Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Weak-coordination-auxiliary aminocatalysis enables directed [3+2] cyclization for 2-acylindolizines

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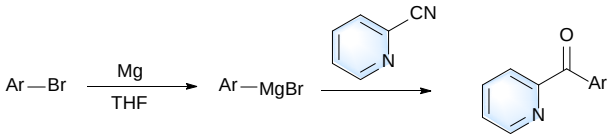
Contents

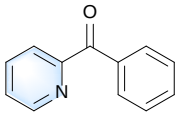
1. General Information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. All reactions were performed under an atmosphere of Ar unless specified otherwise. ^{1}H (300 or 400 MHz), ^{13}C (75 or 100 MHz) spectra were recorded on a 300 MHz or 400 MHz spectrometer with the sample dissolved in $CDCl_3$ and DMSO-d_6. Coupling constants are reported in Hertz (Hz) and signal multiplicity is denoted as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), sextet (sex.), septet (sept.), multiplet (m), and broad (br). Yields refer to isolated compunds estimated to be >95% pure as determined by ^{1}H NMR. ESI mass spectra were recorded on Bruker Daltonic spectrometers maXis (ESI-QTOF-MS) and micrOTOF (ESI-TOF-MS). All chemicals are commercially available and purchased from TH. GEYER Company. It will be mentioned if there is any further purification for the chemicals. FT-IR spectra were recorded on Alpha FT-IR Spectrometer (Bruker, Germany) at room temperature. All samples were measured between 4000 and 500 cm^{-1} with a resolution of 4 cm^{-1} using Platinum ATR and accumulated 24 scans. Melt point were recorded on melting point apparatus, Electrothermal IA 9200.

2. Experimental Procedures for Chemical Feedstocks

2.1 General procedures A for heteroaryl ketones derivatives





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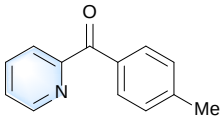

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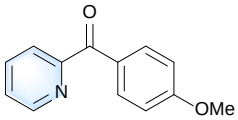

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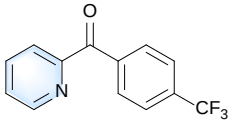
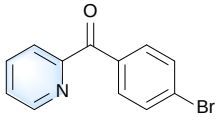


2f



2g

The following starting chemicals (**2c**-**2g**) were synthesized according to previously described methods.[1] A solution of the bromobenzene (10.0 mmol, 1.00 equiv.) in 15 mL of dry THF was dropwised into magnesium (12 mmol, 1.2 equiv.) and stirred in Ar gas in room temperature. After the formation of the Grignard reagent (the color changed to gray), then stopped it. At the same time, carbonitrile (8 mmol, 0.8 equiv.) was dissolved in THF (10 mL), which was dropwised into the mixture solution of Grignard reagent at 0 ˚C. After that, the reaction was quenched by a solution of saturated NH_4Cl. The organic layer was separated and extracted twice by CH_2Cl_2. After evaporation, the organic layer was redissolved in Et_2O (30 mL) and 6 M HCl (6 mL) was added into the solution. After 30 min, the organic layer was separated, and the aqueous layer was basified by saturated $NaHCO_3$ and then extracted three times by CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated in rotary evaporator. The residue was purified by column chromatography with *n*-hexane and ethyl acetate to afford **2c**. Other pyridine ketones **2d**−**2g** were prepared with the similar procedures, and characterized by NMR analysis.

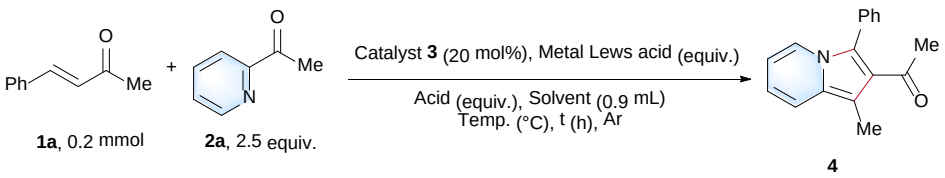
3. Experimental General Procedures B for Indolizine

A mixture of α,β-unsaturated ketones (0.2 mmol), heteroaryl ketones (2.5 equiv.), catalyst **3i** (0.04 mmol), propionic acid (2.0 equiv.) and $LiBF_4$ (3.0 equiv.) in the CF_3CH_2OH (0.9 mL) were stirred at 140 ˚C under Ar atmosphere for 18 h.

Workup: The reactions were conducted in a sealed Schlenk tube and heated by an IKA magnetic heating agitator with heating block. The reaction temperature was directly read from temperature detector of IKA apparatus and was calibrated by thermometer. After cooling to room temperature, the reaction mixture was basified up to pH 7 via stad. Na_2CO_3 aqueous solution, then extracted by diether (3×3 mL) and dried over anhydrous Na_2SO_4. After filtration and concentrated in rotary evaporator, the crude product was purified with flash chromatography on silica gel (ethyl acetate : *n*-hexane) to give products. Here need to mention that all the indolizine products are sensitive and easy to be oxidized in air atmosphere.

4. Optimization of Reaction Conditions.

Table S1. Optimization of organocatalyzed dehydration [3+2]-cyclization

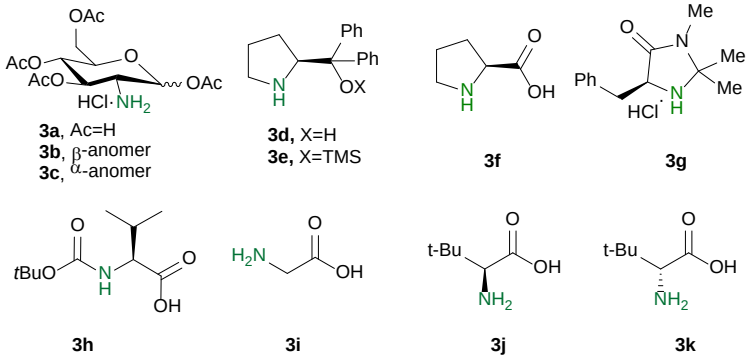


1a, 0.2 mmol **2a**, 2.5 equiv. **4**

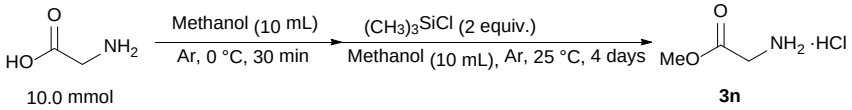
Entry	Catalyst (20%)	Metal Lews acid (equiv.)	Acid (equiv.)	Solvent (mL)	T/h	Yield (%)[a]
1	-	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	13
2	3a	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	27
3	3b	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	35
4	3c	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	25
5	3d	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	21
6	3e	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	30
7	3f	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	32
8	3g	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	45
9	3h	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	57
10	**3i**	**$LiBF_4$ (3.0)**	**PA (2)**	**CF_3CH_2OH (0.9)**	**140/ 18**	**56**
11	3j	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	58
12	3k	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	53
13	3g	$LiSO_3CF_3$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	25
14	3g	LiCl (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	18
15	3g	LiBr (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	39
16	3g	LiI (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	22
17	3g	$LiBF_4$ (3.0)	AcOH (2)	CF_3CH_2OH (0.9)	140/ 18	42
18	3g	$LiBF_4$ (3.0)	CF_3COOH (2)	CF_3CH_2OH (0.9)	140/ 18	16
19	3g	$LiBF_4$ (3.0)	HCOOH (2)	CF_3CH_2OH (0.9)	140/ 18	23
20	3g	$LiBF_4$ (3.0)	CF_3SO_2OH (2)	CF_3CH_2OH (0.9)	140/ 18	2
21	3g	$LiBF_4$ (3.0)	PA (2)	HFIP (0.9)	140/ 18	31
22	3g	$LiBF_4$ (3.0)	PA (2)	EtOH (0.9)	140/ 18	38
23	3g	$LiBF_4$ (3.0)	PA (2)	*n*-BuOH (0.9)	140/ 18	13
24	3g	$LiBF_4$ (3.0)	PA (2)	Dioxide (0.9)	140/ 18	17
25	3g	$LiBF_4$ (3.0)	PA (2)	CH_3CN (0.9)	140/ 18	13
26	3g	$LiBF_4$ (3.0)	PA (2)	DCM (0.9)	140/ 18	7
27	3g	$LiBF_4$ (3.0)	PA (2)	toluene (0.9)	140/ 18	n.d.
28	3g	$LiBF_4$ (3.0)	PA (2)	DMF (0.9)	140/ 18	n.d.
29	3g	$LiBF_4$ (3.0)	PA (2)	H_2O (0.9)	140/ 18	3
30	3g	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	100/ 18	34

31	3g	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	120/ 18	49
32	3g	$LiBF_4$ (3.0)	PA (5)	CF_3CH_2OH (0.9)	140/ 18	49
33	3g	$LiBF_4$ (3.0)	PA (10)	CF_3CH_2OH (0.9)	140/ 18	41
34	3g	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 36	55
35	3g (40%)	$LiBF_4$ (3.0)	PA (2)	CF_3CH_2OH (0.9)	140/ 18	63

[a]Reactions were carried out at 140 ˚C with 4-phenylbut-3-en-2-one (0.2 mmol), 2-acetylpyridine (0.5 mmol), catalyst (0.02 mmol) in CF_3CH_2OH (0.9 mL), under Ar gas condition with stirring for 18 h. Yield was determined by ^{1}H-NMR analysis with CH_2Br_2 as internal standard. [b] 2-Acetylpyridine (0.3 mmol). PA means propionic acid.



5. Preparation of the Intermediates 3n and Unsuccessful or Low Yielding Substrates



1) Glycine (10.0 mmol) was added in a three neck round bottom flask and dissolved in anhydrous methanol (10 mL) for 30 min at 0 ˚C under Ar gas atmosphere. Then, Chlorotrimethylsilane (2 equiv.) was dissolved in anhydrous methanol (10 mL), which was added slowly into the glycine solution. The mixture solution was stirred for 4 days at 25 ˚C under Ar gas atmosphere. After the completion of reaction monitored by TLC, the reaction mixture was concentrate to give a product glycine ester hydrochloride. Work-up gave product **3n** (1.2 g, 9.7 mmol, isolated yield 97%) as a white solid. **^{1}H-NMR** (400 MHz, D_2O) δ 3.98 (s, 2H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, D_2O) δ 168.7, 53.4, 40.1. The compound is known, and the NMR data is in accordance with the previous literature.[2]

2) Unsuccessful or low yielding substrates

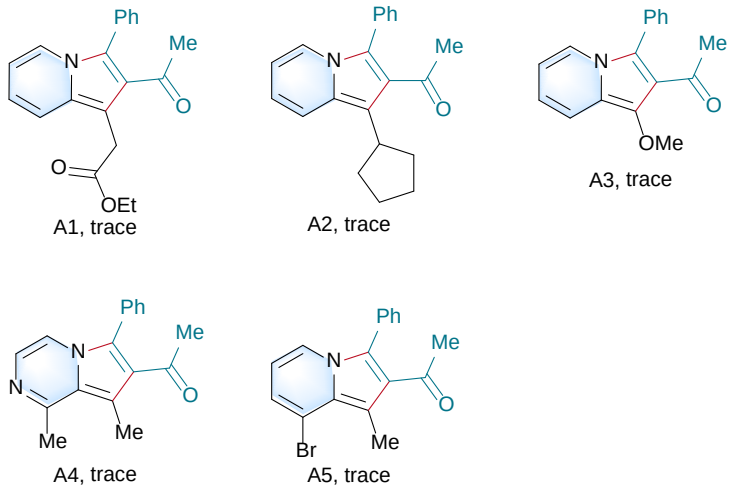
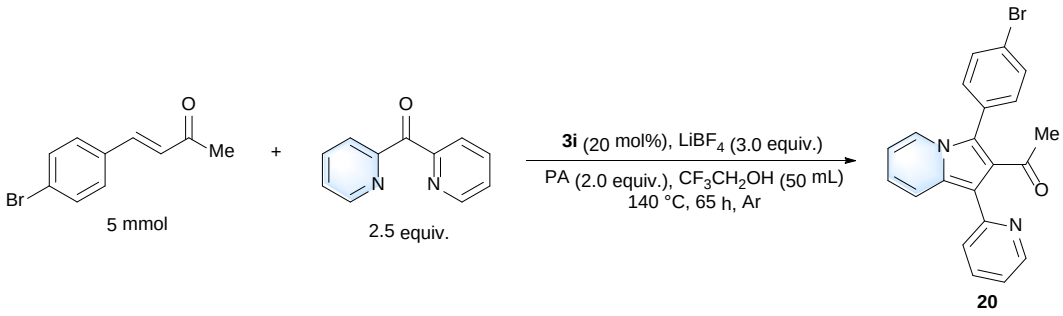


Figure S1. Unsuccessful or low yielding substrates under standard conditions.

6. Large Scale Synthesis and Late-stage Diversifications

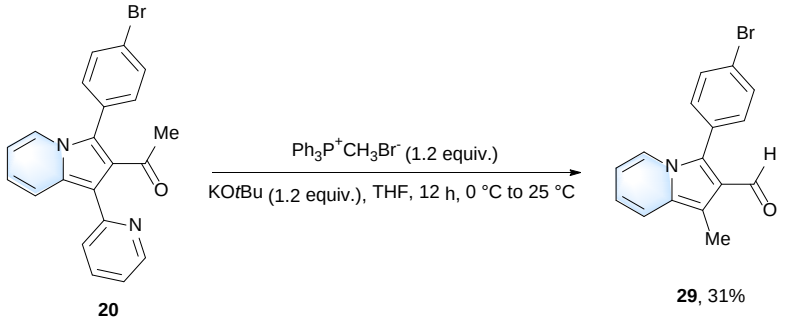
1) Large scale synthesis for product **20**



Preparation of A mixture of 1-(3-(4-bromophenyl)-1-(pyridin-2-yl)indolizin-2-yl)ethan-1-one (**25**): (*E*)-4-(4-bromophenyl)but-3-en-2-one (5.0 mmol), di(pyridin-2-yl)methanone (2.5 equiv.), catalyst **3i** (1.0 mmol), propinic acid (2.0 equiv.) and $LiBF_4$ (3.0 equiv.) in the CF_3CH_2OH (50 mL) were stirred at 140 ˚C under Ar atmosphere for 65 h. The reaction was monitored by TLC.

Workup: The reactions were conducted in a sealed Schlenk tube and heated by an IKA magnetic heating agitator with heating block. The reaction temperature was directly read from temperature detector of IKA apparatus and was calibrated by thermometer. After cooling to room temperature, the reaction mixture was concentrated in rotary evaporator, the crude product was purified with flash chromatography on silica gel (ethyl acetate : *n*-hexane) to give products. Work-up gave product **25** (1.03 mg, 2.65 mmol, isolated yield 53%) as a yellow liquid.

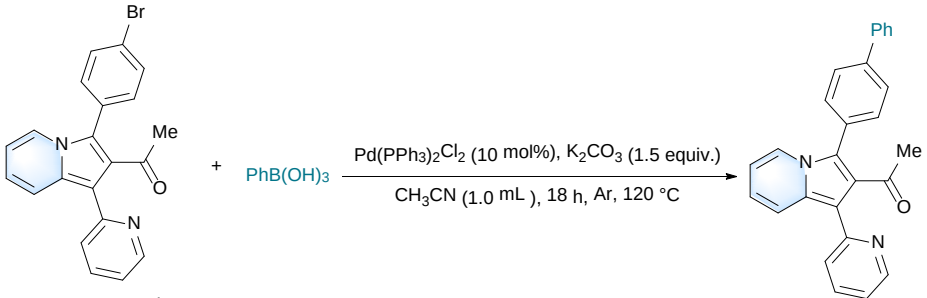
2) Late-stage transformation of **20** for product **29**



20 **29**, 31%

Preparation of 3-(4-bromophenyl)-1-methylindolizine-2-carbaldehyde (**29**): A mixture of **20** (0.2 mmol), $Ph_3P^+CH_3Br$ (1.2 equiv.) and KO*t*Bu in anhydrous THF solution (2.0 mL) were stirred at 0 ˚C to 25 ˚C under air atmosphere for 12 h. The reactions were conducted in a sealed Schlenk tube and stirred by an IKA magnetic heating agitator with heating block. The reaction temperature was calibrated by thermometer. After the reaction, the solution was concentrated under rotary evaporator. The crude product was purified with flash chromatography on silica gel (ethyl acetate : *n*-hexane) to give products. Work-up gave product **29** (18.8 mg, 0.06 mmol, isolated yield 31%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2916, 2743, 1663, 1525, 1506, 1469, 1434, 1397, 1377, 1350, 1319, 1247, 1218, 1181, 1152, 1142, 1115, 1105, 1072, 1055, 1008, 938, 876, 835, 808, 736, 721, 709, 699, 678, 633, 620, 569, 550, 534, 492, 437, 418. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.35 – 7.28 (m, 3H), 6.61 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.43 – 6.40 (m, 1H), 2.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.1, 132.4, 132.3, 130.8, 129.4, 127.8, 123.4, 123.3, 122.0, 119.2, 117.8, 113.1, 110.4, 9.6. **ESI-HRMS**: m/z calcd. for $C_{16}H_{12}NOBr$ $[M+Na]^+$: 336.0000, found 335.9992.

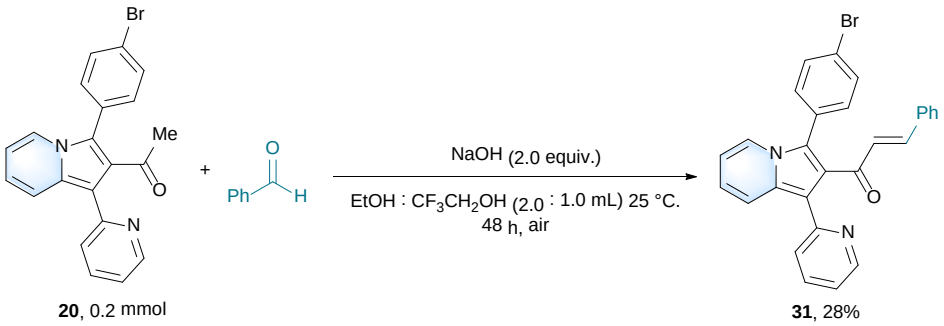
3) Late-stage transformation of **20** for product **30**



20, 0.2 mmol 2.0 equiv. **30**, 80%

Preparation of 1-(3-([1,1'-biphenyl]-4-yl)-1-(pyridin-2-yl)indolizin-2-yl)ethan-1-one (**30**): A mixture of **20** (0.2 mmol), phenylboronic acid (2.0 equiv.), catalyst $Pd(PPh_3)_2Cl_2$ (10% mmol), and K_2CO_3 (1.5 equiv.) in the CH_3CN (1.0 mL) were stirred at 120 ˚C under Ar atmosphere for 18 h. The reactions were conducted in a sealed Schlenk tube and heated by an IKA magnetic heating agitator with heating block. The reaction temperature was directly read from temperature detector of IKA apparatus and was calibrated by thermometer. After cooling to room temperature, the reaction mixture was basified up to pH 7 via stad. Na_2CO_3 aqueous solution, then extracted by diether (3×3 mL) and dried over anhydrous Na_2SO_4. After filtration and concentrated in rotary evaporator, the crude product was purified with flash chromatography on silica gel (ethyl acetate : *n*-hexane) to give products. Work-up gave product **30** (62.1 mg, 0.16 mmol, isolated yield 80%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 3027, 1675, 1587, 1515, 1473, 1445, 1409, 1346, 1261, 1245, 1193, 1152, 1053, 1008, 909, 861, 837, 800, 764, 725, 696, 645, 577, 505, 406. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.8 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.69 – 7.64 (m, 3H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.11 (dd, *J* = 7.2, 5.1 Hz, 1H), 6.78 (dd, *J* = 9.0, 6.6 Hz, 1H), 6.50 (t, *J* = 6.8 Hz, 1H), 2.13 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.8, 153.8, 149.2, 141.6, 140.2, 136.4, 131.3, 131.1, 129.0, 128.9, 127.7, 127.6, 127.1, 125.2, 124.3, 123.1, 120.7, 120.6, 119.3, 112.9, 112.9, 32.1. **ESI-HRMS**: *m/z* calcd. for $C_{27}H_{20}N_2O$ $[M+H]^+$: 389.1654, found 389.1659.

4) Late-stage transformation of **20** for product **31**

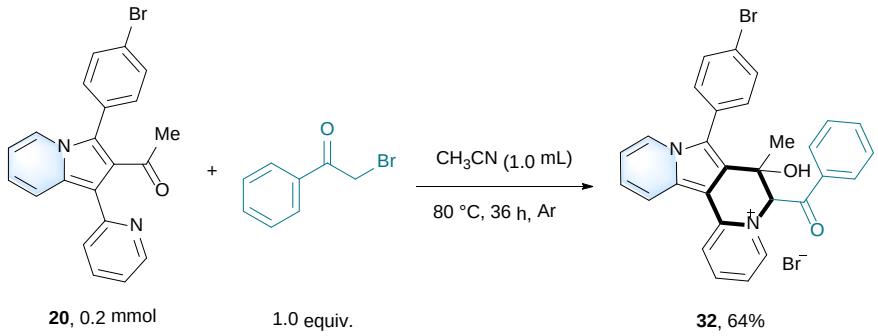


20, 0.2 mmol **31**, 28%

Preparation of (E)-1-(3-(4-bromophenyl)-1-(pyridin-2-yl)indolizin-2-yl)-3-phenylprop-2-en-1-one (**29**): A mixture of **20** (0.2 mmol), benzaldehyde (3.0 equiv.) and NaOH (3.0 equiv.) in the EtOH : CF_3CH_2OH (2.0 : 1.0 mL) were stirred at 25 ˚C under air atmosphere for 48 h. The reactions were conducted in a glass tube and stirred by an IKA magnetic heating agitator. The

reaction was monitored by TLC. After filtration and concentrated in rotary evaporator, the crude product was purified with flash chromatography on silica gel (ethyl acetate : *n*-hexane) to give products. Work-up gave product **31** (26.8 mg, 0.06 mmol, isolated yield 28%) as a yellow solid. **mp**: 103−105 ˚C. **FT-IR**: *v* (cm^{-1}): 2924, 2850, 1720, 1632, 1587, 1513, 1475, 1447, 1331, 1263, 1162, 1090, 1069, 1010, 977, 907, 828, 727, 690, 563, 509, 486, 406. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.23 – 7.17 (m, 4H), 7.14 – 7.12 (m, 2H), 7.08 – 7.05 (m, 1H), 6.91 – 6.85 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.59 – 6.56 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.9, 148.9, 144.1, 136.7, 134.7, 132.3, 132.3, 130.3, 129.0, 128.7, 128.2, 128.1, 126.7, 125.5, 124.8, 123.1, 122.7, 121.1, 120.7, 119.9, 114.1, 113.3. **ESI-HRMS**: m/z calcd. for $C_{28}H_{19}N_2OBr$ [M+H]+: 479.0759, found 479.0754.

5) Late-stage transformation of **20** for product **32**

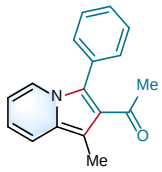


20, 0.2 mmol 1.0 equiv. **32**, 64%

Preparation of (6S)-6-benzoyl-8-(4-bromophenyl)-7-hydroxy-7-methyl-6,7-dihydroindolizino [1,2-a]quinolizin-5-ium bromide (**32**): A mixture of **20** (0.2 mmol) and 2-bromo-1-phenylethan-1-one (1.0 equiv.) in the CH_3CN (1.0 mL) were stirred at 80 ˚C under Ar atmosphere for 36 h. The reactions were conducted in a sealed Schlenk tube and heated by an IKA magnetic heating agitator with heating block. The reaction temperature was directly read from temperature detector of IKA apparatus and was calibrated by thermometer. After cooling to room temperature, resulting precipitate was filtered off, washed with *n*-hexane and washed with ethyl acetate, then gave product **29** (75.3 mg, 0.13 mmol, isolated yield 64%) as a yellow solid. **mp**: 345−346 ˚C. **FT-IR**: *v* (cm^{-1}): 3264, 2990, 1690, 1624, 1597, 1539, 1498, 1445, 1360, 1317, 1269, 1234, 1199, 1150, 1137, 1121, 1098, 1069, 1012, 989, 948, 917, 878, 828, 767, 736, 688, 631, 614, 583, 560,

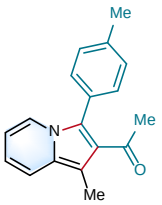
515, 476, 445, 416. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.91 (d, *J* = 6.4 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.46 – 8.39 (m, 2H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 6.8 Hz, 1H), 6.93 (s, 1H), 6.55 (s, 1H), 1.03 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 192.3, 147.8, 144.8, 144.3, 136.1, 134.6, 134.2, 133.2, 132.5, 131.9, 129.2, 129.1, 128.1, 126.5, 126.0, 123.7, 123.6, 122.6, 122.4, 120.8, 117.9, 114.7, 101.8, 77.9, 67.4, 25.7. **ESI-HRMS**: *m/z* calcd. for $C_{29}H_{22}N_2O_2Br^+$ [M]: 510.0937, found 510.0895.

7. Characterization of Products



4

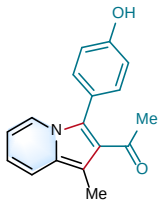
1-(1-methyl-3-phenylindolizin-2-yl)ethan-1-one: According to the general procedure B, work-up gave product **4** (26.9 mg, 0.11 mmol, isolated yield 54%) as a yellow solid. **mp**: 93−94 ˚C. **FT-IR**: *v* (cm^{-1}): 2920, 1655, 1517, 1469, 1447, 1424, 1350, 1323, 1241, 1168, 954, 859, 767, 738, 701, 647, 589, 554, 495, 422. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.35 – 7.31 (m, 3H), 6.57 – 6.53 (m, 1H), 6.32 (t, *J* = 6.4 Hz, 1H), 2.46 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.3, 131.8, 131.1, 129.9, 129.3, 129.0, 126.2, 126.1, 122.5, 118.6, 116.8, 112.2, 110.1, 31.4, 10.2. **ESI-HRMS**: *m/z* calcd. for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1232, found 250.1227.



5

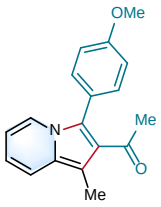
1-(1-methyl-3-(p-tolyl)indolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **5** (31.0 mg, 0.12 mmol, isolated yield 59%) as a yellow liquid. **FT-IR**: *v*

(cm^{-1}): 2916, 1657, 1529, 1475, 1422, 1350, 1327, 1245, 1210, 1183, 1168, 1109, 1043, 1020, 952, 913, 870, 808, 734, 703, 657, 635, 581, 560, 505, 427, 408. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.19 (m, 5H), 6.54 – 6.50 (m, 1H), 6.29 (t, *J* = 6.7 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.4, 138.9, 130.9, 130.0, 129.8, 128.7, 126.3, 125.9, 122.6, 118.6, 116.6, 112.0, 110.0, 31.3, 21.4, 10.2. **ESI-HRMS**: *m/z* calcd. for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1388, found 264.1377.



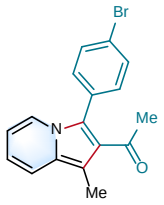
6

1-(3-(4-hydroxyphenyl)-1-methylindolizin-2-yl)ethan-1-one: According to the general procedure B, work-up gave product **6** (15.9 mg, 0.06 mmol, isolated yield 30%) as a yellow solid. **mp**: 101−103 ˚C. **FT-IR**: *v* (cm^{-1}): 2922, 1714, 1653, 1636, 1599, 1587, 1529, 1428, 1403, 1377, 1352, 1323, 1278, 1234, 1168, 1102, 1047, 1022, 997, 822, 740, 705, 661, 635, 618, 560, 528, 427, 408. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.70 – 6.66 (m, 1H), 6.52 (t, *J* = 6.7 Hz, 1H), 2.42 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 196.8, 158.1, 132.2, 129.0, 126.5, 125.2, 122.5, 121.2, 118.5, 117.0, 116.2, 112.4, 108.7, 30.9, 10.2. **ESI-HRMS**: *m/z* calcd. for $C_{17}H_{15}NO_2$ $[M+H]^+$: 266.1181, found 266.1169.



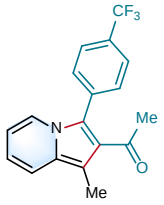
7

1-(3-(4-methoxyphenyl)-1-methylindolizin-2-yl)ethan-1-one: According to the general procedure B, work-up gave product **7** (18.4 mg, 0.07 mmol, isolated yield 33%) as a yellow solid. **mp**: 129−130 ˚C. **FT-IR**: *v* (cm^{-1}): 1654, 1607, 1529, 1469, 1442, 1422, 1401, 1350, 1304, 1230, 1177, 1123, 1107, 1030, 981, 954, 865, 828, 816, 764, 744, 705, 643, 583, 563, 530, 427. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.55 – 6.51 (m, 1H), 6.31 (t, *J* = 6.4 Hz, 1H), 3.82 (s, 3H), 2.46 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.3, 160.1, 132.3, 129.7, 126.1, 125.9, 123.7, 122.6, 118.6, 116.6, 114.7, 112.0, 110.0, 55.3, 31.3, 10.3. **ESI-HRMS**: *m/z* calcd. for $C_{18}H_{17}NO_2$ $[M+Na]^+$: 302.1157, found 302.1146.



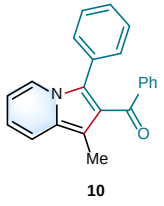
8

1-(3-(4-bromophenyl)-1-methylindolizin-2-yl)ethan-1-one: According to the general procedure B, work-up gave product **8** (37.3 mg, 0.11 mmol, isolated yield 57%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2920, 1659, 1583, 1510, 1469, 1426, 1350, 1323, 1243, 1168, 1100, 1067, 1010, 952, 936, 907, 872, 814, 732, 703, 651, 624, 565, 501, 422. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.59 – 6.55 (m, 1H), 6.35 (t, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.9, 132.6, 132.5, 130.7, 130.2, 126.3, 124.4, 123.3, 122.2, 118.7, 117.0, 112.5, 110.2, 31.5, 10.3. ESI-HRMS: *m/z* calcd. for $C_{17}H_{14}BrNO$ $[M+H]^+$: 328.0337, found 328.0340.



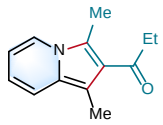
9

1-(1-methyl-3-(4-(trifluoromethyl)phenyl)indolizin-2-yl)ethan-1-one: According to the general procedure B, work-up gave product **9** (39.3 mg, 0.12 mmol, isolated yield 62%) as a yellow solid. **mp**: 112−113 ˚C. **FT-IR**: *v* (cm^{-1}): 2936, 1657, 1616, 1539, 1477, 1440, 1416, 1354, 1319, 1257, 1160, 1115, 1105, 1063, 1016, 977, 938, 857, 816, 744, 703, 684, 647, 596, 573, 501, 420. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.35 (d, *J* = 9.2 Hz, 1H), 6.63 – 6.59 (m, 1H), 6.40 – 6.37 (m, 1H), 2.46 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.9, 135.6 (q, $^{4}J_{C\text{-}F}$ = 1.2 Hz), 131.4, 130.8 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 130.5, 126.7, 126.1 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $^{1}J_{C\text{-}F}$ = 270.4 Hz), 123.9, 122.1, 118.8, 117.3, 112.8, 110.3, 31.6, 10.3. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.69. **ESI-HRMS**: *m/z* calcd. for $C_{18}H_{14}NOF_3$ $[M+H]^+$: 318.1106, found 318.1100.



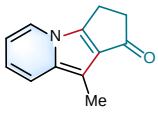
10

methyl-3-phenylindolizin-2-yl)(phenyl)methanone: According to the general procedure B, work-up gave product **10** (29.2 mg, 0.09 mmol, isolated yield 47%) as a yellow solid. **mp**: 87−88 ˚C. **FT-IR**: *v* (cm^{-1}): 2918, 2850, 1634, 1597, 1578, 1519, 1469, 1447, 1422, 1401, 1348, 1327, 1311, 1247, 1197, 1170, 1100, 1074, 1026, 942, 925, 849, 746, 729, 694, 647, 610, 587, 528, 476, 431. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.19 – 7.08 (m, 5H), 6.63 – 6.59 (m, 1H), 6.39 (t, *J* = 6.8 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.3, 139.0, 132.1, 130.6, 130.4, 130.2, 129.9, 128.6, 127.8, 127.7, 125.8, 125.1, 122.3, 118.5, 117.0, 111.9, 109.9, 9.6. ESI-HRMS: *m/z* calcd. for $C_{22}H_{17}NO$ $[M+H]^+$: 312.1388, found 312.1389.



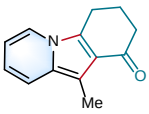
11

1-(1,3-dimethylindolizin-2-yl)propan-1-one: According to the general procedure B, work-up gave product **11** (35.4 mg, 0.18 mmol, isolated yield 88%) as a yellow solid. **mp**: 85−86 ˚C. **FT-IR**: *v* (cm^{-1}): 2976, 2932, 1651, 1581, 1490, 1409, 1366, 1317, 1214, 1152, 1022, 942, 802, 732, 420. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.51 – 6.48 (m, 1H), 6.43 (t, *J* = 6.8 Hz, 1H), 2.83 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.42 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 129.3, 124.8, 122.5, 121.5, 118.5, 115.4, 111.9, 107.4, 36.7, 11.3, 11.0, 8.3. **FTMS + c EI Full ms**: *m/z* calcd. for $C_{13}H_{15}NO$ [M]: 201.2690, found 201.1148.



12

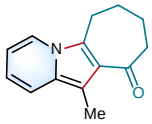
9-methyl-2,3-dihydro-1H-cyclopenta[b]indolizin-1-one: According to the general procedure B, work-up gave product **12** (15.9 mg, 0.09 mmol, isolated yield 43%) as a yellow solid. **mp**: 132−133 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 6.53 – 6.50 (m, 1H), 6.42 – 6.38 (m, 1H), 2.98 – 2.92 (m, 4H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 146.2, 135.6, 128.4, 122.3, 119.7, 116.7, 111.5, 103.3, 41.4, 19.4, 8.7. **ESI-HRMS**: *m/z* calcd. for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0919, found 186.0915.



13

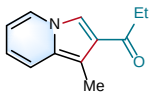
10-methyl-3,4-dihydropyrido[1,2-a]indol-1(2H)-one: According to the general procedure B, work-up gave product **13** (34.2 mg, 0.17 mmol, isolated yield 86%) as a yellow solid. **mp**:

111−112 ˚C. **FT-IR**: *v* (cm^{-1}): 2918, 1646, 1525, 1432, 1368, 1331, 1263, 1228, 1183, 1140, 1084, 925, 894, 812, 736, 713, 626, 577,530, 468, 418. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.4 Hz, 1H), 7.25 (d, *J* = 9.2 Hz, 1H), 6.51 – 6.41 (m, 2H), 2.87 – 2.85 (m, 2H), 2.54 – 2.47 (m, 5H), 2.20 – 2.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.2, 130.8, 129.9, 121.8, 121.0, 119.1, 116.0, 112.1, 107.8, 39.4, 23.5, 21.1, 9.6. **ESI-HRMS**: *m/z* calcd. for $C_{13}H_{13}NO$ $[M+H]^+$: 200.1075, found 200.1071.



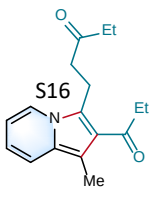
14

11-methyl-6,7,8,9-tetrahydro-10H-cyclohepta[b]indolizin-10-one: According to the general procedure B, work-up gave product **14** (24.3 mg, 0.11 mmol, isolated yield 57%) as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 6.51 – 6.42 (m, 2H), 2.96 (t, *J* = 6.0 Hz, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.96 (p, *J* = 6.0 Hz, 2H), 1.87 (p, *J* = 6.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.8, 129.4, 127.3, 124.9, 121.6, 118.9, 115.4, 112.1, 110.0, 44.3, 25.3, 25.0, 22.5, 10.1. ESI-HRMS: *m/z* calcd. for $C_{14}H_{15}NO$ $[M+H]^+$: 214.1232, found 214.1227.



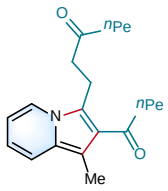
15

1-(1-methylindolizin-2-yl)propan-1-one: According to the general procedure A, work-up gave product **15** (5.6 mg, 0.03 mmol, isolated yield 15%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2926, 1716, 1657, 1617, 1455, 1416, 1374, 1317, 1208, 1150, 1076, 1032, 921, 781, 732, 429. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.65 (s, 1H), 7.26 (d, *J* = 9.0 Hz, 1H), 6.55 – 6.50 (m, 1H), 6.42 – 6.37 (m, 1H), 2.83 (q, *J* = 7.3 Hz, 2H), 2.47 (s, 3H), 1.15 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9, 131.1, 125.6, 125.1, 118.9, 116.6, 115.2, 112.3, 110.1, 33.8, 10.2, 8.5. The compound is known, and the NMR data is in accordance with the previous literature.[3]



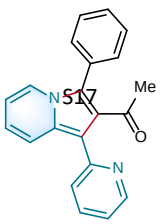
16

1-(1-methyl-2-propionylindolizin-3-yl)pentan-3-one: According to the general procedure A, work-up gave product **16** (19.0 mg, 0.07 mmol, isolated yield 35%) as a yellow solid. **mp**: 92−93 ˚C. **FT-IR**: *v* (cm^{-1}): 2974, 2936, 1710, 1657, 1587, 1490, 1449, 1416, 1374, 1321, 1255, 1214, 1150, 1113, 1028, 940, 812, 734, 420. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.54 – 6.43 (m, 2H), 3.28 (t, *J* = 7.3 Hz, 2H), 2.86 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.44 (s, 3H), 2.36 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 201.0, 129.6, 126.5, 124.5, 121.8, 118.6, 115.9, 112.1, 107.2, 40.4, 36.6, 36.0, 19.4, 11.5, 8.2, 7.7. The compound is known, and the NMR data is in accordance with the previous literature.[3]



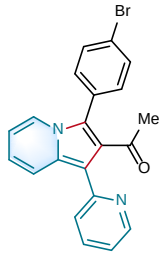
18

1-(2-hexanoyl-1-methylindolizin-3-yl)octan-3-one: According to the general procedure A, work-up gave product **18** (21.3 mg, 0.06 mmol, isolated yield 31%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2930, 2738, 2603, 2498, 1708, 1605, 1475, 1442, 1397, 1383, 1173, 1074, 1034, 917, 851, 808, 734, 462. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 9.2 Hz, 1H), 6.55 – 6.51 (m, 1H), 6.45 (t, *J* = 6.8 Hz, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.66 (p, *J* = 7.2 Hz, 2H), 1.47 (p, *J* = 7.2 Hz, 2H), 1.30 – 1.29 (m, 4H), 1.20 – 1.17 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.79 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.9, 200.9, 129.6, 126.3, 124.7, 121.8, 118.6, 115.9, 112.1, 107.1, 43.5, 42.9, 40.7, 31.6, 31.3, 24.1, 23.4, 22.6, 22.4, 19.3, 13.9, 13.8, 11.4. **ESI-HRMS**: *m/z* calcd. for $C_{23}H_{33}NO_2$ $[M+H]^+$: 356.2590, found 356.2588.



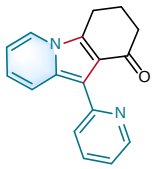
19

1-(3-phenyl-1-(pyridin-2-yl)indolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **19** (54.9 mg, 0.18 mmol, isolated yield 88%) as a yellow solid. **mp**: 137−138 ˚C **FT-IR**: *v* (cm^{-1}): 2992, 2916, 1690, 1585, 1515, 1471, 1447, 1412, 1344, 1325, 1241, 1187, 1148, 1080, 1049, 1032, 1010, 985, 964, 944, 923, 853, 797, 771, 756, 743, 725, 717, 701, 664, 645, 610, 577, 536, 511, 447, 406. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.8 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.64 – 7.60 (m, 1H), 7.45 – 7.36 (m, 6H), 7.08 – 7.05 (m, 1H), 6.73 (dd, *J* = 8.8, 6.8 Hz, 1H), 6.44 (t, *J* = 6.8 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.6, 153.9, 149.4, 136.0, 131.0, 130.7, 130.2, 129.0, 128.9, 127.5, 125.3, 124.2, 122.9, 120.5, 120.3, 119.3, 113.1, 112.7, 32.0. **ESI-HRMS**: *m/z* calcd. for $C_{21}H_{16}N_2O$ $[M+H]^+$: 313.1341, found 313.1340.



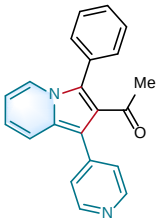
20

1-(3-(4-bromophenyl)-1-(pyridin-2-yl)indolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **20** (66.3 mg, 0.17 mmol, isolated yield 84%) as a yellow solid. **mp**: 129−130 ˚C. FT-IR: *v* (cm^{-1}): 3023, 1681, 1585, 1515, 1471, 1445, 1407, 1344, 1325, 1259, 1247, 1193, 1148, 1123, 1098, 1069, 1010, 987, 966, 942, 857, 828, 793, 771, 740, 715, 703, 672, 618, 577, 556, 505, 455, 437, 414. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 (d, *J* = 3.2 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.10 – 7.07 (m, 1H), 6.79 – 6.75 (m, 1H), 6.48 (t, J = 6.8 Hz, 1H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.5, 153.7, 149.5, 136.1, 132.4, 132.2, 131.2, 129.1, 127.7, 124.1, 123.8, 123.1, 122.7, 120.7, 120.5, 119.3, 113.3, 113.0, 32.0. **ESI-HRMS**: *m/z* calcd. for $C_{21}H_{15}BrN_2O$ $[M+H]^+$: 391.0446, found 391.0450.



21

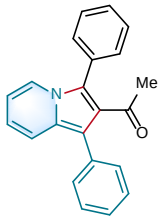
10-(pyridin-2-yl)-3,4-dihydropyrido[1,2-a]indol-1(2H)-one: According to the general procedure A, work-up gave product **21** (36.7 mg, 0.14 mmol, isolated yield 70%) as a yellow solid. **mp**: 136−137 ˚C. **FT-IR**: *v* (cm^{-1}): 2947, 1655, 1587, 1560, 1515, 1477, 1453, 1426, 1399, 1321, 1276, 1232, 1193, 1156, 1123, 1078, 1045, 1018, 991, 958, 942, 909, 892, 835, 791, 775, 746, 727, 709, 686, 637, 616, 563, 540, 473, 447, 427, 412. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.07 – 7.04 (m, 1H), 6.72 (dd, *J* = 9.0, 6.6 Hz, 1H), 6.58 (t, *J* = 6.8 Hz, 1H), 2.93 (t, *J* = 6.2 Hz, 2H), 2.61 – 2.57 (m, 2H), 2.25 (p, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 153.7, 148.4, 135.5, 132.8, 132.3, 125.9, 121.9, 121.3, 120.5, 120.0, 119.8, 113.3, 111.5, 39.8, 23.1, 21.4. ESI-HRMS: *m/z* calcd. for $C_{17}H_{14}N_2O$ $[M+H]^+$: 263.1184, found 263.1183.



22

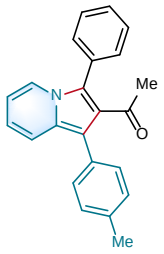
1-(3-phenyl-1-(pyridin-4-yl)indolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **22** (53.7 mg, 0.17 mmol, isolated yield 86%) as a yellow solid. **mp**: 100−101 ˚C. **FT-IR**: *v* (cm^{-1}): 1663, 1591, 1519, 1469, 1412, 1346, 1311, 1257, 1243, 1216, 1154, 1135, 1076, 1016, 989, 969, 909, 855, 830, 785, 752, 727, 703, 680, 661, 637, 606, 577, 521, 439, 422. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.39 (m, 6H), 7.28 (d, *J* = 4.8 Hz, 2H), 6.75 – 6.71 (m, 1H), 6.47 (t, *J* = 6.8 Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.4, 149.5, 142.9, 130.7, 130.4, 130.1, 129.2, 126.5,

126.5, 124.8, 123.1, 120.4, 118.2, 112.9, 111.4, 31.7. **ESI-HRMS**: *m/z* calcd. for $C_{21}H_{16}N_2O$ $[M+H]^+$: 313.1341, found 313.1337.



23

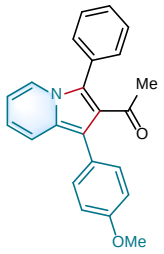
1-(1,3-diphenylindolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **23** (19.3 mg, 0.06 mmol, isolated yield 31%) as a yellow solid. **mp**: 125−126 ˚C. **FT-IR**: *v* (cm^{-1}): 1677, 1599, 1519, 1488, 1473, 1445, 1416, 1346, 1251, 1241, 1181, 1152, 1133, 1076, 1030, 1010, 960, 942, 911, 849, 791, 762, 754, 725, 699, 663, 606, 575, 552, 507, 441, 420. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.37 (m, 10H), 7.27 – 7.26 (d, *J* = 3.6 Hz, 1H), 6.66 – 6.62 (m, 1H), 6.42 (t, *J* = 6.8 Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 134.6, 130.8, 130.7, 130.3, 130.1, 129.0, 128.8, 128.4, 126.9, 126.6, 125.4, 122.7, 119.0, 118.9, 114.8, 112.6, 31.8. **ESI-HRMS**: *m/z* calcd. for $C_{22}H_{17}NO$ $[M+H]^+$: 312.1381, found 312.1388.



24

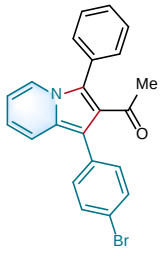
1-(3-phenyl-1-(p-tolyl)indolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **24** (24.7 mg, 0.08 mmol, isolated yield 38%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2918, 1669, 1601, 1525, 1469, 1420, 1393, 1348, 1323, 1255, 1245, 1212, 1181, 1152, 1133, 1074, 1010, 962, 909, 855, 822, 773, 727, 699, 661, 647, 567, 509, 412. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.34 (m, 6H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J*

= 6.8 Hz, 2H), 6.61 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.40 (t, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 136.2, 131.6, 130.8, 130.7, 130.1, 130.0, 129.2, 129.0, 128.7, 126.8, 125.3, 122.6, 119.1, 118.6, 114.8, 112.5, 31.8, 21.2. **ESI-HRMS**: *m/z* calcd. for $C_{23}H_{19}NO$ $[M+H]^+$: 326.1545, found 326.1541.



25

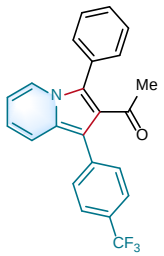
1-(1-(4-methoxyphenyl)-3-phenylindolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **25** (20.5 mg, 0.06 mmol, isolated yield 32%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2932, 2833, 1669, 1609, 1572, 1535, 1525, 1504, 1465, 1442, 1420, 1393, 1350, 1284, 1241, 1175, 1152, 1131, 1107, 1074, 1028, 962, 909, 853, 833, 802, 775, 744, 727, 699, 659, 620, 575, 530, 433, 412. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.34 – 7.29 (m, 3H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.63 – 6.59 (m, 1H), 6.41 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 158.5, 131.4, 130.8, 130.1, 129.0, 128.7, 126.9, 126.8, 125.3, 122.6, 119.1, 118.5, 114.5, 113.9, 112.5, 55.3, 31.8. **ESI-HRMS**: *m/z* calcd. for $C_{23}H_{19}NO_2$ $[M+H]^+$: 342.1494, found 342.1492.



26

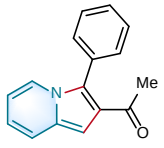
1-(1-(4-bromophenyl)-3-phenylindolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **26** (35.8 mg, 0.09 mmol, isolated yield 46%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2926, 1653, 1578, 1523, 1486, 1449, 1428, 1395, 1352, 1317, 1255,

1216, 1173, 1131, 1069, 1010, 907, 833, 791, 771, 725, 692, 645, 618, 552. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.6 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.45 – 7.41 (m, 4H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.67 (ddd, *J* = 10.0, 8.4, 1.2 Hz, 1H), 6.47 – 6.42 (m, 1H), 2.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.6, 133.6, 131.9, 131.5, 130.8, 130.6, 129.1, 129.0, 126.6, 125.9, 122.8, 120.6, 119.3, 118.7, 113.4, 112.7, 31.8. ESI-HRMS: *m/z* calcd. for $C_{22}H_{16}BrNO$ $[M+H]^+$: 390.0494, found 390.0494.



27

1-(3-phenyl-1-(4-(trifluoromethyl)phenyl)indolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **27** (34.9 mg, 0.09 mmol, isolated yield 46%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 2924, 2852, 1669, 1616, 1527, 1467, 1409, 1350, 1321, 1259, 1243, 1162, 1119, 1107, 1065, 1018, 964, 843, 791, 773, 748, 701, 664, 600, 560, 507453, 406. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.42 (m, 7H), 7.36 (d, *J* = 9.2 Hz, 1H), 6.72 – 6.68 (m, 1H), 6.49 – 6.45 (m, 1H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.5, 138.6, 130.9, 130.5, 130.4, 130.4, 129.2, 129.2, 128.4 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 126.6, 126.2, 125.27 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 124.4 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 123.0, 119.8, 118.5, 113.2, 112.8, 31.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.30. **ESI-HRMS**: *m/z* calcd. for $C_{23}H_{16}F_3NO$ $[M+H]^+$: 380.1262, found 380.1257.



28

1-(3-phenylindolizin-2-yl)ethan-1-one: According to the general procedure A, work-up gave product **28** (8.9 mg, 0.04 mmol, isolated yield 19%) as a yellow liquid. **FT-IR**: *v* (cm^{-1}): 3056, 2920, 2850, 1679, 1657, 1581, 1449, 1430, 1381, 1356, 1302, 1257, 1228, 1212, 1175, 1096,

1072, 1022, 995, 973, 907, 775, 727, 692, 645, 614, 577, 536, 486. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.38 – 7.32 (m, 3H), 6.86 (s, 1H), 6.65 – 6.61 (m, 1H), 6.38 (t, J = 6.7 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.8, 131.8, 131.2, 131.0, 129.0, 129.0, 128.5, 126.3, 123.0, 120.4, 118.4, 112.4, 100.7, 29.5. ESI-HRMS: *m/z* calcd. for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1075, found 236.1069.

8. The X-ray Data and Crystal Structure

Crystal data and details of the data collections are given in Table S3. X-ray data were collected on a BRUKER D8-QUEST diffractometer (monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of ω and ϕ scans at low temperature. The structures were solved with SHELXT and refined on F^2 using all reflections with SHELXL.[4] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.5/1.2 U_{eq}(C). Absorption corrections were performed by the multi-scan method with SADABS.[5]

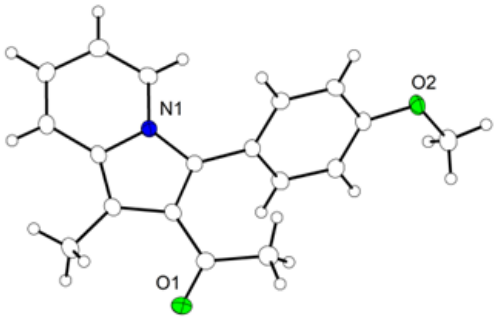


Figure S2. Plot (50% probability thermal ellipsoids) of the molecular structure of **7** (CCDC: 2115159).

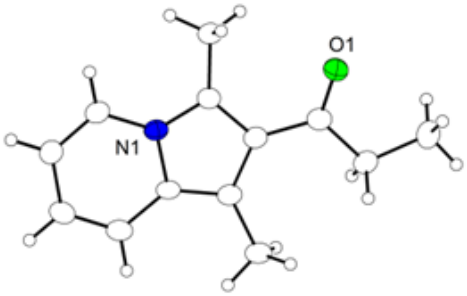


Figure S3. Plot (50% probability thermal ellipsoids) of the molecular structure of **11** (CCDC: 2115160).

Table S2. Crystal data collection and refinement details for **7** and **11**.

Compound	**7** (CCDC: 2115159)	**11** (CCDC: 2115160)
empirical formula	$C_{18}H_{17}NO_2$	$C_{13}H_{15}FNO$
moiety formula	$C_{18}H_{17}NO_2$	$C_{13}H_{15}FNO$
formula weight	279.32	201.26
T [K]	100(2)	100(2)
Crystal size [mm³]	0.320 x 0.233 x 0.060	0.347 x 0.188 x 0.124
Crystal system	Monoclinic	Monoclinic
Space group	*P2₁/c*	*P2₁/c*
a [Å]	7.985(2)	7.5190(13)
b [Å]	8.521(2)	12.050(2)
c [Å]	21.601(5)	11.678(2)
α [°]	90	90
β [°]	96.717(9)	100.317(6)
γ [°]	90	90
V [Å³]	1459.6(6)	1041.0(3)
Z	4	4
ρ [g·cm^{-3}]	1.271	1.284
F(000)	592	432
μ [mm^{-1}]	0.083	0.081
T_{min} / T_{max}	0.96 / 0.99	0.80 / 0.99
θ-range [°]	2.568 - 27.824	2.449 - 27.885
hkl-range	±10, ±11, ±28	±9, ±15, ±15
Measured refl.	35121	31200
Unique refl. [R_{int}]	3462 [0.0432]	2483 [0.1020]
Observed refl. ($I > 2\sigma(I)$)	2967	1762
Data / restr. / param.	3462 / 0 / 193	2483 / 0 / 139
Goodness-of-fit (F^2)	1.026	1.078
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0378 / 0.0883	0.0505 / 0.1167
*R*1, *wR*2 (all data)	0.0469 / 0.0942	0.0863 / 0.1372
Res. el. dens. [e·Å^{-3}]	-0.222 / 0.257	-0.258 / 0.229

9. Computational studies

Calculation method details

All DFT calculations were performed using Gaussian 16, Revision A.03 package.[6] Geometry optimizations were performed at the TPSS[7] level of theory in combination with Grimme's D3 dispersion corrections with a Becke-Johnson damping scheme (D3BJ)[8] in the gas phase. All atoms were described with a def2-SVP basis set.[9] Analytical frequencies were carried out at the same level of theory to identify each stationary point as either an intermediate (no imaginary frequencies) or a transition state (only one imaginary frequency). These also provided thermal and non-thermal corrections to the Gibbs free energy at 413.15 K temperature and at a pressure of 1 atm. The electronic energy was then refined through single-point calculations with the PW6B95[10] functional on the optimized geometries with a def2-TZVP basis set[9] in combination with a standalone version of Grimme's dispersion correction D4.[11] Solvent effects were included implicitly through the use of the SMD model[12] with a dielectric constant of ε = 26.726, which corresponds to 2,2,2-trifluoroethanol. Energies reported in the energy profiles are based on gas-phase Gibbs free energies with a def2-SVP basis set for which the electronic energies were corrected to PW6B95-D4 with a def2-TZVP basis set including solvent effects. Additionally, energy refinement with the DFT hybrid M06-2X,[13] and double-hybrid DSD-PBEP86-D3(BJ))[14] functionals were also considered.

Table S3: Calculated electronic energies at the PW6B95-D4/def2-TZVP+SMD(2,2,2-trifluoroethanol)//TPSS-D3(BJ)/def2-SVP level of theory and Gibbs free energies with dispersion corrections for all structures in the present work (all in Hartree).[a]

Structure	Electronic Energy	Total Gibbs Free Energy
Int1^{A}	-1073.496497	-1073.240599
Int1^{B}	-1073.500726	-1073.245385
Int1^{C}	-1073.484541	-1073.23231
TS1^{A}	-1073.466305	-1073.205136
TS1^{B}	-1073.467973	-1073.211768
TS1^{C}	-1073.470705	-1073.211576
Int2^{A}	-1073.479846	-1073.218615
Int2^{B}	-1073.485482	-1073.223778
Int2^{C}	-1073.489309	-1073.225529
TS2^{B}	-1073.479450	-1073.217361
TS2^{C}	-1073.490247	-1073.225814
Int3^{C}	-1073.496324	-1073.233267

TS3^{C}	-1073.494375	-1073.233632
Int3^{B}	-1073.510713	-1073.24865
Int4^{C}	-1073.505424	-1073.243838

[a] Superscripted A, B, and C represents the respective pathway.

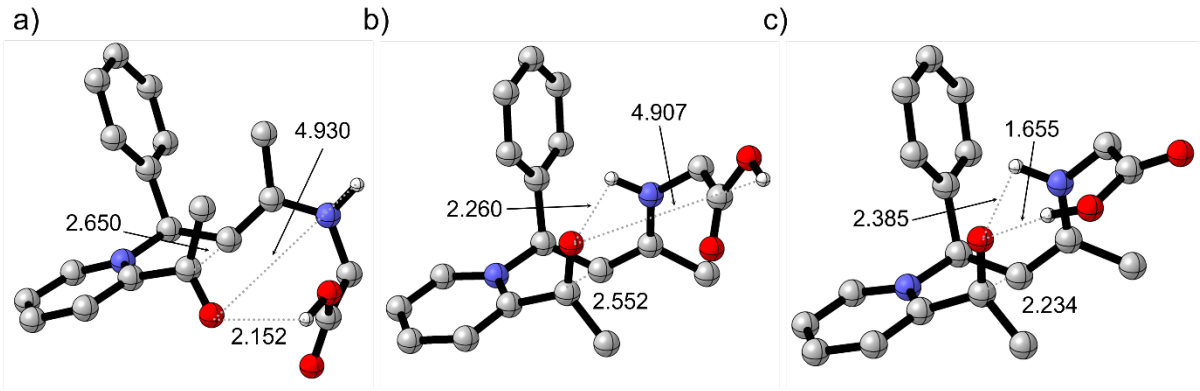


Fig. S4: Computed structures for **Int2** optimized at the TPSS-D3(BJ)/def2-SVP level of theory present in pathways A, B, and C. Non-relevant hydrogens were omitted for clarity and key distances are given in Å. Structures were generated with help of the CYLview[15] software.

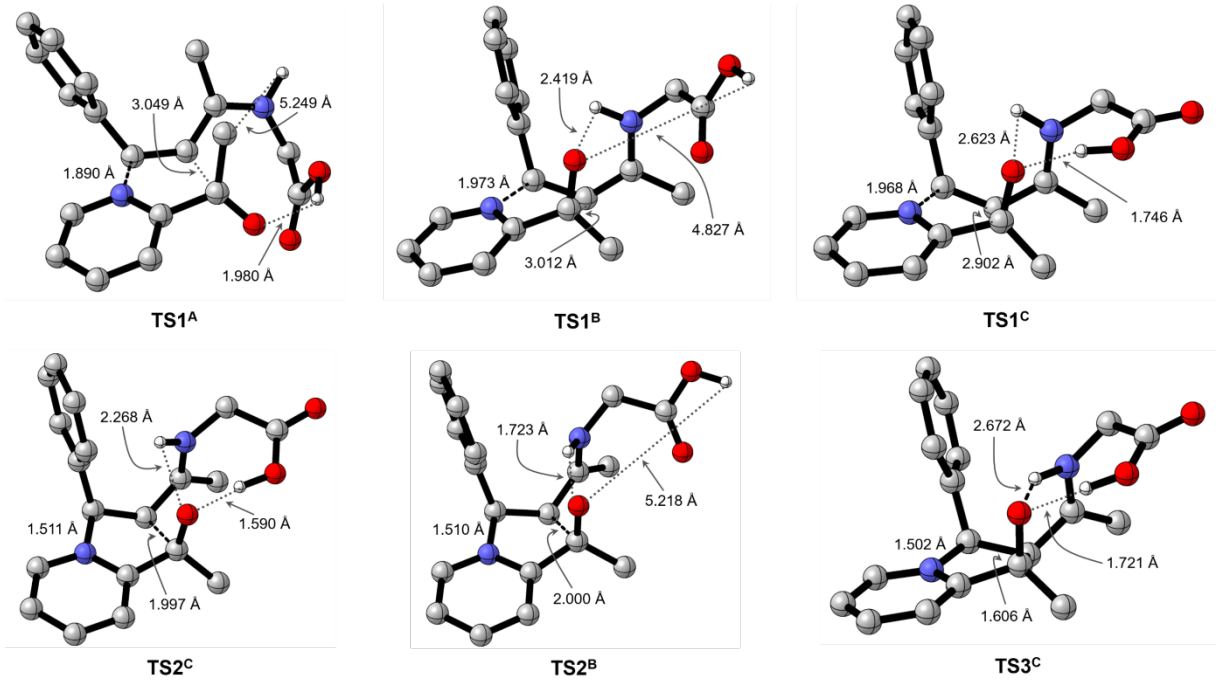


Figure S5. Computed structures for the relevant transition states optimized at the TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogens were omitted for clarity and key distances are given in Å.

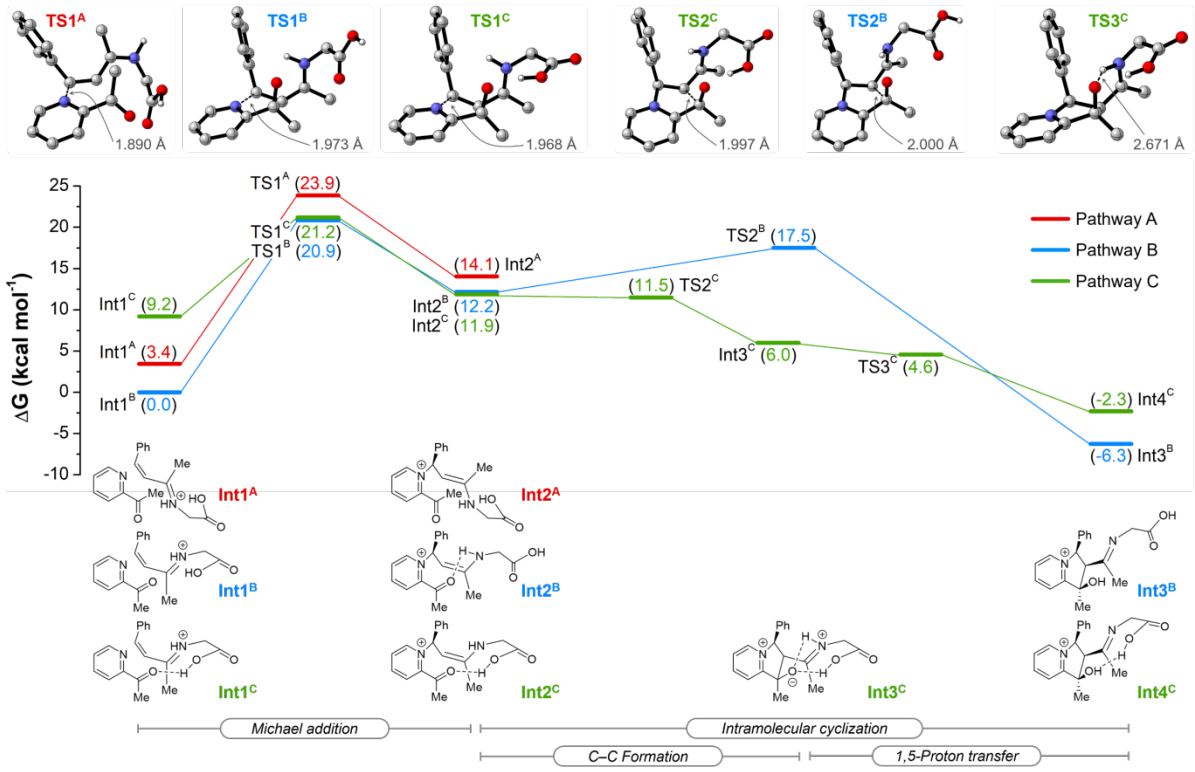


Figure S6. Computed relative Gibbs free energies ($\Delta G_{413.15}$) in kcal mol^{-1} for the amino-catalyzed 2-acylindolizine formation for the three considered plausible pathways. Calculation was performed at the M06-2X/def2-TZVPP+SMD(2,2,2-trifluoroethanol)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogens in the transition state structures were omitted for clarity.

Table S4: Calculated electronic energies at the M06-2X/def2-TZVPP+SMD(2,2,2-trifluoroethanol)//TPSS-D3(BJ)/def2-SVP level of theory and Gibbs free energies for all structures in the present work (all in Hartree).[a]

Structure	Electronic Energy	Total Gibbs Free Energy
Int1^{A}	-1071.673937	-1071.401477
Int1^{B}	-1071.678954	-1071.406952

Int1^{C}	-1071.661689	-1071.392271
TS1^{A}	-1071.648248	-1071.368898
TS1^{B}	-1071.648191	-1071.373699
TS1^{C}	-1071.650701	-1071.373143
Int2^{A}	-1071.664219	-1071.38453
Int2^{B}	-1071.668098	-1071.387533
Int2^{C}	-1071.671121	-1071.388004
TS2^{B}	-1071.660783	-1071.379035
TS2^{C}	-1071.67285	-1071.388618
Int3^{C}	-1071.679827	-1071.397368
TS3^{C}	-1071.679762	-1071.399668
Int3^{B}	-1071.698161	-1071.416914
Int4^{C}	-1071.69122	-1071.410595

[a] Superscripted A, B, and C represents the respective pathway.

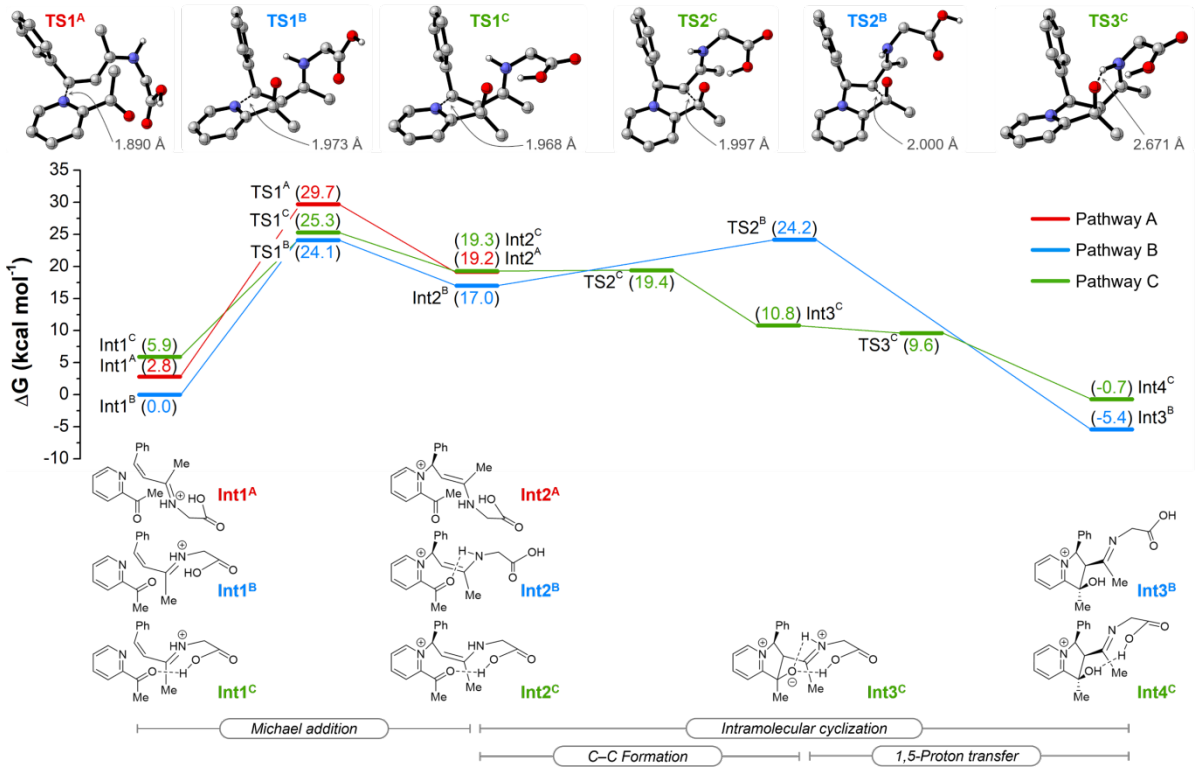


Figure S7. Computed relative Gibbs free energies ($\Delta G_{413.15}$) in kcal mol^{-1} for the amino-catalyzed 2-acylindolizine formation for the three considered plausible pathways. Calculation was performed at the DSD-PBEP86-D3(BJ))/def2-TZVPP+SMD(2,2,2-trifluoroethanol) //TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogens in the transition state structures were omitted for clarity.

Table S5: Calculated electronic energies at the DSD-PBEP86-D3(BJ))/def2-TZVPP+SMD(2,2,2-trifluoroethanol)//TPSS-D3(BJ)/def2-SVP level of theory and Gibbs free energies with dispersion corrections for all structures in the present work (all in Hartree).[a]

Structure	Electronic Energy	Total Gibbs Free Energy
Int1^{A}	-1068.102279	-1067.829819
Int1^{B}	-1068.106213	-1067.834211
Int1^{C}	-1068.09422	-1067.824802
TS1^{A}	-1068.066247	-1067.786897
TS1^{B}	-1068.070291	-1067.795799
TS1^{C}	-1068.071455	-1067.793897
Int2^{A}	-1068.083264	-1067.803575
Int2^{B}	-1068.087627	-1067.807062
Int2^{C}	-1068.086604	-1067.803487
TS2^{B}	-1068.077395	-1067.795647
TS2^{C}	-1068.087451	-1067.803219
Int3^{C}	-1068.099425	-1067.816966
TS3^{C}	-1068.09901	-1067.818916
Int3^{B}	-1068.124071	-1067.842824
Int4^{C}	-1068.115973	-1067.835348

[a] Superscripted A, B, and C represents the respective pathway.

Cartesian Coordinates of the optimized structures

Int1^{A}

Lowest frequency = 16.1695 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	1.603706	0.739069	3.612900
C	2.591250	1.404820	2.864796
C	2.213082	2.082968	1.698226
C	0.864630	2.075247	1.328821
C	-0.047635	1.383469	2.148025
H	1.870438	0.200233	4.531269
H	3.634040	1.390829	3.196956
H	2.956690	2.610619	1.092799
H	0.496136	2.587163	0.435778
C	-1.495868	1.334522	1.773984
C	-2.425378	0.529481	2.634667
H	-2.140409	-0.534988	2.573702
H	-2.308531	0.821115	3.691430
H	-3.464668	0.661082	2.301516
O	-1.871009	1.940041	0.757567
C	-0.244704	-0.547937	-2.805989
H	-0.833015	0.106654	-3.461811
C	1.743231	-0.519599	-1.224508
C	1.152007	-1.213515	-0.134865
C	3.132829	-0.229794	-1.188134
C	1.942640	-1.648592	0.929633
H	0.064680	-1.338275	-0.105611
C	3.919467	-0.691579	-0.132269
H	3.588474	0.333160	-2.009688
C	3.326313	-1.403073	0.925873

H	1.478146	-2.156155	1.780291
H	4.995044	-0.490536	-0.122865
H	3.942442	-1.744987	1.763619
C	-0.796399	-1.860881	-2.595993
C	0.042626	-3.101243	-2.456852
H	1.113213	-2.862926	-2.455247
H	-0.211428	-3.640437	-1.528966
H	-0.169426	-3.771641	-3.310498
N	-2.113600	-2.026957	-2.693147
C	-3.065838	-0.941104	-2.490906
H	-2.993475	-0.182054	-3.287629
H	-4.087850	-1.350021	-2.517756
C	-2.785786	-0.278154	-1.118076
O	-2.068745	-0.818347	-0.288211
O	-3.377442	0.888883	-1.006428
H	-2.980655	1.367847	-0.182180
H	-2.473311	-2.981236	-2.627183
N	0.311279	0.721655	3.266351
C	0.942083	-0.039960	-2.333240
H	1.292247	0.883851	-2.813461

Int1^{B}

Lowest frequency = 21.9550 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	-0.877639	-1.745701	-1.388698
C	-0.454598	-3.053008	-1.677147
C	0.912352	-3.342382	-1.604070

C	1.805096	-2.315985	-1.264707
C	1.298673	-1.033252	-0.998481
H	1.282077	-4.350222	-1.816819
H	-1.938193	-1.469750	-1.432393
H	-1.184355	-3.819351	-1.954127
H	2.878845	-2.512424	-1.214382
C	2.177729	0.153352	-0.670595
C	3.671566	-0.049533	-0.573714
H	3.911149	-0.815426	0.184769
H	4.080359	-0.400385	-1.538422
H	4.145751	0.903768	-0.302030
C	-1.946064	-0.779816	1.761663
H	-2.502704	-1.663189	2.103469
C	-2.731320	0.192080	1.203316
H	-3.814293	0.038094	1.287363
C	-2.403902	1.420387	0.495475
N	-0.025984	-0.770268	-1.050225
N	-1.307156	1.537235	-0.216148
C	-3.412248	2.535494	0.522253
H	-2.927866	3.495477	0.771142
H	-3.873632	2.637964	-0.476541
H	-4.199462	2.336364	1.261971
O	1.662579	1.252954	-0.502066
H	-1.803996	3.236101	-4.159314
C	-1.001014	2.649526	-1.097227
H	0.085922	2.652936	-1.266651
H	-1.284818	3.617131	-0.651479
C	-1.743510	2.478346	-2.429788
O	-2.623696	1.666240	-2.622684
O	-1.289865	3.361412	-3.331957

C	-0.514425	-0.845809	2.046402
C	0.073285	-2.129709	2.168572
C	0.291594	0.293972	2.274965
C	1.432878	-2.268660	2.459718
H	-0.548344	-3.019550	2.022766
C	1.642459	0.151177	2.598049
H	-0.147427	1.293807	2.229857
C	2.220085	-1.127295	2.680784
H	1.874617	-3.266611	2.541052
H	2.249829	1.040877	2.789218
H	3.278310	-1.233084	2.941150
H	-0.688685	0.677391	-0.398628

Int1[C]

Lowest frequency = 20.5035 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.394556	-3.507464	-0.314021
C	0.776821	-4.535718	-1.197567
C	1.242405	-4.185551	-2.468752
C	1.310271	-2.827017	-2.808107
C	0.912029	-1.871880	-1.852852
H	1.549752	-4.952908	-3.185662
H	0.024349	-3.749015	0.691245
H	0.708047	-5.583098	-0.888169
H	1.674177	-2.524606	-3.793721
C	0.975170	-0.399907	-2.129348
C	1.345080	0.096224	-3.504829

H	2.384583	-0.196365	-3.740640
H	0.698438	-0.358836	-4.274993
H	1.264037	1.191704	-3.547978
C	-1.919945	-0.750940	1.211384
H	-2.592797	-1.617351	1.280062
C	-2.260168	0.140093	0.219928
H	-3.100025	-0.156363	-0.415451
C	-1.836692	1.500145	-0.008312
N	0.457197	-2.211800	-0.626713
N	-0.796467	2.049037	0.602301
C	-2.639434	2.354557	-0.945823
H	-3.001833	3.267357	-0.439897
H	-2.001301	2.681491	-1.787454
H	-3.502223	1.803744	-1.342476
O	0.725385	0.393166	-1.208913
H	0.636498	2.011700	-1.406692
C	-0.371910	3.440043	0.491739
H	0.398509	3.614649	1.258883
H	-1.211463	4.121342	0.701031
C	0.217225	3.897344	-0.879897
O	0.277919	5.080663	-1.104685
O	0.627521	2.964038	-1.740052
C	-0.891937	-0.708902	2.247607
C	-1.243798	-1.124903	3.556364
C	0.449248	-0.323372	1.987833
C	-0.306300	-1.071538	4.591922
H	-2.265759	-1.461673	3.760270
C	1.387914	-0.300421	3.024963
H	0.754802	-0.159319	0.947322
C	1.008926	-0.653748	4.330825

H	-0.596886	-1.367703	5.604489
H	2.426318	-0.027439	2.811338
H	1.744637	-0.627153	5.140784
H	-0.224723	1.428158	1.191203

TS1^{A}

Lowest frequency = -219.0786 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	1.358001	0.957327	6.144863
C	1.416854	1.979707	7.091753
C	0.217264	2.456019	7.638968
C	-0.987396	1.866186	7.242566
C	-0.973303	0.803908	6.322970
H	2.253609	0.576058	5.641684
H	2.384360	2.405904	7.370290
H	0.220150	3.278258	8.360918
H	-1.950855	2.198798	7.638287
C	-2.304308	0.136379	6.016914
C	-2.442820	-1.349367	6.238617
H	-1.484047	-1.880884	6.175577
H	-2.847250	-1.486974	7.260252
H	-3.171598	-1.760765	5.523854
O	-3.257008	0.868235	5.780221
C	-0.876634	-0.789789	3.486892
H	-1.308113	0.110568	3.037780
C	1.336010	-1.665394	4.515374
C	1.323188	-2.351838	5.743468

C	2.284819	-2.030099	3.537481
C	2.220936	-3.400976	5.980867
H	0.617787	-2.057159	6.526793
C	3.175358	-3.086097	3.772917
H	2.314394	-1.494070	2.582433
C	3.143150	-3.776634	4.993494
H	2.202044	-3.923607	6.942356
H	3.902348	-3.362920	3.003038
H	3.843310	-4.596859	5.179316
C	-1.489497	-2.011553	3.183056
C	-1.008316	-3.373022	3.622666
H	-0.010247	-3.580432	3.202316
H	-0.915763	-3.443328	4.715455
H	-1.701663	-4.158368	3.280687
N	-2.574344	-2.047121	2.374498
C	-3.204120	-0.893512	1.748090
H	-2.489697	-0.352410	1.105046
H	-4.028918	-1.260492	1.116545
C	-3.761165	0.115433	2.761988
O	-3.583687	1.310097	2.681314
O	-4.435863	-0.504810	3.750974
H	-4.565403	0.160377	4.473031
H	-2.988842	-2.959961	2.199093
N	0.191832	0.387246	5.780744
C	0.372827	-0.569774	4.160529
H	0.891969	0.297781	3.729532

TS1^{B}

Lowest frequency = -182.7696 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	-0.564960	-7.416251	2.094756
C	0.008938	-8.320200	1.195494
C	0.422933	-7.842581	-0.054293
C	0.273940	-6.480299	-0.348664
C	-0.276119	-5.621895	0.616879
H	0.858604	-8.521803	-0.793451
H	-0.942538	-7.731161	3.074772
H	0.108368	-9.374258	1.468368
H	0.607768	-6.076369	-1.308575
C	-0.234280	-4.110541	0.429156
C	-0.775087	-3.521126	-0.846250
H	-0.097977	-3.765798	-1.687070
H	-1.763319	-3.948079	-1.088330
H	-0.827944	-2.428610	-0.736102
C	-1.950827	-5.131568	2.961135
H	-2.543310	-6.052561	3.041926
C	-2.646817	-4.125242	2.232392
H	-3.487142	-4.471047	1.623328
C	-2.516036	-2.726913	2.325603
N	-0.693542	-6.113427	1.800864
N	-1.509437	-2.129383	2.983991
C	-3.577412	-1.852999	1.711338
H	-4.087944	-1.263953	2.495204
H	-3.128874	-1.150617	0.990332
H	-4.332836	-2.465327	1.200225
O	0.339570	-3.455640	1.288470
H	0.379171	1.370889	1.245285

C	-1.261896	-0.705712	3.079755
H	-0.587443	-0.517544	3.928396
H	-2.197020	-0.154386	3.283498
C	-0.649594	-0.114094	1.801047
O	-0.818258	-0.549777	0.681298
O	0.057905	0.990241	2.091804
C	-1.148846	-4.865271	4.202523
C	-1.858720	-4.863577	5.422639
C	0.233993	-4.592213	4.213070
C	-1.201356	-4.573469	6.624682
H	-2.932485	-5.080093	5.427326
C	0.887074	-4.307187	5.421788
H	0.789472	-4.590794	3.271547
C	0.173221	-4.293361	6.628076
H	-1.765479	-4.573216	7.562698
H	1.962395	-4.102062	5.416855
H	0.686711	-4.073674	7.569292
H	-0.756295	-2.733522	3.321111

TS1[c]

Lowest frequency = -207.9941 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.253943	-3.558995	-0.143820
C	0.881237	-4.501829	-0.965225
C	1.365541	-4.082774	-2.210198
C	1.229272	-2.736943	-2.580553
C	0.617408	-1.839466	-1.691787

H	1.846884	-4.793462	-2.888845
H	-0.176159	-3.826231	0.828567
H	0.967701	-5.541185	-0.637046
H	1.621869	-2.379142	-3.536525
C	0.642396	-0.347099	-1.962772
C	0.122565	0.168282	-3.275788
H	0.778768	-0.185324	-4.094264
H	-0.887713	-0.224242	-3.479739
H	0.129704	1.268200	-3.277670
C	-1.152487	-1.212431	0.530946
H	-1.803069	-2.094856	0.591319
C	-1.722001	-0.191797	-0.286479
H	-2.528218	-0.511224	-0.953615
C	-1.513810	1.199519	-0.230675
N	0.135839	-2.274386	-0.510230
N	-0.554283	1.775434	0.514141
C	-2.409166	2.107414	-1.030582
H	-2.961047	2.793069	-0.362955
H	-1.823645	2.734978	-1.725244
H	-3.138447	1.523622	-1.608525
O	1.221840	0.359081	-1.135221
H	1.046472	2.093438	-1.226364
C	-0.286750	3.205722	0.589366
H	0.433115	3.369195	1.407729
H	-1.196407	3.776769	0.833634
C	0.302253	3.844835	-0.695703
O	0.173296	5.026671	-0.897686
O	0.956202	3.032349	-1.545479
C	-0.419122	-0.961433	1.814928
C	-1.180926	-0.999159	3.002216

C	0.958068	-0.661804	1.891077
C	-0.582576	-0.714966	4.236658
H	-2.248700	-1.239156	2.956914
C	1.551819	-0.385664	3.131564
H	1.558420	-0.646097	0.976851
C	0.783841	-0.406300	4.304945
H	-1.186675	-0.742339	5.148863
H	2.622379	-0.162336	3.179062
H	1.250715	-0.192231	5.271264
H	0.042424	1.154566	1.068838

Int2^{A}

Lowest frequency = 24.8671 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	2.087381	1.903892	1.101929
C	2.119538	2.756276	2.193632
C	0.954533	2.909612	2.963491
C	-0.191428	2.199628	2.603702
C	-0.175978	1.325351	1.503654
H	2.946771	1.743323	0.445678
H	3.038315	3.301476	2.423745
H	0.940206	3.584407	3.824737
H	-1.126262	2.310247	3.159103
C	-1.499982	0.628785	1.168789
C	-1.699864	-0.820393	1.541976
H	-0.768529	-1.403261	1.521312
H	-2.106952	-0.843080	2.571705

H	-2.450441	-1.262768	0.869037
O	-2.424346	1.397269	0.926398
C	-0.250349	0.016757	-1.086338
H	-0.691455	0.915406	-1.532478
C	2.011553	-0.866067	-0.116063
C	2.111972	-1.397051	1.182481
C	2.783002	-1.426816	-1.150721
C	2.947911	-2.494761	1.435093
H	1.541424	-0.959975	2.009109
C	3.615756	-2.523634	-0.897478
H	2.721352	-1.008713	-2.161833
C	3.695004	-3.064702	0.395047
H	3.016819	-2.901830	2.448686
H	4.210469	-2.952748	-1.709907
H	4.347806	-3.920273	0.593214
C	-0.775850	-1.205877	-1.481572
C	-0.289595	-2.576784	-1.069802
H	0.438327	-2.958368	-1.806979
H	0.200632	-2.582571	-0.089894
H	-1.140173	-3.279481	-1.038797
N	-1.823472	-1.264270	-2.351918
C	-2.446202	-0.119131	-2.989562
H	-1.701506	0.479195	-3.541867
H	-3.188367	-0.491876	-3.714474
C	-3.145982	0.826404	-2.006190
O	-3.079397	2.033326	-2.070721
O	-3.815808	0.135962	-1.057436
H	-4.043955	0.781693	-0.349298
H	-2.270768	-2.169596	-2.474036
N	0.962816	1.206136	0.775897

C	1.084932	0.288746	-0.465538
H	1.639221	0.949761	-1.157118

Int2^{B}

Lowest frequency = 29.0617 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.085503	-3.537720	-0.241134
C	0.809687	-4.366747	-1.086276
C	1.339587	-3.826417	-2.269642
C	1.146712	-2.470436	-2.548334
C	0.421182	-1.662915	-1.659887
H	1.900178	-4.458714	-2.965003
H	-0.376903	-3.884603	0.686924
H	0.939602	-5.420260	-0.826764
H	1.567713	-2.016077	-3.449167
C	0.413579	-0.143966	-1.814444
C	-0.142073	0.462538	-3.076250
H	0.622032	0.383758	-3.874714
H	-1.056148	-0.048146	-3.416851
H	-0.320494	1.533055	-2.894364
C	-0.996288	-1.388462	0.389148
H	-1.769155	-2.122348	0.678563
C	-1.692518	-0.304041	-0.382445
H	-2.537002	-0.661152	-0.980921
C	-1.658003	1.068546	-0.165770
N	-0.106511	-2.226895	-0.542919
N	-0.693827	1.678430	0.565187

C	-2.730603	1.936710	-0.773786
H	-3.316241	2.432063	0.022302
H	-2.289758	2.717675	-1.413912
H	-3.423147	1.328581	-1.372355
O	1.160315	0.449797	-1.033228
H	1.088749	5.354732	-0.925258
C	-0.513071	3.104249	0.728297
H	0.117604	3.286021	1.611749
H	-1.479595	3.603093	0.921484
C	0.117038	3.794064	-0.489624
O	0.019928	3.417983	-1.639563
O	0.754856	4.916535	-0.112238
C	-0.238719	-1.018414	1.657832
C	-1.005355	-0.699584	2.795991
C	1.164637	-0.954697	1.729974
C	-0.377921	-0.312064	3.985177
H	-2.098748	-0.746374	2.744371
C	1.789821	-0.567596	2.925744
H	1.775113	-1.173193	0.850036
C	1.022684	-0.243674	4.052636
H	-0.983446	-0.067636	4.863543
H	2.882270	-0.519599	2.971309
H	1.513533	0.056540	4.983598
H	0.096539	1.099952	0.852103

Int2[C]

Lowest frequency = 40.7269 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.003799	-3.521840	-0.100017
C	0.787502	-4.365852	-0.873499
C	1.387254	-3.856938	-2.039084
C	1.196242	-2.515334	-2.382654
C	0.398704	-1.695387	-1.573412
H	2.002863	-4.504851	-2.670625
H	-0.500726	-3.836625	0.817340
H	0.918229	-5.407606	-0.570376
H	1.668292	-2.086343	-3.270207
C	0.292976	-0.191600	-1.772640
C	-0.188397	0.318641	-3.114617
H	0.621509	0.180558	-3.856632
H	-1.086608	-0.208717	-3.470927
H	-0.377922	1.400927	-3.051059
C	-1.076266	-1.320332	0.364052
H	-1.944611	-1.959651	0.598686
C	-1.563820	-0.199075	-0.529646
H	-2.396020	-0.501814	-1.175194
C	-1.512914	1.182131	-0.259457
N	-0.182578	-2.227339	-0.469965
N	-0.565075	1.715589	0.524735
C	-2.453454	2.120363	-0.966407
H	-3.065341	2.671618	-0.229692
H	-1.906928	2.873056	-1.561137
H	-3.130037	1.565154	-1.630487
O	1.132345	0.448431	-1.077474
H	1.039316	2.095891	-1.206190
C	-0.295016	3.139569	0.674444
H	0.401655	3.263355	1.518959

H	-1.212843	3.695549	0.919898
C	0.327077	3.837722	-0.567911
O	0.221952	5.035349	-0.685263
O	0.964351	3.068661	-1.458131
C	-0.393560	-0.974229	1.680027
C	-1.211550	-0.709040	2.794857
C	1.005970	-0.864410	1.803091
C	-0.639763	-0.326745	4.014754
H	-2.300171	-0.795422	2.705474
C	1.573442	-0.483543	3.028772
H	1.653421	-1.041279	0.939340
C	0.753767	-0.212004	4.133751
H	-1.283820	-0.123648	4.875877
H	2.661070	-0.399785	3.116686
H	1.200121	0.083399	5.088236
H	0.085326	1.066526	0.974150

TS2^{B}

Lowest frequency = -348.3832 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.121355	-3.558654	-0.167284
C	0.879420	-4.375854	-0.991602
C	1.382731	-3.849043	-2.197923
C	1.129555	-2.517413	-2.533073
C	0.358633	-1.723114	-1.672443
H	1.973283	-4.482153	-2.867387
H	-0.307376	-3.882646	0.784674

H	1.068894	-5.411029	-0.697767
H	1.525464	-2.075430	-3.450727
C	0.195388	-0.210578	-1.770727
C	-0.237883	0.386550	-3.098912
H	0.594880	0.295723	-3.820498
H	-1.130124	-0.106865	-3.518032
H	-0.424283	1.461825	-2.950997
C	-0.986535	-1.362821	0.311962
H	-1.876005	-1.965672	0.562276
C	-1.440866	-0.235345	-0.620290
H	-2.299592	-0.552172	-1.226032
C	-1.528065	1.132583	-0.206829
N	-0.131755	-2.275054	-0.535580
N	-0.475834	1.656071	0.419540
C	-2.721558	1.979174	-0.544616
H	-3.198157	2.344655	0.384436
H	-2.426944	2.854254	-1.146794
H	-3.467782	1.391524	-1.097315
O	1.139732	0.350212	-1.103897
H	0.854127	5.558175	-0.937752
C	-0.293186	3.058036	0.736544
H	0.491549	3.155987	1.502170
H	-1.219104	3.482515	1.161312
C	0.086057	3.888177	-0.499572
O	-0.140880	3.565630	-1.646403
O	0.667202	5.039098	-0.125116
C	-0.288541	-1.007581	1.613383
C	-1.091289	-0.731861	2.735863
C	1.111365	-0.917113	1.721952
C	-0.503839	-0.356645	3.950388

H	-2.181991	-0.810503	2.659182
C	1.696017	-0.547917	2.941726
H	1.743027	-1.100289	0.848029
C	0.892279	-0.263599	4.055167
H	-1.136224	-0.147498	4.818914
H	2.785773	-0.481392	3.019556
H	1.352824	0.022381	5.006005
H	0.401595	1.108267	0.255607

TS2[C]

Lowest frequency = -295.1499 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.113471	-3.597037	-0.096640
C	0.923456	-4.413385	-0.871465
C	1.502840	-3.887215	-2.042197
C	1.264520	-2.556531	-2.396006
C	0.436549	-1.765950	-1.589295
H	2.140386	-4.517579	-2.669756
H	-0.370489	-3.920999	0.828458
H	1.096092	-5.447852	-0.564545
H	1.717153	-2.114803	-3.287168
C	0.231420	-0.265761	-1.747844
C	-0.204630	0.228111	-3.120109
H	0.637712	0.110647	-3.826241
H	-1.077174	-0.318860	-3.511731
H	-0.426975	1.305300	-3.070679
C	-1.005480	-1.398806	0.331770

H	-1.904425	-1.997879	0.553498
C	-1.415900	-0.272020	-0.618450
H	-2.256862	-0.576130	-1.253931
C	-1.453655	1.114139	-0.271270
N	-0.118364	-2.313484	-0.480758
N	-0.499917	1.629225	0.499219
C	-2.435233	2.042555	-0.926770
H	-3.028997	2.574494	-0.161324
H	-1.919044	2.812462	-1.528124
H	-3.124766	1.486154	-1.576147
O	1.146547	0.374024	-1.101456
H	1.082528	1.954606	-1.264147
C	-0.210747	3.048270	0.657211
H	0.476905	3.163188	1.509746
H	-1.126473	3.613192	0.885962
C	0.436760	3.729495	-0.589354
O	0.379622	4.933421	-0.678617
O	1.020813	2.947071	-1.494547
C	-0.339577	-1.049944	1.653963
C	-1.163890	-0.806860	2.768465
C	1.058494	-0.915865	1.779231
C	-0.600828	-0.421950	3.992089
H	-2.250596	-0.915127	2.678121
C	1.616615	-0.532617	3.008000
H	1.708313	-1.074538	0.913374
C	0.789983	-0.282817	4.113484
H	-1.249405	-0.236930	4.853884
H	2.702417	-0.430193	3.098831
H	1.229585	0.014125	5.070647
H	0.194013	0.970930	0.868517

Int3^{C}

Lowest frequency = 32.9426 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.047953	-3.547569	-0.022814
C	0.886151	-4.351397	-0.779428
C	1.465270	-3.828691	-1.955019
C	1.198738	-2.513009	-2.340624
C	0.338247	-1.737927	-1.556295
H	2.126639	-4.455210	-2.561349
H	-0.428288	-3.862954	0.909011
H	1.088458	-5.374448	-0.453143
H	1.648867	-2.074204	-3.234048
C	0.024314	-0.252314	-1.670802
C	-0.284534	0.231571	-3.091770
H	0.619434	0.133711	-3.715321
H	-1.111878	-0.328020	-3.560253
H	-0.539101	1.303797	-3.064564
C	-1.089076	-1.330990	0.320370
H	-2.044617	-1.849437	0.497661
C	-1.325311	-0.193460	-0.727039
H	-2.196679	-0.474584	-1.336888
C	-1.485970	1.195225	-0.227917
N	-0.212570	-2.279769	-0.441616
N	-0.429261	1.680342	0.378212
C	-2.675853	2.038120	-0.558059
H	-2.951914	2.695349	0.283468

H	-2.440168	2.694631	-1.419271
H	-3.539454	1.413843	-0.828253
O	1.086447	0.375995	-1.086235
H	1.127460	1.904673	-1.381721
C	-0.106913	3.081079	0.579949
H	0.598597	3.162784	1.422232
H	-1.003037	3.672952	0.809696
C	0.563326	3.726223	-0.688524
O	0.554981	4.931423	-0.771589
O	1.098129	2.917270	-1.593594
C	-0.475068	-0.972937	1.659739
C	-1.338636	-0.706191	2.738031
C	0.917884	-0.861782	1.838527
C	-0.818272	-0.320307	3.980187
H	-2.422826	-0.803409	2.608180
C	1.433971	-0.481520	3.084916
H	1.597252	-1.042733	0.999572
C	0.569007	-0.206958	4.154841
H	-1.496456	-0.118734	4.815093
H	2.517049	-0.399267	3.219065
H	0.976198	0.087830	5.126970
H	0.408322	1.037610	0.248161

TS3^{C}

Lowest frequency = -869.0916 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	0.124245	-3.584302	-0.093106

C	0.980519	-4.381801	-0.837796
C	1.582155	-3.851101	-1.997189
C	1.318465	-2.533439	-2.381529
C	0.441071	-1.766568	-1.609992
H	2.258997	-4.471560	-2.592563
H	-0.369343	-3.906060	0.827472
H	1.178988	-5.406219	-0.513276
H	1.785189	-2.088783	-3.263483
C	0.104162	-0.286915	-1.726681
C	-0.179713	0.192305	-3.152033
H	0.736767	0.108516	-3.758807
H	-0.989956	-0.379660	-3.635331
H	-0.454940	1.259889	-3.126667
C	-1.019121	-1.367905	0.244305
H	-1.983738	-1.879509	0.388726
C	-1.200732	-0.210123	-0.793759
H	-2.079220	-0.455876	-1.410951
C	-1.361526	1.174719	-0.220565
N	-0.129962	-2.315422	-0.508603
N	-0.258381	1.664445	0.256768
C	-2.669707	1.891550	-0.327786
H	-2.690004	2.827998	0.247358
H	-2.869675	2.129863	-1.390210
H	-3.489407	1.236007	0.013662
O	1.196651	0.372914	-1.157784
H	1.253128	2.060223	-1.491085
C	0.030340	3.050844	0.554651
H	0.769914	3.089800	1.372035
H	-0.857918	3.624740	0.856686
C	0.647117	3.789515	-0.680773

O	0.601756	4.994069	-0.716133
O	1.202220	3.052828	-1.651003
C	-0.437299	-1.028413	1.601510
C	-1.325003	-0.822517	2.673088
C	0.946915	-0.867965	1.802392
C	-0.836762	-0.447593	3.931900
H	-2.402787	-0.959288	2.525633
C	1.431552	-0.501457	3.064759
H	1.644910	-1.004085	0.970023
C	0.542457	-0.286809	4.128860
H	-1.533328	-0.293024	4.761670
H	2.508746	-0.381287	3.216649
H	0.925277	-0.001512	5.113639
H	0.649744	0.979244	-0.188781

Int3^{B}

Lowest frequency = 14.4680 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	-0.081719	-3.570400	-0.127337
C	0.681822	-4.465663	-0.864343
C	1.345021	-4.014172	-2.021771
C	1.236862	-2.675091	-2.412353
C	0.456031	-1.809024	-1.645031
H	1.949388	-4.710935	-2.610657
H	-0.617221	-3.829525	0.789672
H	0.757570	-5.505012	-0.535340
H	1.754635	-2.290400	-3.293949

C	0.296097	-0.300181	-1.754909
C	0.083956	0.234189	-3.173934
H	0.998634	0.078301	-3.768483
H	-0.770156	-0.248392	-3.679824
H	-0.102808	1.319810	-3.115561
C	-0.975727	-1.233655	0.191472
H	-1.998033	-1.631377	0.288967
C	-0.956430	-0.060919	-0.841887
H	-1.843850	-0.201825	-1.483874
C	-1.065718	1.326018	-0.223631
N	-0.181448	-2.283382	-0.544760
N	0.033116	1.959742	-0.012863
C	-2.461793	1.811328	0.062795
H	-2.481001	2.643594	0.781766
H	-2.919488	2.163282	-0.879161
H	-3.082530	0.987234	0.455046
O	1.502757	0.190954	-1.198401
H	-0.308533	6.096500	-1.188274
C	0.044922	3.335554	0.434778
H	1.053581	3.605368	0.784849
H	-0.654037	3.531068	1.272290
C	-0.353099	4.269040	-0.716440
O	-0.924005	3.912907	-1.726869
O	-0.006609	5.537704	-0.439510
C	-0.423007	-0.980762	1.577559
C	-1.314369	-0.984876	2.666154
C	0.942892	-0.713468	1.793624
C	-0.849316	-0.715650	3.961172
H	-2.377151	-1.199661	2.502246
C	1.404149	-0.456974	3.090020

H	1.631563	-0.686338	0.943042
C	0.511125	-0.453837	4.173622
H	-1.548566	-0.720318	4.803036
H	2.466759	-0.253034	3.255448
H	0.877633	-0.250553	5.184773
H	1.211434	1.025425	-0.692045

Int4[C]

Lowest frequency = 21.5340 cm^{-1}

Charge = 1, Multiplicity = 1

45

C	-0.096765	-3.590020	-0.039540
C	0.710797	-4.457692	-0.762491
C	1.360914	-3.989318	-1.920780
C	1.193897	-2.661222	-2.328709
C	0.367594	-1.823639	-1.577514
H	1.999647	-4.664485	-2.498485
H	-0.624502	-3.863514	0.877755
H	0.831540	-5.488851	-0.421300
H	1.699064	-2.266106	-3.213134
C	0.119726	-0.326875	-1.718144
C	-0.086510	0.155128	-3.153162
H	0.843038	0.017515	-3.729163
H	-0.910982	-0.376401	-3.657637
H	-0.308021	1.235518	-3.138700
C	-1.078296	-1.288541	0.250716
H	-2.077457	-1.726899	0.401139
C	-1.158272	-0.148184	-0.820098

H	-2.027071	-0.378161	-1.459642
C	-1.336102	1.249744	-0.243414
N	-0.253826	-2.313644	-0.474183
N	-0.257001	1.816266	0.173886
C	-2.728619	1.817689	-0.236251
H	-2.807809	2.748679	0.342013
H	-3.050860	2.022795	-1.274528
H	-3.435815	1.077103	0.178180
O	1.282757	0.279465	-1.163994
H	1.151825	2.481267	-1.362648
C	-0.159588	3.195853	0.594290
H	0.537826	3.254995	1.448493
H	-1.112457	3.661469	0.894986
C	0.428397	4.083890	-0.537558
O	0.288954	5.279184	-0.523630
O	1.100558	3.449570	-1.523828
C	-0.482155	-0.945154	1.600243
C	-1.362634	-0.632819	2.651929
C	0.907332	-0.870879	1.809931
C	-0.860602	-0.235275	3.898159
H	-2.445977	-0.701610	2.498087
C	1.405603	-0.482689	3.060294
H	1.603789	-1.096836	0.996211
C	0.524589	-0.159369	4.103265
H	-1.551971	0.003888	4.712034
H	2.487140	-0.429794	3.219072
H	0.918006	0.144126	5.078352
H	0.927115	0.860441	-0.402760

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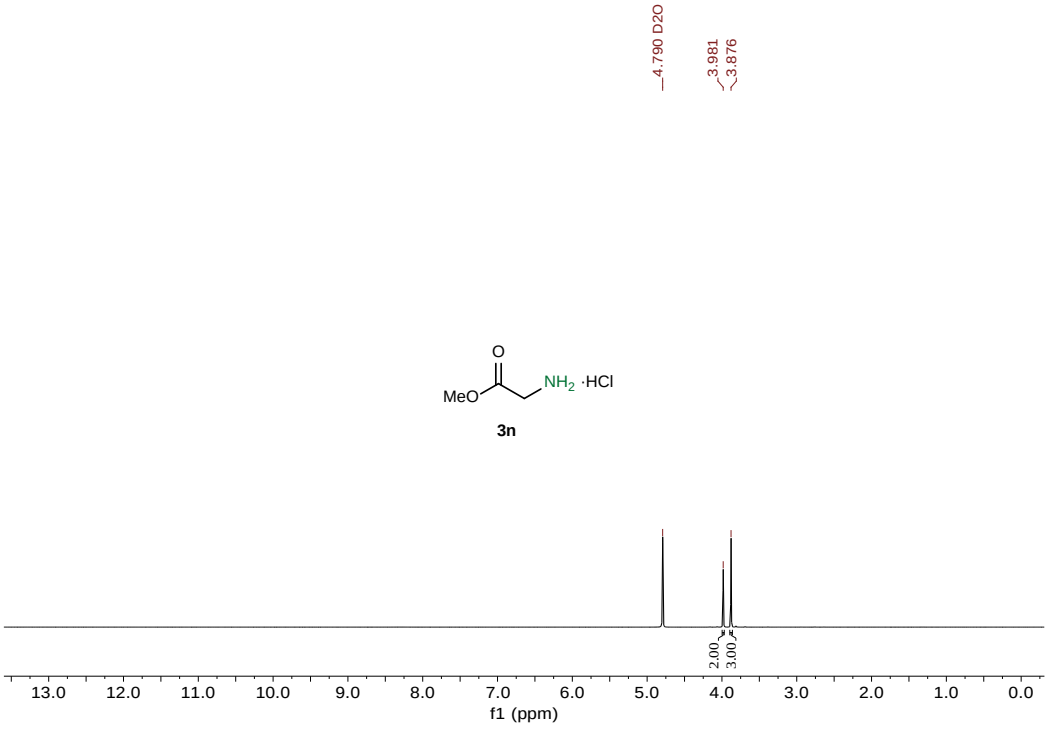
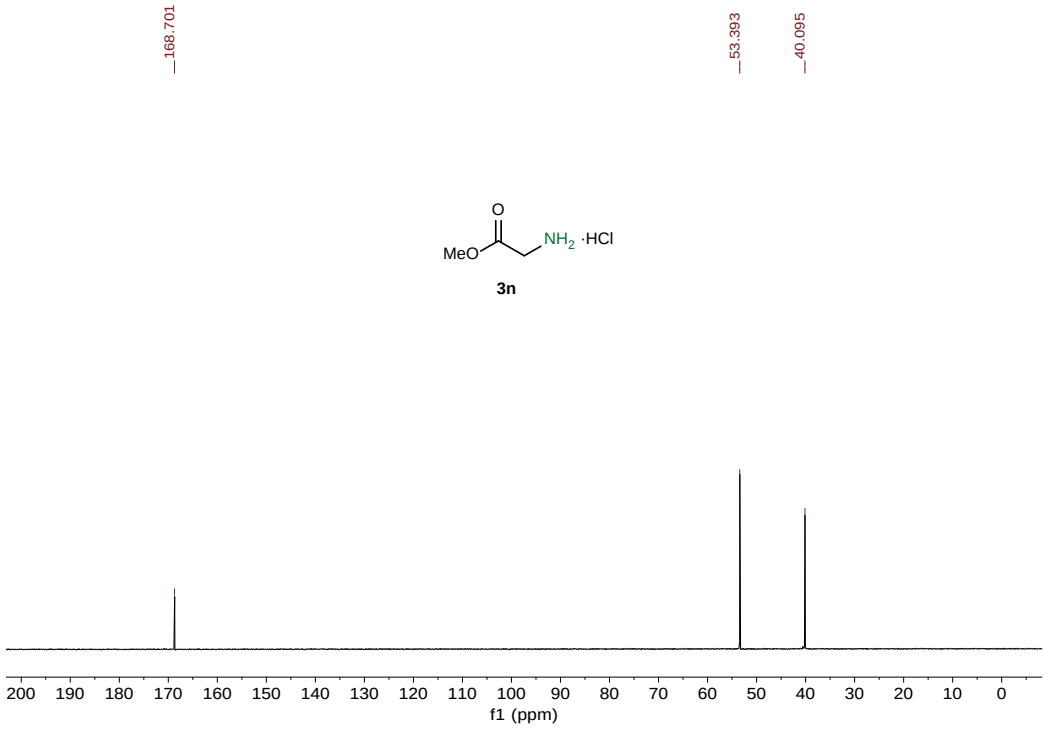
11. NMR Spectra of Compounds.

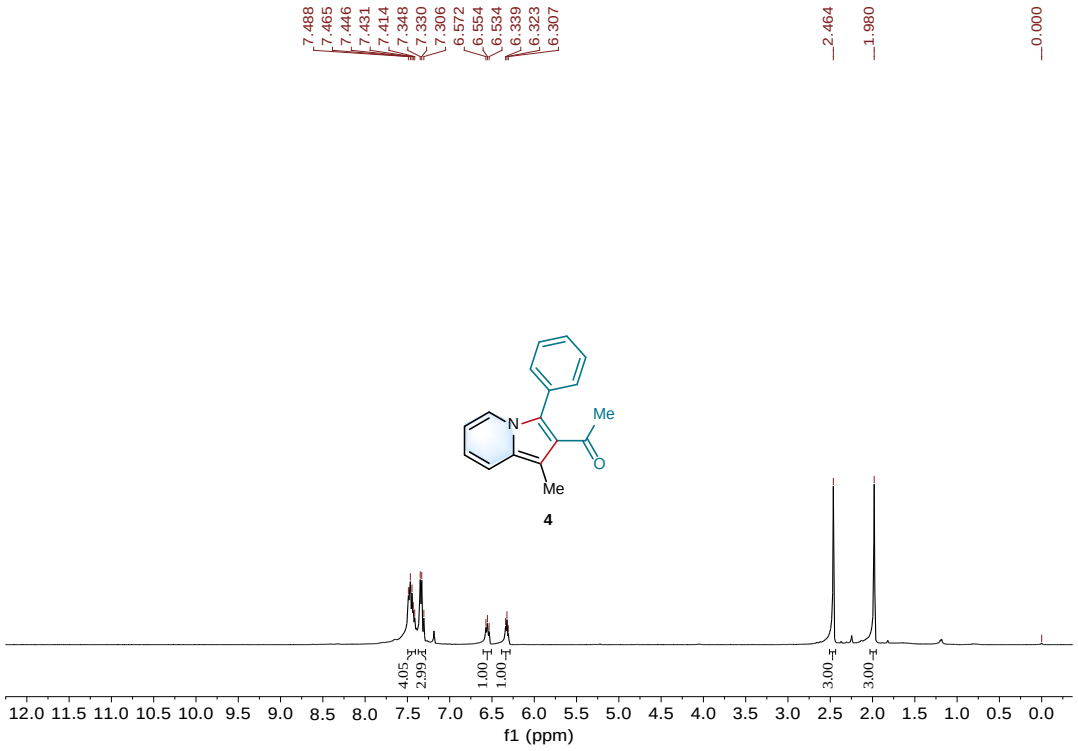
^{1}H NMR spectra of 3n (400 MHz, D_2O)



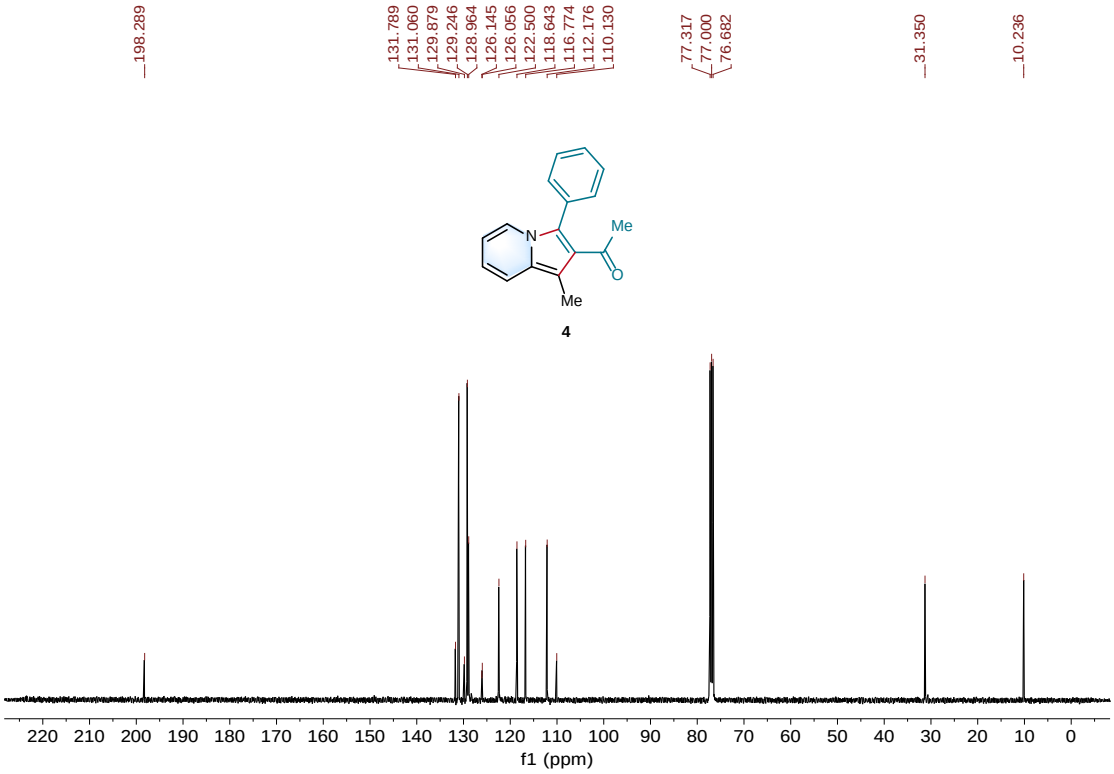
^{13}C NMR spectra of 3n (100 MHz, D_2O)



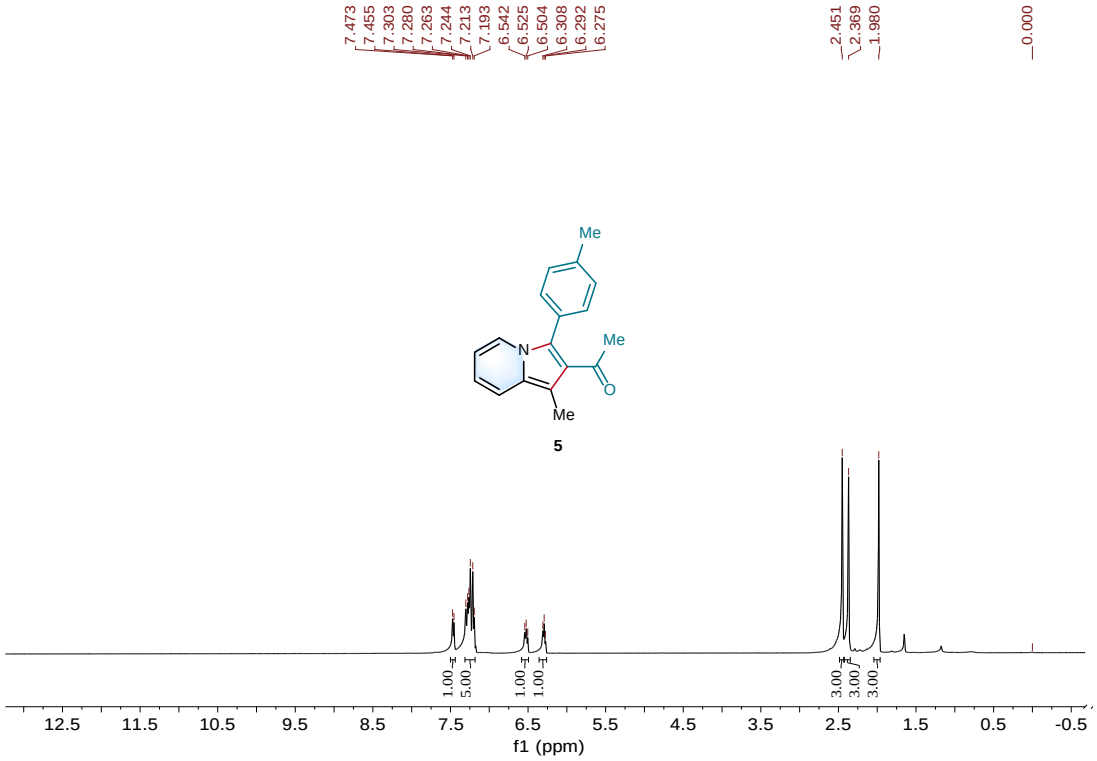
^{1}H NMR spectra of 4 (400 MHz, $CDCl_3$)



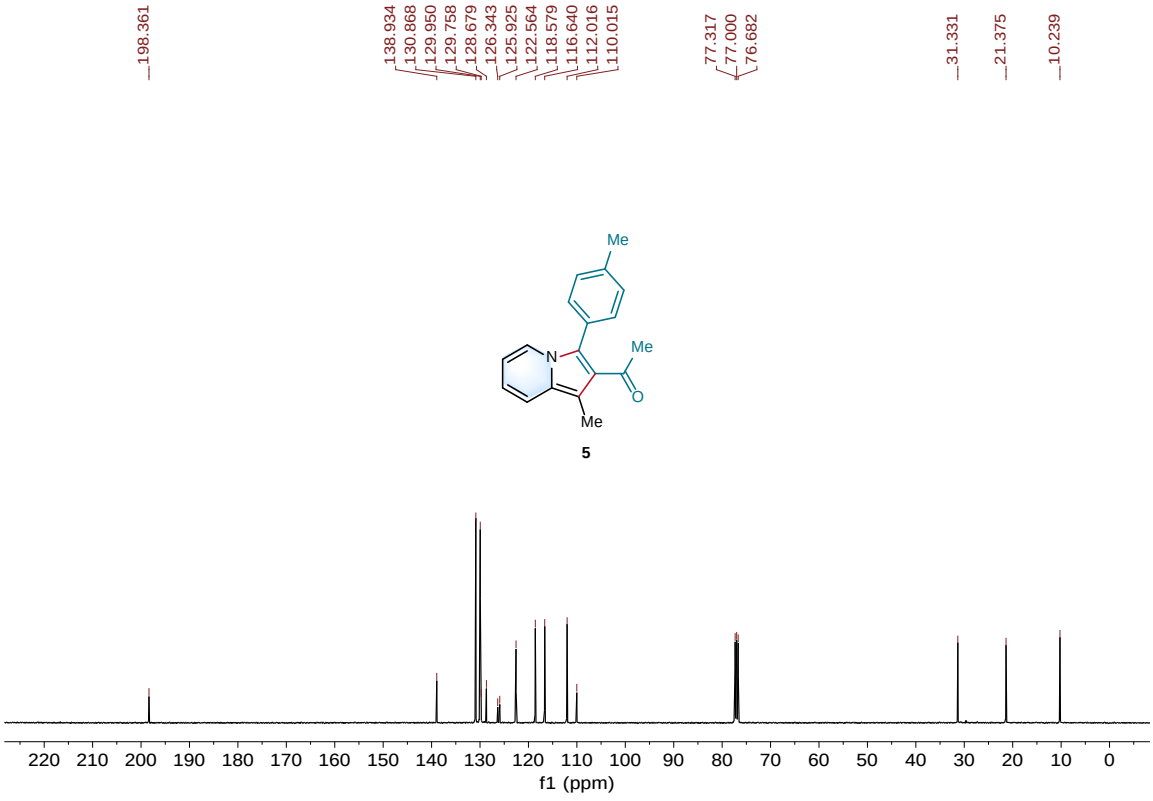
^{13}C NMR spectra of 4 (100 MHz, $CDCl_3$)



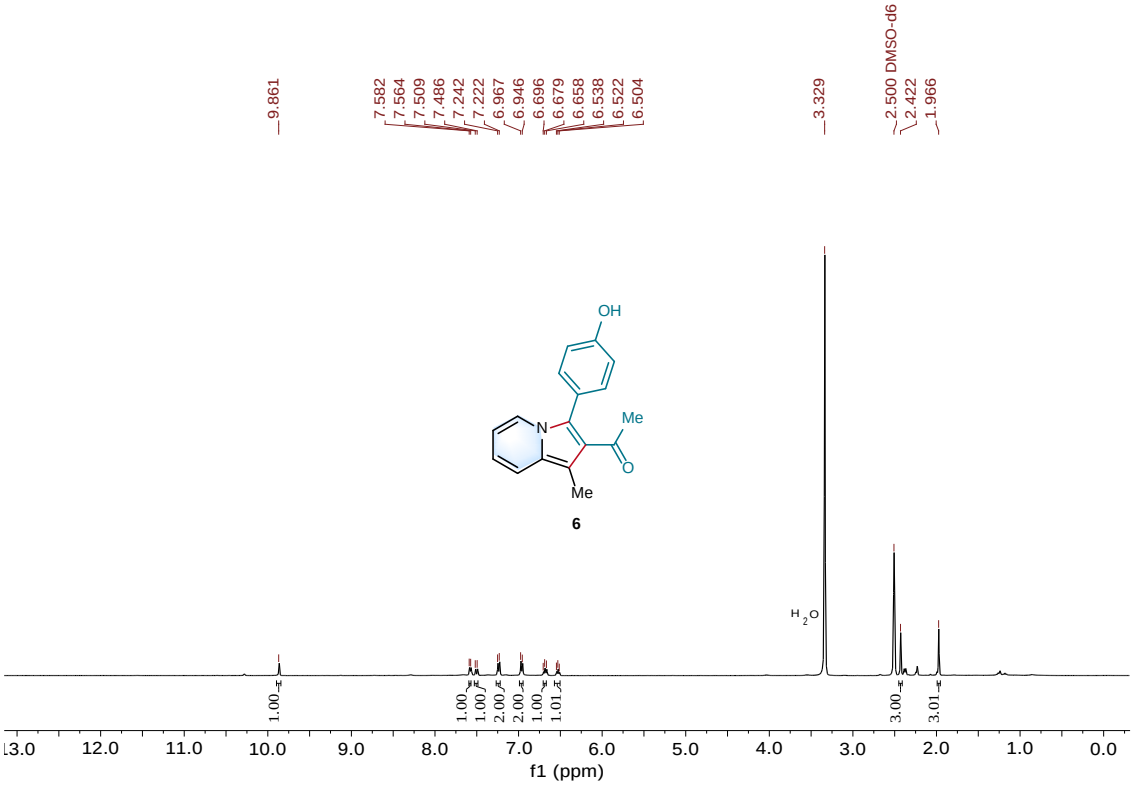
^{1}H NMR spectra of 5 (400 MHz, $CDCl_3$)



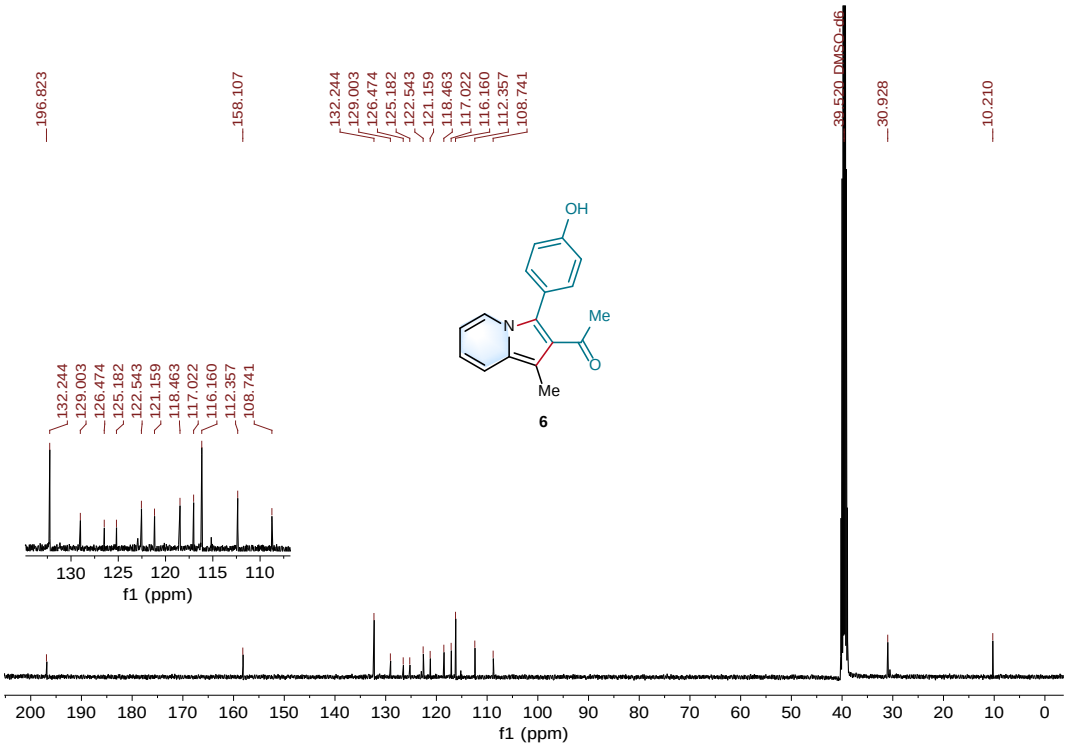
^{1}H NMR spectra of 5 (400 MHz, $CDCl_3$)



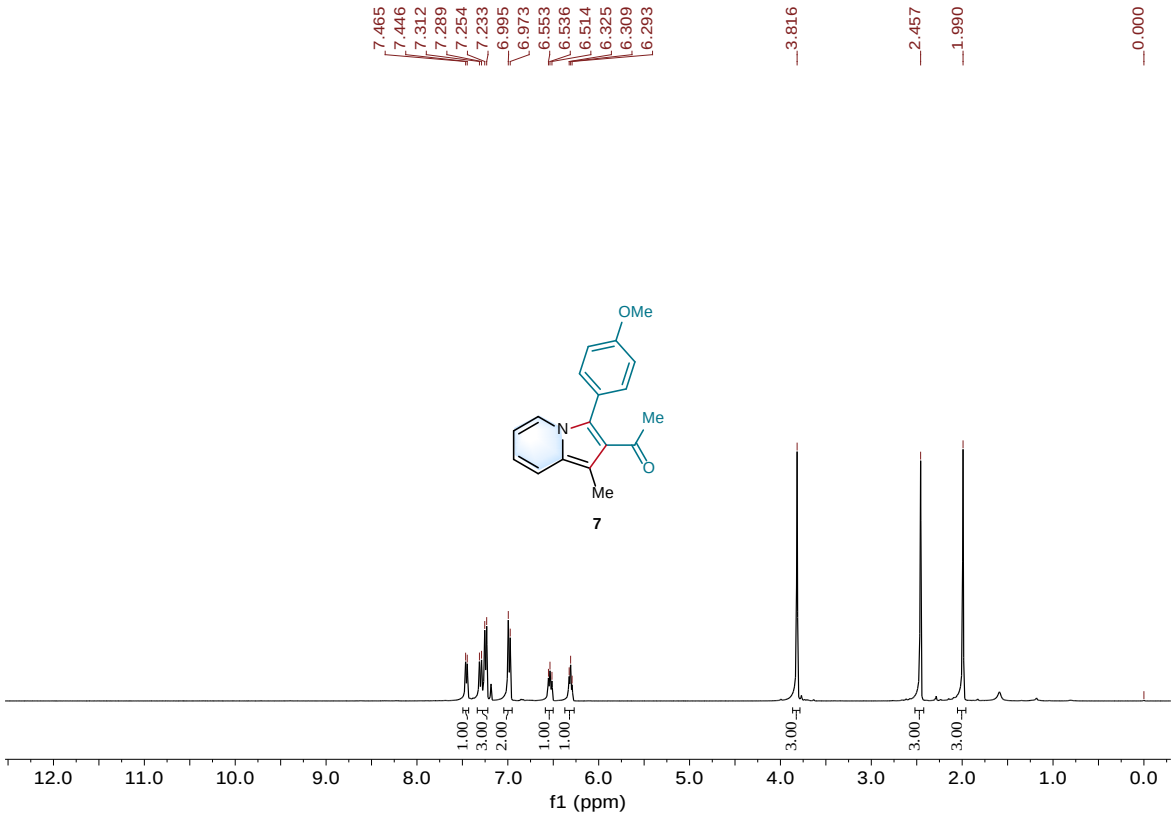
^{1}H NMR spectra of 6 (400 MHz, DMSO-d_6)



^{13}C NMR spectra of 6 (100 MHz, DMSO-d_6)



^{1}H NMR spectra of 7 (400 MHz, $CDCl_3$)



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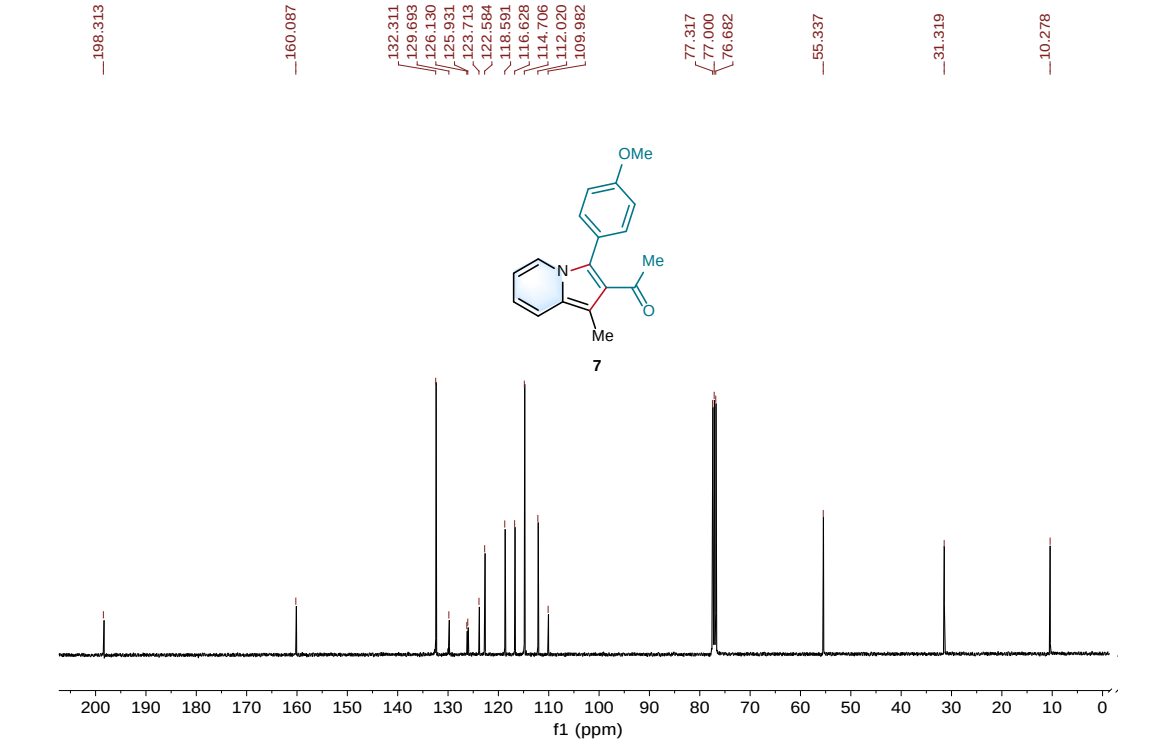
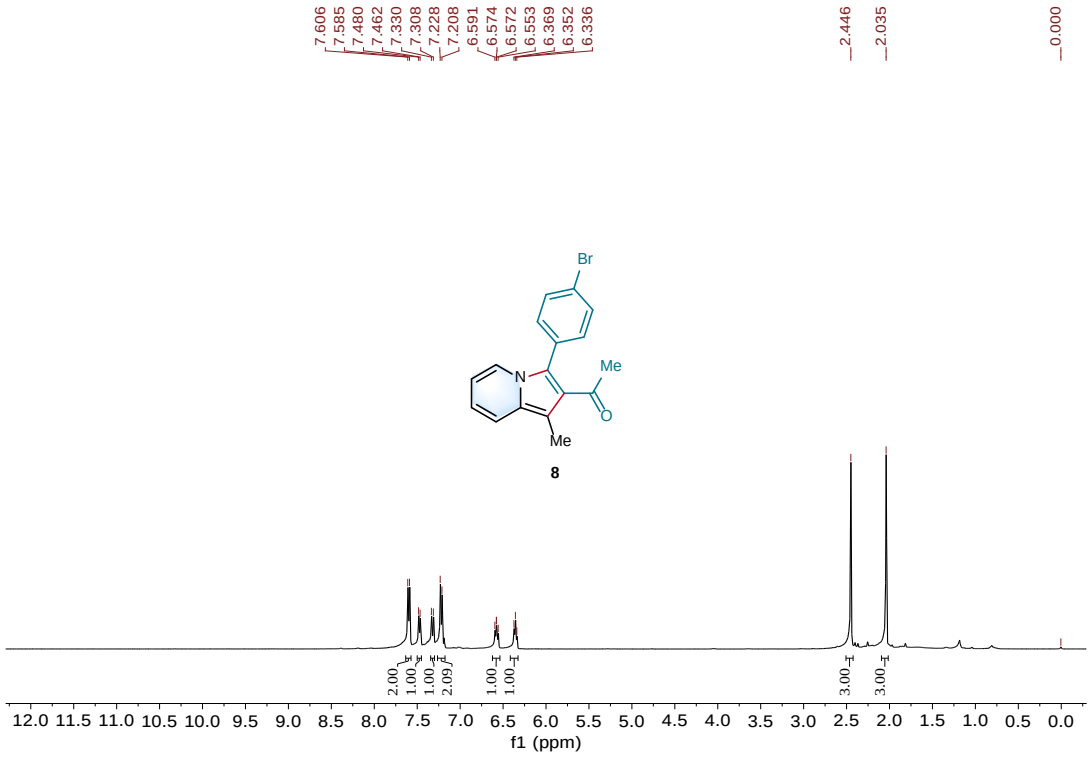


^{1}H NMR spectra of 8 (400 MHz, $CDCl_3$)



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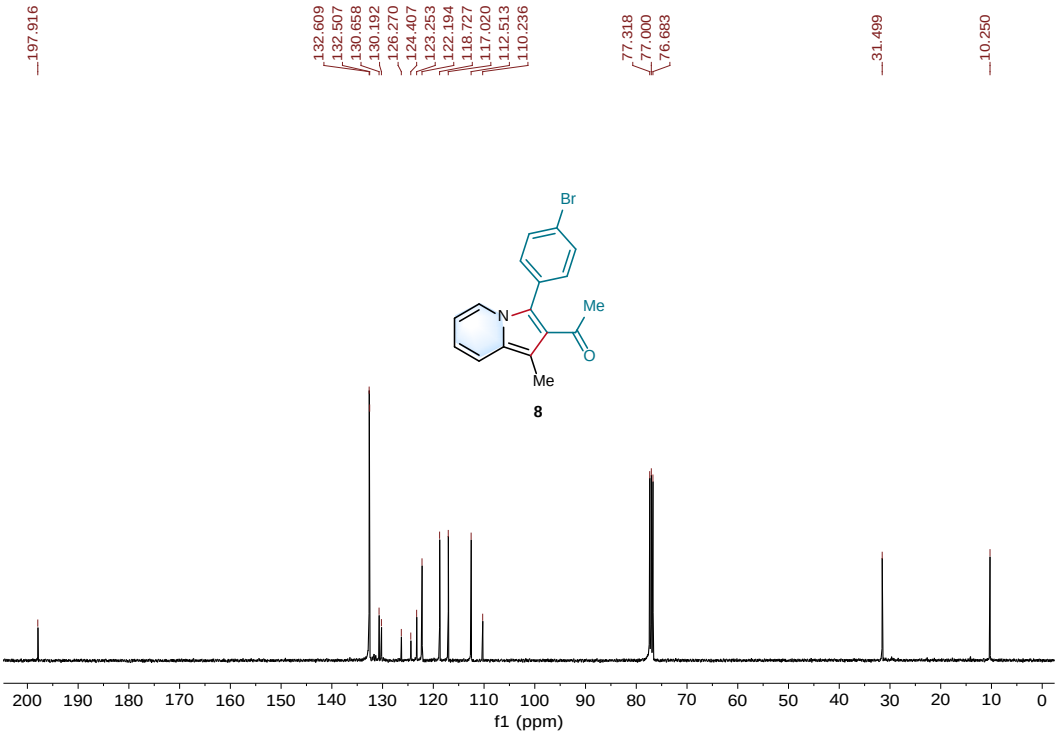
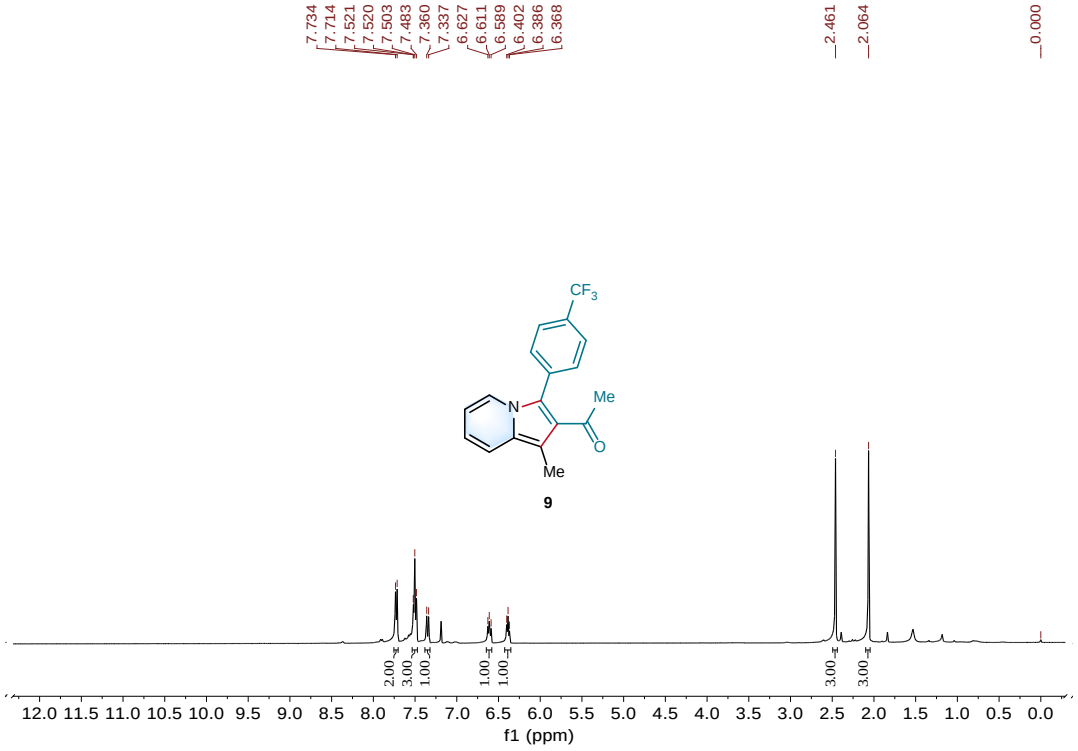


^{1}H NMR spectra of 9 (400 MHz, $CDCl_3$)



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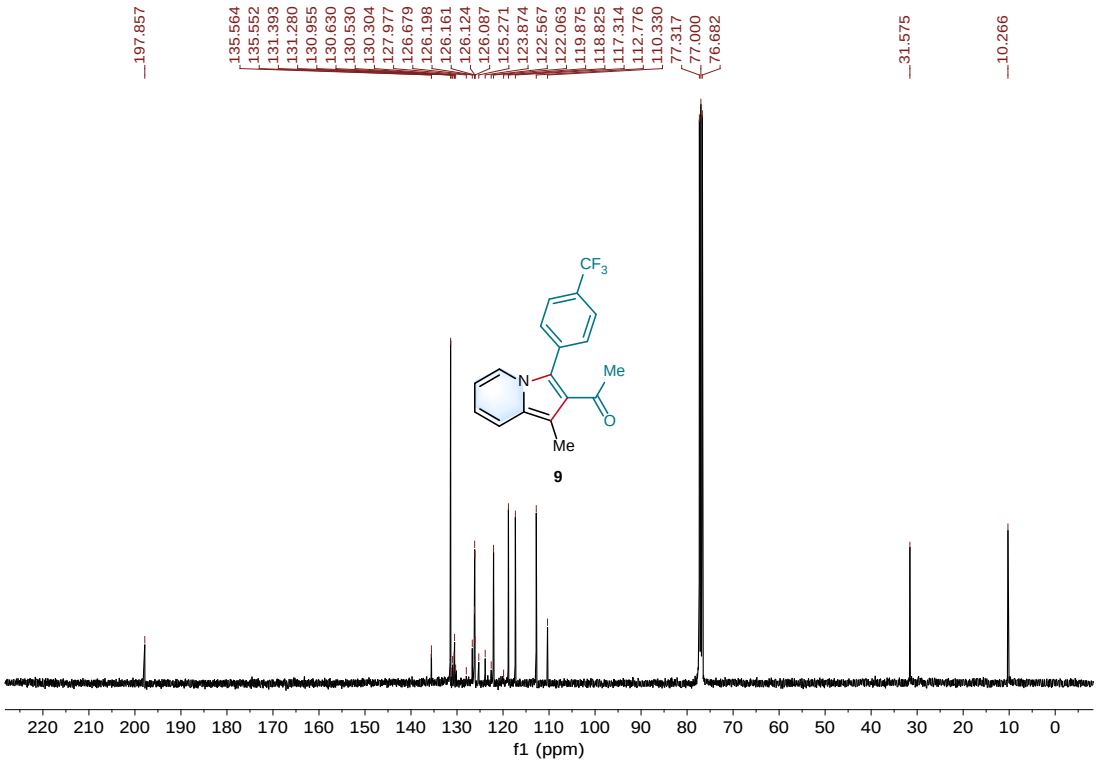
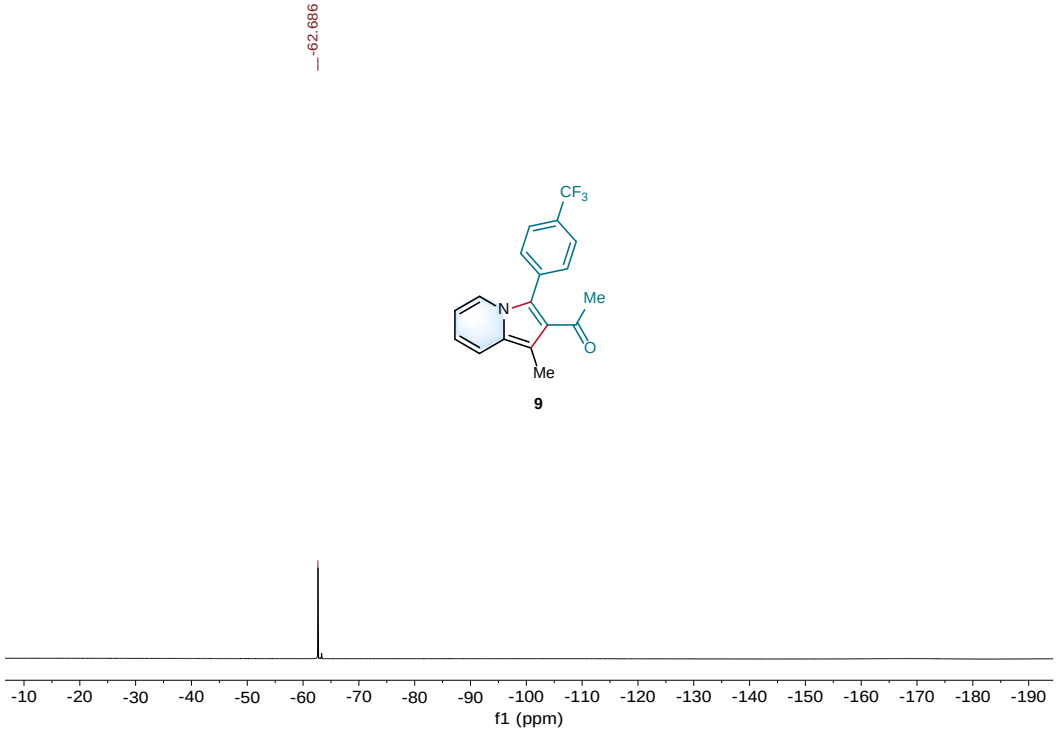


^{19}F NMR spectra of 9 (375 MHz, $CDCl_3$)



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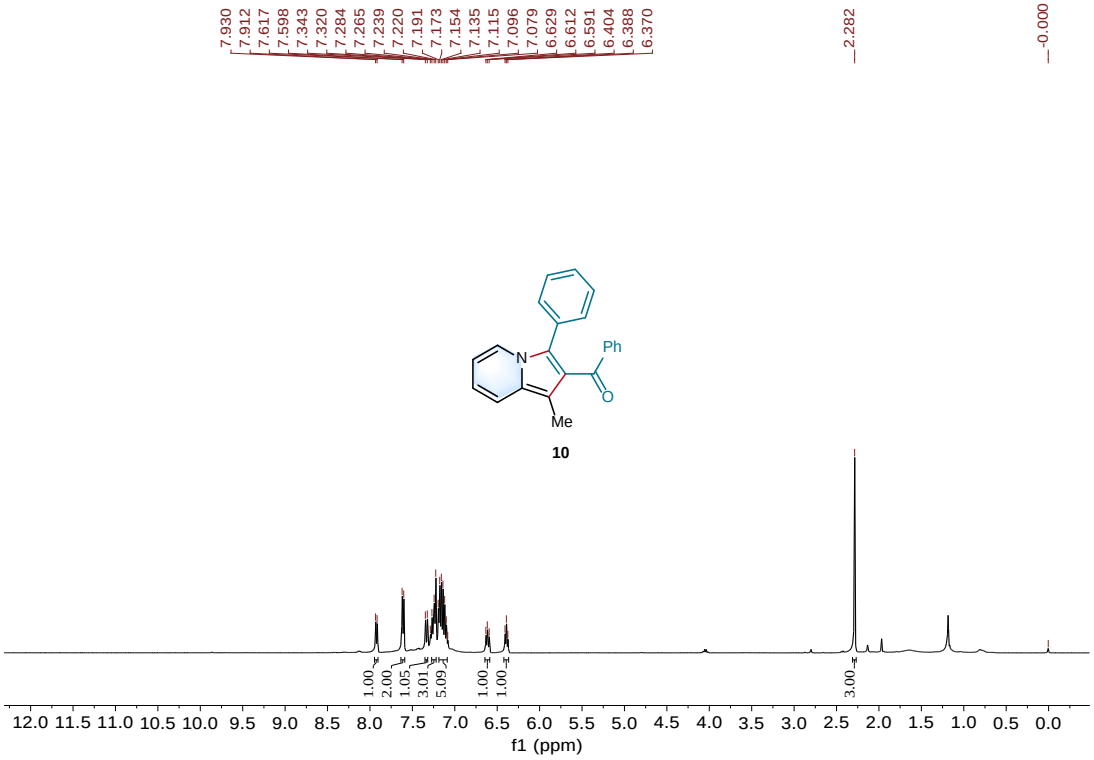
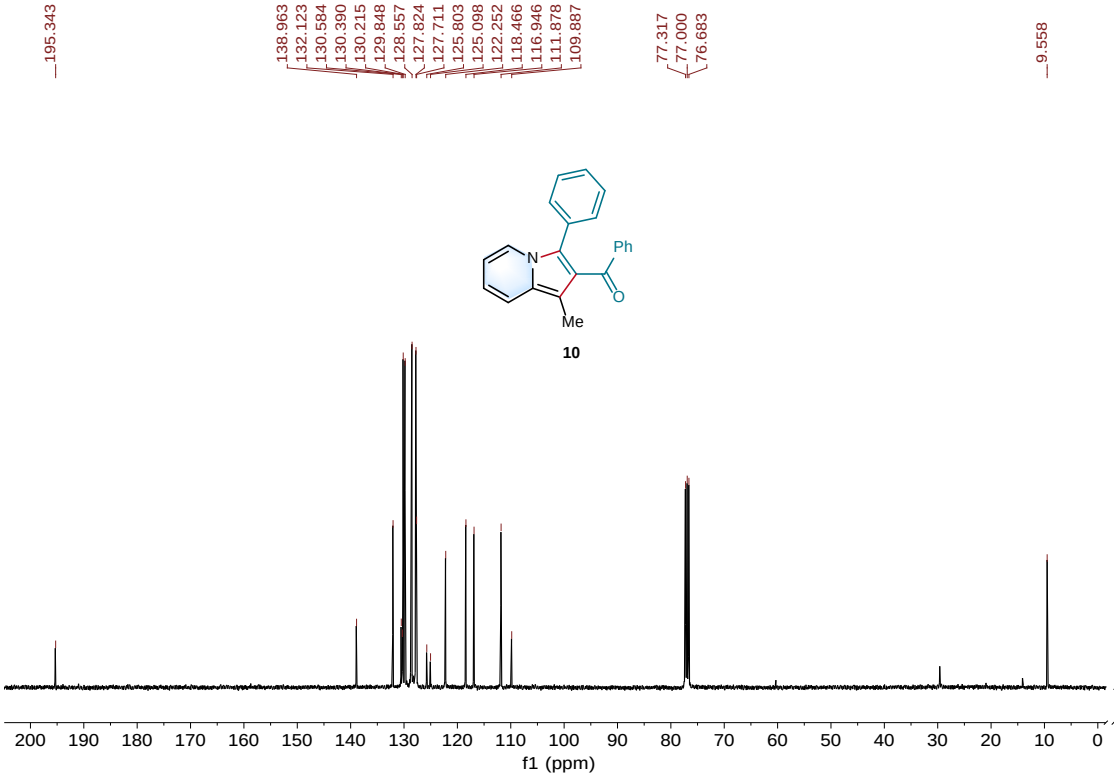
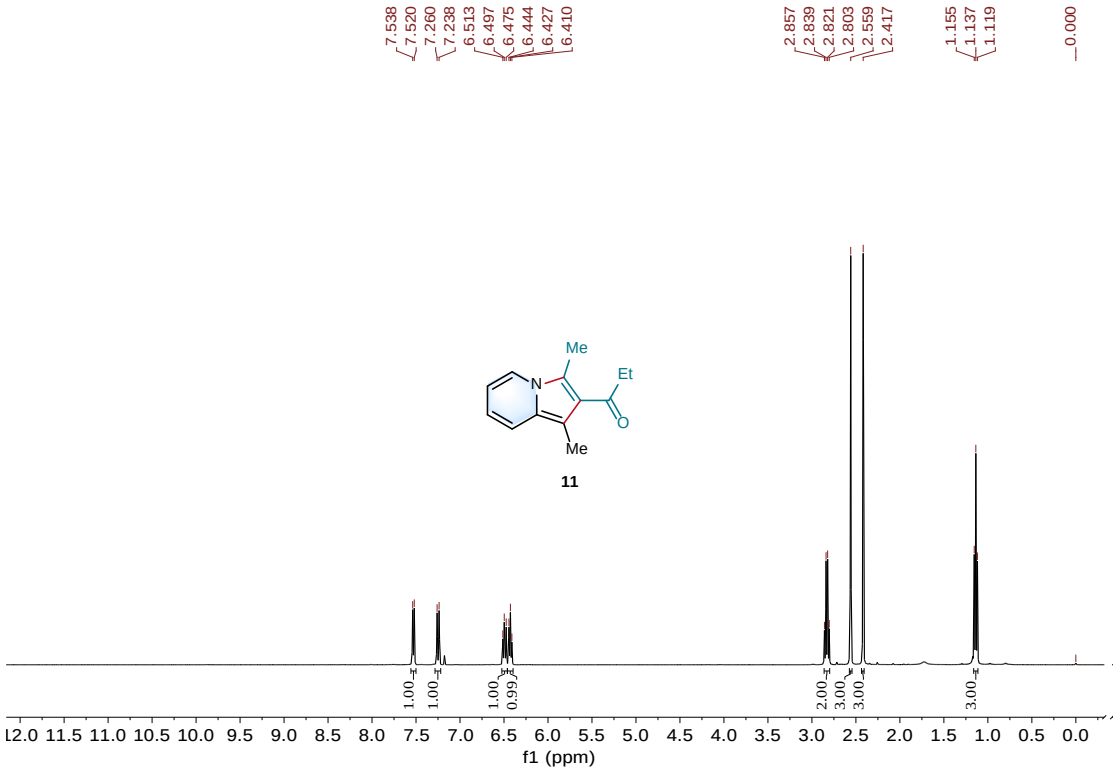


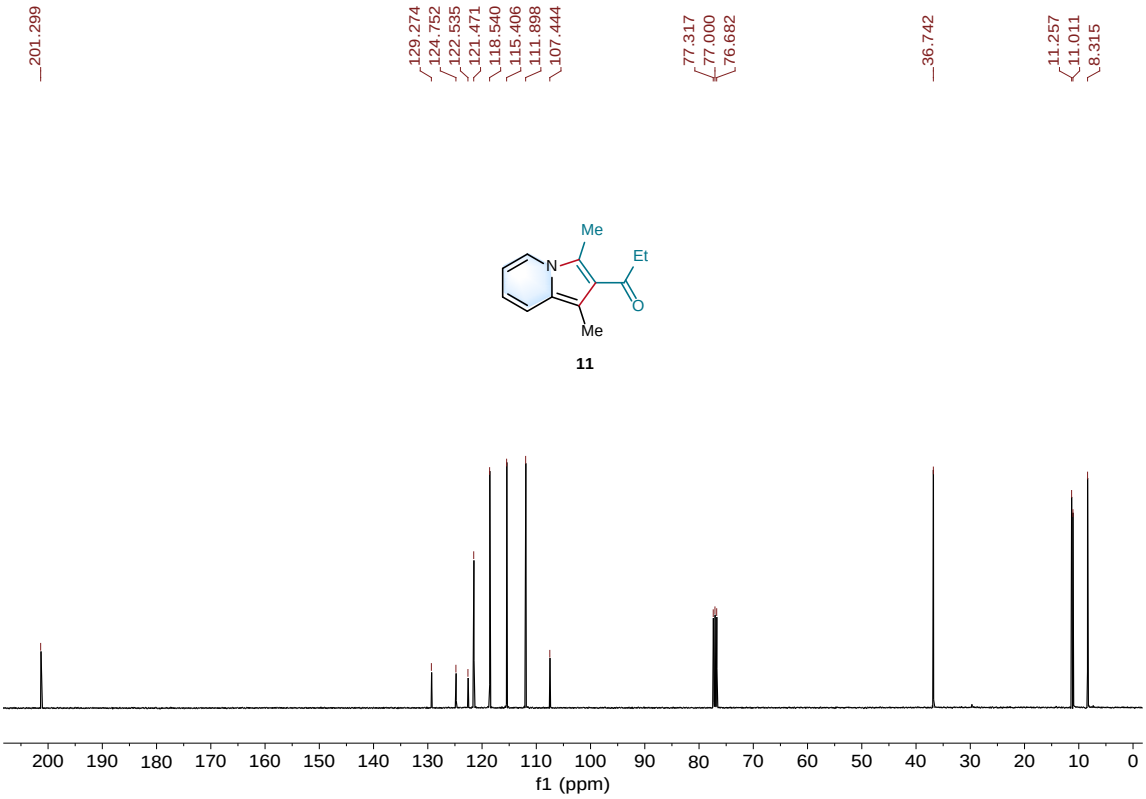
^{13}C NMR spectra of 10 (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 11 (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 11 (100 MHz, $CDCl_3$)



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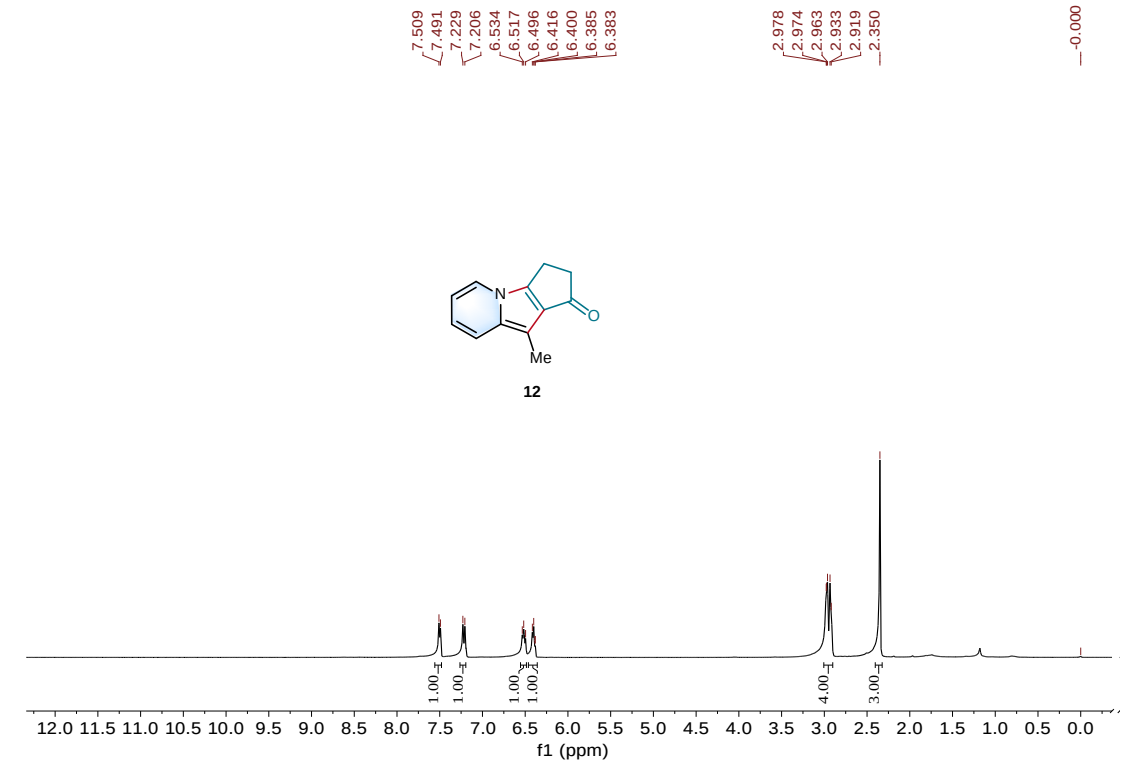
^{1}H NMR spectra of 12 (400 MHz, $CDCl_3$)



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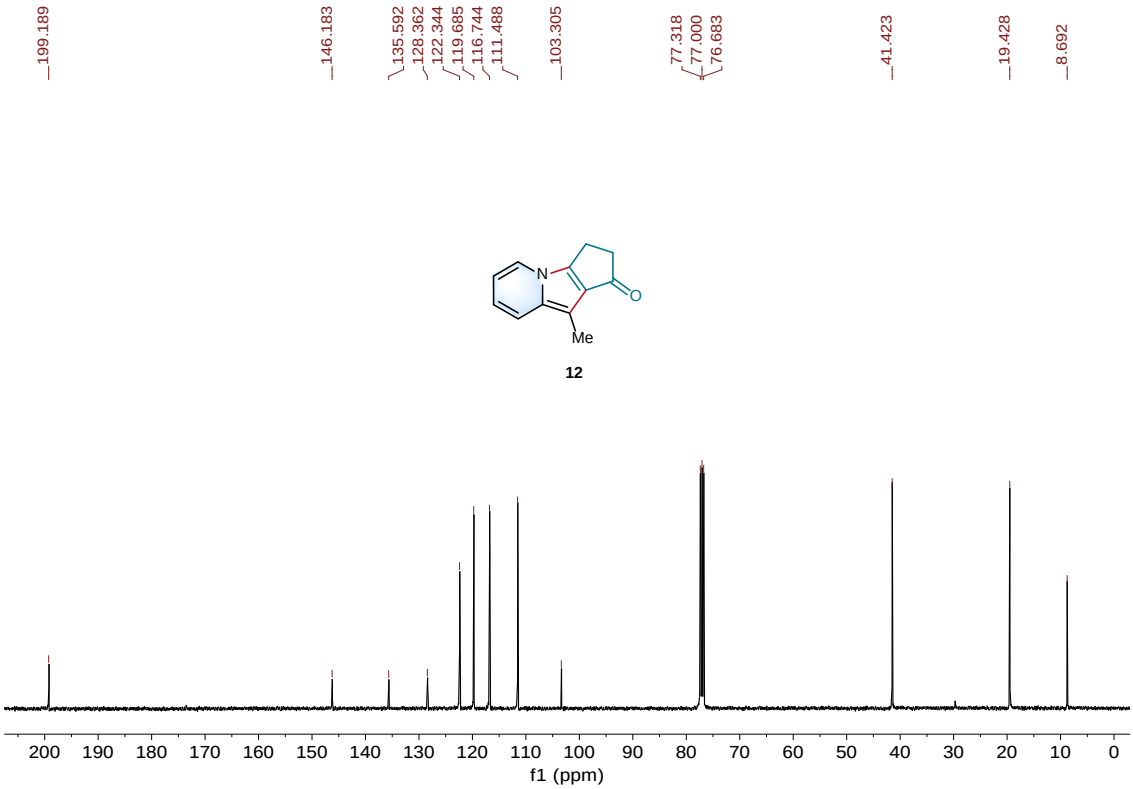
^{13}C NMR spectra of 12 (100 MHz, $CDCl_3$)



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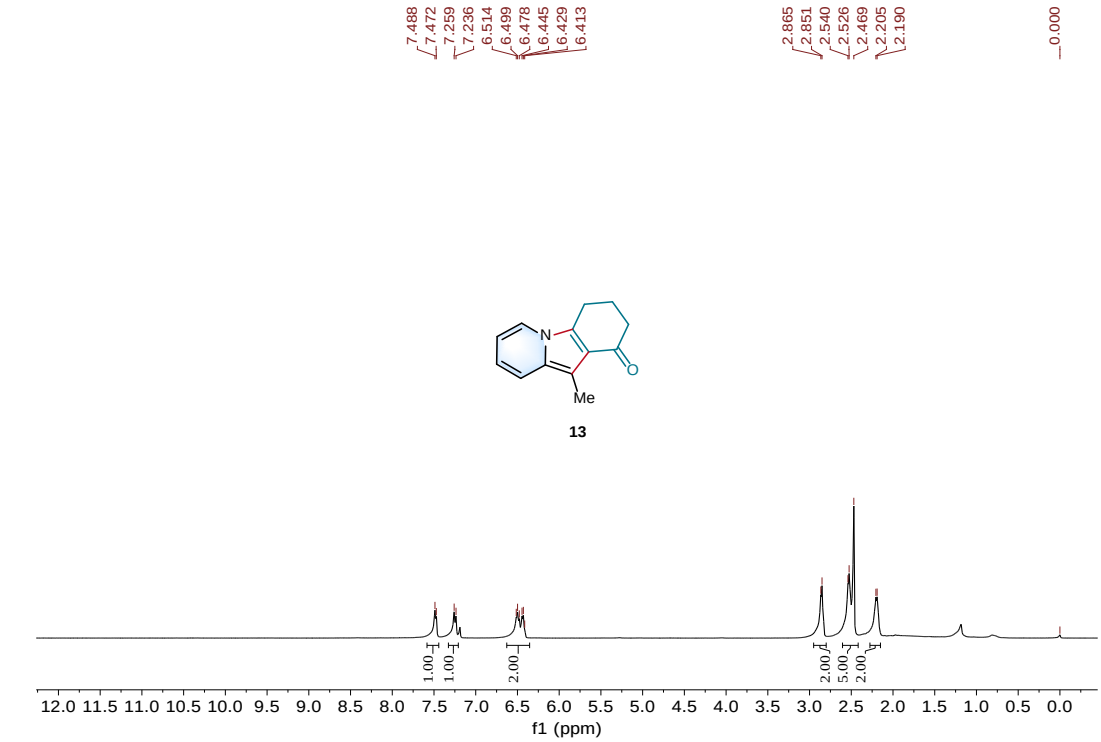

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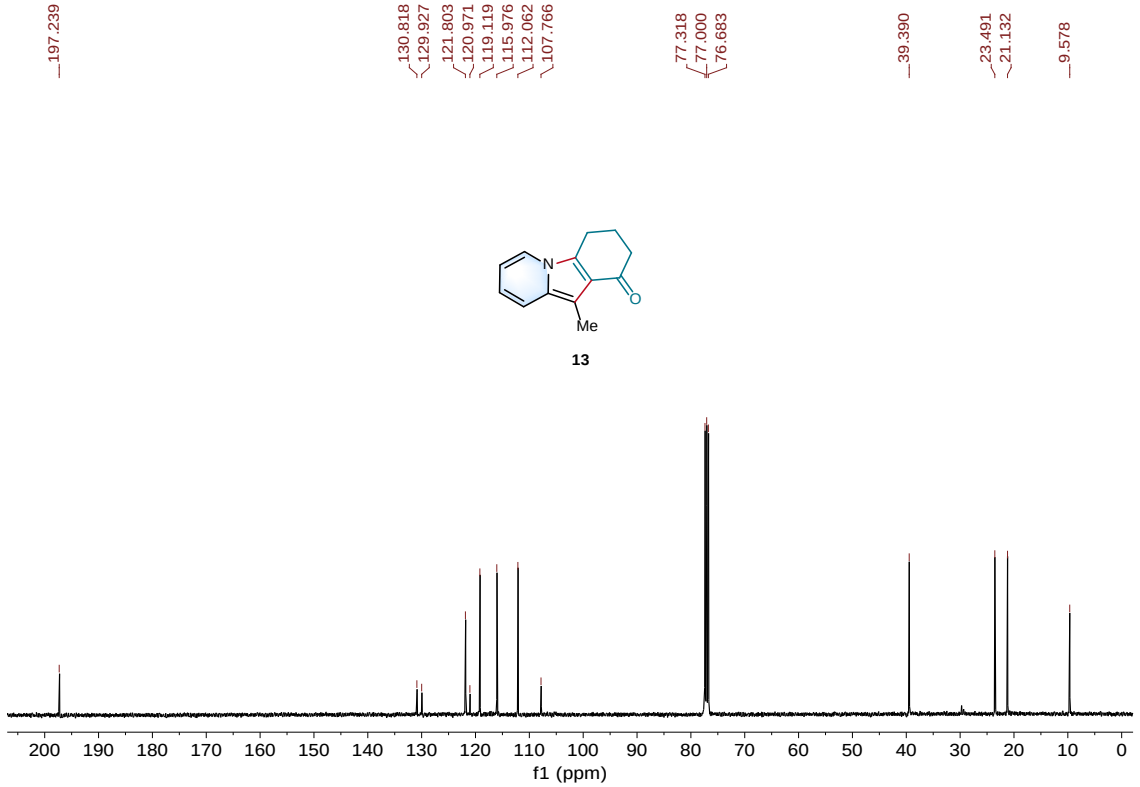

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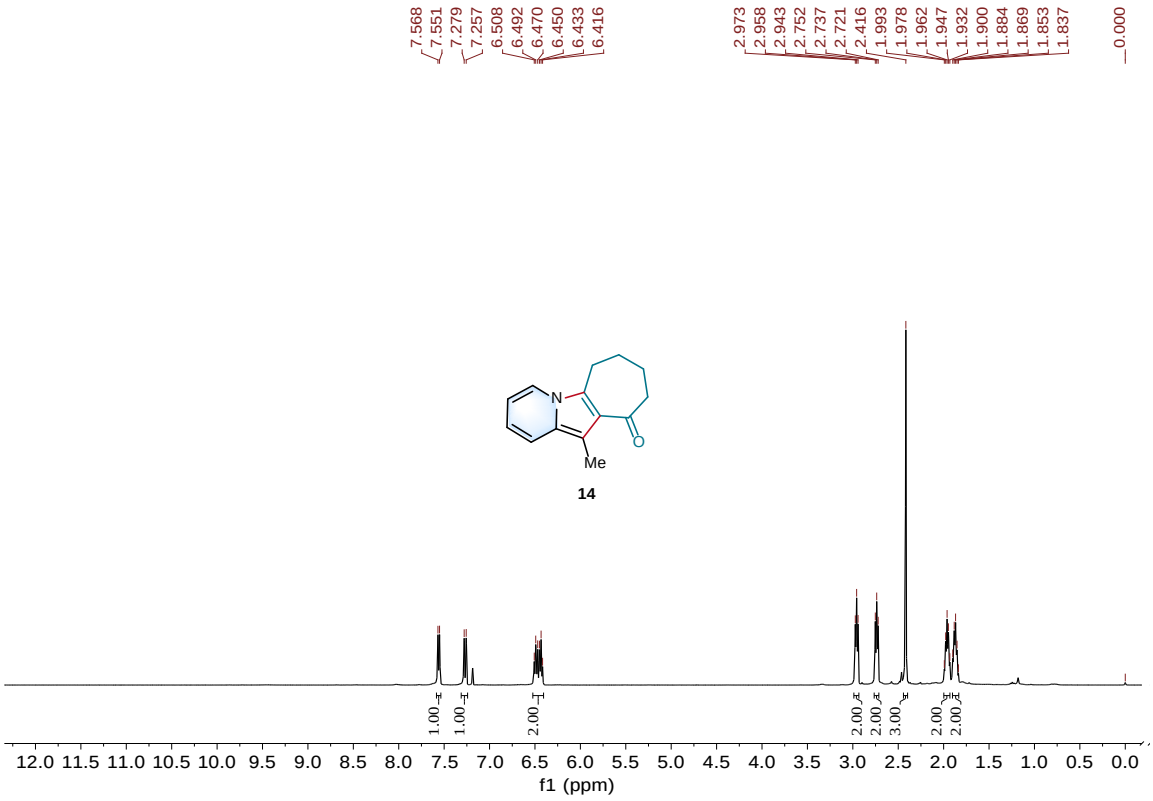
^{1}H NMR spectra of 14 (400 MHz, $CDCl_3$)



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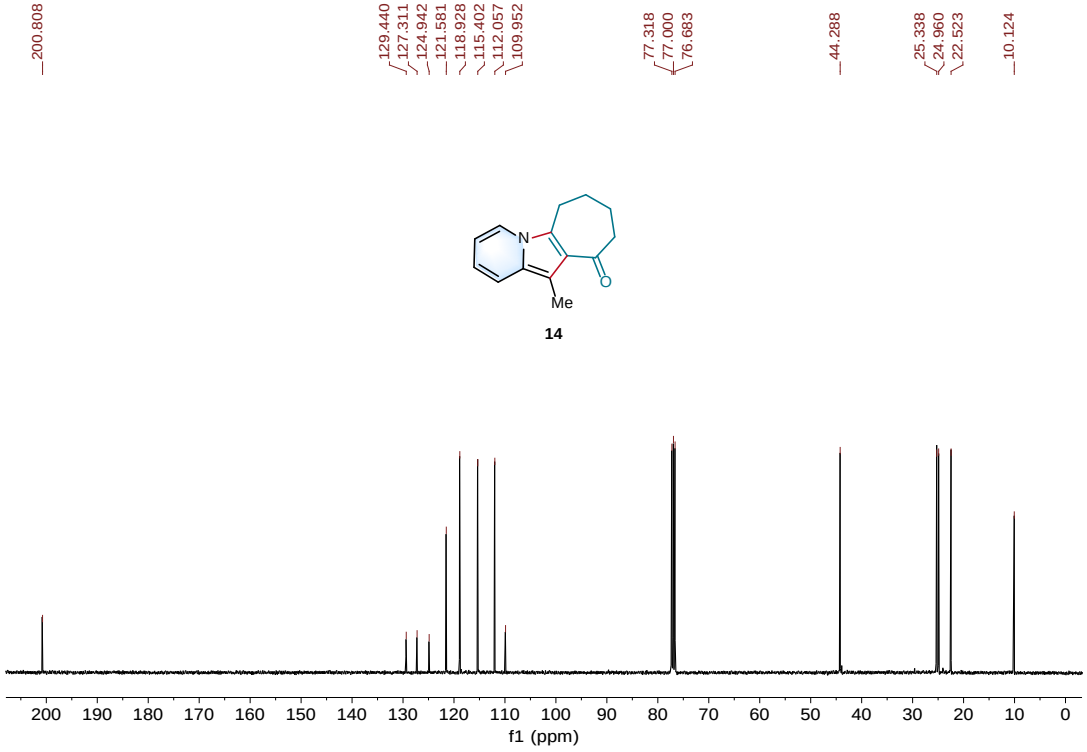
^{13}C NMR spectra of 14 (100 MHz, $CDCl_3$)



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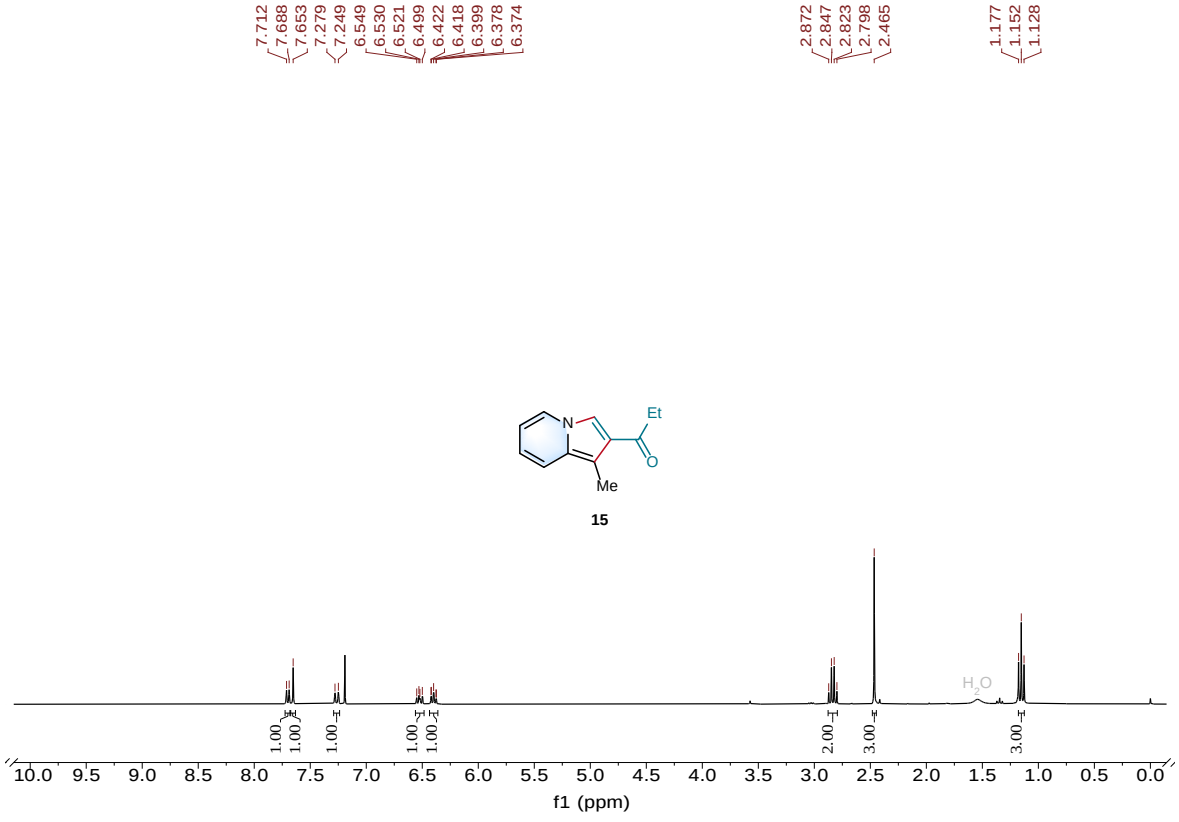

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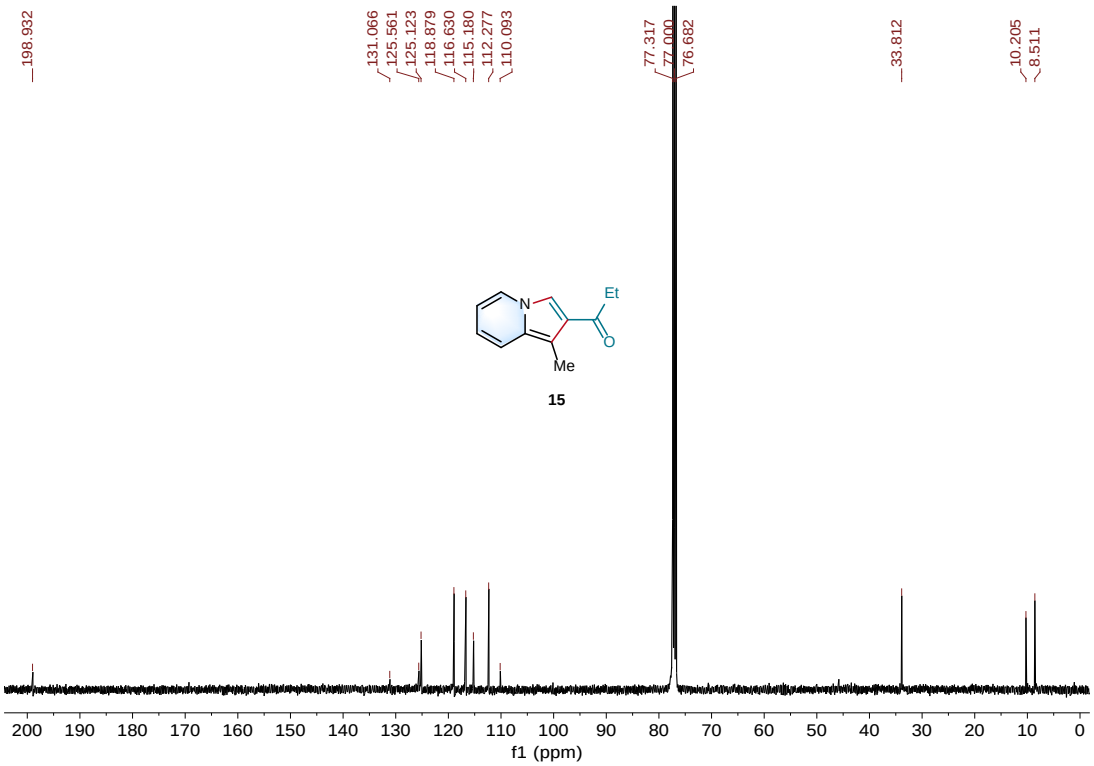

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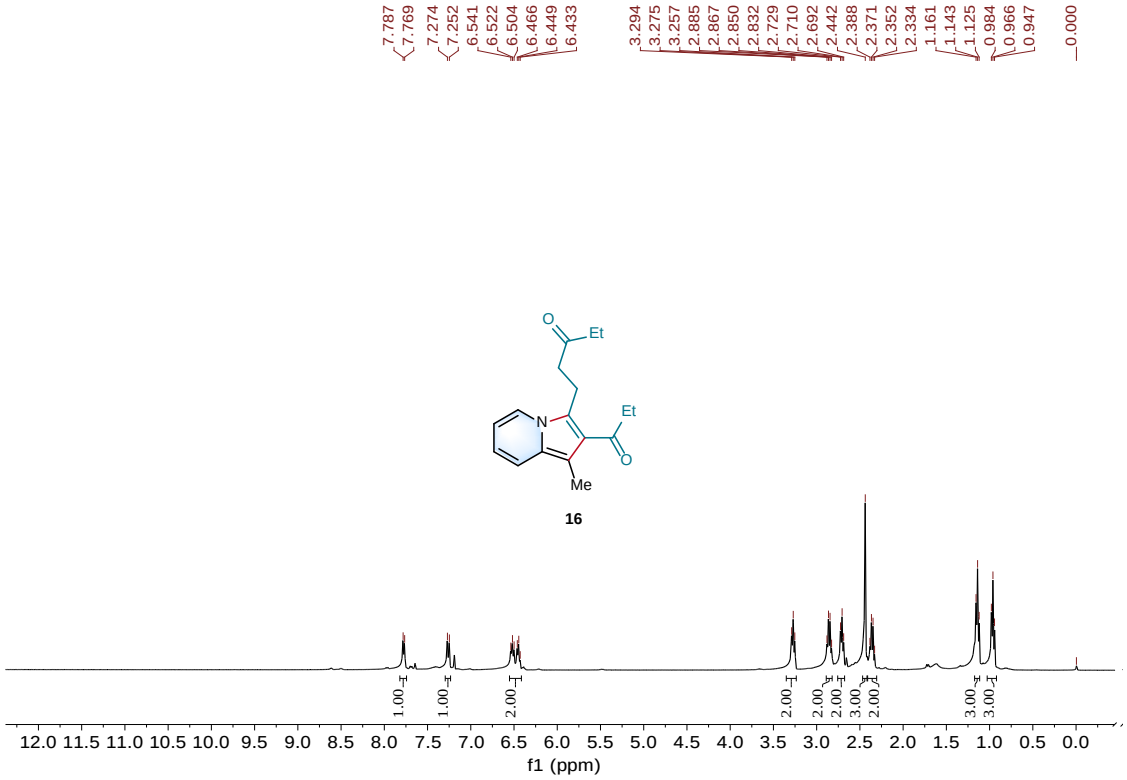

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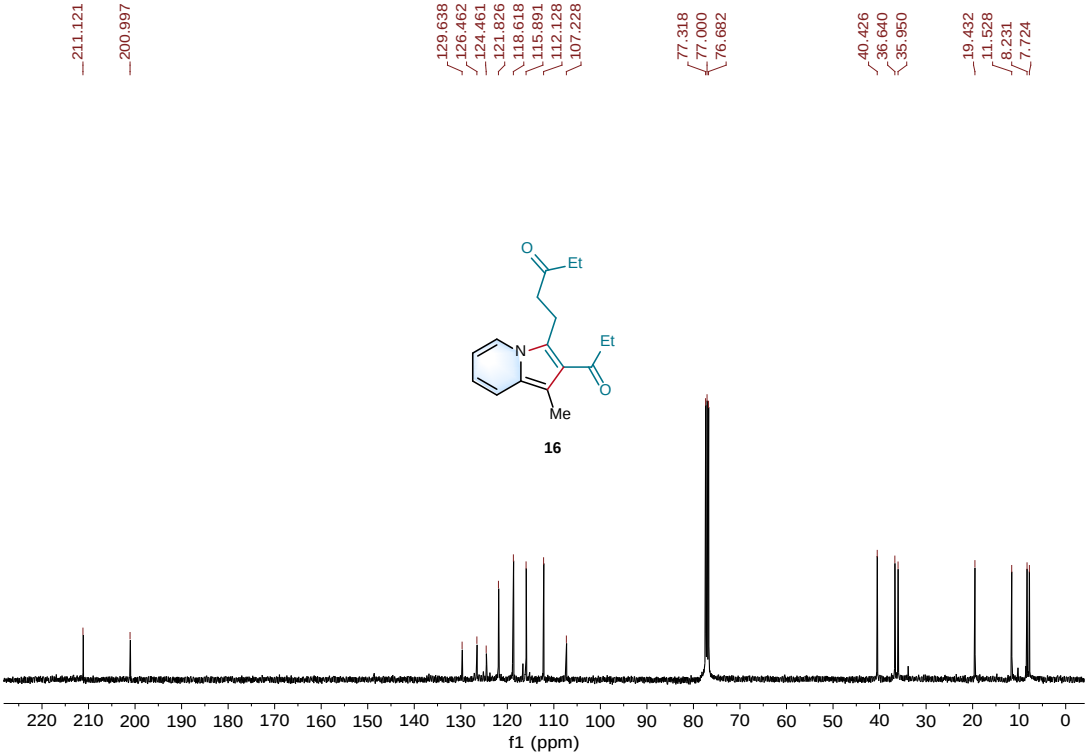

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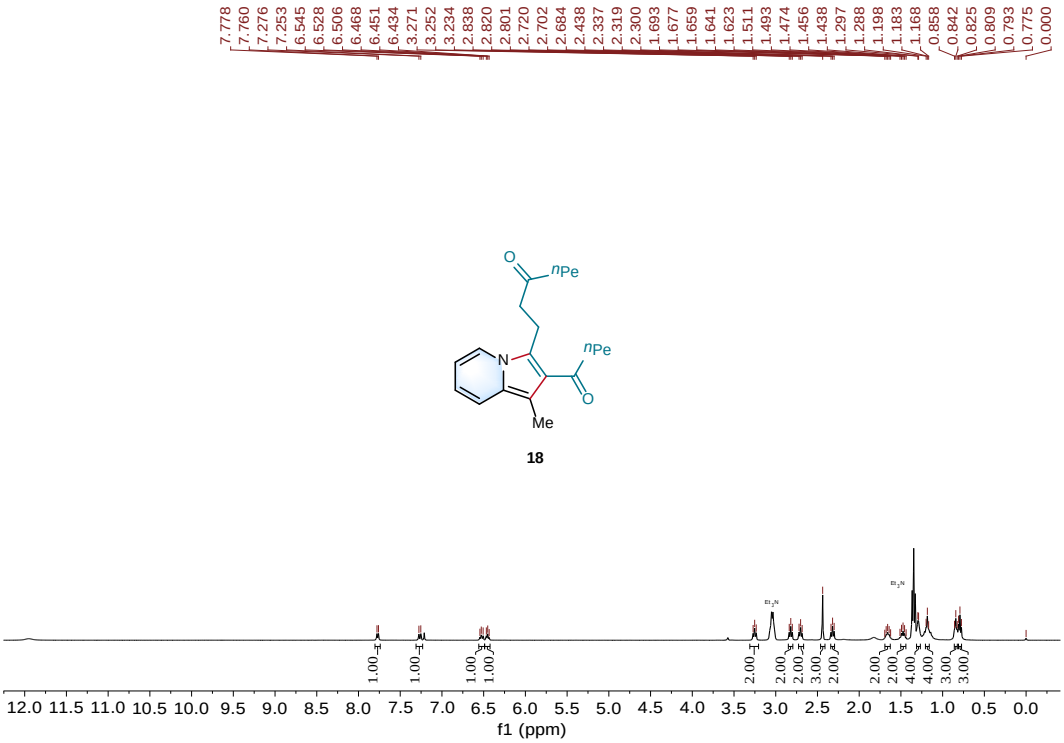
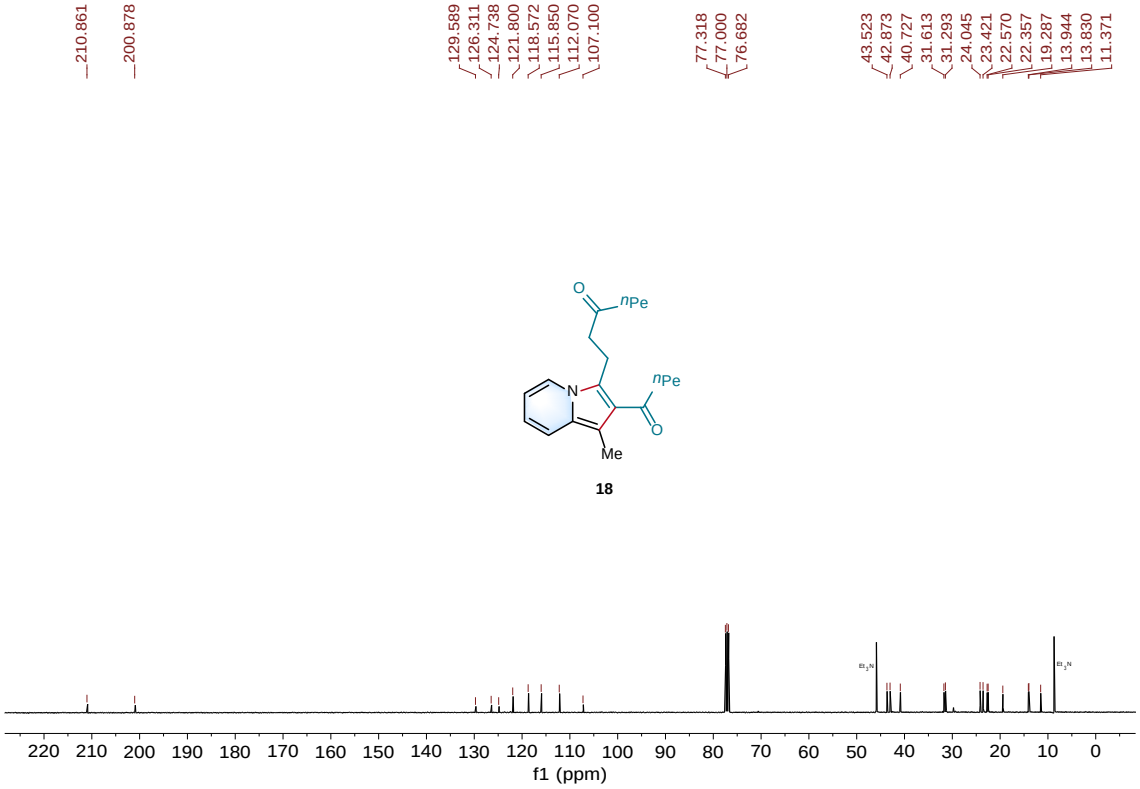
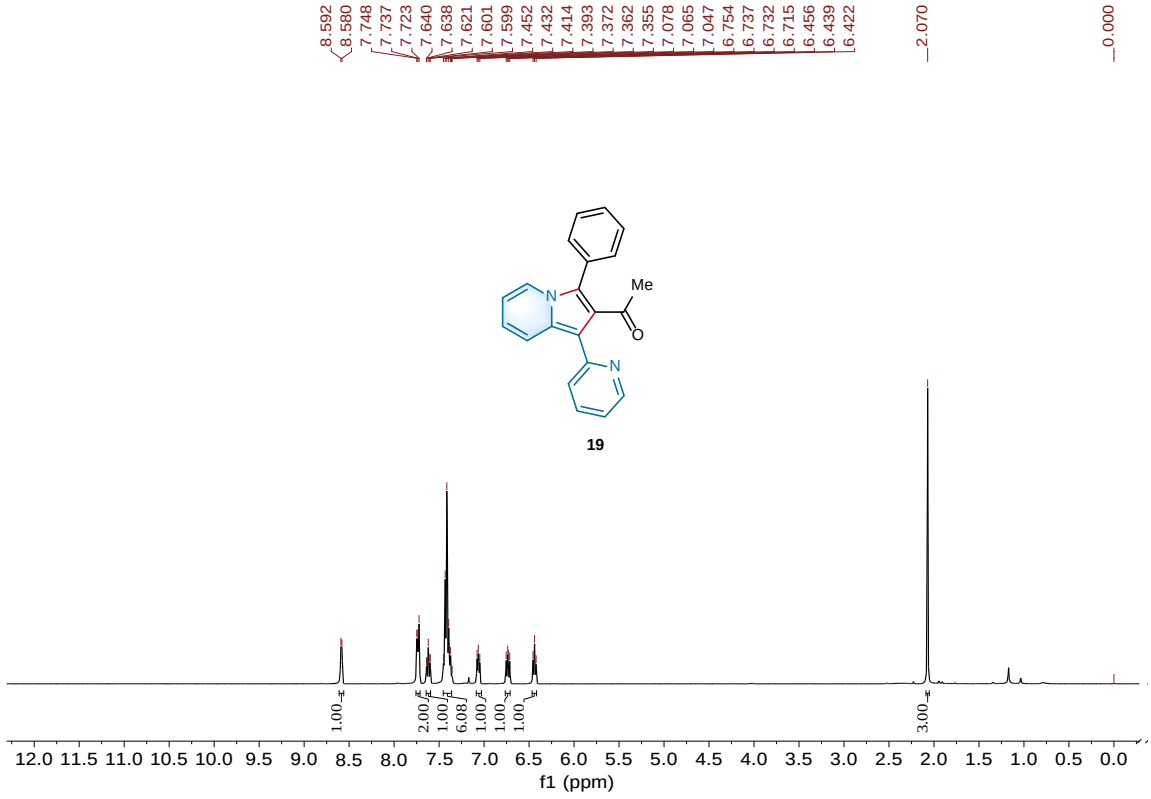


^{1}H NMR spectra of 18 (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 19 (400 MHz, $CDCl_3$)



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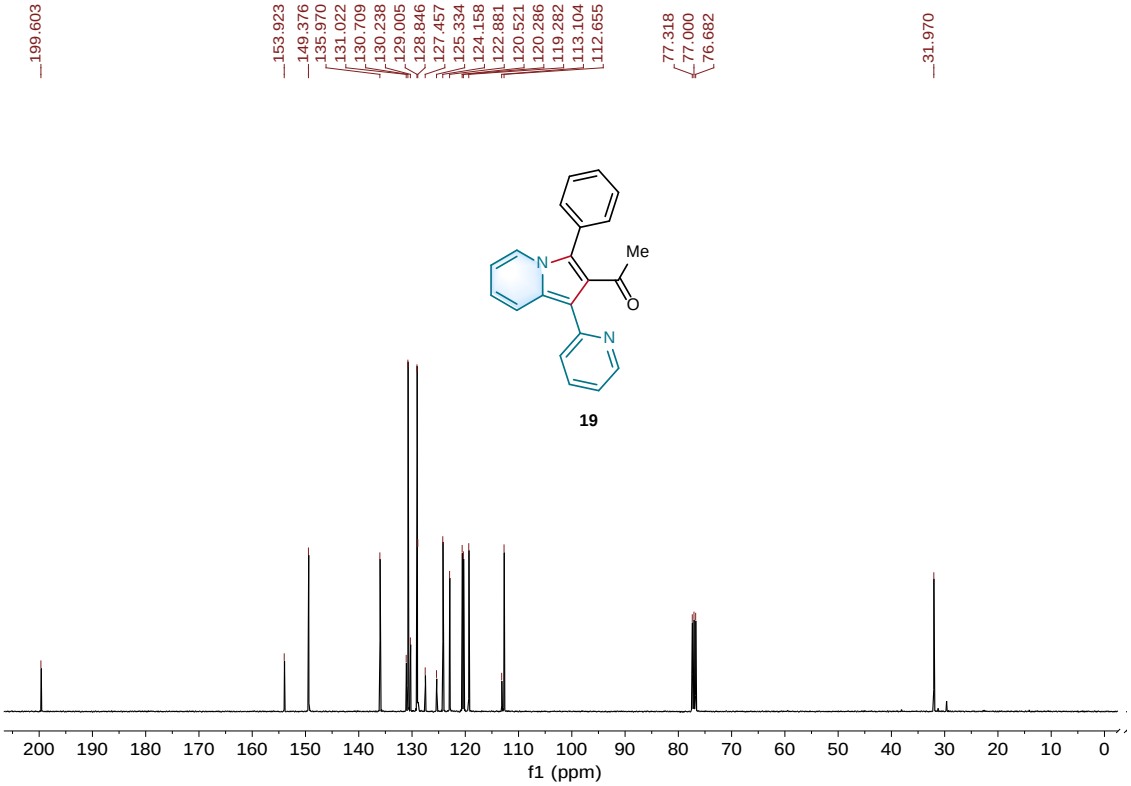
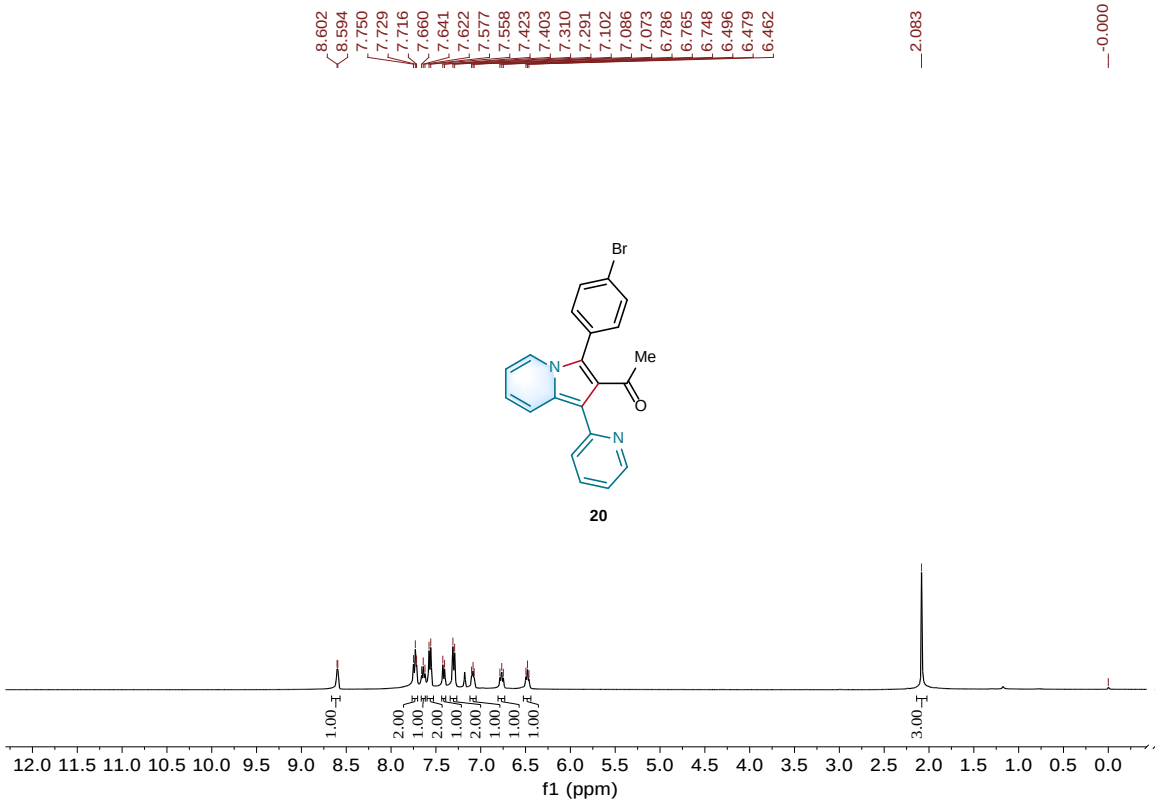


^{1}H NMR spectra of 20 (400 MHz, $CDCl_3$)



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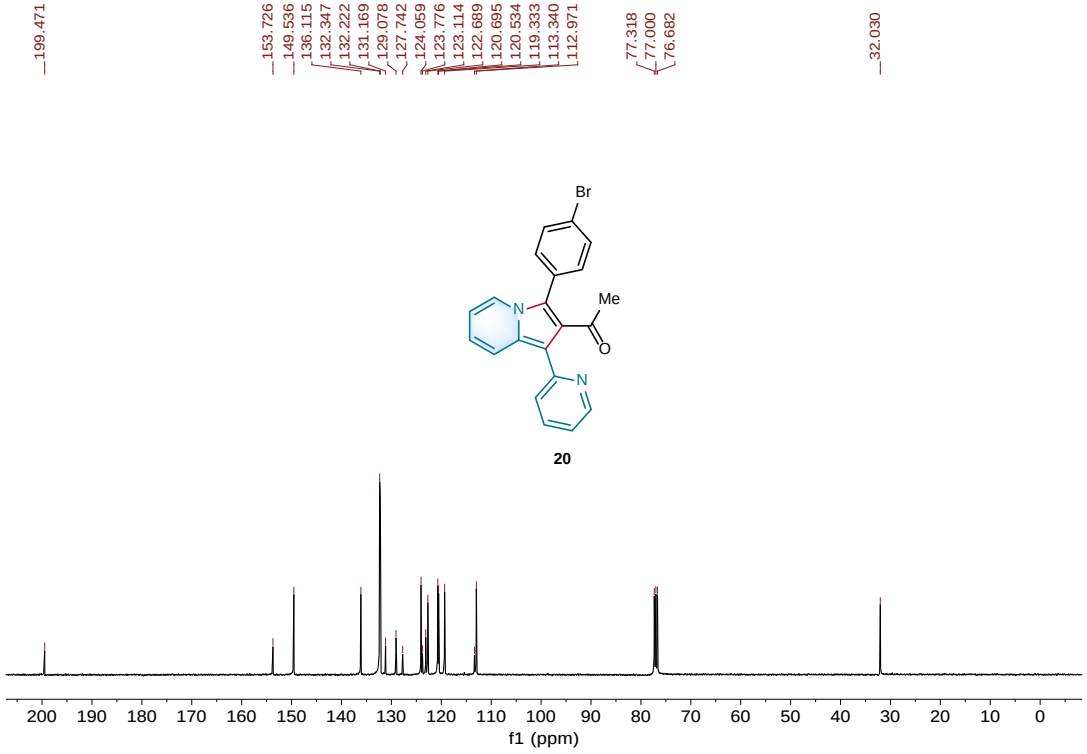

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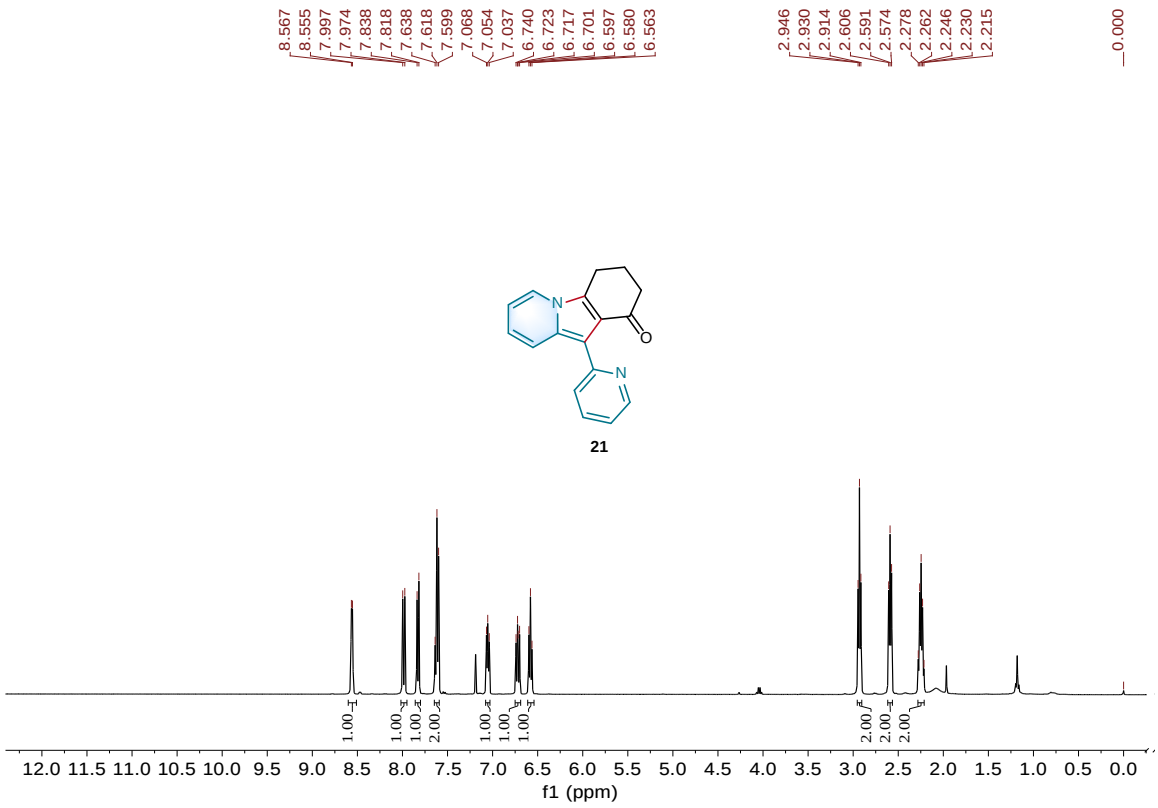

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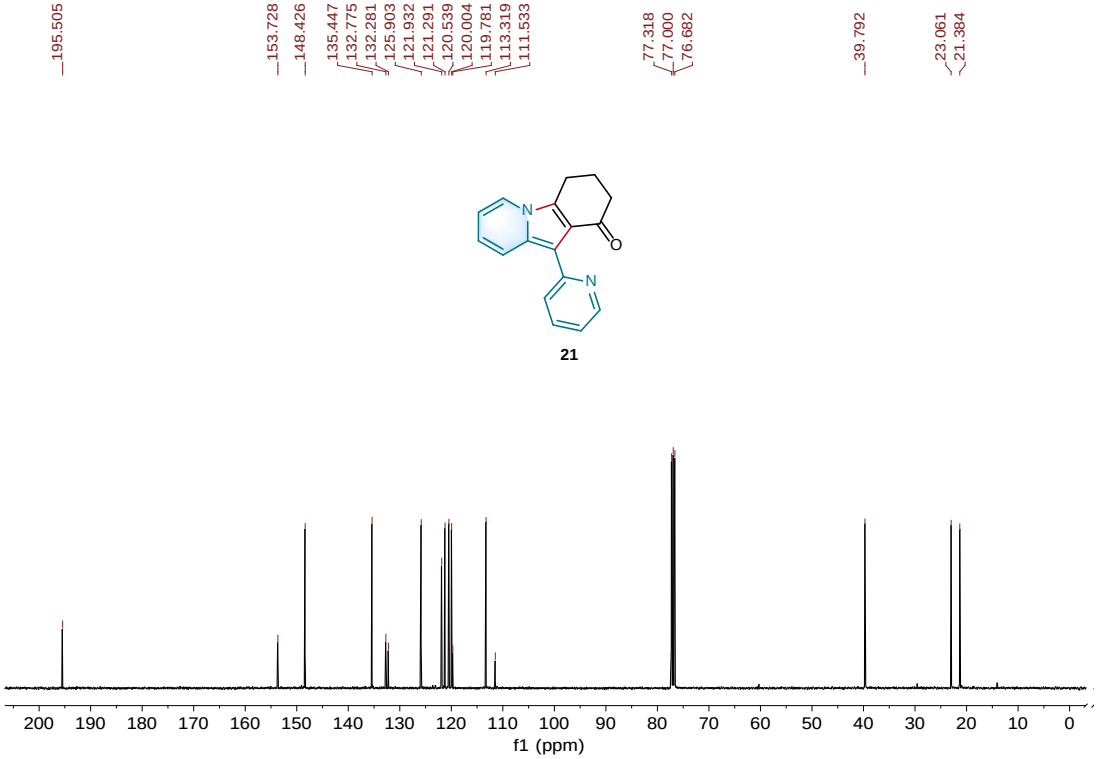

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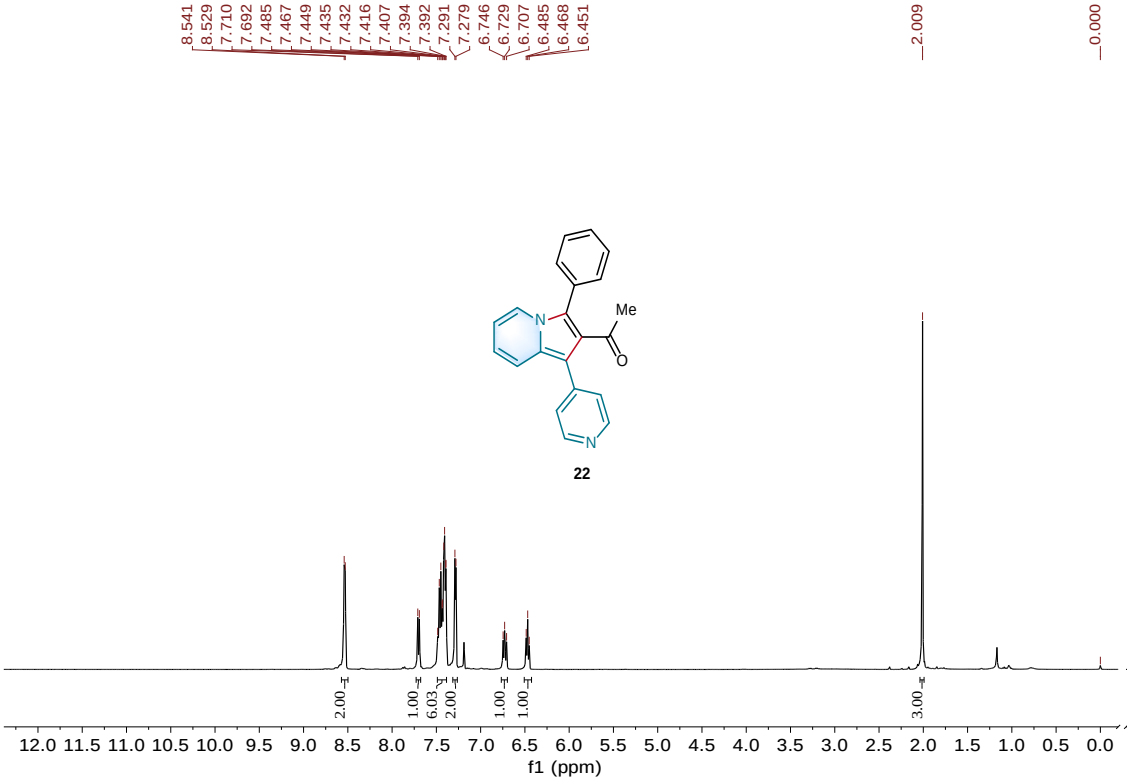

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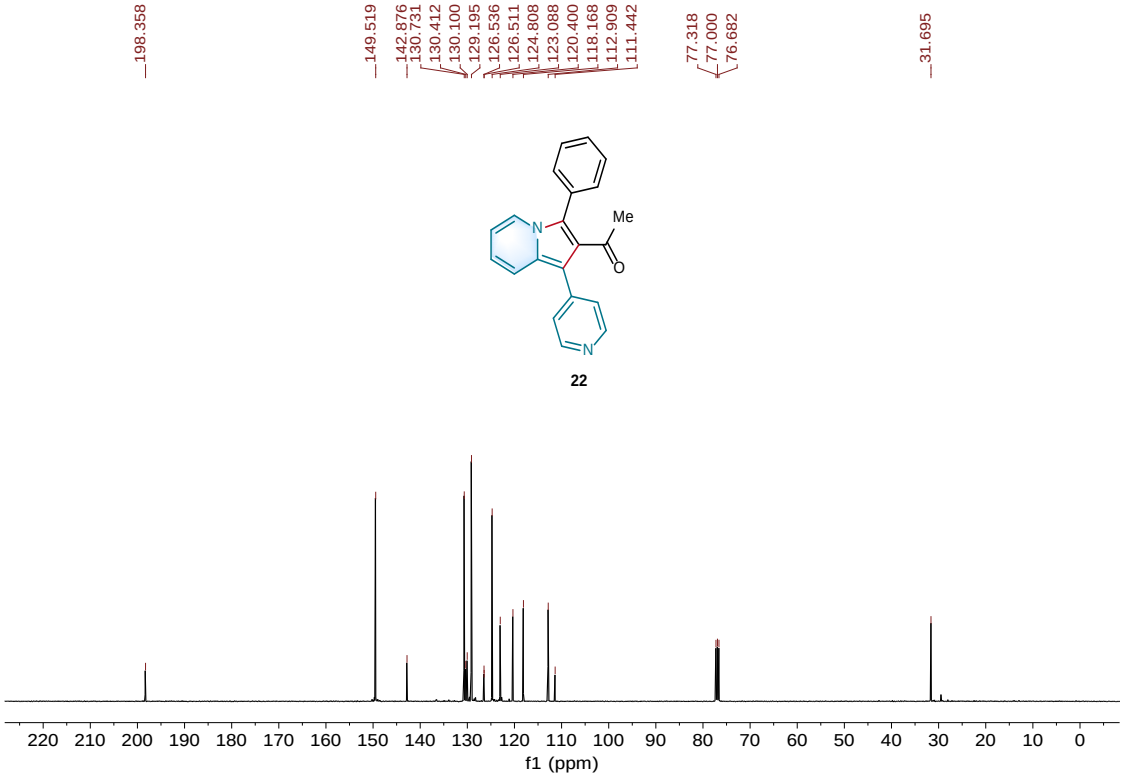
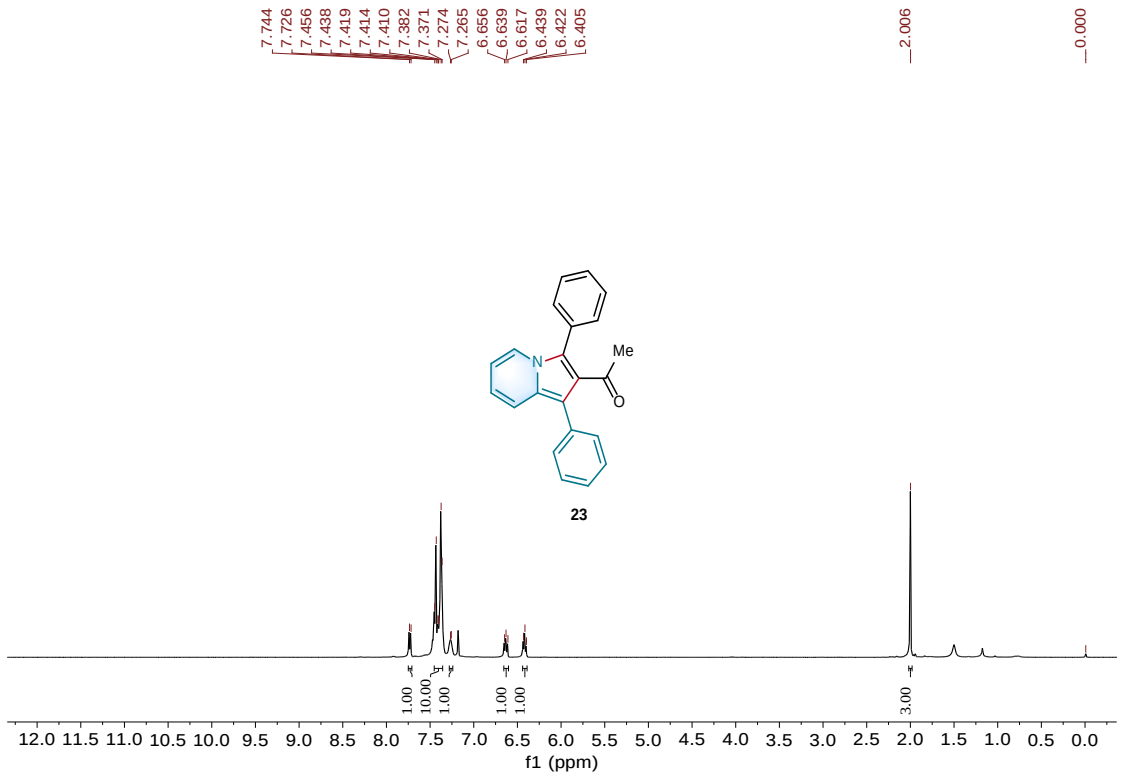
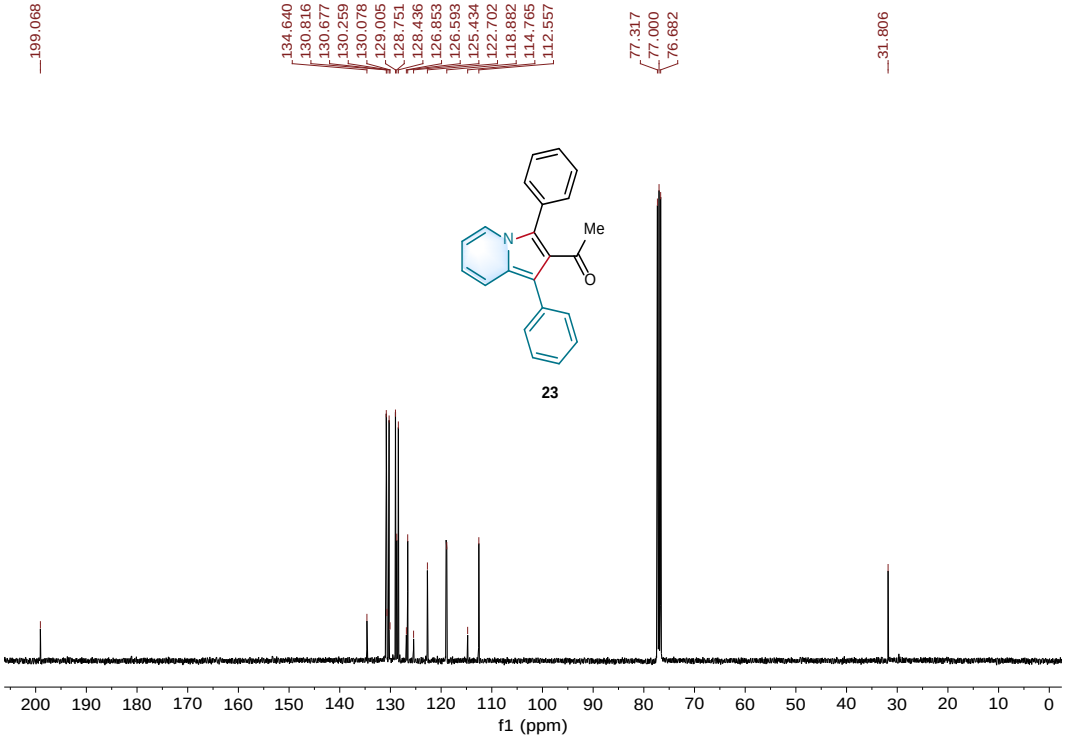


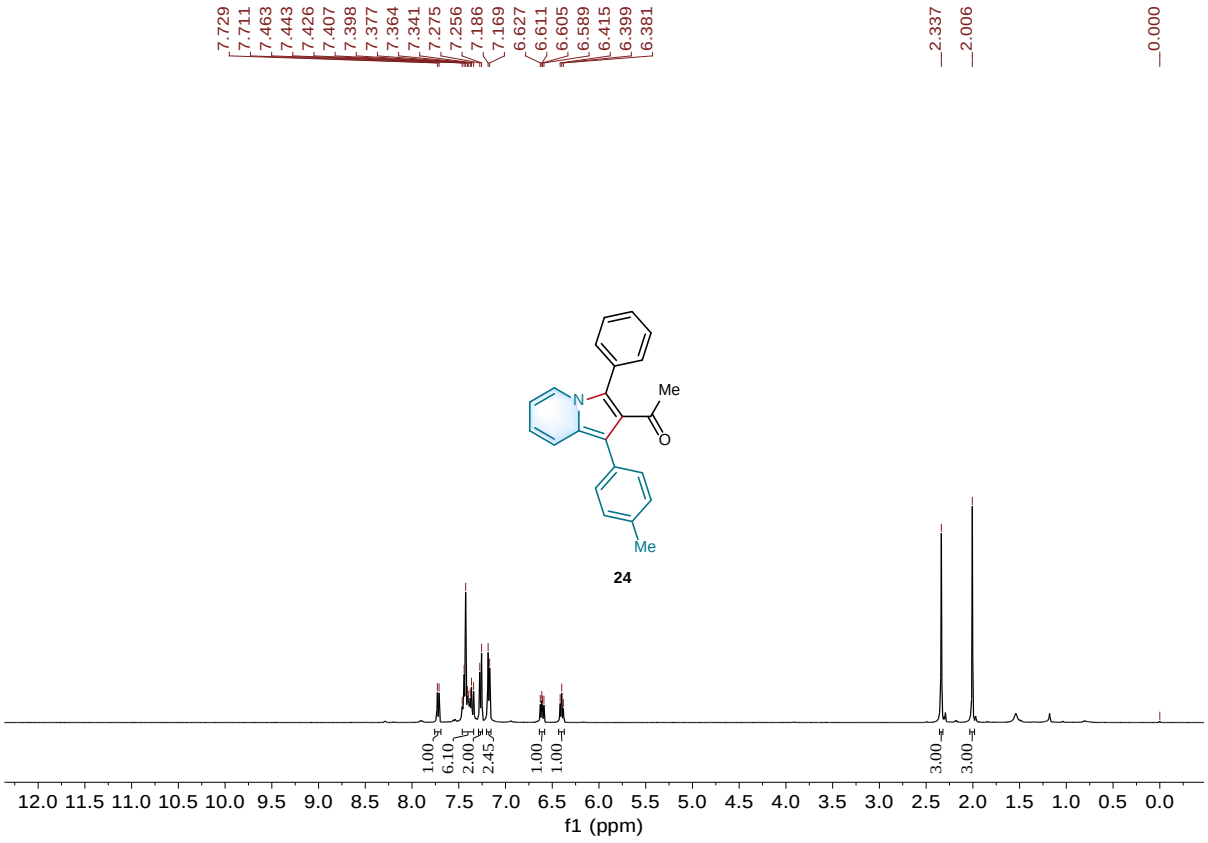
^{1}H NMR spectra of 23 (400 MHz, $CDCl_3$)



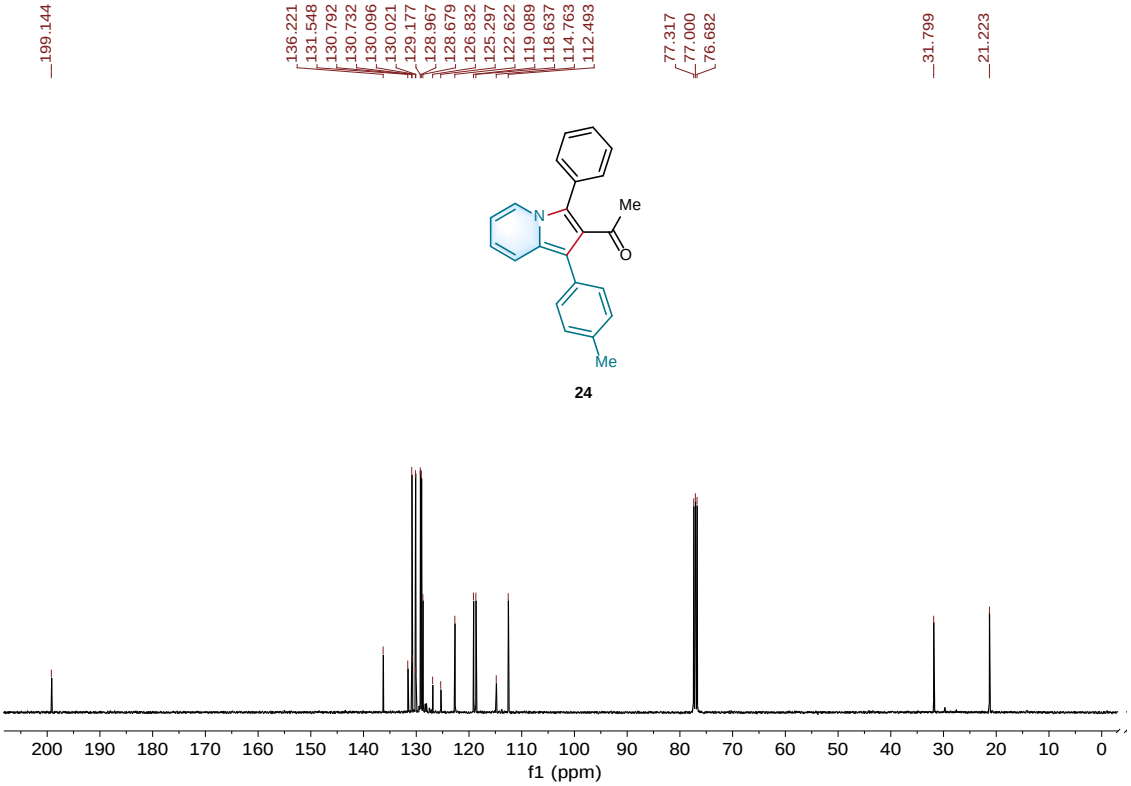
^{13}C NMR spectra of 23 (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 24 (400 MHz, $CDCl_3$)

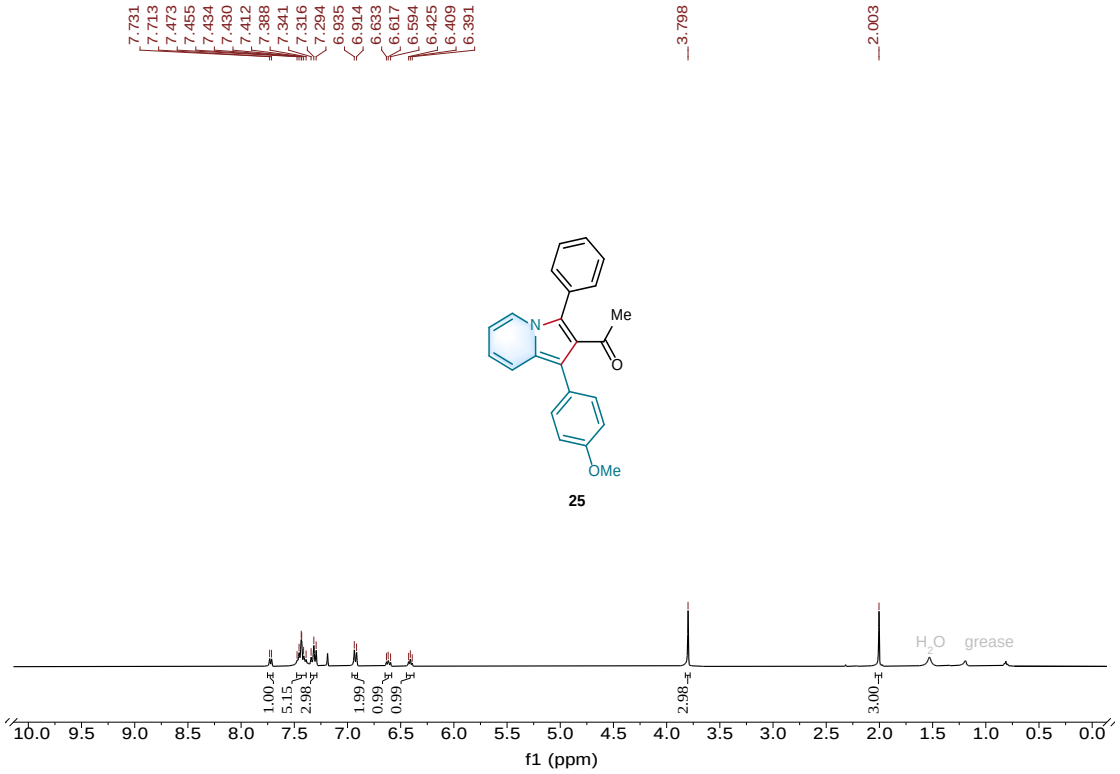


^{13}C NMR spectra of 24 (100 MHz, $CDCl_3$)



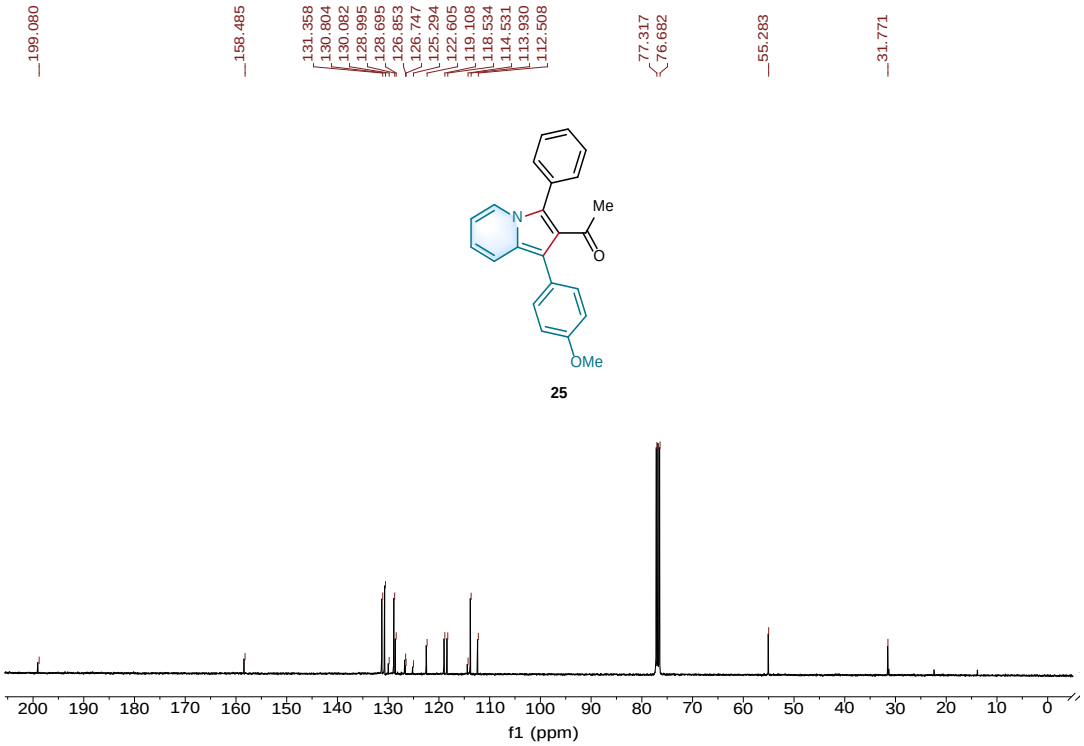
24

^{1}H NMR spectra of 25 (400 MHz, $CDCl_3$)



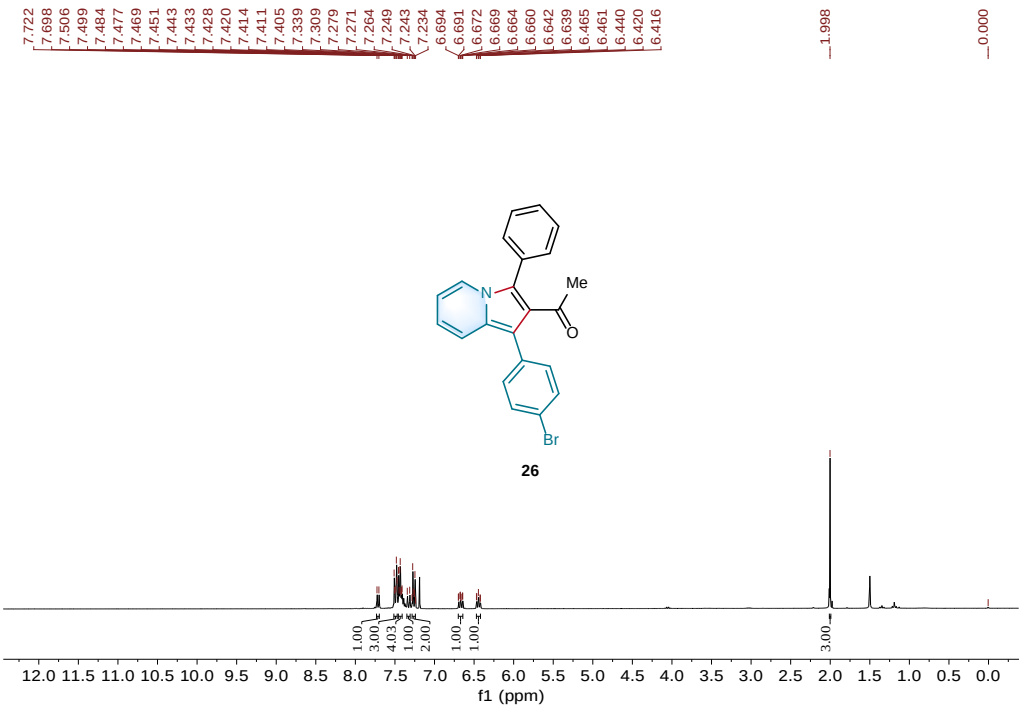
25

^{13}C NMR spectra of 25 (100 MHz, $CDCl_3$)



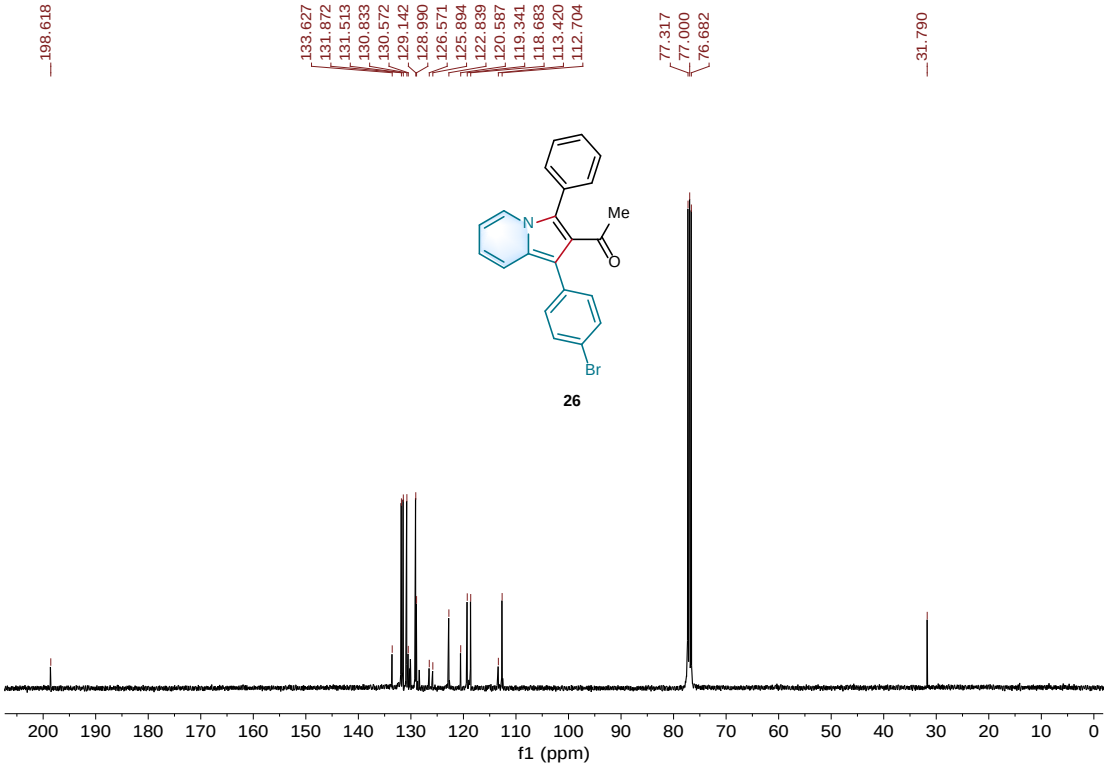
25

^{1}H NMR spectra of 26 (400 MHz, $CDCl_3$)

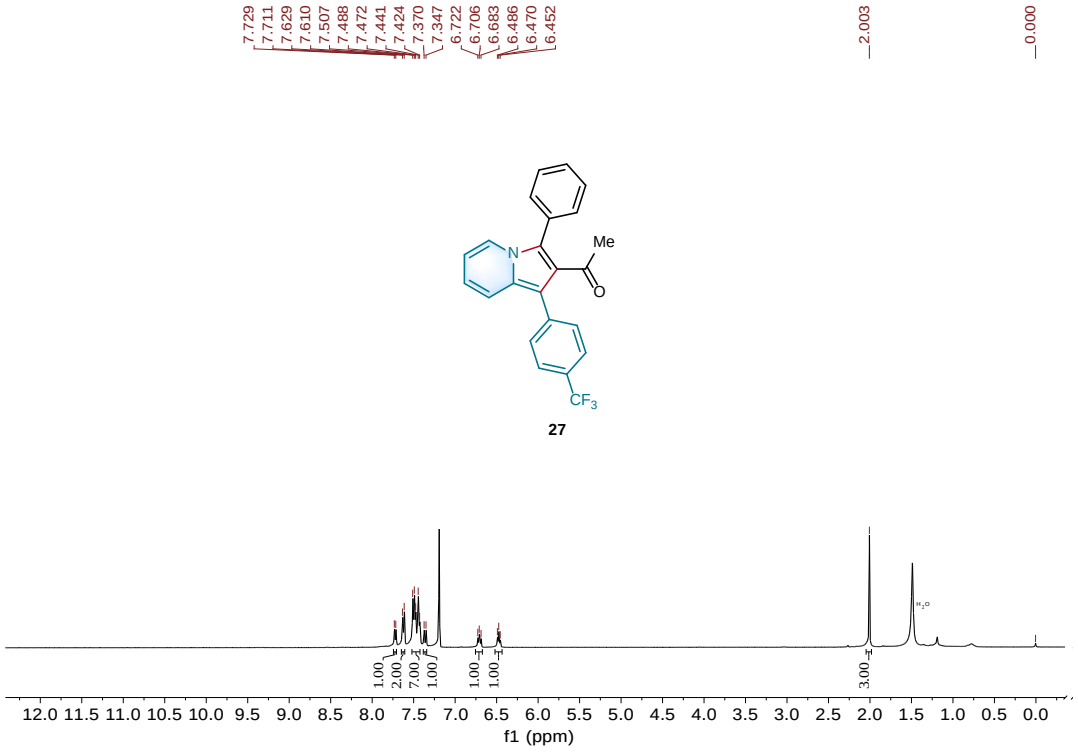


26

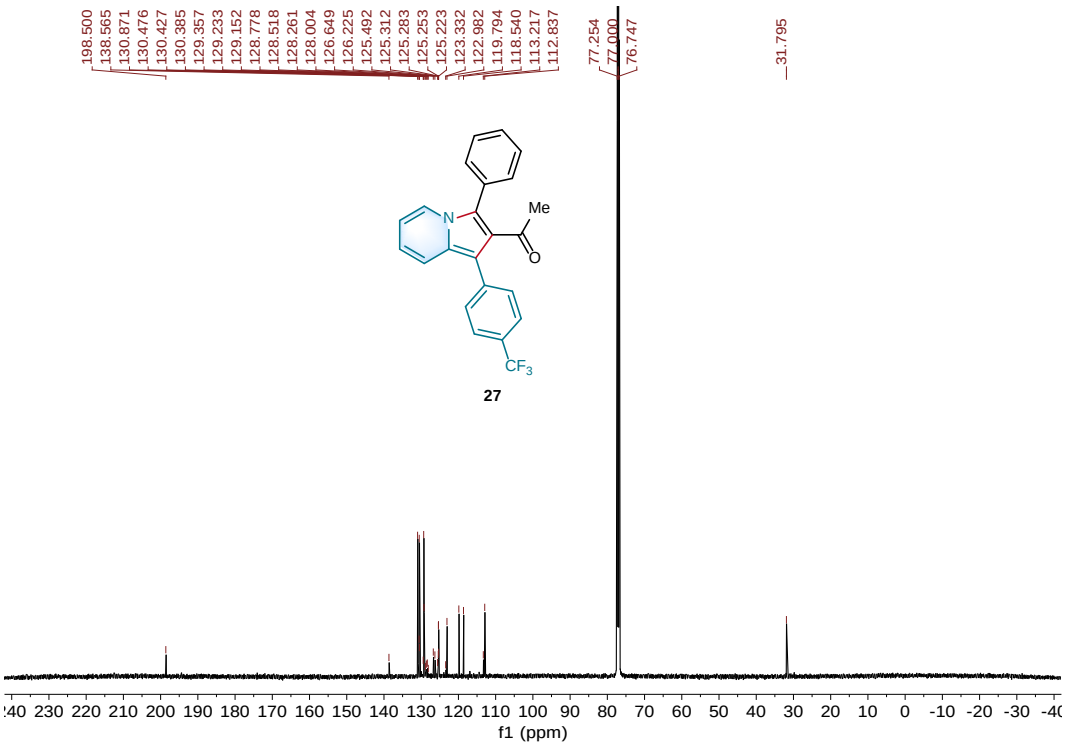
^{13}C NMR spectra of 26 (100 MHz, $CDCl_3$)



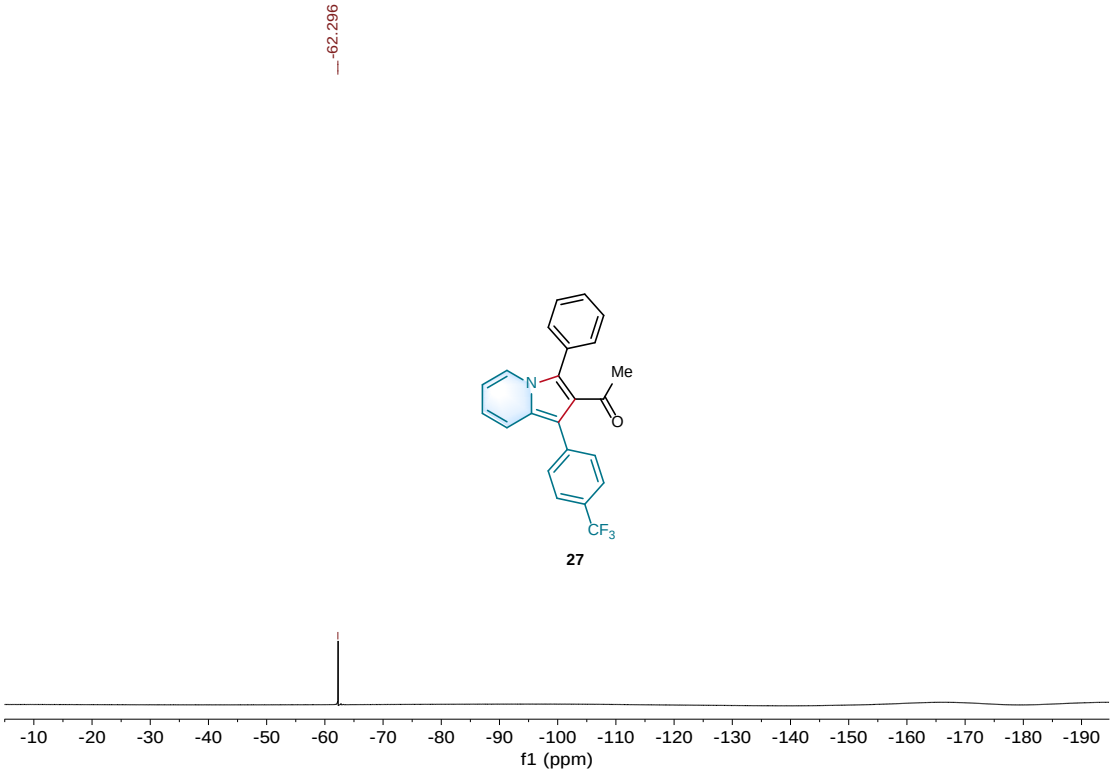
^{1}H NMR spectra of 27 (400 MHz, $CDCl_3$)



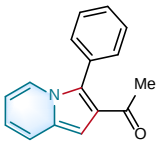
^{13}C NMR spectra of 27 (126 MHz, $CDCl_3$)



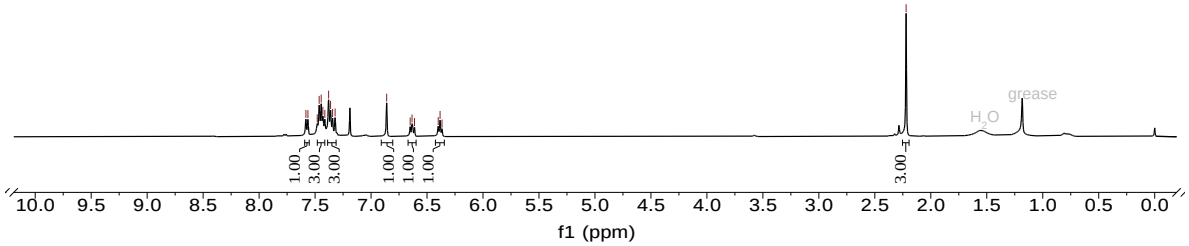
^{19}F NMR spectra of 27 (377 MHz, $CDCl_3$)



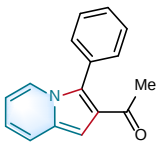
^{1}H NMR spectra of 28 (400 MHz, $CDCl_3$)



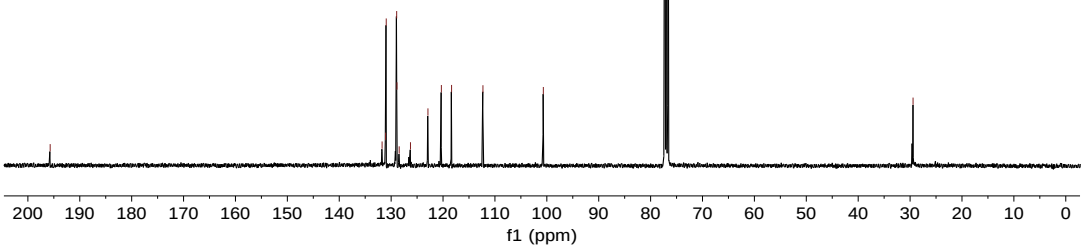
28



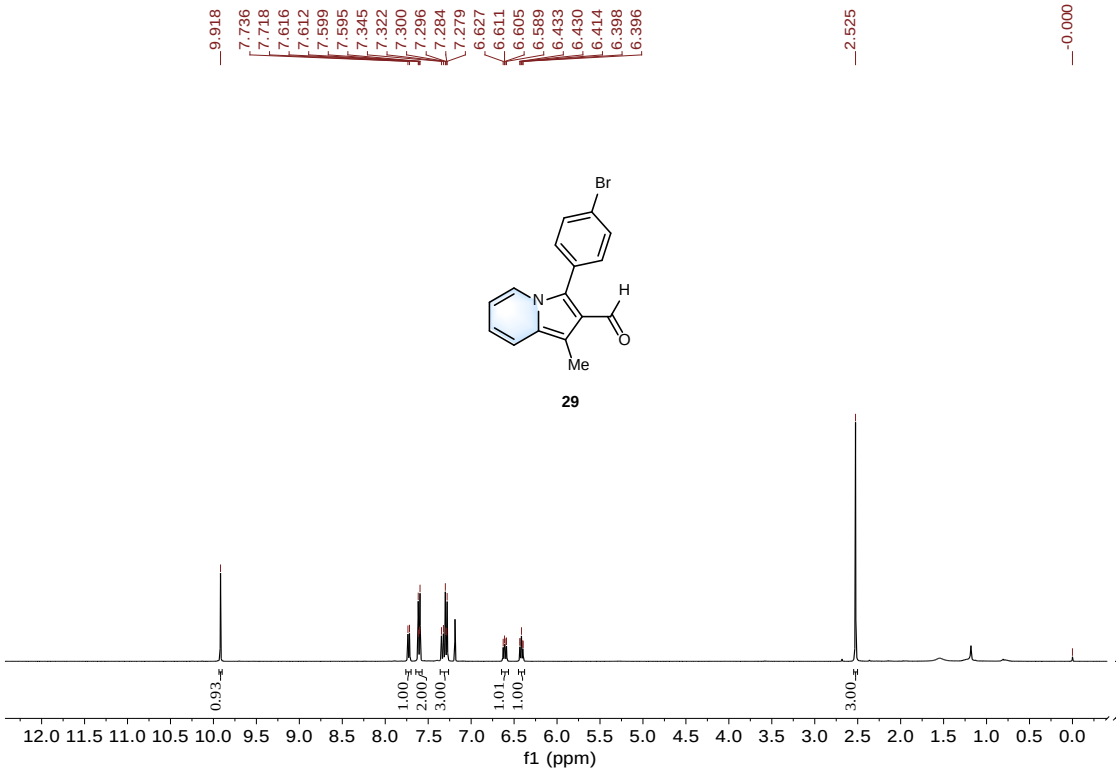
^{13}C NMR spectra of 28 (100 MHz, $CDCl_3$)



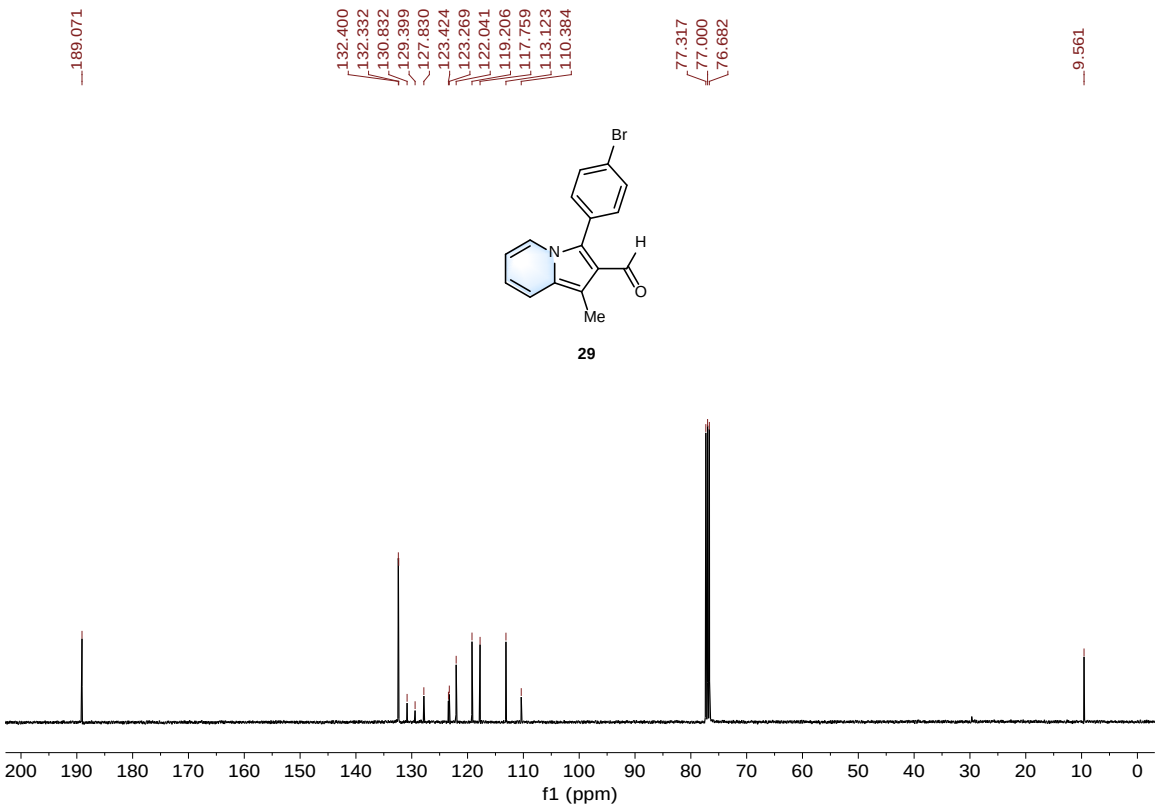
28



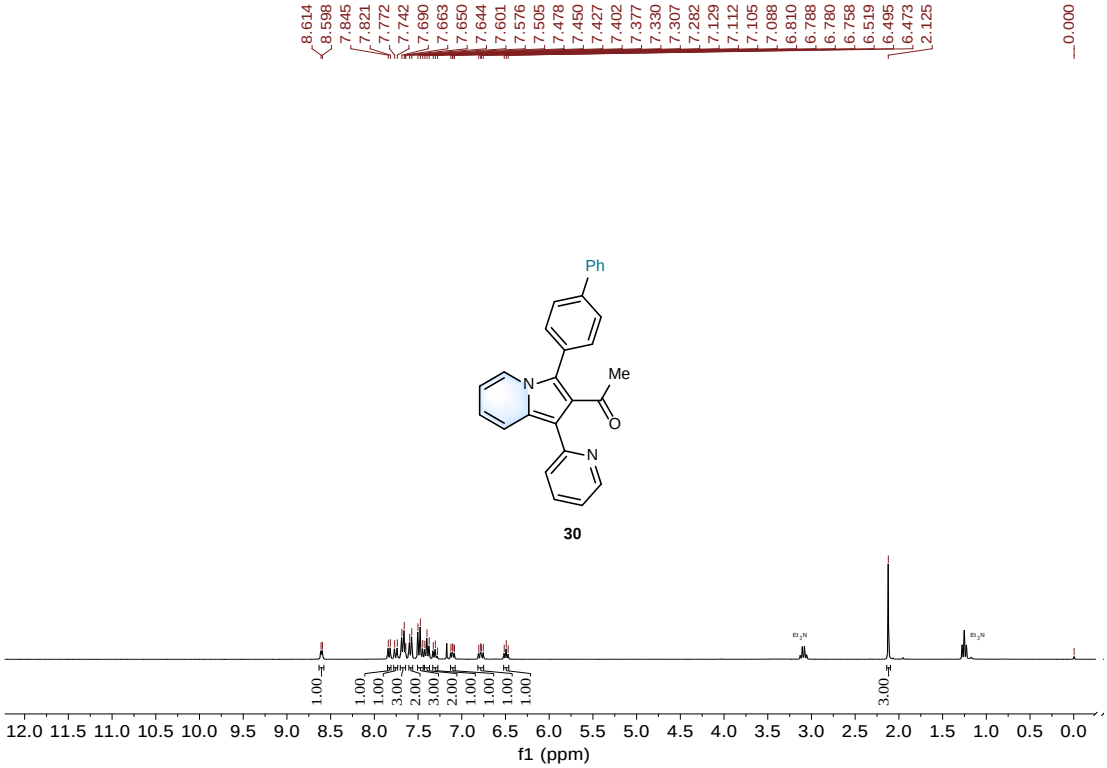
^{1}H NMR spectra of 29 (400 MHz, $CDCl_3$)



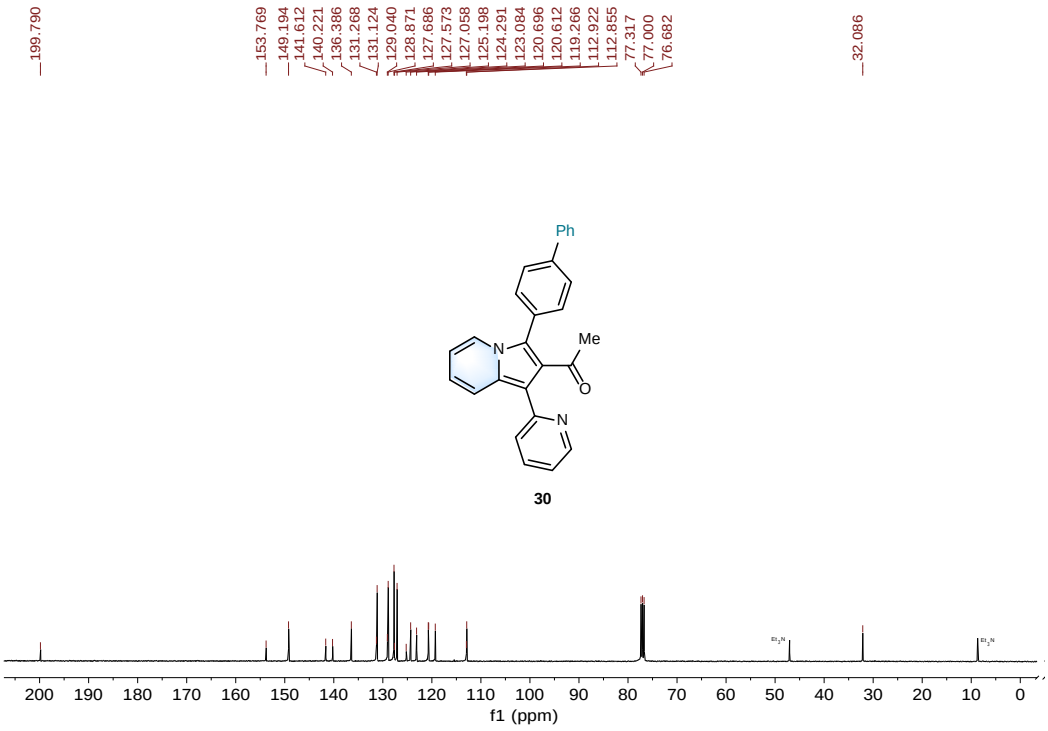
^{13}C NMR spectra of 29 (400 MHz, $CDCl_3$)



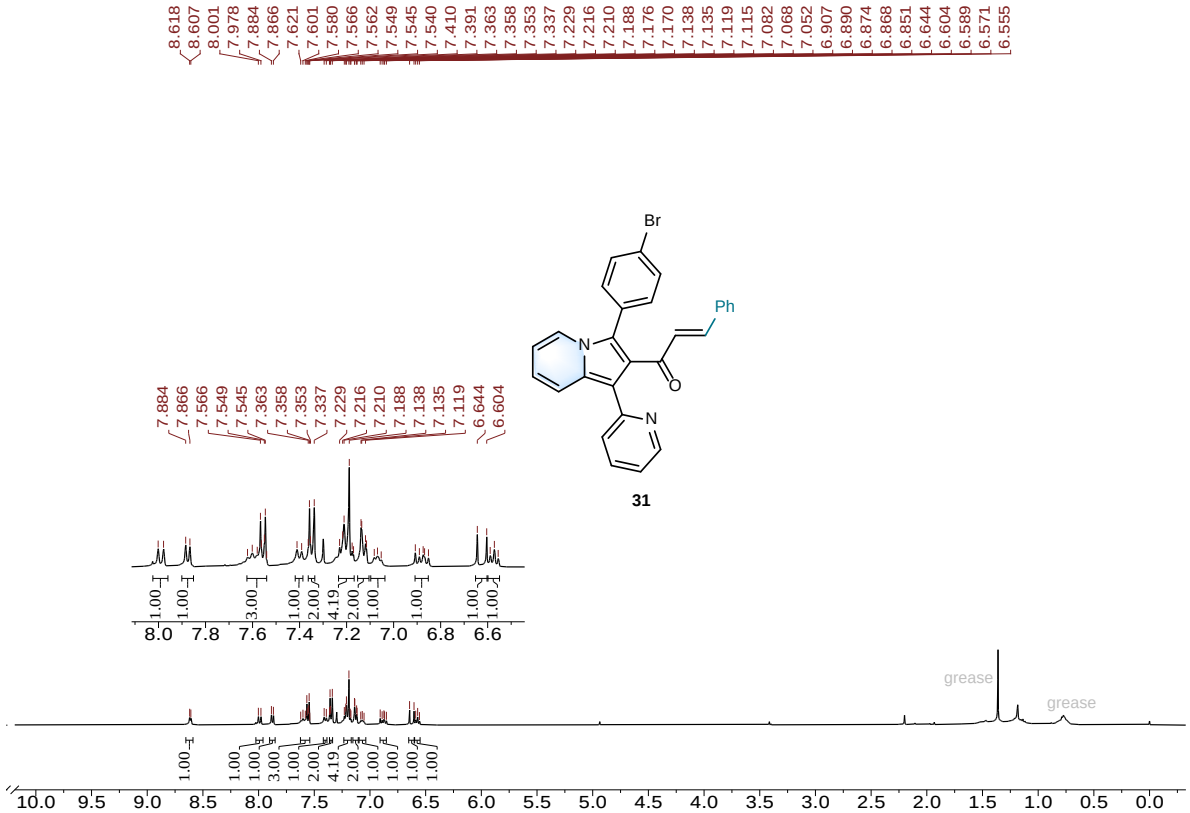
^{1}H NMR spectra of 30 (300 MHz, $CDCl_3$)



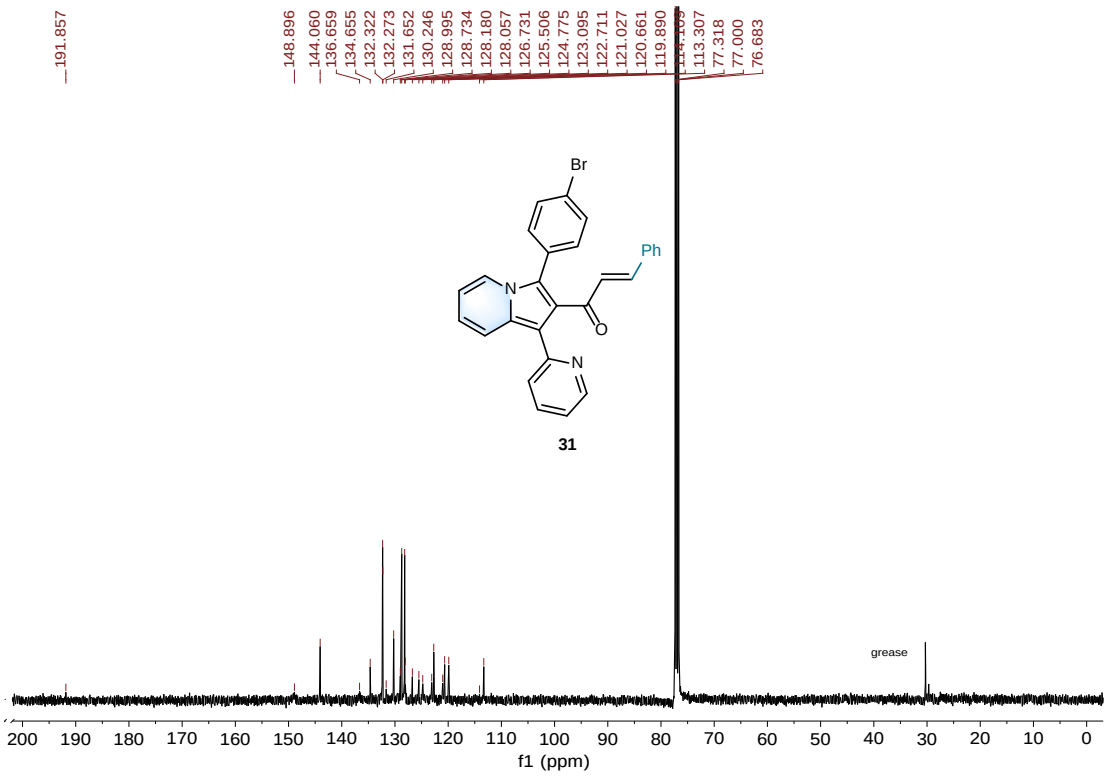
^{13}C NMR spectra of 30 (400 MHz, $CDCl_3$)



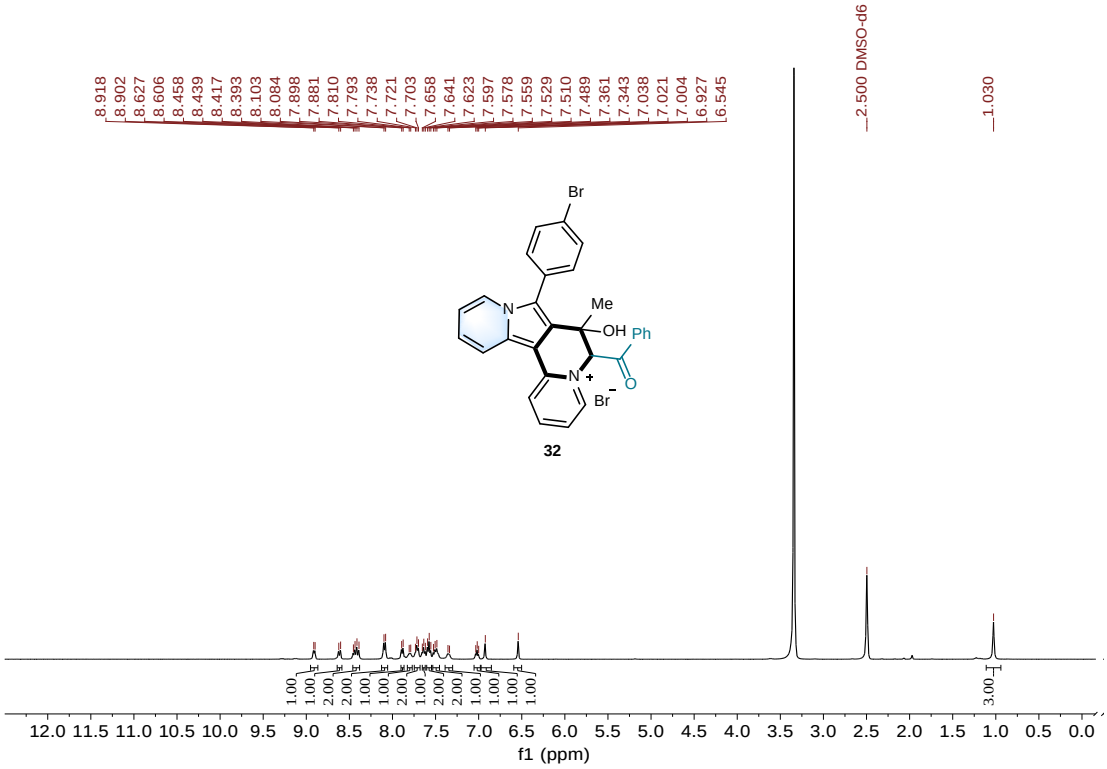
^{1}H NMR spectra of 31 (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 31 (400 MHz, $CDCl_3$)



^{1}H NMR spectra of 32 (400 MHz, DMSO-d_6)



^{13}C NMR spectra of 32 (100 MHz, DMSO-d_6)