procedures of 3-Methoxypropyne-alkyne Synthesis (GP3)

Regarding to Nilsson[3] or Krupadanam[4], the corresponding 3-methoxypropyne-alkyne were obtained by adding K_2CO_3 (3.0 equiv.) and propargyl bromide (1.5 equiv., 80 wt% in PhMe) to a solution of hydroxyl coumarin or chromone (3–6 mmol, 1.0 equiv.) in dry acetone (0.05 M). The reaction mixture was heated to 60 °C for 16 h. After cooling to room temperature, volatiles were removed under reduced pressure. The residue was extracted in EtOAc by water (1 x 100 mL), brine (2 x 80 mL), and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by *flash*-column chromatography (*n*-hexane/EtOAc).

Optimization Studies

Table S-1 Optimization of the manganese catalyzed alkenylation with coumarin **2**.



1 **2** **3**

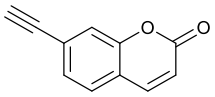
Entry	Catalyst Loading (mol%)	Catalyst	RCO_2H	Solvent	Temperature (°C)	Time (h)	Yield (%)[a], *E*/*Z*[b]
1	20	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	92, 9/1[a]
2	15	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	92, 9/1[a]
3	10	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	91, 9/1[a]
4	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	91, 9/1[a]
5	5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	82, 8/2[a]
6	2.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	68, 8/2[a]
7	0	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	120	24	-,-
8	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	*m*-xylene	120	24	15, 8/2
9	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	DCE	120	24	69, 8/2[a]
10	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	DMF	120	24	traces,-
11	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	DMSO	120	24	-,-
12	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	PhMe	120	24	-,-
13	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	100	24	91, 9/1[a]

14	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	90	24	89, >9/1[a]
15	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	80	24	74, 8/2[a]
16	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	60	24	55, 8/2[a]
17	**7.5**	**$MnBr(CO)_5$**	**1-Ad-CO_2H**	**1,4-dioxane**	**90**	**20**	90, >9/1[a]
18	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	55	71	79, 8/2[a]
19	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	90	16	66, 8/2[a]
20	7.5	$MnBr(CO)_5$	1-Ad-CO_2H	1,4-dioxane	90	12	53, 8/2
21	7.5	$Pd(OAc)_2$	1-Ad-CO_2H	1,4-dioxane	90	24	-,-
22	7.5	$[RuCl_2(p\text{-cymene})]_2$	1-Ad-CO_2H	1,4-dioxane	90	24	-,-
23	7.5	$Co(OAc)_2$	1-Ad-CO_2H	1,4-dioxane	90	24	-,-
24	7.5	$MnBr(CO)_5$	NaOAc	1,4-dioxane	90	24	42, 8/2
25	7.5	$MnBr(CO)_5$	KOAc	1,4-dioxane	90	24	33, 8/2

Reaction conditions: 0.10 mmol of **1**, 0.12 mmol of **2**, 40 mol% of acid and 1.0 mL of solvent were used. [a] Isolated yields. [b] Determined by ^{1}H NMR spectroscopy.

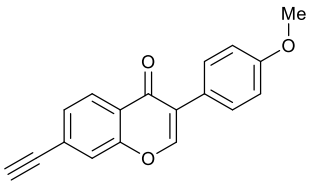
Characterization Data

7-Ethynyl-2*H*-chromen-2-one (2)



Following **GP2** and starting from 7-hydroxy-2*H*-chromen-2-one (1.0 g, 6.2 mmol) the crude was purified by a final *flash*-column chromatography (*n*-hexane/EtOAc, 2:1 to 0:1) to give the desired product **2** (0.81 g, 77%) over three steps as a yellow solid. **Mp.**: 109 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 1.2 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 3.27 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.9, 154.0, 133.7, 128.0, 127.7, 125.6, 120.2, 119.1, 117.2, 82.0, 80.6. **IR (ATR)**: 3109, 3052, 1997, 1667, 1112, 777, 689, 618, **MS (ESI) *m/z* (relative intensity)**: 192.9 (100) $[M+Na]^+$, **HRMS (ESI) *m/z***: Calcd. for $C_{11}H_6O_2$ $[M+Na]^+$ 193.0265; found 193.0261. The data are consistent with the literature.[1]

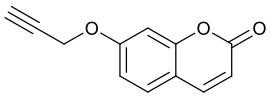
7-Ethynyl-3-(4-methoxyphenyl)-4*H*-chromen-4-one (2a)



Following **GP2** and starting from 7-hydroxy-3-(4-methoxyphenyl)-4*H*-chromen-4-one **2a** (1.5 g, 5.6 mmol) the crude was purified by a final *flash*-column chromatography (*n*-hexane/EtOAc, 2:1 to 0:1) to give the desired product **2a** (1.31 g, 85%) over three steps as an orange solid. **Mp.:** = 186 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.79 – 7.63 (m, 1H), 7.60 (s,

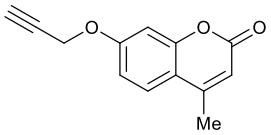
1H), 7.50 – 7.48 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 3.31 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.8, 159.9, 155.8, 152.7, 132.7, 132.1, 130.0, 128.7, 127.5, 126.6, 125.4, 124.5, 123.9, 121.6, 114.0, 81.9, 81.0, 55.3. **IR (ATR)**: 3259, 1641, 1509, 1429, 1244, 1176, 1110, 881, 696 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 277.1 (100) $[M+H]^+$. **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ Calcd. for $C_{18}H_{13}O_3$ 277.0859; found 277.0854. The data are consistent with the literature.[2]

7-(Prop-2-yn-1-yloxy)-2*H*-chromen-2-one (11)



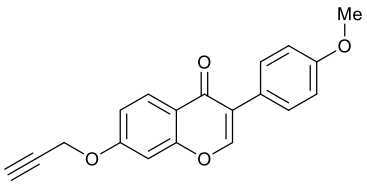
The reaction was performed regarding to **GP3**, starting from the corresponding alcohol (0.5 g, 2.8 mmol) the crude was purified by *flash*-column chromatography (*n*-heptane/EtOAc 4:1 to 1:1) yielding the desired product **11** (0.49 g, 88%) as a beige solid. **Mp.:** = 106 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.27 (d, *J* = 9.6 Hz, 1H), 4.76 (s, 2H), 2.57 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.1, 160.7, 155.8, 143.4, 129.0, 113.8, 113.3, 113.2, 102.3, 77.5, 76.7, 56.3. **IR (ATR)**: 3259, 1642, 1519, 1428, 1284, 1276, 1210, 880, 697 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 201.1 (100) $[M+H]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+H]^+$ Calcd. for $C_{12}H_9O_3$ 201.0552; found: 201.0553. The data are consistent with the literature.[3]

4-Methyl-7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one (11a)



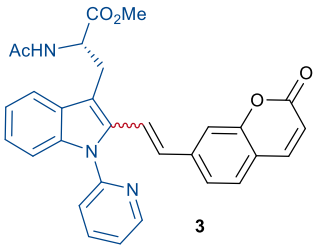
The reaction was performed regarding to **GP3**, starting from the corresponding alcohol (0.5 g, 2.8 mmol) the crude was purified by *flash*-column chromatography (*n*-heptane/EtOAc 4:1 to 1:1) yielding the desired product **11a** (0.47 g, 79%) as a beige solid. **Mp.:** = 111 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.2 Hz, 1H), 7.29 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 4.79 (s, 2H), 2.60 (s, 1H), 2.43 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$,) δ 161.2, 160.5, 155.2, 152.5, 125.7, 114.4, 112.8, 112.5, 102.3, 77.5, 76.6, 56.3, 18.8. **IR (ATR)**: 3258, 1642, 1512, 1433, 1274, 1196, 1101, 883, 696 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 215.1 (100) $[M+H]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+H]^+$ Calcd. for $C_{13}H_{11}O_3$ 215.0708; found 215.0704. The data are consistent with the literature.[3]

3-(4-Methoxyphenyl)-7-(prop-2-yn-1-yloxy)-4*H*-chromen-4-one (11b)



The reaction was performed regarding to GP3, starting from the corresponding alcohol (0.5 g, 1.9 mmol) to crude was purified by *flash*-column chromatography (*n*-heptane/EtOAc 4:1 to 1:1) yielding the desired product **11b** (0.46 g, 79%) as a beige solid. **Mp.:** = 146–147 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.5 Hz, 1H), 7.93 (s, 1H), 7.71 (d, *J* = 9.5 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 7.51 Hz, 1H), 7.28 (s, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.95(d, *J* = 2 Hz, 1H), 4.83 (s, 1H), 4.80 (s, 2H), 3.94 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.0, 160.6, 155.5, 152.2, 143.3, 130.1, 128.8, 128.0, 114.8, 114.0, 113.7, 113.2, 113.1, 102.2, 101.6, 56.2, 55.4. **IR (ATR)**: 3279, 1671, 1529, 1439, 1245, 1076, 1010, 899, 697 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 307.1 (100) $[M+H]^+$. **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ Calcd. for $C_{19}H_{15}O_4$ 307.0965; found: 307.0960. The data are consistent with the literature.[4]

Methyl (*S*)-2-acetamido-3-{2-[2-(2-oxo-2*H*-chromen-7-yl)vinyl]-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (3)

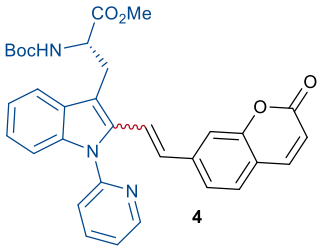


3

Following the general procedure **GP1** the corresponding tryptophane (33.4 mg, 0.10 mmol, 1.0 equiv.) and alkyne (18.7 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.1) yielded **3** (46.7 mg, 92%, *E*/*Z* = >9:1) as a bright yellow solid. **Mp**.: = 113°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 7.0 Hz, 0.9H, *major*), 8.38 (d, *J* = 5.0 Hz, 0.06H, *minor*), 7.92 (*t*, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 9.6 Hz, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.48 – 7.32 (m, 5H), 7.32 – 7.06 (m, 4H), 6.97 – 6.87 (m, 0.06H, *minor*), 6.77 (d, *J* = 12.0 Hz, 0.06H, *minor*), 6.61 (d, *J* = 12.2 Hz, 0.09H, *minor*), 6.45 (d, *J* = 16.7 Hz, 0.98H, *major*), 6.37 (d, *J* = 9.5 Hz, 1H), 6.20 (d, *J* = 7.7 Hz, 1H), 5.00 (td, *J* = 7.2, 5.0 Hz, 1H), 3.67 – 3.56 (m, 2H), 3.55 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.4, 169.8, 160.9, 154.6, 152.0, 150.0, 143.1, 141.3, 138.7, 138.6, 134.2, 129.7, 129.0, 128.3, 124.5, 122.8, 122.5, 122.3, 121.5, 120.0, 119.0, 118.3, 116.1, 114.4, 114.1, 111.0, 53.1, 52.7, 27.9, 23.3. **IR (ATR)**: 1728, 1656, 1605, 1586, 1468, 1435, 1350, 1127,

907, 723, 646 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 530.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{30}H_{25}N_3O_5$ 530.1686; found 530.1685.

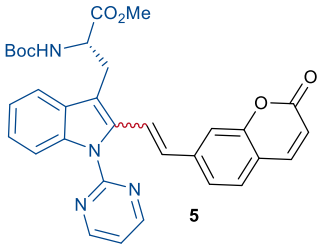
Methyl (*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-[2-(2-oxo-2*H*-chromen-7-yl)vinyl]-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (4)



4

Following the general procedure **GP1** the corresponding tryptophane (39.5 mg, 0.10 mmol, 1.0 equiv.) and alkyne (18.7 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.1) yielded **4** (50.3 mg, 89%, *E*/*Z* = 8:2) as a bright yellow solid. **Mp**.: = 120°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.9 Hz, 0.8H, *major*), 8.39 (d, *J* = 4.9 Hz, 0.2 H, *minor*), 7.91 (td, *J* = 7.8 Hz, 2.0, 1H), 7.71–7.55 (m, 3H), 7.50 – 7.31 (m, 4H), 7.28 – 7.15 (m, 4H), 6.79 (d, *J* = 12.0 Hz, 0.2 H, *minor*), 6.63 (d, *J* = 12.0 Hz, 0.2 H, *minor*), 6.50 (d, *J* = 16.6 Hz, 1H, *major*), 6.37 (d, *J* = 9.5 Hz, 1H), 5.26 (d, *J* = 8.4 Hz, 0.8 H, *major*), 5.15 (d, *J* = 8.1 Hz, 0.2 H, *minor*), 4.75 (q, *J* = 6.9 Hz, 0.8 H, *major*), 4.64 (q, *J* = 6.7 Hz, 0.2 H, *minor*), 3.74 – 3.27 (m, 5H), 1.38 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.7, 172.6 (*minor*), 160.9, 160.9 (*minor*), 155.1, 154.6, 153.9 (*minor*), 152.0, 151.0 (*minor*), 149.9, 148.9 (*minor*), 143.1 (minor), 141.4, 138.6, 138.5 (*minor*), 137.5, 137.4 (*minor*), 134.0, 129.8, 129.1, 128.1, 127.7, 124.6 (*minor*), 124.4, 124.0 (*minor*), 122.7, 122.6, 122.3, 121.8 (*minor*), 121.5, 121.3 (*minor*), 120.7 (*minor*), 120.2, 119.3, 118.2, 117.9 (*minor*), 116.4, 116.0, 114.7, 114.1, 111.3 (*minor*), 111.0, 80.1, 54.4, 54.1 (*minor*), 52.6, 52.5 (*minor*), 28.9 (*minor*), 28.4. **IR (ATR)**: 1729, 1606, 1453, 1366, 1167, 1101, 907, 722, 646 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 566.2 (10) $[M+H]^+$, 588.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{33}H_{31}N_3O_6$ 588.2105; found 588.2105.

Methyl (*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-[2-(2-oxo-2*H*-chromen-7-yl)vinyl]-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (5)

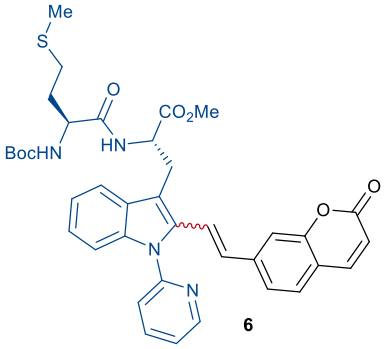


5

Following the general procedure **GP1** the corresponding tryptophane (39.7 mg, 0.10 mmol, 1.0 equiv.) and alkyne (18.7 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.1) yielded **5** (46.5 mg, 82%, *E*/*Z* = 8:2) as a bright

yellow solid. **Mp**.: = 119.8°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 1.56H, major), 8.63 (d, *J* = 4.8 Hz, 0.44H, minor), 8.23 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 9.5 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.42 (s, 2H), 7.34 – 7.27 (m, 1H), 7.24 – 7.11 (m, 2H), 7.07 – 6.90 (m, 1H), 6.82 (d, *J* = 16.5 Hz, 0.67H, major), 6.64 (d, *J* = 12.0 Hz, 0.23H, minor), 6.36 (d, *J* = 9.5 Hz, 0.78H, major), 6.31 (d, *J* = 9.5 Hz, 0.21H, minor), 5.23 (d, *J* = 8.3 Hz, 1H), 4.71 (q, *J* = 7.3 Hz, 1H), 3.52 (s, 3H), 3.45 (d, *J* = 7.5 Hz, 2H), 1.38 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.9, 172.6 (*minor*), 161.0, 160.9 (*minor*), 158.5, 158.2 (*minor*), 158.0, 157.7 (*minor*), 155.1, 154.6, 154.0 (*minor*), 143.2, 143.1 (*minor*), 141.8, 141.2 (*minor*), 137.0, 136.8 (*minor*), 134.6, 130.0 (*minor*), 129.6, 129.4 (*minor*), 128.1 (*minor*), 127.7 (*minor*), 124.8, 124.5, 124.0 (*minor*), 123.2, 122.91, 122.4, 122.3 (*minor*), 119.1, 118.2, 117.8 (*minor*), 117.7, 117.1, 116.5, 116.3, 116.0, 115.8, 114.2 (*minor*), 113.9, 113.8 (*minor*), 80.1, 79.9 (*minor*), 54.2, 53.7 (*minor*), 52.5, 52.4 (*minor*), 29.1, 28.4. **IR (ATR)**: 1729, 1688, 1606, 1454, 1419, 1153, 1126, 907, 723, 647 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 589.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{32}H_{30}N_4O_6$ 589.2058; found 589.2051.

Methyl (*S*)-2-[(*S*)-2-[(*tert*-butoxycarbonyl)amino]-4-(methylthio)butanamido]-3-{2-[2-(2-oxo-2*H*-chromen-7-yl)vinyl]-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (6)

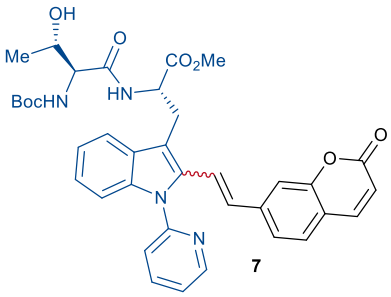


6

Following the general procedure **GP1** the corresponding dipeptide (52.7 mg, 0.10 mmol, 1.0 equiv.) and alkyne (20.4 mg, 0.12 mmol, 1.2 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **6** (43.9 mg, 63%, *E*/*Z* = 9:1) as a bright yellow solid. **Mp**.: = 114.8°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.2 Hz , 0.86H *major*), 8.53 (d, *J* = 4.2 Hz, 0.07H *minor*), 8.19 – 7.76 (m, 1H), 7.63 (dd, *J* = 8.7, 4.0 Hz, 3H), 7.50 – 7.33 (m, 5H), 7.30 – 7.06 (m, 5H), 6.77 – 6.62 (m, 1H), 6.33 (d, *J* = 9.5 Hz, 1H), 6.19 (s, 1H), 5.47 (d, *J* = 7.7 Hz, 1H), 4.58 – 4.44 (m, 1H), 4.38 (d, *J* = 6.4 Hz, 1H), 3.58 (d, *J* = 4.3 Hz, 1H), 3.49 – 3.33 (m, 3H), 2.40 – 2.12 (m, 3H), 1.96 (s, 3H), 1.44 (d, *J* = 7.1 Hz, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 171.2, 161.0, 155.3, 154.6, 151.8, 149.9, 149.0, 143.1, 141.6, 138.6, 138.3, 133.9, 129.8, 128.9, 128.1, 127.7 (*minor*), 124.3, 122.9, 122.7, 122.4, 121.6, 121.5 (*minor*), 120.2, 119.2, 118.2, 115.9, 114.1, 114.0, 110.9, 80.3, 55.5, 52.6 (*minor*), 52.5, 51.8, 51.7 (*minor*), 32.0, 29.8, 29.6, 29.1, 28.5, 28.3 (*minor*) 15.4. **IR (ATR)**: 1729, 1665, 1606, 1469, 1435, 1366, 1163, 1126, 1101, 906, 833, 721, 646, 616 cm^{-1}. **MS**

(ESI-TOF) *m/z* (relative intensity): 719.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{38}H_{40}N_4O_7S$ 719.2502; found 719.2510.

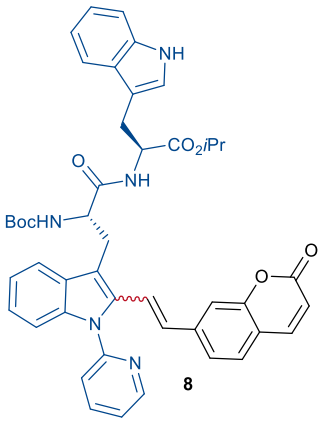
Methyl (*S*)-2-{(2*S*,3*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-hydroxybutanamido}-3-{2-[2-(2-oxo-2*H*-chromen-7-yl)vinyl]-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (7)



7

Following the general procedure **GP1** the corresponding diepeptide (49.6 mg, 0.10 mmol, 1.0 equiv.) and alkyne (20.4 mg, 0.12 mmol, 1.2 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) and purification by GPC yielded **7** (34.0 mg, 51%, *E*/*Z* = >9:1) as a bright yellow solid. **Mp**.: = 132°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.90 Hz, 0.93 H, *major*), 8.39 (d, *J* = 4.90 Hz, 0.05H *minor*), 7.94 (td, *J* = 7.7, 1.9 Hz, 1H), 7.72 (dd, *J* = 6.7, 1.9 Hz, 1H), 7.63 (d, *J* = 9.5 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.30 (m, 5H), 7.24 – 7.07 (m, 3H), 6.55 (d, *J* = 16.6 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 6.33 (d, *J* = 9.5 Hz, 1H), 5.50 (d, *J* = 7.3 Hz, 1H), 4.57 (q, *J* = 7.0 Hz, 1H), 4.29 (dd, *J* = 7.7, 3.6 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.61 – 3.35 (m, 5H), 2.94 (d, *J* = 6.0 Hz, 1H), 1.44 (s, 8.59H *major*), 1.34 (s, 0.71H *minor*), 1.06 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.8, 170.4, 161.0, 155.5, 154.5, 151.8, 149.9, 143.2, 141.5, 138.9, 138.5, 134.1, 129.9, 128.9, 128.1, 124.4, 122.9, 122.8, 122.5, 121.7, 120.4, 119.5, 118.2, 116.0, 114.8, 114.2, 110.7, 80.3, 68.3, 58.0, 55.5, 52.5, 28.9, 28.3, 20.1. **IR (ATR)**: 1729, 1699, 1663, 1605, 1469, 1454, 1436, 1366, 1165, 1165, 1127, 908, 726, 646 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 689.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{37}H_{38}N_4O_8$ 689.2573; found 689.2582.

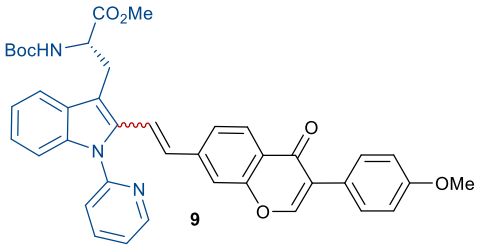
Isopropyl {(*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-(2-[2-(2-oxo-2*H*-chromen-7-yl)vinyl]-1-(pyridin-2-yl)-1*H*-indol-3-yl]propanoyl}-L-tryptophanate (8)



8

Following the general procedure **GP1** the corresponding dipeptide (60.9 mg, 0.10 mmol, 1.0 equiv.) and alkyne (20.4 mg, 0.12 mmol, 1.2 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) and purification by GPC yielded **8** (40.2 mg, 51%, *E*/*Z* = 8:2) as a bright yellow solid. **Mp**.: = 111°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.0 Hz, 0.8 H, *major*), 8.68 (s, 0.8 H, *major*), 8.56 (s, 0.2 H, *minor*), 8.42 (d, *J* = 5.0 Hz, 0.2 H, *minor*), 7.88 (td, *J* = 7.8 Hz, 2.0, 1H), 7.77 – 7.69 (m, 1H), 7.64 (d, *J* = 9.4 Hz, 1H), 7.50 – 7.32 (m, 6H), 7.25–7.15 (m, 3H), 7.18 – 6.81 (m, 4H), 6.75 (d, *J* = 12.0 Hz, 0.2 H, *minor*), 6.57 (d, *J* = 12.0 Hz, 0.2 H, *minor*), 6.52 – 6.42 (m, 1H), 6.42 – 6.27 (m, 2H), 6.20 (d, *J* = 7.0 Hz, 1H), 5.27 (d, *J* = 7.1 Hz, 0.8 H, *major*), 5.03 (d, *J* = 7.1, 0.2 H, *minor*), 4.95 – 4.73 (m, 1H), 4.69 (q, *J* = 6.1 Hz, 0.2 H, *minor*), 4.66 – 4.38 (m, 2H), 3.71 – 3.46 (m, 1H), 3.44 – 3.27 (m, 1H), 3.21 – 3.09 (m, 1H), 3.08 – 2.92 (m, 1H), 1.85 (s, 1H), 1.42 (s, 7.47H *major*), 1.31 (s, 1.86H *minor*), 1.14 – 1.00 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.9 (*minor*), 170.9, 170.6, 161.0, 160.9 (*minor*), 155.3, 154.5 (*minor*), 153.9 (*minor*), 152.0, 149.7, 148.8, 143.1, 141.4 (*minor*), 138.9, 138.6, 136.1 (*minor*), 136.1, 134.1, 133.1, 132.4, 129.8, 129.0, 128.0, 127.7 (*minor*), 127.6, 124.5, 124.4 (*minor*), 124.0 (*minor*), 123.0, 122.8, 122.7, 122.0, 121.6, 121.5 (*minor*), 120.9 (*minor*), 120.3, 119.7, 119.4, 118.6 (*minor*), 118.6, 118.1, 118.0 (*minor*), 116.5, 116.3, 115.9, 114.6, 114.3, 111.3 (*minor*), 111.3, 110.8, 109.7 (*minor*), 109.6, 80.1, 69.3 (*minor*), 69.2, 55.3, 53.3, 53.2 (*minor*), 28.4, 28.3 (*minor*), 27.4 (*minor*), 27.4, 21.7, 21.7. **IR (ATR)**: 1729, 1699, 1454, 1226, 1103, 905, 724, 646, 616 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 802.3 $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M + Na]^+$ Calcd. for $C_{46}H_{45}N_5O_7$ 802.3203; found 802.3211.

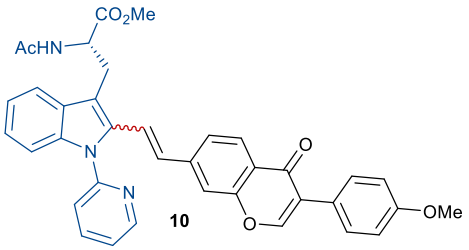
Methyl (*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{2-[3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl]vinyl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (9)



9

Following the general procedure **GP1** the corresponding tryptophane (39.6 mg, 0.10 mmol, 1.0 equiv.) and alkyne (30.4 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **9** (56.5 mg, 84%, *E*/*Z* = 9:1) as an orange solid. **Mp**.: = 115°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.9 Hz, 0.9H, *major*), 8.43 (d, *J* = 4.9 Hz, 0.1 H, *minor*), 8.23 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.92 (td, *J* = 7.8 Hz, 2.1, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.33 (m, 5H), 7.21 (t, *J* = 6.7 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 3H), 6.85 (d, *J* = 12.0 Hz, 0.1 H, *minor*), 6.67 (d, *J* = 12.0 Hz, 0.1 H, *minor*), 6.54 (d, *J* = 16.6 Hz, 0.9 H, *major*), 5.28 (d, *J* = 8.3 Hz, 1H), 4.79 – 4.77 (m, 1H), 3.86 (s, 3H), 3.66 – 3.45 (m, 5H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.1, 172.7, 159.8, 156.7, 155.2, 152.6, 152.1, 149.9, 143.0, 138.6, 134.0, 130.2, 129.6, 129.1, 126.7, 125.2, 124.5, 124.2, 123.5, 123.1, 122.6, 122.3, 121.5, 120.8, 119.4, 115.4, 115.0, 114.1, 111.0, 80.1, 55.5, 54.5, 52.6, 28.9, 28.4. **IR (ATR):** 1745, 1608, 1555, 1468, 1431, 1366, 1177, 1149, 907, 724, 646, 614 cm^{-1}. **MS (ESI-TOF) *m*/*z* (relative intensity):** 694.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF)** *m*/*z*: $[M+Na]^+$ Calcd. for $C_{40}H_{37}N_3O_7$ 694.2521; found 694.2524.

Methyl (*S*)-2-acetamido-3-{2-{2-[3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl]vinyl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (10)

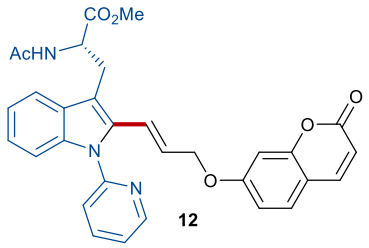


10

Following the general procedure **GP1** the corresponding tryptophane (39.6 mg, 0.10 mmol, 1.0 equiv.) and alkyne (30.4 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **10** (41.7 mg, 68%, *E*/*Z* = 8:2) as an orange solid. **Mp**.: = 109.8°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.6 Hz, 0.82H, *major*), 8.39 (d, *J* = 4.9 Hz, 0.18H, *minor*), 8.19 (d, *J* = 8.8 Hz, 1H), 7.99 – 7.86 (m, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.26 Hz, 2H), 7.43 – 7.30 (m, 5H), 7.29 – 7.04 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 12.0 Hz, 0.19H, *minor*), 6.63 (d, *J* = 12.2 Hz, 0.17H, *minor*), 6.44 (d, *J* = 16.6 Hz, 0.82H, *major*), 6.26 (d, *J* = 7.9 Hz, 0.74H, *major*), 6.15 (d, *J* = 7.6 Hz, 0.20H, *minor*), 5.06 – 4.87 (m, 1H), 3.82 (s,

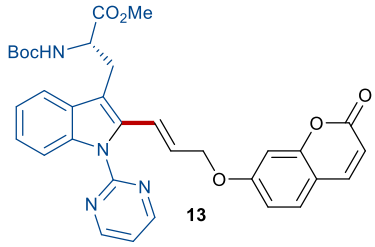
3H), 3.63 – 3.54 (m, 2H), 3.53 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.1, 172.4 (*minor*), 172.3, 169.9, 169.8 (*minor*), 159.7, 156.7, 156.1 (*minor*), 152.6, 152.0, 150.9 (*minor*), 149.9, 149.1, 142.8, 142.2 (*minor*), 138.7, 137.7, 137.4 (*minor*), 134.1, 133.0, 131.3 (*minor*), 130.2, 129.5, 129.0, 126.8, 126.2 (*minor*), 125.4 (*minor*), 125.2, 125.0 (*minor*), 124.6, 124.2, 124.0 (*minor*), 123.5, 123.4 (*minor*), 122.9, 122.8, 122.4, 122.2 (*minor*), 121.5, 120.7 (*minor*), 120.5, 119.1, 117.4, 115.3, 114.7, 114.1, 112.7 (*minor*), 111.3 (*minor*), 111.0, 55.4, 53.1, 52.9 (*minor*), 52.7, 52.5 (*minor*), 27.9, 27.6 (*minor*), 23.3. **IR (ATR)**: 1637, 1608, 1433, 1248, 1227, 1177, 1028, 904, 885, 724, 646, 547 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 636.2 (100) $[M+H]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+H]^+$ Calcd. for $C_{37}H_{31}N_3O_6$ 636.2105; found 636.2106.

Methyl (*S*,*E*)-2-acetamido-3-{2-{3-[(2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (12)



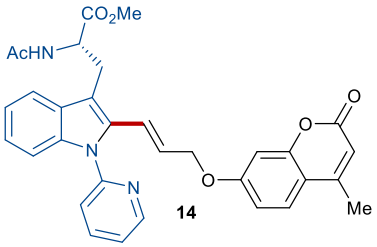
Following the general procedure **GP1** the corresponding amino acid (33.7 mg, 0.10 mmol, 1.0 equiv.) and alkyne (22.2 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **12** (50.0 mg, 93%, *E*/*Z* = >20:1) as a light orange solid. **Mp**.: = 110°C **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 6.0 Hz, 1H), 7.86 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.65 (d, *J* = 9.6 Hz, 1H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.46 – 7.29 (m, 4H), 7.28 – 7.16 (m, 2H), 6.93 – 6.74 (m, 3H), 6.27 (d, *J* = 9.5 Hz, 1H), 6.18 (d, *J* = 7.8 Hz, 1H), 5.77 (dt, *J* = 16.3, 5.4 Hz, 1H), 4.96 (q, *J* = 6.6 Hz, 1H), 4.70 (d, *J* = 5.5 Hz, 2H), 3.61 (s, 3H), 3.57 – 3.41 (m, 2H), 1.96 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.4, 169.8, 161.6, 161.2, 155.9, 151.8, 149.7, 143.5, 138.5, 138.1, 133.6, 128.9, 128.8, 127.2, 124.1, 122.6, 122.2, 122.1, 121.3, 119.0, 113.4, 113.3, 112.8, 112.8, 111.0, 101.8, 69.0, 53.0, 52.6, 27.6, 23.3. **IR (ATR)**: 1723, 1656, 1609, 1505, 1469, 1454, 1435, 1274, 1228, 1121, 908, 834, 725, 616 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity):** 560.2 (100) $[M+Na]^+$. HR-MS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{31}H_{27}N_3O_6$ 560.1792; found 560.1794.

Methyl (*S*,*E*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{3-[(2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (13)



Following the general procedure **GP1** the corresponding tryptophane (34.1 mg, 0.10 mmol, 1.0 equiv.) and alkyne (22.2 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **13** (52.4 mg, 88%, *E*/*Z* = >20:1) as a light orange solid. **Mp**.: = 111–112°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 9.5 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.35 – 7.13 (m, 3H), 7.09 (d, *J* = 16.3 Hz, 1H), 6.92 (dq, *J* = 4.5, 2.4 Hz, 2H), 6.26 (d, *J* = 9.5 Hz, 1H), 6.05 (dt, *J* = 16.6, 5.6 Hz, 1H), 5.17 (d, *J* = 8.2 Hz, 1H), 4.84 (d, *J* = 7.4 Hz, 2H), 4.65 (q, *J* = 6.8 Hz, 1H), 3.60 (s, 3H), 3.39 (d, *J* = 6.9 Hz, 2H), 1.40 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.9, 161.9, 161.2, 158.4, 158.0, 155.9, 155.1, 143.5, 136.6, 134.3, 129.8, 128.9, 127.1, 124.8, 124.4, 122.2, 119.0, 117.5, 117.4, 114.6, 113.9, 113.6, 113.3, 113.2, 112.7, 101.9, 80.0, 69.3, 54.2, 52.4, 28.4. **IR (ATR)**: 1700, 1610, 1560, 1420, 1343, 1154, 1120, 906, 833, 724, 647 cm^{-1}**. MS (ESI-TOF) *m*/*z* (relative intensity)**: 619.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m*/*z*:** $[M+Na]^+$ Calcd. for $C_{33}H_{32}N_4O_7$ 619.2172; found 619.2163.

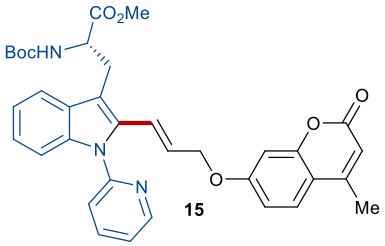
Methyl (*S*,*E*)-2-acetamido-3-{2-{3-[(2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (14)



14

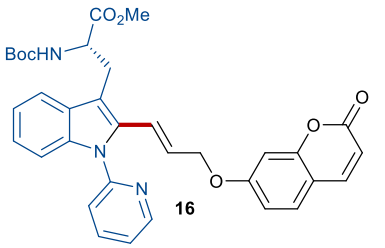
Following the general procedure **GP1** the corresponding tryptophane (33.7 mg, 0.10 mmol, 1.0 equiv.) and alkyne (23.5 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **14** (44.1 mg, 80%, *E*/*Z* = >20:1) as a light orange solid. **Mp.:** 121°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.84 (td, *J* = 7.6, 1.9 Hz, 1H), 7.53 (dd, *J* = 6.2, 1.5 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.12 (m, 2H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.76 (dd, *J* = 16.1, 2.1 Hz, 2H), 6.18 (d, *J* = 7.8 Hz, 1H), 6.13 (d, *J* = 1.3 Hz, 1H), 5.74 (dt, *J* = 16.4, 5.6 Hz, 1H), 4.96 – 4.88 (m, 1H), 4.65 (dd, *J* = 5.6, 1.6 Hz, 2H), 3.59 (s, 3H), 3.51 – 3.39 (m, 2H), 2.39 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 169.8, 161.3, 161.2, 155.2, 152.6, 151.7, 149.6, 138.6, 138.5, 138.0, 133.5, 128.7, 127.2, 125.7, 124.0, 122.5, 122.2, 122.0, 121.2, 118.9, 113.8, 112.9, 112.9, 112.8, 112.1, 110.9, 101.8, 77.1, 68.9, 53.0, 52.5, 27.5, 23.2, 18.7. **IR (ATR):** 1723, 1656, 1609, 1505, 1469, 1454, 1435, 1274, 1228, 1121, 908, 834, 725, 616 cm^{-1}. **MS (ESI-TOF) *m*/*z* (relative intensity):** 574.2 (100) $[M+Na]^+$, **HR-MS (ESI-TOF) *m*/*z*:** $[M+Na]^+$ Calcd. for $C_{32}H_{29}N_3O_6$ 574.1949; found 574.1949.

Methyl (*S*,*E*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{3-[(4-methyl-2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (15)



Following the general procedure **GP1** the corresponding amino acid (39.6 mg, 0.10 mmol, 1.0 equiv.) and alkyne (23.5 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **15** (41.4 mg, 68%, *E*/*Z* = >20:1) as a light orange solid. **Mp**.: = 118–119°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.9 Hz, 1H), 7.83 (td, *J* = 7.8 Hz, 2.0, 1H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.18 (dq, *J* = 8.7, 3.8, 2.4 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.81 – 6.65 (m, 2H), 6.14 (s, 1H), 5.77 (dt, *J* = 16.3, 5.6 Hz, 1H), 5.15 (d, *J* = 8.3 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 2H), 3.60 (s, 3H), 3.39 (d, *J* = 6.3 Hz, 2H), 2.39 (s, 3H), 1.51 – 1.19 (m, 10H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.7, 161.5, 161.3, 155.3, 155.2, 152.6, 151.8, 149.7, 138.4, 138.0, 133.5, 128.9, 127.4, 125.7, 124.0, 122.4, 122.3, 122.1, 121.3, 119.2, 113.9, 113.1, 112.9, 112.2, 111.0, 101.9, 80.0, 69.1, 54.3, 52.5, 38.9, 36.6, 28.4, 18.8. **IR (ATR)**: 1747, 1699, 1611, 1469, 1435, 1366, 1135, 907, 723, 646 cm^{-1}. **MS (ESI-TOF) *m*/*z* (relative intensity)**: 632.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m*/*z***: $[M+Na]^+$ Calcd. for $C_{35}H_{35}N_3O_7$ 632.2363; found 632.2367.

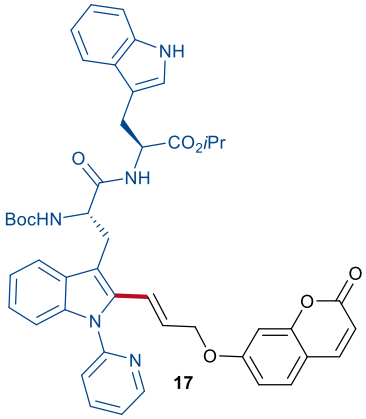
Methyl (*S*,*E*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{3-[(2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (16)



Following the general procedure **GP1** the corresponding amino acid (39.6 mg, 0.10 mmol, 1.0 equiv.) and alkyne (22.2 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **16** (53.0 mg, 89%, *E*/*Z* = >20:1) as a light orange solid. **Mp**.: = 111°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.4 Hz, 1H), 7.82 (td, *J* = 7.7 Hz, 2.0, 1H), 7.63 (d, *J* = 9.7 Hz, 1H),7.57 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.24 (m, 4H), 7.24 – 7.08 (m, 2H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.80 – 6.69 (m, 2H), 6.26 (d, *J* = 9.5 Hz, 1H), 5.78 (dt, *J* = 16.4, 5.6 Hz, 1H), 5.14 (d, *J* = 8.3 Hz, 1H), 4.66 (d, *J* = 4.2 Hz, 2H), 3.60 (s, 3H), 3.40 (d, *J* = 6.3 Hz, 2H), 1.70 (s, 1H), 1.39 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.8, 161.7, 161.2, 155.9, 155.2, 151.8, 149.7,

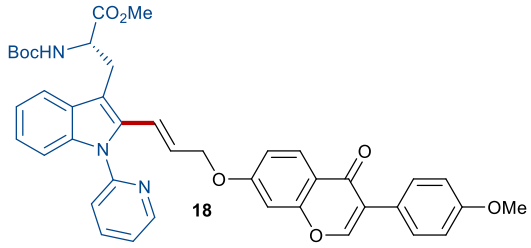
143.5, 138.5, 138.0, 133.5, 128.9, 127.3, 124.0, 122.5, 122.3, 122.2, 121.3, 119.2, 113.4, 113.3, 113.1, 112.8, 111.0, 101.9, 80.0, 69.1, 54.3, 52.5, 28.4. **IR (ATR)**: 1741, 1701, 1610, 1505, 1155, 1121, 1015, 908, 834, 725, 647 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 618.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{34}H_{33}N_3O_7$ 618.2203; found 618.2211.

Isopropyl {(*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{(*E*)-3-[(2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoyl}-L-tryptophanate (17)



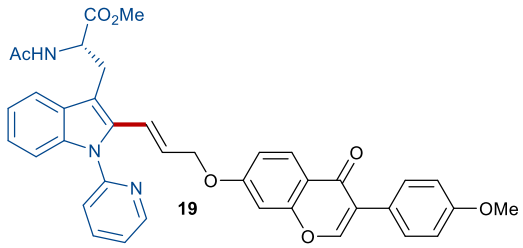
Following the general procedure **GP1** the corresponding dipeptide (61.0 mg, 0.10 mmol, 1.0 equiv.) and alkyne (22.2 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **17** (53.0 mg, 66%, *E*/*Z* = >20:1) as a light orange solid. **Mp**.: = 131–132°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.9, 2.0 Hz, 2H), 7.80 (td, *J* = 7.8 Hz, 2.0, 1H), 7.75 – 7.65 (m, 1H), 7.60 (d, *J* = 9.5 Hz, 1H), 7.46 – 7.28 (m, 4H), 7.25 –7.14 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.75 – 6.66 (m, 1H), 6.49 (s, 1H), 6.24 (d, *J* = 9.4 Hz, 2H), 5.67 (dt, *J* = 16.4, 5.6 Hz, 1H), 5.15 (s, 1H), 4.95 – 4.72 (m, 1H), 4.64 – 4.38 (m, 4H), 3.48 (d, *J* = 13.5 Hz, 1H), 3.38 – 3.22 (m, 1H), 3.12 (qd, *J* = 14.9, 5.8 Hz, 2H), 1.80 (s, 1H), 1.38 (s, 9H), 1.10 (d, *J* = 3.8 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.0, 170.8, 161.7, 161.3, 155.8, 155.2, 151.8, 149.5, 143.5, 138.7, 138.1, 136.1, 133.5, 128.8, 128.7, 127.7, 124.1, 123.0, 122.7, 122.6, 122.3, 122.0, 121.5, 119.7, 119.4, 118.6, 113.3, 113.2, 112.7, 111.3, 110.9, 109.7, 102.0, 69.2, 69.1, 55.1, 53.3, 28.4, 28.1, 27.3, 21.8, 21.7. **IR (ATR)**: 1729, 1703, 1610, 1469, 1454, 1228, 1123, 1103, 906, 834, 723, 647, 616 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 832.3 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{47}H_{47}N_5O_8$ 832.3309; found 832.3317.

Methyl (*S*,*E*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{3-{[3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl]oxy}prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (18)



Following the general procedure **GP1** the corresponding amino acid (39.5 mg, 0.10 mmol, 1.0 equiv.) and alkyne (33.7 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **18** (56.7 mg, 80%, *E*/*Z* = >20:1) as a dark orange solid. **Mp**.: = 141 °C. **^{1}H NMR** (300 MHz, CH_2Cl_2) δ 8.63 (d, *J* = 5.4 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 1H), 7.99 – 7.73 (m, 2H), 7.72 – 7.47 (m, 4H), 7.47 – 7.36 (m, 7H), 7.33 – 7.14 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.81 (d, *J* = 16.3 Hz, 1H) 5.19 (d, *J* = 7.9 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 2H), 3.87 (s, 3H), 3.63 (s, 3H), 3.43 (d, *J* = 6.7 Hz, 2H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 172.8, 162.8, 159.8, 157.9, 152.2, 151.9, 149.7, 138.4, 138.1, 133.5, 130.1, 128.9, 128.0, 127.2, 125.1, 124.3, 124.1, 122.4, 122.2, 121.4, 119.3, 118.7, 115.1, 114.1, 113.2, 111.0, 101.3, 80.0, 69.2, 55.5, 54.3, 52.5, 28.4. **IR (ATR)**: 1701, 1608, 1436, 1366, 1244, 1177, 1029, 906, 832, 724, 548 cm^{-1}. **MS (ESI-TOF) *m*/*z* (relative intensity):** 724.2 $[M+Na]^+$. HR-MS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{41}H_{39}N_3O_8$ 724.2619; found 724.2629.

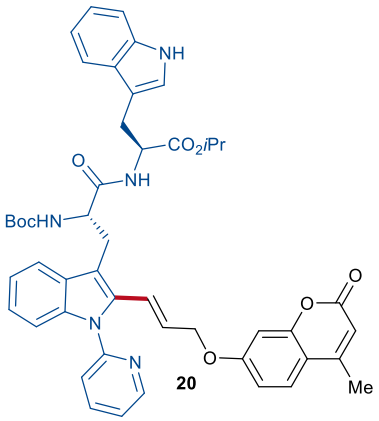
Methyl (*S*,*E*)-2-acetamido-3-{2-{3-{[3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl]oxy}prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoate (19)



Following the general procedure **GP1** the corresponding tryptophane (33.7 mg, 0.10 mmol, 1.0 equiv.) and alkyne (33.7 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded in **19** (53.5 mg, 83%, *E*/*Z* = >20:1) as a dark orange solid. **Mp**.: = 126 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.8 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.92 (s, 1H), 7.87 – 7.72 (m, 1H), 7.58 – 7.42 (m, 3H), 7.42 – 7.34 (m, 1H), 7.33 – 7.26 (m, 2H), 7.23 – 7.14 (m, 2), 7.07 – 6.89 (m, 3H), 6.86 – 6.71 (m, 2H), 6.22 (d, *J* = 7.8 Hz, 1H), 5.77 (td, *J* = 16.0, 5.7 Hz, 1H) 4.97 – 4.87 (m, 1H), 4.69 (d, *J* = 1.5 Hz, 2H), 3.83 (s, 3H), 3.60 (s, 3H), 3.47 (d, *J* = 9.2 Hz, 2H), 1.95 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.8, 172.4, 169.8, 162.6, 159.7, 157.8, 152.2, 151.7, 149.6, 138.4, 138.0, 133.6, 130.2, 128.8, 127.9, 127.0, 124.9, 124.2, 124.0,

122.5, 122.2, 122.0, 121.3, 118.9, 118.6, 114.9, 114.0, 112.9, 111.0, 101.3, 69.0, 55.4, 53.0, 52.6, 27.5, 23.20. **IR (ATR)**: 1623, 1512, 1246, 1177, 1030, 903, 834, 723, 646, 547 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 666.2 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z*:** $[M+Na]^+$ Calcd. for $C_{38}H_{33}N_3O_7$ 666.2211; found 666.2206.

Isopropyl {(*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{2-{(*E*)-3-[(4-methyl-2-oxo-2*H*-chromen-7-yl)oxy]prop-1-en-1-yl}-1-(pyridin-2-yl)-1*H*-indol-3-yl}propanoyl}-L-tryptophanate (20)



Following the general procedure **GP1** the corresponding dipeptide (61.0 mg, 0.10 mmol, 1.0 equiv.) and alkyne (23.5 mg, 0.11 mmol, 1.1 equiv.) were used. Purification by *flash*-column chromatography on silica gel (DCM/MeOH 10:0.15) yielded **20** (53.6 mg, 65%, *E*/*Z* = >20:1) as a light orange solid. **Mp**.: = 130–131 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.67 (d, *J* = 5.0 Hz, 1H), 7.79 (td, *J* = 7.8, 1.9 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.49 – 7.28 (m, 4H), 7.25 – 7.12 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.75 – 6.64 (m, 1H), 6.52 (s, 1H), 6.40 – 6.20 (m, 1H), 6.11 (s, 1H), 5.69 (dt, *J* = 16.3, 5.6 Hz, 1H), 5.17 (d, *J* = 7.9 Hz, 1H), 4.90 – 4.77 – 4.79 (m, 1H), 4.71 – 4.35 (m, 4H), 3.47 (d, *J* = 14.4 Hz, 1H), 3.39 – 3.23 (m, 1H), 3.12 (dq, *J* = 13.3, 5.9 Hz, 2H), 2.36 (s, 3H), 1.38 (s, 9H), 1.18 – 1.00 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.0, 170.7, 161.4, 161.4, 155.2, 155.1, 152.7, 151.7, 149.4, 138.6, 138.0, 136.1, 133.5, 128.6, 127.7, 127.6, 125.6, 124.0, 123.1, 122.6, 122.5, 122.2, 121.2, 121.4, 119.6, 119.3, 118.5, 113.7, 113.1, 112.9, 112.0, 111.3, 110.9, 109.5, 102.0, 80.0, 69.2, 69.0, 55.0, 53.3, 28.3, 28.1, 27.3, 21.7, 18.7. **IR (ATR)**: 1700, 1666, 1469, 1454, 1069, 905, 724, 646 cm^{-1}. **MS (ESI-TOF) *m/z* (relative intensity)**: 846.3 (100) $[M+Na]^+$. **HR-MS (ESI-TOF) *m/z***: $[M+Na]^+$ Calcd. for $C_{48}H_{49}N_5O_8$ 846.3468; found 846.3473.

Computational Studies

Calculations were performed using the Gaussian 16, Revision A.03 package.[5] All structures were optimized at the TPSS[5] level of theory in combination with Grimme's D3 dispersion corrections with the Becke-Johnson damping scheme [D3(BJ)][7] in combination with a def2-SVP basis set.[8] Analytical frequency calculations were carried out at the same level of theory in order to identify

the stationary points either as intermediates (no imaginary frequencies) or transition states (only one imaginary frequency), as well as to provide thermal and non-thermal corrections to the free energy in gas-phase at 363 K and 1 atm. The electronic energy was then refined through PW6B95[9] single-point calculations on the optimized geometries in combination with a standalone version of Grimme's D4[10] dispersion corrections with a def2-TZVP basis set.[8] Solvent effects were included through the use of the implicit solvation model SMD[11] with a dielectric constant of ε = 2.2099, which corresponds to 1,4-dioxane, the solvent of choice used in the experimental work. Unless otherwise stated, the energies herein provided are based on gas-phase Gibbs free energies with def2-SVP basis set for which the electronic energies were improved at the PW6B95-D4/def2-TZVP+SMD(1,4-dioxane) level of theory. The first transition state was found to be facile with an energy barrier of 14.2 kcal·mol^{-1}. Upon alkyne coordination, migratory insertion was proven to be exergonic with a barrier of 19 kcal·mol^{-1}, revealing it to be the rate determining step. Afterwards proto-demetalation (TS(5-6)), takes place leading to the formation of the desired product (complex I-6). The transition state for the corresponding *Z*-isomer could not be calculated. The diastereoselectivity of the hydroarylation likely due to isomerization of secondary intermediates.

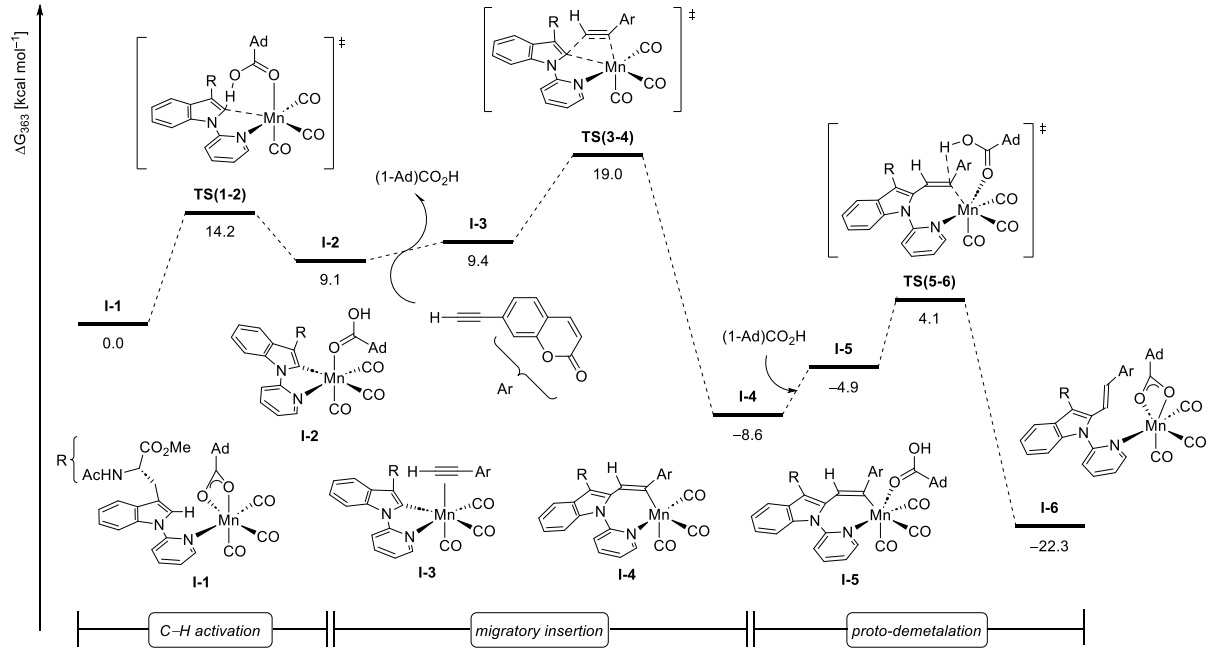


Figure S1. Computed Gibbs free energies (ΔG_{363}) in kcal·mol^{-1} between the C–H activation and proto-demetalation elementary steps at the PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/def2-SVP level of theory.

Cartesian Coordinates and Energies

(1-Ad)CO_2H

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]

= −580.273221 E_h

Total Gibbs Free Energy = −580.106185 E_h

Lowest frequency = 36.370 cm^{-1}

Charge = 0, Multiplicity =1

29

C	0.242656	-0.690697	1.262500
H	0.604330	-0.171242	2.169678

H	0.668974	-1.709214	1.271252
C	0.741843	0.068183	-0.000056
C	-1.298093	-0.747457	1.260150
H	-1.638195	-1.284354	2.164932
C	-1.868690	0.685629	1.259634
H	-1.541116	1.224569	2.168688
H	-2.974369	0.652424	1.280240
C	0.156419	1.496820	-0.000611
H	0.524373	2.043885	-0.886901
H	0.524432	2.044583	0.885216
C	-1.383688	1.432070	-0.000557
H	-1.788368	2.460738	-0.000955
C	-1.868731	0.684641	-1.260143
H	-2.974411	0.651421	-1.280692
H	-1.541183	1.222856	-2.169636
C	0.242612	-0.691712	-1.261974
H	0.668910	-1.710244	-1.269910
H	0.604267	-0.173012	-2.169594
C	-1.781453	-1.495843	0.000608
H	-1.390639	-2.530911	0.001007
H	-2.885672	-1.562905	0.000658
C	-1.298138	-0.748447	-1.259541
H	-1.638274	-1.286065	-2.163883
C	2.261682	0.133883	-0.000041
O	2.827888	-1.106722	-0.000011
H	3.796237	-0.953790	0.000065
O	2.934887	1.146576	0.000014

alkyne

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]

= –574.133008 E_h

Total Gibbs Free Energy = –574.069466 E_h

Lowest frequency = 80.730 cm^{-1}

Charge = 0, Multiplicity =1

C	-4.062851	-1.175797	-0.006714
C	-4.016355	1.267874	-0.012569
C	-3.297185	0.044593	-0.006153
C	-1.883040	0.096639	0.000355
H	-1.320501	-0.842988	0.005330
C	-1.212127	1.313295	0.000480
C	-1.944640	2.533733	-0.005991
C	-3.354318	2.500981	-0.012526
H	-3.529853	-2.133465	-0.001832
H	-0.119789	1.348774	0.005519
H	-3.940226	3.422600	-0.017566
O	-5.378324	1.288276	-0.019010
C	-6.169129	0.116393	-0.019810
O	-7.370489	0.251472	-0.025782
C	-5.425732	-1.141384	-0.013196
H	-6.035652	-2.048112	-0.013804
C	-1.254874	3.784902	-0.005863
C	-0.658894	4.850766	-0.005714
H	-0.136903	5.791261	-0.005600

Int1

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]

= –3199.299899 E_h

Total Gibbs Free Energy = –3198.889640 E_h

Lowest frequency = 15.080 cm^{-1}

Charge = 0, Multiplicity =1

C	0.750694	-4.573352	-1.419440
C	0.389928	-3.635253	-0.454026
C	1.785601	-2.016668	-1.381706
C	2.209482	-2.912902	-2.380909
C	1.700055	-4.210910	-2.387982
H	0.299129	-5.568700	-1.403189
H	-0.342410	-3.858239	0.327264
H	2.891886	-2.558226	-3.156774

H	2.011078	-4.919739	-3.161856
C	3.478101	-0.152743	-1.602545
C	1.968442	1.583165	-1.278904
N	2.191905	-0.678876	-1.406396
Mn	0.690384	-1.421047	1.541975
C	2.303904	-0.635479	1.467612
O	3.372616	-0.175272	1.495072
O	1.872211	-3.790558	2.844223
C	3.362900	1.270259	-1.516112
C	4.527449	2.054213	-1.636625
C	5.758069	1.418145	-1.824363
H	4.468871	3.145864	-1.574464
C	4.711551	-0.797377	-1.763573
C	5.849782	0.009438	-1.881765
H	6.669303	2.017923	-1.918460
H	4.792980	-1.887964	-1.780990
H	6.828673	-0.462978	-2.012944
N	0.923460	-2.389197	-0.398989
O	0.203478	-0.060475	4.118708
C	0.390533	-0.620308	3.118070
C	1.424465	-2.847181	2.329508
O	-0.795188	-0.082337	0.695891
O	-1.334382	-2.096375	1.362844
C	1.299998	0.385588	-1.220527
H	0.243127	0.181684	-1.068995
C	1.304671	2.927504	-1.167656
H	0.746888	3.139330	-2.096530
H	2.051964	3.731144	-1.048093
C	0.251501	2.995724	-0.015750
H	-0.226333	2.003499	0.077570
C	2.459065	2.671052	2.954774
H	3.282546	1.946648	2.985023
H	2.830839	3.706798	2.995195
H	1.756414	2.498481	3.786037
O	1.790194	2.430189	1.697644
C	0.881226	3.342598	1.326198
O	0.605712	4.339528	1.974559
N	-0.781392	3.987393	-0.262740
H	-0.783125	4.789527	0.371096
C	-1.833833	3.716425	-1.086726
C	-2.939169	4.760966	-1.119363
H	-3.830500	4.343629	-0.618583
H	-2.660896	5.705706	-0.624283
H	-3.211188	4.958423	-2.168400
O	-1.890708	2.676783	-1.753270
C	-4.010009	-1.958468	0.543141
H	-4.119167	-2.019831	1.641210
H	-3.576175	-2.918406	0.210228
C	-3.050440	-0.804841	0.181990
C	-5.379075	-1.722864	-0.126260
H	-6.060406	-2.550818	0.143648
C	-5.972007	-0.384399	0.363400
H	-6.119911	-0.415552	1.459749
H	-6.965302	-0.220512	-0.095722
C	-3.650084	0.545607	0.660428
H	-2.951865	1.357611	0.399460
H	-3.759419	0.530699	1.761280
C	-5.019345	0.769606	-0.011859
H	-5.439143	1.729567	0.343640
C	-4.839433	0.818760	-1.543973
H	-5.816001	1.001205	-2.031810
H	-4.158032	1.642250	-1.821699
C	-2.876242	-0.735306	-1.365921
H	-2.414027	-1.674872	-1.725363
H	-2.203314	0.102726	-1.615799
C	-5.199102	-1.677719	-1.658173
H	-4.788133	-2.640435	-2.018400
H	-6.179542	-1.536619	-2.151273
C	-4.249817	-0.521214	-2.031182
H	-4.111884	-0.487209	-3.127630
C	-1.679828	-1.004327	0.790554

TS(1-2)

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]

= –3199.270444 E_h

Total Gibbs Free Energy = –3198.866987 E_h

Lowest frequency = –1125.970 cm^{-1}

Charge = 0, Multiplicity =1

79

C	0.855007	-4.637080	-1.945375
C	0.442337	-4.026401	-0.762344
C	1.968783	-2.275026	-1.036446
C	2.425662	-2.822614	-2.251403
C	1.867084	-4.019057	-2.698443
H	0.386247	-5.569454	-2.270055
H	-0.349942	-4.455227	-0.143169
H	3.164548	-2.285596	-2.846568
H	2.203067	-4.455796	-3.644203
C	3.577621	-0.350895	-0.692010
C	2.166856	0.816432	0.727849
N	2.394175	-1.067252	-0.512359
Mn	0.388177	-1.905115	1.457895
C	1.954891	-2.153419	2.283639
O	2.985288	-2.297768	2.804979
O	-0.788808	-4.307095	2.746909
C	3.454322	0.845836	0.081213
C	4.515747	1.773663	0.100569
C	5.674436	1.492537	-0.626651
H	4.429180	2.696571	0.681919
C	4.751601	-0.645634	-1.404528
C	5.790444	0.291895	-1.363546
H	6.510369	2.199614	-0.616821
H	4.877407	-1.577439	-1.959658
H	6.716196	0.082780	-1.909507
N	0.993248	-2.882623	-0.301552
O	-0.629263	-0.100542	3.574752
C	-0.212723	-0.818278	2.757486
C	-0.341739	-3.361611	2.236119
O	-0.810735	0.240997	-0.635247
O	-1.491381	-1.617822	0.431564
C	1.522236	-0.373719	0.387179
H	0.276170	-0.131040	-0.112278
C	1.503660	1.960562	1.427741
H	2.230556	2.554901	2.009516
H	0.727129	1.599706	2.118634
C	0.812524	2.901635	0.381088
H	0.126453	2.280583	-0.219782
C	-1.838048	4.385583	2.504117
H	-2.639841	3.783714	2.952395
H	-1.219051	4.858768	3.283646
H	-2.252642	5.168638	1.848535
O	-1.046819	3.459024	1.733612
C	0.020725	3.983942	1.097670
O	0.321919	5.163883	1.130372
N	1.752033	3.535809	-0.520250
H	2.041890	4.482401	-0.272033
C	2.012389	3.024599	-1.770781
C	3.002080	3.829664	-2.599489
H	3.987657	3.336272	-2.528253
H	2.685658	3.805127	-3.653523
H	3.104632	4.874957	-2.262683
O	1.525216	1.967596	-2.164466
C	-3.224366	0.357261	-2.078214
H	-2.857714	-0.377220	-2.819608
H	-2.554658	1.232515	-2.130993
C	-3.151126	-0.261050	-0.661498
C	-4.679497	0.755064	-2.396385
H	-4.721779	1.189290	-3.412240
C	-5.583707	-0.493327	-2.326589
H	-5.255093	-1.240440	-3.073819
H	-6.627126	-0.221163	-2.574885
C	-4.065011	-1.503051	-0.584981
H	-3.995802	-1.947752	0.422531

H	-3.708899	-2.267336	-1.300679
C	-5.517828	-1.099844	-0.909348
H	-6.162483	-1.996600	-0.858350
C	-6.003516	-0.056418	0.118553
H	-7.053458	0.222715	-0.090973
H	-5.976128	-0.487123	1.137212
C	-3.648281	0.795655	0.373201
H	-2.983200	1.677124	0.342480
H	-3.580560	0.366829	1.390371
C	-5.163131	1.798902	-1.367956
H	-4.528795	2.703877	-1.420782
H	-6.198822	2.110412	-1.601396
C	-5.101318	1.192979	0.049469
H	-5.442483	1.940648	0.789870
C	-1.715223	-0.591305	-0.273724

Int2

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]

= –3199.284875 E_h

Total Gibbs Free Energy = –3198.879973 E_h

Lowest frequency = 9.610 cm^{-1}

Charge = 0, Multiplicity =1

79

C	1.942313	2.470080	3.616732
C	1.310762	1.258842	3.338994
C	0.340605	2.101918	1.383586
C	0.978846	3.344997	1.579072
C	1.778843	3.525514	2.706216
H	2.556328	2.572472	4.514929
H	1.427004	0.396346	3.999856
H	0.871620	4.138404	0.841890
H	2.280743	4.485014	2.866590
C	-1.086451	2.611837	-0.652501
C	-1.701262	0.391230	-0.974055
N	-0.483628	1.791685	0.318731
Mn	-0.178597	-0.792386	1.623013
C	-1.792685	-0.638594	2.355023
O	-2.851456	-0.504144	2.819647
O	0.863738	-2.282660	3.996261
C	-1.845971	1.739539	-1.489662
C	-2.587060	2.268767	-2.562746
C	-2.574681	3.651477	-2.781523
H	-3.186491	1.610904	-3.199273
C	-1.092635	4.000305	-0.858474
C	-1.841401	4.504712	-1.933340
H	-3.148876	4.076608	-3.611127
H	-0.562462	4.696358	-0.207170
H	-1.856186	5.585665	-2.106895
N	0.531015	1.065756	2.253437
O	-0.741514	-3.350934	0.237318
C	-0.572869	-2.340658	0.788152
C	0.483642	-1.699147	3.062988
O	1.348675	-0.471380	-1.413283
O	1.859530	-0.819058	0.758142
C	-0.867866	0.420118	0.138946
H	0.429184	-0.325624	-1.011829
C	-2.476219	-0.788197	-1.481297
H	-1.913462	-1.726311	-1.363668
H	-2.702885	-0.669885	-2.555802
C	-3.833918	-0.993358	-0.726989
H	-3.616916	-1.263219	0.317177
C	-4.984751	2.411705	0.187148
H	-4.735229	2.886468	1.145389
H	-4.566943	2.989669	-0.653728
H	-6.074778	2.312650	0.063084
O	-4.366303	1.109644	0.231864
C	-4.665567	0.279633	-0.780709
O	-5.473014	0.527948	-1.661798
N	-4.607518	-2.069789	-1.311934
H	-5.246783	-1.810698	-2.063709
C	-4.626186	-3.325214	-0.753049

C	-5.531392	-4.332023	-1.451641
H	-6.126568	-3.895091	-2.270690
H	-4.906417	-5.147245	-1.854262
H	-6.207490	-4.776300	-0.702823
O	-3.948321	-3.616771	0.228774
C	4.564565	-1.052447	0.354041
H	4.290895	-2.056849	0.723684
H	4.387155	-0.347328	1.185228
C	3.659456	-0.677491	-0.839175
C	6.041929	-1.017512	-0.084361
H	6.679082	-1.290491	0.776379
C	6.264216	-2.022862	-1.233379
H	6.025160	-3.047485	-0.891851
H	7.327129	-2.020506	-1.539512
C	3.888883	-1.680219	-2.003732
H	3.231563	-1.416789	-2.850412
H	3.611042	-2.697719	-1.671729
C	5.369650	-1.642183	-2.431098
H	5.521714	-2.363308	-3.254808
C	5.728334	-0.221084	-2.913039
H	6.782762	-0.189196	-3.245318
H	5.102612	0.054210	-3.782693
C	4.028448	0.753674	-1.333335
H	3.849590	1.479060	-0.517170
H	3.370090	1.030170	-2.175570
C	6.402359	0.403525	-0.565393
H	6.262342	1.129202	0.258104
H	7.467459	0.446174	-0.860661
C	5.508200	0.784039	-1.763415
H	5.758275	1.804413	-2.107718
C	2.202346	-0.673390	-0.425699

Int3

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]
= –3193.135189 E_h

Total Gibbs Free Energy = –3192.838002 E_h

Lowest frequency = 5.430 cm^{-1}

Charge = 0, Multiplicity =1

69

C	-3.448619	-0.806340	0.991760
H	-4.541305	-0.708070	1.117553
H	-3.050581	-1.182036	1.946676
C	-3.167159	-1.889465	-0.095047
H	-2.167205	-2.323726	0.056805
C	-4.716455	-4.972829	1.257086
H	-4.270285	-5.552901	2.076325
H	-5.709772	-4.588229	1.542434
H	-4.818984	-5.590827	0.350160
O	-3.807372	-3.883213	1.011778
C	-4.183802	-3.026429	0.039566
O	-5.218518	-3.115030	-0.590962
N	-3.219434	-1.321716	-1.431541
H	-3.798071	-0.494162	-1.577163
C	-2.911163	-2.122422	-2.512052
C	-3.231136	-1.524726	-3.873224
H	-3.295217	-0.423801	-3.852413
H	-2.462061	-1.844194	-4.592703
H	-4.202350	-1.927275	-4.212291
O	-2.409933	-3.232887	-2.361904
C	2.293735	3.975480	0.371644
C	1.983019	2.696764	0.827969
C	-0.259693	2.902164	0.184584
C	-0.020680	4.211149	-0.287594
C	1.263390	4.743170	-0.192973
H	3.314255	4.354570	0.465024
H	2.746686	2.061155	1.282136
H	-0.831920	4.803015	-0.704045
H	1.455586	5.758727	-0.553130
C	-2.730699	2.637120	-0.365529
C	-2.875359	0.533637	0.632098
N	-1.477322	2.253577	0.158445

Mn	0.230099	0.266215	1.389396
C	-0.298240	-1.396714	1.835462
O	-0.602572	-2.477417	2.136706
C	-0.425371	0.937633	2.931990
O	-0.876652	1.376568	3.905666
C	1.867364	-0.055611	2.120385
O	2.892135	-0.251866	2.634721
C	-1.565659	0.953798	0.748358
C	-3.622863	1.561185	-0.067596
C	-4.965253	1.629661	-0.490399
C	-5.400330	2.755870	-1.199866
H	-5.659642	0.811995	-0.267262
C	-3.168218	3.762458	-1.078513
C	-4.510343	3.807155	-1.489674
H	-6.441131	2.820524	-1.533320
H	-2.511691	4.592711	-1.340113
H	-4.863020	4.679025	-2.049721
N	0.744772	2.162489	0.741595
C	0.022842	-0.384571	-0.663840
H	-0.913974	-0.600256	-1.166974
C	1.269165	-0.328679	-0.544138
C	2.675574	-0.258215	-0.821368
C	3.171656	0.830860	-1.592598
C	4.530667	0.928773	-1.867035
H	2.469746	1.580634	-1.965436
H	4.913513	1.764489	-2.462490
C	4.931249	-1.126505	-0.626006
C	5.440896	-0.042726	-1.389137
C	3.566576	-1.237054	-0.339129
H	3.213591	-2.081717	0.255806
O	5.752448	-2.097996	-0.141911
C	7.150598	-2.105632	-0.353100
O	7.784482	-3.017694	0.123178
C	7.672124	-0.988222	-1.137427
C	6.860974	-0.009510	-1.629601
H	8.752421	-0.993305	-1.302000
H	7.277938	0.816747	-2.216756

TS(3-4)

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)] = –3193.121100 E_h

Total Gibbs Free Energy = –3192.822654 E_h

Lowest frequency = –283.260 cm^{-1}

Charge = 0, Multiplicity =1

69

C	-3.356936	-0.855611	0.786821
H	-4.459708	-0.808116	0.766675
H	-3.066160	-1.100358	1.821061
C	-2.900976	-2.030759	-0.121277
H	-1.869481	-2.325884	0.128278
C	-4.157337	-5.089349	1.552631
H	-3.684856	-5.509417	2.450791
H	-5.199089	-4.791752	1.757535
H	-4.148426	-5.819370	0.726943
O	-3.366560	-3.937890	1.200328
C	-3.794729	-3.250549	0.122809
O	-4.786782	-3.525535	-0.522148
N	-2.946906	-1.635317	-1.519053
H	-3.597353	-0.894031	-1.779701
C	-2.541357	-2.540130	-2.483054
C	-2.869096	-2.153982	-3.915914
H	-2.954595	-1.062833	-4.053195
H	-2.091371	-2.558162	-4.580761
H	-3.832539	-2.618720	-4.192533
O	-1.957342	-3.573602	-2.175086
C	2.274169	4.056146	0.144406
C	1.911004	2.912444	0.851873
C	-0.222040	2.893467	-0.098193
C	0.086274	4.024900	-0.881205
C	1.342816	4.612248	-0.746612
H	3.270631	4.484297	0.277659

H	2.614116	2.421061	1.528435
H	-0.636433	4.407221	-1.600610
H	1.599545	5.490527	-1.347064
C	-2.691111	2.591236	-0.602296
C	-2.806652	0.472165	0.355234
N	-1.424159	2.214289	-0.133279
Mn	0.159838	0.496864	1.590800
C	-0.323298	-1.126088	2.196689
O	-0.618671	-2.174739	2.604120
C	-0.735897	1.316456	2.937654
O	-1.339294	1.854522	3.769670
C	1.708983	0.373035	2.522307
O	2.697213	0.293656	3.130604
C	-1.484329	0.909453	0.451193
C	-3.567519	1.496947	-0.310817
C	-4.930444	1.588534	-0.670250
C	-5.394531	2.753002	-1.288151
H	-5.617269	0.762891	-0.455275
C	-3.165788	3.772132	-1.191885
C	-4.524204	3.835351	-1.535544
H	-6.448954	2.834422	-1.571183
H	-2.525577	4.637171	-1.371175
H	-4.912376	4.747786	-1.999028
N	0.692533	2.338432	0.744464
C	-0.157890	-0.194490	-0.451718
H	-0.860598	-0.722125	-1.097127
C	1.101296	-0.114800	-0.182642
C	2.445062	-0.239089	-0.668280
C	2.780858	0.373219	-1.913254
C	4.074424	0.292332	-2.410364
H	2.003594	0.911606	-2.462484
H	4.328008	0.765081	-3.365531
C	4.740594	-1.007491	-0.465121
C	5.086088	-0.400682	-1.702606
C	3.446141	-0.921329	0.055369
H	3.230483	-1.397700	1.013186
O	5.665152	-1.690275	0.266654
C	7.012136	-1.844794	-0.135901
O	7.745750	-2.469475	0.595516
C	7.361799	-1.220017	-1.407779
C	6.445868	-0.533237	-2.151071
H	8.401469	-1.340412	-1.721812
H	6.734732	-0.073931	-3.103592

Int4

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)] = –3193.167416 E_h

Total Gibbs Free Energy = –3192.866623 E_h

Lowest frequency = 10.850 cm^{-1}

Charge = 0, Multiplicity =1

69

C	1.837626	1.940642	0.677883
H	2.356292	2.219050	1.611352
H	0.767910	2.163369	0.801764
C	2.365131	2.832518	-0.495990
H	1.715714	2.645094	-1.368649
C	0.824474	6.038656	0.551024
H	-0.260313	6.162117	0.666596
H	1.342616	6.188180	1.512001
H	1.225616	6.748327	-0.190460
O	1.011324	4.682576	0.091751
C	2.286131	4.299083	-0.093627
O	3.254303	5.016962	0.084048
N	3.728642	2.539160	-0.880353
H	4.446906	3.159111	-0.503978
C	4.016011	1.623212	-1.861672
C	5.495644	1.395892	-2.120319
H	6.121341	2.257085	-1.832077
H	5.815094	0.518227	-1.529971
H	5.641017	1.164669	-3.186160
O	3.134647	0.991206	-2.445528

C	-0.548375	-4.801685	-1.271685
C	-0.814284	-3.784568	-0.351624
C	1.114444	-2.647155	-0.968919
C	1.446088	-3.613467	-1.924118
C	0.603222	-4.720860	-2.067707
H	-1.242926	-5.641497	-1.359714
H	-1.704320	-3.809702	0.282333
H	2.332193	-3.470028	-2.546847
H	0.830805	-5.497373	-2.804316
C	3.145482	-1.489241	-0.111737
C	2.051948	0.493042	0.372425
N	1.893344	-1.501191	-0.731103
Mn	-0.248606	-1.156741	1.184223
C	-0.503868	0.302269	2.188954
O	-0.701188	1.255066	2.832197
C	0.938189	-1.918673	2.356215
O	1.691630	-2.383225	3.110788
C	-1.701728	-1.896668	1.876498
O	-2.673251	-2.380641	2.308734
C	1.209599	-0.294185	-0.419202
C	3.275133	-0.246467	0.574221
C	4.463712	0.034391	1.278964
C	5.474607	-0.927654	1.301485
H	4.586968	0.988603	1.800262
C	4.140781	-2.475972	-0.060728
C	5.308408	-2.171282	0.645889
H	6.404710	-0.727999	1.842858
H	4.016473	-3.441897	-0.557568
H	6.111702	-2.913659	0.693836
N	0.010295	-2.728468	-0.179333
C	-0.051596	0.093478	-1.112648
H	0.007146	0.616368	-2.082713
C	-1.150462	-0.224954	-0.388565
C	-2.538652	0.008303	-0.784221
C	-2.940464	-0.135457	-2.143593
C	-4.261088	0.074002	-2.521686
H	-2.193284	-0.431123	-2.886270
H	-4.565113	-0.045843	-3.567637
C	-4.832456	0.586624	-0.214242
C	-5.238663	0.444758	-1.567027
C	-3.508725	0.357543	0.175788
H	-3.241802	0.466834	1.229464
O	-5.723415	0.943647	0.755976
C	-7.087880	1.193274	0.498925
O	-7.787353	1.509501	1.435361
C	-7.503558	1.038904	-0.892294
C	-6.624217	0.683138	-1.873048
H	-8.560995	1.229214	-1.091916
H	-6.961827	0.575513	-2.910562

Int5

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)] = –3773.470295 E_h

Total Gibbs Free Energy = –3772.966993 E_h

Lowest frequency = 12.850 cm^{-1}

Charge = 0, Multiplicity =1

98

C	1.407647	-2.114980	4.991092
C	1.771263	-2.164662	3.648542
C	-0.117626	-0.999468	2.983227
C	-0.544976	-0.896043	4.323582
C	0.215189	-1.466059	5.340939
H	2.054470	-2.578162	5.740850
H	2.695220	-2.662206	3.348133
H	-1.466962	-0.348988	4.534511
H	-0.103388	-1.387412	6.384957
C	-2.318816	-0.548759	1.963262
C	-1.696559	1.154426	0.529449
N	-0.925082	-0.418220	1.991103
Mn	1.776522	-1.946932	0.644915
C	1.570753	-3.751610	0.910256

O	1.462378	-4.894642	1.085119
O	4.579269	-1.962782	1.547010
C	-0.546479	0.615248	1.100185
C	-2.824409	0.424182	1.051043
C	-4.210981	0.461169	0.780580
C	-5.046418	-0.454704	1.426430
H	-4.617899	1.193742	0.076625
C	-3.153158	-1.477897	2.603464
C	-4.524076	-1.414023	2.325778
H	-6.122332	-0.440705	1.223913
H	-2.750129	-2.243164	3.272962
H	-5.199753	-2.131726	2.801920
N	1.030096	-1.632586	2.641171
C	0.832387	0.985550	0.818375
H	0.987201	2.071644	0.704181
C	1.881324	0.143179	0.543534
C	3.186352	0.809532	0.317538
C	3.693768	1.703883	1.301738
C	4.927243	2.326153	1.140050
H	3.104061	1.875080	2.207586
H	5.312712	3.002048	1.911601
O	2.729876	-2.477999	-2.103429
C	2.358394	-2.237284	-1.025252
C	3.465622	-1.956889	1.200318
C	3.964188	0.565727	-0.830837
H	3.627156	-0.112252	-1.617527
C	5.194616	1.209191	-0.998458
C	5.707246	2.096819	-0.016490
O	5.889229	0.946712	-2.143083
C	7.146539	1.518411	-2.432863
O	7.672051	1.216912	-3.480959
C	6.990513	2.697379	-0.268024
C	7.674973	2.423165	-1.415720
H	7.409022	3.381467	0.479517
H	8.650130	2.863448	-1.637959
C	-1.751408	2.270941	-0.470127
H	-2.659954	2.187240	-1.086466
H	-0.893307	2.233393	-1.159363
C	-1.773526	3.667024	0.202456
H	-0.790903	3.860107	0.669888
C	-1.967197	4.753301	-0.866477
O	-1.741045	4.589995	-2.047534
O	-2.341619	5.930127	-0.319667
C	-2.600699	6.979928	-1.270467
H	-1.713657	7.159653	-1.899798
H	-3.449346	6.697439	-1.914821
H	-2.845687	7.868670	-0.672583
N	-2.760564	3.777826	1.267968
H	-2.447054	3.740311	2.233775
C	-4.097856	3.800748	0.982362
O	-4.500816	3.795898	-0.183140
C	-2.787370	-2.757557	-0.964543
H	-3.134054	-2.112616	-0.140007
H	-2.210094	-3.582855	-0.512778
C	-1.870902	-1.944299	-1.905470
C	-3.990664	-3.301817	-1.757842
H	-4.641170	-3.872717	-1.070349
C	-4.782962	-2.124559	-2.363273
H	-5.153190	-1.466647	-1.555399
H	-5.665593	-2.503134	-2.912467
C	-2.666411	-0.771273	-2.530666
H	-2.007531	-0.182425	-3.191289
H	-3.015482	-0.102460	-1.726154
C	-3.870082	-1.326524	-3.316787
H	-4.432245	-0.479281	-3.749749
C	-3.367079	-2.248141	-4.446644
H	-4.223039	-2.633538	-5.031645
H	-2.724186	-1.678291	-5.143401
C	-1.365759	-2.877644	-3.053853
H	-0.779740	-3.707552	-2.617941
H	-0.693904	-2.308368	-3.720535
C	-3.489132	-4.225067	-2.886983

H	-2.933765	-5.080791	-2.458849
H	-4.346431	-4.639512	-3.449927
C	-2.575646	-3.423850	-3.837333
H	-2.204094	-4.082530	-4.643641
C	-0.638832	-1.468450	-1.173667
O	-0.249189	-2.003323	-0.119721
O	0.044673	-0.506866	-1.776511
H	0.790131	-0.249248	-1.155603
C	-5.033497	3.788211	2.179430
H	-5.936076	4.364855	1.927917
H	-5.335532	2.744182	2.378133
H	-4.569214	4.199553	3.091423

TS(5-6)

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)]

= –3773.452028 E_h

Total Gibbs Free Energy = –3772.952631 E_h

Lowest frequency = –1108.780 cm^{-1}

Charge = 0, Multiplicity =1

98

C	1.071882	-2.300138	5.051909
C	1.571998	-2.214007	3.756680
C	-0.341442	-1.175459	2.970038
C	-0.913409	-1.217852	4.259459
C	-0.210565	-1.796087	5.311990
H	1.683103	-2.755976	5.835250
H	2.566858	-2.600482	3.527967
H	-1.899544	-0.770859	4.405945
H	-0.641265	-1.830262	6.317468
C	-2.451989	-0.768669	1.756098
C	-1.807661	1.110000	0.571775
N	-1.081220	-0.562609	1.945238
Mn	1.836606	-1.924948	0.774134
C	1.889515	-3.697191	1.103734
O	1.920153	-4.838675	1.317382
O	4.511284	-1.480105	1.956347
C	-0.693547	0.590434	1.219761
C	-2.926802	0.257354	0.887897
C	-4.275471	0.236766	0.467215
C	-5.109477	-0.780006	0.938872
H	-4.653660	1.003448	-0.216035
C	-3.284068	-1.798913	2.222424
C	-4.619908	-1.785476	1.806510
H	-6.156606	-0.811221	0.620872
H	-2.900639	-2.601486	2.858672
H	-5.292016	-2.581470	2.142618
N	0.886883	-1.681944	2.708802
C	0.680509	1.076713	1.125917
H	0.823776	2.146080	1.353185
C	1.711389	0.365718	0.571871
C	3.020434	1.027766	0.397329
C	3.605861	1.766512	1.460661
C	4.847976	2.372121	1.307083
H	3.079807	1.823155	2.418714
H	5.301044	2.926681	2.136199
O	3.172238	-2.434430	-1.820291
C	2.637355	-2.203133	-0.816043
C	3.451605	-1.644712	1.500583
C	3.718822	0.915136	-0.820428
H	3.302435	0.360472	-1.664649
C	4.962171	1.537660	-0.972826
C	5.555028	2.274192	0.086395
O	5.586986	1.407432	-2.177600
C	6.848213	1.975358	-2.460122
O	7.309104	1.797799	-3.564859
C	6.844712	2.865700	-0.155950
C	7.459363	2.724279	-1.365161
H	7.324717	3.433708	0.649489
H	8.437026	3.161633	-1.582113
C	-1.826428	2.298570	-0.342385
H	-2.640118	2.199179	-1.077473

H	-0.886880	2.370723	-0.912385
C	-2.042290	3.631201	0.417576
H	-1.145461	3.852662	1.024358
C	-2.179834	4.784238	-0.589201
O	-1.791699	4.731577	-1.737407
O	-2.711884	5.885560	-0.015746
C	-2.930388	6.986607	-0.917770
H	-1.987838	7.275871	-1.410812
H	-3.665912	6.697449	-1.686236
H	-3.318143	7.806581	-0.297585
N	-3.163325	3.591319	1.347285
H	-2.975096	3.515931	2.342887
C	-4.451614	3.555701	0.888882
O	-4.700279	3.610467	-0.317496
C	-2.440460	-2.908247	-1.240936
H	-2.887463	-2.334693	-0.412182
H	-1.893081	-3.755411	-0.792384
C	-1.453130	-2.010886	-2.016637
C	-3.544879	-3.410863	-2.191760
H	-4.247967	-4.045227	-1.620819
C	-4.301265	-2.204217	-2.784893
H	-4.768179	-1.618176	-1.971784
H	-5.113955	-2.554069	-3.449554
C	-2.210103	-0.808995	-2.630690
H	-1.496625	-0.163185	-3.170270
H	-2.653144	-0.206734	-1.819364
C	-3.316578	-1.317460	-3.575119
H	-3.854136	-0.448725	-3.997466
C	-2.681459	-2.139237	-4.715321
H	-3.464728	-2.491608	-5.412794
H	-1.985416	-1.505921	-5.296672
C	-0.817230	-2.841769	-3.175003
H	-0.257291	-3.694307	-2.747636
H	-0.095474	-2.209079	-3.721784
C	-2.910324	-4.234041	-3.331520
H	-2.378836	-5.110869	-2.915456
H	-3.696968	-4.618455	-4.008051
C	-1.926102	-3.345381	-4.119704
H	-1.460803	-3.933002	-4.932641
C	-0.296977	-1.546804	-1.143655
O	-0.017961	-2.200316	-0.084389
O	0.403798	-0.557026	-1.548643
H	1.161749	-0.275157	-0.512939
C	-5.530002	3.400856	1.948099
H	-6.430966	3.937124	1.614807
H	-5.781353	2.328946	2.040429
H	-5.216996	3.774763	2.937416

Int6

E[(PW6B95-D4/def2-TZVP+SMD(1,4-dioxane)] = –3773.497271 E_h

Total Gibbs Free Energy = –3772.994663 E_h

Lowest frequency = 10.790 cm^{-1}

Charge = 0, Multiplicity =1

98

C	0.994504	-3.875875	-4.207280
C	0.324659	-3.608147	-3.017583
C	1.334862	-1.530385	-2.786749
C	2.011837	-1.710665	-4.013168
C	1.858282	-2.897698	-4.722018
H	0.824488	-4.825602	-4.720772
H	-0.376992	-4.336883	-2.606376
H	2.622294	-0.892667	-4.400254
H	2.380724	-3.046578	-5.672017
C	2.747003	0.314380	-1.883624
C	1.100994	1.387066	-0.644900
N	1.517781	-0.334804	-2.088876
Mn	-0.635796	-2.371476	-0.445460
C	-0.137559	-4.043593	-0.062023
O	0.198560	-5.122144	0.207337
O	-3.063916	-3.328207	-1.847131

C	0.526937	0.318160	-1.323249
C	2.498478	1.409794	-1.005373
C	3.564887	2.246001	-0.612147
C	4.851183	1.953616	-1.071787
H	3.382472	3.101658	0.044747
C	4.044006	-0.003648	-2.314574
C	5.087927	0.832486	-1.898609
H	5.691636	2.587172	-0.771482
H	4.254351	-0.883761	-2.926248
H	6.109804	0.603241	-2.217116
N	0.484718	-2.470953	-2.292555
C	-0.856863	-0.115251	-1.402703
H	-1.241420	-0.369368	-2.399989
C	-1.723037	-0.009035	-0.327591
C	-3.185997	-0.066277	-0.379186
C	-3.912850	-0.230164	-1.589579
C	-5.299342	-0.281988	-1.577494
H	-3.379405	-0.322718	-2.539354
H	-5.855812	-0.416073	-2.511017
O	-2.175641	-2.423730	2.100946
C	-1.526364	-2.325411	1.146047
C	-2.116451	-2.928158	-1.294748
C	-3.891568	0.062612	0.833587
H	-3.361772	0.189260	1.781088
C	-5.290349	0.013660	0.837951
C	-6.021076	-0.163852	-0.364743
O	-5.921537	0.142530	2.037432
C	-7.326590	0.106337	2.178424
O	-7.784003	0.233489	3.290242
C	-7.457394	-0.209229	-0.269767
C	-8.076685	-0.082946	0.938195
H	-8.043778	-0.348924	-1.185142
H	-9.163624	-0.114598	1.046840
C	0.426721	2.418641	0.210448
H	1.185469	2.977055	0.778357
H	-0.245389	1.971286	0.954972
C	-0.366941	3.440045	-0.639799
H	-1.220624	2.926015	-1.118057
C	-0.966087	4.518622	0.274350
O	-1.171552	4.361512	1.459878
O	-1.306273	5.628131	-0.415856
C	-1.827864	6.701093	0.390997
H	-2.710577	6.364034	0.958784
H	-1.054974	7.045986	1.097237
H	-2.094632	7.500353	-0.314213
N	0.428280	4.014886	-1.716510
H	0.265866	3.702205	-2.669474
C	1.481087	4.844274	-1.437745
O	1.723067	5.202043	-0.283487
C	3.688641	-1.401084	1.191796
H	3.730814	-0.713337	0.330909
H	3.505378	-2.412760	0.789461
C	2.524118	-0.999222	2.119903
C	5.021159	-1.352860	1.967016
H	5.846359	-1.635450	1.286402
C	5.256165	0.077138	2.496448
H	5.310097	0.785572	1.648767
H	6.222683	0.130176	3.033604
C	2.768309	0.425617	2.670524
H	1.921544	0.708567	3.318927
H	2.793485	1.142225	1.830373
C	4.102104	0.472741	3.441190
H	4.266477	1.498696	3.820116
C	4.044975	-0.513598	4.625860
H	4.990118	-0.473832	5.200536
H	3.228893	-0.228425	5.316016
C	2.477976	-1.989148	3.321426
H	2.287987	-3.011716	2.943498
H	1.633549	-1.713629	3.978008
C	4.965666	-2.338826	3.152058
H	4.813379	-3.369773	2.779471
H	5.925548	-2.327969	3.703133

C	3.810423	-1.942970	4.094468
H	3.761101	-2.651803	4.942209
C	1.147066	-1.080584	1.446633
O	1.100637	-1.785314	0.351785
O	0.164199	-0.547476	1.992943
H	-1.277888	0.231121	0.645522
C	2.341908	5.247163	-2.623424
H	2.701433	6.275191	-2.466570
H	3.220680	4.578387	-2.659882
H	1.808212	5.181020	-3.58640

Isomerization Studies by Light

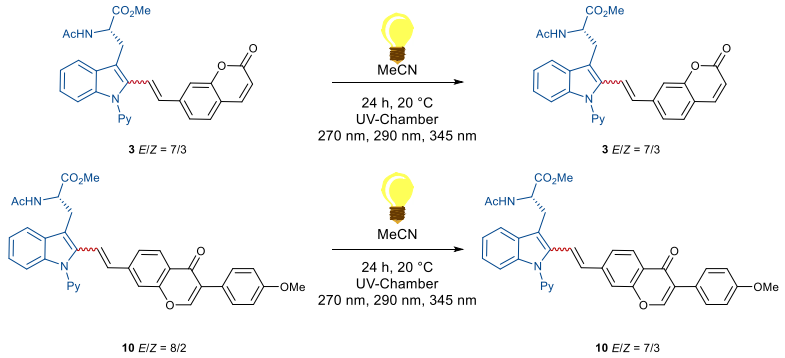


Figure S2. Isomerization of compounds 3 and 10.

Further synthetic isomerization studies were conducted with compounds **3** and **10** to evaluate the influence of UV-light on the *E*/*Z* ratio. Therefore, a UV-chamber with a mercury lamp was used with the wavelengths of 270 nm, 290 nm and 345 nm on a 0.05 mmol scale in dry MeCN (0.1 M). However, the excitation of the isomers led to a poorer ratio of *E*- and *Z* and decomposition.

Isomerization Studies Thermal Conditions

For further investigation of the isomerization, the compound **3** (*E*/*Z*, 8/2) was treated with 40 mol% of $AdCO_2H$, 7.5 mol% of $MnBr(CO)_5$ at 90 °C under N_2-atmosphere in 1,4-dioxane. After 20 h the mixture was flushed over a short plug of celite (EA/MeOH 9/0.2) and exceeded solvent was removed under reduced pressure and the product was reisolated in 96% with the same *E*/*Z* ratio of 8/2.

Removal of the Pyridyl-Directing Group

R.P 1 According to the well-established two-step sequence[12], a stirring solution of the amino acid (1.0 equiv) in CH_2Cl_2 (0.25 M) was treated with MeOTf (1.0 equiv) at 0 °C. After 30-60 min, the mixture was allowed to warm up to 25 °C and stirred for 16-18 h. The crude mixture was concentrated under reduced pressure to afford a bright yellow solid. **R.P 2** For the final removal, in a sealed-tube, the crude product, $Pd(OH)_2/C$ (20 wt.%, 0.1 equiv) or Pd/C (20 wt.%, 0.1 equiv) and ammonium formate (10.0 equiv) or a H_2 (1 atm) saturated solution were dissolved in ethanol (0.5 M) and stirred at 50-60 °C for 16-21 h. This method resulted in fragmentation of compounds **3**, **4**, and **10**.

Besides palladium catalyzed protocols the Raney-Nickel catalyst was investigated. The pyridyl was methylated according to the introduced procedure **R.P 1** treated and further implemented. **R.P 3** Therefore, the Raney-Nickel catalyst was activated with a NaOH (2 M) solution and dried under vacuum. The methylated amino acid (1.0 equiv) was treated with 20 mol% of the activated Raney-Nickel catalyst in MeOH (0.2 M) at 50 °C.[13] This method resulted in fragmentation of compounds **3** and **4**.

Spectrophotometer Data

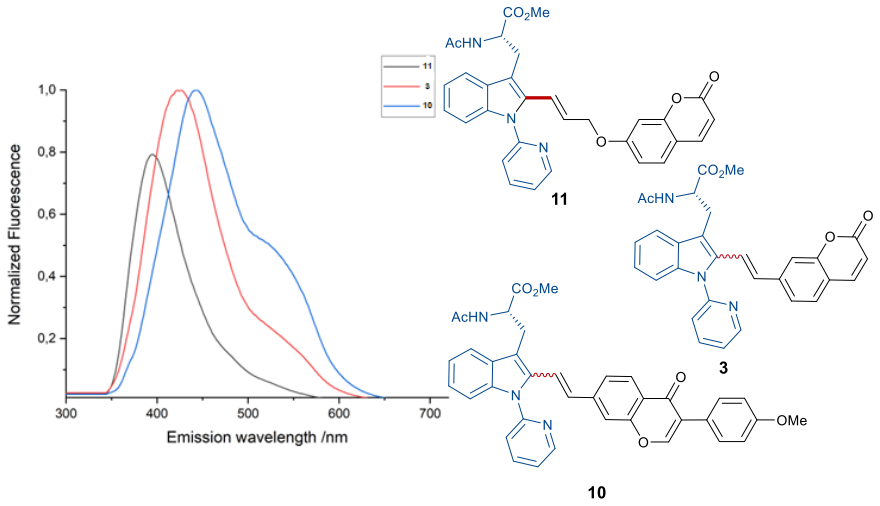


Figure S3. Fluorescence Studies compound **3**, **10**, **11**.

Fluorescent studies showed an emission wavelengths of $\lambda_{em.}$= 426 nm, $\lambda_{em.}$= 396 nm and $\lambda_{em.}$= 443 nm for products **3**, **10** and **11**, respectively within an excitation wavelength of $\lambda_{exc.}$= 330 nm. All here listed Data are given as raw data.

Raw Data of Compound **3**, **10**, **11**:

200	0	0	0	0
201	0,25884	0,38441	0,515	0,00182
202	0,25884	0,38441	0,515	0,00364
203	0,25884	0,38441	0,515	0,00545
204	0,25884	0,38441	0,515	0,00727
205	0,25884	0,38441	0,515	0,00909
206	0,25884	0,38441	0,515	0,01091
207	0,25884	0,38441	0,515	0,01273
208	0,25884	0,38441	0,515	0,01455
209	0,25884	0,38441	0,515	0,01636
210	0,25884	0,38441	0,515	0,01818
211	0,25884	0,38441	0,515	0,02
212	0,25884	0,38441	0,515	0,02182
213	0,25884	0,38441	0,515	0,02364
214	0,25884	0,38441	0,515	0,02545
215	0,25884	0,38441	0,515	0,02727
216	0,25884	0,38441	0,515	0,02909
217	0,25884	0,38441	0,515	0,03091
218	0,25884	0,38441	0,515	0,03273

219	0,25884	0,38441	0,515	0,03455
220	0,25884	0,38441	0,515	0,03636
221	0,25884	0,38441	0,515	0,03818
222	0,25884	0,38441	0,515	0,04
223	0,25884	0,38441	0,515	0,04182
224	0,25884	0,38441	0,515	0,04364
225	0,25884	0,38441	0,515	0,04545
226	0,25884	0,38441	0,515	0,04727
227	0,25884	0,38441	0,515	0,04909
228	0,25884	0,38441	0,515	0,05091
229	0,25884	0,38441	0,515	0,05273
230	0,25884	0,38441	0,515	0,05455
231	0,25884	0,38441	0,515	0,05636
232	0,25884	0,38441	0,515	0,05818
233	0,25884	0,38441	0,515	0,06
234	0,25884	0,38441	0,515	0,06182
235	0,25884	0,38441	0,515	0,06364
236	0,25884	0,38441	0,515	0,06545
237	0,25884	0,38441	0,515	0,06727
238	0,25884	0,38441	0,515	0,06909
239	0,25884	0,38441	0,515	0,07091
240	0,25884	0,38441	0,515	0,07273
241	0,25884	0,38441	0,515	0,07455
242	0,25884	0,38441	0,515	0,07636
243	0,25884	0,38441	0,515	0,07818
244	0,25884	0,38441	0,515	0,08
245	0,25884	0,38441	0,515	0,08182
246	0,25884	0,38441	0,515	0,08364
247	0,25884	0,38441	0,515	0,08545
248	0,25884	0,38441	0,515	0,08727
249	0,25884	0,38441	0,515	0,08909
250	0,25884	0,38441	0,515	0,09091
251	0,25884	0,38441	0,515	0,09273
252	0,25884	0,38441	0,515	0,09455

253	0,25884	0,38441	0,515	0,09636
254	0,25884	0,38441	0,515	0,09818
255	0,25884	0,38441	0,515	0,1
256	0,25884	0,38441	0,515	0,10182
257	0,25884	0,38441	0,515	0,10364
258	0,25884	0,38441	0,515	0,10545
259	0,25884	0,38441	0,515	0,10727
260	0,25884	0,38441	0,515	0,10909
261	0,25884	0,38441	0,515	0,11091
262	0,25884	0,38441	0,515	0,11273
263	0,25884	0,38441	0,515	0,11455
264	0,25884	0,38441	0,515	0,11636
265	0,25884	0,38441	0,515	0,11818
266	0,25884	0,38441	0,515	0,12
267	0,25884	0,38441	0,515	0,12182
268	0,25884	0,38441	0,515	0,12364
269	0,25884	0,38441	0,515	0,12545
270	0,25884	0,38441	0,515	0,12727
271	0,25884	0,38441	0,515	0,12909
272	0,25884	0,38441	0,515	0,13091
273	0,25884	0,38441	0,515	0,13273
274	0,25884	0,38441	0,515	0,13455
275	0,25884	0,38441	0,515	0,13636
276	0,25884	0,38441	0,515	0,13818
277	0,25884	0,38441	0,515	0,14
278	0,25884	0,38441	0,515	0,14182
279	0,25884	0,38441	0,515	0,14364
280	0,25884	0,38441	0,515	0,14545
281	0,25884	0,38441	0,515	0,14727
282	0,25884	0,38441	0,515	0,14909
283	0,25884	0,38441	0,515	0,15091
284	0,25884	0,38441	0,515	0,15273
285	0,25884	0,38441	0,515	0,15455
286	0,25884	0,38441	0,515	0,15636

287	0,25884	0,38441	0,515	0,15818
288	0,25884	0,38441	0,515	0,16
289	0,25884	0,38441	0,515	0,16182
290	0,25884	0,38441	0,515	0,16364
291	0,25884	0,38441	0,515	0,16545
292	0,25884	0,38441	0,515	0,16727
293	0,25884	0,38441	0,515	0,16909
294	0,25884	0,38441	0,515	0,17091
295	0,25884	0,38441	0,515	0,17273
296	0,25884	0,38441	0,515	0,17455
297	0,25884	0,38441	0,515	0,17636
298	0,25884	0,38441	0,515	0,17818
299	0,25884	0,38441	0,515	0,18
300	0,25884	0,38441	0,515	0,18182
301	0,25884	0,38441	0,515	0,18364
302	0,25884	0,38441	0,515	0,18545
303	0,25884	0,38441	0,515	0,18727
304	0,25884	0,38441	0,515	0,18909
305	0,25884	0,38441	0,515	0,19091
306	0,25884	0,38441	0,515	0,19273
307	0,25884	0,38441	0,515	0,19455
308	0,25884	0,38441	0,515	0,19636
309	0,25884	0,38441	0,515	0,19818
310	0,25884	0,38441	0,515	0,2
311	0,25884	0,38441	0,515	0,20182
312	0,25884	0,38441	0,515	0,20364
313	0,25884	0,38441	0,515	0,20545
314	0,25884	0,38441	0,515	0,20727
315	0,25884	0,38441	0,515	0,20909
316	0,25884	0,38441	0,515	0,21091
317	0,25884	0,38441	0,515	0,21273
318	0,25884	0,38441	0,515	0,21455
319	0,25884	0,38441	0,515	0,21636
320	0,25884	0,38441	0,515	0,21818

321	0,25884	0,38441	0,515	0,22
322	0,25884	0,38441	0,515	0,22182
323	0,25884	0,38441	0,515	0,22364
324	0,25884	0,38441	0,515	0,22545
325	0,25884	0,38441	0,515	0,22727
326	0,25884	0,38441	0,515	0,22909
327	0,25884	0,38441	0,515	0,23091
328	0,25884	0,38441	0,515	0,23273
329	0,25884	0,38441	0,515	0,23455
330	0,25884	0,38441	0,515	0,23636
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336	0,25884	0,38441	0,515	0,24727
337	0,25884	0,38441	0,515	0,24909
338	0,25884	0,38441	0,515	0,25091
339	0,25884	0,38441	0,515	0,25273
340	0,25884	0,38441	0,515	0,25455
341	0,25884	0,38441	0,515	0,25636
342	0,25884	0,38441	0,515	0,25818
343	0,27491	0,40015	0,52531	0,26
344	0,27491	0,40019	0,52474	0,26182
345	0,27692	0,40192	0,52547	0,26364
346	0,27968	0,40397	0,52625	0,26545
347	0,28281	0,406	0,52674	0,26727
348	0,2865	0,40834	0,52728	0,26909
349	0,29072	0,41087	0,5278	0,27091
350	0,29577	0,41368	0,52838	0,27273
351	0,30157	0,4166	0,52905	0,27455
352	0,30844	0,41988	0,52944	0,27636
353	0,31642	0,42329	0,53005	0,27818
354	0,32494	0,42694	0,53092	0,28

355	0,33501	0,43124	0,53194	0,28182
356	0,34657	0,43594	0,53316	0,28364
357	0,359	0,44096	0,53464	0,28545
358	0,37249	0,44666	0,53649	0,28727
359	0,38762	0,45254	0,53896	0,28909
360	0,40385	0,45929	0,54158	0,29091
361	0,41701	0,46526	0,54383	0,29273
362	0,43468	0,47274	0,54739	0,29455
363	0,45423	0,48041	0,55133	0,29636
364	0,47399	0,48823	0,55512	0,29818
365	0,49323	0,49657	0,55871	0,3
366	0,51252	0,50516	0,56196	0,30182
367	0,5306	0,51275	0,56488	0,30364
368	0,54572	0,51776	0,56538	0,30545
369	0,55438	0,51739	0,56061	0,30727
370	0,5512	0,50822	0,54623	0,30909
371	0,53104	0,48455	0,51807	0,31091
372	0,49174	0,44383	0,47411	0,31273
373	0,42903	0,38374	0,41108	0,31455
374	0,34163	0,30431	0,32881	0,31636
375	0,24766	0,21988	0,24132	0,31818
376	0,15627	0,13661	0,15571	0,32
377	0,07815	0,06803	0,08379	0,32182
378	0,02814	0,02392	0,03512	0,32364
379	5,50486E-4	8,68548E-5	0,00567	0,32545
380	0	0	0	0,32727
381	0,02731	0,02445	0,01837	0,32909
382	0,08444	0,07484	0,06133	0,33091
383	0,16783	0,15047	0,1281 0,33273	
384	0,27253	0,24633	0,21315	0,33455
385	0,39947	0,36041	0,31703	0,33636
386	0,53433	0,48056	0,4285 0,33818	
387	0,64914	0,58484	0,52417	0,34
388	0,73347	0,66434	0,59588	0,34182

389	0,78973	0,72103	0,64456	0,34364
390	0,81939	0,75564	0,67223	0,34545
391	0,83267	0,77637	0,68708	0,34727
392	0,83873	0,79044	0,69594	0,34909
393	0,84177	0,80315	0,70318	0,35091
394	0,84285	0,81525	0,7103 0,35273	
395	0,84234	0,82507	0,71774	0,35455
396	0,84204	0,83696	0,72442	0,35636
397	0,83975	0,84866	0,73106	0,35818
398	0,83659	0,85918	0,73654	0,36
399	0,83432	0,87021	0,74354	0,36182
400	0,83137	0,88062	0,75106	0,36364
401	0,82744	0,89047	0,75777	0,36545
402	0,82262	0,90165	0,76529	0,36727
403	0,81606	0,91145	0,77236	0,36909
404	0,80987	0,91919	0,77906	0,37091
405	0,80348	0,92733	0,78471	0,37273
406	0,79657	0,93676	0,79121	0,37455
407	0,78943	0,94526	0,79863	0,37636
408	0,7826	0,95354	0,80644	0,37818
409	0,77375	0,96128	0,81335	0,38
410	0,76548	0,96761	0,82027	0,38182
411	0,75732	0,97178	0,8274	0,38364
412	0,74899	0,97625	0,83476	0,38545
413	0,74075	0,98172	0,84247	0,38727
414	0,73295	0,98669	0,85001	0,38909
415	0,7231	0,99077	0,85681	0,39091
416	0,71164	0,99288	0,86354	0,39273
417	0,7022	0,99471	0,87056	0,39455
418	0,69423	0,99538	0,87748	0,39636
419	0,68545	0,99712	0,88455	0,39818
420	0,67524	0,99903	0,8919	0,4
421	0,66465	1	0,89894	0,40182
422	0,65198	0,99909	0,90459	0,40364

423	0,64066	0,99649	0,91054	0,40545
424	0,63123	0,99449	0,91713	0,40727
425	0,62203	0,99271	0,92296	0,40909
426	0,61216	0,99324	0,92891	0,41091
427	0,60197	0,99224	0,93549	0,41273
428	0,59178	0,9903	0,94205	0,41455
429	0,58332	0,98833	0,94804	0,41636
430	0,5765	0,98642	0,954	0,41818
431	0,57019	0,98405	0,96081	0,42
432	0,56452	0,98178	0,968	0,42182
433	0,55854	0,98033	0,9733	0,42364
434	0,55294	0,97909	0,97815	0,42545
435	0,547	0,97676	0,98207	0,42727
436	0,54035	0,97292	0,98529	0,42909
437	0,53415	0,96681	0,98854	0,43091
438	0,52784	0,96206	0,9925 0,43273	
439	0,52331	0,95818	0,99512	0,43455
440	0,51834	0,95411	0,99606	0,43636
441	0,51236	0,94973	0,99795	0,43818
442	0,50693	0,94274	0,99877	0,44
443	0,50227	0,93521	0,99908	0,44182
444	0,49678	0,92783	1	0,44364
445	0,49144	0,92158	0,99944	0,44545
446	0,48629	0,91451	0,99842	0,44727
447	0,48043	0,9072	0,99689	0,44909
448	0,47514	0,89871	0,99488	0,45091
449	0,46989	0,88919	0,99296	0,45273
450	0,46417	0,88058	0,9905	0,45455
451	0,45853	0,87228	0,9877	0,45636
452	0,45392	0,86389	0,98418	0,45818
453	0,44901	0,85555	0,97992	0,46
454	0,44396	0,84701	0,97625	0,46182
455	0,43871	0,83706	0,97277	0,46364
456	0,43405	0,82778	0,96838	0,46545

457	0,4293	0,81842	0,96323	0,46727
458	0,42505	0,80997	0,95837	0,46909
459	0,42114	0,80236	0,9527	0,47091
460	0,41615	0,7945	0,94867	0,47273
461	0,41162	0,78623	0,94509	0,47455
462	0,40833	0,77808	0,94119	0,47636
463	0,40489	0,77066	0,93586	0,47818
464	0,40219	0,76301	0,93168	0,48
465	0,3984	0,75509	0,92701	0,48182
466	0,39551	0,74762	0,92316	0,48364
467	0,39309	0,74061	0,91813	0,48545
468	0,39016	0,73328	0,91349	0,48727
469	0,38751	0,7267	0,91012	0,48909
470	0,38536	0,72063	0,90654	0,49091
471	0,38288	0,7134	0,90194	0,49273
472	0,38006	0,70625	0,89637	0,49455
473	0,37824	0,70062	0,89171	0,49636
474	0,37573	0,69395	0,88627	0,49818
475	0,37348	0,68743	0,88153	0,5
476	0,37172	0,68063	0,87766	0,50182
477	0,36971	0,67547	0,87331	0,50364
478	0,36811	0,67043	0,86932	0,50545
479	0,36533	0,66458	0,86445	0,50727
480	0,36343	0,65779	0,85863	0,50909
481	0,36164	0,65106	0,85329	0,51091
482	0,35964	0,64557	0,84923	0,51273
483	0,35788	0,64063	0,84561	0,51455
484	0,35558	0,63545	0,84017	0,51636
485	0,35288	0,62933	0,83581	0,51818
486	0,35082	0,62425	0,83167	0,52
487	0,34873	0,6191	0,82652	0,52182
488	0,3466	0,61393	0,82161	0,52364
489	0,3441	0,61003	0,81808	0,52545
490	0,3422	0,606	0,81451	0,52727

491	0,34021	0,6013	0,8108	0,52909
492	0,33811	0,59639	0,80664	0,53091
493	0,3363	0,59265	0,8032	0,53273
494	0,33455	0,58901	0,79926	0,53455
495	0,33264	0,58577	0,79599	0,53636
496	0,33054	0,58294	0,79441	0,53818
497	0,32871	0,57968	0,79237	0,54
498	0,32714	0,57624	0,79006	0,54182
499	0,32579	0,57342	0,7875	0,54364
500	0,32371	0,56997	0,78487	0,54545
501	0,32235	0,56715	0,78247	0,54727
502	0,32093	0,56496	0,78096	0,54909
503	0,31964	0,56312	0,78008	0,55091
504	0,31834	0,56138	0,77891	0,55273
505	0,31703	0,55855	0,77701	0,55455
506	0,31579	0,55672	0,77539	0,55636
507	0,31466	0,55537	0,77495	0,55818
508	0,3137	0,55401	0,77429	0,56
509	0,3126	0,55252	0,77376	0,56182
510	0,31182	0,55085	0,77332	0,56364
511	0,31074	0,5486	0,77179	0,56545
512	0,3096	0,54696	0,77021	0,56727
513	0,309	0,54543	0,76939	0,56909
514	0,30816	0,544	0,76932	0,57091
515	0,30739	0,54293	0,76872	0,57273
516	0,30653	0,54207	0,7679	0,57455
517	0,30539	0,54041	0,76708	0,57636
518	0,30457	0,53849	0,7657	0,57818
519	0,30382	0,53715	0,76469	0,58
520	0,30296	0,53557	0,76398	0,58182
521	0,30239	0,53424	0,76308	0,58364
522	0,30161	0,5332	0,76249	0,58545
523	0,30071	0,53127	0,76147	0,58727
524	0,30025	0,52991	0,75964	0,58909

525	0,29953	0,52843	0,75842	0,59091
526	0,29842	0,52719	0,75726	0,59273
527	0,29766	0,52564	0,7562	0,59455
528	0,29669	0,52436	0,75476	0,59636
529	0,29588	0,52311	0,75342	0,59818
530	0,29508	0,52137	0,75194	0,6
531	0,29397	0,51981	0,74994	0,60182
532	0,29318	0,5183	0,7488	0,60364
533	0,2924	0,51704	0,74693	0,60545
534	0,29171	0,51575	0,74499	0,60727
535	0,29083	0,51427	0,74337	0,60909
536	0,29008	0,51272	0,74196	0,61091
537	0,28933	0,51111	0,74019	0,61273
538	0,28832	0,50951	0,73834	0,61455
539	0,28773	0,50784	0,73663	0,61636
540	0,28674	0,50644	0,73433	0,61818
541	0,28586	0,50493	0,73142	0,62
542	0,28525	0,50338	0,73022	0,62182
543	0,28461	0,50142	0,7287	0,62364
544	0,28373	0,49971	0,72626	0,62545
545	0,28281	0,49837	0,7238	0,62727
546	0,28203	0,49706	0,7216	0,62909
547	0,28144	0,49556	0,7196	0,63091
548	0,28075	0,49358	0,71748	0,63273
549	0,28028	0,49181	0,71482	0,63455
550	0,27958	0,4904	0,71245	0,63636
551	0,27896	0,48858	0,70974	0,63818
552	0,27843	0,48731	0,70732	0,64
553	0,27773	0,48556	0,70438	0,64182
554	0,27723	0,48385	0,70178	0,64364
555	0,27657	0,48209	0,69945	0,64545
556	0,27574	0,48029	0,69619	0,64727
557	0,2752	0,47871	0,69297	0,64909
558	0,27501	0,47729	0,69012	0,65091

559	0,27443	0,47522	0,68798	0,65273
560	0,27397	0,47298	0,68532	0,65455
561	0,27348	0,4713	0,68216	0,65636
562	0,27273	0,46951	0,67879	0,65818
563	0,27244	0,46732	0,67495	0,66
564	0,27187	0,46532	0,67113	0,66182
565	0,27129	0,46343	0,66805	0,66364
566	0,27097	0,46098	0,66478	0,66545
567	0,27054	0,45871	0,66049	0,66727
568	0,26995	0,4571	0,65639	0,66909
569	0,2696	0,45502	0,6525	0,67091
570	0,26913	0,45277	0,6483	0,67273
571	0,2687	0,45035	0,64428	0,67455
572	0,26812	0,4481	0,64036	0,67636
573	0,26775	0,44609	0,63649	0,67818
574	0,26747	0,44419	0,63309	0,68
575	0,26711	0,44183	0,62903	0,68182
576	0,26668	0,43973	0,62474	0,68364
577	0,26624	0,43749	0,62108	0,68545
578	0,26593	0,43576	0,61716	0,68727
579	0,26558	0,4339	0,61306	0,68909
580	0,26516	0,43191	0,60956	0,69091
581	0,26475	0,42971	0,60601	0,69273
582	0,2645	0,42806	0,60259	0,69455
583	0,26426	0,42657	0,59932	0,69636
584	0,26399	0,42472	0,59589	0,69818
585	0,26372	0,42308	0,59239	0,7
586	0,26347	0,42154	0,58923	0,70182
587	0,26317	0,41992	0,58632	0,70364
588	0,26291	0,41858	0,58378	0,70545
589	0,26273	0,41717	0,58099	0,70727
590	0,26254	0,4159	0,57833	0,70909
591	0,26234	0,41455	0,57596	0,71091
592	0,26217	0,41359	0,57385	0,71273

593	0,262	0,41241	0,57184	0,71455
594	0,26177	0,41101	0,56954	0,71636
595	0,26164	0,41001	0,56738	0,71818
596	0,26153	0,409	0,56548	0,72
597	0,26136	0,40807	0,56363	0,72182
598	0,26122	0,40726	0,56174	0,72364
599	0,26115	0,40638	0,55982	0,72545
600	0,26104	0,40542	0,55806	0,72727
601	0,26089	0,40466	0,55673	0,72909
602	0,26079	0,40381	0,55516	0,73091
603	0,26067	0,40305	0,55387	0,73273
604	0,26059	0,40245	0,55224	0,73455
605	0,26055	0,40175	0,55037	0,73636
606	0,26045	0,4009	0,54917	0,73818
607	0,26032	0,40033	0,54786	0,74
608	0,26023	0,39957	0,54643	0,74182
609	0,2602	0,39887	0,54511	0,74364
610	0,26008	0,39835	0,54423	0,74545
611	0,26001	0,39776	0,543	0,74727
612	0,25993	0,39721	0,54171	0,74909
613	0,25989	0,39662	0,54074	0,75091
614	0,25986	0,3962	0,53973	0,75273
615	0,25983	0,39574	0,53853	0,75455
616	0,25978	0,39525	0,53764	0,75636
617	0,25971	0,39475	0,53686	0,75818
618	0,25968	0,39438	0,53594	0,76
619	0,25963	0,39405	0,53505	0,76182
620	0,25961	0,39368	0,5342	0,76364
621	0,25958	0,39327	0,53347	0,76545
622	0,2595	0,39277	0,53259	0,76727
623	0,25944	0,39247	0,53181	0,76909
624	0,25942	0,39211	0,53111	0,77091
625	0,25939	0,39177	0,53038	0,77273
626	0,25934	0,39146	0,52971	0,77455

627	0,25931	0,39119	0,52922	0,77636
628	0,25932	0,39088	0,52853	0,77818
629	0,25925	0,39055	0,52791	0,78
630	0,25924	0,39024	0,52726	0,78182
631	0,25922	0,39003	0,52675	0,78364
632	0,2592	0,38974	0,52626	0,78545
633	0,25919	0,3894	0,52574	0,78727
634	0,25917	0,38921	0,52522	0,78909
635	0,25915	0,389	0,52483	0,79091
636	0,25912	0,38881	0,5244	0,79273
637	0,2591	0,38861	0,52388	0,79455
638	0,25907	0,38841	0,52338	0,79636
639	0,25905	0,38822	0,52308	0,79818
640	0,25903	0,38803	0,5228	0,8
641	0,25903	0,38784	0,52238	0,80182
642	0,25902	0,38768	0,5221	0,80364
643	0,259	0,38754	0,52172	0,80545
644	0,25898	0,38741	0,52133	0,80727
645	0,25898	0,38726	0,52102	0,80909
646	0,25896	0,3871	0,52082	0,81091
647	0,25895	0,38694	0,52046	0,81273
648	0,25896	0,38684	0,52015	0,81455
649	0,25894	0,38674	0,51988	0,81636
650	0,25893	0,38665	0,51969	0,81818
651	0,25892	0,38647	0,51944	0,82
652	0,25891	0,3864	0,51921	0,82182
653	0,2589	0,38631	0,51899	0,82364
654	0,2589	0,38621	0,5188	0,82545
655	0,2589	0,38612	0,51858	0,82727
656	0,2589	0,38598	0,5184	0,82909
657	0,2589	0,38593	0,51829	0,83091
658	0,25889	0,38587	0,51811	0,83273
659	0,25887	0,3858	0,51795	0,83455
660	0,25887	0,38576	0,51782	0,83636

661	0,25888	0,38569	0,51769	0,83818
662	0,25887	0,38559	0,51753	0,84
663	0,25886	0,38554	0,5174	0,84182
664	0,25885	0,38547	0,51726	0,84364
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666	0,25882	0,38536	0,51702	0,84727
667	0,25883	0,3853	0,51689	0,84909
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669	0,25883	0,38518	0,51673	0,85273
670	0,25882	0,38513	0,51666	0,85455
671	0,25882	0,38509	0,51653	0,85636
672	0,25881	0,38506	0,51645	0,85818
673	0,25881	0,38503	0,51642	0,86
674	0,25882	0,38499	0,51632	0,86182
675	0,2588	0,38496	0,51624	0,86364
676	0,2588	0,38494	0,51616	0,86545
677	0,25881	0,38489	0,51611	0,86727
678	0,25879	0,38484	0,51606	0,86909
679	0,25879	0,38485	0,51599	0,87091
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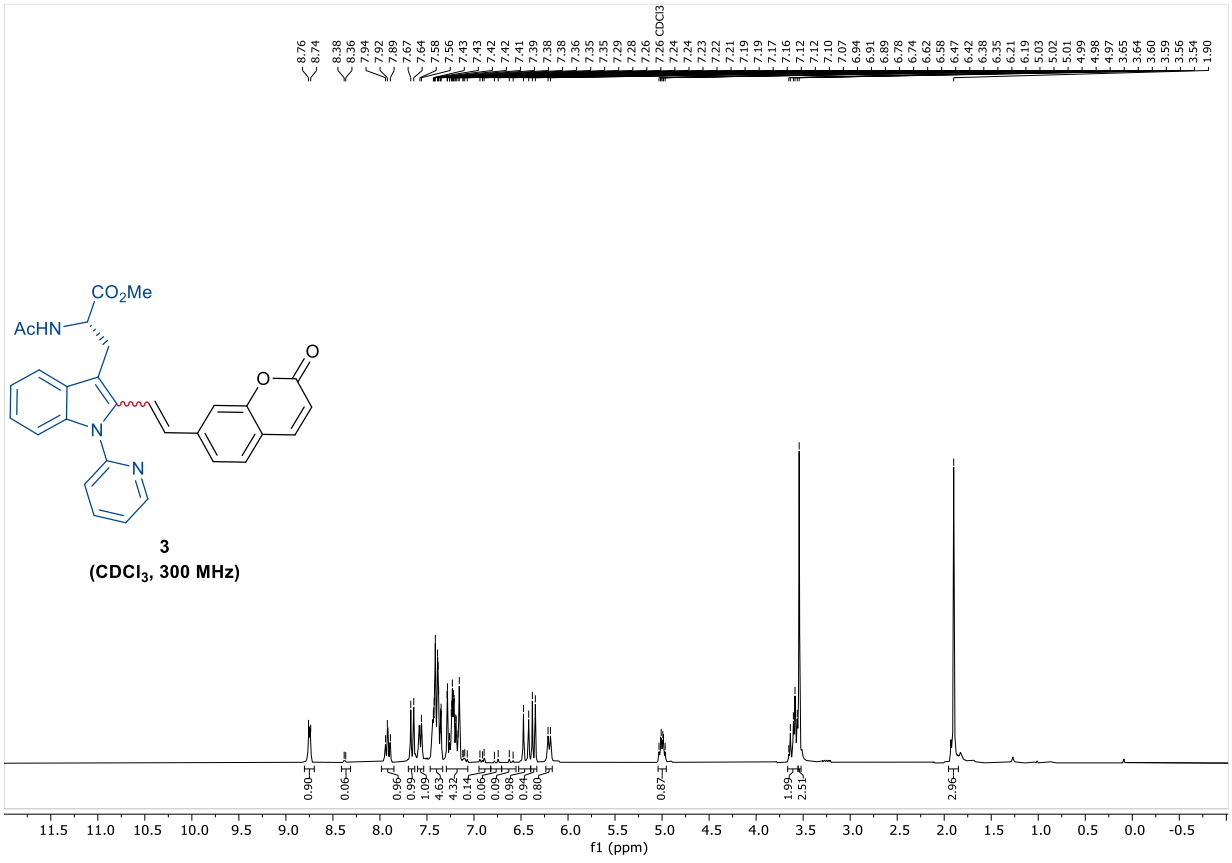
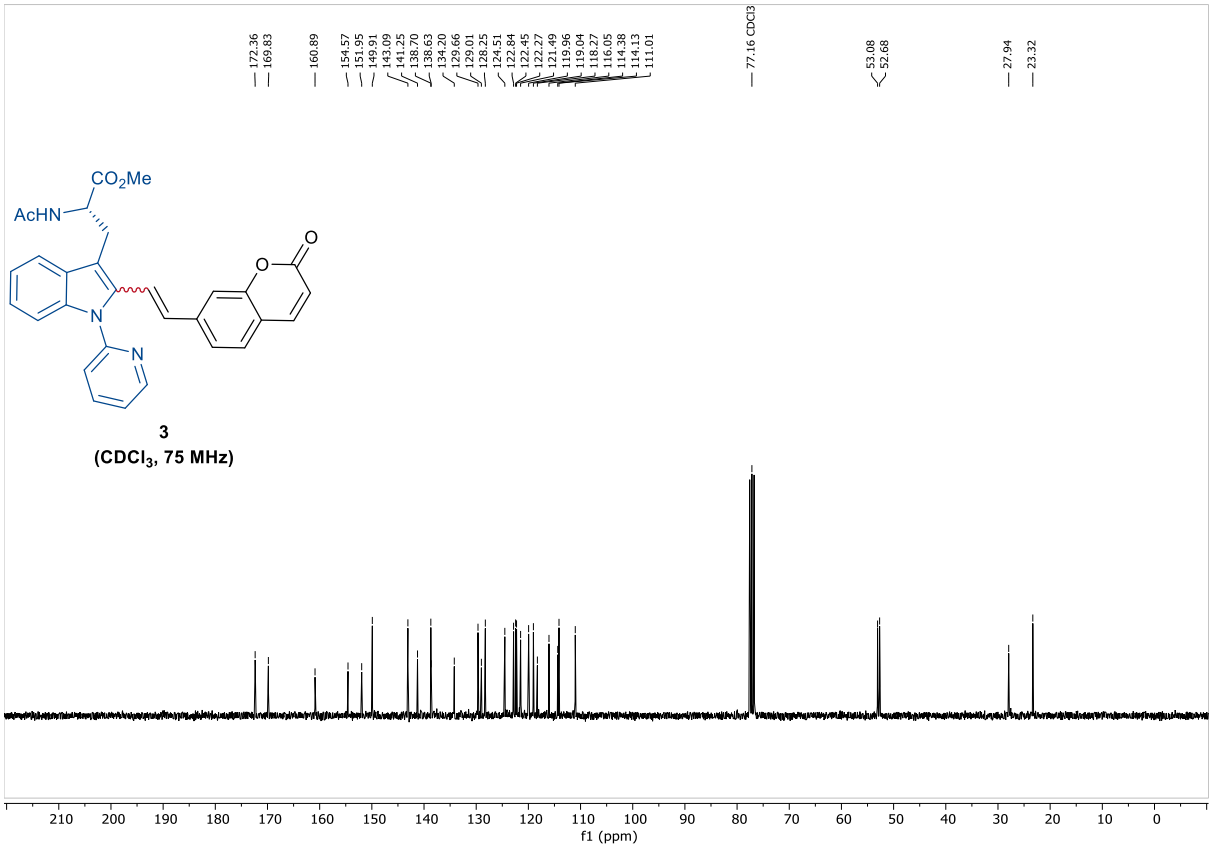
683	0,25879	0,38475	0,51579	0,87818
684	0,25879	0,38474	0,51574	0,88
685	0,25879	0,38472	0,51572	0,88182
686	0,25879	0,38471	0,51566	0,88364
687	0,25879	0,38469	0,51563	0,88545
688	0,25878	0,38467	0,51561	0,88727
689	0,25878	0,38464	0,51557	0,88909
690	0,25878	0,38464	0,51554	0,89091
691	0,25878	0,38463	0,51549	0,89273
692	0,25878	0,38461	0,51546	0,89455
693	0,25878	0,3846	0,51545	0,89636
694	0,25878	0,38457	0,51544	0,89818

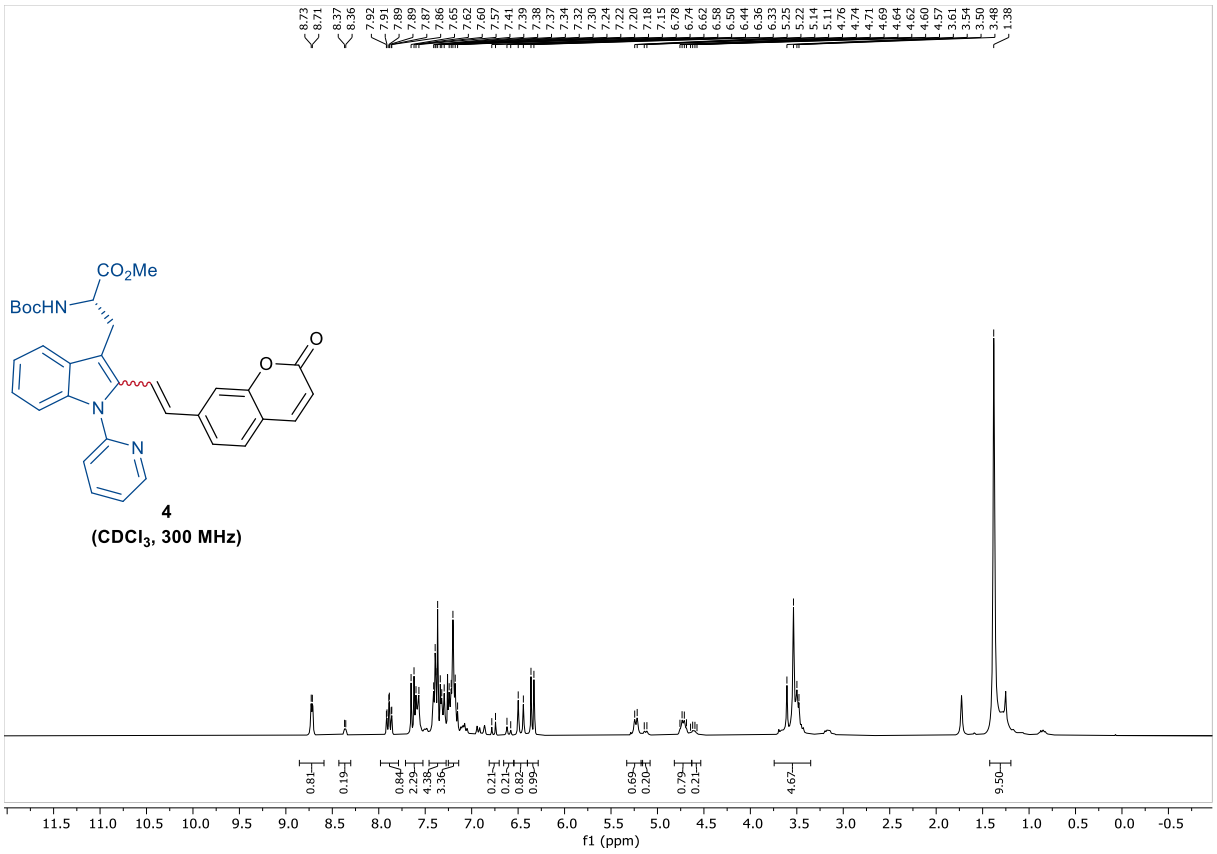
695	0,25877	0,38456	0,5154	0,9
696	0,25878	0,38456	0,51536	0,90182
697	0,25877	0,38457	0,51536	0,90364
698	0,25877	0,38456	0,51532	0,90545
699	0,25877	0,38454	0,51531	0,90727
700	0,25879	0,38453	0,5153	0,90909
701	0,25878	0,38452	0,5153	0,91091
702	0,25877	0,38453	0,51528	0,91273
703	0,25877	0,38451	0,51527	0,91455
704	0,25878	0,38449	0,51523	0,91636
705	0,25878	0,38448	0,51521	0,91818
706	0,25877	0,38448	0,51519	0,92
707	0,25877	0,38448	0,51519	0,92182
708	0,25877	0,38446	0,51518	0,92364
709	0,25877	0,38446	0,51517	0,92545
710	0,25877	0,38445	0,51515	0,92727
711	0,25877	0,38446	0,51514	0,92909
712	0,25877	0,38445	0,51514	0,93091
713	0,25877	0,38444	0,51511	0,93273
714	0,25878	0,38443	0,51511	0,93455
715	0,25877	0,38444	0,51511	0,93636
716	0,25878	0,38442	0,51511	0,93818
717	0,25878	0,38443	0,5151	0,94
718	0,25877	0,38442	0,51508	0,94182
719	0,25876	0,38443	0,51508	0,94364
720	0,25877	0,38442	0,51507	0,94545
721	0,25877	0,38443	0,51506	0,94727
722	0,25878	0,38442	0,51507	0,94909
723	0,25877	0,38441	0,51505	0,95091
724	0,25877	0,3844	0,51504	0,95273
725	0,25877	0,3844	0,51504	0,95455
726	0,25876	0,3844	0,51503	0,95636
727	0,25877	0,3844	0,51503	0,95818
728	0,25878	0,38441	0,51503	0,96

729	0,25878	0,3844	0,51502	0,96182
730	0,25878	0,3844	0,51502	0,96364
731	0,25877	0,38441	0,51502	0,96545
732	0,25876	0,38439	0,51502	0,96727
733	0,25876	0,38439	0,51502	0,96909
734	0,25877	0,38439	0,51502	0,97091
735	0,25877	0,38439	0,51501	0,97273
736	0,25878	0,38439	0,515	0,97455
737	0,25877	0,38438	0,51499	0,97636
738	0,25877	0,38438	0,51499	0,97818
739	0,25878	0,38439	0,515	0,98
740	0,25877	0,38438	0,515	0,98182
741	0,25877	0,38439	0,51499	0,98364
742	0,25876	0,38439	0,51499	0,98545
743	0,25877	0,38439	0,51499	0,98727
744	0,25878	0,38439	0,51498	0,98909
745	0,25878	0,38439	0,51499	0,99091
746	0,25876	0,38438	0,51498	0,99273
747	0,25877	0,38438	0,51497	0,99455
748	0,25876	0,38437	0,51497	0,99636
749	0,25876	0,38438	0,51497	0,99818
750	0,25877	0,38438	0,51498	1

NMR-Spectra

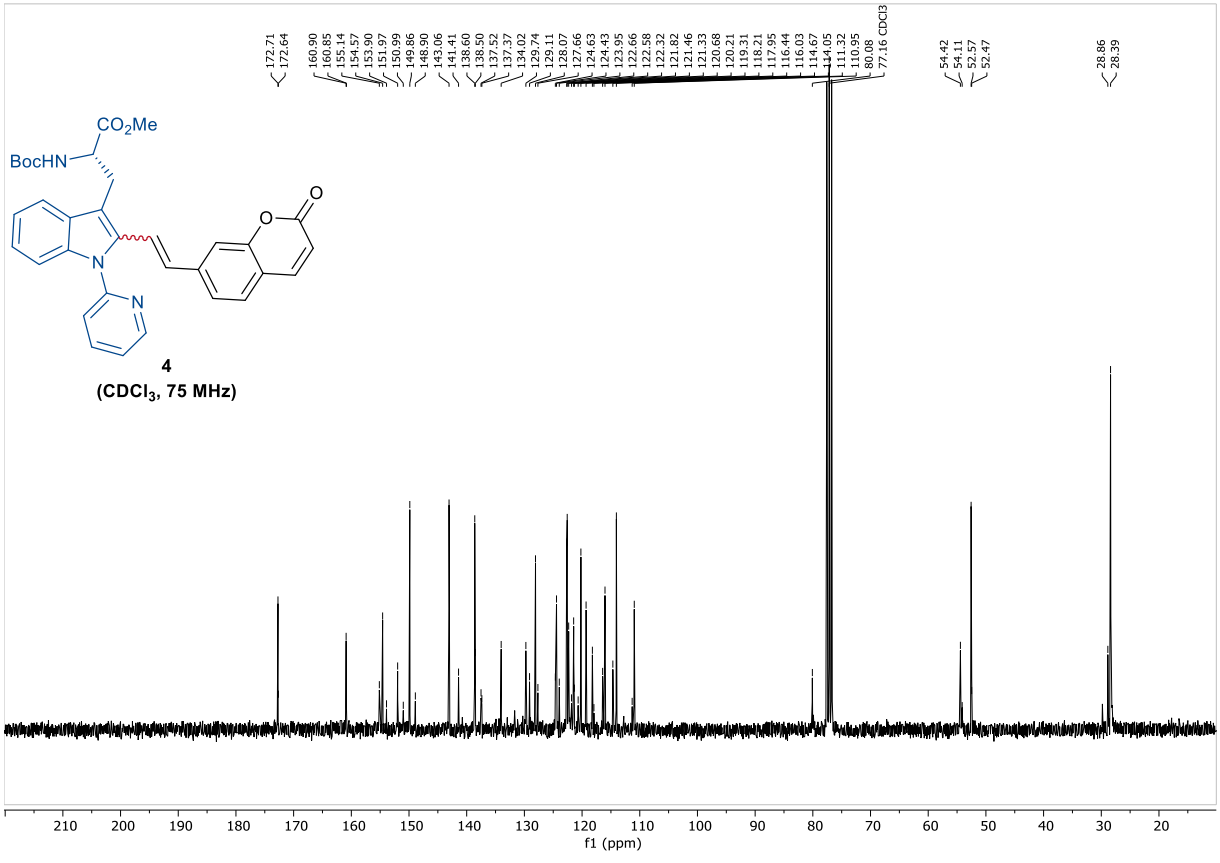

CO2Me
AcHN
O
O
N
N
3
(CDCl3, 300 MHz)
f1 (ppm)


CO2Me
AcHN
O
O
N
N
3
(CDCl3, 75 MHz)
f1 (ppm)



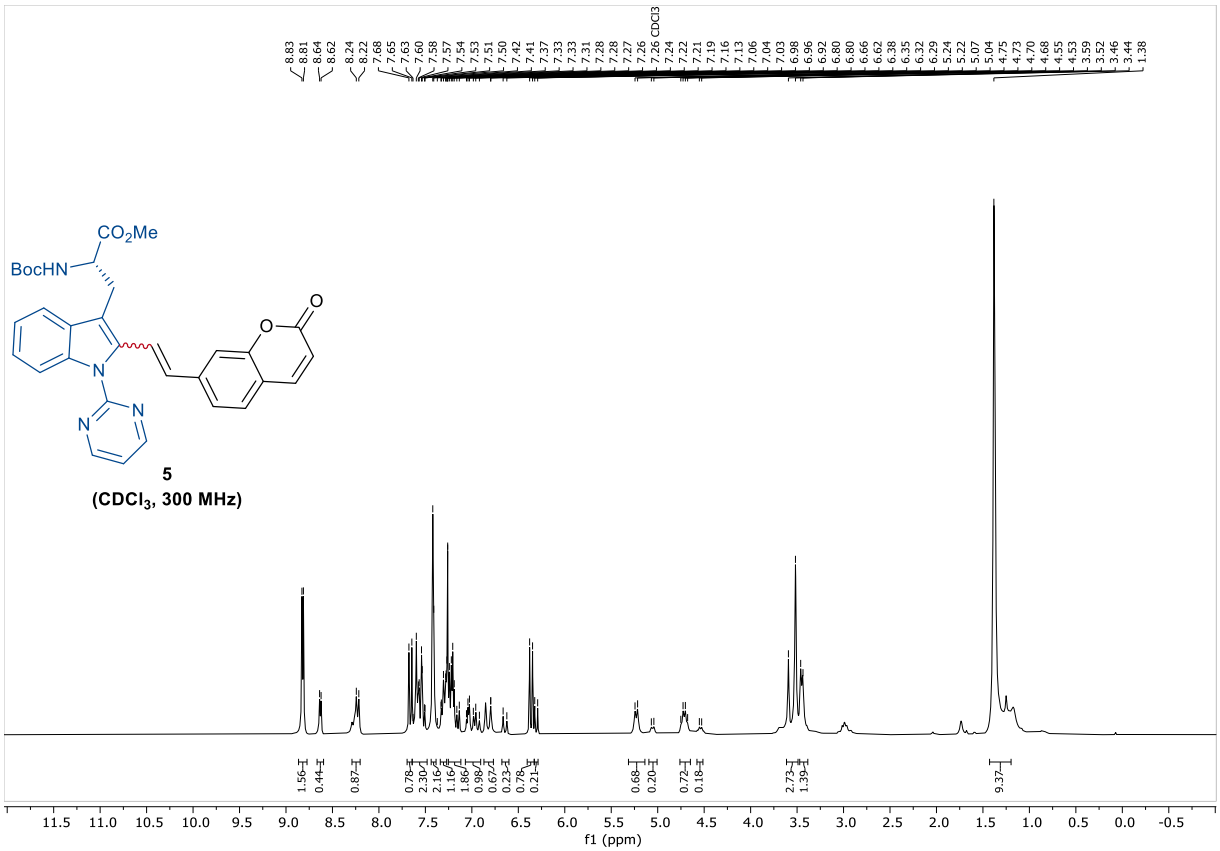
4

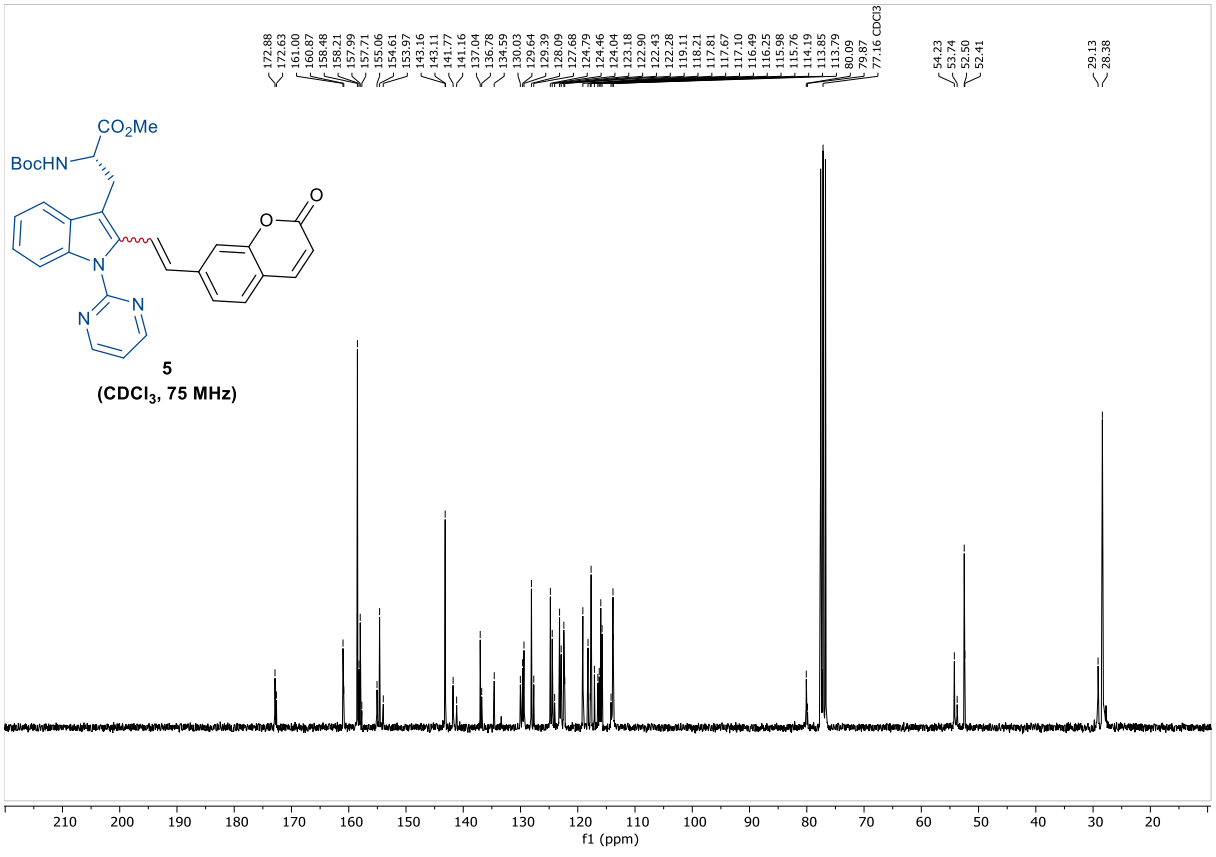
($CDCl_3$, 300 MHz)

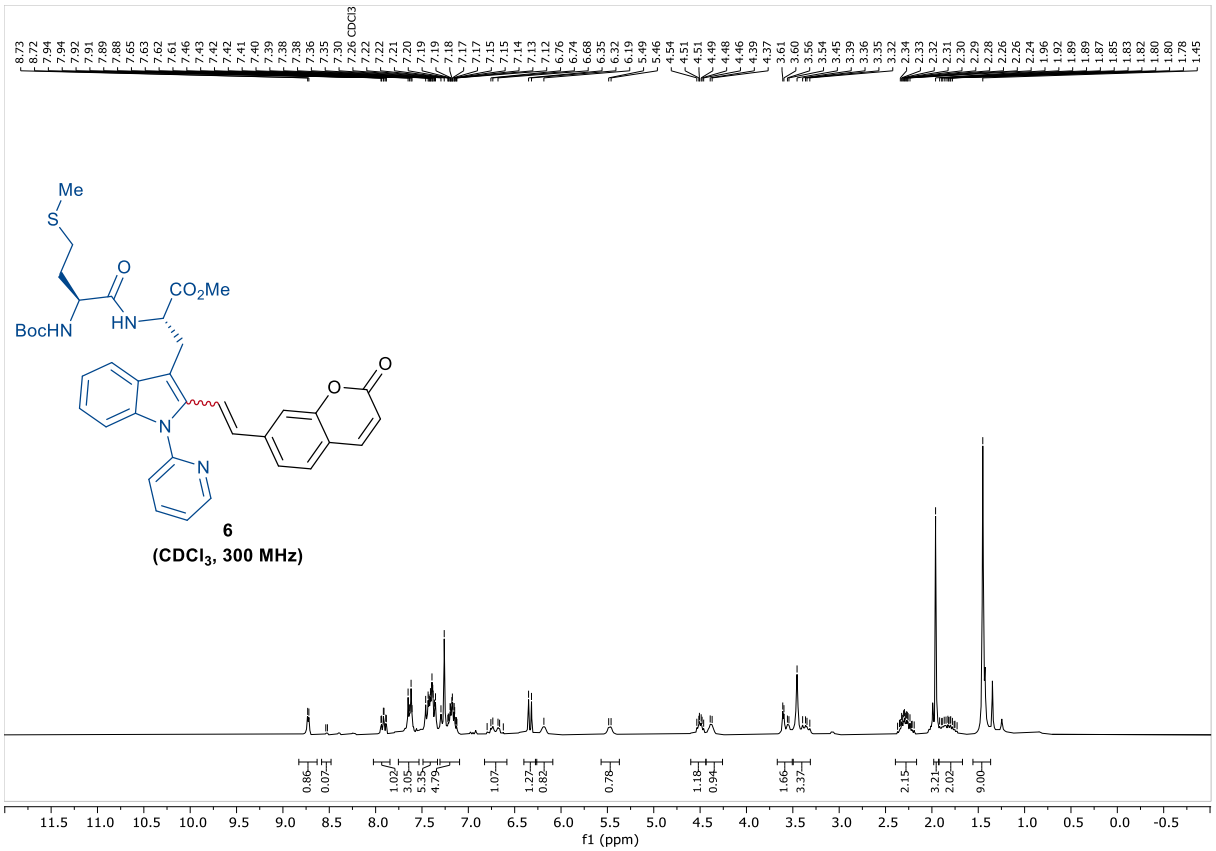


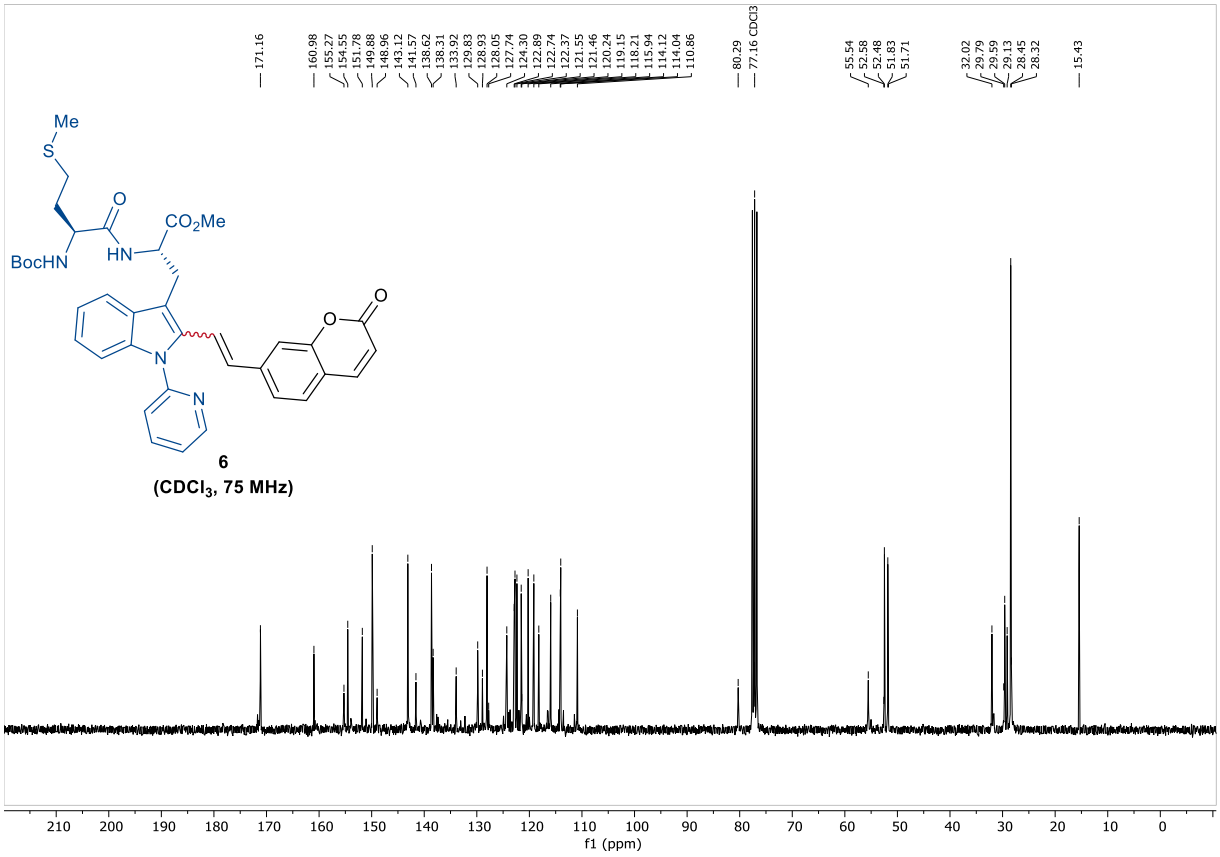
4

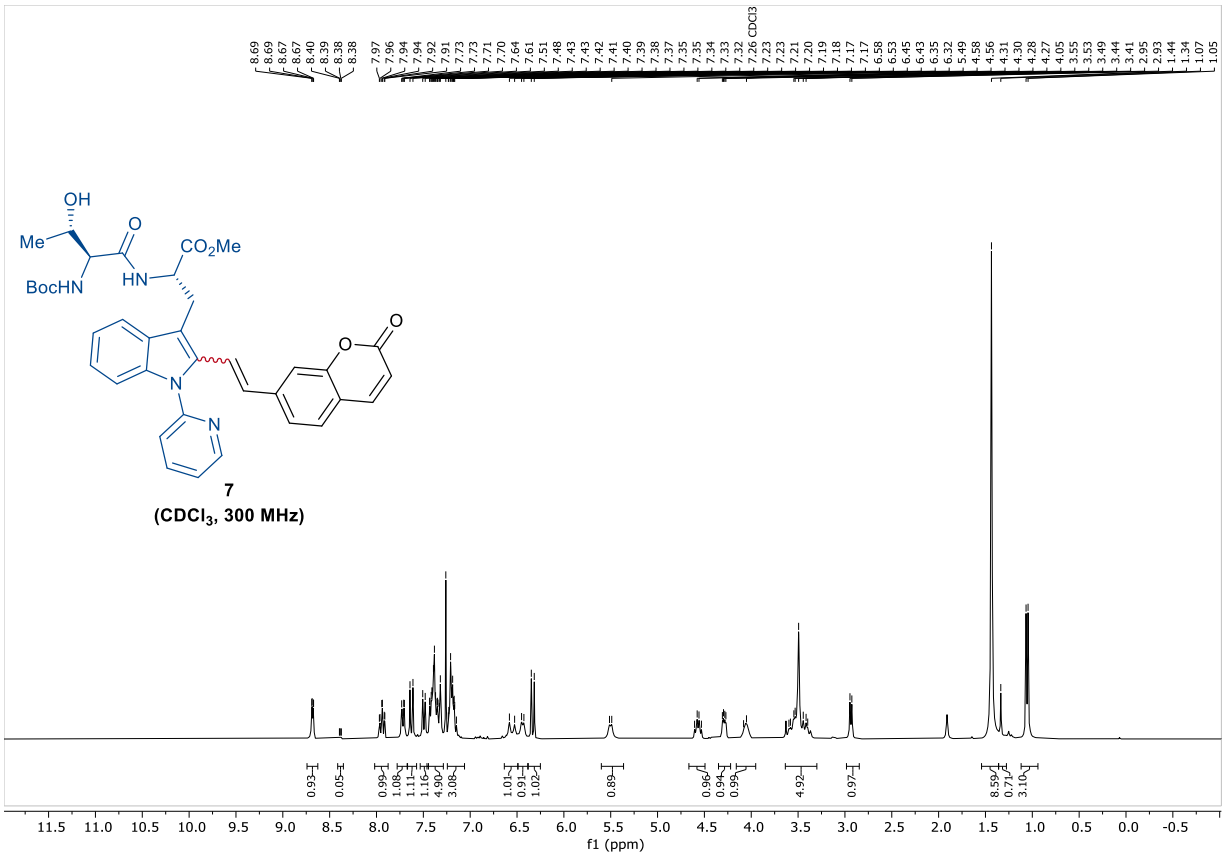
($CDCl_3$, 75 MHz)

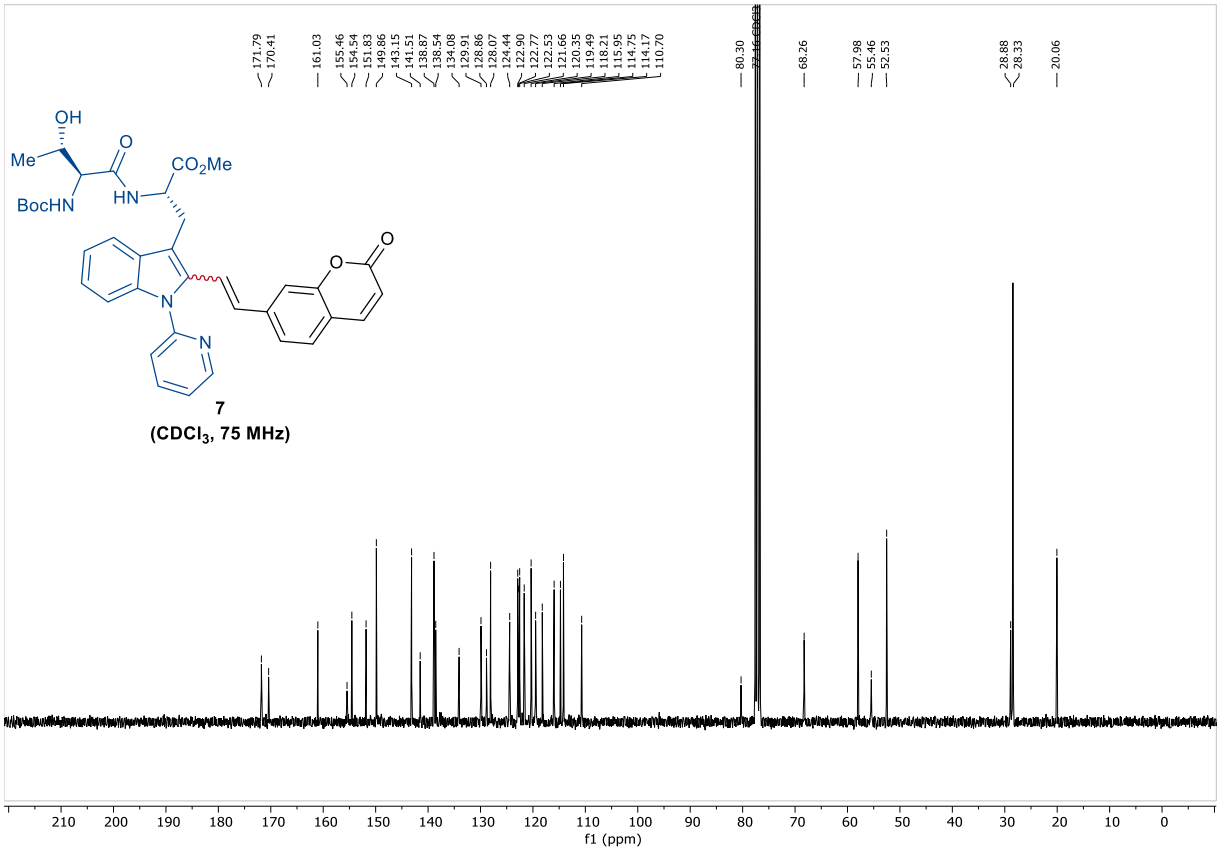

CO2Me
BocHN
O
O
N
N
N
5
(CDCl3, 300 MHz)
f1 (ppm)

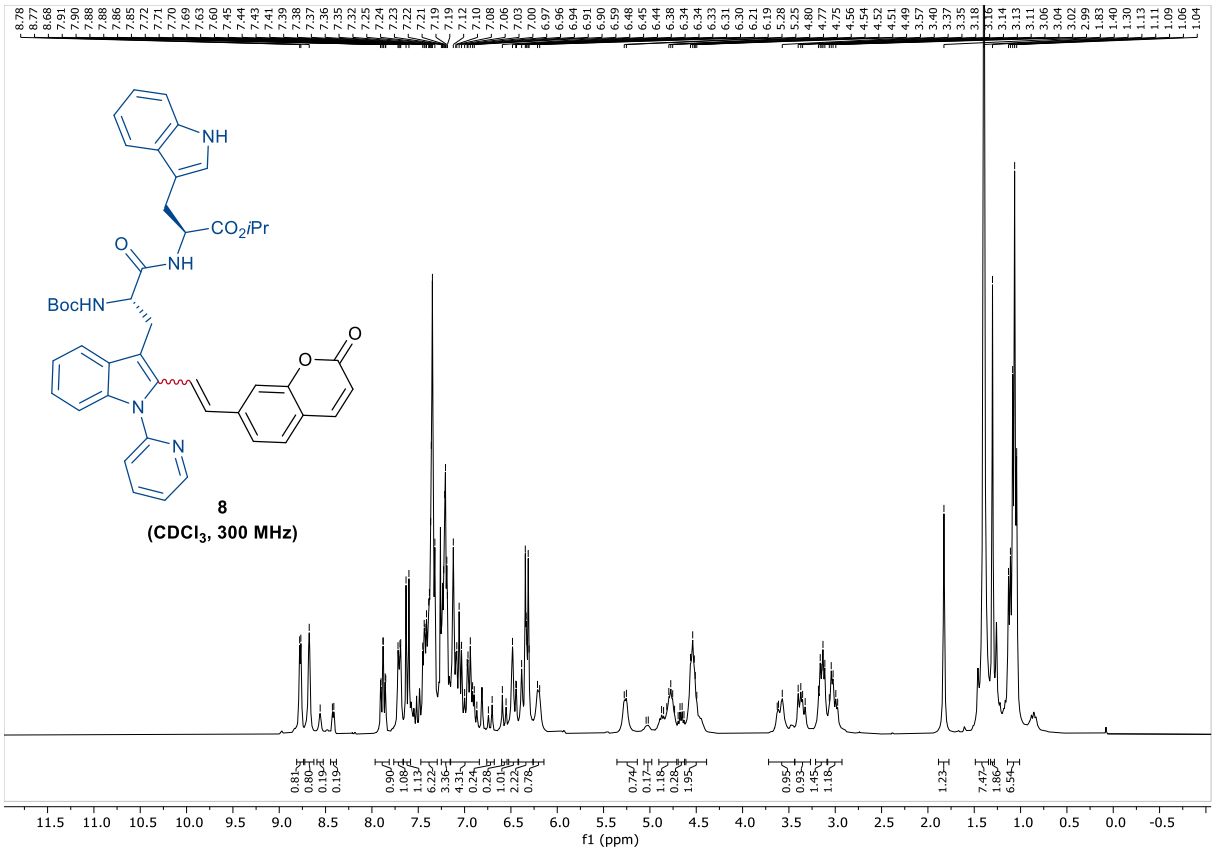

CO2Me
BocHN
O
O
N
N
N
5
(CDCl3, 75 MHz)
f1 (ppm)

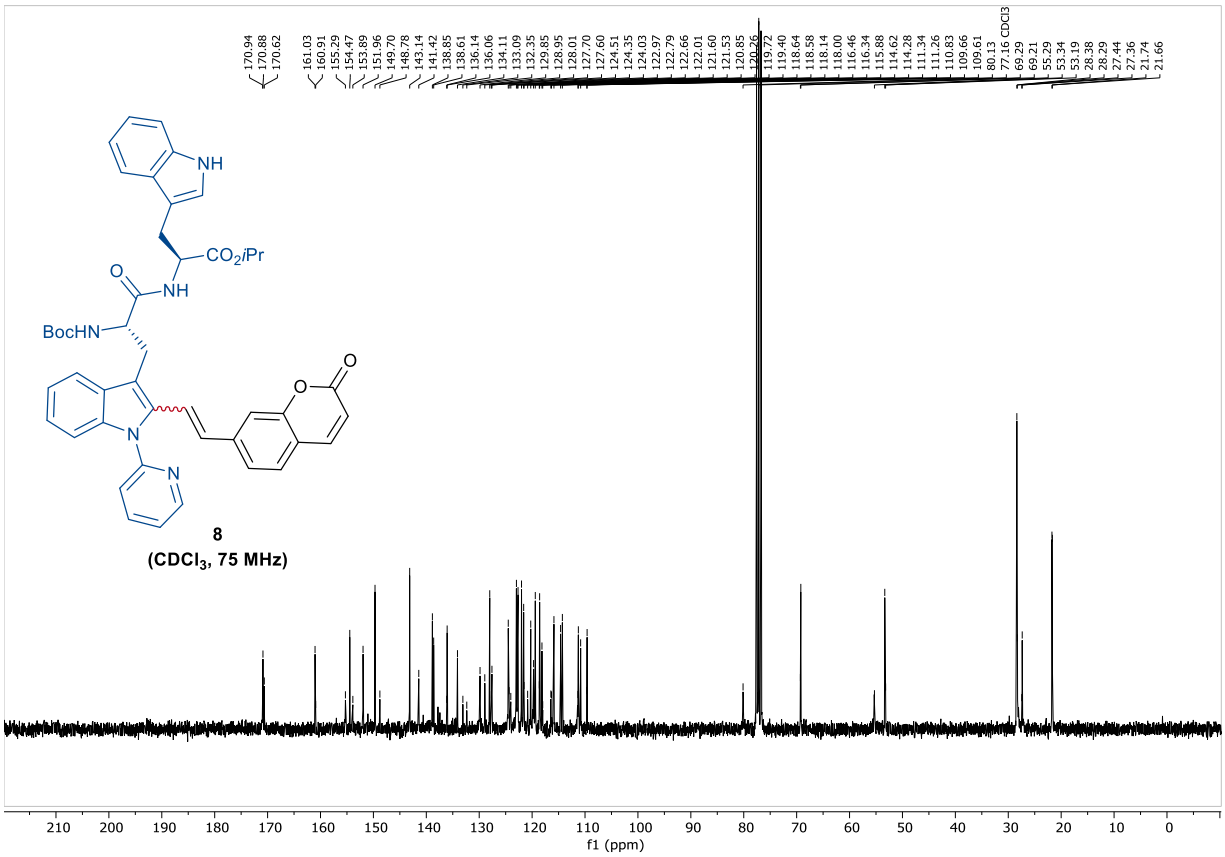

Me
S
O
CO2Me
BocHN
HN
O
O
N
N
6
(CDCl3, 300 MHz)
f1 (ppm)

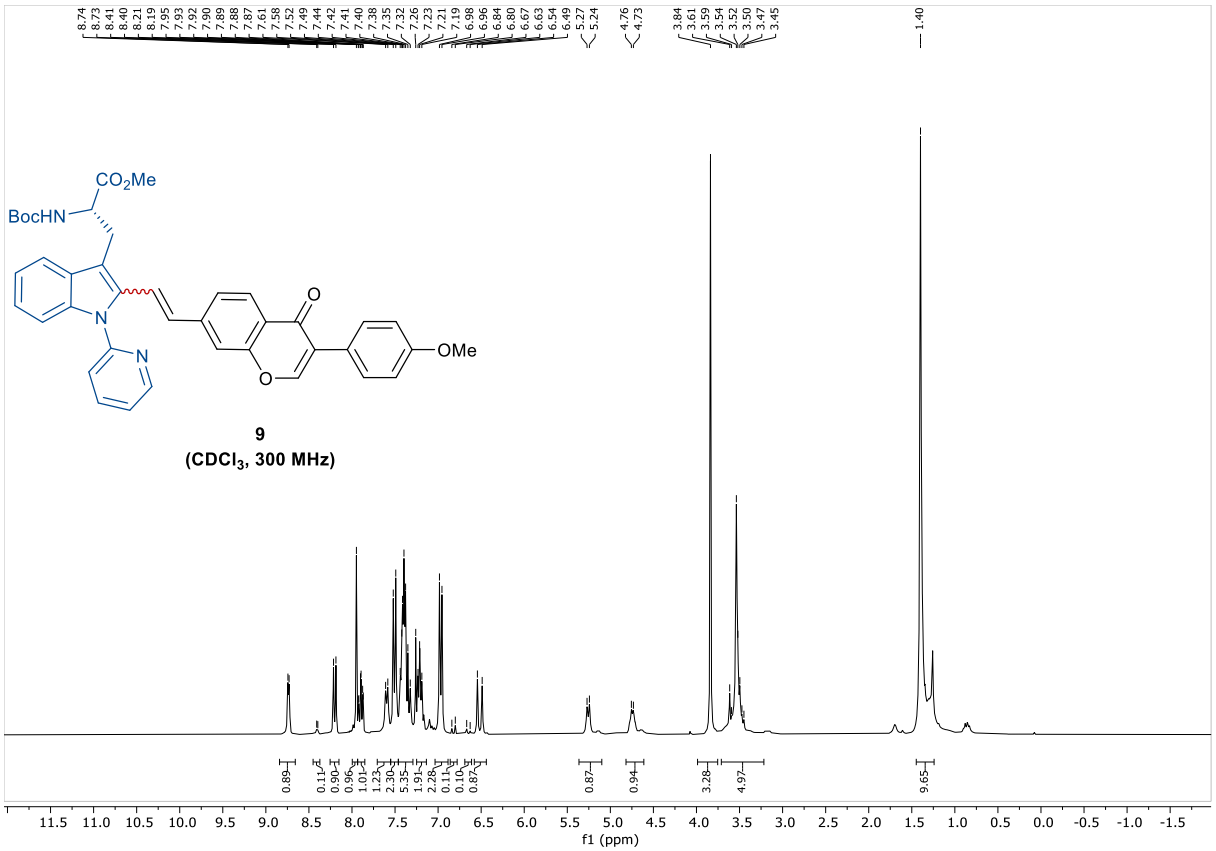

Me
S
O
CO2Me
BocHN
HN
O
O
N
N
6
(CDCl3, 75 MHz)
f1 (ppm)


OH
Me
O
CO2Me
BocHN
HN
O
O
N
N
7
(CDCl3, 300 MHz)
f1 (ppm)

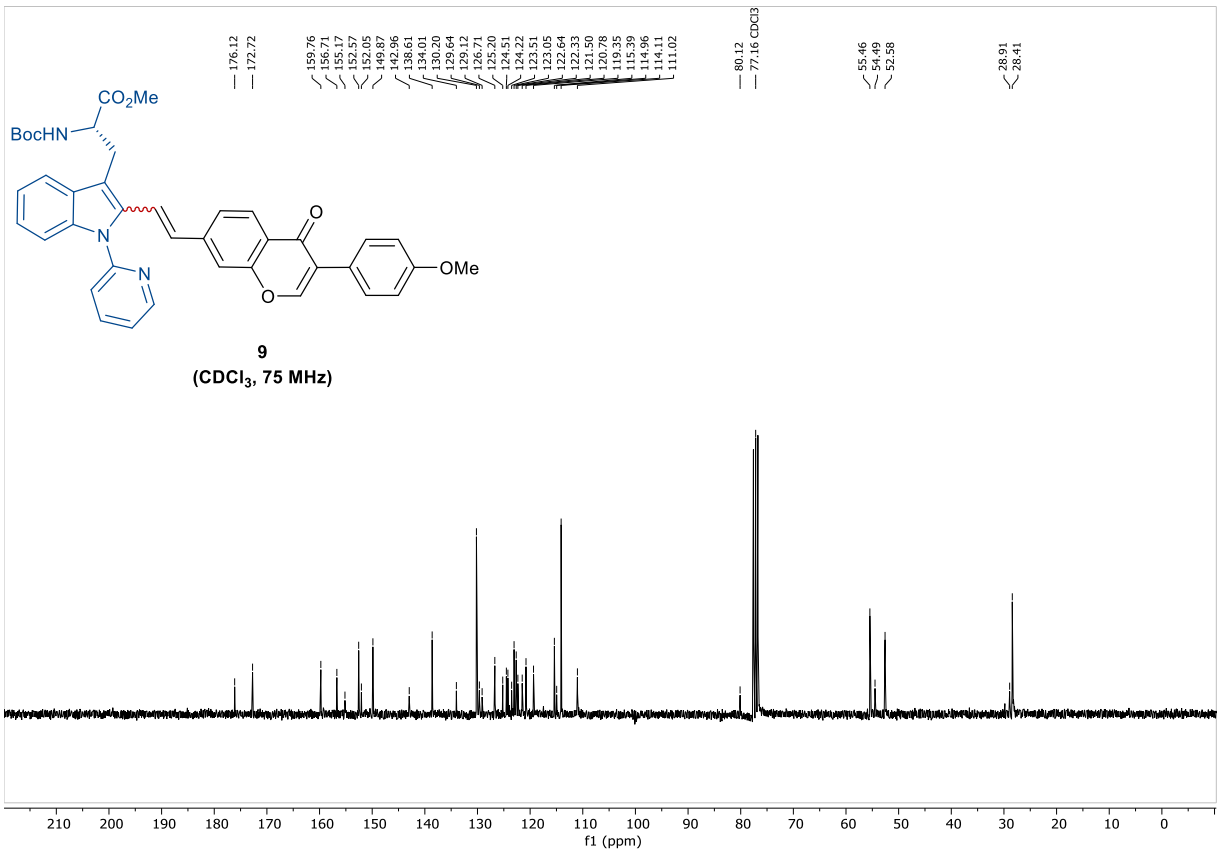

OH
Me
O
CO2Me
BocHN
HN
O
O
N
N
7
(CDCl3, 75 MHz)
f1 (ppm)


NH
CO2iPr
O
NH
BocHN
O
O
N
N
8
(CDCl3, 300 MHz)
f1 (ppm)

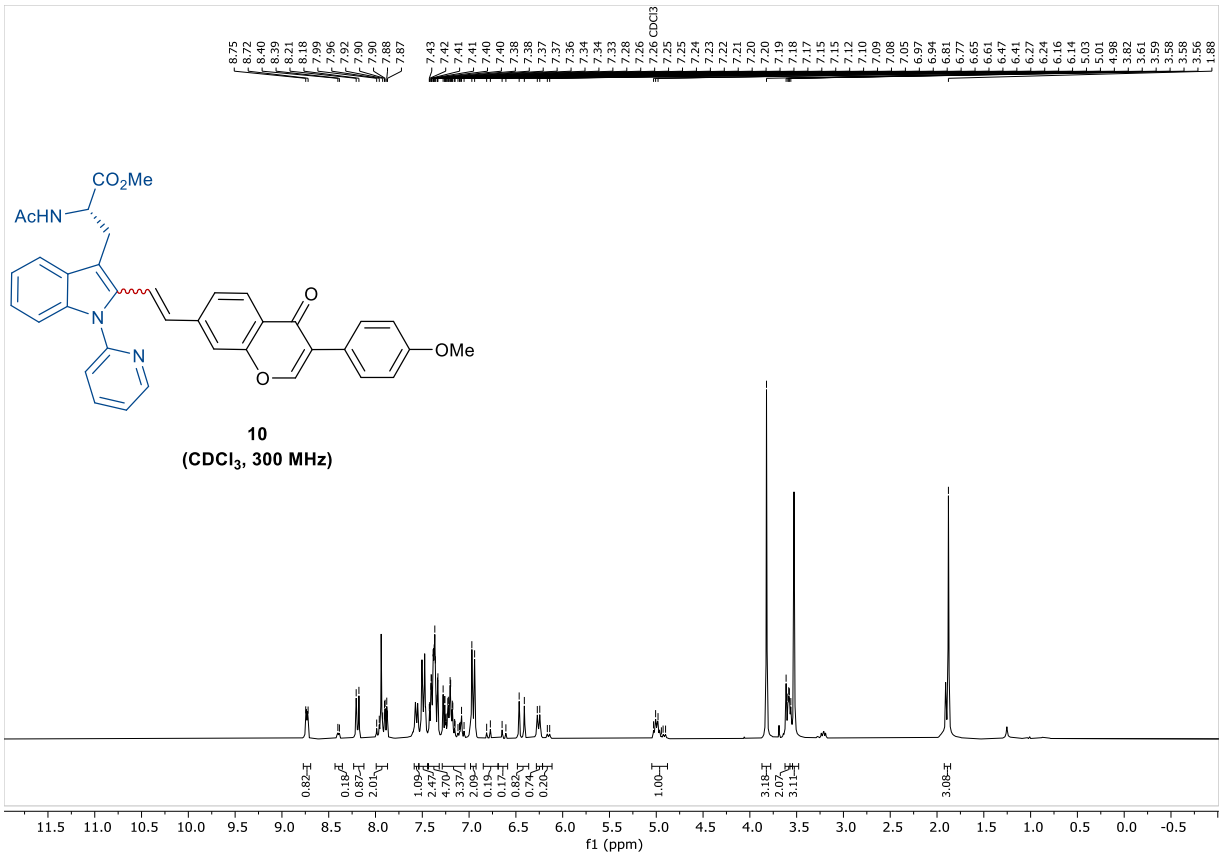

NH
CO2iPr
O
NH
BocHN
O
O
N
N
8
(CDCl3, 75 MHz)
f1 (ppm)



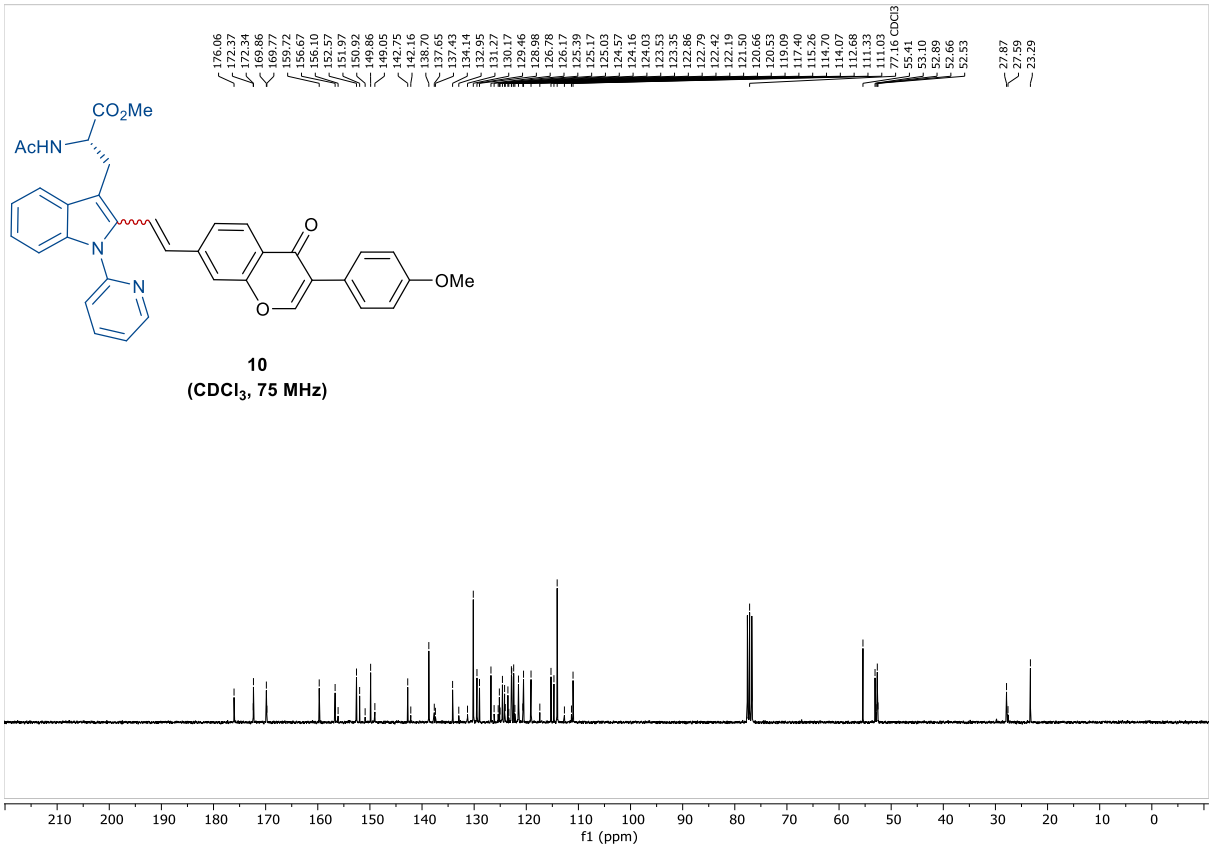
9
($CDCl_3$, 300 MHz)



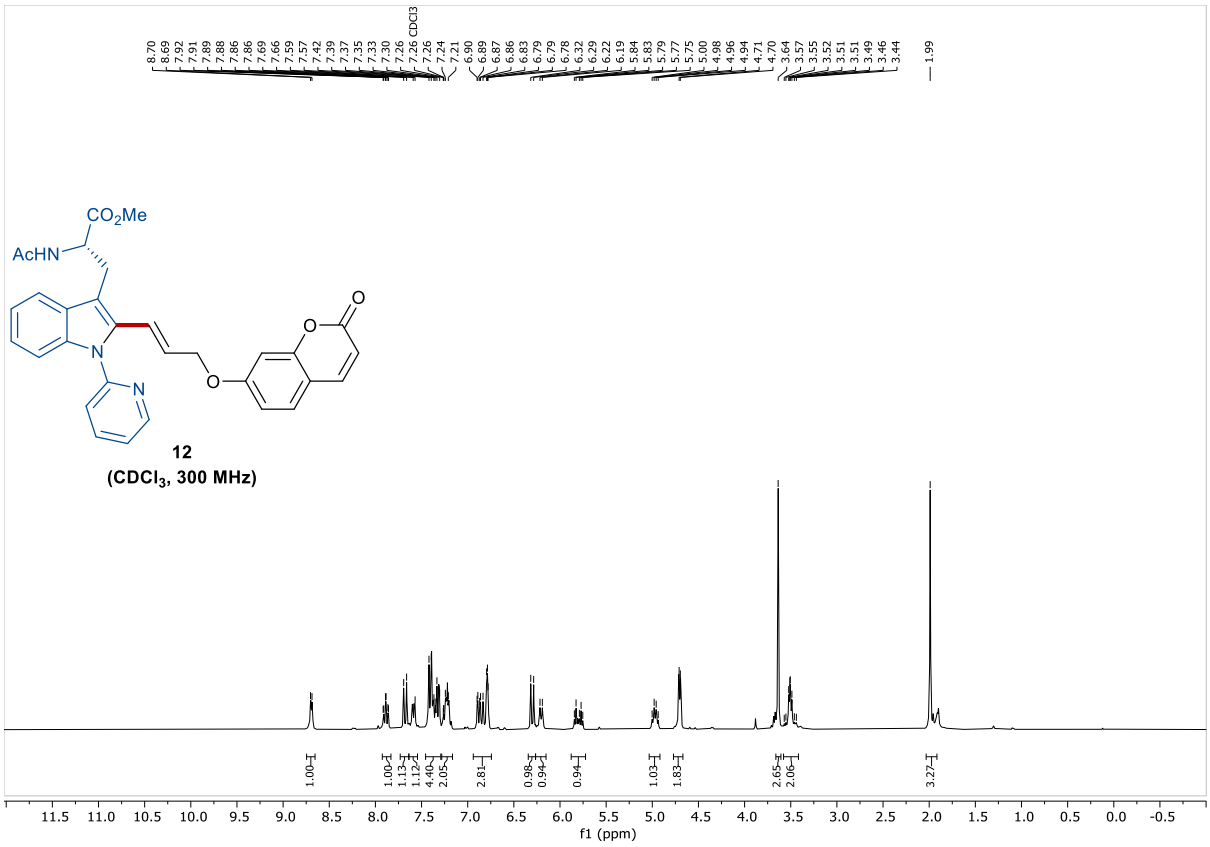
9
($CDCl_3$, 75 MHz)

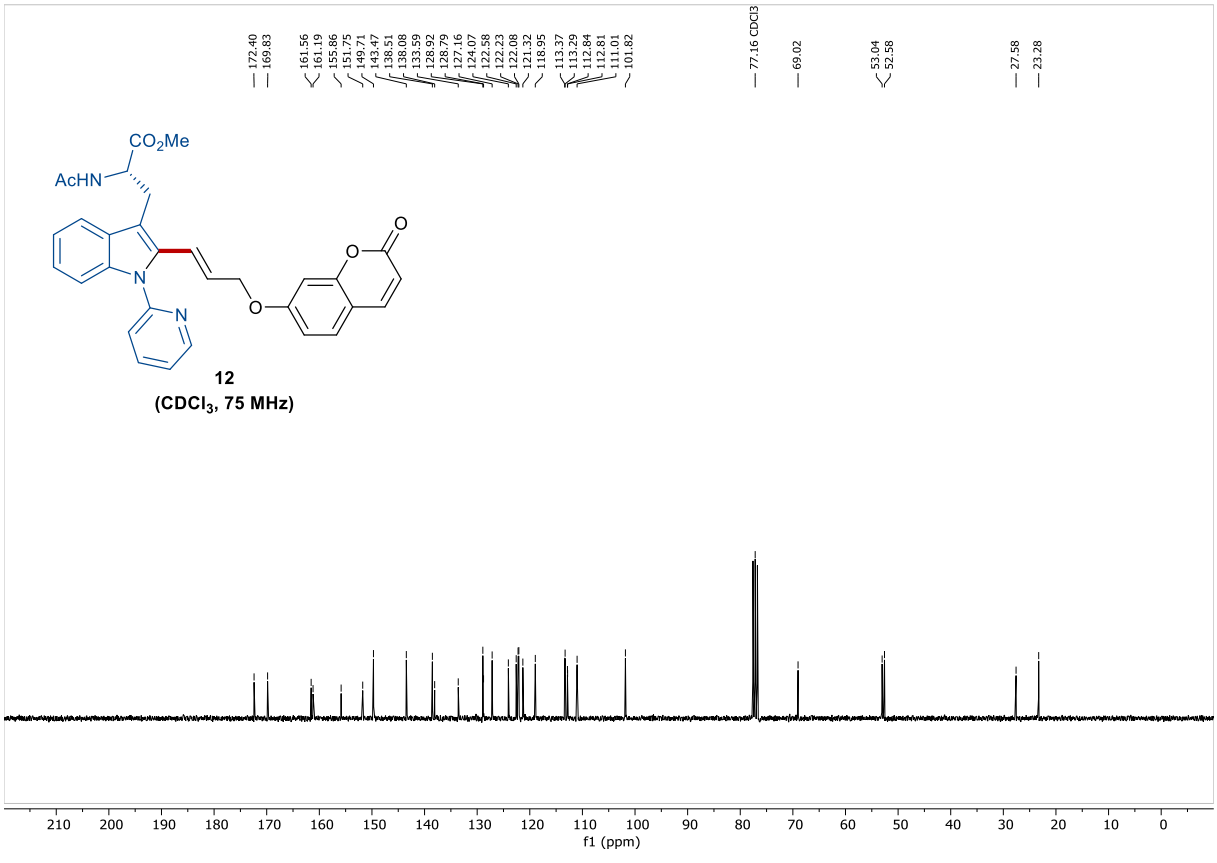


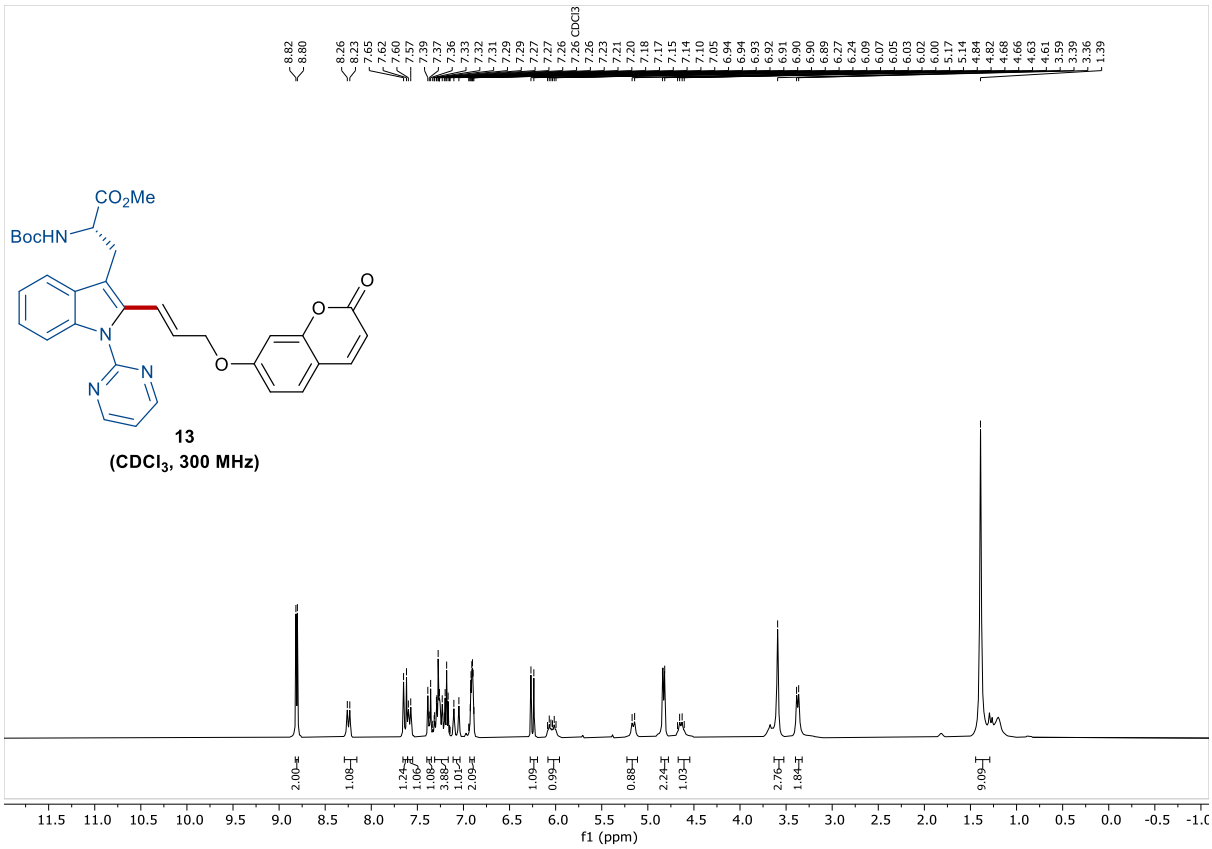
10
($CDCl_3$, 300 MHz)



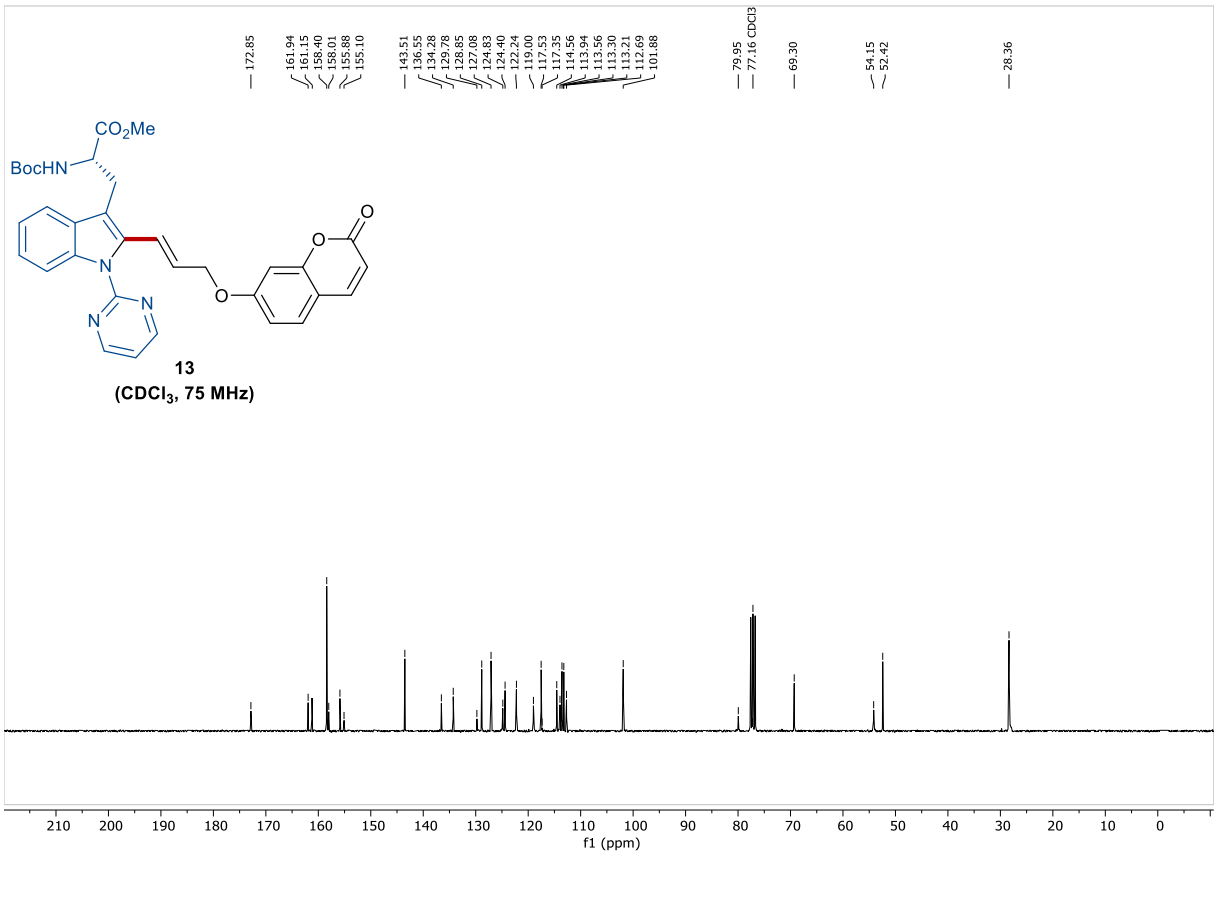
10
($CDCl_3$, 75 MHz)


CO2Me
AcHN
O
O
N
N
12
(CDCl3, 300 MHz)
f1 (ppm)

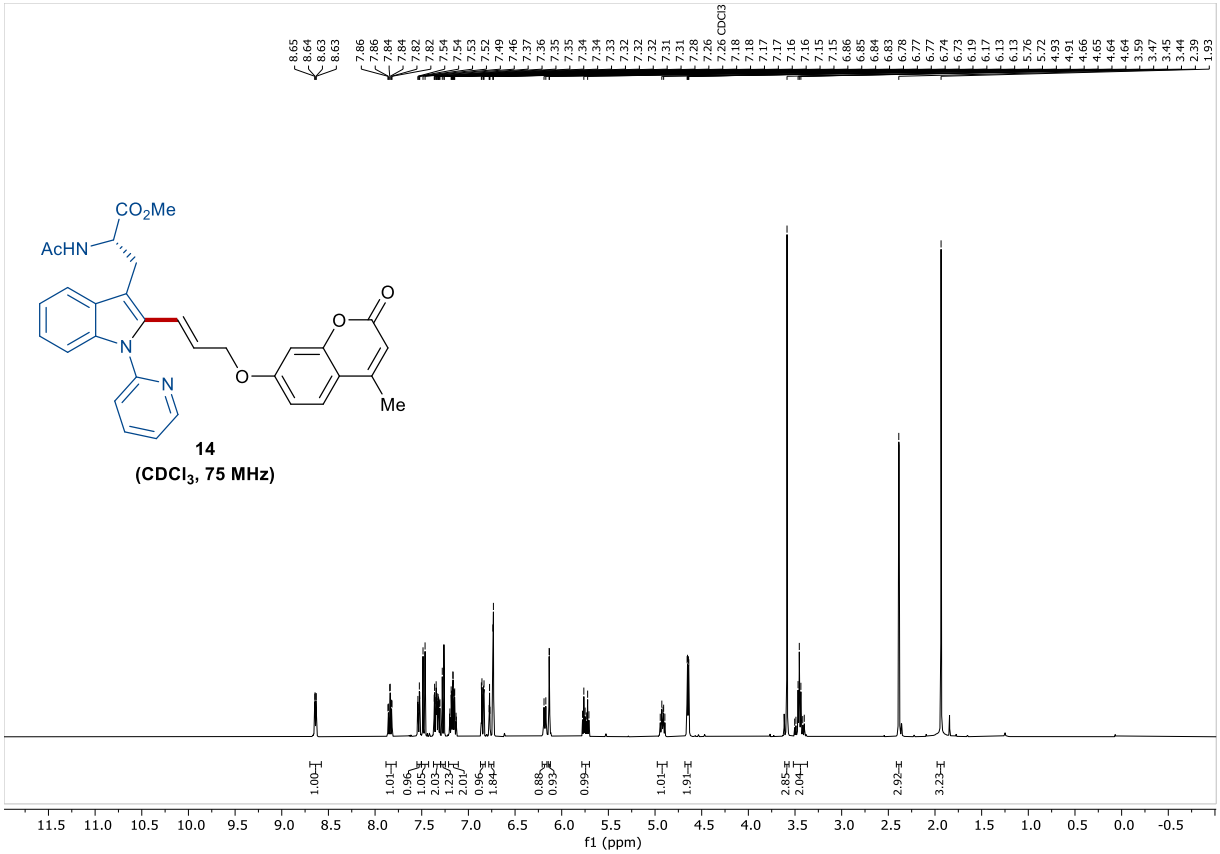

CO2Me
AcHN
O
O
N
N
12
(CDCl3, 75 MHz)
f1 (ppm)

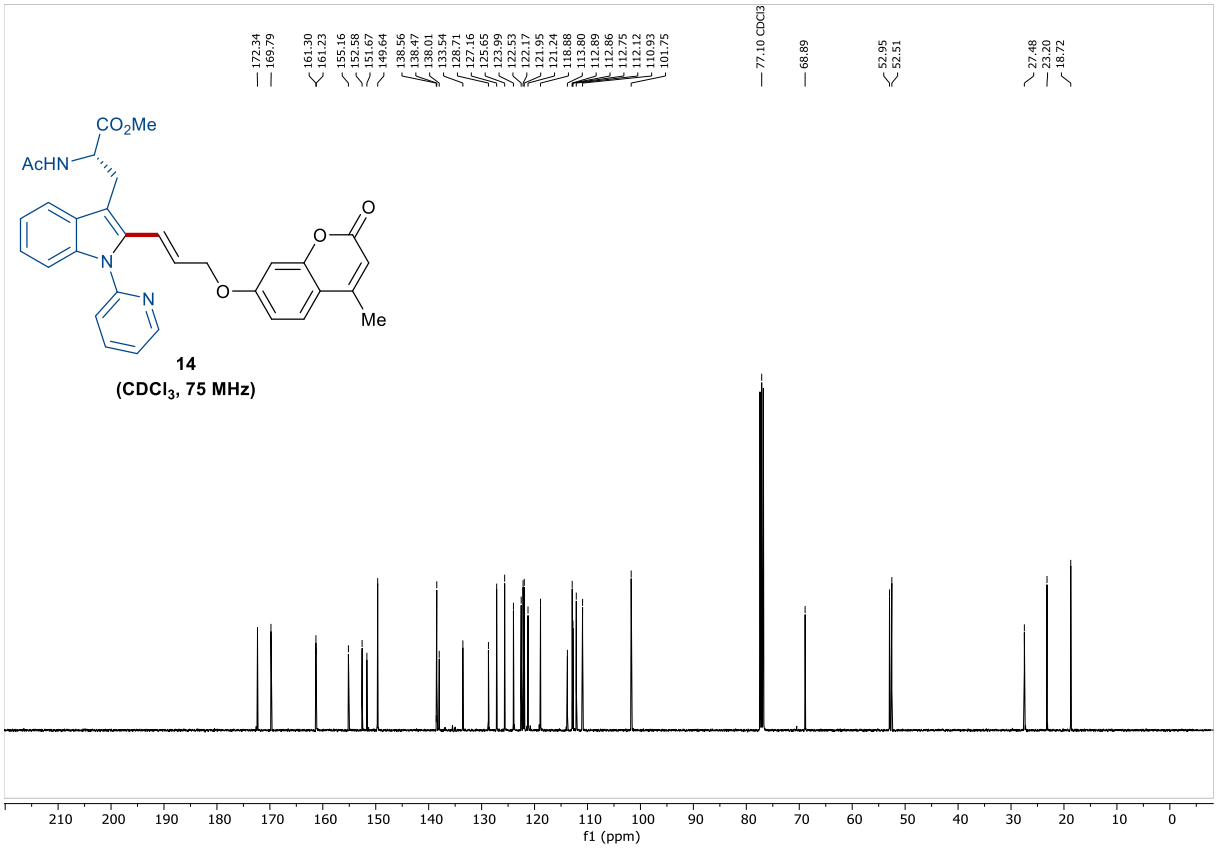


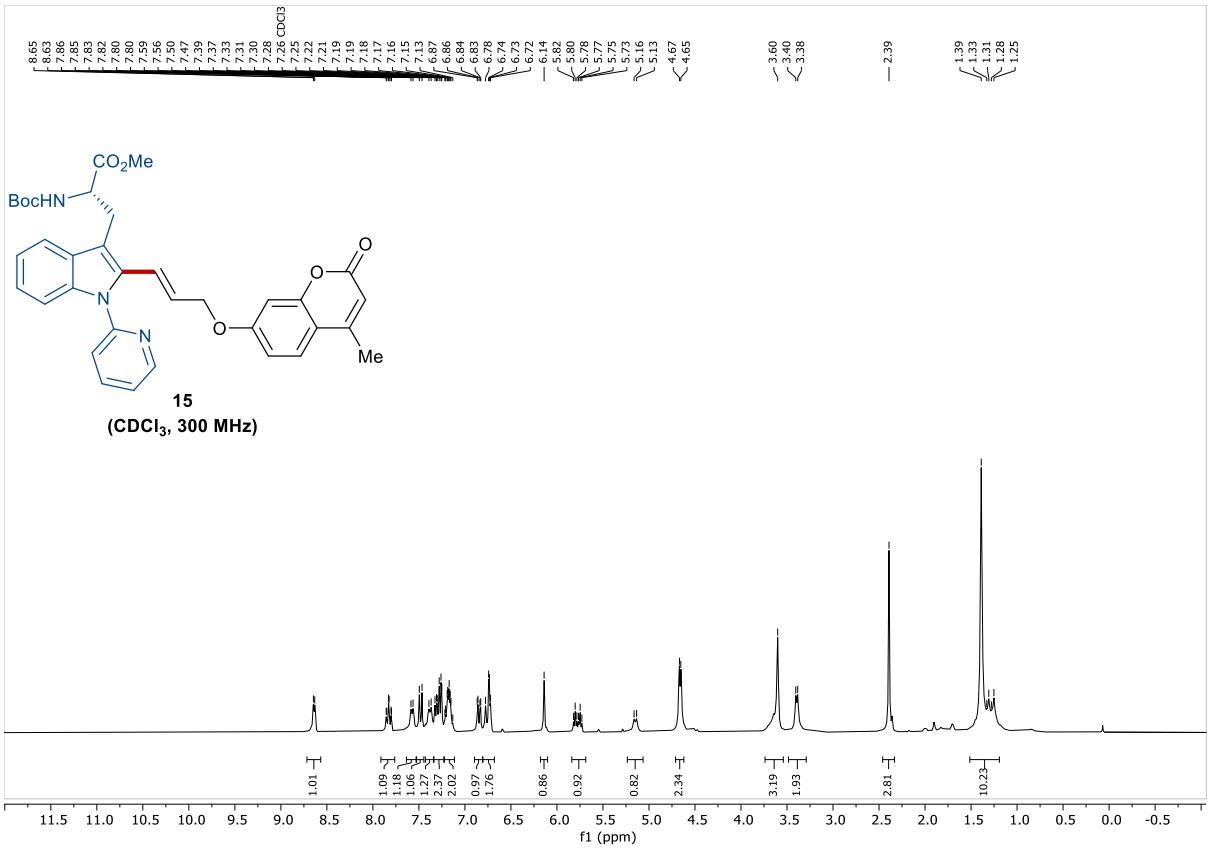
13
($CDCl_3$, 300 MHz)

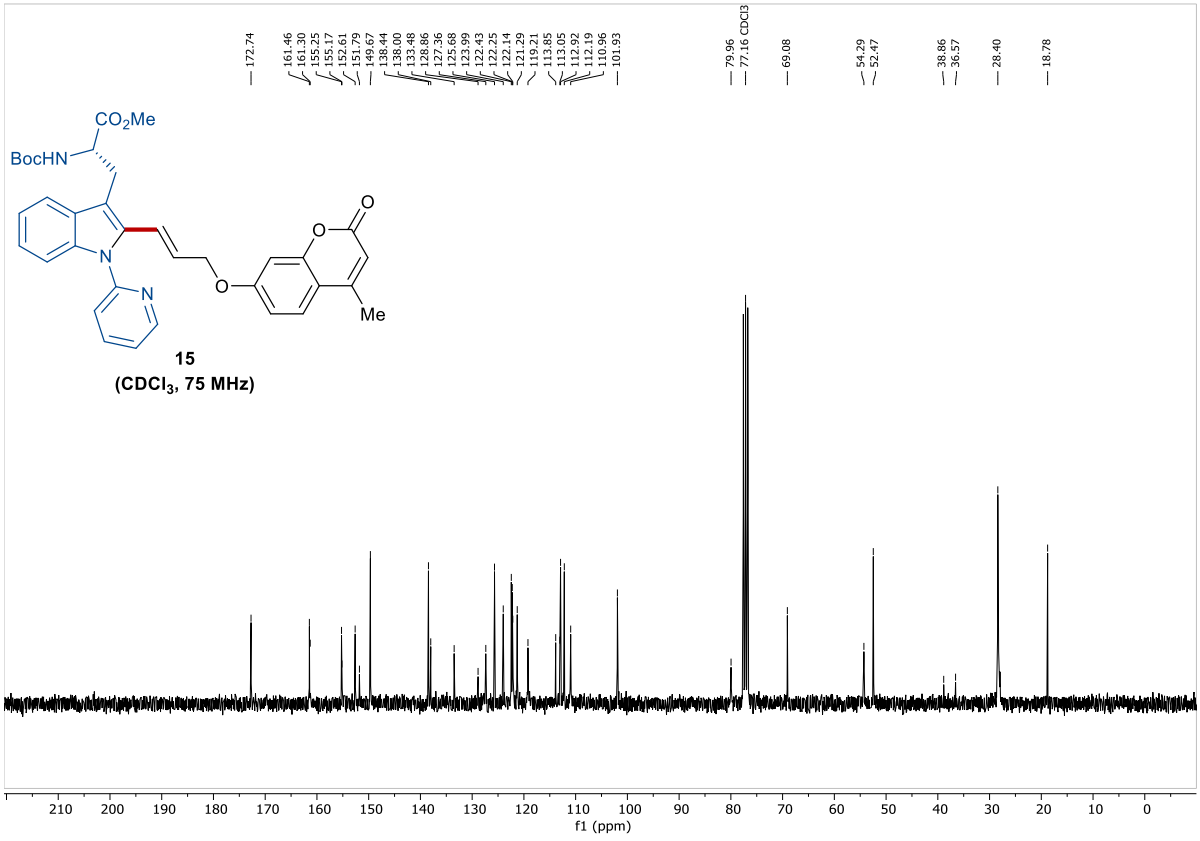


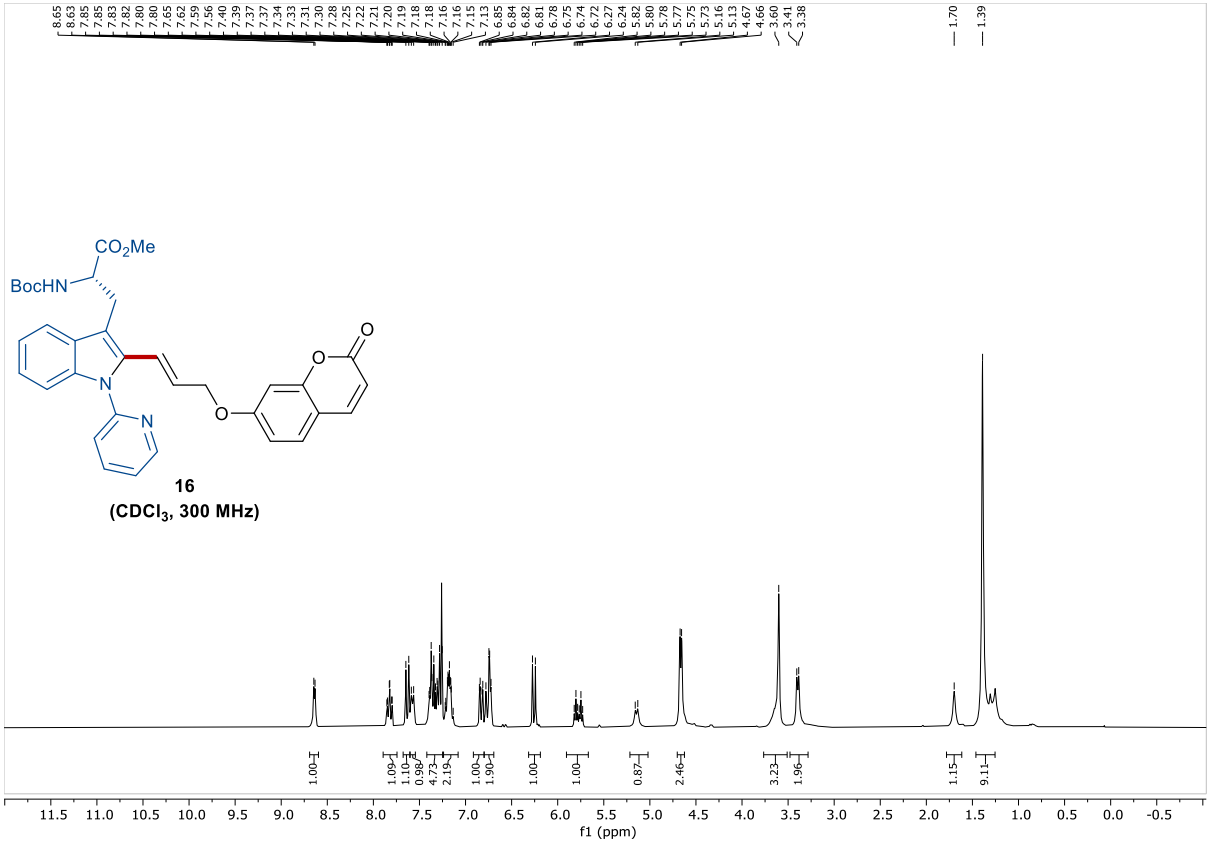
13
($CDCl_3$, 75 MHz)

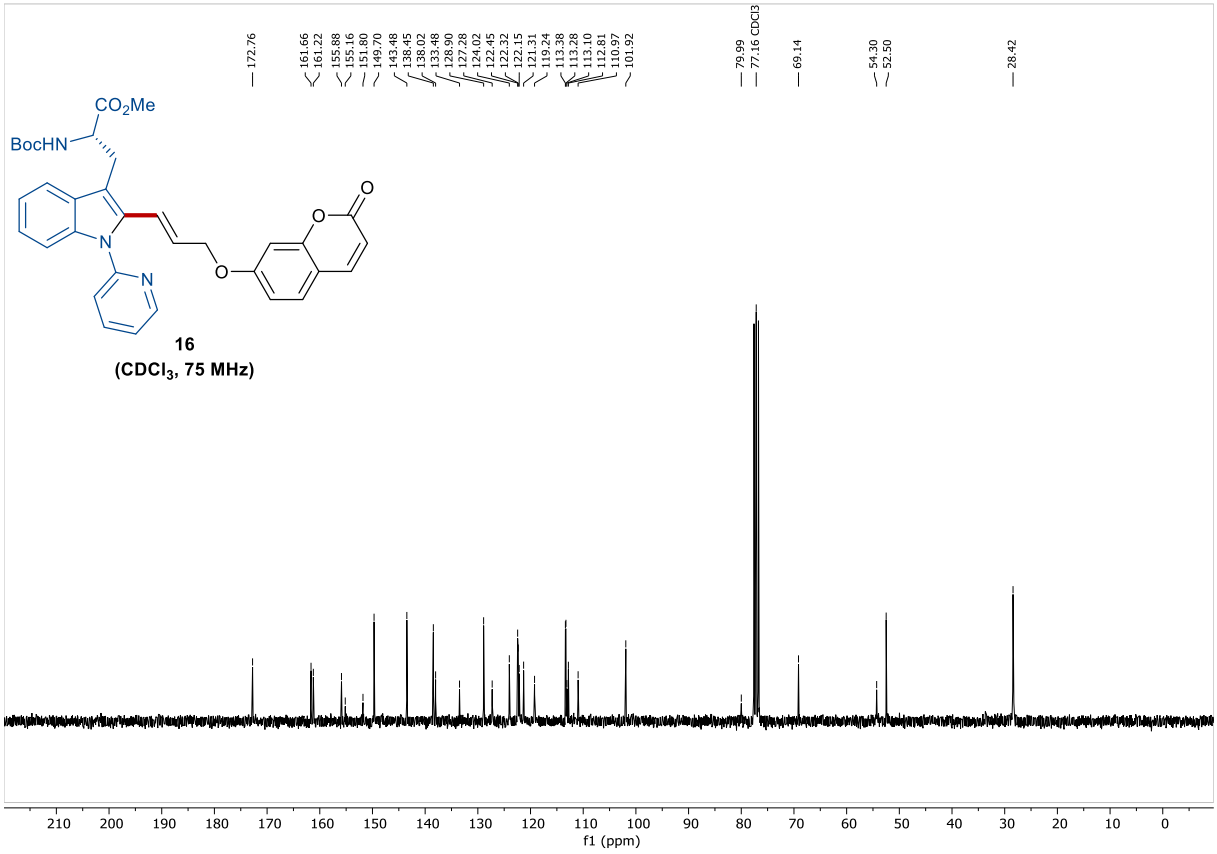

CO2Me
AcHN
O
O
N
N
O
Me
14
(CDCl3, 75 MHz)
f1 (ppm)

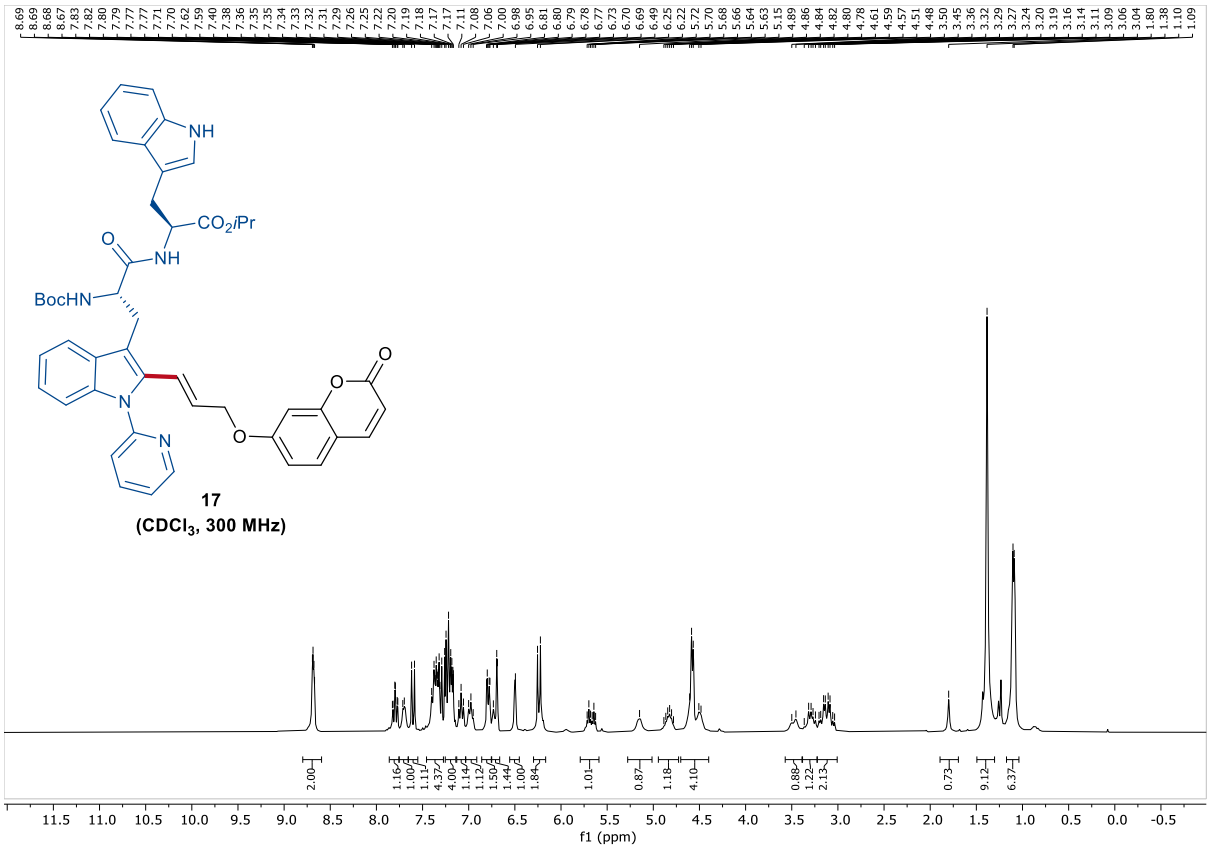

CO2Me
AcHN
O
O
N
N
O
Me
14
(CDCl3, 75 MHz)
f1 (ppm)

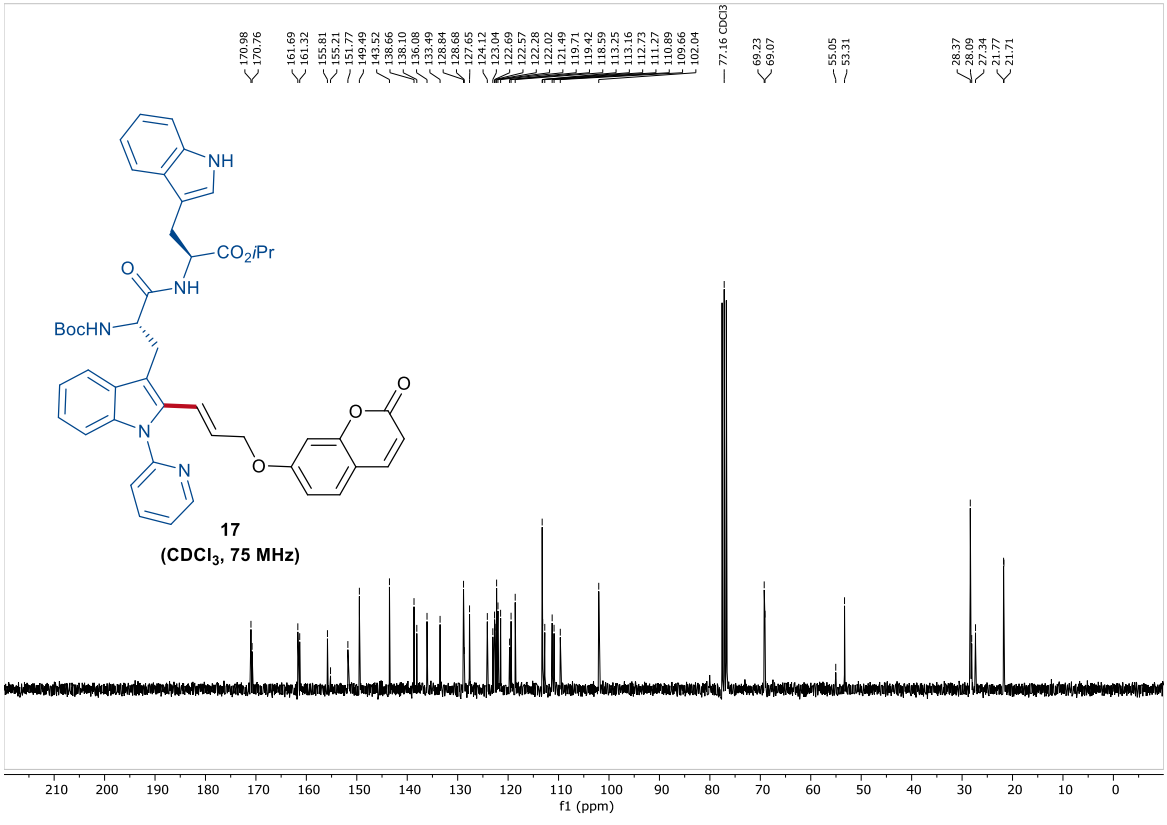

8.65
8.63
7.86
7.85
7.83
7.82
7.80
7.80
7.59
7.56
7.50
7.47
7.39
7.37
7.33
7.31
7.30
7.28
7.26 CDCl3
7.25
7.22
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.13
6.87
6.86
6.84
6.83
6.78
6.74
6.73
6.72
6.44
5.82
5.80
5.78
5.77
5.75
5.73
5.16
5.13
4.67
4.65
3.60
3.40
3.38
2.39
1.39
1.33
1.31
1.28
1.25
CO2Me
BocHN
O
O
N
O
N
Me
15
(CDCl3, 300 MHz)
1.01
1.09
1.18
1.06
1.27
2.37
2.02
0.97
1.76
0.86
0.92
0.82
2.34
3.19
1.93
2.81
10.23
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

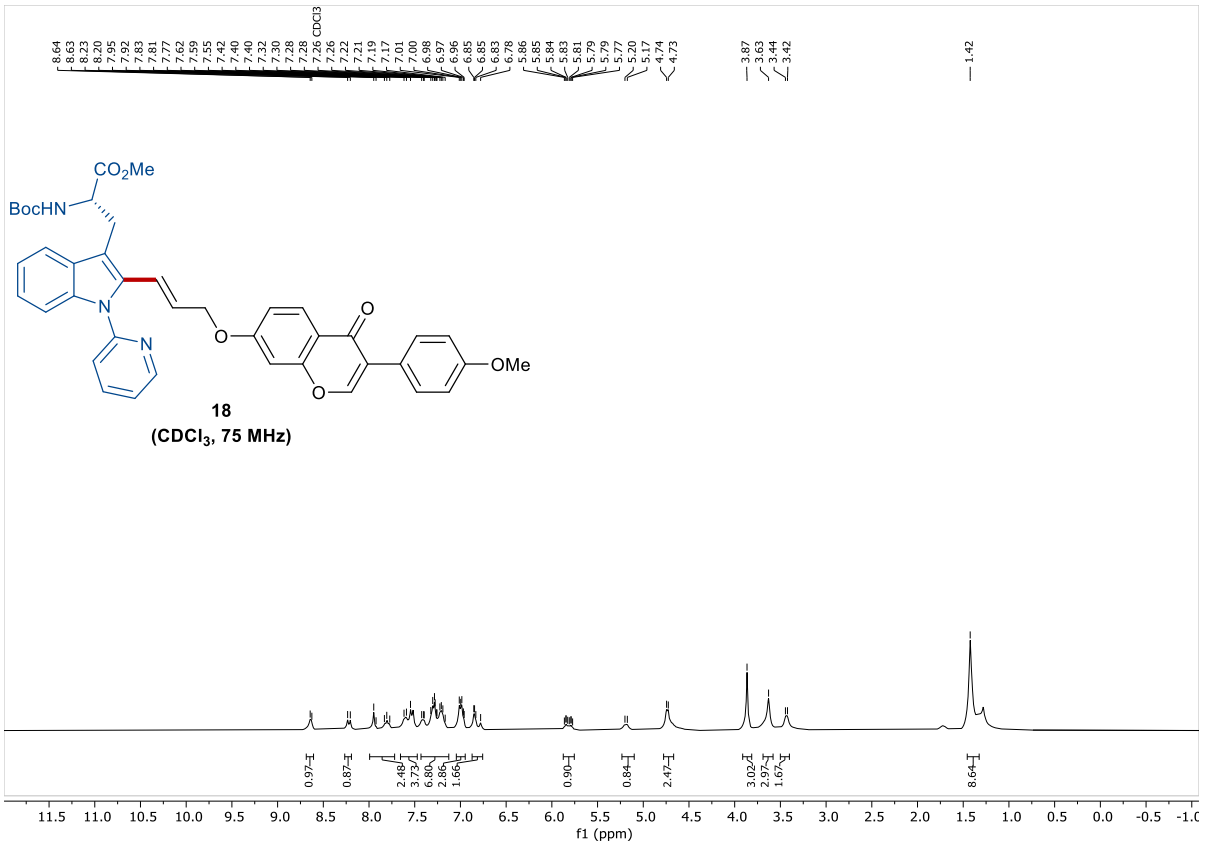

172.74
161.46
161.30
155.25
155.17
152.61
151.79
149.67
138.44
138.00
133.48
128.86
127.36
125.68
123.99
122.43
122.25
122.14
121.29
119.21
113.85
113.05
112.92
112.19
110.96
101.93
79.96
77.16 CDCl3
69.08
54.29
52.47
38.86
36.57
28.40
18.78
CO2Me
BocHN
O
O
N
O
N
Me
15
(CDCl3, 75 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CO2Me
BocHN
O
O
N
O
N
16
(CDCl3, 300 MHz)
f1 (ppm)

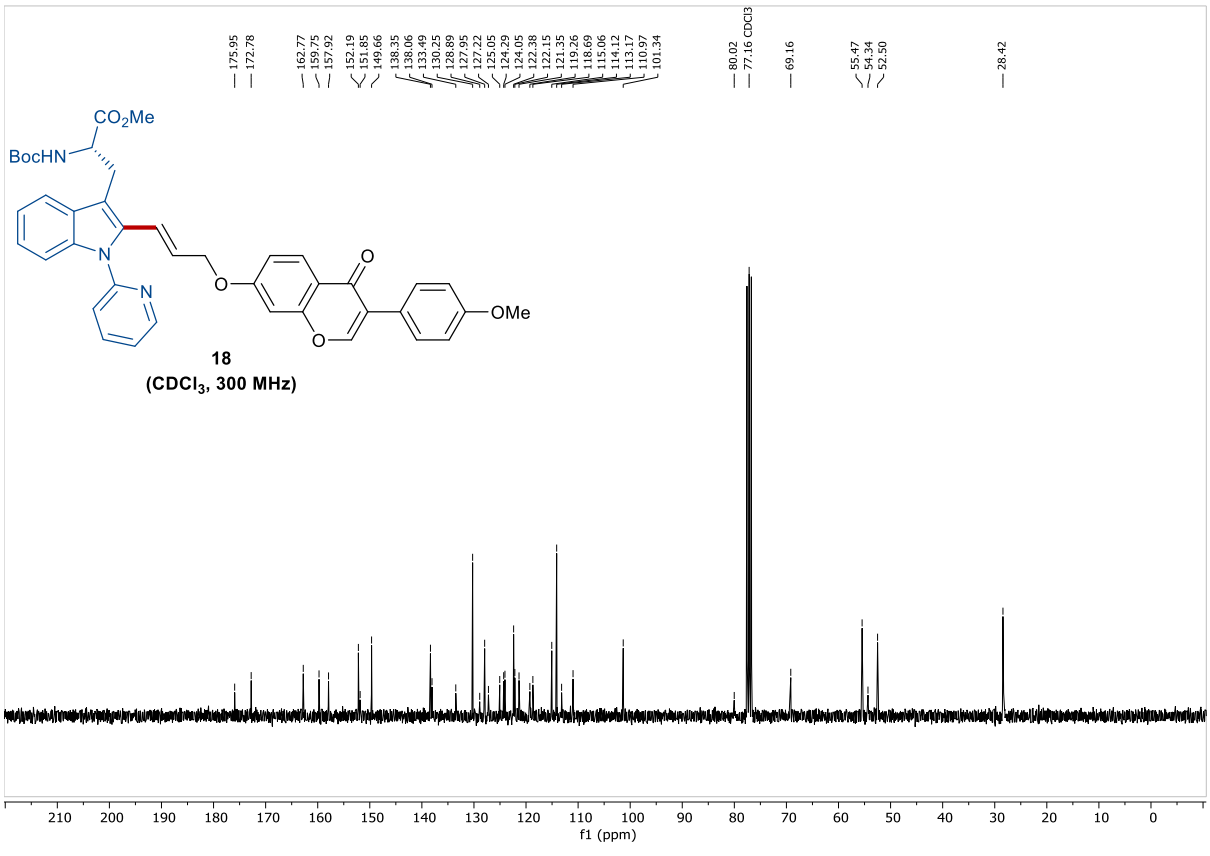

CO2Me
BocHN
O
O
N
O
N
16
(CDCl3, 75 MHz)
f1 (ppm)


NH
CO2iPr
O
NH
BocHN
O
O
N
O
N
17
(CDCl3, 300 MHz)
f1 (ppm)

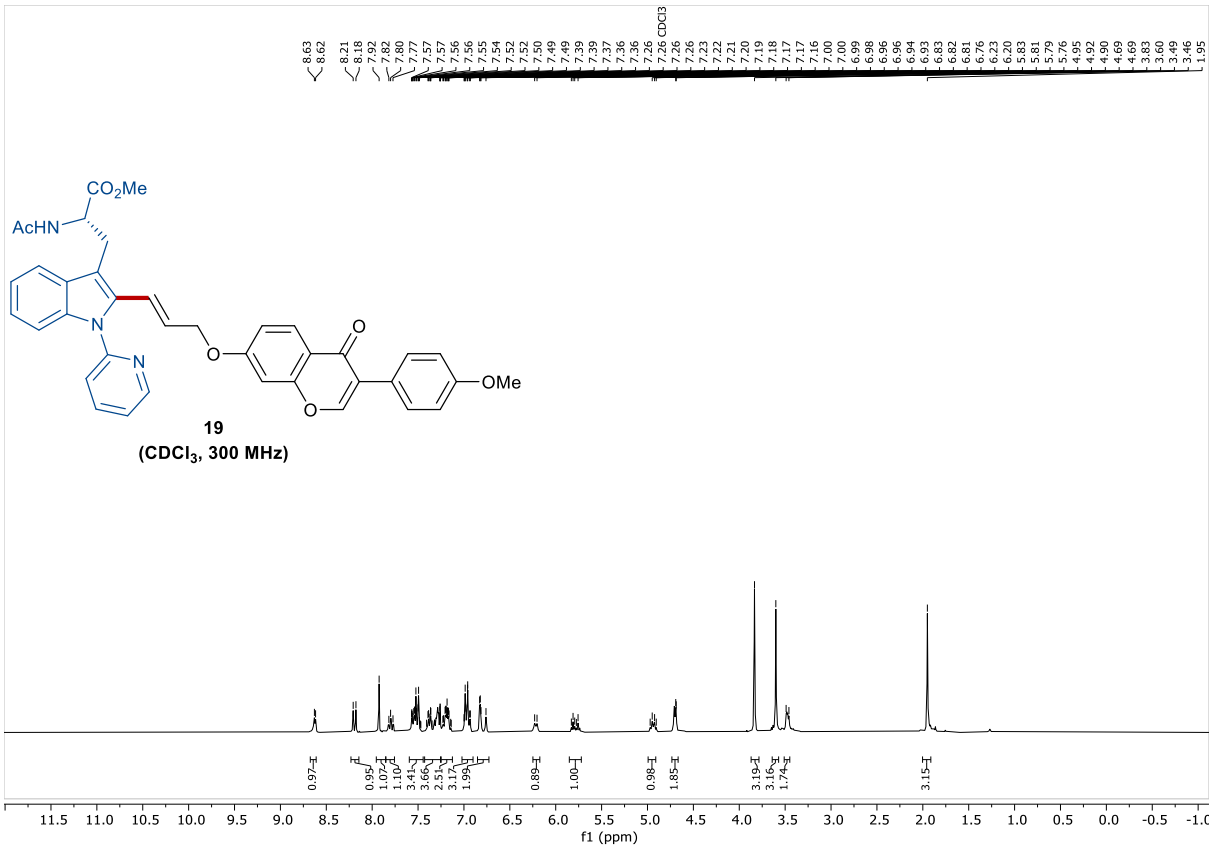

NH
CO2iPr
O
NH
BocHN
O
O
N
O
N
17
(CDCl3, 75 MHz)
f1 (ppm)



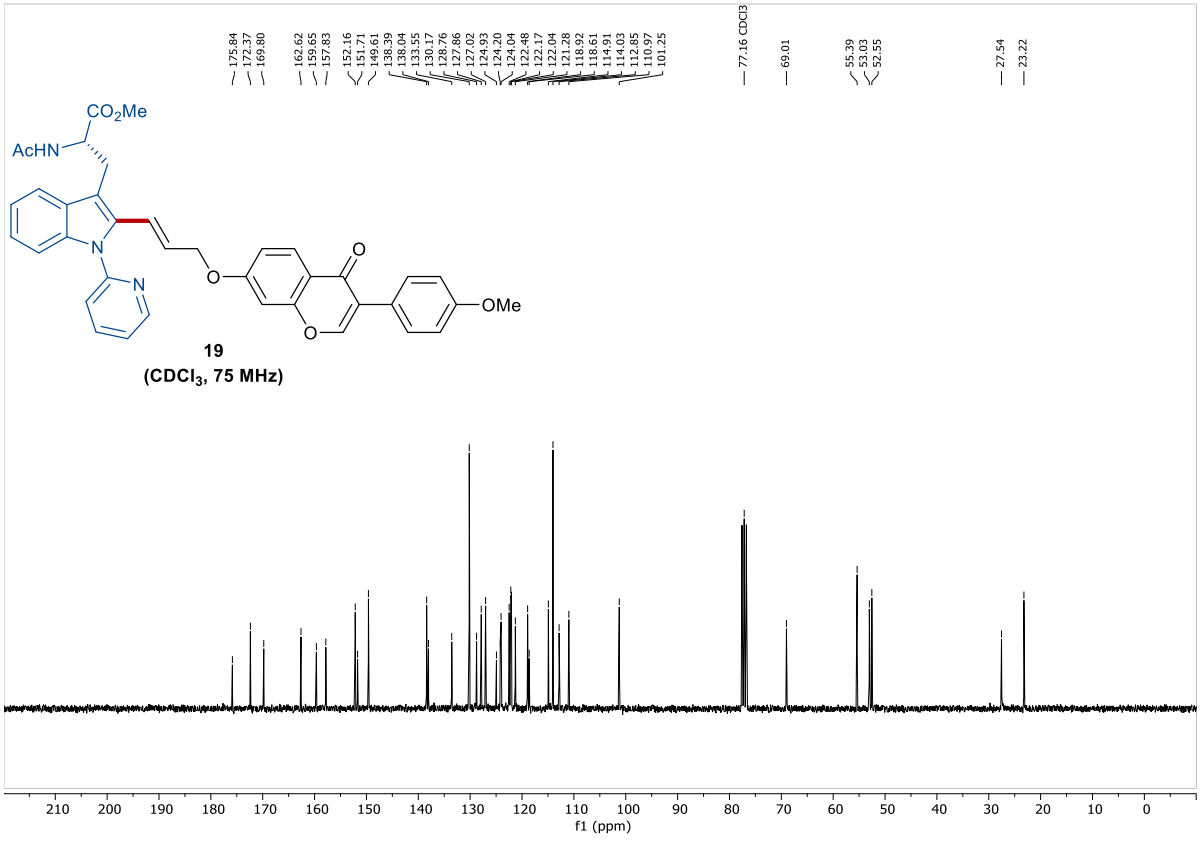
18
($CDCl_3$, 75 MHz)



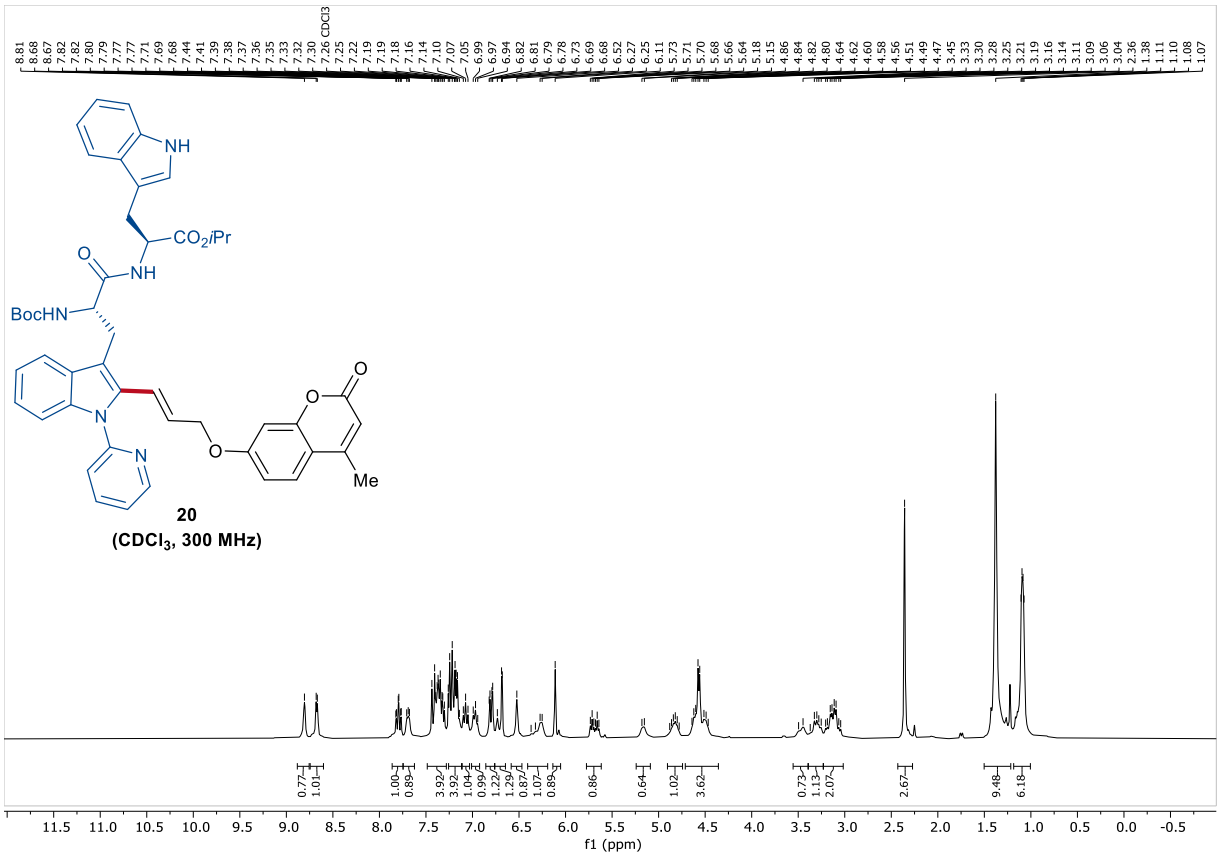
18
($CDCl_3$, 300 MHz)

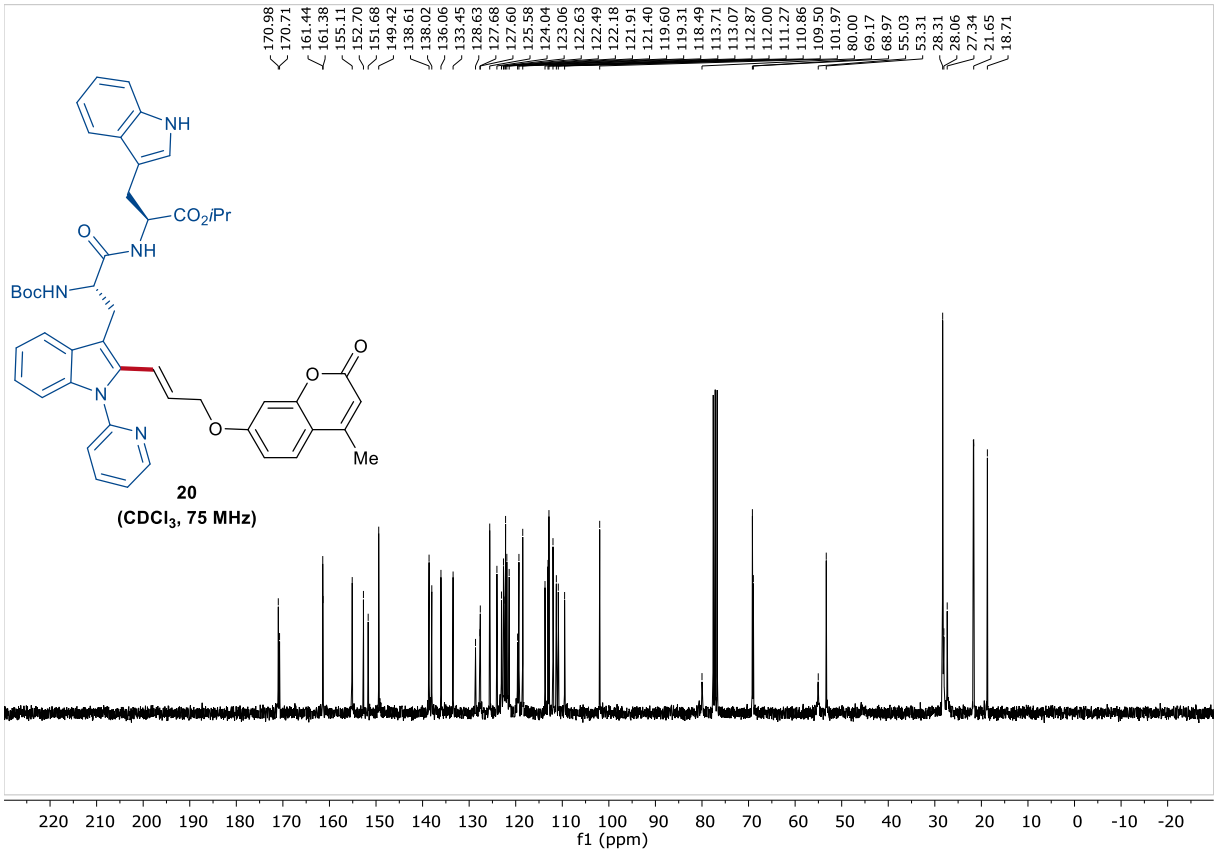


19
($CDCl_3$, 300 MHz)



19
($CDCl_3$, 75 MHz)


NH
CO2iPr
O
NH
BocHN
O
O
N
N
O
Me
20
(CDCl3, 300 MHz)
f1 (ppm)


NH
CO2iPr
O
NH
BocHN
O
O
N
N
O
Me
20
(CDCl3, 75 MHz)
f1 (ppm)

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