Electronic Supplementary Material (ESI) for Chemical Science.

Cobalt-Catalyzed Acylation-Reactions of (Hetero)Arylzinc Pivalates with Thiopyridyl Ester Derivatives

Ferdinand H. Lutter, Lucie Grokenberger, Maximilian S. Hofmayer, and Paul Knochel*

Ludwig-Maximilians-University Munich
Department of Chemistry
Butenandtstr. 5-13, 81377 Munich, Germany
Paul.Knochel@cup.uni-muenchen.de

Supporting Information

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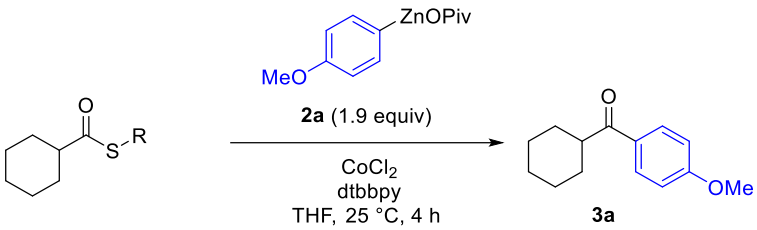
General Information

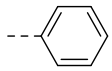
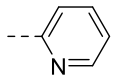
Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under argon. Syringes used to transfer reagents and solvents were purged with argon prior to use. All reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC were performed using aluminum plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Purification *via* column chromatography was performed using Merck silica gel 60 (40–63 mm 230–400 mesh ASTM from Merck). THF was used from Acros, 99.5%, extra dry over molecular sieves. Acetonitrile was used from VWR, HPLC-SUPER GRADIENT. Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. Chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and high-resolution mass spectra (HR-MS) were recorded using electroionization (EI) except where otherwise noted. GCs were recorded on machines of the type Hewlett-Packard 6890 (Hewlett Packard, 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm; film thickness: 0.25 µm). $CoCl_2$ (97% purity) was purchased from Alfa Aesar; $CoCl_2$ (99.99% purity) was purchased from Sigma Aldrich. Infrared spectra were recorded on a *Perkin* 281 IR spectrometer and samples were measured neat (ATR, Smiths Detection DuraSample IR II Diamond ATR). The absorption bands are reported in wave numbers (cm^{-1}). Optical rotation values were recorded on a *PerkinElmer*241 or *Anton Paar* MCP 200 polarimeter. The specific rotation is calculated as follows:

$$[\alpha]_{\lambda}^{\varphi} = \frac{[\alpha] \cdot 100}{c \cdot d}$$

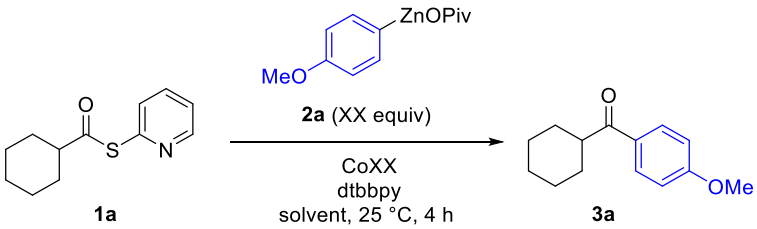
Thereby, the wavelength λ is reported in nm and the measuring temperature φ in °C. α represents the recorded optical rotation, *c* the concentration of the analyte in 10 mg/mL and d the length of the cuvette in dm. Thus, the specific rotation is given in $10^{-1}\cdot deg\cdot cm^2\cdot g^{-1}$. Usage of the sodium D line (λ = 589 nm) is indicated by D instead of the wavelength in nm. The respective concentration as well as the solvent is reported at the relevant section of the experimental section. Enantiomeric excess (*ee*) of the compounds were measured by *Shimazu* HPLC Prominence with *Daicel* Chiralcel.

Optimization of the Reaction Conditions



Entry	R =	GC-Yield[a] [%]
1	Et	8
2		53
3		90

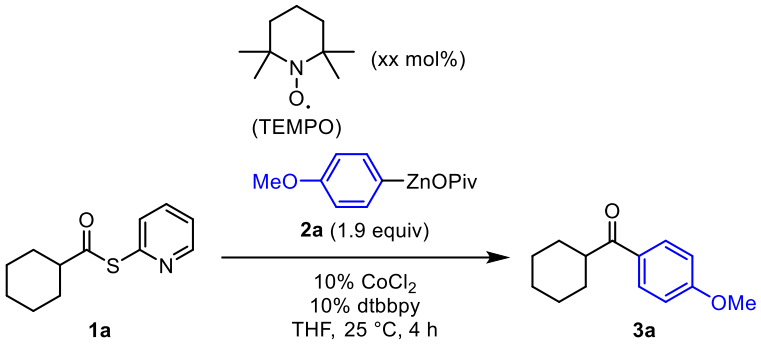
[a] Tetradecane ($C_{14}H_{30}$) was used as internal standard.



Entry	Cobalt salt	$CoCl_2$ [mol%]	dtbbpy [mol%]	Solvent	Amount of **2a** [equiv]	GC-Yield[a] [%]
1	$CoCl_2$	5	5	THF	1.9	81
2	**$CoCl_2$**	**10**	**10**	**THF**	**1.9**	**90**
3	$CoCl_2$	20	20	THF	1.9	92
4	$CoCl_2$	10	10	THF	1.5	85
5	$CoCl_2$	10	10	THF	2.5	87
6	$CoCl_2$	10	10	MeCN	1.9	89
7	$CoCl_2$	10	10	1,4-dioxane	1.9	90
9	$CoCl_2$	10	10	2-MeTHF	1.9	87
10	$CoCl_2$	10	10	THF	1.9	80[b]
11	$CoCl_2$	10	10	THF	1.9	82[c]
12	$CoBr_2$	10	10	THF	1.9	86
13	$Co(acac)_2$	10	10	THF	1.9	86
14	$Co(acac)_3$	10	10	THF	1.9	84

[a] Tetradecane ($C_{14}H_{30}$) was used as internal standard. [b] ZnCl was used instead of ZnOPiv. [c] The solid zinc pivalate **2a** was weighed out on the bench and added to the reaction mixture under air.

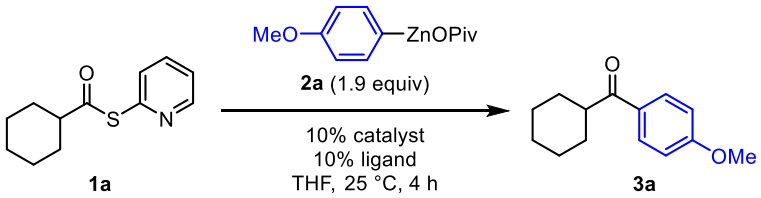
Mechanistic Experiments



entry	TEMPO	GC-yield[a]
1	-	90
2	10%	71
3	150%	6

[a] Tetradecane ($C_{14}H_{30}$) was used as internal standard.

To gain an insight into the reaction mechanism, the reaction was performed in the presence of various amounts of a radical trapping agent (TEMPO). Addition of 10% of the trapping reagent decreases the yield by 19%. To ensure, that TEMPO does not react with the arylzinc species, **2a** was stirred with equimolar amounts of TEMPO. Iodolysis of the reaction mixture after 4 h led to 99% of the iodinated **2a**, determined using GC-analysis with an internal standard ($C_{14}H_{30}$). These findings may indicate an involvement of radicals within the reaction mechanism.

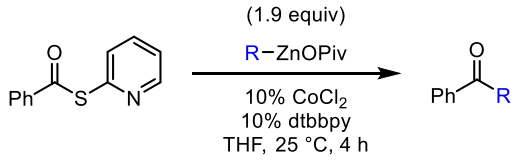


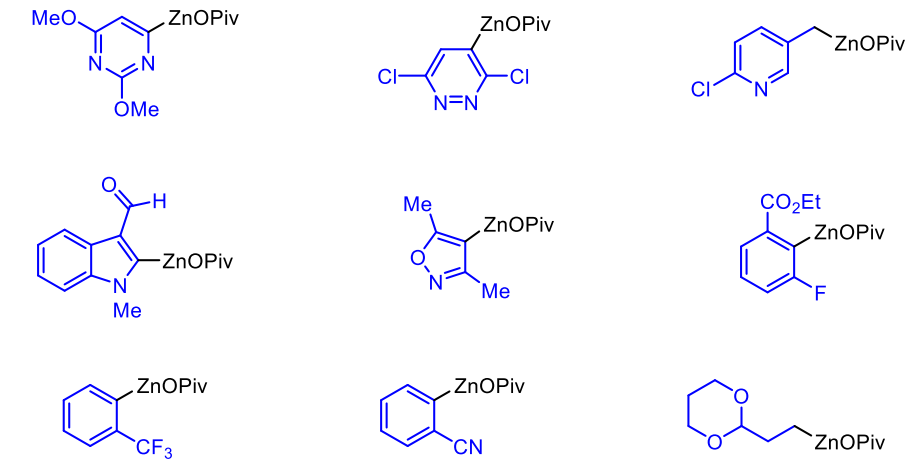
entry	cobalt salt	ligand	GC-yield[a]
1	$CoCl_2$	dtbbpy	90
2	Co powder	dtbbpy	2
3	$CoCl(PPh_3)_3$	-	64
4	$CoCl_2(PPh_3)_3$	-	73

[a] Tetradecane ($C_{14}H_{30}$) was used as internal standard.

These experiments might indicate the involvement of a Co(I) species within the catalytic cycle.

Unsuccessful Acylation Reactions with Several Heterocyclic and Sterically Hindered Organozinc Pivalates





Preparation of Organometallic Reagents

Preparation of $Zn(OPiv)_2$

A dry, tared, 500 mL round-bottomed flask equipped with a magnetic stirring bar and a septum is charged with toluene (250 mL, 0.2 M). Pivalic acid (12.5 mL, 11.3 g, 110 mmol, 2.2 equiv) is added to form a colorless solution. Zinc oxide (4.07 g, 50 mmol, 1.0 equiv) is added in 1 g portions at 25 °C over 15 min to form a colorless suspension. The flask was equipped with a Dean-Stark apparatus (10 mL) wrapped in aluminum foil and topped with a reflux condenser (20 cm) and the suspension is stirred under nitrogen at reflux in an oil bath for 16 h. A viscous colorless suspension was obtained after 12 h. After cooling to 25 °C, the mixture is concentrated by rotary evaporation (50 °C/50 mmHg). The remaining pivalic acid and water were removed in *vacuo* from the reaction mixture using a vacuum line (0.1 mmHg) and a liquid nitrogen cold trap (1000 mL). The white solid was warmed to 100 °C in an oil bath and dried for at least 6 h. Zinc pivalate (13.1–13.2 g, 48.9–49.7 mmol, 98–99% yield), is obtained as a puffy amorphous white solid.[1]

Preparation of *i*PrMgCl·LiCl

Magnesium turnings (2.67 g, 110 mmol) and anhydrous LiCl (4.66 g, 100 mmol) were placed in an argon-flushed flask and THF (50 mL) was added. A solution of *i*PrCl (9.13 mL, 100 mmol) in THF (50 mL) was slowly added at 25 °C. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at 25 °C. The grey solution of *i*PrMgCl·LiCl was cannulated to another flask under argon and removed in this way from excess of magnesium. A yield of ca. 95-98% of *i*PrMgCl·LiCl is obtained.[2]

Preparation of TMPMgCl•LiCl

A dry and argon-flushed 250-mL *Schlenk*-flask, equipped with a magnetic stirring bar and a septum, was charged with freshly titrated *i*PrMgCl·LiCl (100 mL, 1.2 M in THF, 120 mmol). TMPH (17.8 g, 126 mmol, 1.05 equiv) was added dropwise at 25 °C. The reaction mixture was stirred at 25 °C until gas evolution ceased (ca. 24 h).[3]

Preparation of Starting Materials

Preparation of thiopyridyl esters (TP1):[4]

The corresponding carboxylic acid **4** (1.0 equiv), PPh_3 (1.5 equiv) and 2,2'-dipyridyl disulfide (1.1 equiv) were added to a round bottom flask equipped with a magnetic stirring bar. The mixture was dissolved in MeCN (0.3 M) and heated to reflux for 3 h. After solvent evaporation, the resulting thiopyridyl ester was purified by column chromatography (SiO_2, *i*hexane/ethyl acetate) yielding the pure thioester.

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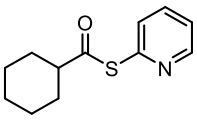
[1] M. Ellwart, Y-H. Chen, C. P. Tüllmann, V. Malakhov, P. Knochel, *Org. Synth.* 2018, **95**, 127-141.
[2] A. Krasovskiy, P. Knochel, *Angew. Chem. Int. Ed.* 2004, **43**, 3333-3336.
[3] A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem. Int. Ed.* 2006, **45**, 2958-2961.
[4] T. Endo, S. Ikenaga, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* 1970, **43**, 2632-2633.

Preparation of α-chiral-thiopyridyl esters (TP2):

The corresponding α-chiral-carboxylic acid **4** (1.0 equiv), PPh_3 (1.0 equiv) and 2,2'-dipyridyl disulfide (1.0 equiv) were added to a round bottom flask equipped with a magnetic stirring bar. The mixture was dissolved in MeCN (0.3 M), cooled to 0 °C and stirred for 16 h. After solvent evaporation, the resulting substrate was purified by column chromatography (SiO_2, *i*hexane/ethyl acetate) yielding the corresponding thioester.

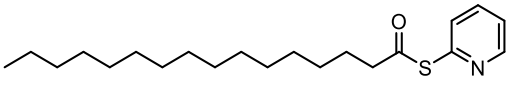
***S*-(Pyridin-2-yl) cyclohexanecarbothioate (1a)**



S-(Pyridin-2-yl) cyclohexanecarbothioate was prepared according to **TP1** from cyclohexanecarboxylic acid (**4a**, 2.21 g, 10.00 mmol) and was obtained as a yellow solid (1.68 g, 7.60 mmol, 76% yield. The analytical data is in full consistency with the data reported in the literature.[5]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.61 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.71 (tt, *J* = 7.7, 1.4 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.17 (m, 1H), 2.62 (tt, *J* = 11.4, 3.5 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.81 (dt, *J* = 12.8, 3.4 Hz, 2H), 1.67 (dt, *J* = 12.6, 3.6 Hz, 1H), 1.53 (qd, *J* = 12.0, 3.3 Hz, 2H), 1.40 – 1.12 (m, 3H).

***S*-(Pyridin-2-yl) hexadecanethioate (1b)**



S-(Pyridin-2-yl) hexadecanethioate was prepared according to **TP1** from palmitic acid (**4b**, 512 mg, 2.00 mmol) and was obtained as a yellow powder (684 mg, 1.96 mmol, 98% yield).

Purification: *i*hexane:ethyl acetate = 8:2.

m.p.: 62.0 – 63.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.66 – 8.58 (m, 1H), 7.73 (td, *J* = 7.7, 1.9 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.33 – 7.26 (m, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.72 (p, *J* = 7.5 Hz, 2H), 1.25 (s, 24H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 196.8, 151.8, 150.5, 137.2, 130.3, 123.6, 44.4, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 25.6, 22.9, 14.3.

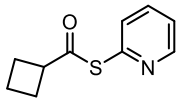
FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ =2916, 2848, 1796, 1739, 1696, 1571, 1472, 1463, 1446, 1421, 1382, 1124, 1107, 1092, 1061, 1049, 981, 945, 905, 762, 718.

MS (EI, 70 eV): *m/z* (%) = 239 (9), 112 (32), 111 (100), 98 (16), 57 (11), 43 (25).

HR-MS (EI, 70eV): [$C_{21}H_{35}NOS$], calcd.: 349.2439; found: 349.2432.

[5] B. Neises, W. Steglich, T. Van Ree, *S. Afr. J. Chem.* 1981, **34**, 58-59.

***S*-(pyridin-2-yl) cyclobutanecarbothioate (1c)**



S-(pyridin-2-yl) cyclobutanecarbothioate was prepared according to **TP1** from cyclobutanecarboxylic acid (**4c**, 200 mg, 2.00 mmol) and was obtained as a yellow oil (305 mg, 1.58 mmol, 79%).

Purification: *i*hexaner:ethyl acetate = 8:2.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.66 – 8.50 (m, 1H), 7.67 (td, *J* = 7.7, 1.9 Hz, 1H), 7.55 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 3.43 (pd, *J* = 8.5, 1.0 Hz, 1H), 2.45 – 2.27 (m, 2H), 2.20 (dtdd, *J* = 12.6, 8.3, 4.2, 2.3 Hz, 2H), 2.02 – 1.72 (m, 2H).

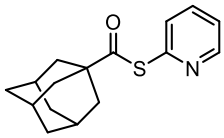
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 198.4, 151.6, 150.4, 137.1, 130.2, 123.4, 47.0, 26.0, 18.00.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2986, 2944, 1698, 1572, 1562, 1448, 1420, 1334, 1280, 1245, 1186, 1139, 1105, 1059, 1046, 988, 956, 885, 813, 763, 722, 677.

MS (EI, 70 eV): *m/z* (%) = 258 (36), 211 (19), 136 (9) 135 (100), 77 (11).

HR-MS (EI, 70eV): [$C_{10}H_{12}NOS$], calcd.: 194.0634; found: 194.0634 [M^++H].

***S*-(pyridin-2-yl)-adamantane-1-carbothioate (1d)**



S-(pyridin-2-yl)-adamantane-1-carbothioate was prepared according to **TP1** from adamantane-1-carboxylic acid (**4d**, 360 mg, 2.00 mmol) and was obtained as a pale yellow powder (464 mg, 1.70 mmol, 85 % yield).

Purification: *i*hexane:ethyl acetate = 9:1 → 8:2.

m.p.: 73.2 – 75.6 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.62 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.17 (m, 1H), 2.09 (p, *J* = 3.1 Hz, 3H), 2.00 (d, *J* = 3.0 Hz, 6H), 1.83 – 1.63 (m, 6H).

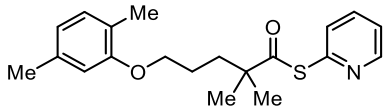
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 203.5, 152.0, 150.5, 137.0, 131.1, 123.4, 49.6, 39.3, 36.5, 28.3.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ =2909, 2848, 1689, 1572, 1562, 1449, 1421, 1342, 1280, 1250, 1188, 1138, 1116, 1102, 1084, 1045, 986, 946, 918, 822, 795, 760, 742, 724, 671.

MS (EI, 70 eV): *m/z* (%) = 273 (2), 244 (6), 136 (8), 135 (100), 93 (8), 79 (9).

HR-MS (EI, 70eV): [$C_{16}H_{19}NOS$], calcd.: 273.1187; found: 273.1176.

***S*-(Pyridin-2-yl) 3-(2,5-dimethylphenoxy)-2,2-dimethylpropanethioate (1e)**



S-(Pyridin-2-yl) 3-(2,5-dimethylphenoxy)-2,2-dimethylpropanethioate was prepared according to **TP1** from 3-(2,5-dimethylphenoxy)-2,2-dimethylpropanoic acid (**4e**, 444 mg, 2.00 mmol) and was obtained as a yellow oil (617 mg, 1.96 mmol, 98% yield).

Purification: *i*hexane:ethyl acetate = 9:1 → 8:2.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.64 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.73 (td, *J* = 7.7, 2.0 Hz, 1H), 7.53 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.29 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.61 (d, *J* = 1.5 Hz, 1H), 3.95 (t, *J* = 5.4 Hz, 2H), 2.31 (s, 3H), 2.19 (s, 3H), 1.91 – 1.79 (m, 4H), 1.36 (s, 6H).

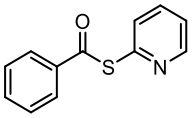
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 203.6, 157.0, 151.9, 150.6, 137.1, 136.6, 131.0, 130.4, 123.7, 123.5, 120.8, 112.0, 67.8, 50.6, 37.6, 25.4, 25.0, 21.6, 16.0.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2966, 2922, 1693, 1614, 1583, 1573, 1563, 1509, 1448, 1419, 1389, 1366, 1285, 1263, 1156, 1129, 1044, 1000, 988, 931, 906, 803, 764, 724.

MS (EI, 70 eV): *m/z* (%) = 258 (36), 211 (19), 136 (9) 135 (100), 77 (11).

HR-MS (EI, 70eV): [$C_{20}H_{26}NO_2S$], calcd.: 344.1679; found: 344.1678 [M^++H].

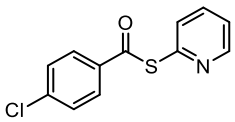
***S*-(Pyridin-2-yl) benzothioate (1f)**



S-(Pyridin-2-yl) benzothioate was prepared according to **TP1** from benzoic acid (**4f**, 1.22 g, 10.0 mmol) and was obtained as a yellow solid (1.81 g, 8.4 mmol, 84% yield). The analytical data was in full consistency with the data reported in the literature.[6]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.72 – 8.62 (m, 1H), 8.08 – 7.97 (m, 2H), 7.79 (td, J = 7.7, 1.9 Hz, 1H), 7.73 (dt, J = 8.0, 1.0 Hz, 1H), 7.67 – 7.56 (m, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.33 (ddt, J = 7.1, 4.8, 1.0 Hz, 1H).

***S*-(Pyridin-2-yl) 4-chlorobenzothioate (1g)**

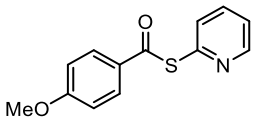


[6] C. M. Lemon, E. Karnas, M. G. Bawendi, D. G. Nocera, *Inorg. Chem.* 2013, **52**, 10394-10406.

S-(Pyridin-2-yl) 4-chlorobenzothioate was prepared according to **TP1** from 4-chlorobenzoic acid (**4g**, 1.55 g, 10.0 mmol) and was obtained as pale yellow needles (1.64 g, 6.6 mmol, 66 % yield). The analytical data was in full consistency with the data reported in the literature.[7]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.68 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 8.03 – 7.92 (m, 2H), 7.79 (td, *J* = 7.7, 1.9 Hz, 1H), 7.71 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.34 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H).

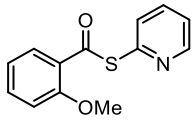
_S_-(Pyridin-2-yl) 4-methoxybenzothioate (1h)



S-(Pyridin-2-yl) 4-methoxybenzothioate was prepared according to **TP1** from 4-methoxybenzoic acid (**4h**, 304 mg, 2.00 mmol) and was obtained as a yellow solid (338 mg, 1.38 mmol, 69% yield). The analytical data was in full consistency with the data reported in the literature.[8]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.59 (ddt, *J* = 3.6, 2.6, 1.4 Hz, 1H), 7.93 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.77 – 7.59 (m, 2H), 7.25 (dtd, *J* = 6.8, 3.2, 1.6 Hz, 1H), 6.89 (dd, *J* = 9.1, 2.6 Hz, 2H), 3.81 (s, 3H).

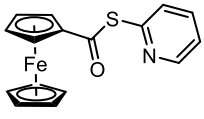
_S_-(Pyridin-2-yl) 4-methoxybenzothioate (1h')



S-(Pyridin-2-yl) 2-methoxybenzothioate was prepared according to **TP1** from 2-methoxybenzoic acid (**4h'**, 304 mg, 2.00 mmol) and was obtained as a yellow oil (470 mg, 1.92 mmol, 96% yield). The analytical data was in full consistency with the data reported in the literature.[9]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.74 – 8.58 (m, 1H), 7.86 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.51 (ddd, *J* = 7.9, 7.0, 1.8 Hz, 1H), 7.30 (ddd, *J* = 6.7, 4.8, 1.9 Hz, 1H), 7.07 – 6.98 (m, 2H), 3.96 (s, 3H).

_S_-(Pyridin-2-yl) ferrocenecarbothioate (1i)



S-(Pyridin-2-yl) ferrocene was prepared according to **TP1** from ferrocene monocarboxylic acid (**4i**, 460 mg, 2.00 mmol) and was obtained as red crystals (588 mg, 1.82 mmol, 91% yield).

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[7] M. Ociepa, O. Baka, J. Nardodowiec, D. Gryko, *Adv. Synth. Catal.* 2017, **359**, 3560-3565.
[8] S. H. H. Zaidi, K. Muthukumaran, S.-I. Taimaru, J. S. Lindsey, *J. Org. Chem.* 2004, **69**, 8356-8365.
[9] M. Ociepa, O. Baka, J. Narodowiec, D. Gryko, *Adv. Synth. Catal*. **2017**, *359*, 3560.

Purification: *i*hexane:ethyl acetate = 9:1 → 8:2.

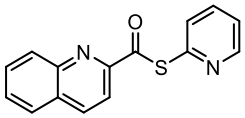
m.p.: 84.6 – 86.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.64 (d, *J* = 5.1 Hz, 1H), 7.75 (d, *J* = 6.5 Hz, 2H), 7.28 (dd, *J* = 11.8, 5.0 Hz, 1H), 4.94 (s, 2H), 4.55 (s, 2H), 4.31 (s, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 190.9, 152.4, 150.4, 150.3, 137.0, 130.4, 123.3, 123.3, 123.3, 78.8, 72.4, 72.4, 71.0, 70.8, 69.4, 69.3.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ =2923, 1652, 1570, 1446, 1422, 1369, 1239, 1121, 1106, 1045, 1024, 1002, 986, 942, 837, 810, 762, 721, 693.

***S*-(Pyridin-2-yl) quinoline-2-carbothioate (1j)**



S-(Pyridin-2-yl) quinoline-2-carbothioate was prepared accordning to **TP1** from quinoline-2-carboxylic acid (**4j**, 856 mg, 5.00 mmol) and was obtained as yellow crystals (998 mg, 3.75 mmol, 75%).

Purification: *i*hexane:ethyl acetate = 9:1 → 8:2.

m.p.: 142.8– 144.2 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.80 – 8.70 (m, 1H), 8.38 – 8.25 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.90 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.87 – 7.73 (m, 3H), 7.69 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.35 (ddd, *J* = 7.3, 4.8, 1.4 Hz, 1H).

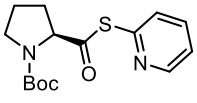
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 192.1, 152.5, 151.1, 150.6, 147.9, 137.8, 137.4, 131.0, 130.7, 130.6, 130.5, 129.2, 127.9, 123.7, 117.3.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2926, 1682, 1668, 1572, 1561, 1502, 1461, 1448, 1419, 1378, 1305, 1279, 1263, 1227, 1206, 1142, 1108, 1082, 1046, 988, 964, 912, 834, 792, 763, 738, 722,702.

MS (EI, 70 eV): *m/z* (%) = 266 (3), 238 (19), 237 (40), 206 (40), 205 (23).

HR-MS (EI, 70eV): [$C_{15}H_{10}N_2OS$], calcd.: 266.0514; found: 266.0509.

***tert*-Butyl (*S*)-2-((pyridin-2-ylthio)carbonyl)pyrrolidine-1-carboxylate (1k)**



tert-Butyl (*S*)-2-((pyridin-2-ylthio)carbonyl)pyrrolidine-1-carboxylate was prepared according to **TP2** from (*tert*-butoxycarbonyl)-*L*-proline (**4k**, 2.15 g, 10.0 mmol) and was obtained as a yellow solid (2.24 g, 7.3 mmol, 73% yield). The analytical data is in full consistency with the data reported in the literature.[10]

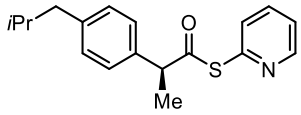
[10] T. Hofmann, P. Schieberle, *J. Agric. Food Chem*. 1998, **46**, 616-619.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm, mixture of rotamers)**:** δ = 8.61 (dd, *J* = 5.0, 2.0 Hz, 0.6 H), 8.60 – 8.56 (m, 0.4 H), 7.72 (qd, *J* = 7.1, 6.5, 1.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 0.4 H), 7.55 (d, *J* = 7.9 Hz, 0.6 H), 7.26 (td, *J* = 9.7, 8.7, 5.0 Hz, 1.1 H), 4.57 (dd, *J* = 8.3, 3.4 Hz, 0.4 H), 4.44 (dd, *J* = 8.8, 3.8 Hz, 0.6 H), 3.54 (dtdd, *J* = 37.3, 18.1, 9.0, 6.1 Hz, 2H), 2.36 – 1.99 (m, 3H), 1.91 (pd, *J* = 7.6, 3.8 Hz, 1H), 1.48 (d, *J* = 7.1 Hz, 9H).

Optical rotation: $[\alpha]_D^{20} = -118$ (c 1.17, $CHCl_3$).

Chiral HPLC: >99% *ee*, AD-H column, *i*PrOH:heptane = 95:5, 1.5 mL/min, 30 °C.

***S*-(Pyridin-2-yl) (S)-2-(4-isobutylphenyl)propanethioate (1l)**



(*S*)-2-(4-Isobutylphenyl)propanethioate was prepared according to **TP2** at 0 °C from (*S*)-2-(4-isobutylphenyl)-propanoic acid (**4l**, 412 mg, 2.00 mmol) and was obtained as a yellow oil (574 mg, 1.96 mmol, 96% yield).

Purification: *i*hexane:ethyl acetate = 9:1 → 8:2.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (t, *J* = 1.8 Hz, 1H), 7.69 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.34 (ddd, *J* = 7.8, 2.0, 1.1 Hz, 1H), 7.32 – 7.23 (m, 1H), 7.20 – 7.14 (m, 2H), 7.09 – 7.02 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 1H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.86 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 198.5, 151.8, 150.2, 141.3, 137.1, 136.2, 130.1, 129.6, 127.9, 123.4, 54.2, 45.1, 30.2, 22.4, 18.4.

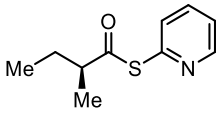
FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954, 2928, 2868, 1706, 1573, 1563, 1511, 1448, 1420, 1368, 1240, 1217, 1183, 1168, 1140, 121, 1097, 1084, 1066, 1045, 998, 988, 930, 847, 802, 763, 738, 724, 663.

HR-MS (ESI, 70eV): [$C_{18}H_{22}NOS$], calcd.: 300.1417; found: 300.1416 [M^++H].

Optical rotation: $[\alpha]_D^{20} = 104$ (c 1.24, $CHCl_3$).

Chiral HPLC: 98% *ee*, OD-H column, *i*PrOH:heptane = 90:10, 1.0 mL/min, 30 °C.

***S*-(Pyridin-2-yl) (*S*)-2-methylbutanethioate (1m)**



S-(Pyridin-2-yl) (*S*)-2-methylbutanethioate was prepared according to **TP2** at 0 °C from *(S)*-2-methylbutanoic acid (**4m**, 510 mg, 5 mmol) and was obtained as a yellow oil (950 mg, 4.87 mmol, 97% yield).

Purification: *i*hexane:ethyl acetate = 9:1 → 8:2.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.61 (ddd, *J* = 5.1, 1.8, 0.9 Hz, 1H), 7.72 (td, *J* = 7.7, 1.9 Hz, 1H), 7.60 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.26 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 2.70 (h, *J* = 6.9 Hz, 1H), 1.82 (dt, *J* = 13.7, 7.2 Hz, 1H), 1.54 (tt, *J* = 14.4, 7.1 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 200.8, 151.8, 150.4, 137.1, 130.3, 123.5, 50.6, 27.2, 17.1, 11.7.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2968, 2934, 2877, 1702, 1573, 15622, 1448, 1418, 1380, 1260, 1201, 1139, 1118, 1084, 1045, 987, 967, 939, 829, 807, 762, 732, 719, 669, 670.

MS (EI, 70 eV): *m/z* (%) = 196 (2), 166 (15), 139 (18), 134 (65), 112 (91), 111 (100), 67 (26).

HR-MS (EI, 70eV): [$C_{10}H_{14}NOS$], calcd.: 196.0791; found: 196.0789 [M^++H].

Optical rotation: $[\alpha]_D^{20} = 19$ (c 1.20, $CHCl_3$).

Chiral HPLC: 98% *ee*, OD-H column, *i*PrOH:heptane = 98:2, 1.0 mL/min, 30 °C.

Cobalt-Catalyzed Acylation-Reactions of (Hetero)arylzinc Pivalates with Organic Thiopyridylester derivatives

Preparation of arylzinc pivalates by insertion (TP3):

Magnesium turnings (1.2 equiv), dry LiCl (1.2 equiv) and dry THF (1.00 M solution relating to the aryl halide) were added to a dry and argon flushed *Schlenk*-tube equipped with a magnetic stirring bar and a septum. The tube was charged with the aromatic bromide **5** (1.0 equiv). For controlling the following initial heat evolution of the insertion reaction, the Schlenk-tube was placed in an ice bath for cooling. To monitor the progress of the insertion reaction, reaction aliquots quenched with iodine and were analyzed as water-quenched samples by GC-analysis. When the insertion was completed, solid $Zn(OPiv)_2$ (1.0 equiv) was added in one portion at 0 °C and stirred at ambient temperature for 15 min.

Preparation of arylzinc pivalates by halogen/magnesium exchange (TP4):

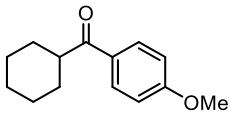
A dry and argon flushed *Schlenk*-tube equipped with a magnetic stirring bar and a septum was charged with the corresponding aryl halide (1.00 mmol) in THF (0.50 M) Then, after stirring for 5 min at ambient temperature, the resulting solution was cooled to -20 °C, *i*PrMgCl (1.11 M in THF, 1.1 equiv) was added dropwise. GC-analysis was used to monitor the progress of the halogen-magnesium exchange, by analysis of reaction aliquots quenched with I_2. The reaction was completed within 60 min. $Zn(OPiv)_2$ (1.0 equiv) was added in one portion at 0 °C and the mixture was slowly warmed to room temperature.

Cobalt-catalyzed acylation of arylzinc pivalates with thiopyridyl esters (TP5):

A dry and argon flushed *Schlenk*-tube equipped with a magnetic stirring bar and a septum was charged with $CoCl_2$ (6.5 mg, 0.05 mmol, 0.10 equiv, dried in *vacuo* at 400 °C prior to use). Then, the ligand 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.0 mg, 0.05 mmol, 0.10 equiv) and the corresponding thiopyridyl ester (**1**, 0.50 mmol, 1.0 equiv) were added to the *Schlenk*-tube. The resulting mixture was dissolved in dry THF (1 mL). Then, the organozinc pivalate,

synthesized *via* **TP2** or **TP3** (**2**, 0.95 mmol, 1.9 equiv) was added and stirring was continued for 4 h, at 25 °C. For substance **3t-3y** the reaction was carried out at 0 °C. The reaction conversion was monitored by GC-analysis of water-quenched reaction aliquots ($C_{14}H_{30}$ was used as an internal standard). Upon consumption of the starting material, sat. aq. NH_4Cl solution (10 mL) was added, the phases were separated and the aqueous phase was extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over $MgSO_4$. The solvents were evaporated and the residue was subjected to column chromatographical purification (pentane/ethyl acetate) on silica yielding the corresponding title compound.

Cyclohexyl(4-methoxyphenyl)methanone (3a)



Following **TP5** *S*-(pyridin-2-yl) cyclohexanecarbothioate (**1a**, 111 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-(methoxy)phenylzinc pivalate (**2a**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 96 mg, 0.44 mmol, 88%, colorless crystals.

Purification: pentane:ethyl acetate = 99:1.

m.p.: 64.2 – 66.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.22 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.85 (tdd, *J* = 11.7, 6.2, 3.0 Hz, 4H), 1.73 (dddt, *J* = 12.8, 5.0, 3.3, 1.7 Hz, 1H), 1.57 – 1.38 (m, 3H), 1.36 – 1.19 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 202.6, 163.3, 130.6, 129.4, 113.8, 55.6, 45.4, 29.7, 26.1, 26.1.

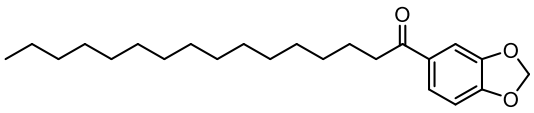
FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3065, 3019, 2973, 2944, 2916, 2846, 1639, 1628, 1594, 1573, 1504, 1499, 1466, 1454, 1442, 1416, 1405, 1302, 1296, 1284, 1256, 1224, 1182, 1175, 1148, 1116, 1094, 1064, 1028, 1013, 967, 959, 949, 928, 856, 842, 828, 815, 789, 763, 682.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2923, 2851, 1658, 1598, 1571, 1505, 1458, 1420, 1370, 1334, 1313, 1299, 1251, 1208, 1163, 1133, 1103, 1025, 972, 896, 844, 825, 791, 770, 742, 687.

MS (EI, 70 eV): *m/z* (%) = 135 (100), 150 (13), 187 (8), 218 (6).

HR-MS (EI, 70eV): [$C_{14}H_{18}O_2$], calcd.: 218.1307; found: 218.1302.

1-(Benzo[*d*][1,3]dioxol-5-yl)hexadecan-1-one (3b)



Following **TP5** *S*-(pyridin-2-yl) hexadecanethioate (**1b**, 175 mg, 0.50 mmol, 1.0 equiv) was coupled with (benzo[*d*][1,3]dioxol-5-yl)zinc pivalate (**2b**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 162 mg, 0.45 mmol, 90%, white solid.

Purification: pentan*e*:ethyl acetate = 100:2.

m.p.: 73.5 – 75.3 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.70 (p, *J* = 7.4 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.7 Hz, 3H).

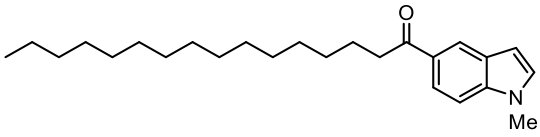
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 198.9, 151.7, 148.3, 132.1, 124.4, 108.1, 108.0, 101.9, 38.6, 32.1, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 24.8, 22.9, 14.3.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2961, 2952, 2914, 2868, 2847, 2774, 1675, 1604, 1497, 1488, 1472, 1462, 1444, 1418, 1373, 1359, 1285, 1279, 1263, 1258, 1250, 1200, 1110, 1092, 1051, 1004, 990, 940, 900, 889, 824, 811, 805, 780, 757, 742, 730, 719, 655.

MS (EI, 70 eV): *m/z* (%) = 281 (21), 225 (8), 209 (8), 208 (10), 207 (84), 191 (16), 165 (10), 164 (100), 149 (57), 121 (12), 44 (7).

HR-MS (EI, 70eV): [$C_{23}H_{36}O_3$], calcd.: 360.2664; found: 360.2662.

1-(1-Methyl-1*H*-indol-5-yl)hexadecan-1-one (3c)



Following **TP5** *S*-(pyridin-2-yl) hexadecanethioate (**1b**, 175 mg, 0.50 mmol, 1.0 equiv) was coupled with ((1-methyl-1*H*-indol-5-yl)zinc pivalate (**2c**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 137 mg, 0.37 mmol, 74%, pale yellow crystals.

Purification: pentan*e*:ethyl acetate = 9:1.

m.p.: 71.6 – 73.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 8.31 (d, *J* = 1.6 Hz, 1H), 7.91 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 6.61 (d, *J* = 3.1 Hz, 1H), 3.82 (s, 3H), 3.03 (t, *J* = 7.5 Hz, 2H), 1.77 (p, *J* = 7.5 Hz, 2H), 1.26 (s, 18H), 0.88 (t, *J* = 6.7 Hz, 3H).

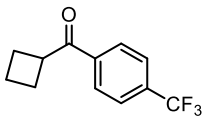
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 200.9, 139.2, 130.4, 129.4, 128.0, 122.9, 121.9, 109.2, 103.1, 38.7, 33.2, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 25.1, 22.9, 14.3.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2948, 2920, 2848, 1657, 1606, 1556, 1513, 1464, 1450, 1212, 1412, 1368, 1343, 1309, 1297, 1264, 1249, 1229, 1163, 1145, 1090, 968, 821, 803, 780, 766, 733, 724.

MS (EI, 70 eV): *m/z* (%) = 130 (14), 158 (72), 173 (100), 174 (14), 369 (11).

HR-MS (EI, 70eV): [$C_{25}H_{39}NO$], calcd.: 369.3032; found: 369.3037.

Cyclobutyl(4-(trifluoromethyl)phenyl)methanone (3d)



Following **TP5** *S*-(pyridin-2-yl) cyclobutanecarbothioate (**1c**, 97 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-(trifluoromethyl)phenyl)zinc pivalate (**2d**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 96 mg, 0.42 mmol, 84% yield, colorless oil.

Purification: pentane:ethyl acetate = 9:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.99 (dt, *J* = 8.1, 1.0 Hz, 2H), 7.74 – 7.68 (m, 2H), 4.13 – 3.93 (m, 1H), 2.50 – 2.26 (m, 4H), 2.18 – 2.05 (m, 1H), 1.99 – 1.86 (m, 1H).

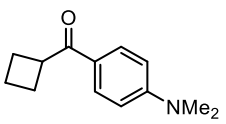
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 199.92, 138.26 , 134.15 (q, *J* = 32.6 Hz), 128.64 , 125.65 (q, *J* = 3.8 Hz), 123.63 (q, *J* = 272.7 Hz), 42.36 , 24.97 , 18.13 .

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2951, 1674, 1510, 1410, 1322, 1252, 1227, 1212, 1166, 1125, 1108, 1065, 1015, 967, 949, 922, 893, 856, 842, 783, 774, 762, 731, 684, 671.

MS (EI, 70 eV): *m/z* (%) = 227 (1), 174 (8), 173 (11), 173 (100), 145 (25).

HR-MS (EI, 70eV): [$C_{12}H_{11}F_3O$], calcd.: 228.0762, found: 228.0758.

Cyclobutyl(4-(dimethylamino)phenyl)methanone (3e)



Following **TP5** *S*-(pyridin-2-yl) cyclobutanecarbothioate (**1c**, 97 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-(dimethylamino)phenyl)zinc pivalate (**2e**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 97 mg, 0.48 mmol, 95% yield, white solid.

Purification: pentane:ethyl acetate = 95:5.

m.p.: 75.2– 77.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 – 7.71 (m, 2H), 6.67 – 6.57 (m, 2H), 3.88 (pd, *J* = 8.6, 1.1 Hz, 1H), 2.98 (s, 6H), 2.42 – 2.27 (m, 2H), 2.18 (dddd, *J* = 12.4, 10.6, 8.8, 3.9 Hz, 2H), 2.08 – 1.91 (m, 1H), 1.81 (ddddd, *J* = 14.6, 9.2, 7.9, 4.0, 1.1 Hz, 1H).

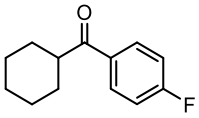
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): 199.4, 153.0, 130.4, 111.0, 110.9, 41.7, 40.3, 25.3, 18.2.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2959, 1667, 1622, 1478, 1387, 1261, 1195, 1167, 1025, 909, 856, 819.

MS (EI, 70 eV): *m/z* (%) = 203 (16), 148 (100), 44 (12), 42 (39).

HR-MS (EI, 70eV): [$C_{13}H_{17}NO$], calcd.: 203.1310, found: 203.1305.

Cyclohexyl(4-fluorophenyl)methanone (3f)



Following **TP5** *S*-(pyridin-2-yl) cyclohexanecarbothioate (**1a**, 111 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-fluorophenyl)zinc pivalate (**2f**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 62 mg, 0.30 mmol, 60%, colorless oil.

Purification: pentane:ethyl acetate = 9:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.07 – 7.85 (m, 2H), 7.21 – 7.03 (m, 2H), 3.21 (tt, *J* = 11.4, 3.2 Hz, 1H), 1.95 – 1.79 (m, 4H), 1.74 (dtt, *J* = 13.0, 3.5, 1.8 Hz, 1H), 1.58 – 1.16 (m, 5H).

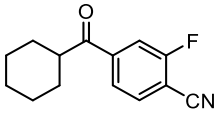
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 202.4, 165.7 (d, J = 254.0 Hz), 132.8 (d, J = 3.0 Hz), 131.0 (d, J = 9.2 Hz), 115.8 (d, J = 21.7 Hz), 45.7, 29.6, 26.1, 26.0.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3068, 2929, 2853, 1678, 1596, 1505, 1463, 1450, 1409, 1371, 1332, 1312, 1295, 1289, 1249, 1233, 1205, 1176, 1154, 1134, 1102, 1027, 1012, 974, 893, 860, 841, 824, 806, 800, 776, 738, 675.

MS (EI, 70 eV): *m/z* (%) = 206 (9), 151 (21), 138 (9), 124 (8), 123 (100), 95 (8).

HR-MS (EI, 70eV): [$C_{13}H_{15}FO$], calcd.: 206.1107; found: 206.1101.

4-(Cyclohexanecarbonyl)-2-fluorobenzonitrile (3g)



Following **TP5** *S*-(pyridin-2-yl) cyclohexanecarbothioate (**1a**, 111 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-cyano-3-fluorophenyl)zinc pivalate (**2g**, 0.95 mmol, 1.9 equiv)prepared according to **TP4** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 91 mg, 0.39 mmol, 79%, colorless crystals.

Purification: pentane:ethyl acetate = 9:1.

m.p.: 54.4 – 56.2 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.85 – 7.68 (m, 3H), 3.16 (tt, *J* = 11.3, 3.1 Hz, 1H), 1.86 (dp, *J* = 9.5, 3.4 Hz, 4H), 1.75 (dddd, *J* = 11.5, 5.2, 3.3, 1.7 Hz, 1H), 1.58 – 1.16 (m, 5H).

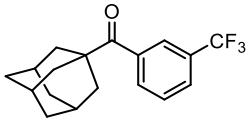
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 201.2 (d, *J* = 1.6 Hz), 163.4 (d, *J* = 261.1 Hz), 142.2 (d, *J* = 6.1 Hz), 134.1, 124.3 (d, *J* = 3.7 Hz), 116.1 (d, *J* = 20.5 Hz), 113.4, 105.2 (d, *J* = 15.9 Hz), 46.2, 29.2, 25.9, 25.7.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3076, 2930, 2855, 2239, 1686, 1618, 1567, 1495, 1463, 1450, 1421, 1415, 1373, 1331, 1313, 1299, 1290, 1274, 1253, 1230, 1192, 1157, 1133, 1120, 1103, 996, 988, 921, 908, 901, 873, 836, 797, 772, 734, 706.

MS (EI, 70 eV): *m/z* (%) = 231 (43), 225 (8), 216 (9), 213 (18), 190 (31), 189 (12), 188 (12), 177 (10), 176 (100), 165 (7), 164 (26), 163 (26), 158 (7), 148 (86), 121 (59), 129 (10), 105 (24), 100 (21), 83 (16), 77 (9), 68 (8), 67 (11), 55 (27).

HR-MS (EI, 70eV): [$C_{14}H_{14}FNO$], calcd.: 231.1059; found: 231.1054.

(Adamantan-1-yl)(3-(trifluoromethyl)phenyl)methanone (3h)



Following **TP5** *S*-(pyridin-2-yl)-adamantane-1-carbothioate (**1d**, 137 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-(trifluoromethyl)phenyl) zinc pivalate (**2h**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 94 mg, 0.31 mmol, 61%, white solid.

Purification: pentane:ethyl acetate = 98:2.

m.p.: 63.6 – 65.3 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.76 (d, *J* = 2.0 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 2.09 (q, *J* = 3.1 Hz, 3H), 1.99 (d, *J* = 2.9 Hz, 6H), 1.82 – 1.68 (m, 6H).

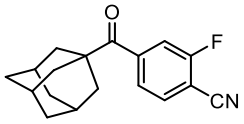
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 209.0, 140.3, 131.7 – 129.7 (m), 130.4 (d, *J* = 1.4 Hz), 128.7, 126.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 272.5 Hz), 47.1, 39.1, 36.5, 28.1.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2943, 2914, 2854, 1661, 1605, 1453, 1329, 1309, 1261, 1225, 1184, 1162, 1119, 1102, 1071, 998, 922, 808, 778, 762, 734, 695, 659.

MS (EI, 70 eV): *m/z* (%) = 308 (1), 136 (12), 135 (100), 93 (12), 79 (12).

HR-MS (EI, 70eV): [$C_{18}H_{19}F_3O$], calcd.: 308.1388; found: 308.1382.

4-(Adamantane-1-carbonyl)-2-fluorobenzonitrile (3i)



Following **TP5** *S*-(pyridin-2-yl)-adamantane-1-carbothioate (**1d**, 137 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-cyano-3-fluorophenyl)zinc pivalate (**2g**, 0.95 mmol, 1.9 equiv) prepared according to **TP4** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 114 mg, 0.41 mmol, 81%, colorless crystals.

Purification: pentane:ethyl acetate = 9:1.

m.p.: 103.9 -105.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.66 (dd, *J* = 7.9, 6.2 Hz, 1H), 7.31 (ddd, *J* = 21.5, 8.5, 1.4 Hz, 2H), 2.07 (q, *J* = 3.1 Hz, 3H), 1.93 (d, *J* = 3.0 Hz, 6H), 1.81 – 1.65 (m, 6H).

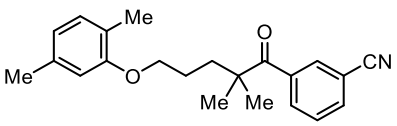
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): 207.6 (d, *J* = 1.4 Hz), 162.6 (d, *J* = 261.2 Hz), 146.3 (d, *J* = 6.2 Hz), 133.5, 123.2 (d, *J* = 3.9 Hz), 115.1 (d, *J* = 20.9 Hz), 113.4, 102.8 (d, *J* = 15.6 Hz), 47.2, 38.8, 36.3, 27.9.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053, 2930, 2901, 2858, 2849, 2673, 2652, 2241, 1682, 1620, 1561, 1497, 1451, 1413, 1344, 1323, 1297, 1276, 1269, 1252, 1225, 1209, 1191, 1179, 1171, 1106, 1099, 1003, 968, 938, 902, 884, 879, 851, 819, 793, 764, 751, 732, 718, 677, 661.

MS (EI, 70 eV): *m/z* (%) = 136 (11), 135 (100), 107 (14), 93 (16), 79 (13).

HR-MS (EI, 70eV): [$C_{18}H_{18}FNO$], calcd.: 283.1372; found: 283.1266.

3-(5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoyl)benzonitrile (3j)



Following **TP5** *S*-(pyridin-2-yl) 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanethioate (**1e**, 172 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-cyanophenyl)zinc pivalate (**2i**, 0.95 mmol, 1.9 equiv) prepared according to **TP4** from the corresponding iodide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 110 mg, 0.33 mmol, 66%, yellow oil.

Purification: pentane:ethyl acetate = 95:5.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.97 (d, *J* = 1.8 Hz, 1H), 7.92 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.74 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.66 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.60 – 6.54 (m, 1H), 3.90 (t, *J* = 6.0 Hz, 2H), 2.29 (s, 3H), 2.13 (s, 3H), 2.02 – 1.91 (m, 2H), 1.80 – 1.67 (m, 2H), 1.37 (s, 6H).

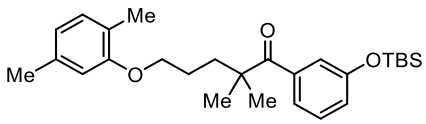
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 206.7, 156.8, 139.8, 136.6, 134.2, 131.8, 131.4, 130.4, 129.3, 123.4, 120.9, 118.2, 112.8, 111.8, 67.5, 47.9, 37.4, 26.0, 25.1, 21.5, 16.0.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2922, 2230, 1677, 1677, 1583, 1508, 1470, 1414, 1388, 1309, 1284, 1262, 1223, 1156, 1128, 1043, 1017, 999, 844, 803, 752, 683.

MS (EI, 70 eV): *m/z* (%) = 335 (4), 214 (100), 144 (13), 130 (26), 122 (17), 102 (10), 83 (12), 55 (15).

HR-MS (EI, 70eV): [$C_{22}H_{25}NO_2$], calcd.: 335.1885, found: 335.1888.

1-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-one (3k)



Following **TP5** *S*-(pyridin-2-yl) 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanethioate (**1e**, 172 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-((*tert*-butyldimethylsilyl)oxy)phenyl)zinc pivalate (**2j**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 158 mg, 0.36 mmol, 78%, pale yellow oil.

Purification: pentane:ethyl acetate = 9:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.13 – 6.99 (m, 2H), 6.93 (t, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.73 (ddd, *J* = 7.8, 2.5, 1.3 Hz, 1H), 6.44 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.37 (d, *J* = 1.5 Hz, 1H), 3.68 (t, *J* = 6.1 Hz, 2H), 2.09 (s, 3H), 1.94 (s, 3H), 1.79 – 1.68 (m, 2H), 1.59 – 1.48 (m, 2H), 1.14 (s, 6H), 0.78 (s, 9H), 0.00 (s, 6H).

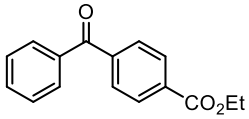
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 208.6, 156.9, 155.4, 140.3, 136.4, 130.3, 129.2, 123.5, 122.7, 120.7, 120.5, 119.3, 111.8, 67.8, 47.7, 37.5, 26.2, 25.7, 25.1, 21.4, 18.2, 15.8, -4.4.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2953, 2927, 1672, 1594, 1576, 1508, 1470, 1421, 1388, 1362, 1251, 1183, 1156, 1129, 1044, 1000, 913, 834, 800, 779, 759, 685.

MS (EI, 70 eV): *m/z* (%) = 320 (23), 319 (100), 235 (32), 83 (8), 73 (14).

HR-MS (EI, 70eV): [$C_{27}H_{40}O_3Si$], calcd.: 440.2747, found: 440.2751.

Ethyl 4-benzoylbenzoate (3l)



Following **TP5** **S**-(pyridin-2-yl) benzothioate (**1f**, 108 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-(ethoxycarbonyl)phenyl)zinc pivalate (**2k**, 0.95 mmol, 1.9 equiv) prepared according to **TP4** at -40 °C from the corresponding iodide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 90 mg, 0.35 mmol, 71% yield, colorless crystals.

Purification: pentane:ethyl acetate = 95:5.

m.p.: 93.6 – 95.4 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.20 – 8.11 (m, 2H), 7.82 (ddd, *J* = 14.6, 7.6, 1.8 Hz, 4H), 7.66 – 7.57 (m, 1H), 7.50 (dd, *J* = 8.4, 7.1 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

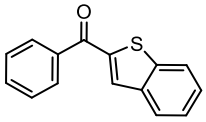
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 196.2, 166.0, 141.3, 137.1, 133.7, 133.1, 130.3, 129.9, 129.6, 128.6, 61.6, 14.5.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2979, 1704, 1660, 1604, 1480, 1446, 1399, 1367, 1266, 1179, 1102, 1019, 1004, 937, 925, 845, 752, 712, 695, 656.

MS (EI, 70 eV): *m/z* (%) = 177 (28), 105 (100), 149 (59), 152 (39), 181 (59), 209 (59), 226 (30), 254 (35).

HR-MS (EI, 70eV): [$C_{16}H_{14}O_3$], calcd.: 254.0943; found:254.0939.

Benzo[*b*]thiophen-2-yl(phenyl)methanone (3m)



Following **TP5**, using TMEDA (10 mol%, 0.05 mmol, 6 mg) as ligand, *S*-(pyridin-2-yl) benzothioate (**1f**, 108 mg, 0.50 mmol, 1.0 equiv) was coupled with (benzo[*b*]thiophen-2-yl)zinc pivalate (**2l**, 0.95 mmol, 1.9 equiv) prepared by directed metalation from benzo[*b*]thiophen and TMPMgCl (1.0 equiv) at 0 °C for 3 h, followed by transmetalation with $Zn(OPiv)_2$ (1.0 equiv) The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 81 mg, 0.34 mmol, 68%, orange oil.

Purification: pentane:ethyl acetate = 9:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.96 – 7.85 (m, 5H), 7.68 – 7.60 (m, 1H), 7.54 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.49 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H).

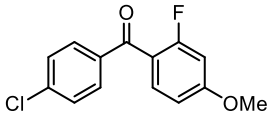
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 189.8, 143.2, 142.8, 139.2, 138.0, 132.6, 132.4, 129.4, 128.7, 127.6, 126.2, 125.2, 123.1.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1631, 1593, 1576, 1509, 1455, 1444, 1425, 1314, 1285, 1245, 1187, 1175, 1157, 1114, 1066, 1025, 880, 869, 833, 790, 746, 731, 708, 701, 664.

MS (EI, 70 eV): *m/z* (%) = 238 (100), 23 (11), 210 (10), 161 (97), 133 (16), 105 (40), 89 (23), 77 (31).

HR-MS (EI, 70eV): [$C_{15}H_{10}OS$], calcd.: 238.0452, found: 238.0454.

(4-Chlorophenyl)(2-fluoro-4-methoxyphenyl)methanone (3n)



Following **TP5** *S*-(pyridin-2-yl) 4-chlorobenzothioate (**1g**, 125 mg, 0.50 mmol, 1.0 equiv) was coupled with (2-fluoro-4-methoxyphenyl)zinc pivalate (**2m**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 121 mg, 0.46, 92%, colorless oil.

Purification: pentan*e*:ethyl acetate = 8:2.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.74 (dd, J = 8.5, 1.6 Hz, 2H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.46 – 7.40 (m, 2H), 6.80 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.66 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.88 (s, 3H).

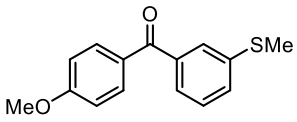
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 191.5 (d, J = 1.0 Hz), 164.2 (d, J = 11.3 Hz), 163.1, 161.9 (d, J = 254.1 Hz), 139.2, 136.7, 132.7 (d, J = 4.4 Hz), 130.9 (d, J = 1.7 Hz), 128.6, 118.9 (d, J = 13.6 Hz), 101.9 (d, J = 25.7 Hz), 55.9.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1671, 1588, 1570, 1560, 1544, 1446, 1426, 1340, 1282, 1235, 1218, 1154, 1116, 1069, 1054, 986, 916, 885, 791, 58, 733, 690.

MS (EI, 70 eV): *m/z* (%) = 139 (16), 153 (100), 154 (9), 187 (9), 220 (11), 264 (25), 266 (8).

HR-MS (EI, 70eV): [$C_{14}H_{10}ClFO_2$], calcd.: 264.0353, found: 264.0351.

(4-Methoxyphenyl)(3-(methylthio)phenyl)methanone (3o)



Following **TP5** *S*-(pyridin-2-yl) 4-methoxybenzothioate (**1h**, 123 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-(methylthio)phenylzinc pivalate (**2n**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 123 mg, 0.48 mmol, 96%, colorless oil.

Purification: pentane:ethyl acetate = 9:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 7.89 – 7.77 (m, 2H), 7.62 (t, *J* = 1.7 Hz, 1H), 7.55 – 7.30 (m, 3H), 7.05 – 6.88 (m, 2H), 3.89 (s, 3H), 2.52 (s, 3H).

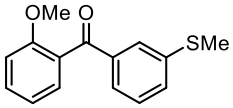
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): 195.3, 163.5, 139.3, 139.0, 132.7, 130.1, 129.8, 128.6, 127.1, 126.5, 113.7, 55.7, 15.8.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2916, 2847, 1650, 1597, 1567, 1507, 1419, 1315, 1282, 1256, 1175, 1154, 1026, 842, 756, 710.

MS (EI, 70 eV): *m/z* (%) = 258 (36), 211 (19), 136 (9) 135 (100), 77 (11).

HR-MS (EI, 70eV): [$C_{15}H_{14}O_2S$], calcd.: 258.0715; found: 258.0709.

(2-Methoxyphenyl)(3-(methylthio)phenyl)methanone (3o')



Following **TP5** *S*-(pyridin-2-yl) 2-methoxybenzothioate (**1h'**, 123 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-(methylthio)phenylzinc pivalate (**2n**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 91 mg, 0.35 mmol, 71%, colorless oil.

Purification: pentane:ethyl acetate = 9:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 7.74 (t, *J* = 1.8 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.39 – 7.29 (m, 2H), 7.04 (td, *J* = 7.4, 0.9 Hz, 1H), 6.99 (dd, *J* = 8.5, 0.9 Hz, 1H), 3.73 (s, 3H), 2.50 (s, 3H).

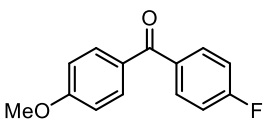
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): 196.2, 157.5, 139.3, 138.5, 132.2, 130.9, 129.8, 128.7, 128.7, 127.0, 127.0, 120.7, 111.6, 55.7, 15.8.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2920, 2836, 1659, 1597, 1581, 1567, 1486, 1462, 1434, 1413, 1294, 1241, 1180, 1154, 1111, 1077, 1047, 1020, 994, 973, 959, 949, 936, 889, 809, 750, 716, 672.

MS (EI, 70 eV): *m/z* (%) = 258 (32), 211 (43), 138 (23), 135 (100), 121 (58), 79 (26), 77 (38)

HR-MS (EI, 70eV): [$C_{15}H_{14}O_2S$], calcd.: 258.0715; found:. 258.0707.

(4-Fluorophenyl)(4-methoxyphenyl)methanone (3p)



Following **TP5** *S*-(pyridin-2-yl) 4-methoxybenzothioate (**1h**, 123 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-fluorophenyl)zinc pivalate (**2f**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 99 mg, 0.43 mmol, 86% yield, white solid.

Purification: pentan*e*:ethyl acetate = 9:1.

m.p.: 97.1 – 98.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (dt, *J* = 8.7, 2.7 Hz, 4H), 7.15 (t, *J* = 8.6 Hz, 2H), 7.03 – 6.92 (m, 2H), 3.89 (s, 3H).

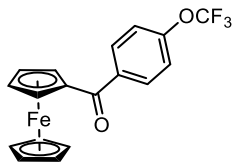
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 194.3, 165.2 (d, *J* = 253.2 Hz), 163.4, 134.6 (d, *J* = 3.1 Hz), 132.6, 132.4 (d, *J* = 9.1 Hz), 130.1, 115.5 (d, *J* = 21.8 Hz), 113.8, 55.7.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3065, 3019, 2973, 2944, 2916, 2846, 1639, 1628, 1594, 1573, 1504, 1499, 1466, 1454, 1442, 1416, 1405, 1302, 1296, 1284, 1256, 1224, 1182, 1175, 1148, 1116, 1094, 1064, 1028, 1013, 967, 959, 949, 928, 856, 842, 828, 815, 789, 763, 682.

MS (EI, 70 eV): *m/z* (%) = 231 (7), 230 (43), 199 (13), 136 (9), 135 (100), 123 (16), 77 (9).

HR-MS (EI, 70eV): [$C_{14}H_{11}FO_2$], calcd.: 230.0743; found: 230.0737.

Ferrocenyl-(4-(trifluoromethoxy)phenyl)methanone (3q)



Following **TP5** *S*-(pyridin-2-yl) ferrocenecarbothioate (**1i**, 162 mg, 0.50 mmol, 1.0 equiv) was coupled with 4-(trifluoromethoxy)phenyl)zinc pivalate (**2o**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 151 mg, 0.40 mmol, 81%, red solid.

Purification: pentan*e*:ethyl acetate = 9:1.

m.p.: 38.2 – 40.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.03 – 7.91 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.89 (t, *J* = 1.9 Hz, 2H), 4.62 (t, *J* = 2.0 Hz, 2H), 4.21 (s, 5H).

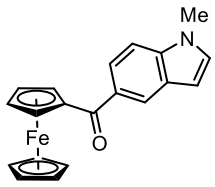
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 197.7, 153.8 – 150.2 (m), 138.2, 130.1, 120.5 (q, *J* = 258.3 Hz), 120.4, 77.9, 73.0, 71.6, 70.4.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2924, 1627, 1598, 1447, 1251, 1213, 1152, 1104, 1054, 1027, 1014, 1002, 968, 951, 923, 852, 822, 767, 713.

MS (EI, 70 eV): *m/z* (%) = 375 (20), 374 (100), 372 (6), 212 (7), 185 (9), 139 (24).

HR-MS (EI, 70eV): [$C_{18}H_{13}F_3FeO_2$], calcd.: 374.0217, found: 374.0214.

Ferrocenyl-(1-methyl-1H-indol-5-yl)methanone (3r)



Following **TP5** *S*-(pyridin-2-yl) ferrocenecarbothioate (**1i**, 162 mg, 0.50 mmol, 1.0 equiv) was coupled with ((1-methyl-1*H*-indol-5-yl)zinc pivalate (**2b**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 144 mg, 0.42, 84%, red oil.

Purification: pentane:ethyl acetate = 8:2.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.32 (d, *J* = 1.8 Hz, 1H), 7.87 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.14 (d, *J* = 3.1 Hz, 1H), 6.62 (d, *J* = 3.1 Hz, 1H), 4.98 (t, *J* = 2.0 Hz, 2H), 4.56 (t, *J* = 2.0 Hz, 2H), 4.21 (s, 5H), 3.85 (s, 3H).

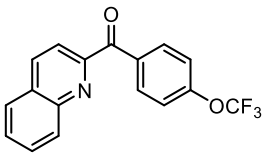
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 199.1, 138.6, 131.6, 130.3, 127.7, 122.7, 122.5, 109.0, 102.7, 79.5, 72.0, 71.9, 70.3, 33.2.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3093, 2920, 1624, 1597, 1564, 1511, 1489, 1441, 1416, 1373, 1337, 1305, 1286, 1267, 1242, 1210, 1149, 1135, 1098, 1081, 1044, 1025, 1000, 900, 841, 818, 776, 753, 736, 722.

MS (EI, 70 eV): *m/z* (%) = 344 (23), 343 (100), 341 (7), 194 (9), 130 (9).

HR-MS (EI, 70eV): [$C_{20}H_{17}FeNO$], calcd.: 343.0660, found: 343.0659.

Quinolin-2-yl(4-(trifluoromethoxy)phenyl)methanone (3s)



Following **TP5** *S*-(pyridin-2-yl) quinoline-2-carbothioate (**1j**, 133 mg, 0.50 mmol, 1.0 equiv) was coupled with 4-(trifluoromethoxy)phenyl)zinc pivalate (**2o**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 108 mg, 0.34 mmol, 68%, colorless oil.

Purification: pentane:ethyl acetate = 99:1.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.41 – 8.33 (m, 3H), 8.20 (dq, *J* = 8.6, 0.9 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.81 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.35 (dq, *J* = 9.1, 1.1 Hz, 2H).

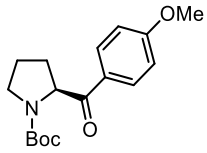
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 192.12, 154.22, 152.76, 152.74, 146.79, 137.48, 134.52, 133.72, 130.65, 130.42, 129.17, 128.85, 127.84, 121.90 – 119.05 (m, 2C)

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1662, 1605, 1587, 1508, 1309, 1295, 1202, 1140, 1112, 967, 957, 920, 850, 835, 794, 769, 743, 669.0

MS (EI, 70 eV): *m/z* (%) = 95, (12), 189 (100), 189 (29), 191 (15), 204 (42), 232 (17), 288 (69), 289 (53), 316 (28), 317 (30).

HR-MS (EI, 70eV): [$C_{17}H_{10}F_3NO_2$], calcd.: 317.0664, found: 317.0660.

***tert*-Butyl (*S*)-2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate (3t)**



Following **TP5** *tert*-butyl (*S*)-2-((pyridin-2-ylthio)carbonyl)pyrrolidine-1-carboxylate (**1k**: 154 mg, 0.50 mmol, 1.0 equiv) was coupled with ((4-methoxyphenyl)zinc pivalate (**2a**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 110 mg, 0.36 mmol, 72%, pale yellow crystals.

Purification: pentane:ethyl acetate = 8:2 → 6:4.

m.p.: 124.8– 126.9 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): (mixture of rotamers) δ = 8.06 – 7.85 (m, 2H), 7.04 – 6.82 (m, 2H), 5.29 (dd, *J* = 9.3, 2.9 Hz, 0H), 5.15 (dd, *J* = 8.8, 3.8 Hz, 1H), 3.87 (s, 2H), 3.85 (s, 1H), 3.71 – 3.58 (m, 1H), 3.54 (dt, *J* = 10.6, 6.6 Hz, 1H), 3.46 (dt, *J* = 10.3, 7.3 Hz, 0H), 2.41 – 2.18 (m, 1H), 1.91 (ttd, *J* = 15.0, 7.2, 3.5 Hz, 3H), 1.46 (s, 3H), 1.25 (s, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): (mixture of rotamers) δ = 197.5, 197.0, 163.7, 163.6, 154.6, 154.0, 130.9, 130.6, 128.3, 128.1, 114.0, 113.9, 79.8, 79.7, 61.1, 60.9, 55.6, 55.6, 46.9, 46.7, 31.1, 30.1, 28.6, 28.3, 24.3, 23.7.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2972, 1680, 1597, 1574, 1510, 1477, 1455, 1391, 1363, 1307, 1254, 1228, 1158, 1115, 1080, 1025, 1010, 988, 918, 880, 838, 809, 771, 688.

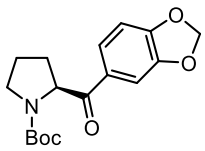
MS (EI, 70 eV): *m/z* (%) = 170 (34), 125 (81), 114 (89), 77 (13), 70 (100), 57 (67), 41 (14).

HR-MS (EI, 70eV): [$C_{17}H_{23}NO_4$], calcd.: 305.1627, found: 305.1624.

Optical rotation: $[\alpha]_D^{20}$ = -23 (c 1.02, $CHCl_3$).

Chiral HPLC: 99% *ee*, OJ-H column, *i*PrOH:heptane = 95:5, 1.0 mL/min, 30 °C.

***tert*-Butyl (*S*)-2-(benzo[*d*][1,3]dioxole-5-carbonyl)pyrrolidine-1-carboxylate (3u)**



Following **TP5** *tert*-butyl 2-((pyridin-2-ylthio)carbonyl)pyrrolidine-1-carboxylate (**1k**, 154 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-(dimethylamino)phenyl)zinc pivalate (**2c**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 130 mg, 0.41 mmol, 82%, brown oil.

Purification: : pentane:ethyl acetate = 8:2.

^{1}H-NMR (400 MHz, DMSO-d6**, ppm):** (mixture of rotamers) δ = 7.66 (ddd, *J* = 8.2, 2.8, 1.7 Hz, 1H), 7.49 (t, *J* = 1.9 Hz, 1H), 7.06 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.15 (s, 2H), 5.25 (ddd, *J* = 10.8, 9.0, 3.8 Hz, 1H), 3.39 (dddd, *J* = 14.2, 11.8, 7.3, 4.6 Hz, 2H), 2.37 – 2.23 (m, 1H), 1.91 – 1.63 (m, 4H), 1.38 (s, 4H), 1.17 (s, 6H).

^{13}C-NMR (100 MHz, DMSO-d$_6$, ppm): δ = (mixture of rotamers)197.3, 196.5, 153.8, 153.4, 152.1, 148.4, 129.7, 129.5, 125.2, 125.0, 108.7, 108.7, 108.2, 108.0, 102.6, 102.6, 79.0, 78.8, 61.0, 61.0, 47.0, 46.9, 31.0, 30.1, 28.6, 28.3, 27.5, 24.3, 23.6.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2974, 1682, 1614, 1605, 1505, 1488, 1442, 1392, 1364, 1245, 1160, 1120, 1108, 1097, 1034, 1000, 973, 927, 910, 884, 856, 807, 772, 740, 718.

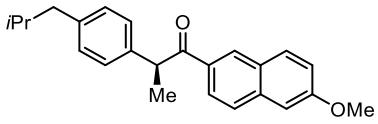
MS (EI, 70 eV): *m/z* (%) = 319 (4), 246 (11), 170 (48), 149 (100), 121 (18), 70 (75), 58 (23), 57 (48), 43 (53).

HR-MS (EI, 70eV): [$C_{17}H_{21}NO_5$], calcd.: 319.1420, found: 319.1411.

Optical rotation: $[\alpha]_D^{20}$ = -29 (c 0,4 $CHCl_3$).

Chiral HPLC: >99% *ee*, OJ-H column, *i*PrOH:heptane = 99:1, 1.0 mL/min, 30 °C.

(*S*)-2-(4-Isobutylphenyl)-1-(6-methoxynaphthalen-2-yl)propan-1-one (3v)



Following **TP5** *S*-(pyridin-2-yl) (*S*)-2-(4-isobutylphenyl)propanethioate (**1l**, 150 mg, 0.50 mmol, 1.0 equiv) was coupled with (6-methoxynaphthalen-2-yl)zinc pivalate (**2p**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 144 mg, 0.42 mmol, 89%, white solid.

Purification: *pentane*:ethyl acetate = 95:5 → 9:1.

m.p.: 70.1 – 72.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.34 (d, J = 1.7 Hz, 1H), 7.92 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.07 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 7.00 – 6.96 (m, 2H), 4.72 (q, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 2.31 (d, *J* = 7.2 Hz, 2H), 1.71 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.49 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 200.4, 159.8, 140.4, 139.1, 137.2, 132.0, 131.3, 130.4, 129.8, 127.9, 127.6, 127.1, 125.5, 119.7, 105.7, 77.1, 55.5, 47.4, 5.1, 30.3, 22.5, 22.5, 19.8.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954, 2923, 1670, 1622, 1508, 1480, 1458, 1438, 1389, 1369, 1337, 1271, 1264, 1231, 1200, 1167, 1150, 1061, 1024, 945, 911, 901, 893, 864, 856, 849, 830, 817, 801, 776, 770, 762, 738, 698.

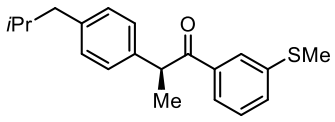
MS (EI, 70 eV): *m/z* (%) = 142 (7), 157 (13), 185 (100), 186 (13), 346 (1).

HR-MS (EI, 70eV): [$C_{24}H_{26}O_2$], calcd.: 346.1933, found: 346.1027.

Optical rotation: $[\alpha]_D^{20}$ = -89 (c 1.02, $CHCl_3$).

Chiral HPLC: 97% *ee*, OD-H column, *i*PrOH:heptane = 98:2, 1.0 mL/min, 30 °C.

(*S*)-2-(4-*iso*-Butylphenyl)-1-(3-(methylthio)phenyl)propan-1-one (3w)



Following **TP5** *S*-(pyridin-2-yl) 2-(4-isobutylphenyl)propanethioate (**1l**, 150 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-(methylthio)phenylzinc pivalate (**2n**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 110 mg, 0.35 mmol, 71%, colourless oil

Purification: pentane:ethyl acetate = 98:2

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (t, J = 1.8 Hz, 1H), 7.69 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.34 (ddd, *J* = 7.8, 2.0, 1.1 Hz, 1H), 7.32 – 7.23 (m, 1H), 7.20 – 7.14 (m, 2H), 7.09 – 7.02 (m, 2H), 4.61 (q, *J* = 6.9 Hz, 1H), 2.45 (s, 3H), 2.40 (d, *J* = 7.2 Hz, 2H), 1.80 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.51 (d, *J* = 6.9 Hz, 3H), 0.86 (dd, J = 6.6, 0.8 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 200.1, 140.4, 139.4, 138.5, 137.1, 130.6, 129.8, 128.7, 127.4, 126.1, 125.4, 47.7, 45.0, 30.2, 22.4, 22.4, 19.5, 15.6.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2957, 2926, 1682, 1584, 1569, 1509, 1465, 1453, 1415, 1384, 1373, 1333, 1215, 1080, 1061, 1014, 960, 882, 848, 795, 747, 686, 667.

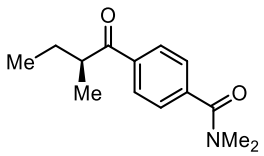
MS (EI, 70 eV): *m/z* (%) = 312 (4), 161 (35), 152 (9), 151 (100), 123 (10).

HR-MS (EI, 70eV): [$C_{20}H_{24}OS$], calcd.: 312. 1548, found: 312.2539.

Optical rotation: $[\alpha]_D^{20}$ = 107 (c 0.53, $CHCl_3$).

Chiral HPLC: 94% *ee*, OD-H column, *i*PrOH:heptane = 98:2, 1.0 mL/min, 30 °C.

(*S*)-*N*,*N*-Dimethyl-4-(2-methylbutanoyl)benzamide (3x)



Following **TP5** *S*-(pyridin-2-yl) (*S*)-2-methylbutanethioate (**1m**, 98 mg, 0.50 mmol, 1.0 equiv) was coupled with (4-(dimethylcarbamoyl)phenyl)zinc pivalate (**2q**, 0.95 mmol, 1.9 equiv) prepared according to **TP4** from the corresponding iodide at 0 °C in 2 h. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 80 mg, 0.34 mmol, 69%, yellow oil

Purification: pentane:ethyl acetate = 6:4, 5% NEt_3

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.03 – 7.94 (m, 2H), 7.54 – 7.47 (m, 2H), 3.38 (h, *J* = 6.7 Hz, 1H), 3.13 (s, 3H), 2.96 (s, 3H), 1.82 (dqd, *J* = 13.8, 7.4, 6.3 Hz, 1H), 1.49 (ddd, *J* = 14.0, 7.6, 6.8 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 203.9, 170.6, 140.4, 137.4, 128.4, 127.3, 42.3, 26.6, 16.6, 11.7.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2963, 2933, 2363, 1684, 1636, 1508, 1458, 1396, 1266, 1219, 1081, 1015, 971, 861, 839, 709, 699.

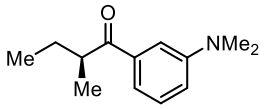
MS (EI, 70 eV): *m/z* (%) = 233 (7), 189 (5), 177 (11), 176 (100), 120 (6), 104 (11).

HR-MS (EI, 70eV): [$C_{14}H_{19}NO_2$], calcd.: 233.1416, found: 233.1407.

Optical rotation: $[\alpha]_D^{20} = 13$ (c 0.1, $CHCl_3$).

Chiral HPLC: >95% *ee*, AD-H column, *i*PrOH:heptane = 99:1, 2.0 mL/min, 30 °C.

(*S*)-1-(3-(Dimethylamino)phenyl)-2-methylbutan-1-one (3y)



Following **TP5** *S*-(pyridin-2-yl) 2-(4-isobutylphenyl)propanethioate (**1m**, 150 mg, 0.50 mmol, 1.0 equiv) was coupled with (3-(methylthio)phenylzinc pivalate (**2r**, 0.95 mmol, 1.9 equiv) prepared according to **TP3** from the corresponding bromide. The solution was stirred for 4 h and was worked-up as usual.

Isolated yield: 110 mg, 0.35 mmol, 71%, colorless oil

Purification: pentane:ethyl acetate = 98:2

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.35 – 7.15 (m, 3H), 6.86 (ddd, *J* = 8.0, 2.6, 1.3 Hz, 1H), 3.34 (h, *J* = 6.7 Hz, 1H), 2.94 (s, 6H), 1.78 (ddd, *J* = 13.9, 7.5, 6.5 Hz, 1H), 1.52 – 1.37 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 205.3, 150.7, 137.6, 129.1, 116.8, 116.5, 111.5, 42.2, 40.6, 39.4, 35.3, 26.8, 17.0, 11.9.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2965, 2932, 2874, 1677, 1597, 1574, 1496, 1460, 1434, 1353, 1261, 1213, 1146, 1062, 986, 943, 865, 773, 7421, 682.

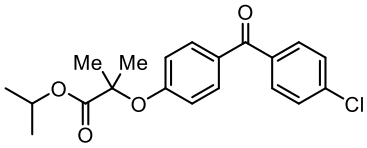
MS (EI, 70 eV): *m/z* (%) = 205 (77), 149 (12), 148 (74), 137 (22), 136 (14), 121 (38), 120 (100), 77 (15).

HR-MS (EI, 70eV): [$C_{13}H_{19}NO$], calcd.: 205.1467, found: 205.1460.

Optical rotation: $[\alpha]_D^{20} = 41$ (c 1.05, $CHCl_3$).

Chiral HPLC: 98% *ee*, OD-H column, *i*PrOH:heptane = 99:1, 1.0 mL/min, 30 °C.

Fenofibrate (3z)



KOH (560 mg, 1.0 equiv, 10 mmol) was added to a solution of 4-iodophenol (**6**, 2.2 g, 10 mmol, 1.0 equiv) in EtOH (20 mL) at 0 °C. After 30 min, isopropyl 2-bromo-2-methylpropanoate (**7**, 2.09 g, 10 mmol, 1.0 equiv) was added and the mixture was refluxed for 16 h. After solvent evaporation the product was subjected to column chromatographical purification with *i*hexane/EtOAc (98:2) as eluent. Isopropyl 2-(4-iodophenoxy)-2-methylpropanoate (**8**) was obtained as a yellow oil (2.44 g, 7 mmol, 70% yield).

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57 – 7.44 (m, 2H), 6.71 – 6.51 (m, 2H), 5.17 – 4.95 (m, 1H), 1.57 (s, 7H), 1.21 (d, J = 6.3 Hz, 6H).

Magnesium turnings (1.2 equiv), dry LiCl (1.2 equiv), $Zn(OPiv)_2$ (1.0 equiv) and dry THF (0.5 M) were added to a dry and argon flushed *Schlenk*-tube equipped with a magnetic stirring bar and a septum. The tube was charged with isopropyl 2-(4-iodophenoxy)-2-methylpropanoate (**8**, 1.0 equiv) at room temperature. To monitor the progress of the insertion reaction, reaction aliquots were quenched with iodine and analyzed by GC-analysis. The insertion was completed within 4 h and the concentration was determined by titration with iodine, yielding (4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenylzinc pivalate **2s** in 70%.

A dry and argon flushed *Schlenk*-tube equipped with a magnetic stirring bar and a septum was charged with $CoCl_2$ (3.25 mg, 0.025 mmol, 0.10 equiv, dried in *vacuo* at 400 °C prior to use). Then, the ligand 4,4'-di-*tert*-butyl-2,2'-dipyridyl (6.5 mg, 0.25 mmol, 0.10 equiv) and *S*-(pyridin-2-yl) 4-chlorobenzothioate (**1g**, 63 mg, 0.25 mmol, 1.0 equiv) added to the *Schlenk*-tube. The resulting mixture was dissolved in dry THF (0.5 mL). Then, (4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenylzinc pivalate (**2t**, 0.48 mmol, 1.9 equiv) was added and stirring

was continued for 4 h, at 25 °C. Upon consumption of the starting material, satured aq. NH_4Cl solution (10 mL) was added, the phases were separated and the aqueous phase was extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over $MgSO_4$. The solvents were evaporated and the residue was subjected to column chromatographical purification.

Isolated yield: 59 mg, 0.16 mmol, 64% yield, colorless solid.

Purification: pentane:ethyl acetate = 90:10.

m.p.:65.6 – 67.4 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 7.75 – 7.71 (m, 2H), 7.71 – 7.66 (m, 2H), 7.50 – 7.41 (m, 2H), 6.91 – 6.82 (m, 2H), 5.08 (h, *J* = 6.3 Hz, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.2 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 194.3, 173.1, 159.7, 138.4, 136.4, 132.0, 131.2, 130.2, 128.5, 117.2, 79.4, 69.4, 25.4, 21.5.

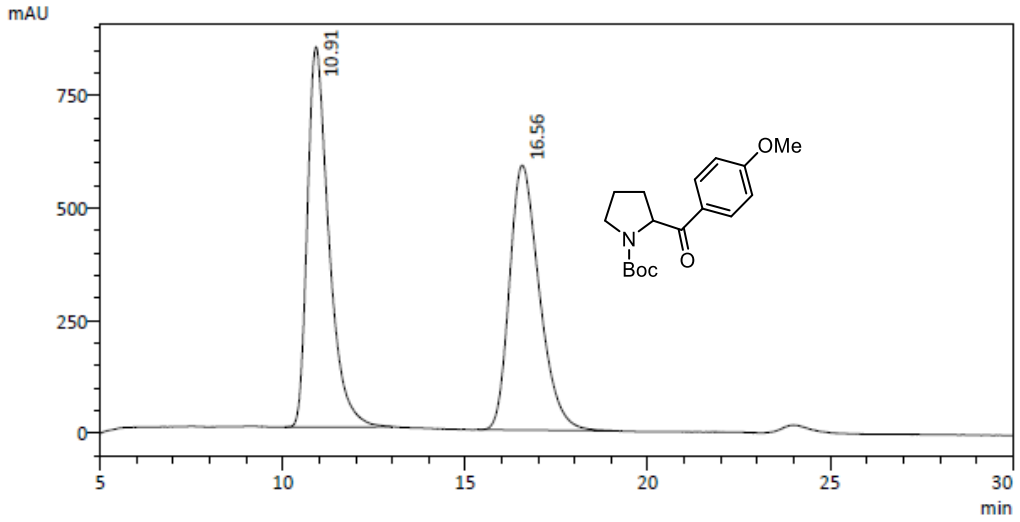
FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2983, 2932, 1728, 1653, 1898, 1496, 1466, 1384, 1285, 1242, 1173, 1143, 4401, 1090, 1014, 972, 926, 898, 843, 825, 762, 740, 682, 655.

MS (EI, 70 eV): *m/z* (%) = 121 (100), 138 (78), 140 26), 197 (70), 232 (66), 234 (21), 273 (65), 275 (26), 360 (5).

HR-MS (EI, 70eV): [$C_{20}H_{21}ClO_4$], calcd.: 360.1128, found: 360.1125.

Chiral HPLC analysis

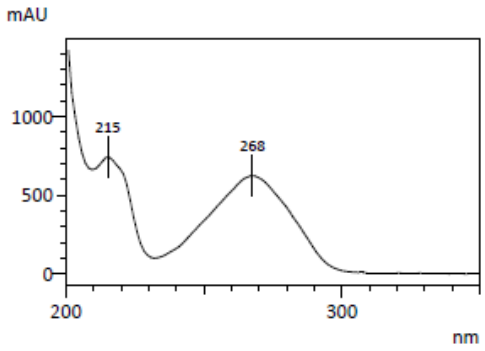
***tert*-Butyl (R/*S*)-2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate (3t)**



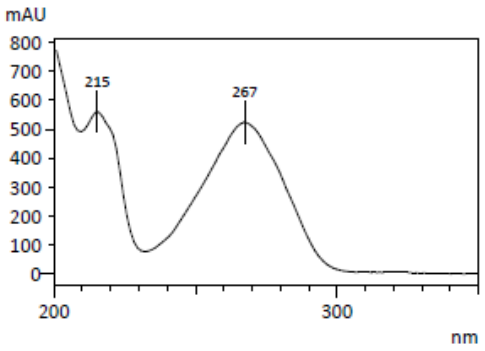
PDA Ch2 205nm

Peak#	Ret. Time	Area	Height	Area%
1	10.91	34590934	845603	50.8
2	16.56	33536738	588075	49.2
Total				100.0

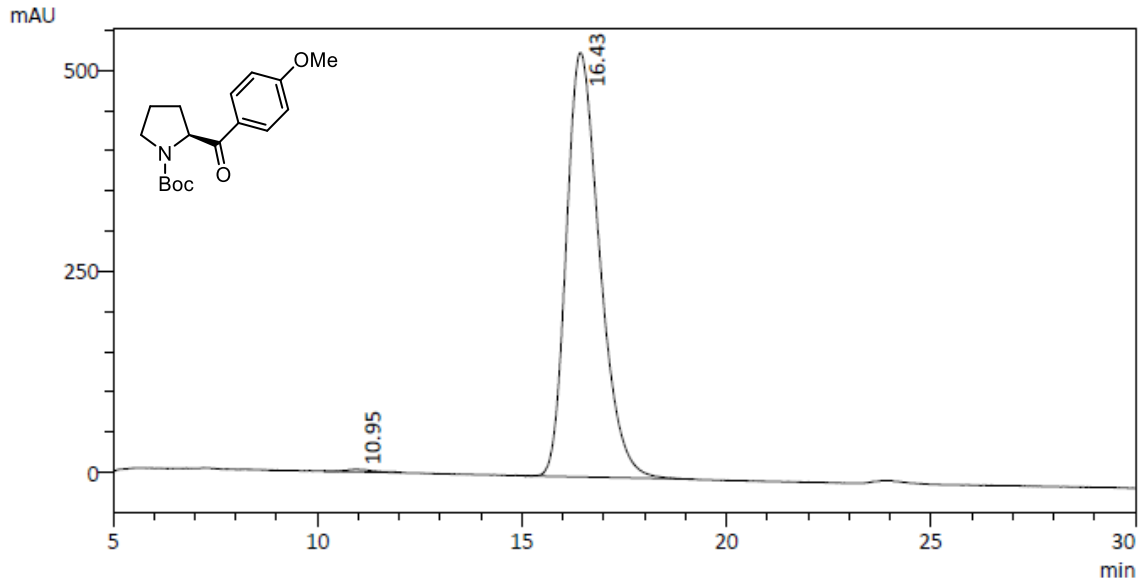
UV Spectrum
Peak#: 1
Retention Time: 10.912 min



UV Spectrum
Peak#: 2
Retention Time: 16.560 min



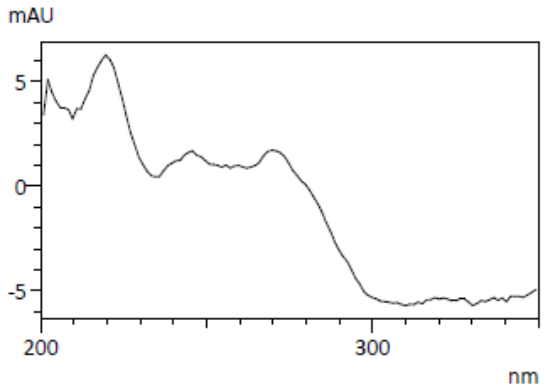
***tert*-Butyl (*S*)-2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate (3t)**



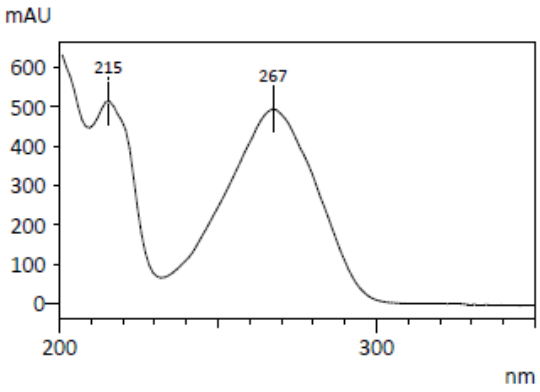
PDA Ch2 205nm

Peak#	Ret. Time	Area	Height	Area%
1	10.95	144744	3265	0.5
2	16.43	29893047	527759	99.5
Total				100.0

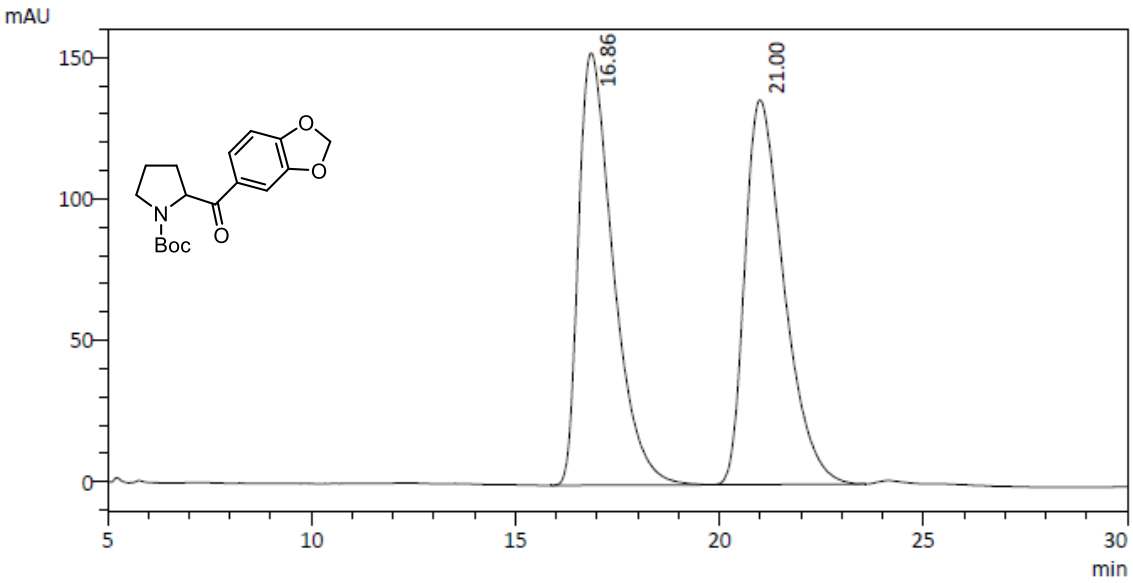
UV Spectrum
Peak#: 1
Retention Time: 10.947 min



UV Spectrum
Peak#: 2
Retention Time: 16.429 min



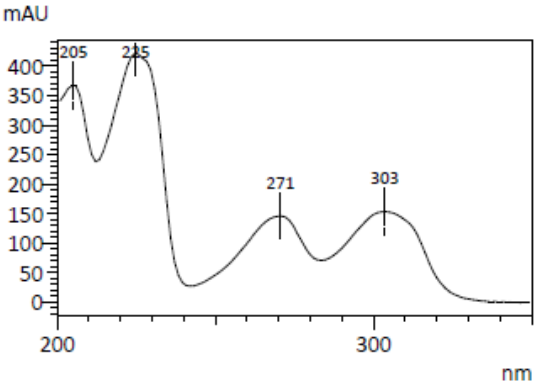
***tert*-Butyl (R/S)-2-(benzo[*d*][1,3]dioxole-5-carbonyl)pyrrolidine-1-carboxylate (3u)**



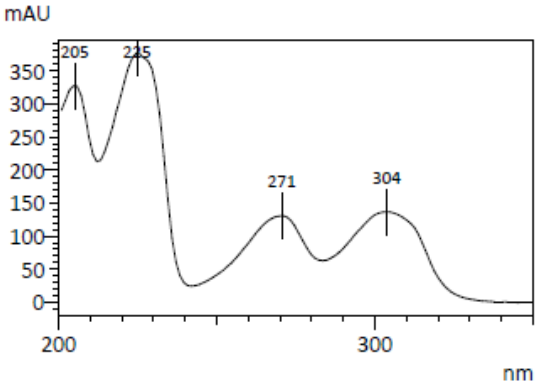
PDA Ch2 303nm

Peak#	Ret. Time	Area	Height	Area%
1	16.86	9027923	152766	49.9
2	21.00	9081683	135945	50.1
Total				100.0

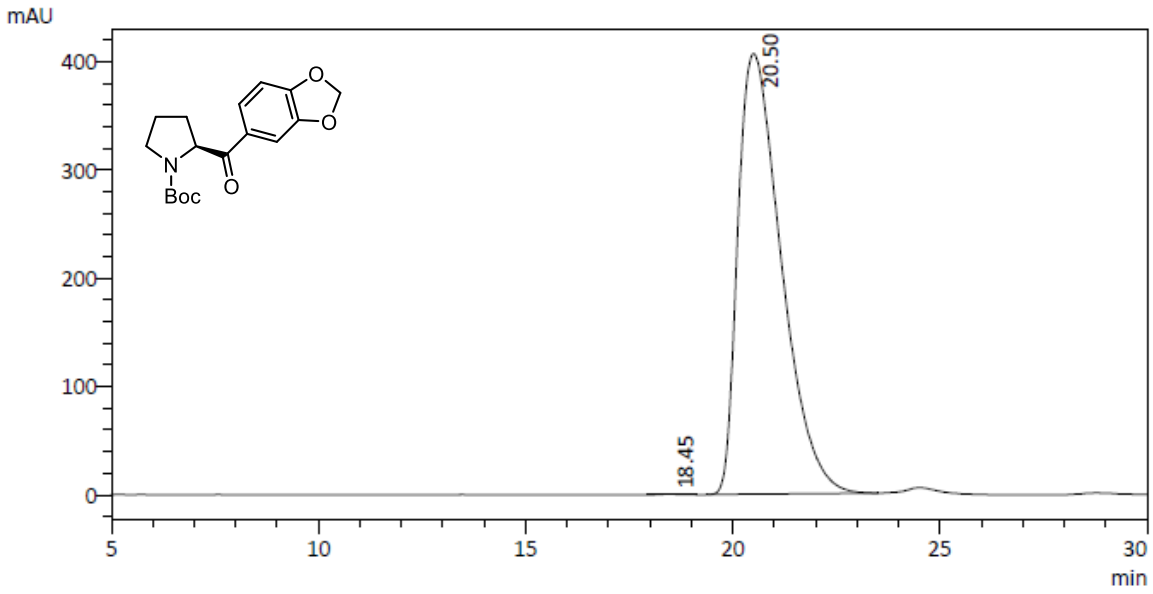
UV Spectrum
Peak#: 1
Retention Time: 16.859 min



UV Spectrum
Peak#: 2
Retention Time: 20.998 min



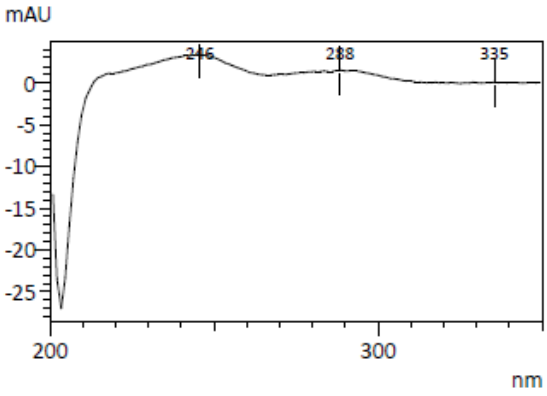
***tert*-Butyl (S)-2-(benzo[*d*][1,3]dioxole-5-carbonyl)pyrrolidine-1-carboxylate (3u)**



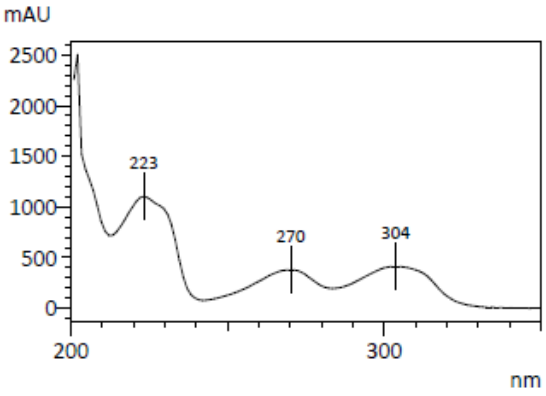
PDA Ch2 303nm

Peak#	Ret. Time	Area	Height	Area%
1	18.45	15261	456	0.1
2	20.50	29617587	406667	99.9
Total				100.0

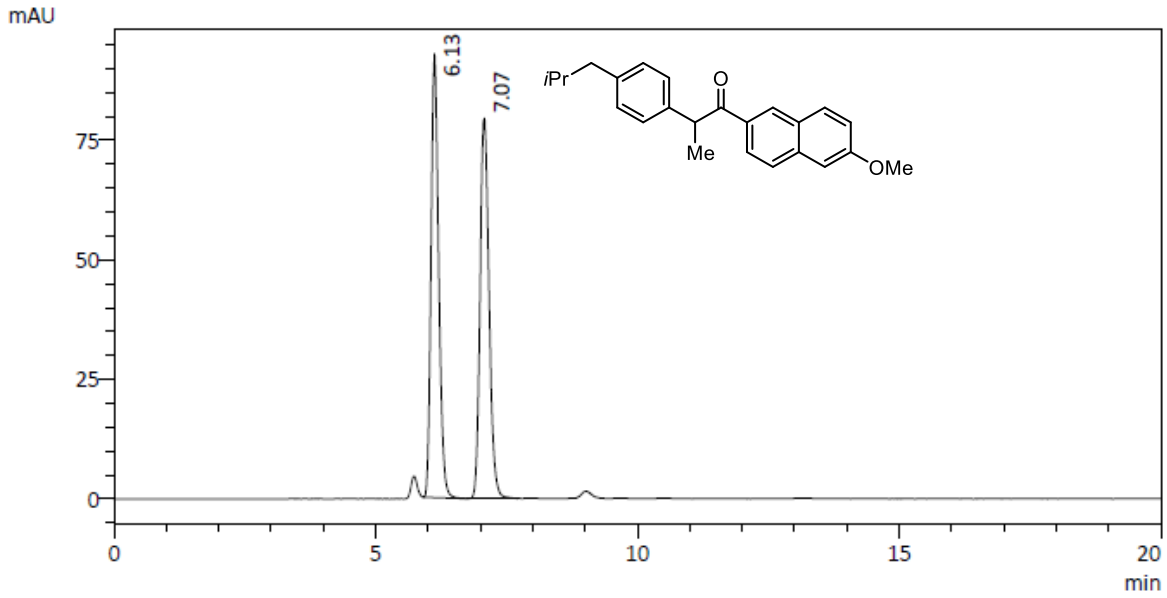
UV Spectrum
Peak#: 1
Retention Time: 18.446 min



UV Spectrum
Peak#: 2
Retention Time: 20.503 min



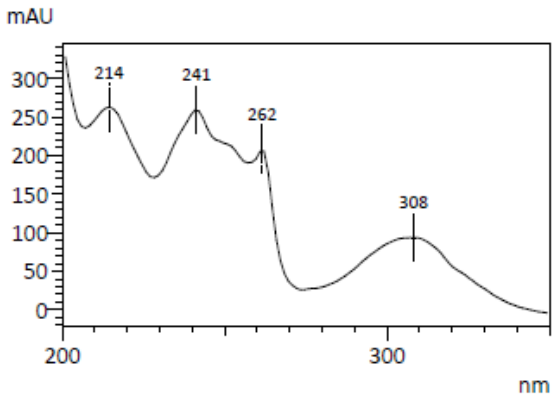
(R/*S*)-2-(4-*iso*-Butylphenyl)-1-(6-methoxynaphthalen-2-yl)propan-1-one (3v)



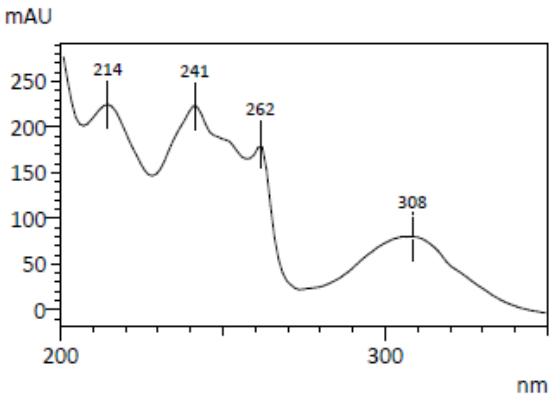
PDA Ch2 308nm

Peak#	Ret. Time	Area	Height	Area%
1	6.13	940487	92827	49.8
2	7.07	948746	79468	50.2
Total				100.0

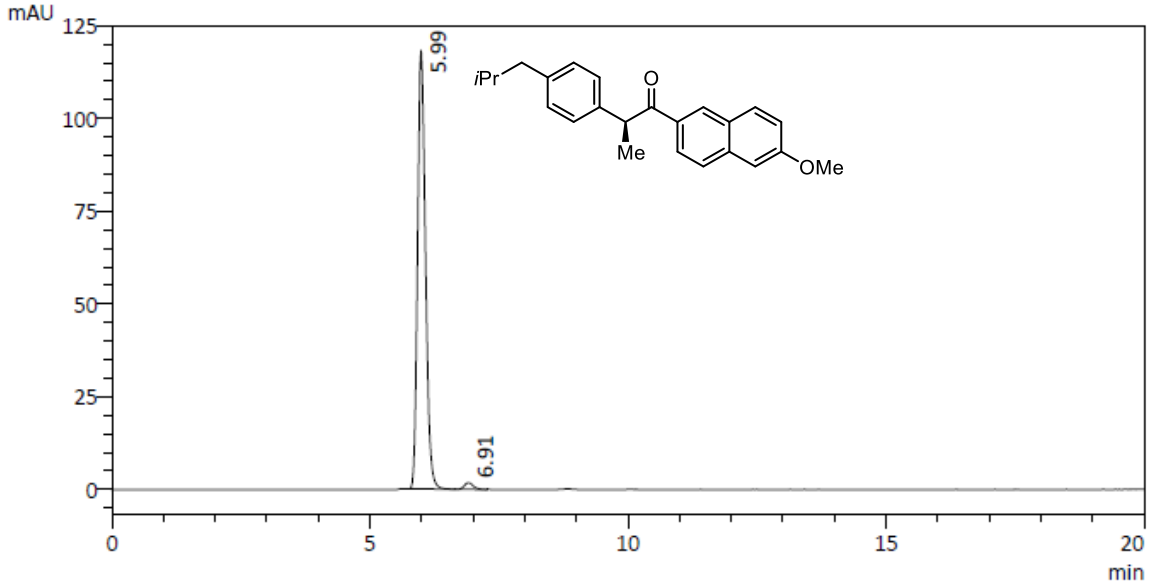
UV Spectrum
Peak#: 1
Retention Time: 6.125 min



UV Spectrum
Peak#: 2
Retention Time: 7.074 min



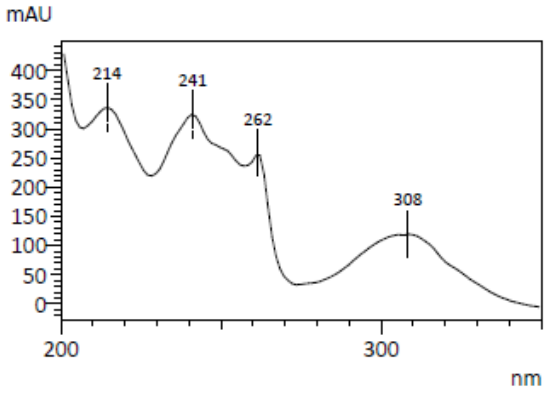
(R/*S*)-2-(4-*iso*-Butylphenyl)-1-(6-methoxynaphthalen-2-yl)propan-1-one (3v)



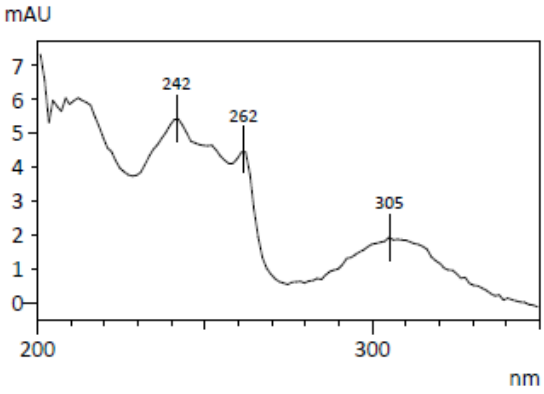
PDA Ch2 308nm

Peak#	Ret. Time	Area	Height	Area%
1	5.99	1260220	118202	98.3
2	6.91	21578	1804	1.7
Total				100.0

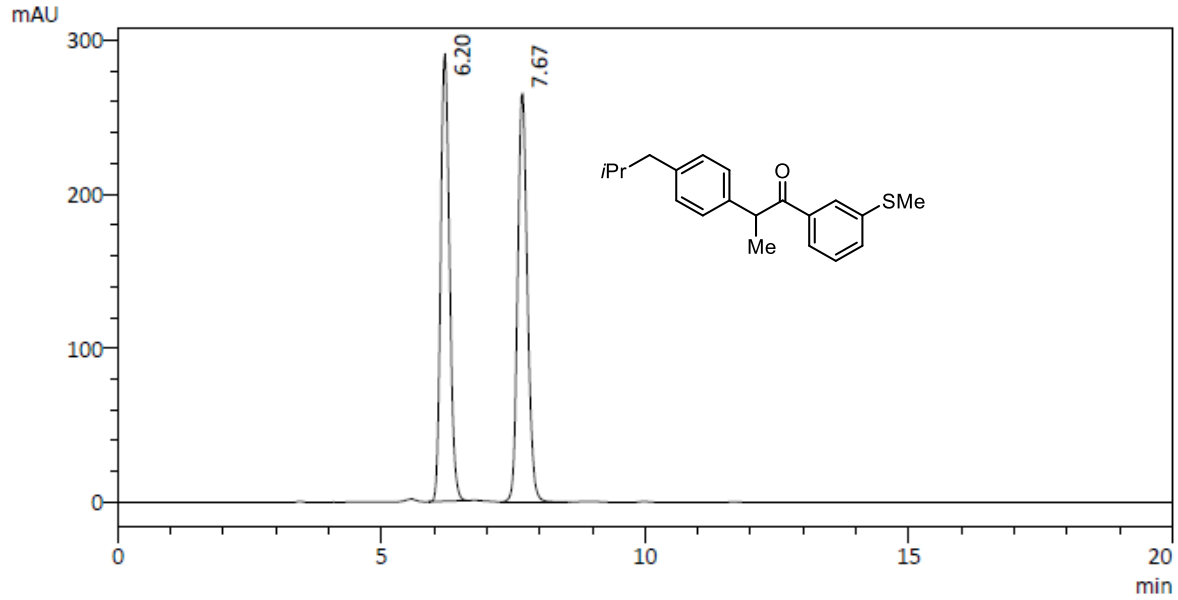
UV Spectrum
Peak#: 1
Retention Time: 5.994 min



UV Spectrum
Peak#: 2
Retention Time: 6.913 min



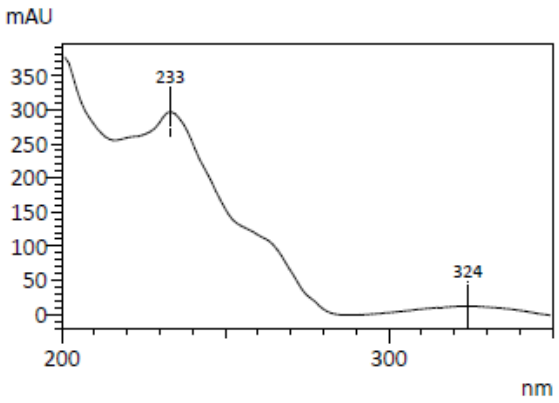
(R/*S*)-2-(4-*iso*-Butylphenyl)-1-(3-(methylthio)phenyl)propan-1-one (3w)



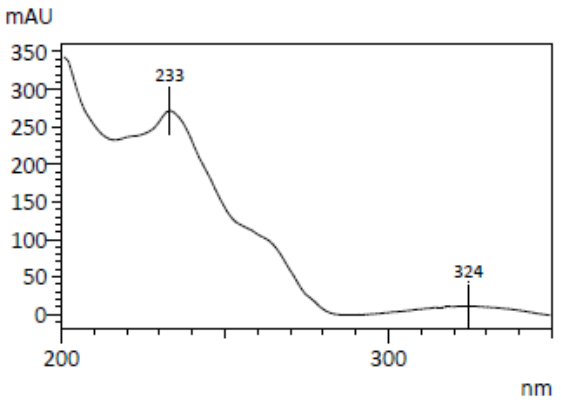
PDA Ch2 233nm

Peak#	Ret. Time	Area	Height	Area%
1	6.20	3372405	290642	49.7
2	7.67	3419067	265543	50.3
Total				100.0

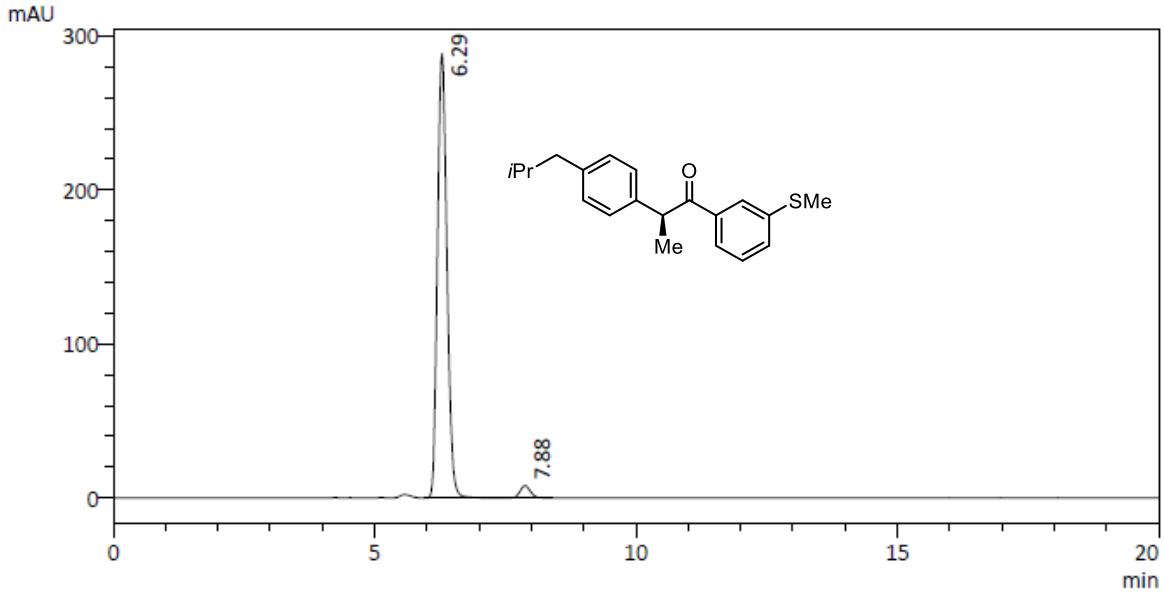
UV Spectrum
Peak#: 1
Retention Time: 6.203 min



UV Spectrum
Peak#: 2
Retention Time: 7.672 min



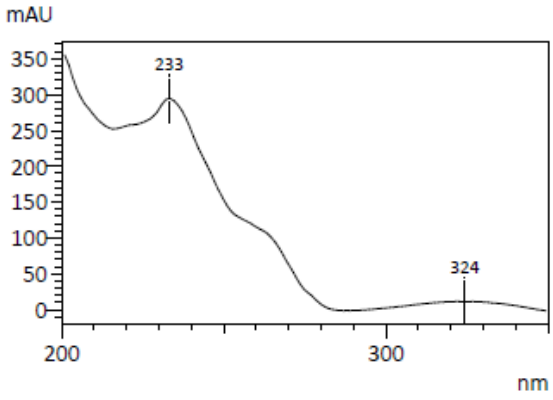
(*S*)-2-(4-*iso*-Butylphenyl)-1-(3-(methylthio)phenyl)propan-1-one (3w)



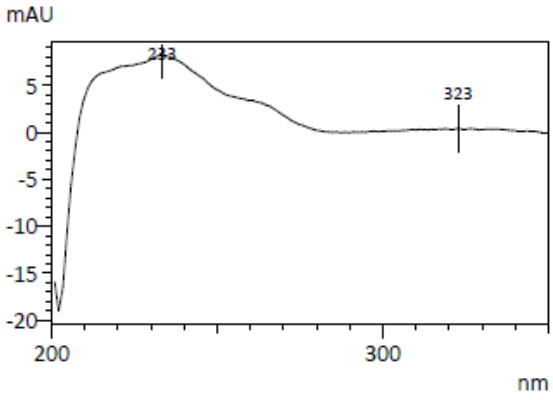
PDA Ch2 233nm

Peak#	Ret. Time	Area	Height	Area%
1	6.29	3644451	288696	97.0
2	7.88	111762	8053	3.0
Total				100.0

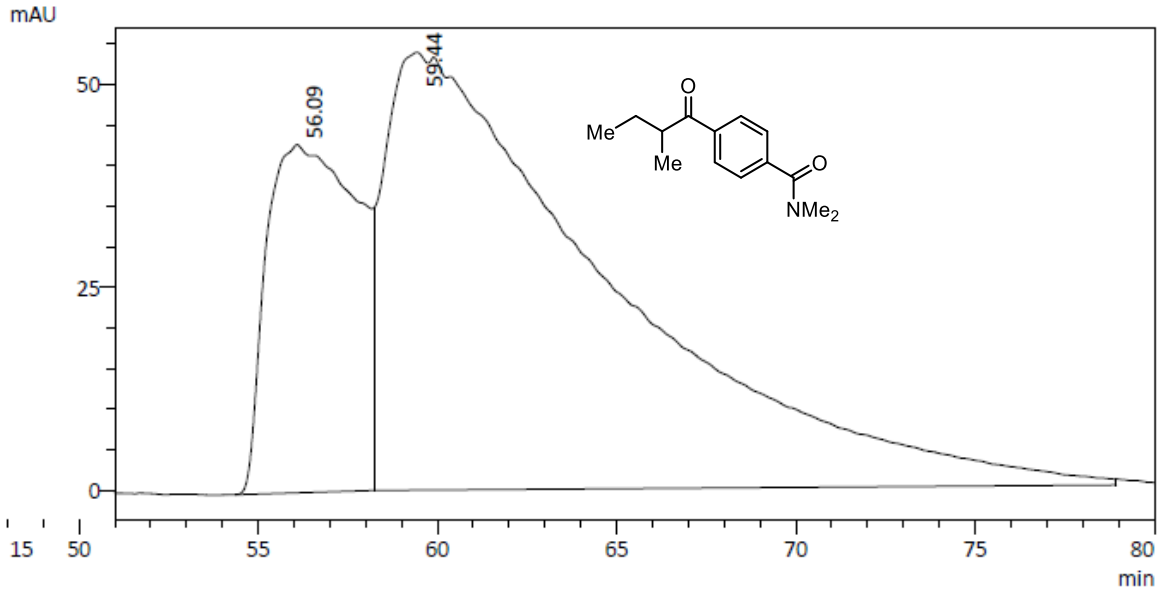
UV Spectrum
Peak#: 1
Retention Time: 6.289 min



UV Spectrum
Peak#: 2
Retention Time: 7.877 min



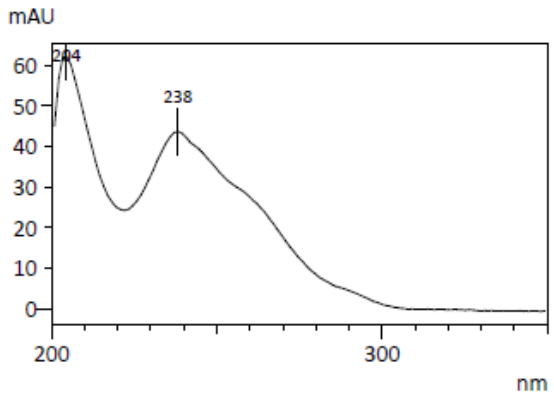
(R/*S*)-*N*,*N*-Dimethyl-4-(2-methylbutanoyl)benzamide (3x)



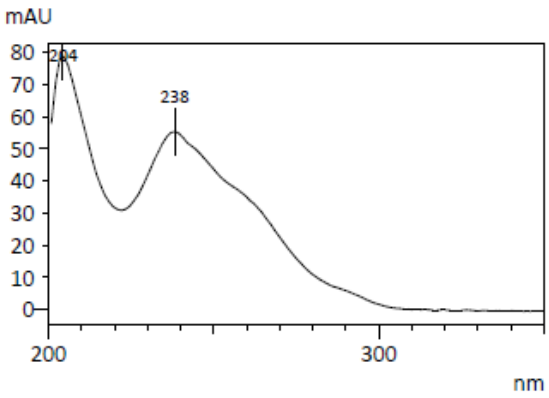
PDA Ch2 238nm

Peak#	Ret. Time	Area	Height	Area%
1	56.09	7545482	42833	24.3
2	59.44	23532946	53869	75.7
Total				100.0

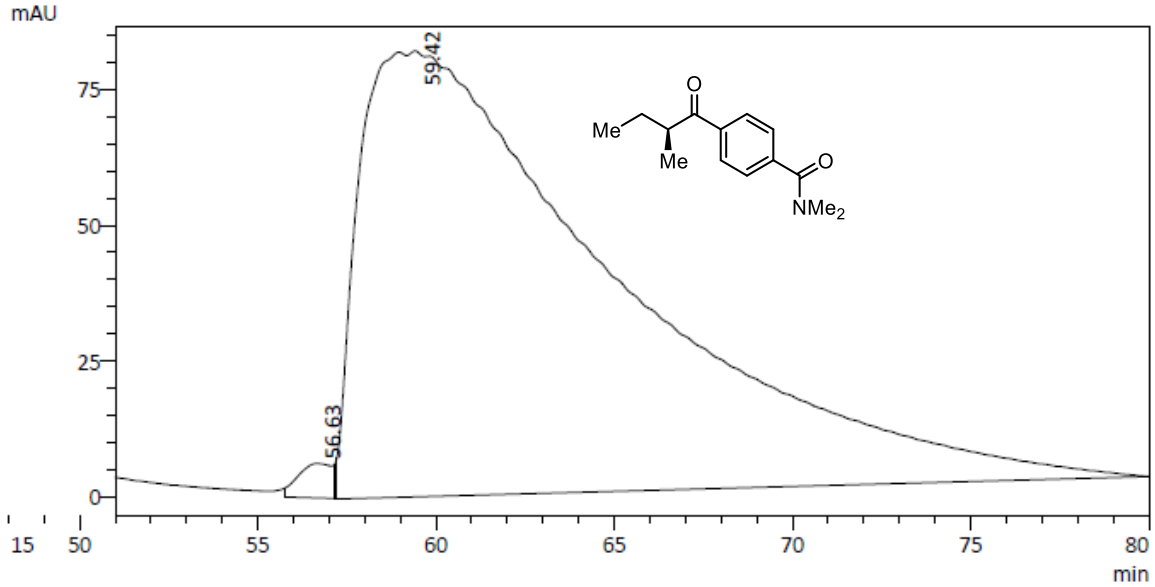
UV Spectrum
Peak#: 1
Retention Time: 56.086 min



UV Spectrum
Peak#: 2
Retention Time: 59.443 min



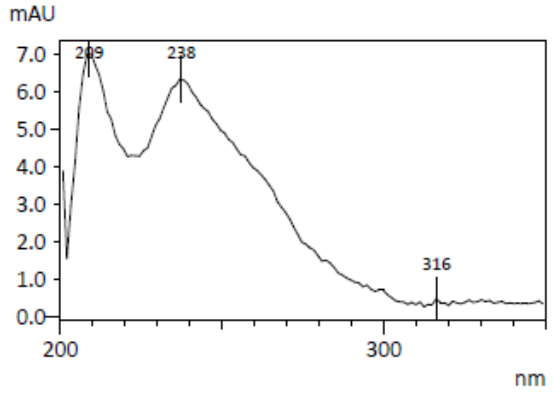
(*S*)-*N*,*N*-Dimethyl-4-(2-methylbutanoyl)benzamide (3x)



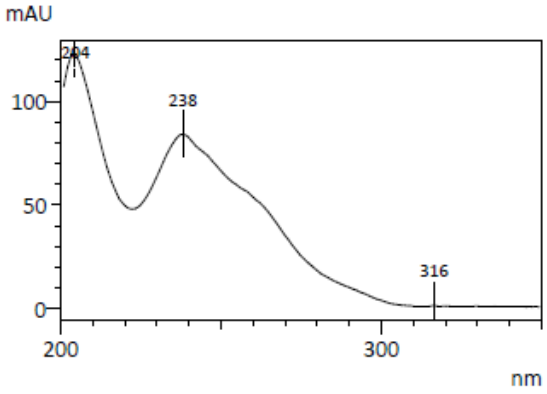
PDA Ch2 238nm

Peak#	Ret. Time	Area	Height	Area%
1	56.63	416671	6326	1.0
2	59.42	41146287	82083	99.0
Total				100.0

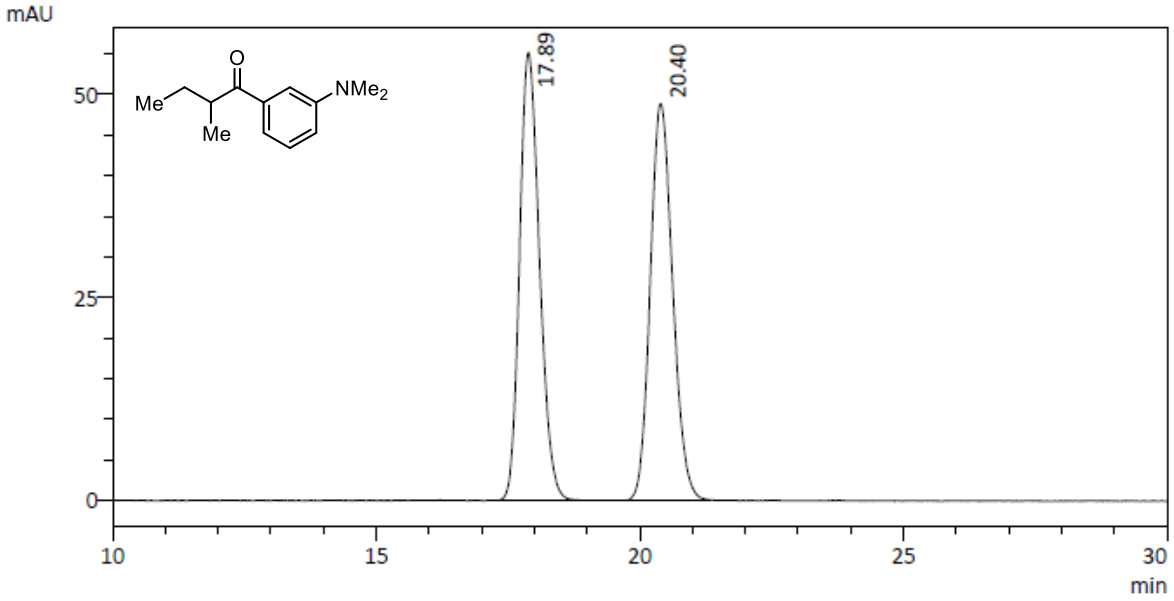
UV Spectrum
Peak#: 1
Retention Time: 56.629 min



UV Spectrum
Peak#: 2
Retention Time: 59.421 min



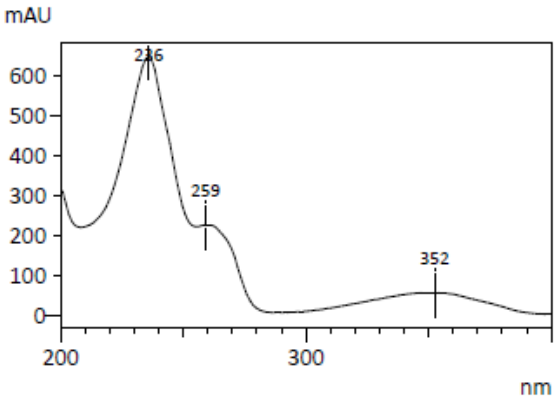
(R/*S*)-1-(3-(Dimethylamino)phenyl)-2-methylbutan-1-one (3y)



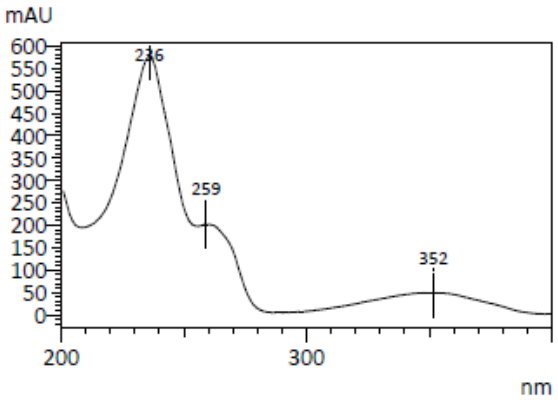
PDA Ch2 352nm

Peak#	Ret. Time	Area	Height	Area%
1	17.89	1445365	55158	50.0
2	20.40	1445361	48838	50.0
Total				100.0

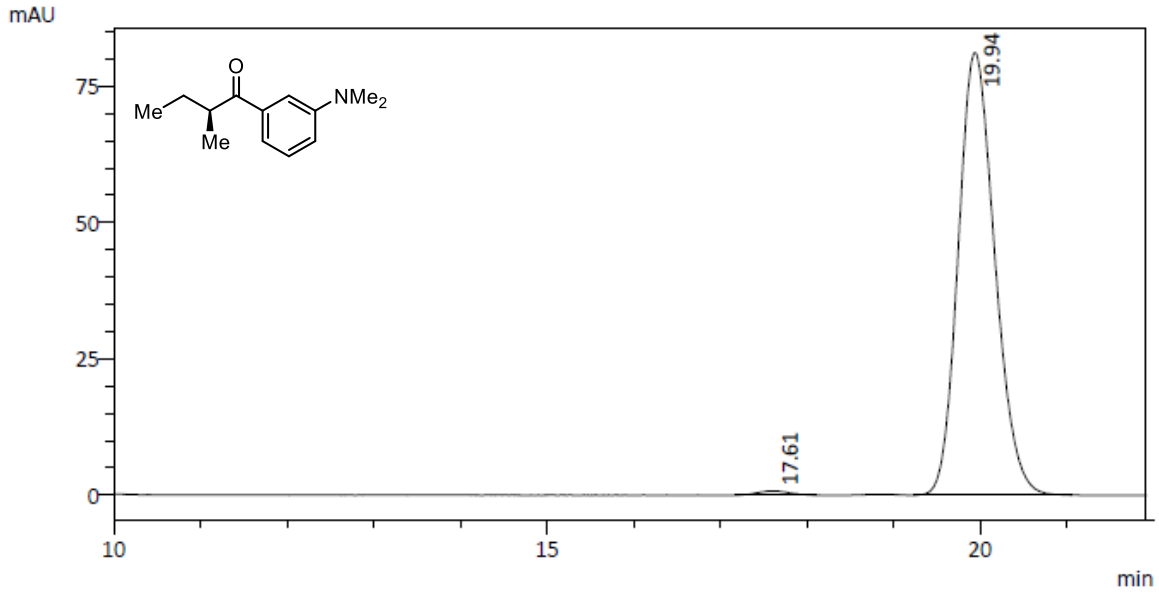
UV Spectrum
Peak#: 1
Retention Time: 17.890 min



UV Spectrum
Peak#: 2
Retention Time: 20.398 min



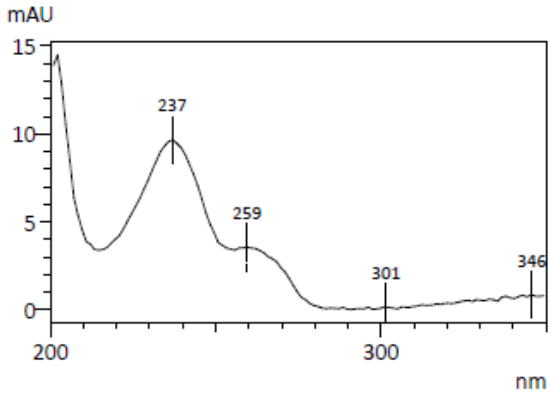
(*S*)-1-(3-(Dimethylamino)phenyl)-2-methylbutan-1-one (3y)



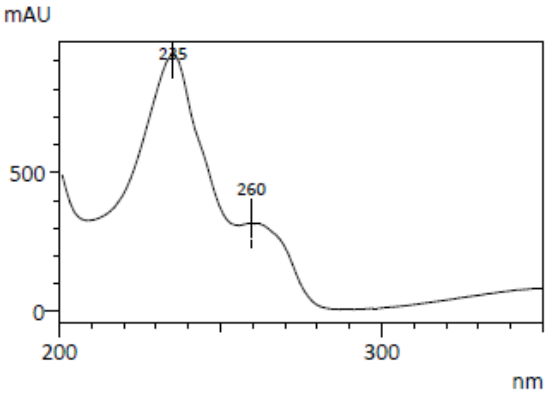
PDA Ch2 353nm

Peak#	Ret. Time	Area	Height	Area%
1	17.61	19705	797	0.8
2	19.94	2384952	81203	99.2
Total				100.0

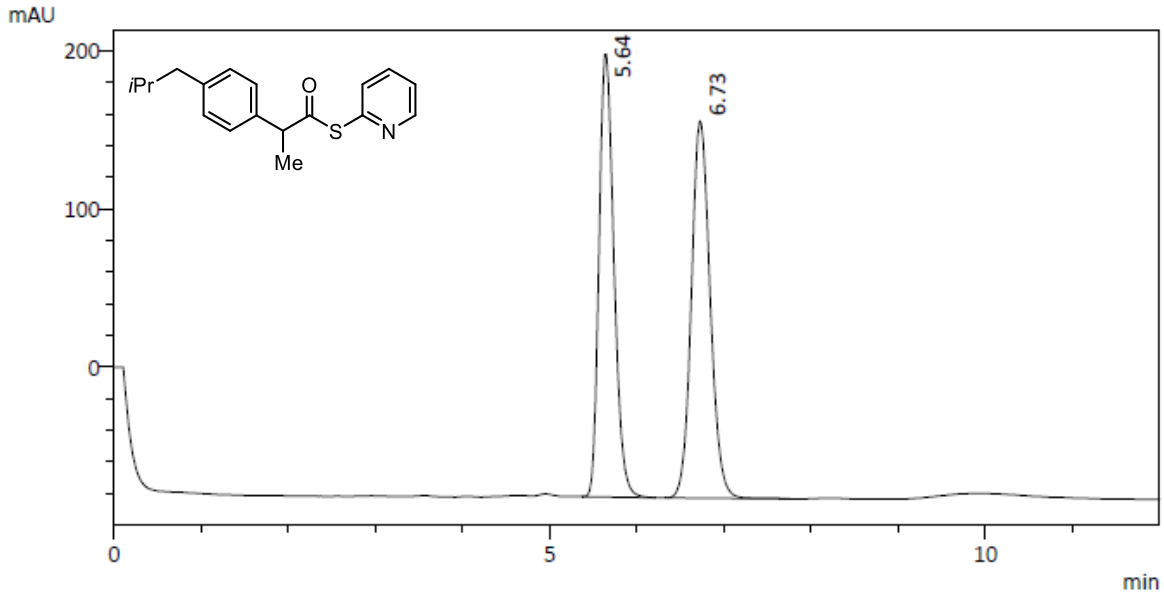
UV Spectrum
Peak#: 1
Retention Time: 17.610 min



UV Spectrum
Peak#: 2
Retention Time: 19.943 min



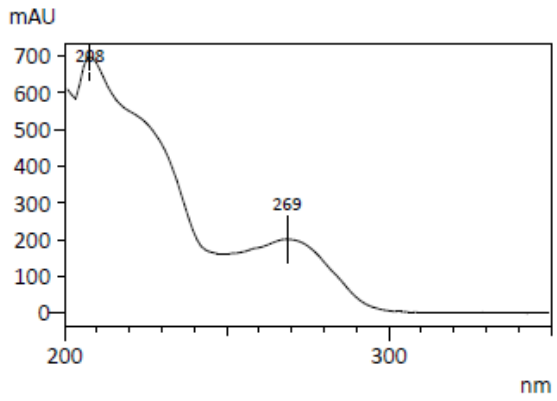
***S*-(Pyridin-2-yl) (R/S)-2-(4-isobutylphenyl)propanethioate (1l)**



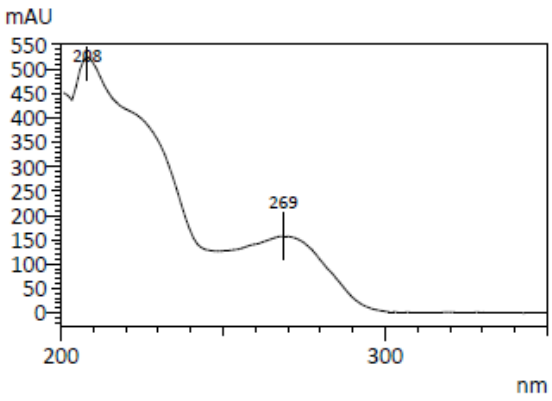
PDA Ch2 268nm

Peak#	Ret. Time	Area	Height	Area%
1	5.64	3345973	279898	48.4
2	6.73	3571156	238609	51.6
Total				100.0

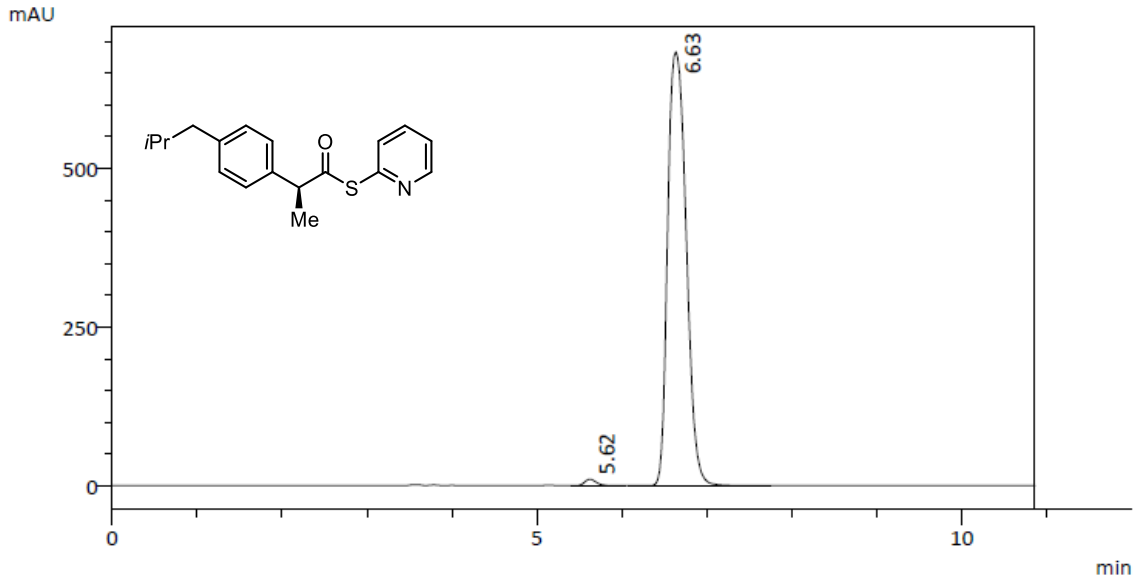
UV Spectrum
Peak#: 1
Retention Time: 5.643 min



UV Spectrum
Peak#: 2
Retention Time: 6.727 min



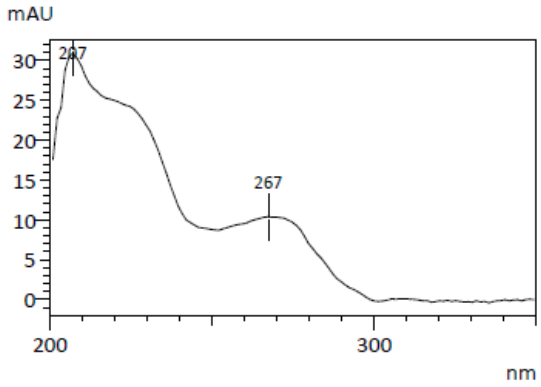
***S*-(Pyridin-2-yl) (S)-2-(4-isobutylphenyl)propanethioate (1l)**



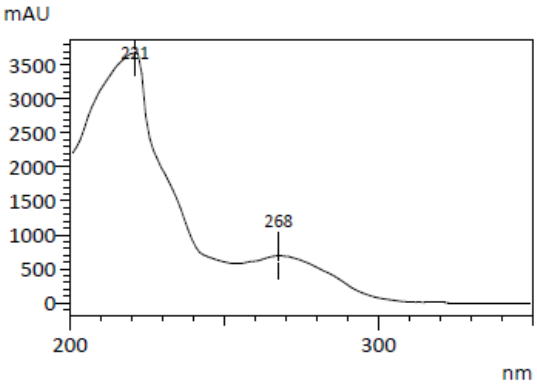
PDA Ch2 268nm

Peak#	Ret. Time	Area	Height	Area%
1	5.62	98756	10149	0.9
2	6.63	10337718	684373	99.1
Total				100.0

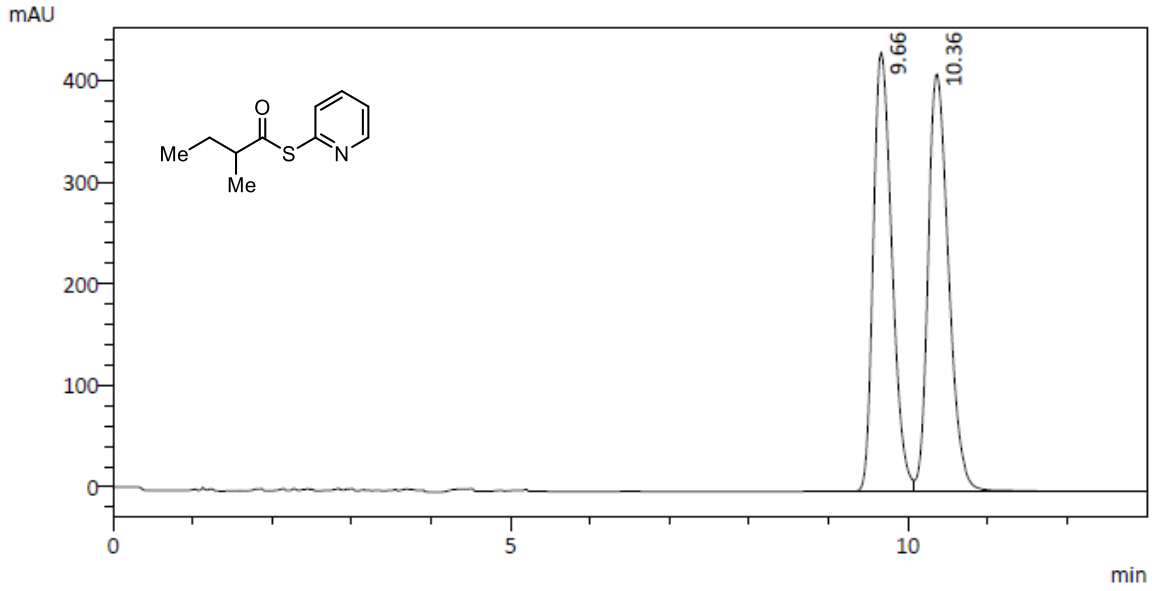
UV Spectrum
Peak#: 1
Retention Time: 5.625 min



UV Spectrum
Peak#: 2
Retention Time: 6.634 min



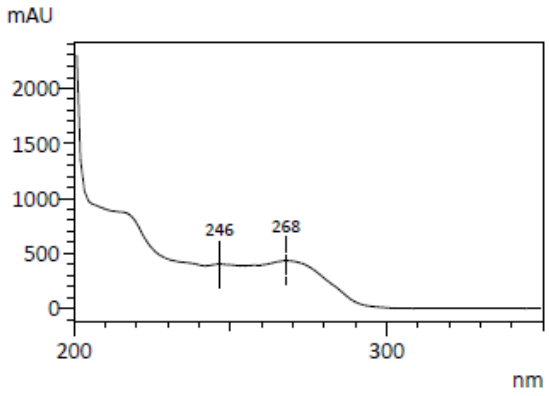
S-(Pyridin-2-yl) (R/S)-2-methylbutanethioate (1m)



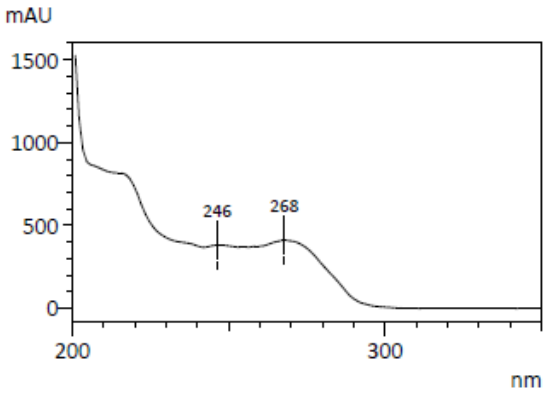
PDA Ch2 268nm

Peak#	Ret. Time	Area	Height	Area%
1	9.66	7082537	432518	49.0
2	10.36	7374118	410870	51.0
Total				100.0

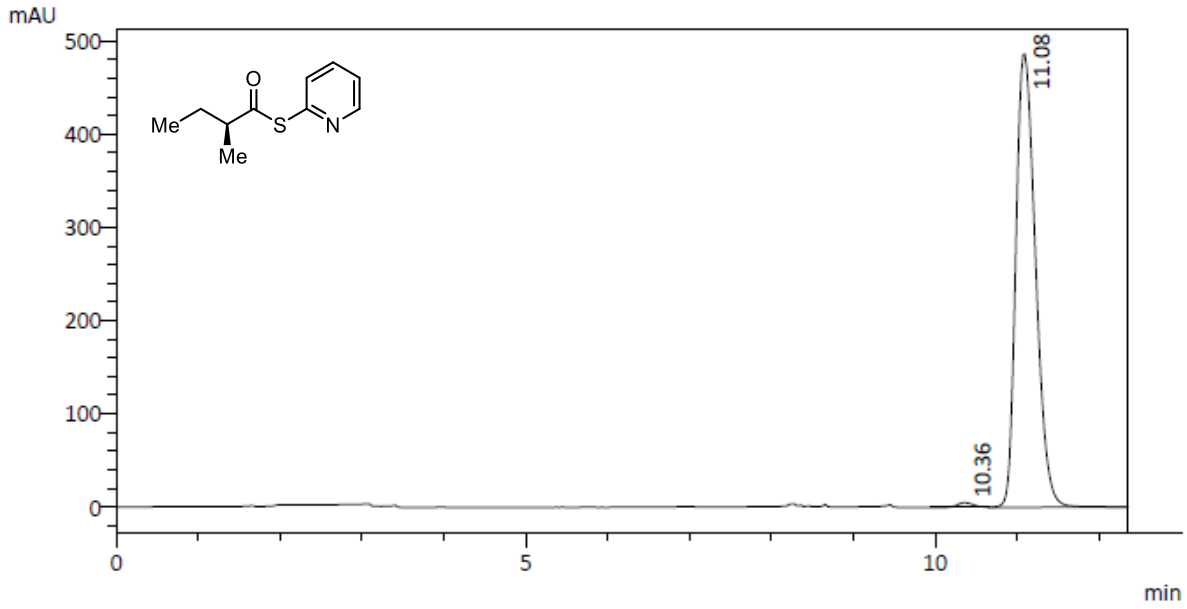
UV Spectrum
Peak#: 1
Retention Time: 9.663 min



UV Spectrum
Peak#: 2
Retention Time: 10.362 min



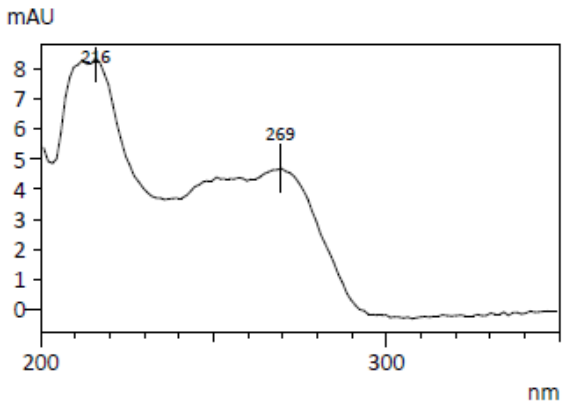
***S*-(Pyridin-2-yl) (*S*)-2-methylbutanethioate (1m)**



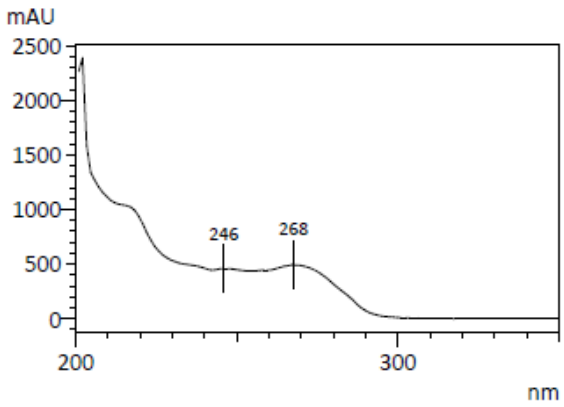
PDA Ch2 268nm

Peak#	Ret. Time	Area	Height	Area%
1	10.36	67843	5002	0.8
2	11.08	8089331	486237	99.2
Total				100.0

UV Spectrum
Peak#: 1
Retention Time: 10.363 min

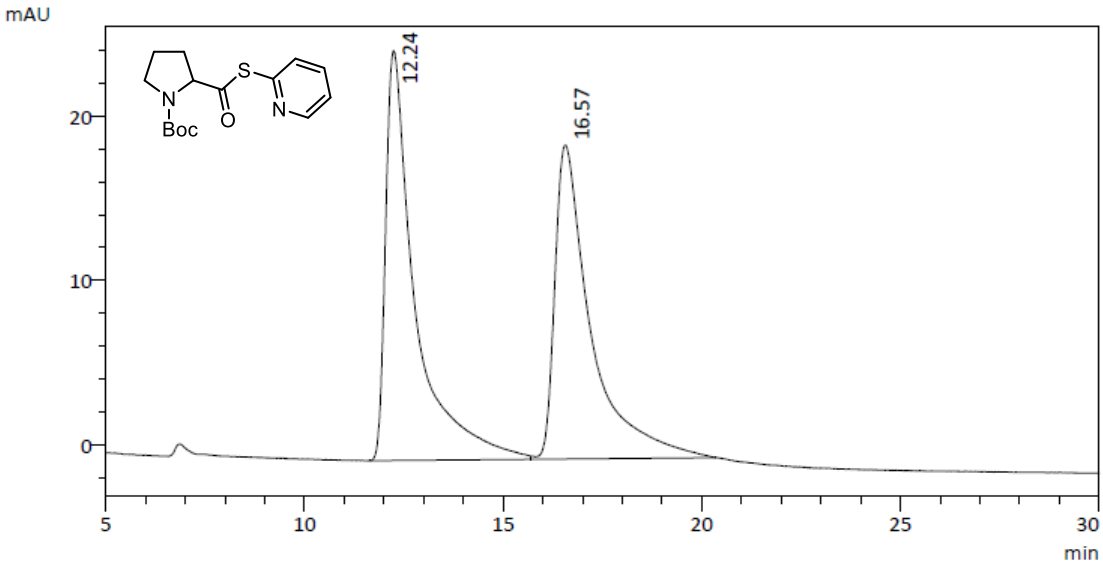


UV Spectrum
Peak#: 2
Retention Time: 11.084 min



***tert*-Butyl (R/*S*)-2-((pyridin-2-ylthio)carbonyl)pyrrolidine-1-carboxylate (1k)**

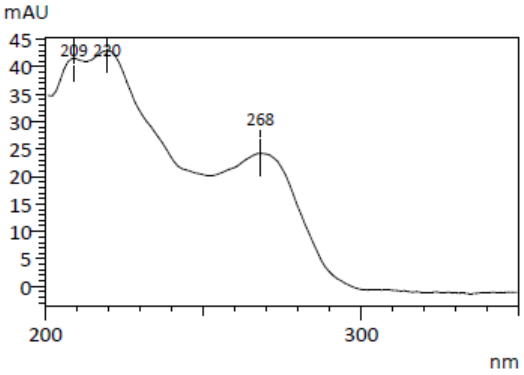
Method File : AD-H_H95_30min.lcm
Date Processed : 03/04/2019 09:07:51



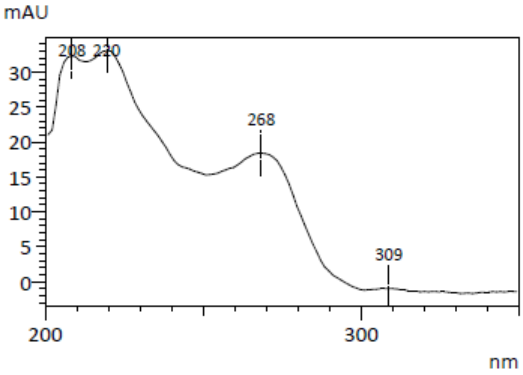
PDA Ch2 268nm

Peak#	Ret. Time	Area	Height	Area%
1	12.24	1282884	24914	51.6
2	16.57	1201484	19082	48.4
Total				100.0

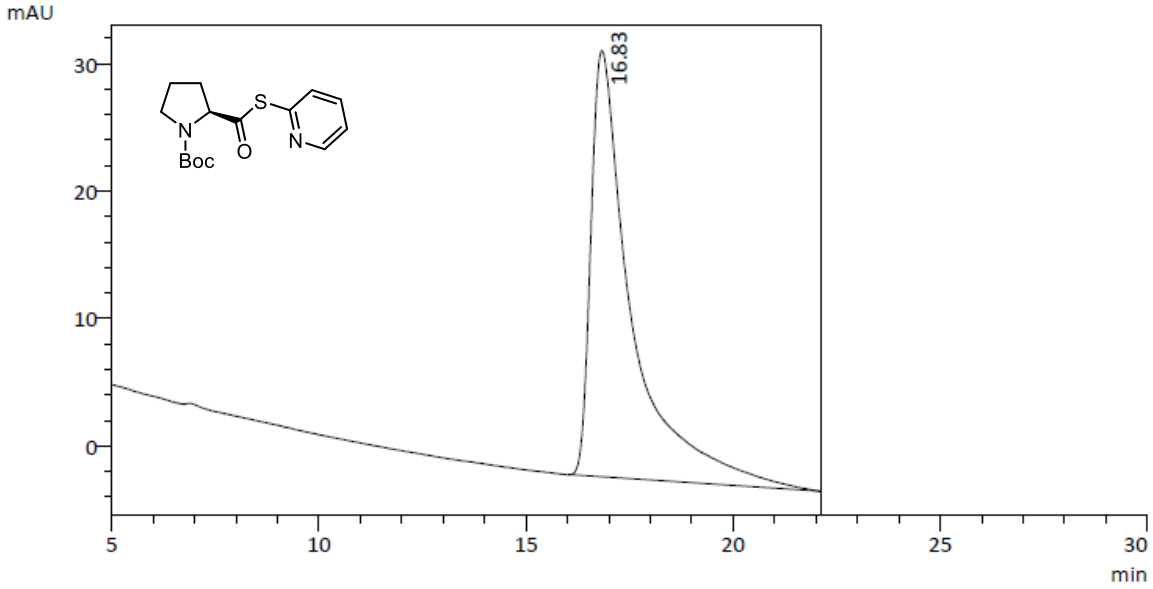
UV Spectrum
Peak#: 1
Retention Time: 12.245 min



UV Spectrum
Peak#: 2
Retention Time: 16.565 min



***tert*-Butyl (*S*)-2-((pyridin-2-ylthio)carbonyl)pyrrolidine-1-carboxylate (1k)**

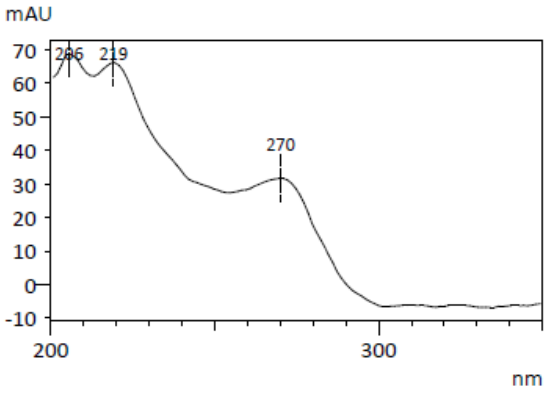


PDA Ch2 267nm

Peak#	Ret. Time	Area	Height	Area%
1	16.83	2292279	33483	100.0
Total				100.0

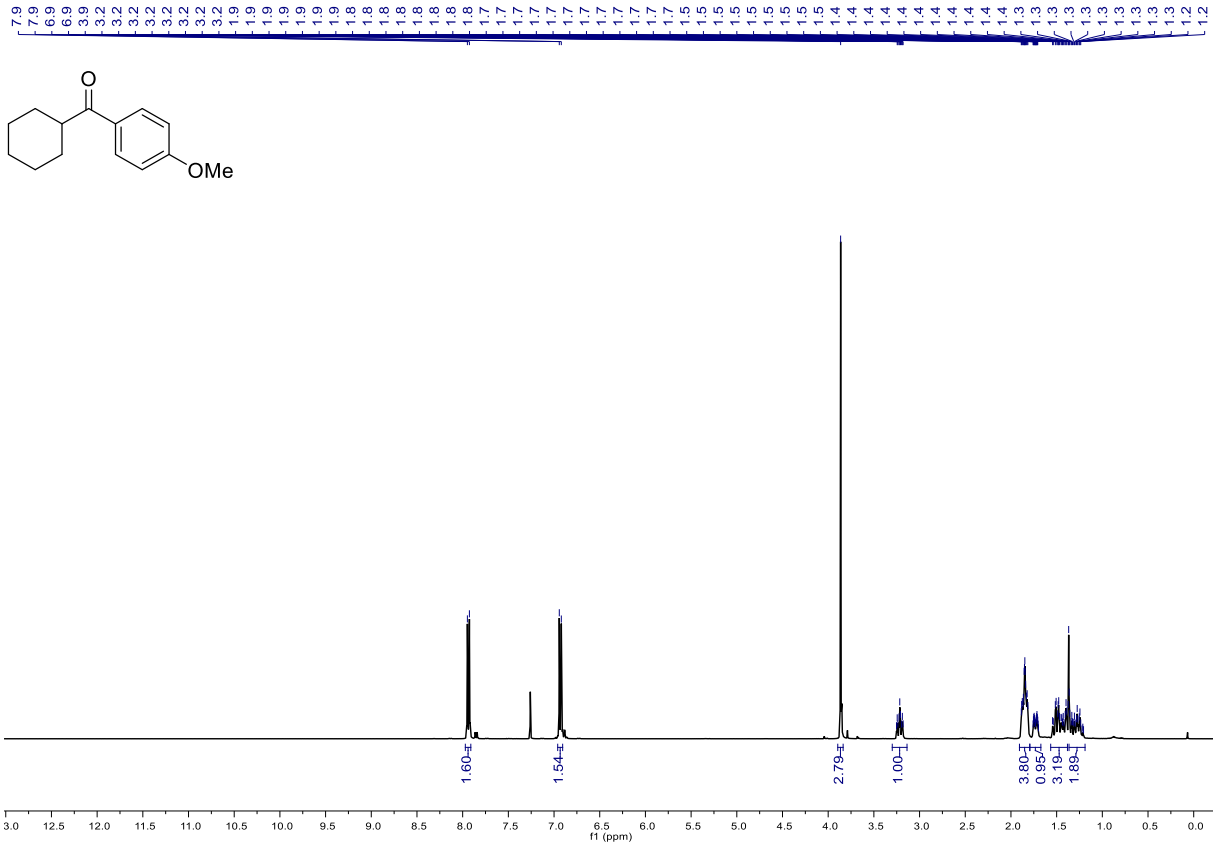
UV Spectrum
Peak#: 1
Retention Time: 16.833 min

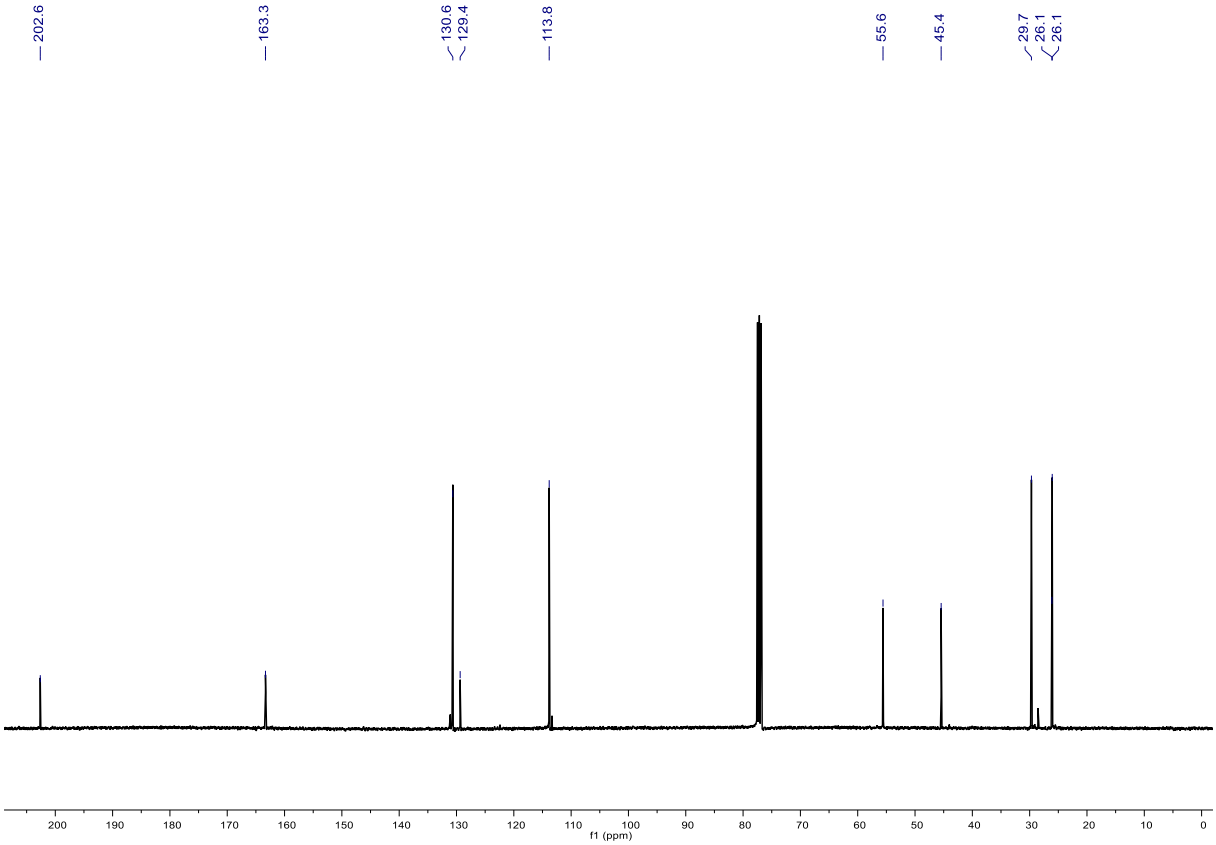
UV Spectrum



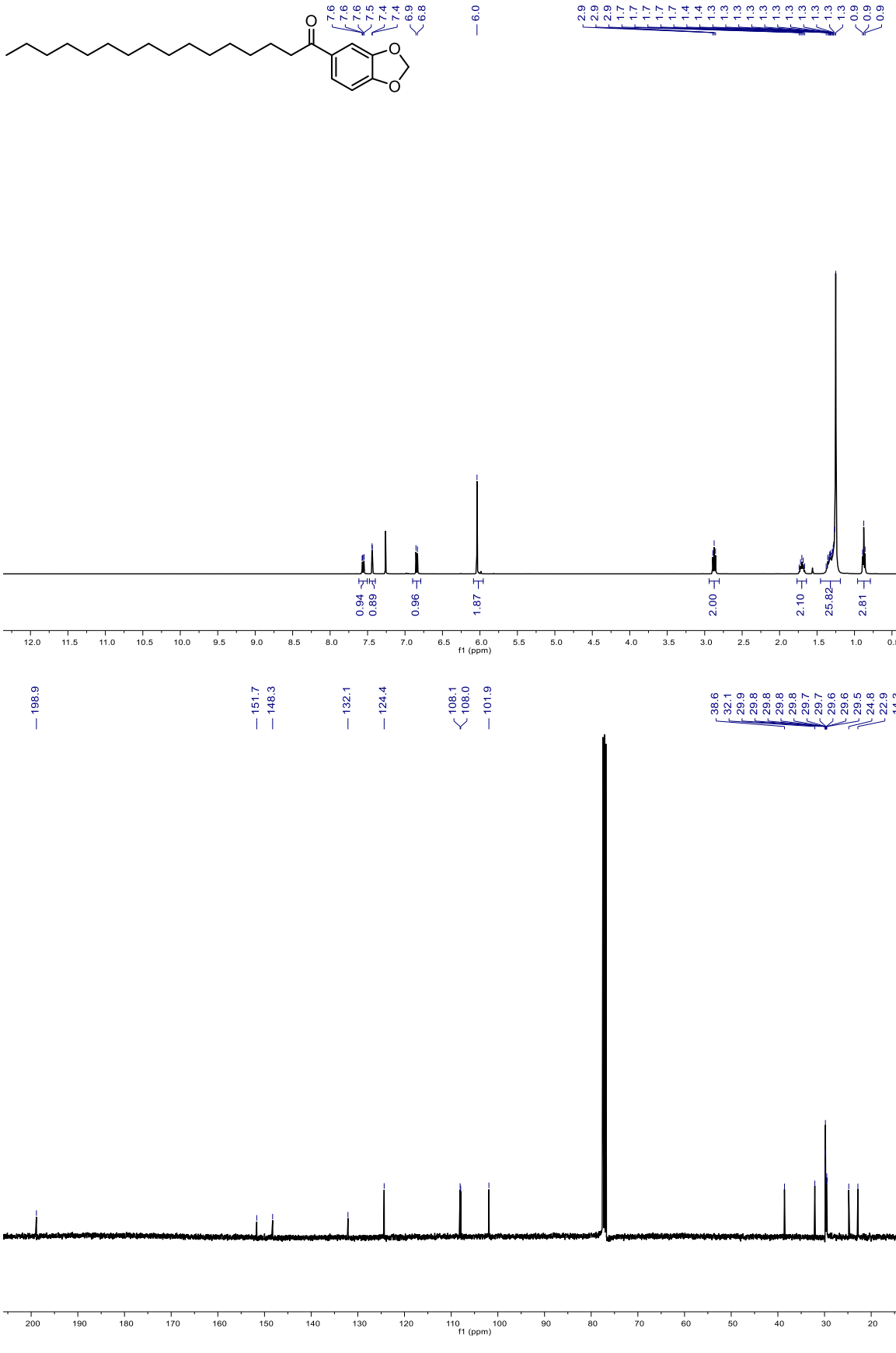
^{1}H-NMR and ^{13}C-NMR Spectra

Cyclohexyl(4-methoxyphenyl)methanone (3a)

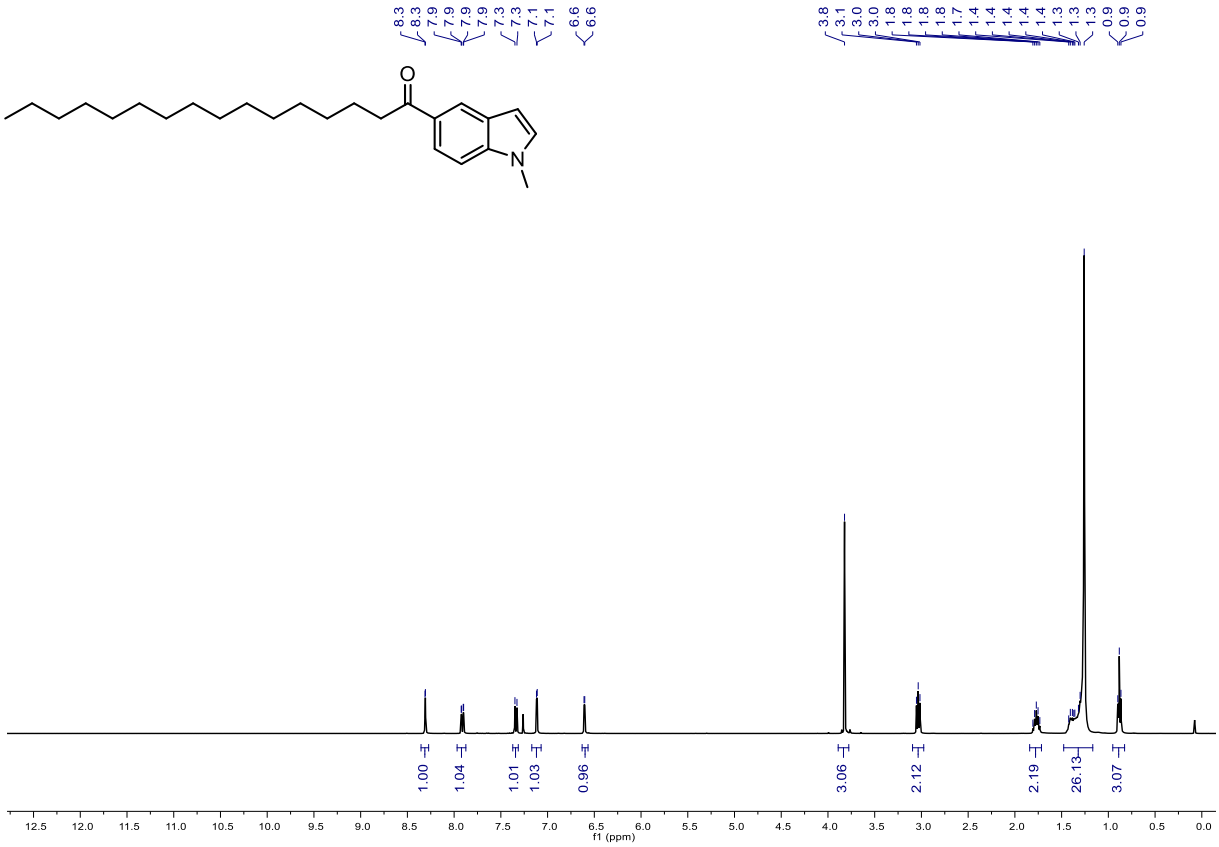


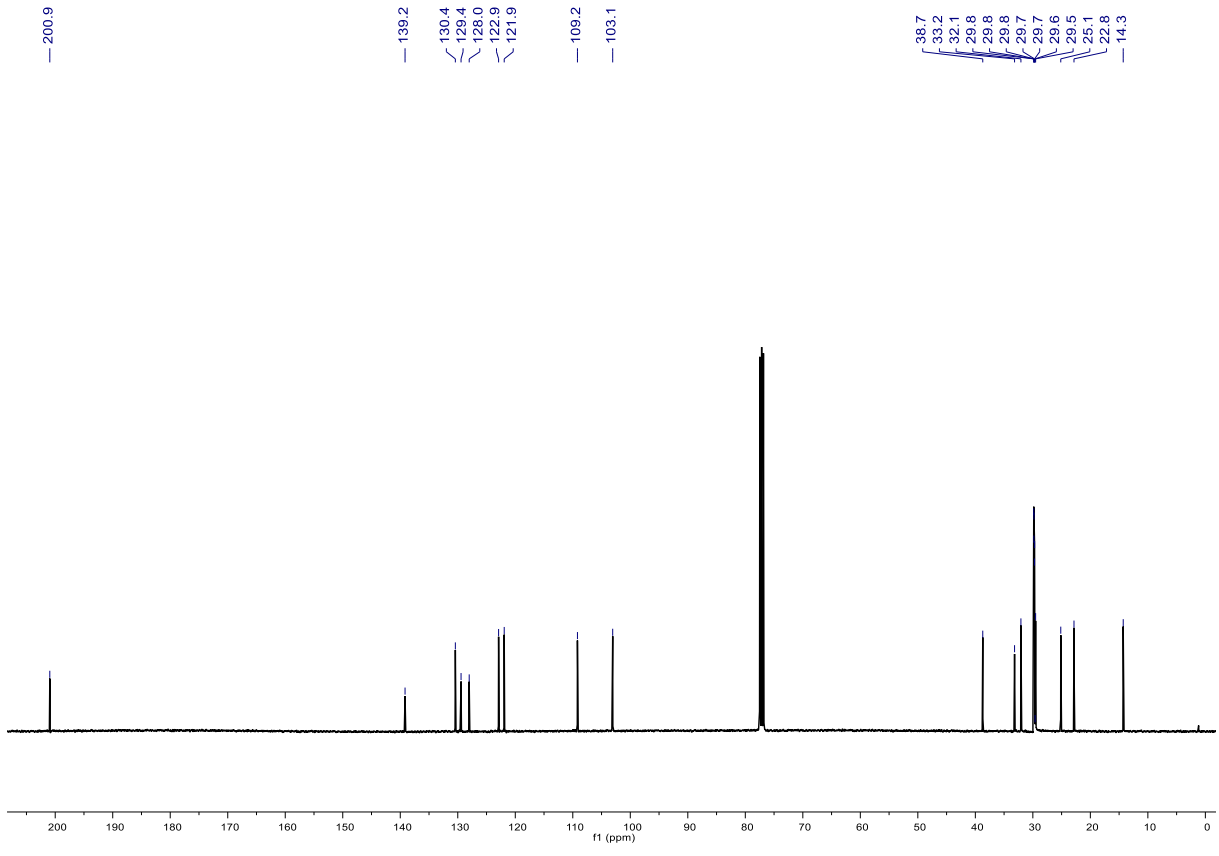


1-(Benzo[*d*][1,3]dioxol-5-yl)hexadecan-1-one (3b)

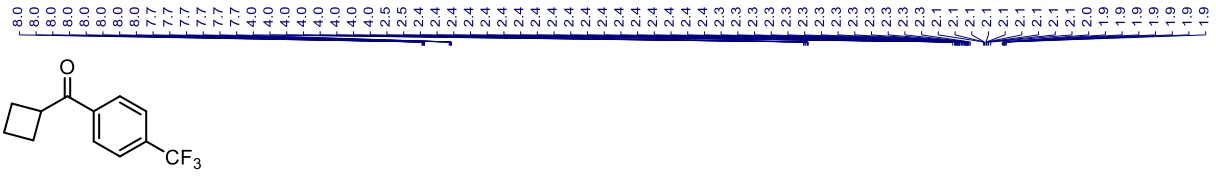


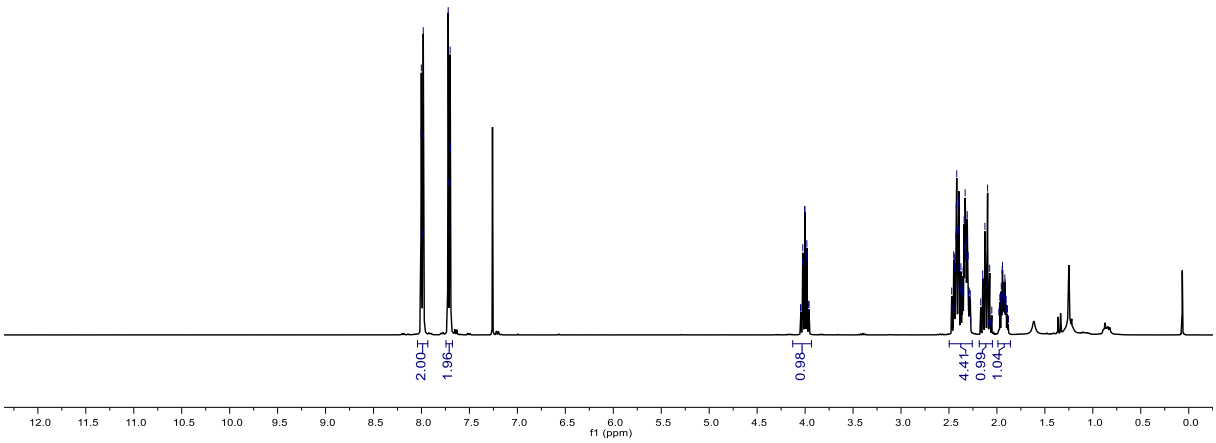
1-(1-Methyl-1*H*-indol-5-yl)hexadecan-1-one (3c)

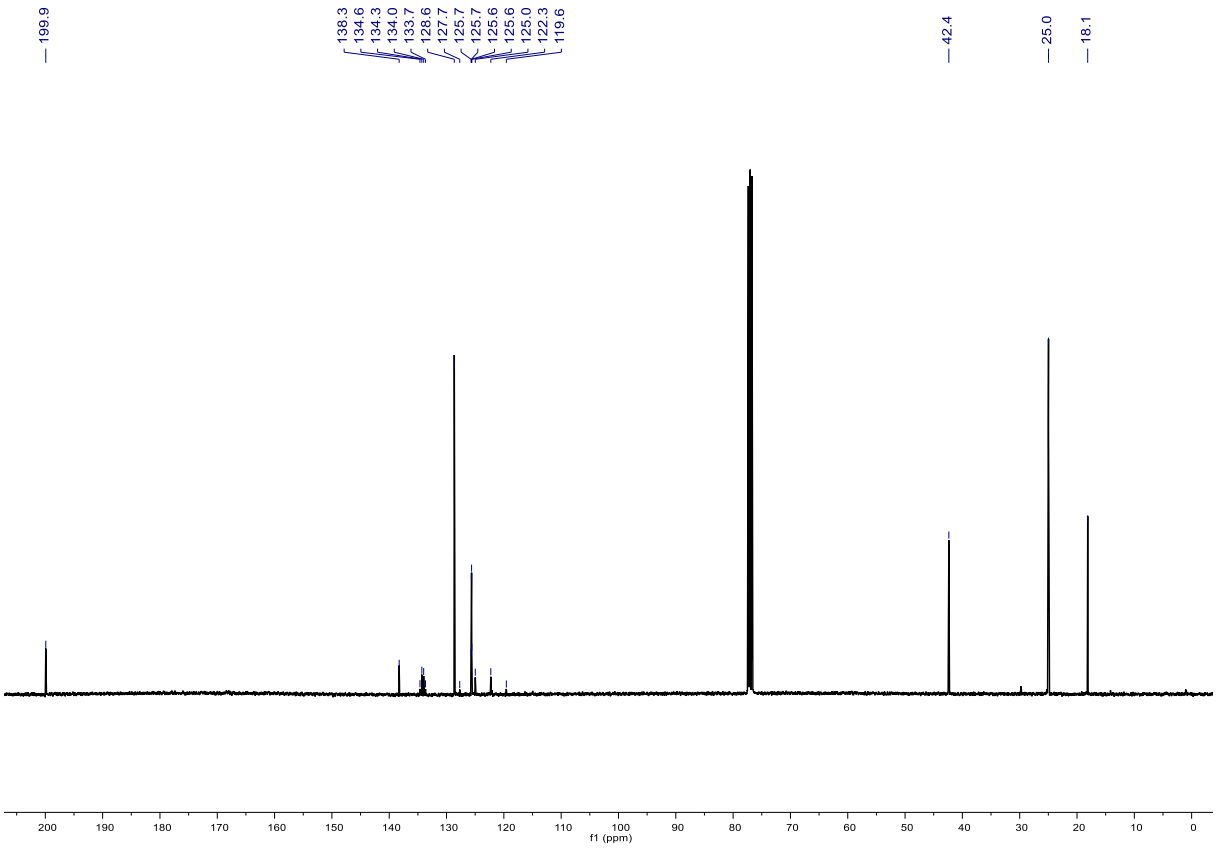




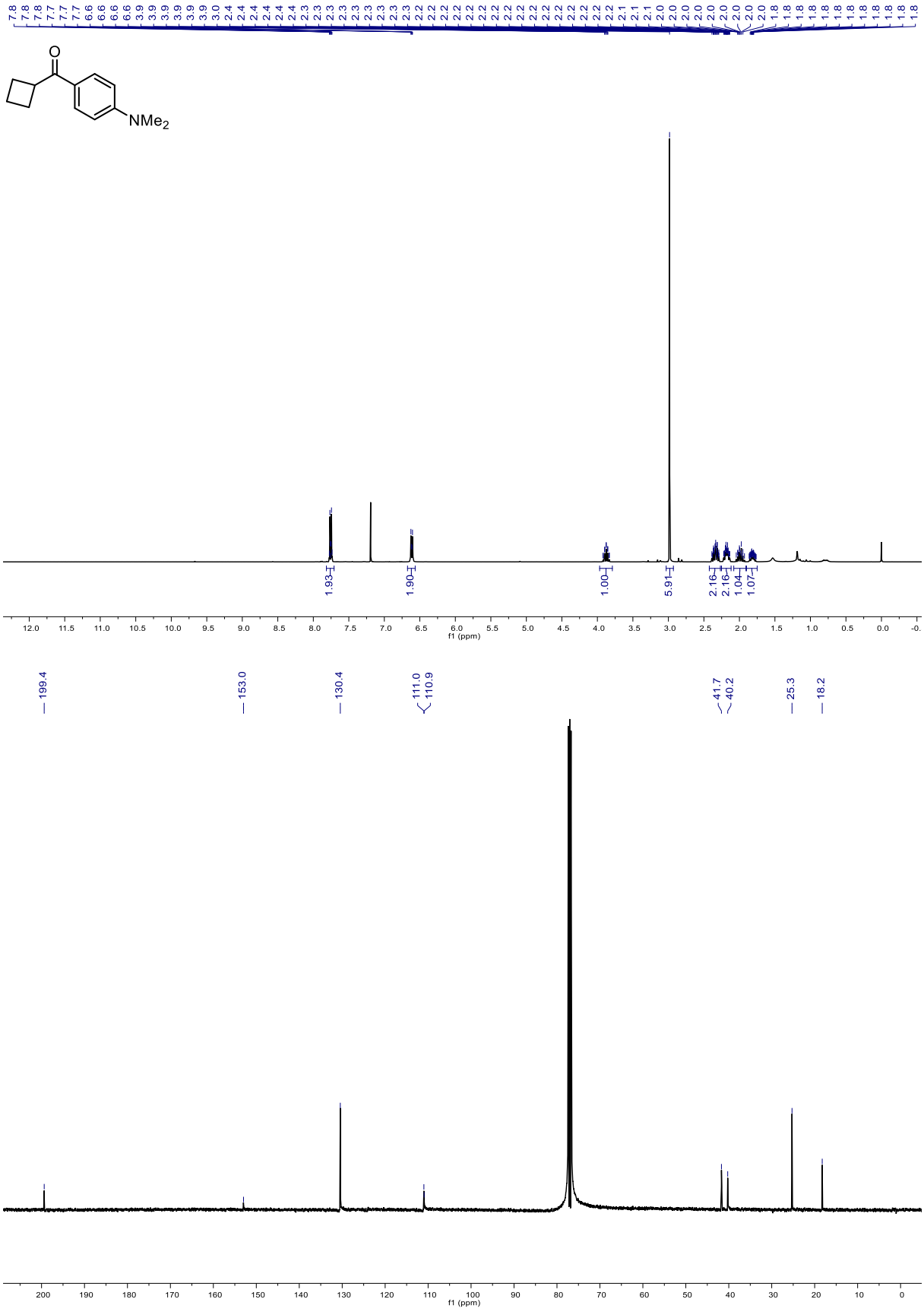
Cyclobutyl(4-(trifluoromethyl)phenyl)methanone (3d)



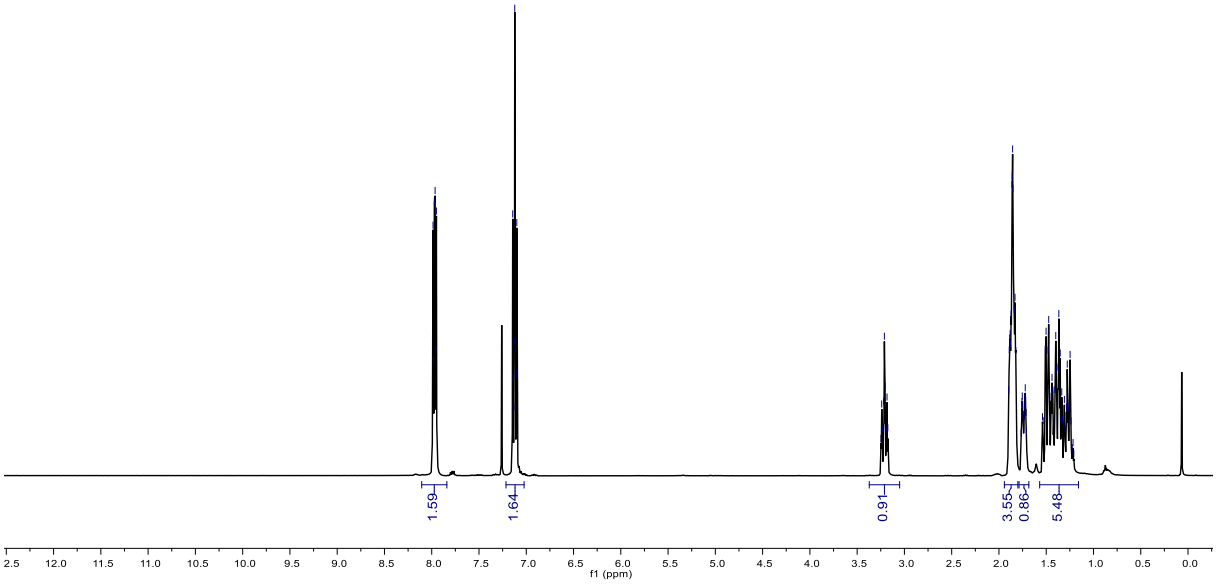


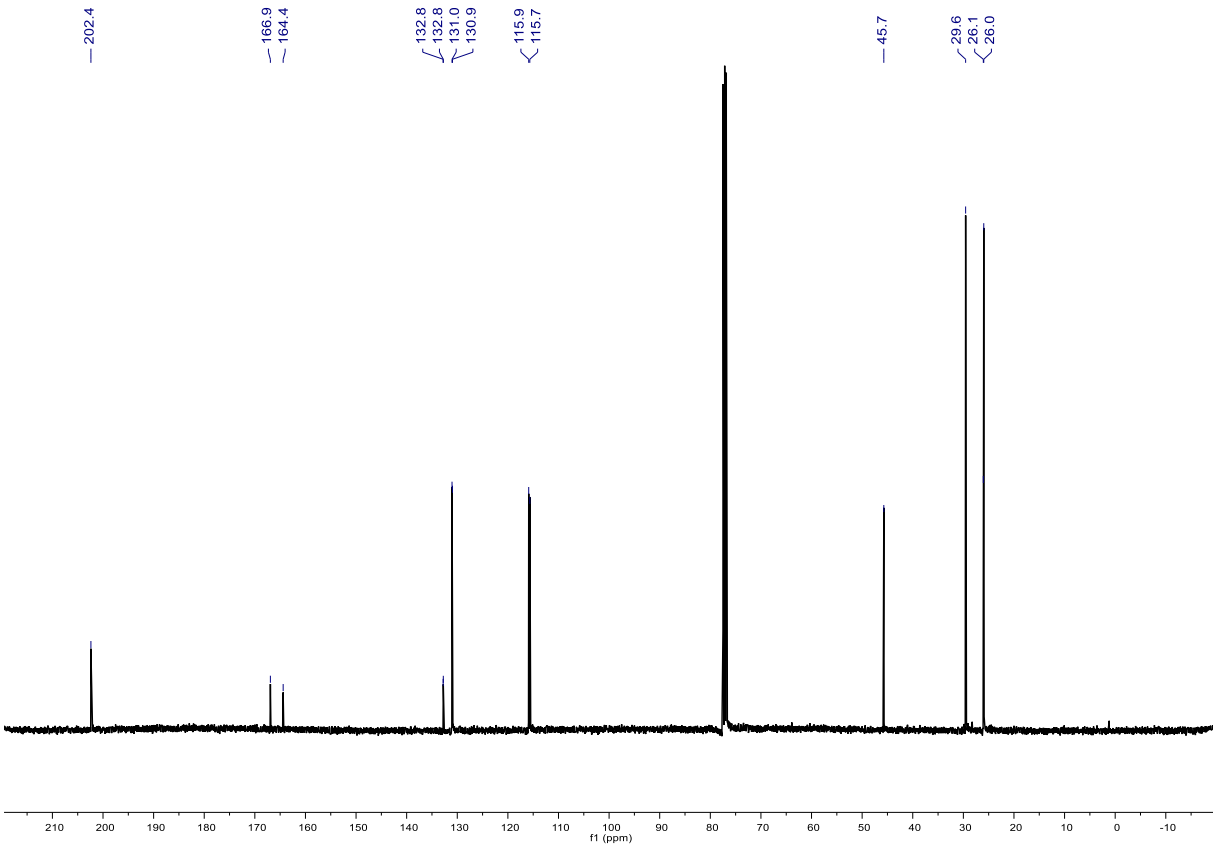


Cyclobutyl(4-(dimethylamino)phenyl)methanone (3e)

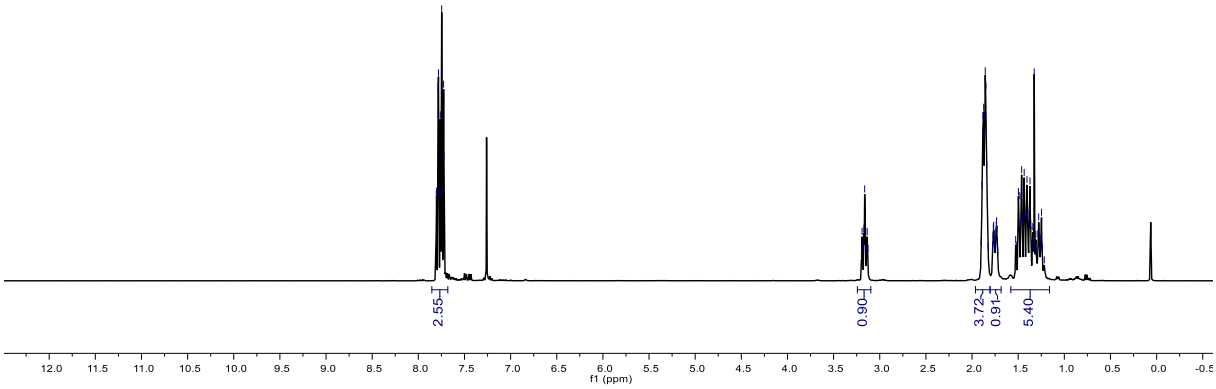


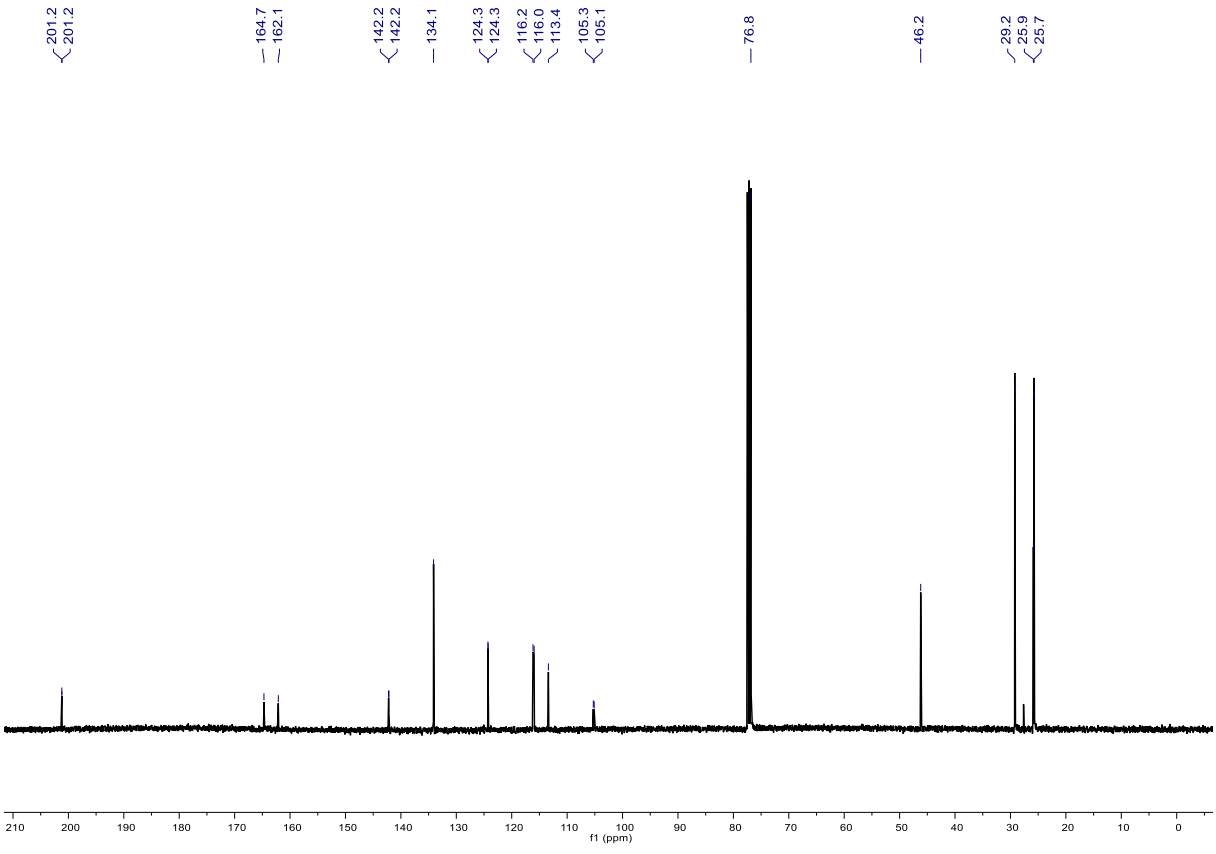
Cyclohexyl(4-fluorophenyl)methanone (3f)



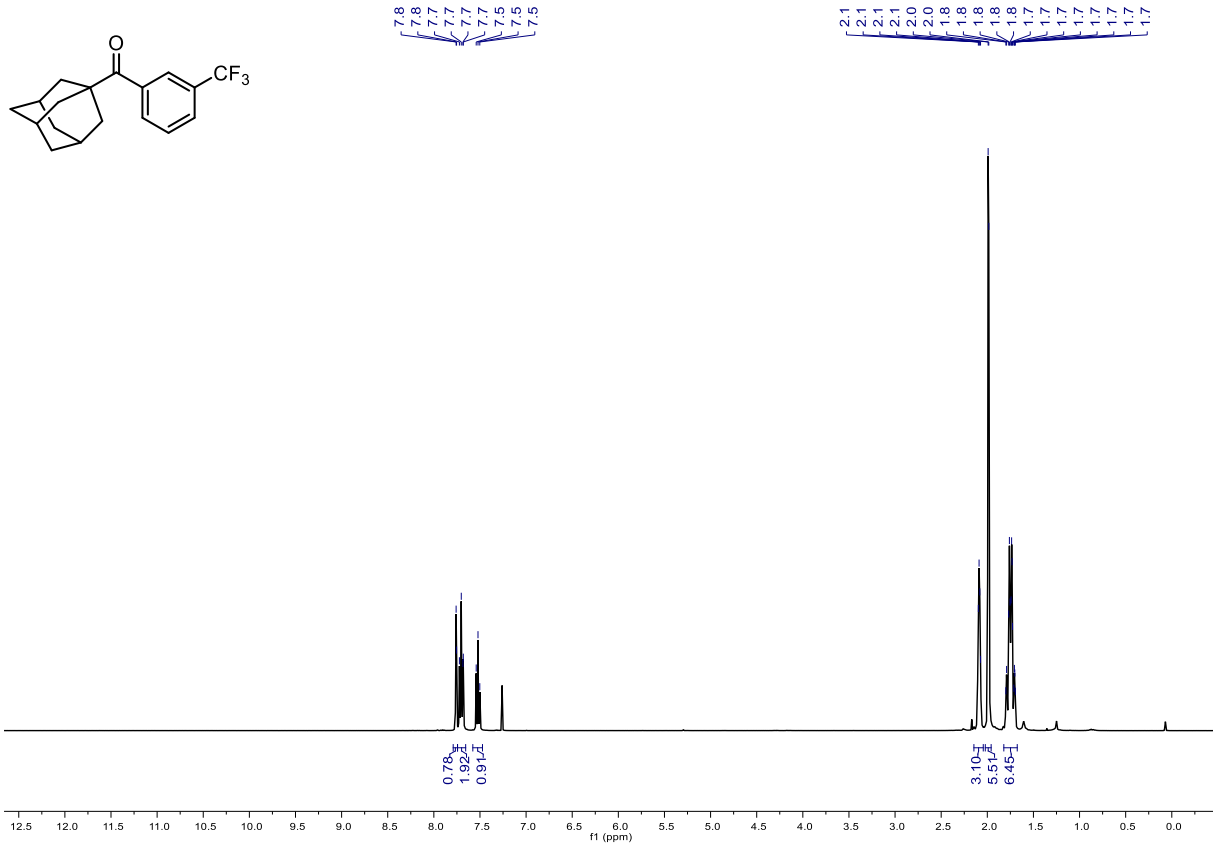


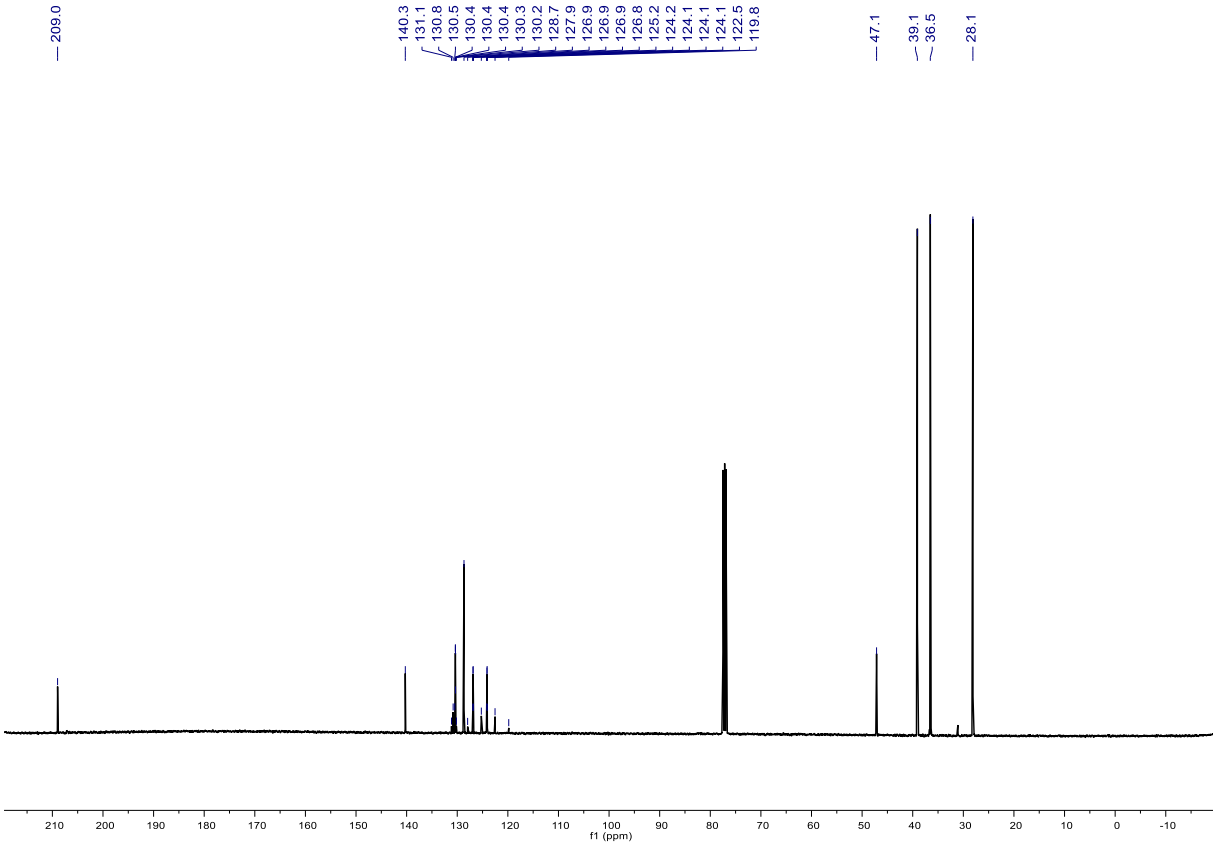
4-(Cyclohexanecarbonyl)-2-fluorobenzonitrile (3g)



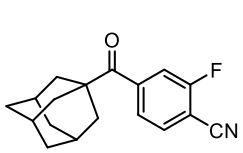


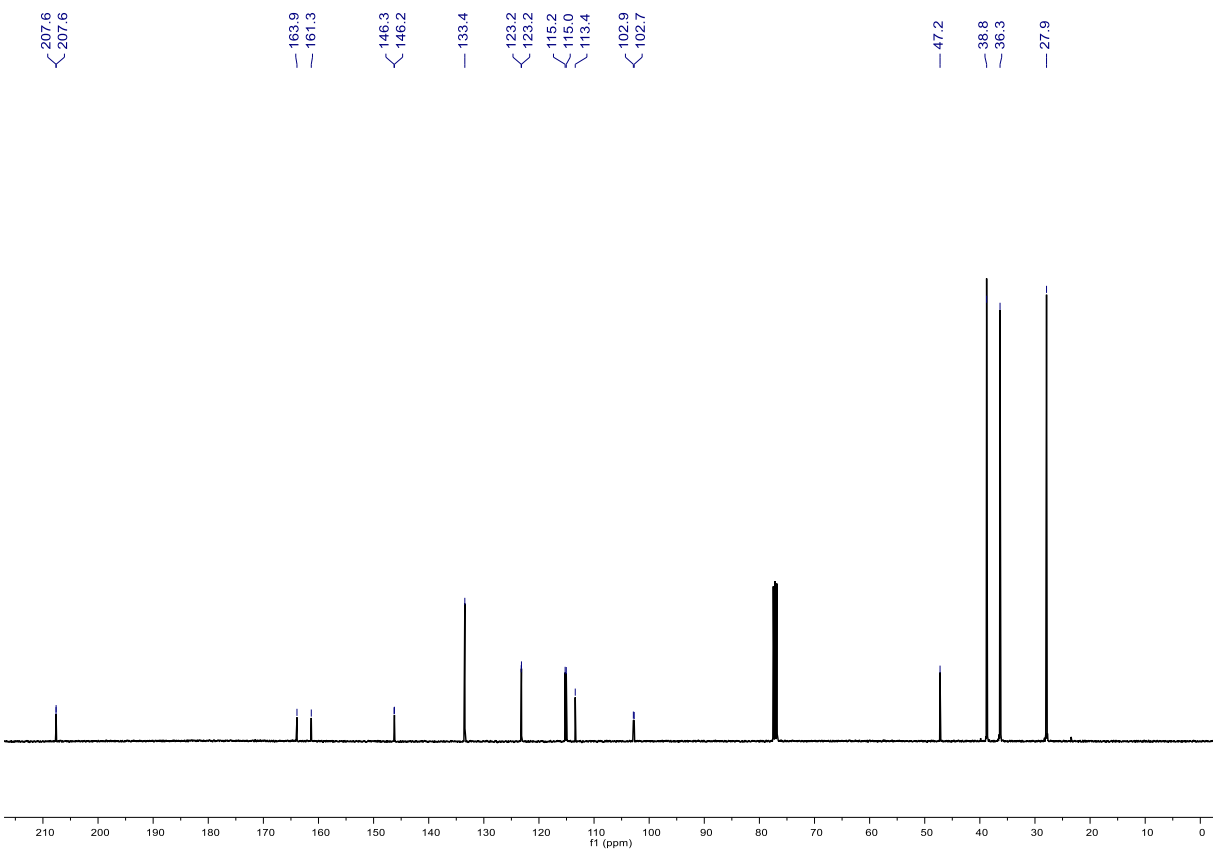
(Adamantan-1-yl)(3-(trifluoromethyl)phenyl)methanone (3h)



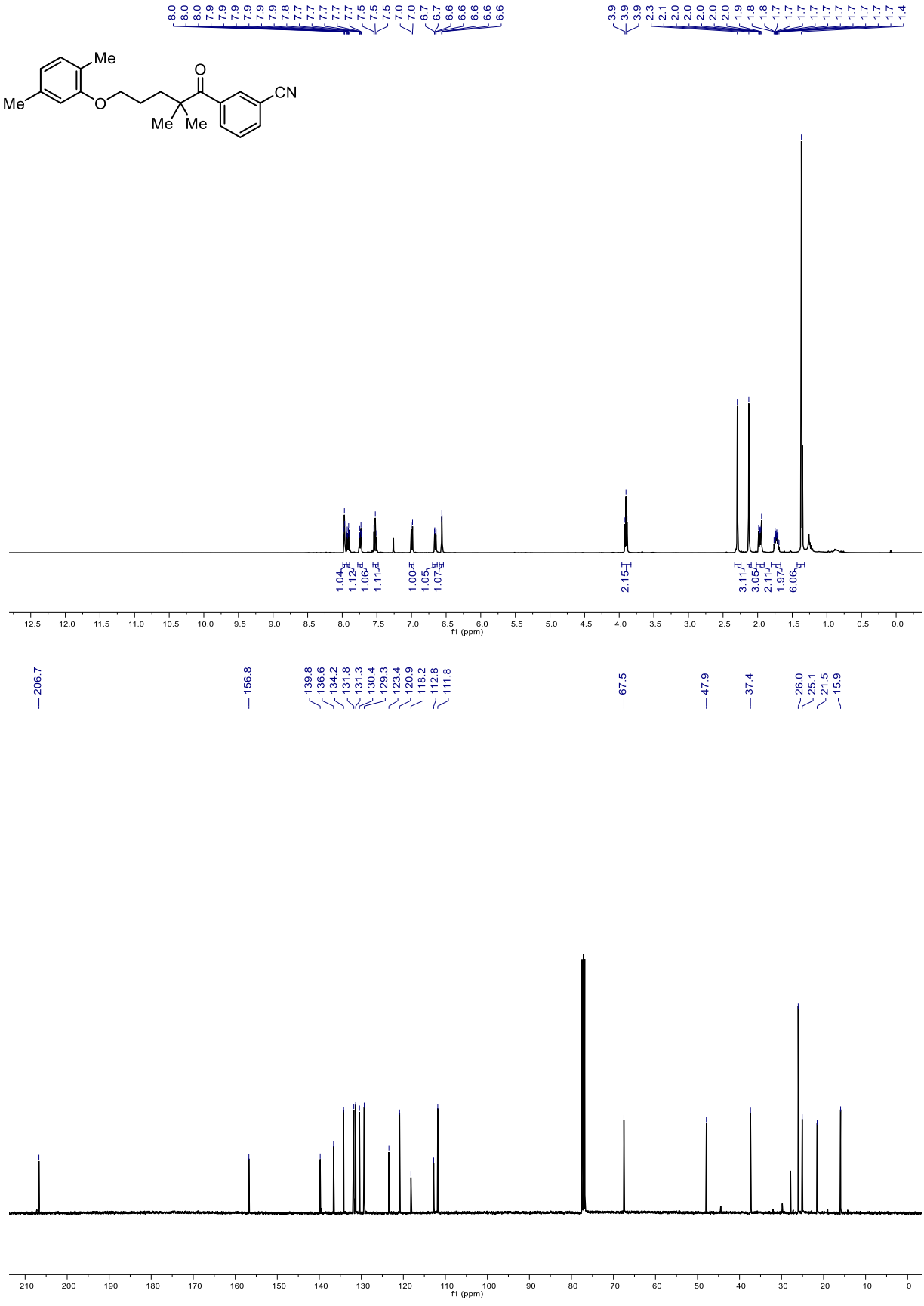


4-(Adamantane-1-carbonyl)-2-fluorobenzonitrile (3i)

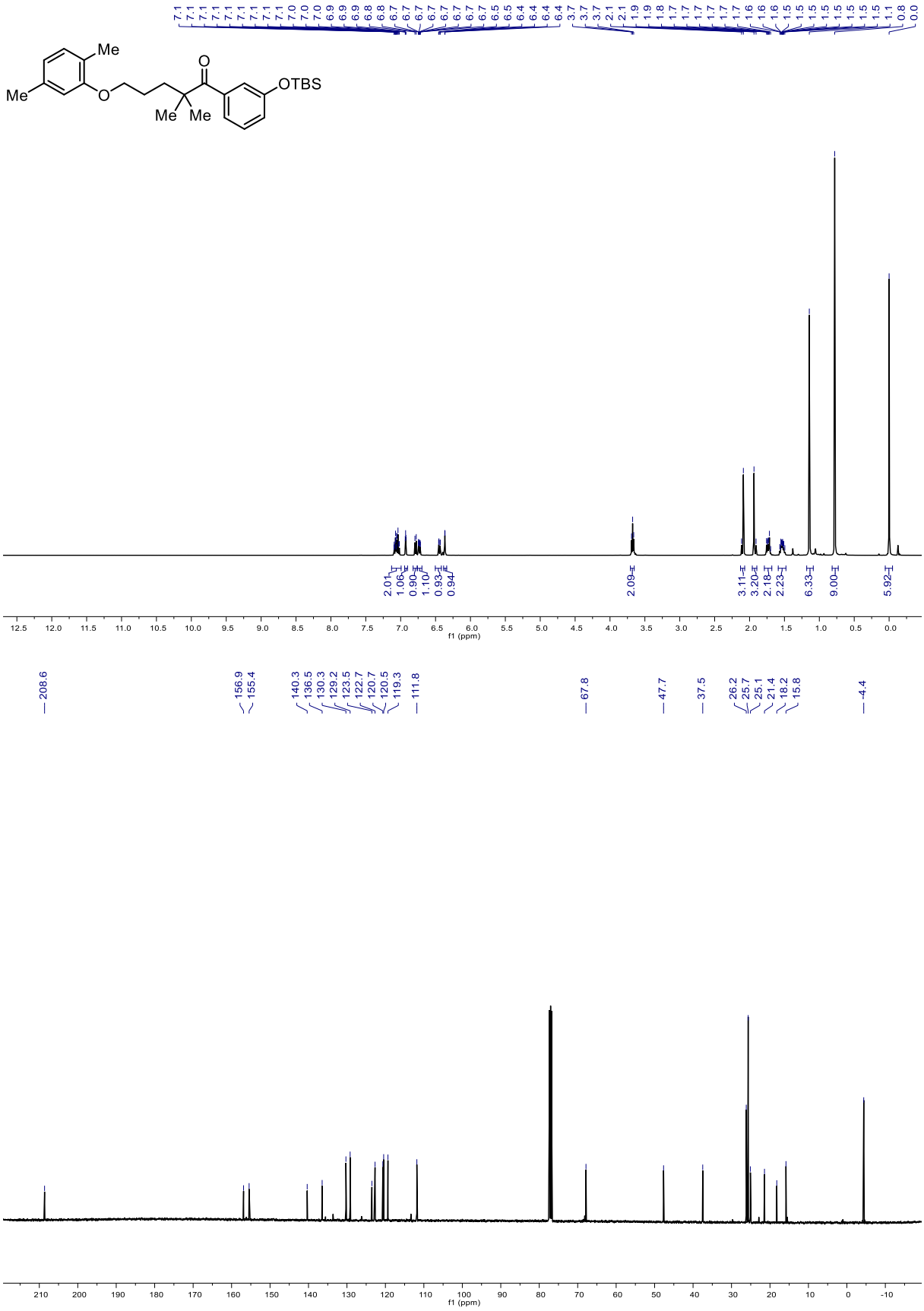




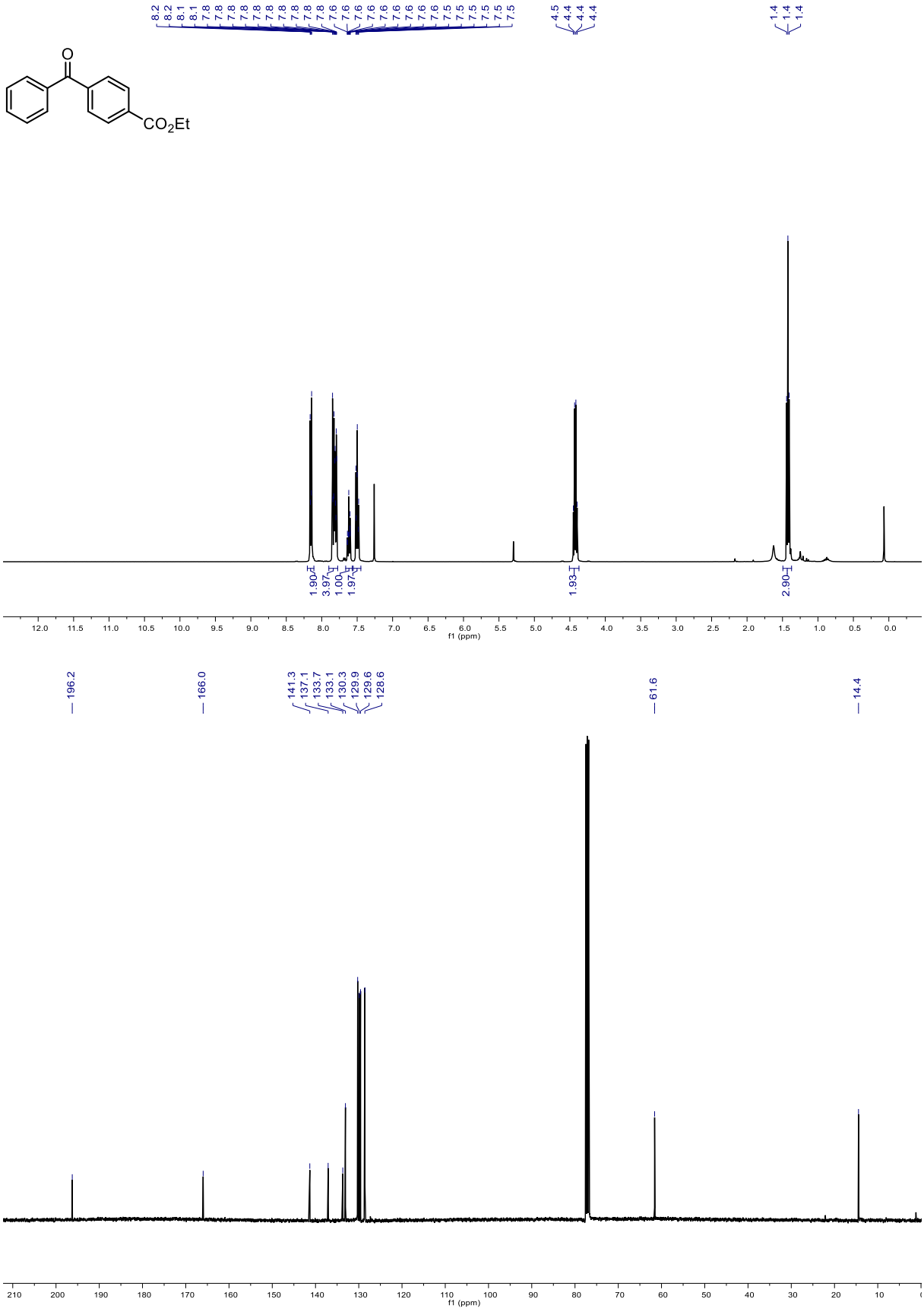
3-(5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoyl)benzonitrile (3j)



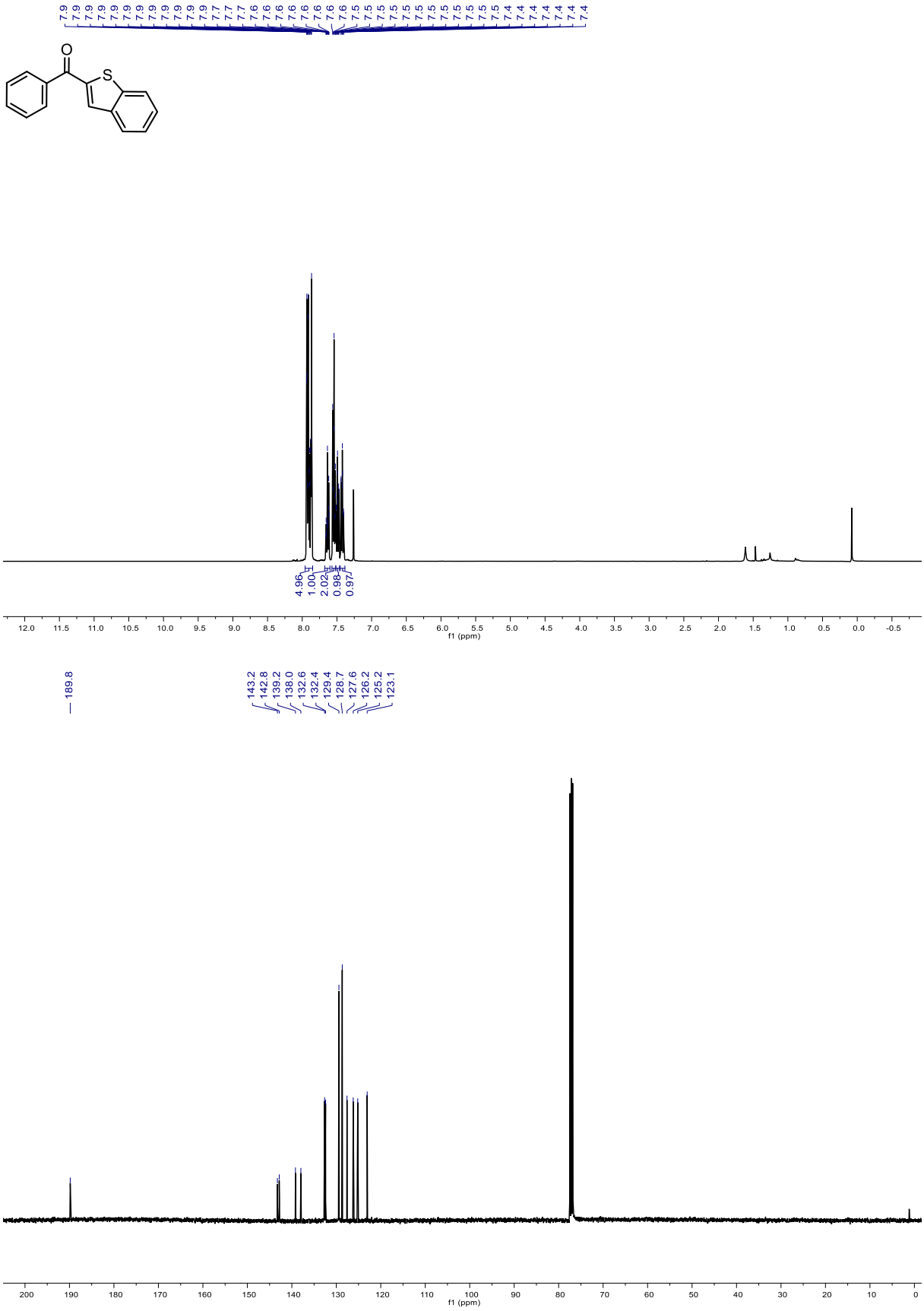
1-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-one (3k)



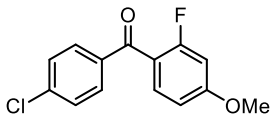
Ethyl 4-benzoylbenzoate (3l)

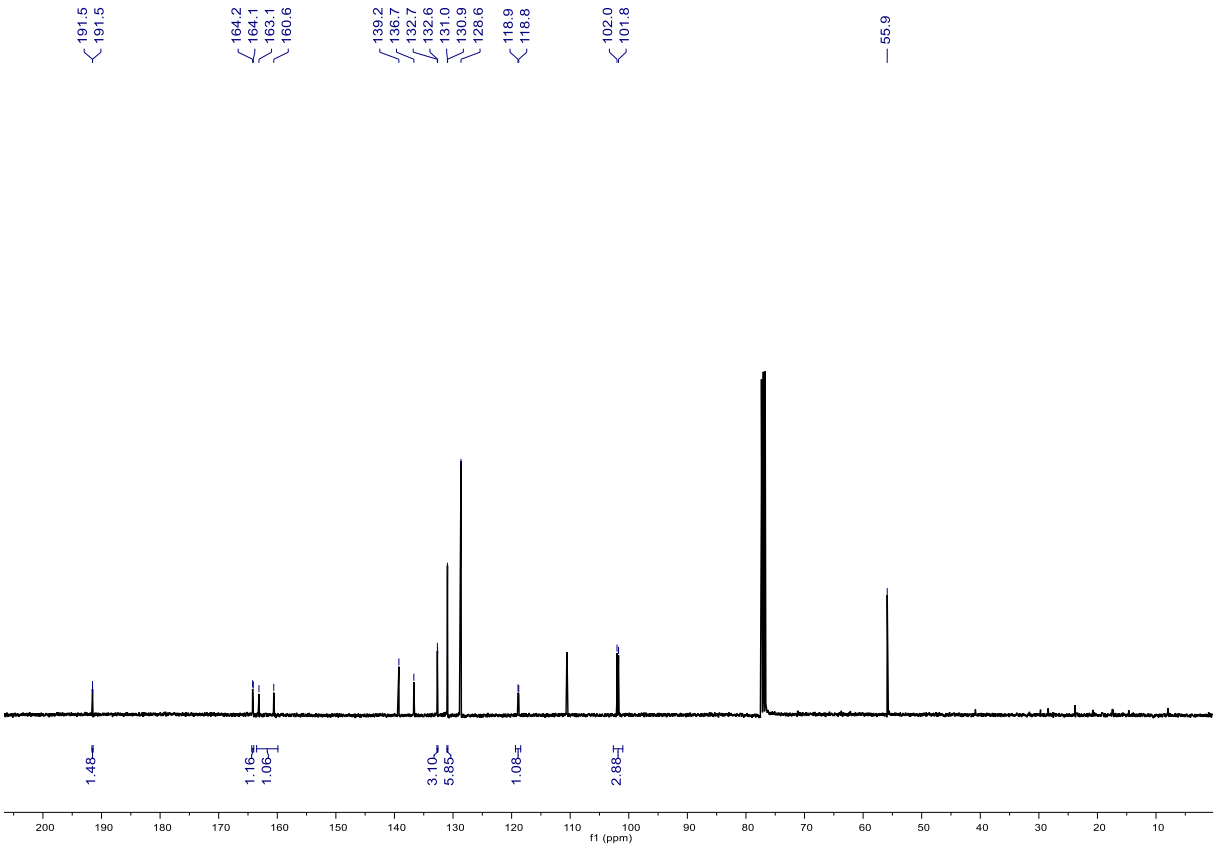


Benzo[*b*]thiophen-2-yl(phenyl)methanone (3m)

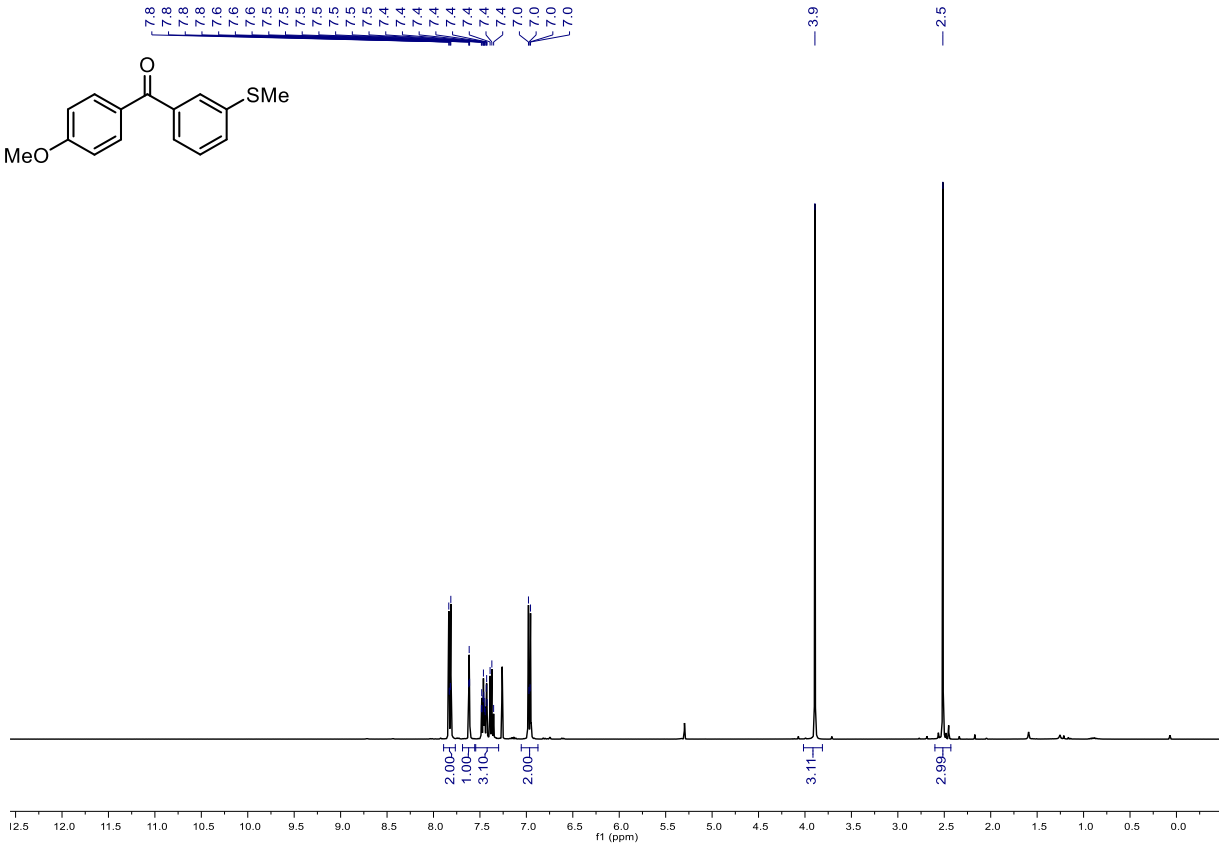


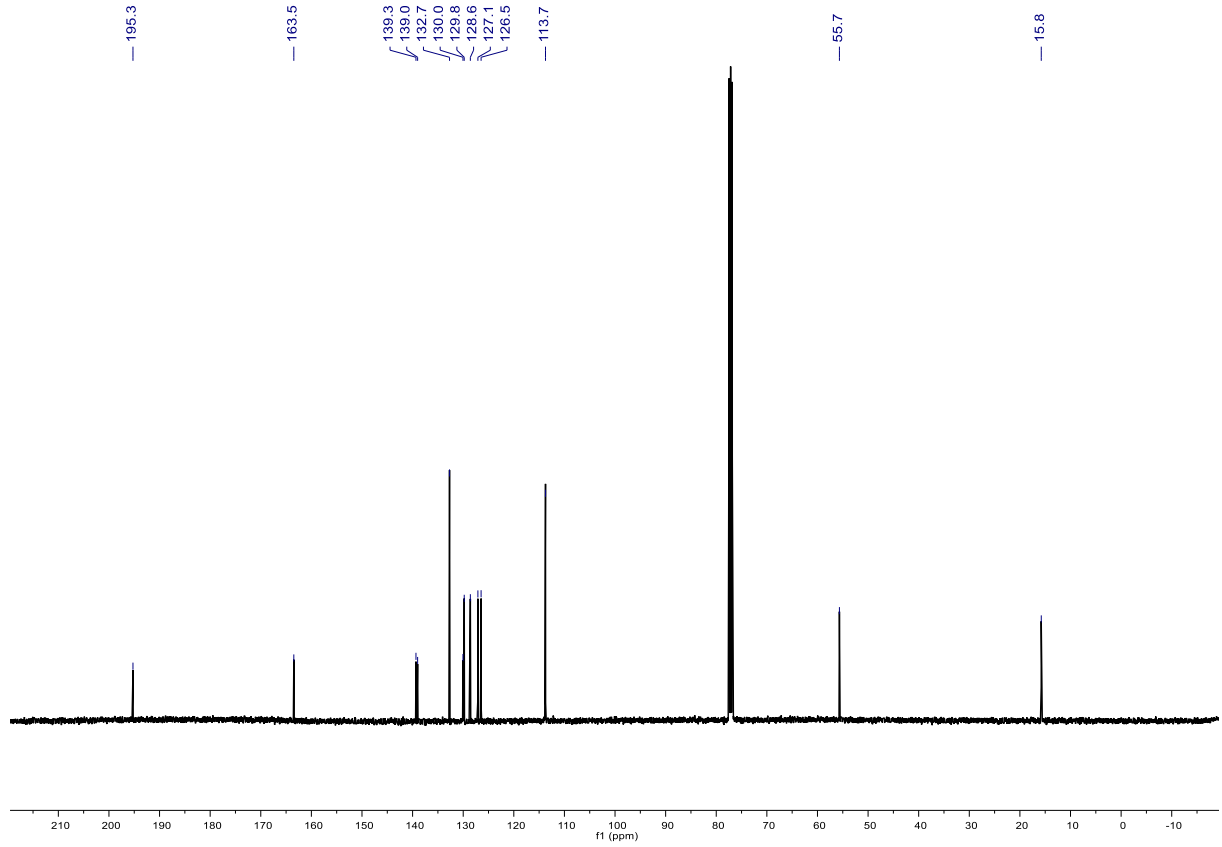
(4-Chlorophenyl)(2-fluoro-4-methoxyphenyl)methanone (3n)



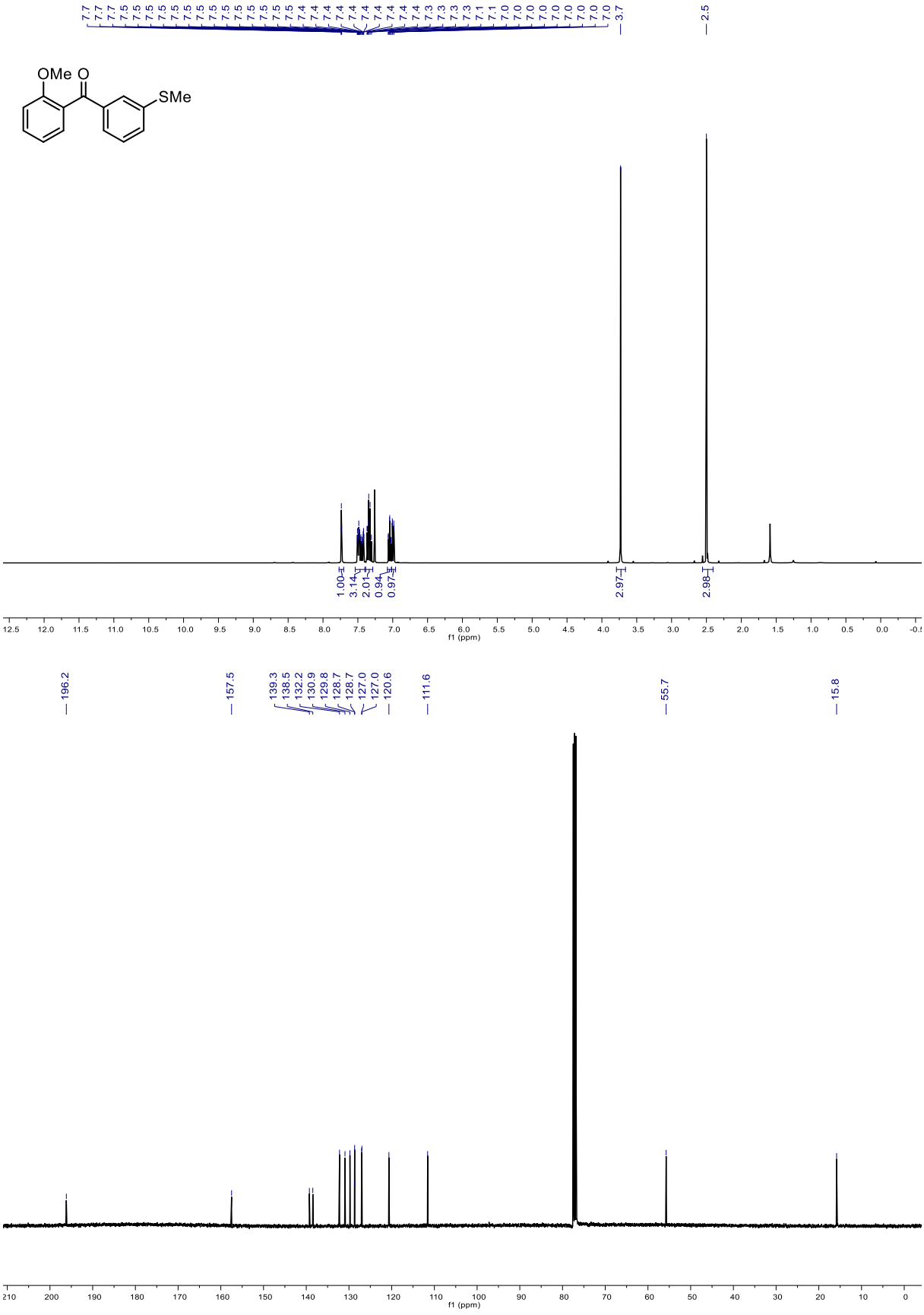


(4-Methoxyphenyl)(3-(methylthio)phenyl)methanone (3o)

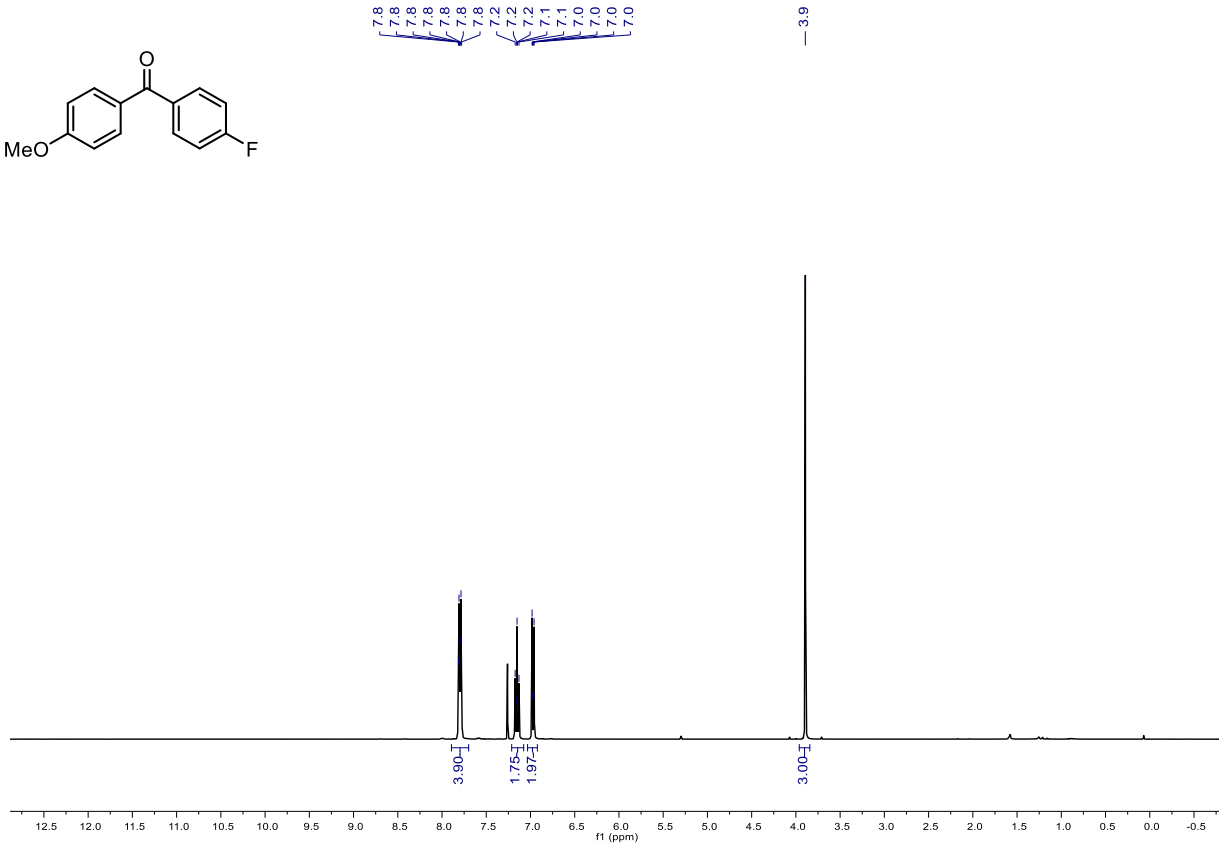


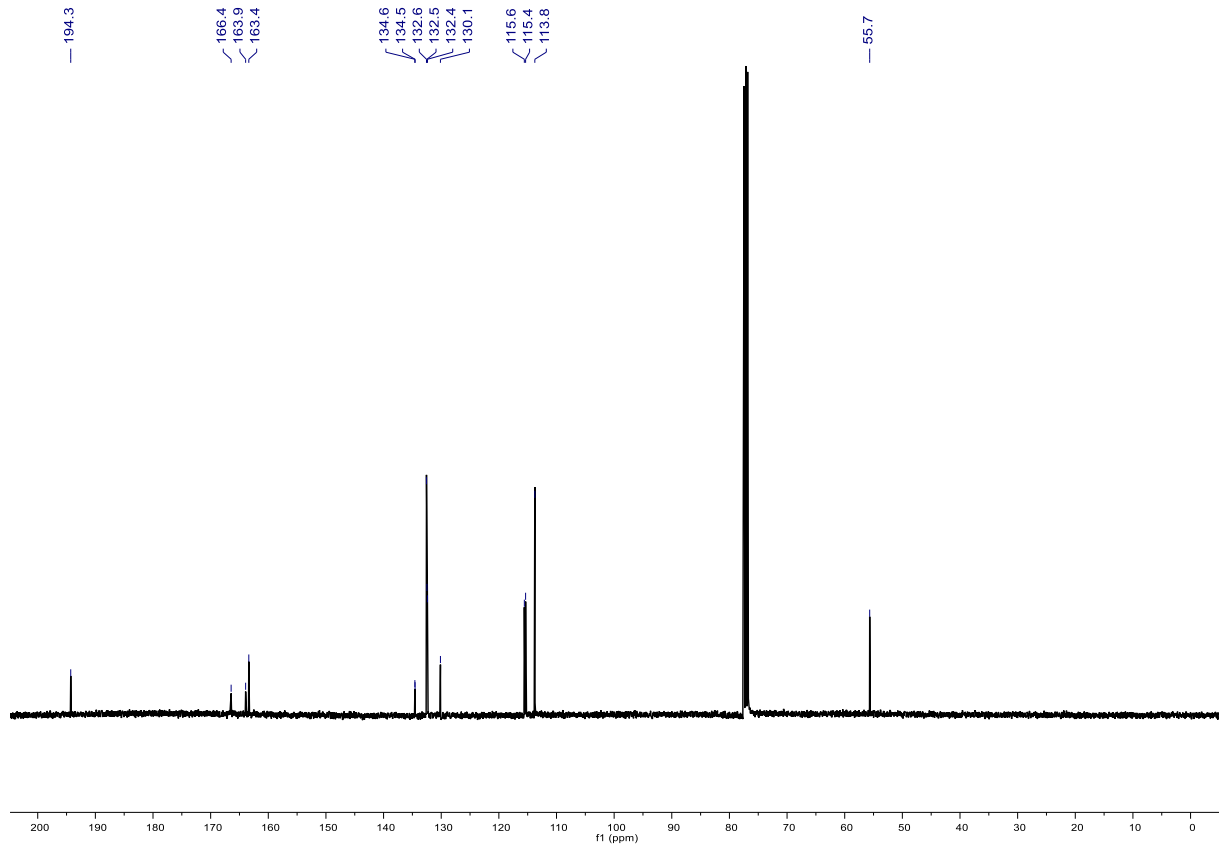


(2-Methoxyphenyl)(3-(methylthio)phenyl)methanone (3o')

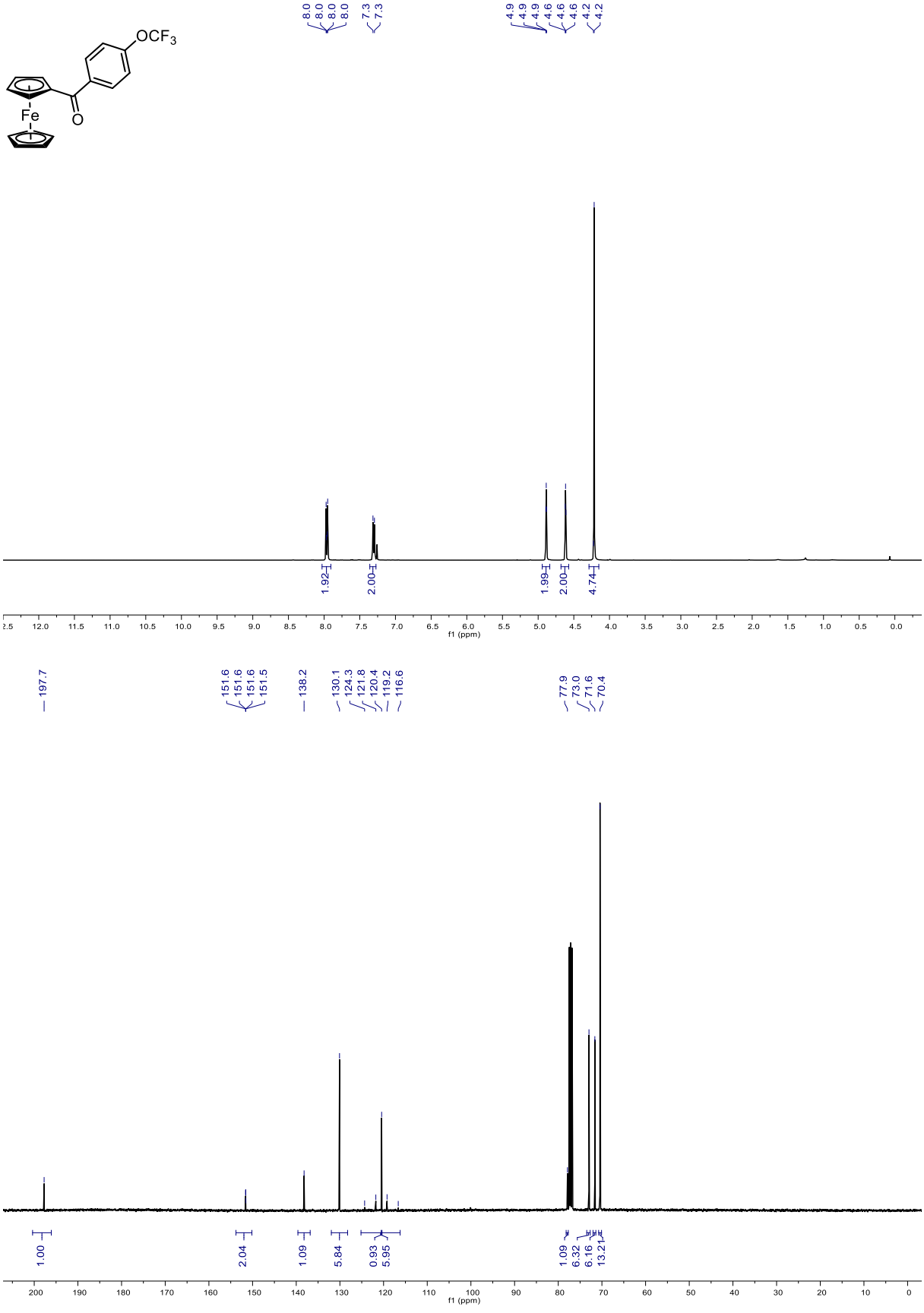


(4-Fluorophenyl)(4-methoxyphenyl)methanone (3p)

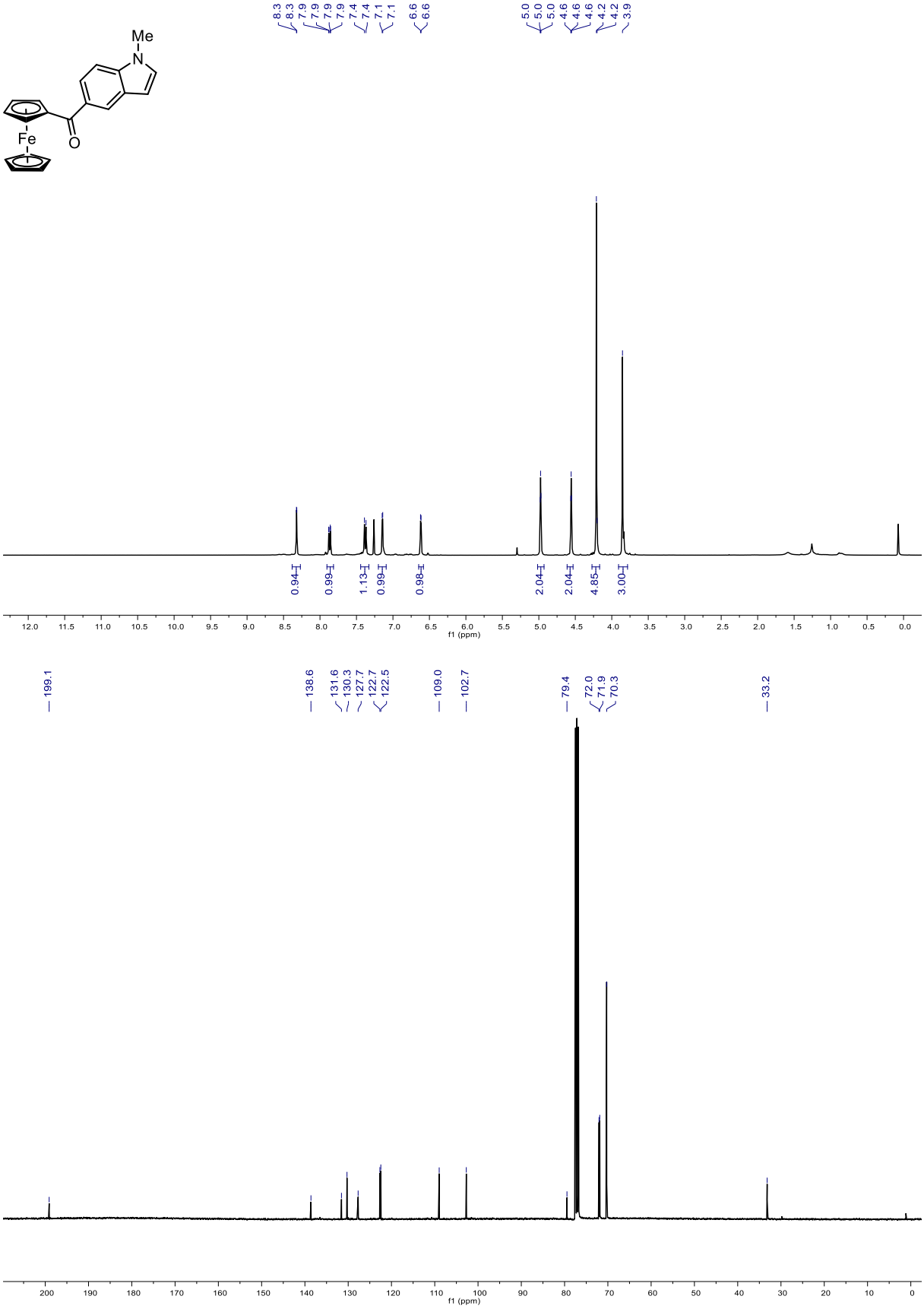




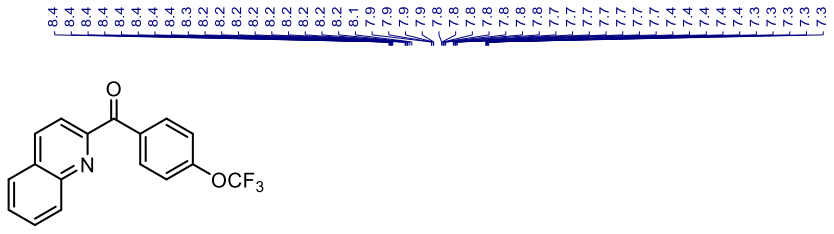
Ferrocenyl-(4-(trifluoromethoxy)phenyl)methanone (3q)

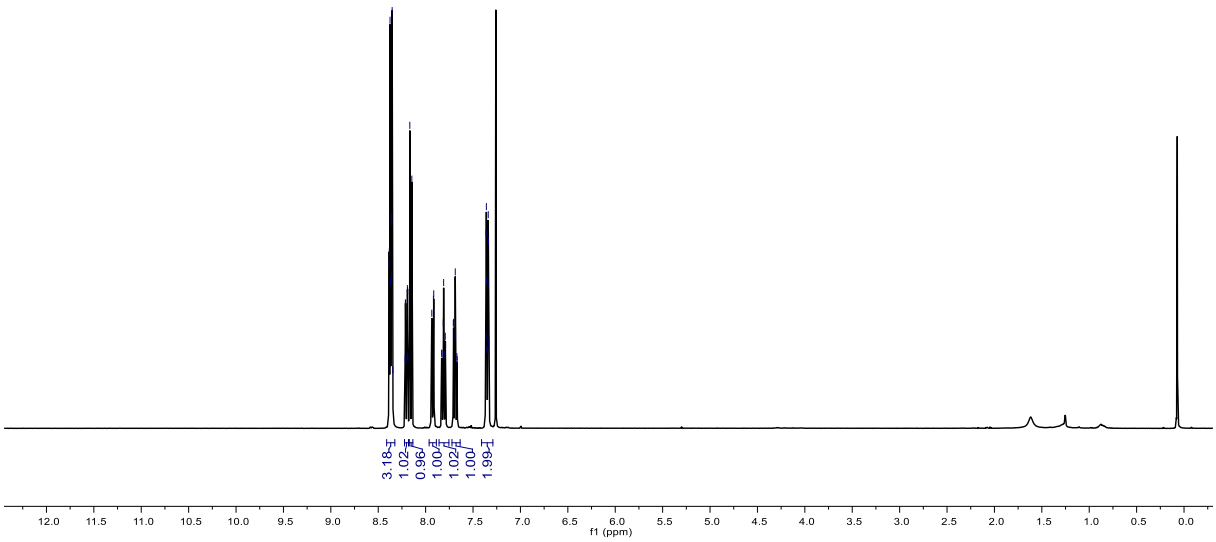


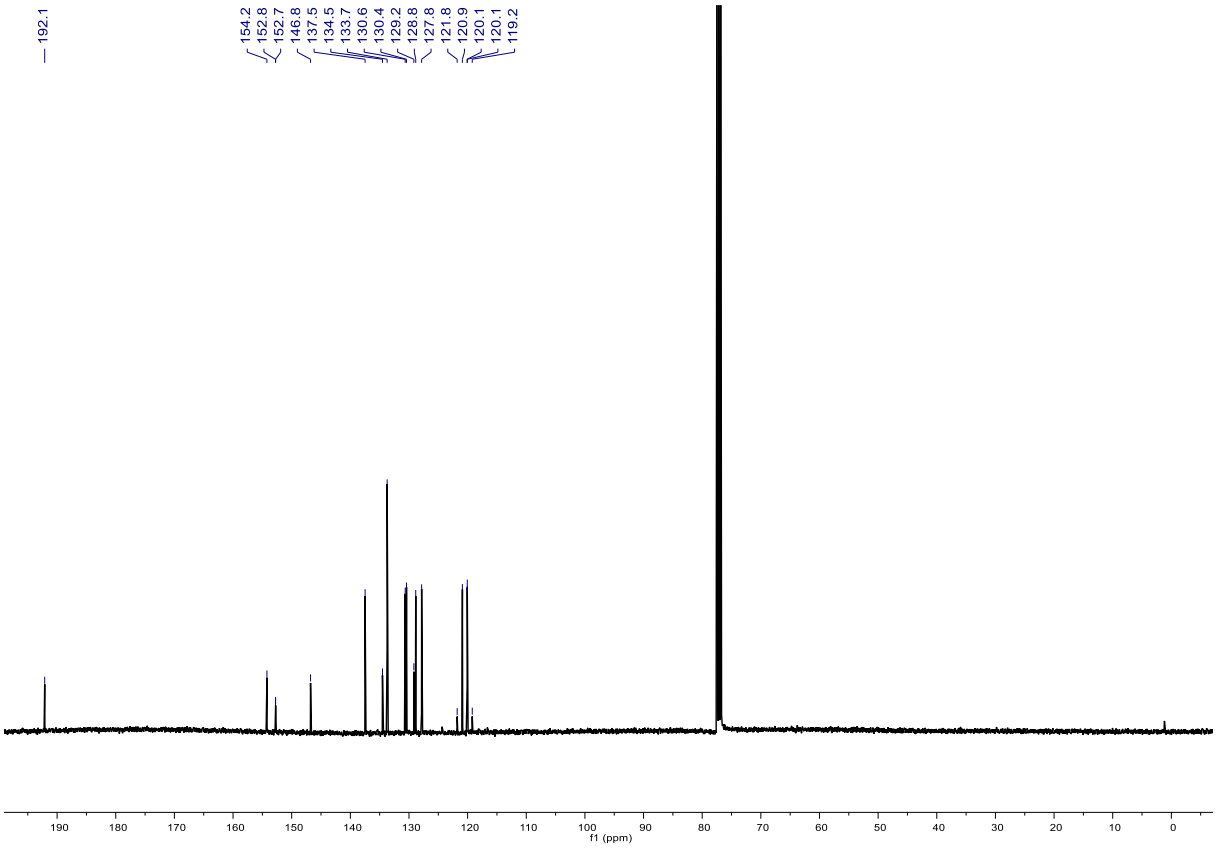
Ferrocenyl-(1-methyl-1*H*-indol-5-yl)methanone (3r)



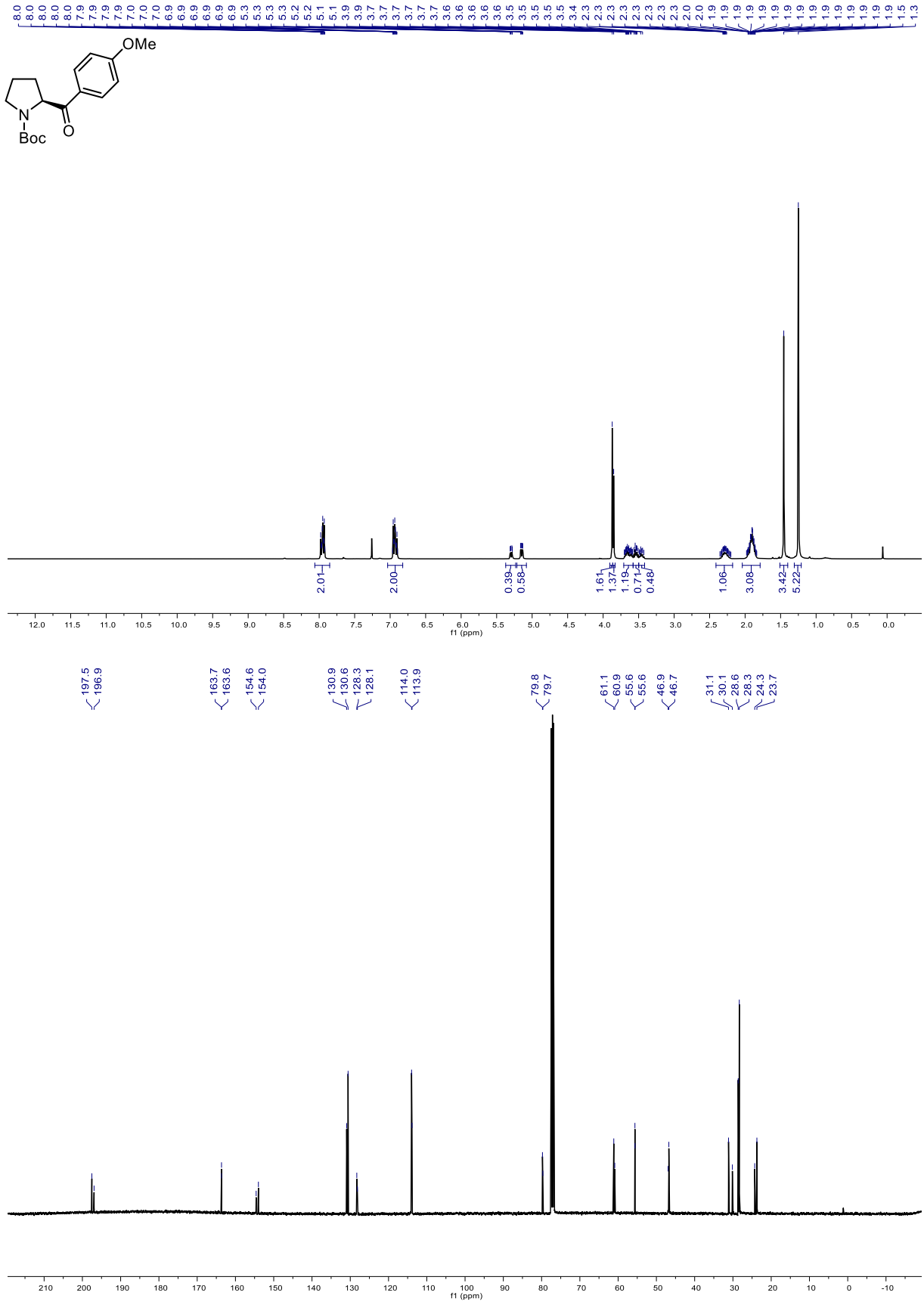
2-(4-*iso*-Butylphenyl)-1-(4-(trifluoromethoxy)phenyl)propan-1-one (3s)



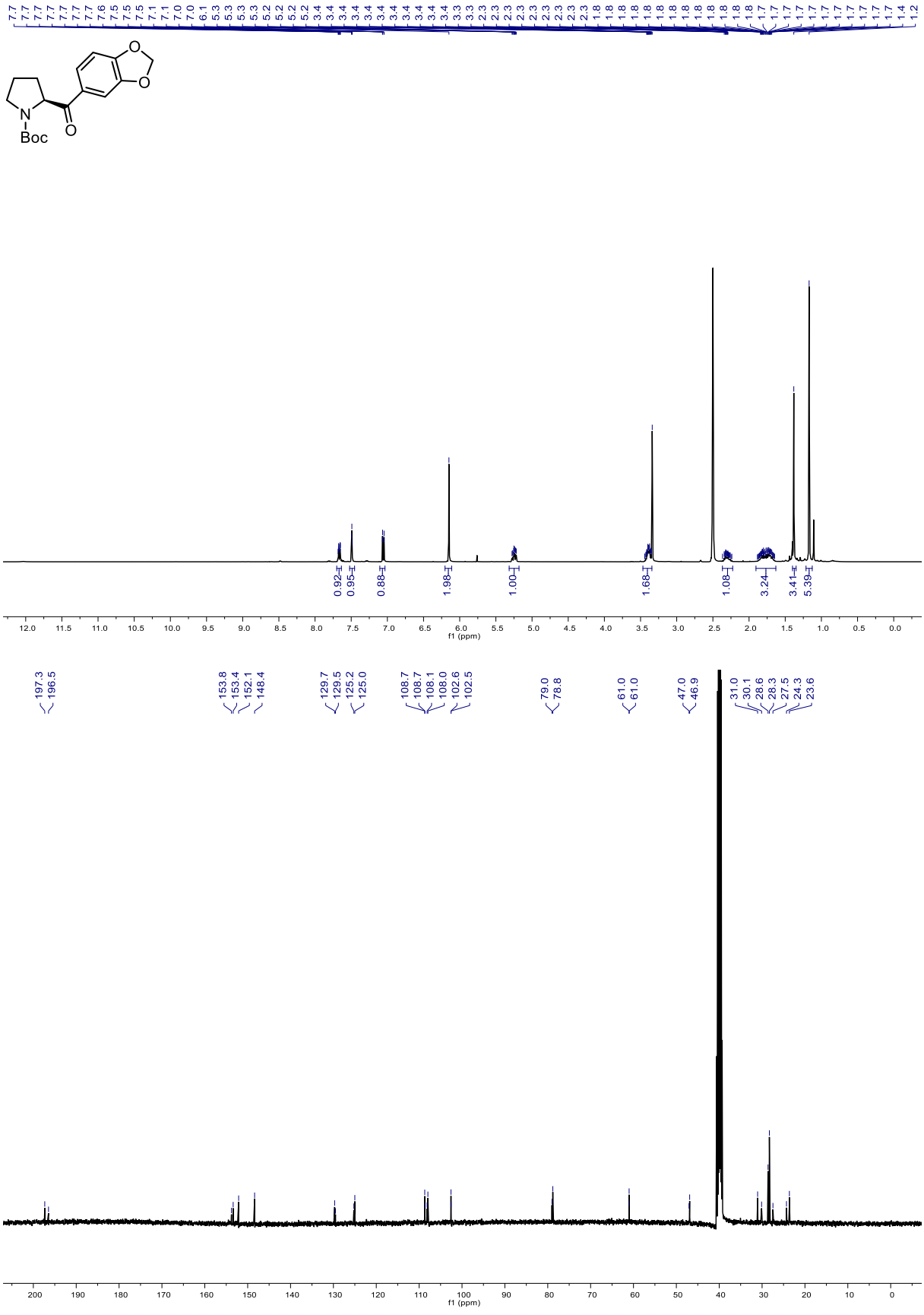




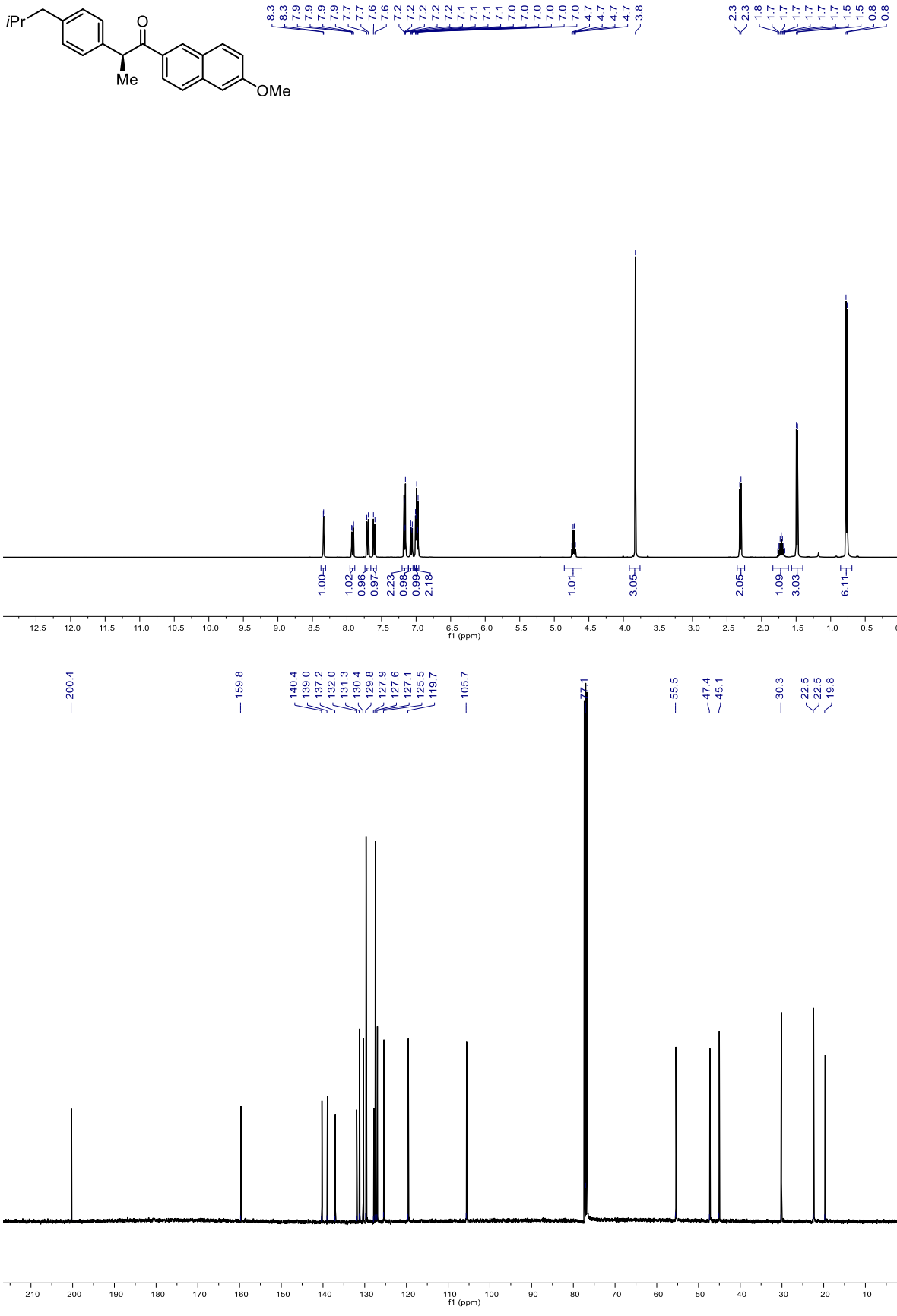
***tert*-Butyl (*S*)-2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate (3t)**



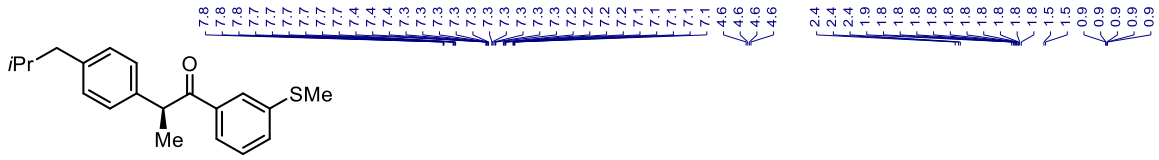
***tert*-Butyl (*S*)-2-(benzo[*d*][1,3]dioxole-5-carbonyl)pyrrolidine-1-carboxylate (3u)**

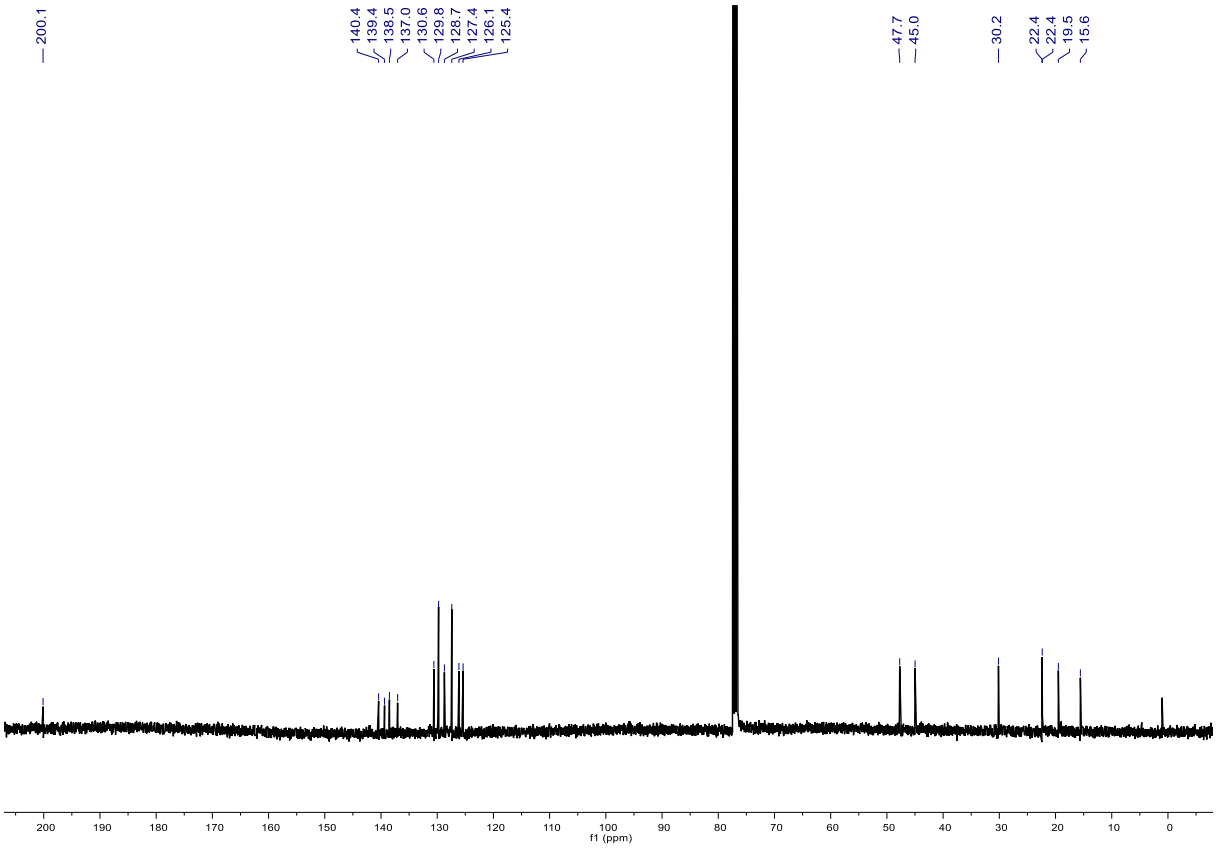


(*S*)-2-(4-*iso*-Butylphenyl)-1-(6-methoxynaphthalen-2-yl)propan-1-one (3v)

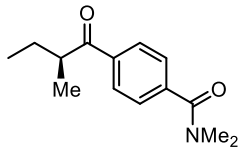


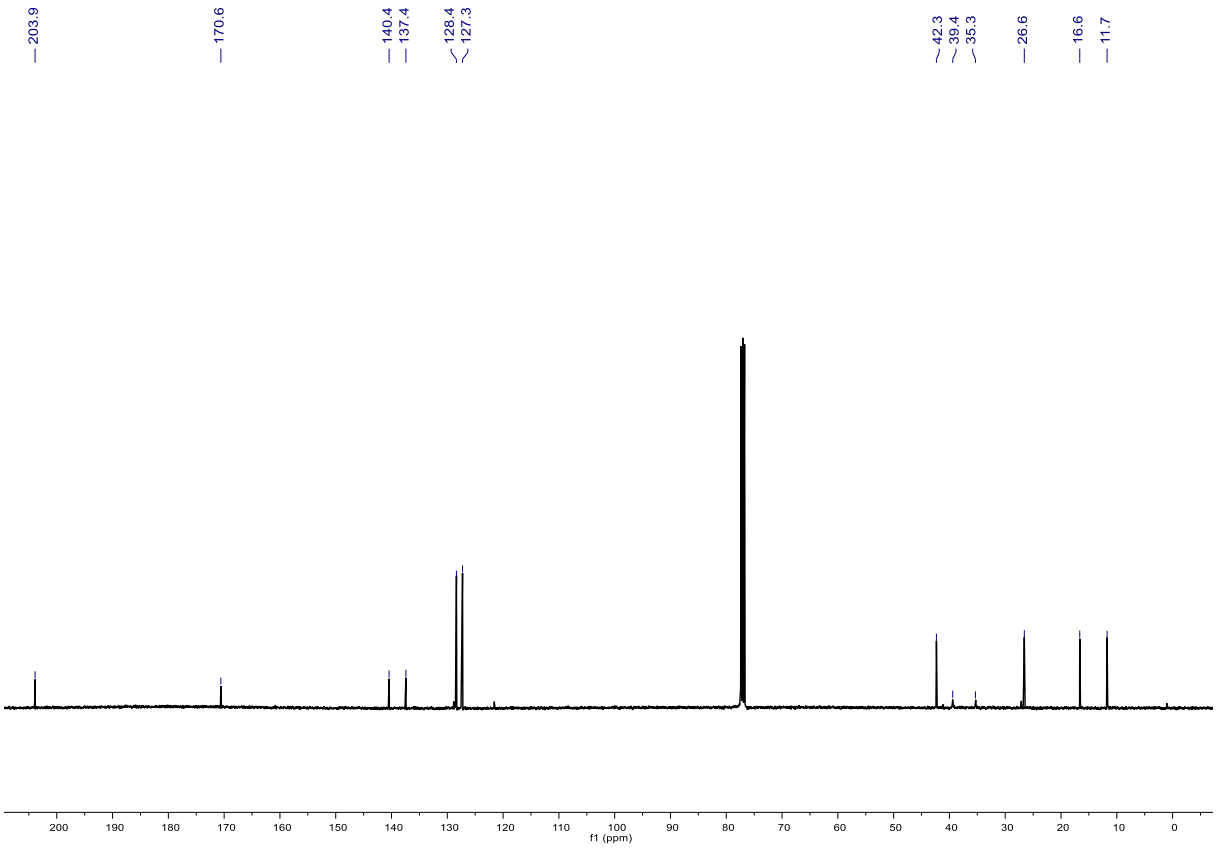
(*S*)-2-(4-*iso*-Butylphenyl)-1-(3-(methylthio)phenyl)propan-1-one (3w)



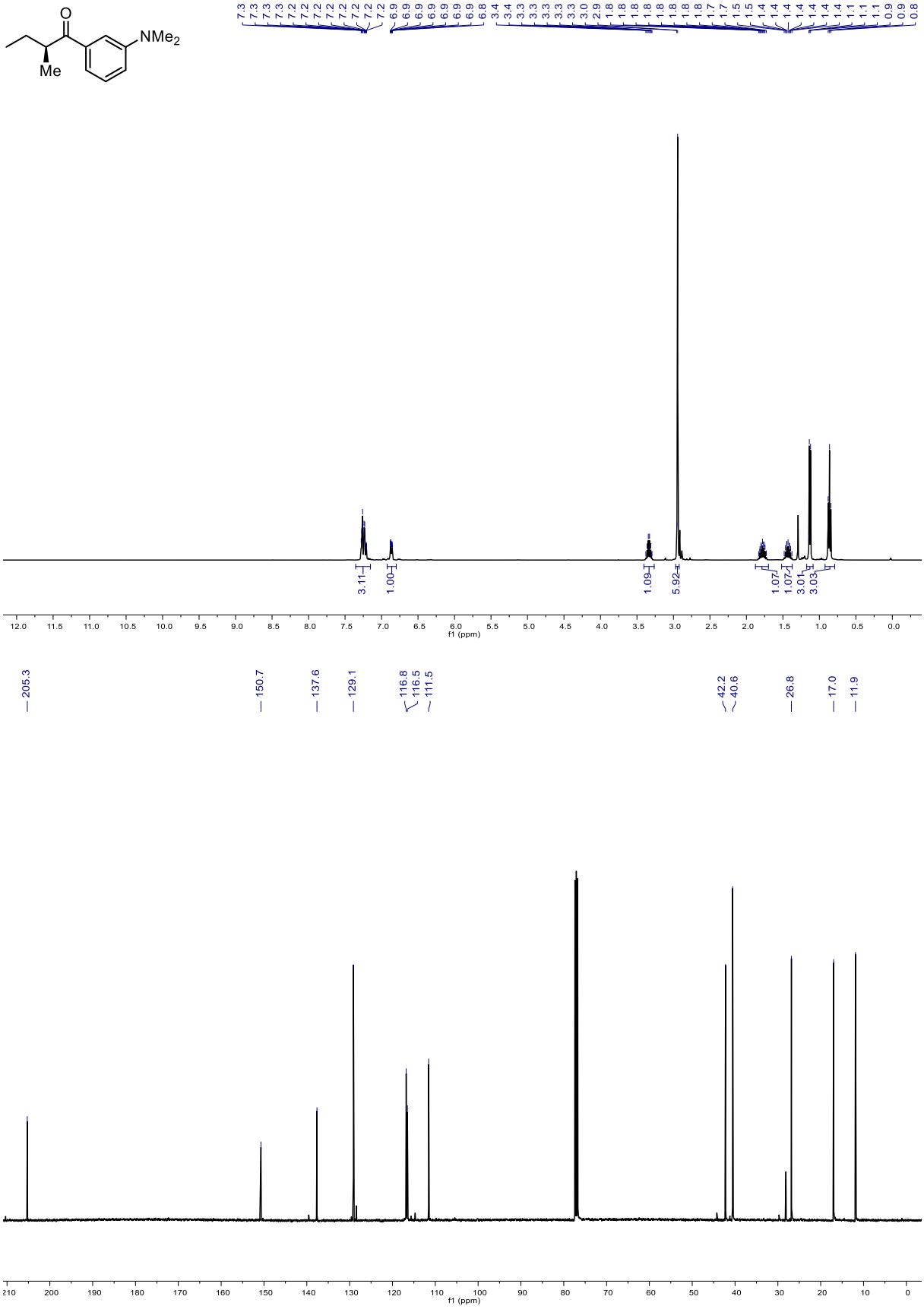


(*S*)-*N*,*N*-Dimethyl-4-(2-methylbutanoyl)benzamide (3x)





(*S*)-1-(3-(Dimethylamino)phenyl)-2-methylbutan-1-one (3y)



Fenofibrate (3z)