Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information for

From acetone metalation to the catalytic α-arylation of ketones with half-sandwich NHC-nickel(II) complexes

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I. General information

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon.

Solution NMR spectra were recorded at 298 K on FT-Bruker Ultra Shield 300 and FT Bruker Spectrospin 400 spectrometers operating at 300.13 or 400.14 MHz for ^1H, at 282 or 376 MHz for $^{19}F\{^1H\}$, and at 75.47 or 100.61 MHz for $^{13}C\{^1H\}$. DEPT ^{13}C spectra and/or $^1H/^{13}C$ HSQC correlations were recorded for the new complex $[Ni\{(iPr_2Ph)_2NHC\}(NCMe)Cp](PF_6)$ **7** and for the 2:1 mixture of 2-(4-methylphenyl)-4-methyl-pentan-3-one and 2-(4-methylphenyl)-2-methyl-pentan-3-one to help in the ^{13}C signal assignments. The chemical shifts are referenced to the residual deuterated or ^{13}C solvent peaks. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively.

The IR spectrum of **7** was recorded on a FT-IR Nicolet 380 spectrometer equipped with a diamond SMART-iTR ATR. Vibrational frequencies are expressed in cm^{-1}.

Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg.

GC analyses were performed with an Agilent 7820A GC system equipped with a 30-m capillary column (Agilent HP-5, cross-linked 5% phenyl silicone gum, 30 m × 0.32 mm × 0.25 μm). H_2/air was used as vector gas. The following GC conditions were used: initial temperature 40 °C, for 2 min, then rate 10 °C/min. until 200 °C, and 20 °C/min until 280 °C. 1,3,5-Trimethoxybenzene was used as an internal standard.

Commercial compounds were used as received. Coupling products that had been reported previously were isolated in greater than 95% purity, as determined by ^1H and ^{13}C NMR spectroscopy (see spectra, pp. S22-S35). New coupling products were characterized by ^1H

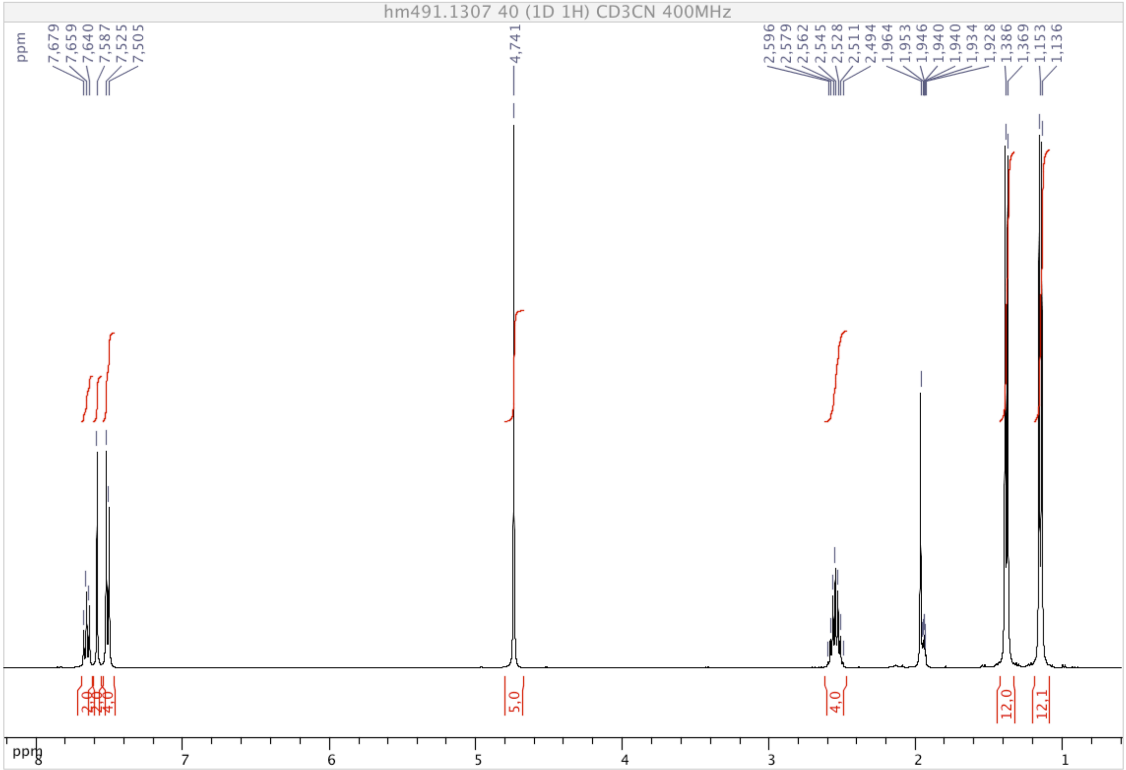
and ^{13}C NMR spectroscopy, and elemental analyses or high-resolution mass spectrometry. Nickelocene,[1] [Ni(Mes$_2$NHC)ClCp] **1**,[2] [Ni(Mes-NHC-*n*Bu)ICp] **5**,[3] [Ni{(*i*Pr$_2$Ph)$_2$NHC}ClCp] **6**,[4] and [Ni{(*i*Pr$_2$Ph)$_2$NHC}ClCp*] **8**[5] were prepared according to published methods.

II. Synthesis and characterization of [Ni{(*i*Pr$_2$Ph)$_2$NHC}(NCMe)Cp](PF$_6$) (7)

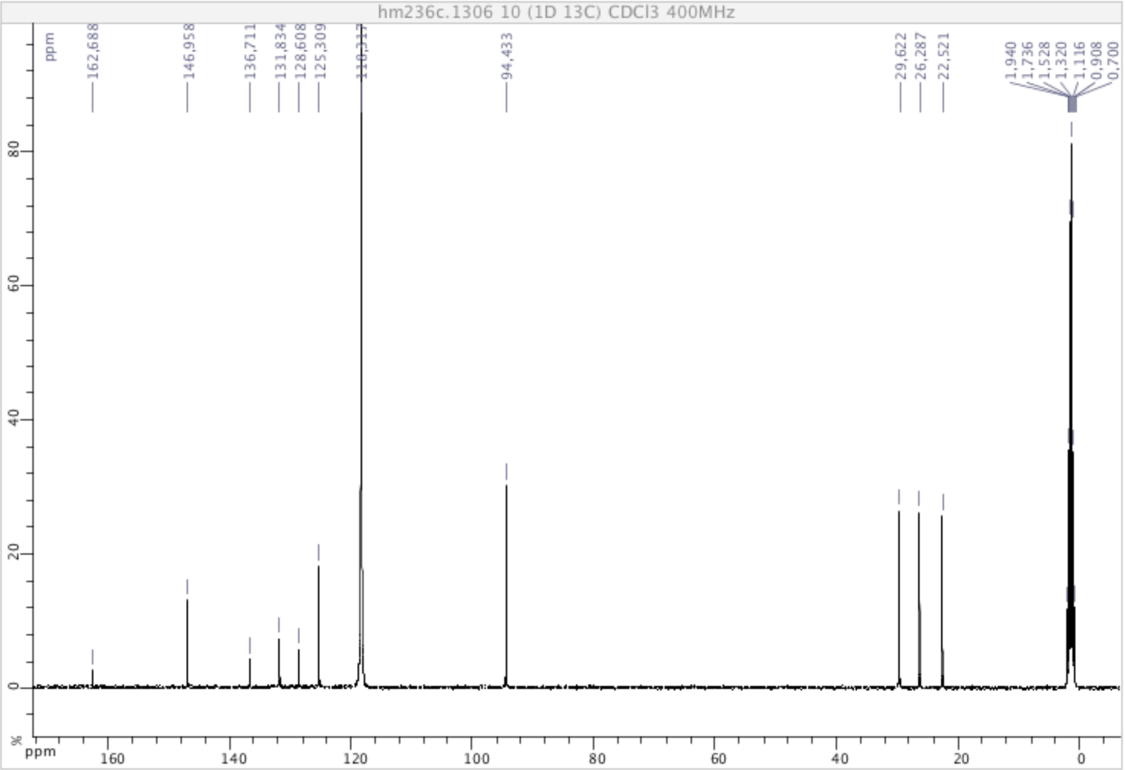
KPF$_6$ (168 mg, 0.913 mmol) and [Ni{(*i*Pr$_2$Ph)$_2$NHC}ClCp] **6** (500 mg, 0.913 mmol) were suspended in acetonitrile (10 mL), and the resulting mixture was stirred at room temperature. A quick colour change from violet to dark yellow was observed. After 15 min, the reaction medium was filtered through Celite, concentrated to ca. 3 mL, and treated with diethylether (10 mL) to yield a dark yellow solid that was washed with diethylether (3 x 10 mL), and dried under vacuum to give **7** (557 mg, 0.798 mmol, 87%). Anal. Calcd for $C_{34}H_{44}F_6N_3NiP$: C, 58.47; H, 6.35; N, 6.02. Found: C, 58.08; H, 6.36; N, 6.11. ^{1}H NMR (CD$_3$CN, 400.14 MHz): δ 7.66 (t, ^3J = 8.0, 2H, *p*-H); 7.59 (s, 2H, NC*H*); 7.52 (d, ^3J = 8.0, 4H, *m-H*); 4.74 (s, 5H, C$_5$*H*$_5$); 2.55 (hept, ^3J = 6.8, 4H, C*H*Me$_2$); 1.38 (d, ^3J = 6.8, 12H, CH*Me*$_2$); 1.14 (d, ^3J = 6.8, 12H, CH*Me*$_2$).[a] ^{13}C{^{1}H} NMR (CD$_3$CN, 100.61 MHz): δ 162.7 (N*C*N), 147.0 (*ipso*- or *o*-C$_{Ar}$), 136.7 (*o*- or *ipso*-C$_{Ar}$), 131.8 (*p*-C$_{Ar}$), 128.6 (N*C*H), 125.3 (*m*-C$_{Ar}$), 94.4 (*C*$_5$H$_5$), 29.6 (*C*HMe$_2$), 26.3 and 22.5 (CH*Me*$_2$). FT-IR: ν(CH) 2963 (m), 2928 (w), 2866 (w); ν(P-F) 835 (s).

[a] Free CH$_3$CN that results from exchange with CD$_3$CN is seen as a singlet (at 1.96 ppm) on the downfield side of the multiplet due to residual CHD$_2$CN observed at 1.94 ppm.

^{1}H NMR spectrum of (7)



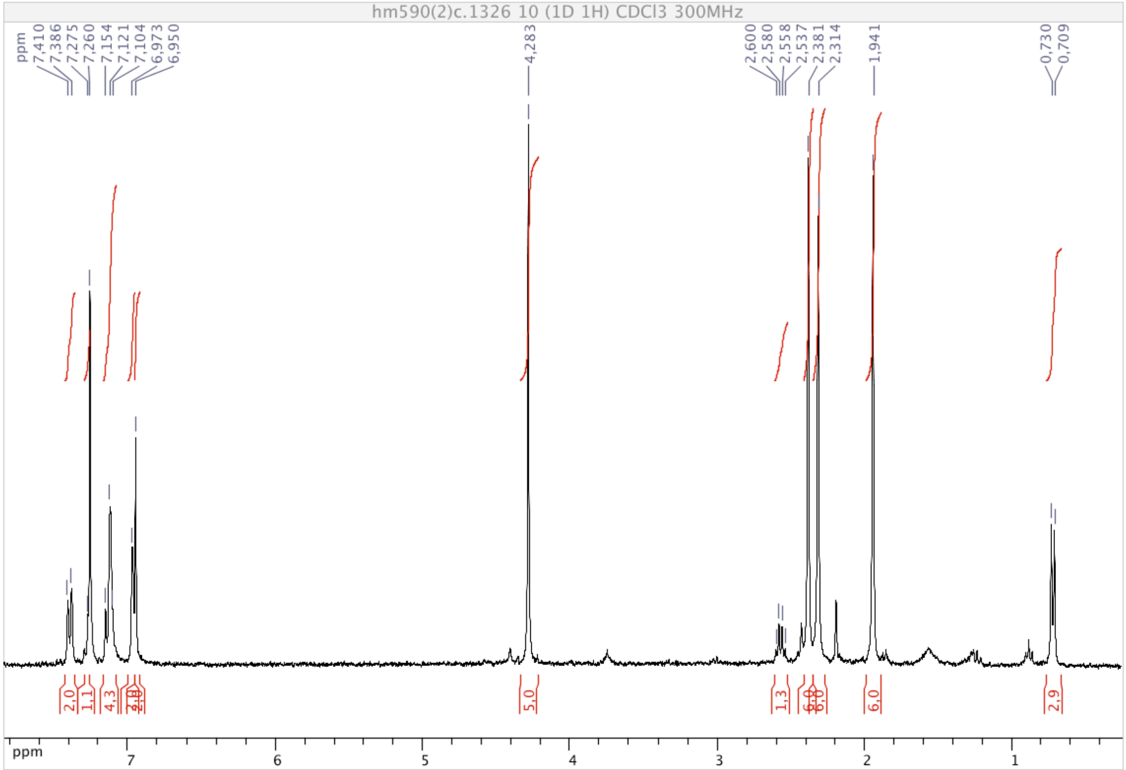
^{13}C{^{1}H} NMR spectrum of (7)



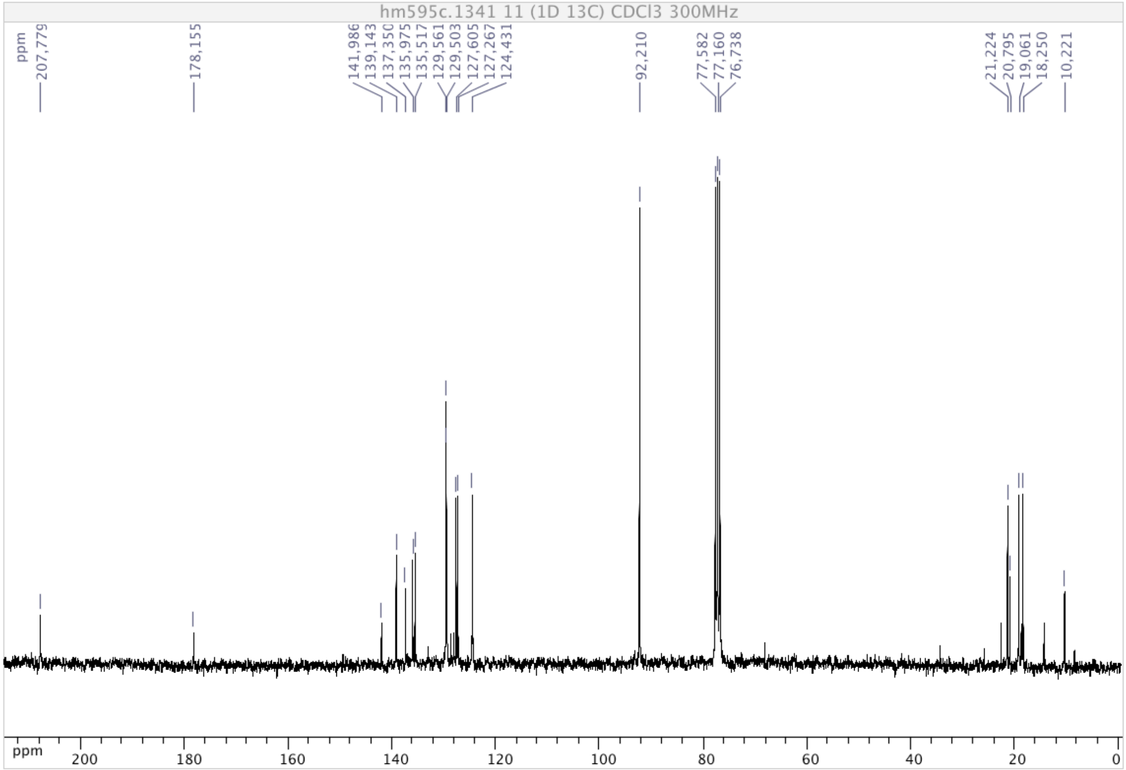
III. Synthesis and characterization of [Ni(Mes$_2$NHC){CH(CH$_3$)C(O)Ph}Cp] (9)

To [Ni(Mes$_2$NHC)ClCp] **1** (500 mg, 1.08 mmol), KO*t*-Bu (121 mg, 1.08 mmol) and propiophenone (145 mL, 1.08 mmol) was added toluene (5 mL). The resulting suspension was stirred at room temperature for 4 h during which a colour change from violet to red-brown was observed. Volatiles were then removed *in vacuo*. Addition of pentane (20 mL) to the residue gave a solid that was collected on a frit, washed with pentane until the washings were colourless, extracted with THF (40 mL) and filtered over Celite. Concentration of the filtrate to *ca*. 5 mL and addition of 20 mL of pentane then gave a reddish solid that was washed with pentane until the washings were colourless. Recrystallization from THF/pentane (1:5) at –28°C finally afforded **9** (273 mg, 0.486 mmol, 45%) as red-brown crystals. Anal. Calcd for $C_{35}H_{38}N_2NiO$: C, 74.88; H, 6.82; N, 4.99. Found: C, 73.54; H, 6.69; N, 4.99. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 7.40 (d, ^3J = 7.5, 2H, Ph), 7.28 (m, 1H, Ph), 7.12 (m, 4H, Ph and *m*-H), 6.97 (br. s, 2H, *m*-H), 6.95 (s, 2H, NC*H*), 4.28 (s, 5H, C_5H_5), 2.57 (q, ^3J = 6.0, 1H, C*H*(CH$_3$)), 2.38 (s, 6H, *o*- or *p*-Me), 2.31 (s, 6H, *o*- or *p*-Me), 1.94 (s, 6H, *o*-Me), 0.72 (d, ^3J = 6.0, 3H, CH(CH_3)). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 207.8 (*C*O), 178.2 (N*C*N), 142.0, 139.1, 137.4, 136.0, 135.5, 129.6, 129.5, 127.6, 127.3, 124.4 (C_{Ar} and N*C*H), 92.2 (C_5H_5), 21.2 (*p*-Me), 20.8 (*C*H(CH$_3$)), 19.1 (*o*-Me), 18.3 (*o*-Me), 10.2 (CH(*C*H$_3$)).

^{1}H NMR spectrum of (9)



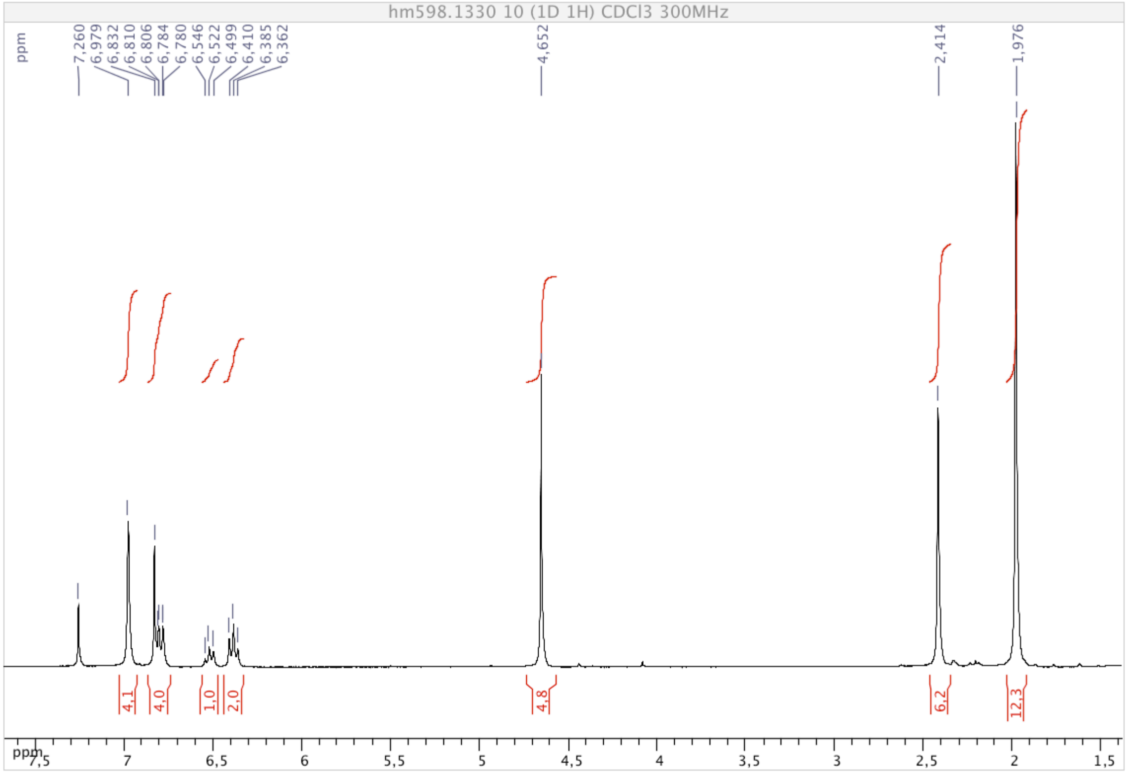
^{13}C{^{1}H} NMR spectrum of (9)



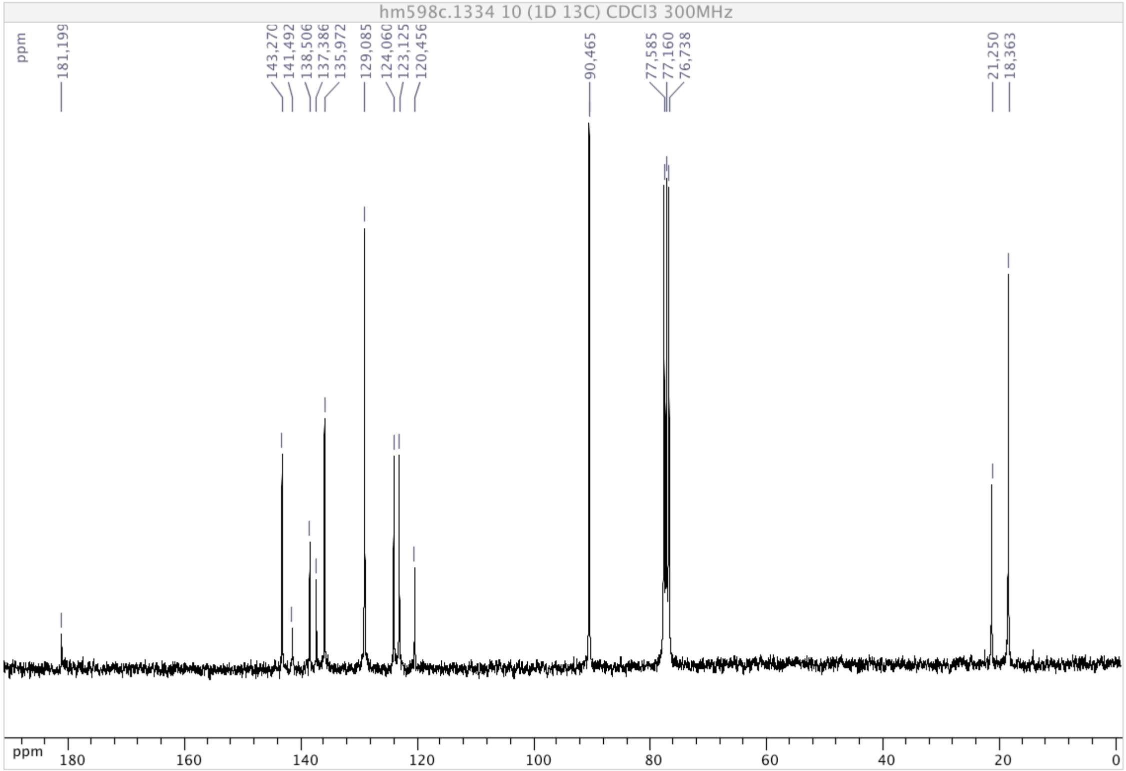
IV. Synthesis and characterization of [Ni(Mes$_2$NHC)PhCp] (10)

[Ni(Mes$_2$NHC)ClCp] **1** (500 mg, 1.08 mmol) was dissolved THF (10 mL). The resulting solution was cooled to –78°C before drop-wise addition of PhLi (1.8 M in Bu$_2$O, 0.60 mL, 1.08 mmol). The reaction medium was then allowed to warm to room temperature, during which time a colour change from violet to brown was observed. The reaction mixture was subsequently filtered over Celite, concentrated under vacuum to *ca*. 3 mL and treated with pentane (10 mL), to yield brown crystals after standing at –28°C for 16 h. The crystals were washed with pentane (2 x 10 mL) and dried under vacuum to give **10** (343 mg, 0.679 mmol, 63%). Anal. Calcd for $C_{32}H_{34}N_2Ni$: C, 76.06; H, 6.78; N, 5.54. Found: C, 75.96; H, 6.98; N, 5.38. ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 6.98 (s, 4H, *m*-H), 6.83 (s, 2H, NC*H*), 6.80 (dd, ^3J = 7.8, ^4J = 1.5, 2H, Ph), 6.52 (tt, ^3J = 7.1, ^4J n.r., 1H, Ph), 6.39 (t, ^3J = 7.2, 2H, Ph), 4.65 (s, 5H, C_5H_5), 2.41 (s, 6H, *p*-Me), 1.98 (s, 12H, *o*-Me). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz): δ 181.2 (N*C*N), 143.3, 141.5, 138.5, 137.4, 136.0, 129.1, 124.1, 123.1, 120.5 (C_{Ar} and N*C*H), 90.5 (C_5H_5), 21.3 (*p*-Me), 18.4 (*o*-Me).

^{1}H NMR spectrum of (10)



^{13}C{^{1}H} NMR spectrum of (10)



V. X-ray diffraction study of (7) and (10): structure determination and refinement

Single crystals of **7** and **10** suitable for X-ray diffraction studies were selected from batches of crystals obtained at 4°C from an acetonitrile / diethylether solution and at RT from a toluene / pentane solution, respectively. Diffraction data were collected at 173(2) K on a Bruker APEX II DUO KappaCCD area detector diffractometer equipped with an Oxford Cryosystem liquid N_2 device using Mo-Kα radiation ($\lambda = 0.71073$ Å). A summary of crystal data, data collection parameters and structure refinements is given in Table S1. The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)[6] from reflections taken from tree sets of twelve frames, each at 10 s exposure. The structure was solved using direct methods with SHELXS-97 and refined against F^2 for all reflections using the SHELXL-97 software.[7] A semi-empirical absorption correction was applied using SADABS in APEX2.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters, using weighted full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters.

The asymmetric unit of **7** contains two independent cationic molecules, $[\mathrm{Ni}\{(i\mathrm{Pr}_2\mathrm{Ph})_2\mathrm{NHC}\}(\mathrm{NCMe})\mathrm{Cp}]^+$, two anions, PF_6^-, and one molecule of acetonitrile. Squeeze instruction was used to suppress a second molecule of acetonitrile that exhibits too much disorder.

Crystallographic data (excluding structure factors) have also been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication nos. CCDC 983811 (**7**) and 983818 (**10**). Copies of the data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. X-Ray Crystallographic Data and Data Collection Parameters for **7** and **10**.

Complex	**7**	**10**
Empirical formula	$2(C_{34}H_{44}N_3Ni)\cdot 2(F_6P)\cdot C_2H_3N$	$C_{32}H_{34}N_2Ni$
Formula weight	1437.86	505.32
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	36.2607 (19)	21.3657 (16)
b (Å)	16.6530 (9)	8.2297 (7)
c (Å)	12.6625 (7)	15.7213 (12)
β (°)	97.198 (1)	104.982 (2)
V (Å^3)	7586.0 (7)	2670.4 (4)
Z	4	4
D_{calcd} (Mg.m^{-3})	1.259	1.257
Absorp coeff (mm^{-1})	0.610	0.749
Crystal habit, color	Prism, green	Prism, red
Crystal size (mm)	0.45 × 0.25 × 0.20	0.28 × 0.20 × 0.15
h, k, l_{max}	47, 22, 16	29, 5, 21
T_{min}, T_{max}	0.771, 0. 888	0.818, 0.896
Reflns collected	96242	19927
R [I > 2σ(I)])	0.0485	0.0432
wR^2 (all data)	0.1099	0.1136
GOF on F^2	1.058	1.004

VI. ORTEP plot of complex (7)

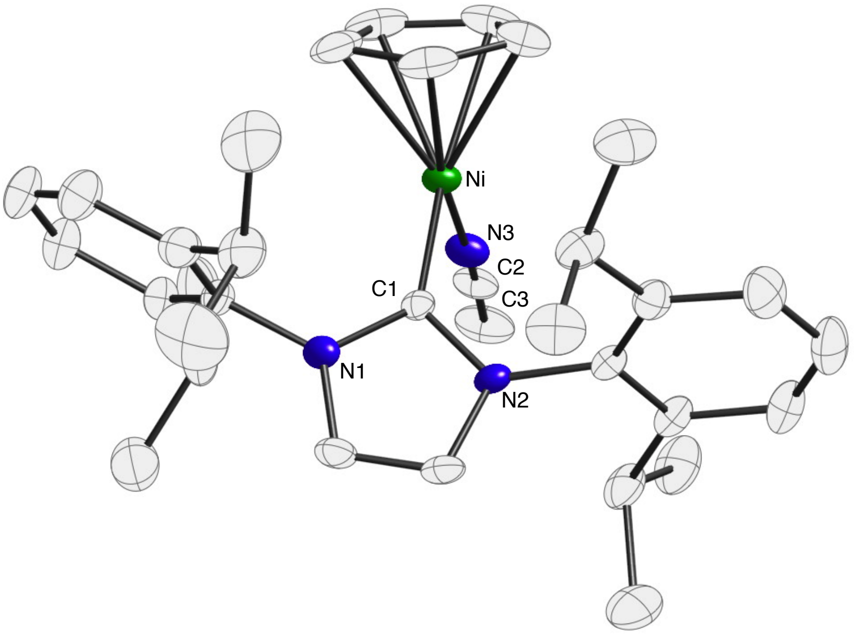


Fig. S1. Molecular structure of one cation of **7** showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labelled. Selected distances (Å) and angles (°) for both cations contained in the asymmetric unit: Ni–C1, 1.8885(19)/1.8912(19); Ni–N3, 1.863(2)/1.8637(19); Ni–Cp_{cent}, 1.746/1.749; C1–Ni–N3, 97.24(8)/96.29(8); C1–Ni–Cp_{cent}, 134.55/135.25; N3–Ni–Cp_{cent}, 127.89/128.16.

VII. Optimisation: solvent and base influence

Table S2. Optimization for the α-arylation of propiophenone with 4-bromotoluene catalyzed by **6**.[a]

Entry	Base	Solvent	Yield (%)[b]
1[c]	-	Toluene	0
2	LiO*t*Bu	Toluene	21
3	LiO*t*Bu	Dioxane	21
4	NaO*t*Bu	Toluene	65
5[c]	NaO*t*Bu	Toluene	78
6[d]	NaO*t*Bu	Toluene	0
7	NaO*t*Bu	Dioxane	3
8	KO*t*Bu	Toluene	0
9	KO*t*Bu	Dioxane	0
10	NaH	Toluene	24
11	NaH	Dioxane	0
12	NaOH	Toluene	4
13	NaOH	Dioxane	0
14	Cs_2CO_3	Toluene	0
15	Cs_2CO_3	Dioxane	0
16	K_3PO_4	Toluene	1
17	K_3PO_4	Dioxane	0

[a] *Reaction conditions:* propiophenone (1.2 mmol), 4-bromotoluene (1.0 mmol), base (1.5 mmol), **6** (5 mol%), solvent (3 mL), reflux, 24 h. [b] Yields determined by GC; average value of two runs. [c] **6** (3 mol%). [d] Reactions run in the absence of **6**.

VIII. General procedure for the α-arylation of ketones

A 10 mL oven dried Schlenk tube containing a stirring bar was loaded with **6** (16 mg, 0.03 mmol), NaO*t*Bu (144 mg, 1.50 mmol), the aryl halide (1.00 mmol), the ketone (1.20 mmol) and toluene (3 mL). The resulting suspension was stirred in a preheated oil bath at 110 °C for 24 h. The reaction mixture was then quenched by the addition of a solution of saturated aqueous NH_4Cl (10 mL), and the product extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The residue was then purified by column chromatography on silica gel (40-63 μm), eluting with toluene to provide the title α-arylated ketone. All yields are the average value of at least two runs.

IX. Control experiments

Each experiment described hereafter was performed twice.

Investigation of the mercury effect

The experiment was performed as per the general procedure using 4-bromotoluene (171 mg, 1.00 mmol), propiophenone (160 μL, 1.20 mmol), **6** (27 mg, 0.05 mmol), and mercury (100 mg, 0.50 mmol). GC analysis indicated 59% yield of 1-phenyl-2-(4-methylphenyl)-propan-1-one.

Reaction of complex (9) with 4-bromotoluene

A suspension of **9** (100 mg, 0.178 mmol) and 4-bromotoluene (31 mg, 0.181 mmol) in toluene (5 mL) was stirred at 110 °C for 24 h, during which a colour change from reddish to brown as well as the formation of a black solid was observed. The reaction medium was purified by flash silica column chromatography using toluene as eluent. Two fractions were collected: one containing propiophenone (15 mg, 0.112 mmol, 63%) and traces of 1-phenyl-2-(4-methylphenyl)-propan-1-one and another yielding a violet solid after solvent removal. The latter (19 mg, 0.037 mmol, 21%) was identified as [Ni(Mes_2NHC)BrCp] by comparison of its NMR data with those of [Ni(Mes_2NHC)ClCp] **1**,[2] and by its mass spectrum. ESI-MS: *m/z* $[M]^+$ calcd for $C_{26}H_{29}N_2NiBr$ 506.09, found 506.08; calcd for $C_{26}H_{29}N_2Ni$ 427,17, found

427,16. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 7.11 (s, 4H, *m*-H), 7.07 (s, 2H, NC*H*), 4.63 (s, 5H, C_5H_5), 2.43 (s, 6H, *p*-Me), 2.19 (s, 12H, *o*-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 167.6 (N*C*N), 139.2, 136.8, 136.0, 129.4 (C_{Ar}), 124.7 (N*C*H), 92.5 (C_5H_5), 21.4 (*p*-Me), 18.9 (*o*-Me).

Catalytic α-arylation of propiophenone with (9) as pre-catalyst

The experiment was performed as per the general procedure using 4-bromotoluene (171 mg, 1.00 mmol), propiophenone (160 μL, 1.20 mmol) and **9** (28 mg, 0.050 mmol). GC analysis indicated 11% yield of 1-phenyl-2-(4-methylphenyl)-propan-1-one.

Reaction of complex (10) with propiophenone

To a suspension of **10** (70 mg, 0.139 mmol) and NaO*t*Bu (13 mg, 0.135 mmol) in toluene (5 mL) was added propiophenone (20 μL, 0.150 mmol). The resulting mixture was stirred at 110 °C for 24 h. No colour change was observed. The reaction was then quenched by the addition of a saturated aqueous solution of NH_4Cl (10 mL), and the product extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was then purified by flash silica column chromatography using toluene as eluent. No coupling product was collected, and 12 mg propiophenone (0.089 mmol, 59%) was recovered.

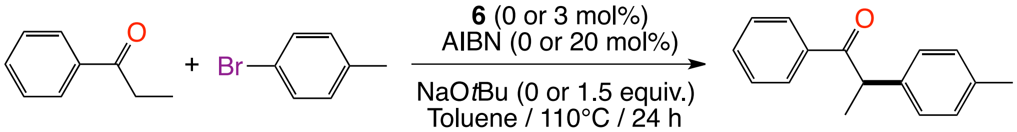
Investigation of radical scavenger effect

The experiments were performed as per the general procedure using 4-bromotoluene (171 mg, 1.00 mmol), propiophenone (160 μL, 1.20 mmol) and TEMPO (156 mg, 1.00 mmol) or galvinoxyl (422 mg, 1.00 mmol). GC analyses indicated no conversion to 1-phenyl-2-(4-methylphenyl)-propan-1-one in both cases.

Investigation of radical initiator effect

The experiment was performed as per the general procedure using 4-bromotoluene (171 mg, 1.00 mmol), propiophenone (160 μL, 1.20 mmol), and AIBN (34 mg, 0.20 mmol), but without NaO*t*Bu and **6**. GC analysis indicated 5% yield of 1-phenyl-2-(4-methylphenyl)-propan-1-one (Table S3, entry 4). In the presence of **6** (16 mg, 0.03 mmol) and/or NaO*t*Bu (144 mg, 1.50 mmol), GC analyses indicated no conversion (entries 2 and 3).

Table S3. α-Arylation of propiophenone with 4-bromotoluene catalyzed by **6** and/or AIBN.[a]

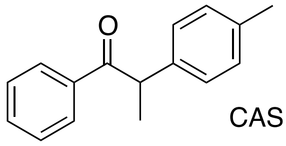


Entry	Catalyst (mol%)	NaO*t*Bu (equiv.)	Yield (%)[b]
1[c]	**6** (3)	1.5	78
2	**6** (3) + AIBN (20)	1.5	< 1
3	AIBN (20)	1.5	< 1
4	AIBN (20)	0	5

[a] Reaction conditions: propiophenone (1.2 mmol), 4-bromotoluene (1 mmol), NaO*t*Bu (0 or 1.5 mmol), **6** (0 or 3 mol%), AIBN (0 or 20 mo%) in toluene (3 mL) at 110 °C for 24 h. [b] Yields determined by GC; average value of two runs.

X. Spectral data of the coupling products

1-phenyl-2-(4-methylphenyl)-propan-1-one[8] (Table 2, entry 1)

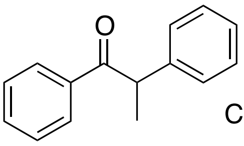


CAS 107271-15-8

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 7.95 (d, ^3J = 7.2, 2H, H$_{Ar}$), 7.47 (t, ^3J = 7.2, 1H, H$_{Ar}$), 7.37 (t, ^3J = 7.3, 2H, H$_{Ar}$), 7.17 (d, ^3J = 8.1, 2H, H$_{Ar}$), 7.10 (d, ^3J = 7.8, 2H, H$_{Ar}$), 4.65 (q, ^3J = 6.9, 1H, C*H*(CH$_3$)), 2.28 (s, 3H, C*H$_3$*), 1.51 (d, ^3J = 6.9, 3H, CH(C*H$_3$*)). ^{13}C{^{1}H} NMR

($CDCl_3$, 75.47 MHz): δ = 200.5 (*C*O), 138.6, 136.7, 136.6, 132.8, 129.8, 128.9, 128.6, 127.7 (C_{Ar}), 47.6 (*C*H(CH_3)), 21.1 (*C*H_3), 19.6 (CH(*C*H_3)).

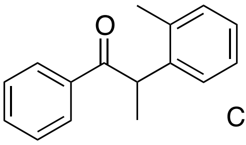
1,2-diphenylpropan-1-one[8] (Table 2, entries 3-4)



CAS 2042-85-5

^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.93 (d, ^3J = 7.2, 2H, H_{Ar}), 7.45 (t, ^3J = 7.5, 1H, H_{Ar}), 7.35 (t, ^3J = 7.5, 2H, H_{Ar}), 7.27-7.24 (m, 4H, H_{Ar}), 7.19 (m, 1H, H_{Ar}), 4.66 (q, ^3J = 6.9, 1H, C*H*(CH_3)), 1.51 (d, ^3J = 6.9, 3H, CH(CH_3)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 200.4 (*C*O), 141.6, 136.6, 132.9, 129.1, 128.9, 128.6, 127.9, 127.0 (C_{Ar}), 48.0 (*C*H(CH_3)), 19.6 (CH(*C*H_3)).

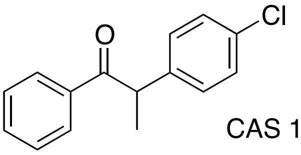
1-phenyl-2-(2-methylphenyl)-propan-1-one[8] (Table 2, entries 5-6)



CAS 53423-27-1

^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.82 (d, ^3J = 7.2, 2H, H_{Ar}), 7.45 (t, ^3J = 7.4, 1H, H_{Ar}), 7.35 (t, ^3J = 7.8, 2H, H_{Ar}), 7.20 (d, ^3J = 6.8, 1H, H_{Ar}), 7.10 (m, 2H, H_{Ar}), 7.02 (dd, ^3J = 7.2, ^4J = 2.0, 1H, H_{Ar}), 4.76 (q, ^3J = 6.8, 1H, C*H*(CH_3)), 2.50 (s, 3H, CH_3), 1.47 (d, ^3J = 6.8, 3H, CH(CH_3)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz): δ = 201.1 (*C*O), 140.3, 136.7, 134.7, 132.8, 131.1, 128.6, 127.1, 127.0, 126.9 (C_{Ar}), 44.7 (*C*H(CH_3)), 19.8 and 18.2 (*C*H_3 and CH(*C*H_3)).

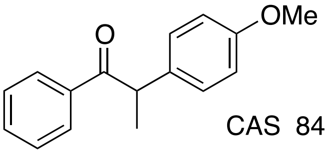
1-phenyl-2-(4-chlorophenyl)-propan-1-one[9] (Table 2, entry 7)



CAS 126866-18-0

^{1}H NMR ($CDCl_3$, 300.14 MHz): δ = 7.93 (d, ^3J = 7.2, 2H, H_{Ar}), 7.50 (t, ^3J = 7.4, 1H, H_{Ar}), 7.39 (t, ^3J = 7.4, 2H, H_{Ar}), 7.27 (d, ^3J = 8.7, 2H, H_{Ar}), 7.22 (d, ^3J = 8.7, 2H, H_{Ar}), 4.67 (q, ^3J = 6.8, 1H, C*H*(CH_3)), 1.52 (d, ^3J = 6.9, 3H, CH(C*H_3*)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 200.1 (*C*O), 140.0, 136.4, 133.1, 133.0, 129.3, 128.8, 128.7 (C_{Ar}), 47.3 (*C*H(CH_3)), 19.6 (CH(*C*H_3)).

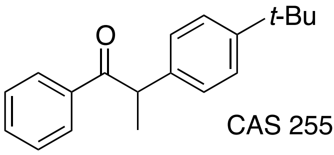
1-phenyl-2-(4-methoxyphenyl)-propan-1-one[8] (Table 2, entries 8-9)



CAS 84839-92-9

^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.95 (d, ^3J = 7.6, 2H, H_{Ar}), 7.47 (t, ^3J = 7.2, 1H, H_{Ar}), 7.38 (t, ^3J = 7.6, 2H, H_{Ar}), 7.20 (d, ^3J = 8.4, 2H, H_{Ar}), 6.83 (d, ^3J = 8.8, 2H, H_{Ar}), 4.64 (q, ^3J = 6.8, 1H, C*H*(CH_3)), 3.75 (s, 3H, OC*H_3*), 1.51 (d, ^3J = 6.8, 3H, CH(C*H_3*)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz): δ = 200.7 (*C*O), 158.6 (OC_{Ar}), 136.7, 133.6, 132.8, 128.9, 128.9, 128.6, 114.5 (C_{Ar}), 55.4 (O*C*H_3), 47.1 (*C*H(CH_3)), 19.7 (CH(*C*H_3)).

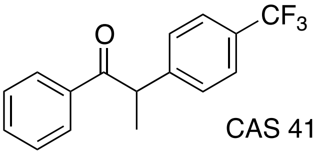
1-phenyl-2-(4-*tert*-butylphenyl)-propan-1-one[9] (Table 2, entries 10-11)



CAS 255836-61-4

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 7.98 (d, ^3J = 7.2, 2H, H$_{Ar}$), 7.49 (t, ^3J = 7.3, 1H, H$_{Ar}$), 7.39 (t, ^3J = 7.3, 2H, H$_{Ar}$), 7.31 (d, ^3J = 8.4, 2H, H$_{Ar}$), 7.22 (d, ^3J = 8.4, 2H, H$_{Ar}$), 4.69 (q, ^3J = 6.9, 1H, C*H*(CH$_3$)), 1.53 (d, ^3J = 6.9, 3H, CH(C*H*$_3$)), 1.28 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz): δ = 200.6 (*C*O), 149.8, 138.3, 136.7, 132.8, 128.6, 128.6, 127.5, 126.0 (C$_{Ar}$), 47.3 (*C*H(CH$_3$)), 34.5 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 19.6 (CH(*C*H$_3$)).

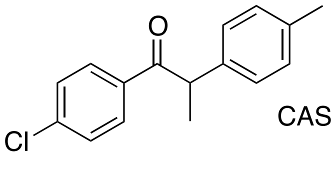
1-phenyl-2-[(4-trifluoromethyl)phenyl]-propan-1-one[10] (Table 2, entry 12)



CAS 413615-60-8

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 7.94 (dt, ^3J = 7.2, ^4J n.r., 2H, H$_{Ar}$), 7.56 (d, ^3J = 8.4, 2H, H$_{Ar}$), 7.50 (d, ^3J = 7.2, ^4J n.r., 1H, H$_{Ar}$), 7.43-7.38 (m, 4H, H$_{Ar}$), 4.77 (q, ^3J = 6.9, 1H, C*H*(CH$_3$)), 1.56 (d, ^3J = 6.9, 3H, CH(C*H*$_3$)). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.61 MHz): δ = 199.8 (*C*O), 145.5, 136.3, 133.3, 132.8, 128.9, 128.8, 128.3 (C$_{Ar}$), 126.1 (q, $^1J_{CF}$ = 3.2, *C*F$_3$), 47.7 (*C*H(CH$_3$)), 19.6 (CH(*C*H$_3$)).

1-(4-chlorophenyl)-2-(4-methylphenyl)-propan-1-one[11] (Table 2, entries 13-14)

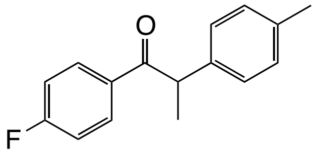


CAS 777038-79-6

ESI-HRMS: *m/z* [M]$^+$ calcd for C$_{16}$H$_{15}$ClONa 281.0704, found 281.0695. ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 7.87 (ddd, ^3J = 8.7, ^4J = 2.4, ^5J = 2.0, 2H, H$_{Ar}$), 7.33 (ddd, ^3J = 8.7, ^4J = 2.4, ^5J = 2.0, 2H, H$_{Ar}$), 7.12 (m, 4H, H$_{Ar}$), 4.57 (q, ^3J = 6.9, 1H, C*H*(CH$_3$)), 2.29 (s, 3H, C*H*$_3$), 1.50 (d, ^3J = 6.9, 3H, CH(C*H*$_3$)). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.61 MHz): δ =

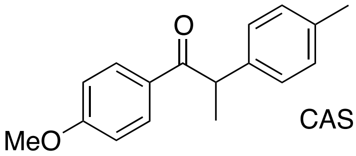
199.3 (CO), 139.2, 138.3, 136.9, 134.9, 130.3, 129.9, 128.9, 127.7 (C_{Ar}), 47.8 ($CH(CH_3)$), 21.2 (CH_3), 19.6 ($CH(CH_3)$).

1-(4-fluorophenyl)-2-(4-methylphenyl)-propan-1-one (Table 2, entry 15)



Anal. Calcd for $C_{16}H_{15}FO$: C, 79.32; H, 6.24. Found: C, 79.34; H, 6.38. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.89 (m, ^3J = 8.8, ^4J = 2.0, $^4J_{HF}$ = 5.6, 2H, H_{ArF}), 7.07 (d, ^3J = 8.2, 2H, H_{Ar}), 7.02 (d, ^3J = 8.2, 2H, H_{Ar}), 6.95 (m, ^3J = 8.8, ^4J = 2.0, $^3J_{HF}$ = 6.6, 2H, H_{ArF}), 4.51 (q, ^3J = 6.8, 1H, $CH(CH_3)$), 2.21 (s, 3H, CH_3), 1.42 (d, ^3J = 6.8, 3H, $CH(CH_3)$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 198.9 (CO), 165.5 (d, $^1J_{CF}$ = 254.4, C_{ArF}), 138.5, 136.8 (C_{Ar}), 133.0 (d, $^4J_{CF}$ = 2.4, C_{ArF}), 131.5 (d, $^3J_{CF}$ = 9.3, C_{ArF}), 129.9, 127.7 (C_{Ar}), 115.7 (d, $^2J_{CF}$ = 21.9, C_{ArF}), 47.7 ($CH(CH_3)$), 21.1 (CH_3), 19.6 ($CH(CH_3)$). ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ = –105.70 (s, F).

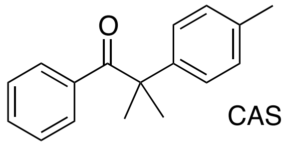
1-(4-methoxyphenyl)-2-(4-methylphenyl)-propan-1-one[12] (Table 2, entries 16-17)



CAS 921929-32-0

^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.95 (d, ^3J = 8.8, 2H, H_{Ar}), 7.18 (d, ^3J = 8.0, 2H, H_{Ar}), 7.10 (d, ^3J = 8.0, 2H, H_{Ar}), 6.85 (d, ^3J = 8.8, 2H, H_{Ar}), 4.61 (q, ^3J = 6.8, 1H, $CH(CH_3)$), 3.81 (s, 3H, OCH_3), 2.28 (s, 3H, CH_3), 1.50 (d, ^3J = 6.8, 3H, $CH(CH_3)$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz): δ = 199.1 (CO), 163.2 (OC_{Ar}), 139.0, 136.5, 131.1, 129.7, 129.6, 127.7, 113.7 (C_{Ar}), 55.5 (OCH_3), 47.2 ($CH(CH_3)$), 21.1 (CH_3), 19.7 ($CH(CH_3)$).

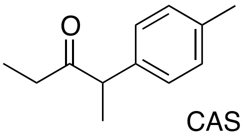
1-phenyl-2-methyl-2-(4-methylphenyl)-propan-1-one[13] (Table 2, entries 18-19)



CAS 14271-33-1

^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.49 (dd, ^3J = 8.4, 2H, H_{Ar}), 7.36 (tt, ^3J = 7.3, 1H, H_{Ar}), 7.25-7.14 (m, 6H, H_{Ar}), 2.34 (s, 3H, $\mathrm{C}\mathit{H_3}$), 1.58 (s, 6H, $\mathrm{C(C}\mathit{H_3}\mathrm{)_2}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz): δ = 204.1 ($\mathit{C}\mathrm{O}$), 142.3, 136.5, 131.7, 129.8, 128.9, 128.0, 125.7 (C_{Ar}), 51.2 ($\mathit{C}\mathrm{(CH_3)_2}$), 28.0 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$), 21.2 ($\mathit{C}\mathrm{H_3}$).

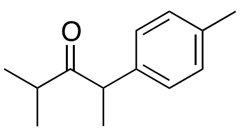
2-(4-methylphenyl)-pentan-3-one[14] (Table 2, entries 21-22)



CAS 395116-78-6

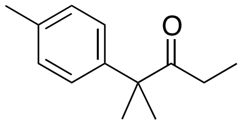
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.14 (d, ^3J = 8.4, 2H, H_{Ar}), 7.09 (d, ^3J = 8.4, 2H, H_{Ar}), 3.72 (q, ^3J = 6.9, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)}$), 2.37 (m, 2H, ^3J = 7.5, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 2.33 (s, 3H, $\mathrm{C}\mathit{H_3}$), 1.37 (d, ^3J = 6.9, 3H, $\mathrm{CH(C}\mathit{H_3}\mathrm{)}$), 0.96 (t, ^3J = 7.5, 3H, $\mathrm{CH_2C}\mathit{H_3}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz): δ = 211.9 ($\mathit{C}\mathrm{O}$), 138.1, 136.9, 129.7, 127.8 (C_{Ar}), 52.4 ($\mathit{C}\mathrm{H(CH_3)}$), 34.3 ($\mathit{C}\mathrm{H_2CH_3}$) 21.2 ($\mathit{C}\mathrm{H_3}$), 17.7 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)}$), 8.1 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$).

2-(4-methylphenyl)-4-methyl-pentan-3-one (Table 2, entry 23)



ESI-HRMS: *m/z* $[M]^+$ calcd for $C_{13}H_{18}ONa$ 213.1250, found 213.1241. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.16-7.08 (m, 4H, H_{Ar}), 3.88 (q, ^3J = 6.8, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)}$), 2.68 (sept., 1H, ^3J = 6.8, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 2.32 (s, 3H, $\mathrm{C}\mathit{H_3}$), 1.35 (d, ^3J = 6.8, 3H, $\mathrm{CH(C}\mathit{H_3}\mathrm{)}$), 1.07 (d, ^3J = 6.8, 3H, CH(CH_3)$_2$), 0.91 (d, ^3J = 6.8, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz): δ = 215.0 (*C*O), 137.9, 136.8, 129.7, 128.0 (C_{Ar}), 50.9 (*C*H(CH_3)), 39.2 (*C*H(CH_3)$_2$), 21.2 (*C*H_3), 19.4 (CH(*C*H_3)$_2$), 18.4 and 18.3 (CH(*C*H_3)$_2$ and CH(*C*H_3)).

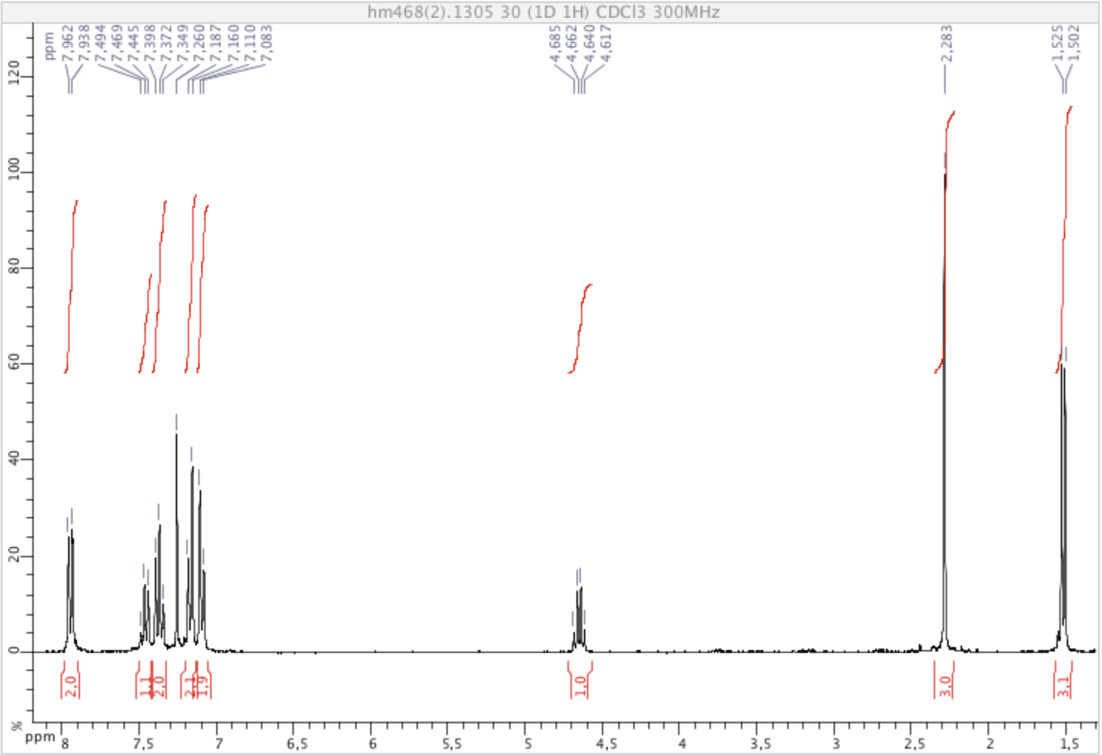
2-(4-methylphenyl)-2-methyl-pentan-3-one (Table 2, entry 23)

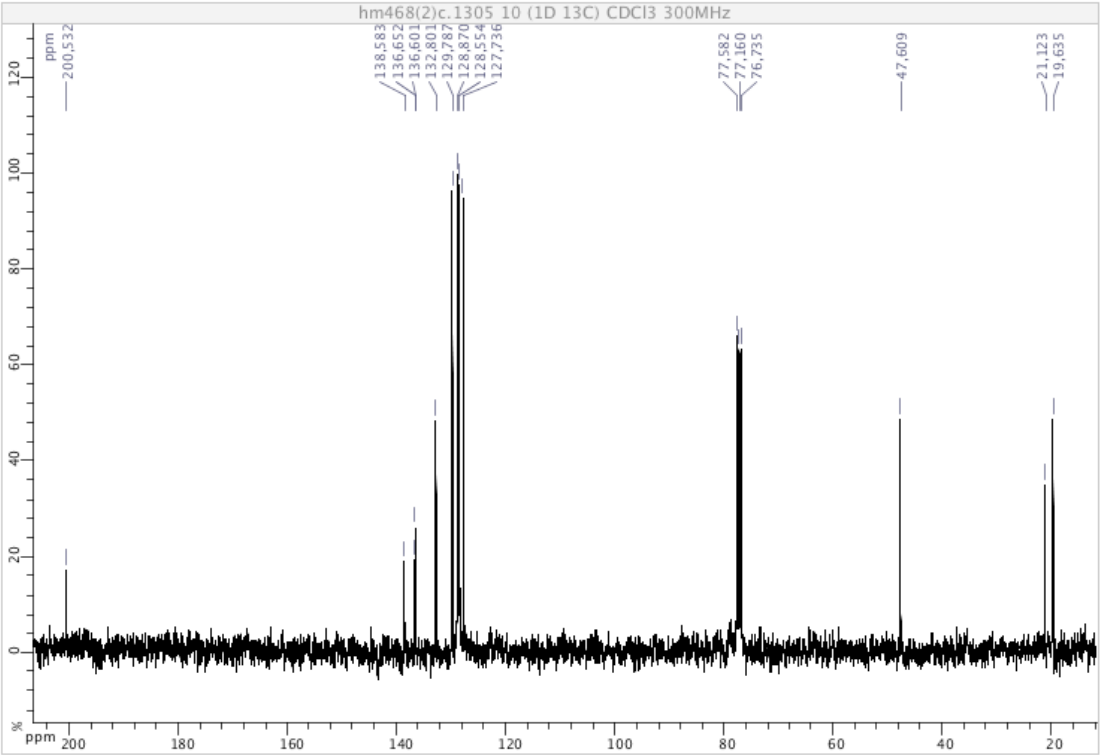


ESI-HRMS: *m/z* $[M]^+$ calcd for $C_{13}H_{18}ONa$ 213.1250, found 213.1241. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.16-7.08 (m, 4H, H_{Ar}), 2.33 (s, 3H, CH_3), 2.22 (q, ^3J = 7.4, 2H, C$H_2$$CH_3$), 1.46 (s, 6H, C(C$H_3$)$_2$), 0.93 (t, ^3J = 7.4, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz): δ = 214.3 (*C*O), 141.5, 136.5, 129.5, 126.0 (C_{Ar}), 52.0 (*C*(CH_3)$_2$), 30.7 (*C*$H_2$$CH_3$) 25.4 (C(*C*$H_3$)$_2$), 21.1 (*C*$H_3$), 8.8 ($CH_2$*C*$H_3$).

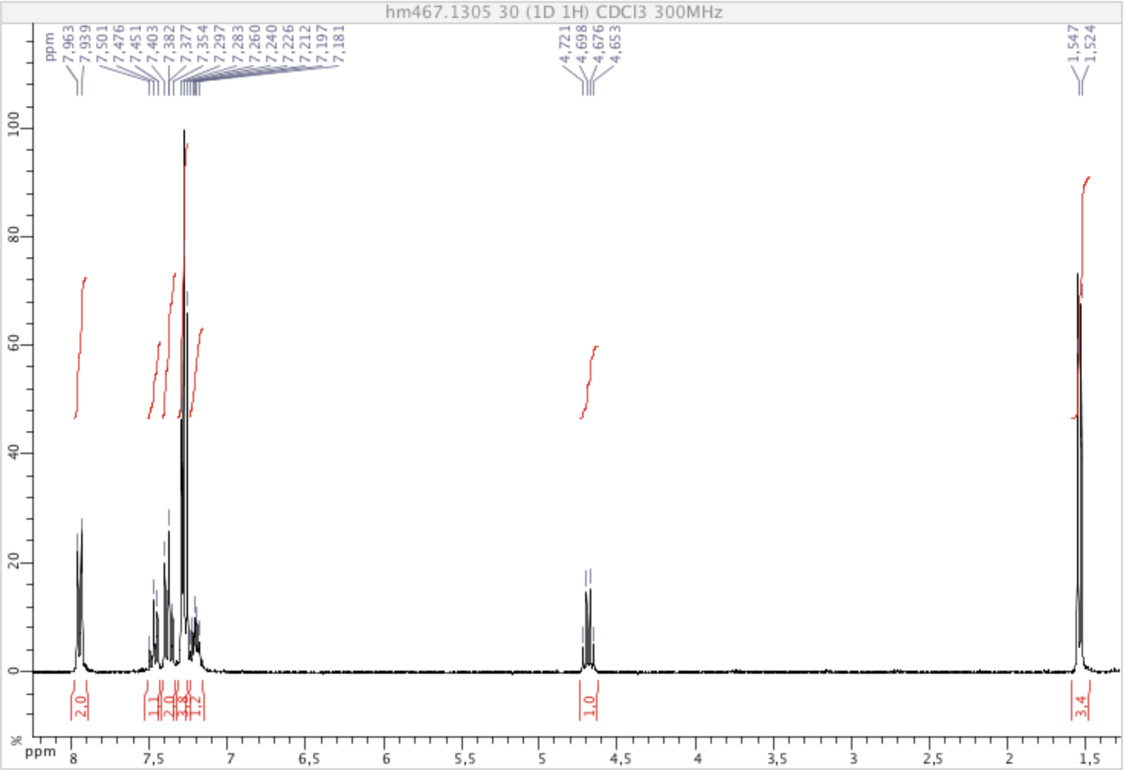
XI. ^{1}H and ^{13}C{^{1}H} NMR spectra of the coupling products

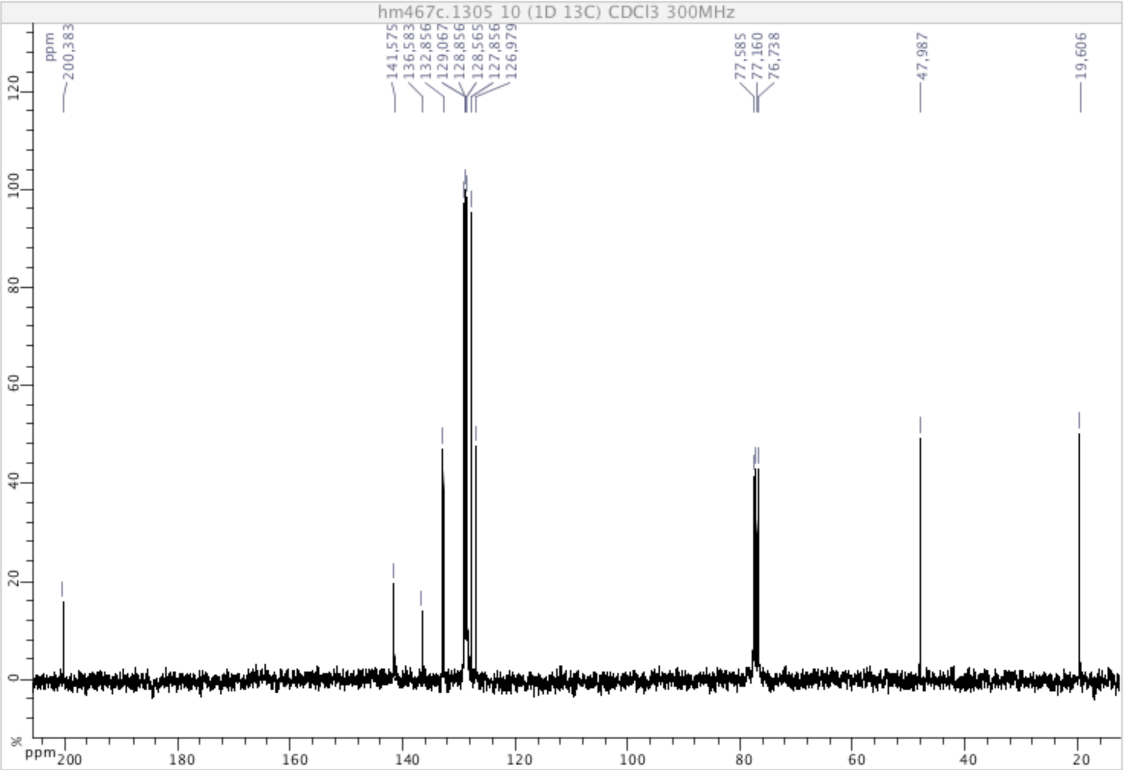
NMR spectra of 1-phenyl-2-(4-methylphenyl)-propan-1-one (Table 2, entry 1)



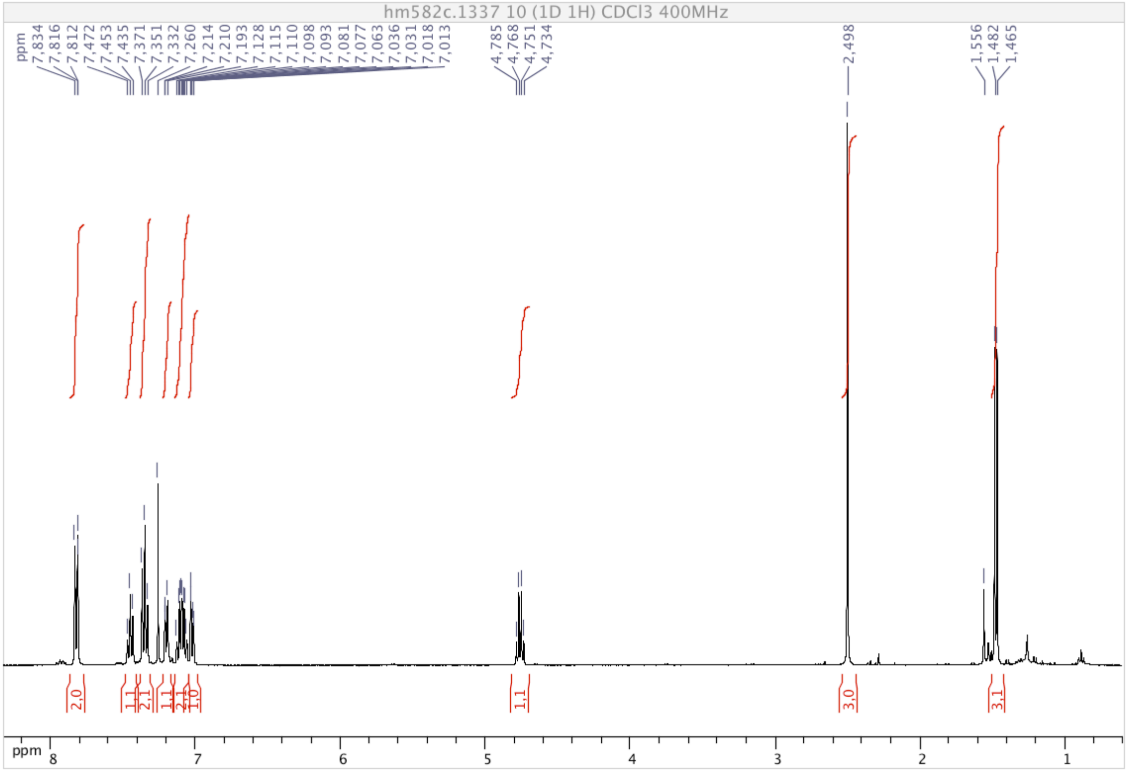


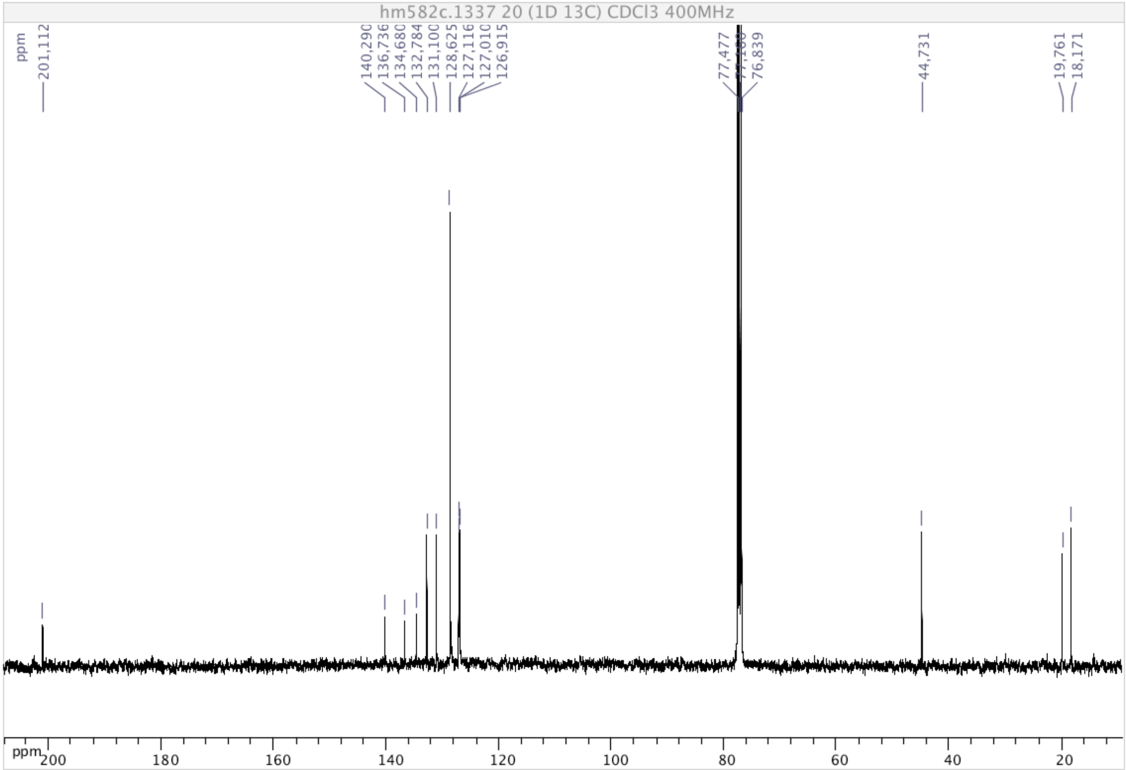
NMR spectra of 1,2-diphenylpropan-1-one (Table 2, entries 3-4)



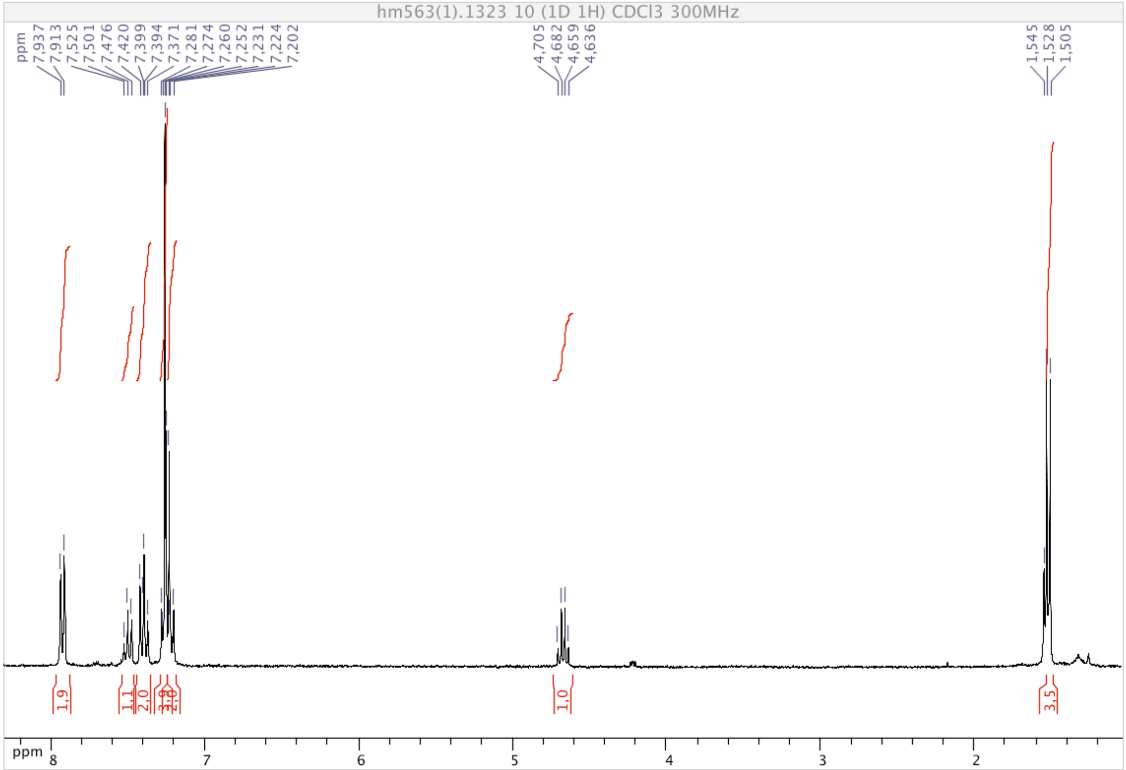


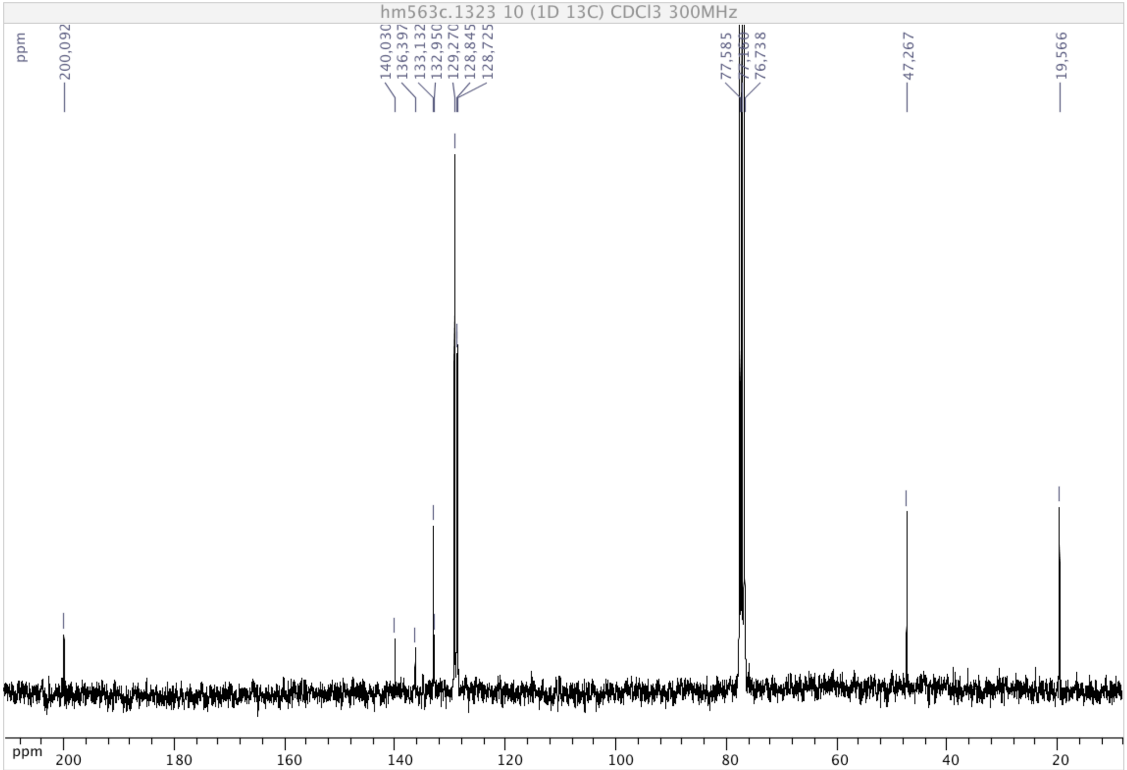
NMR spectra of 1-phenyl-2-(2-methylphenyl)-propan-1-one (Table 2, entries 5-6)



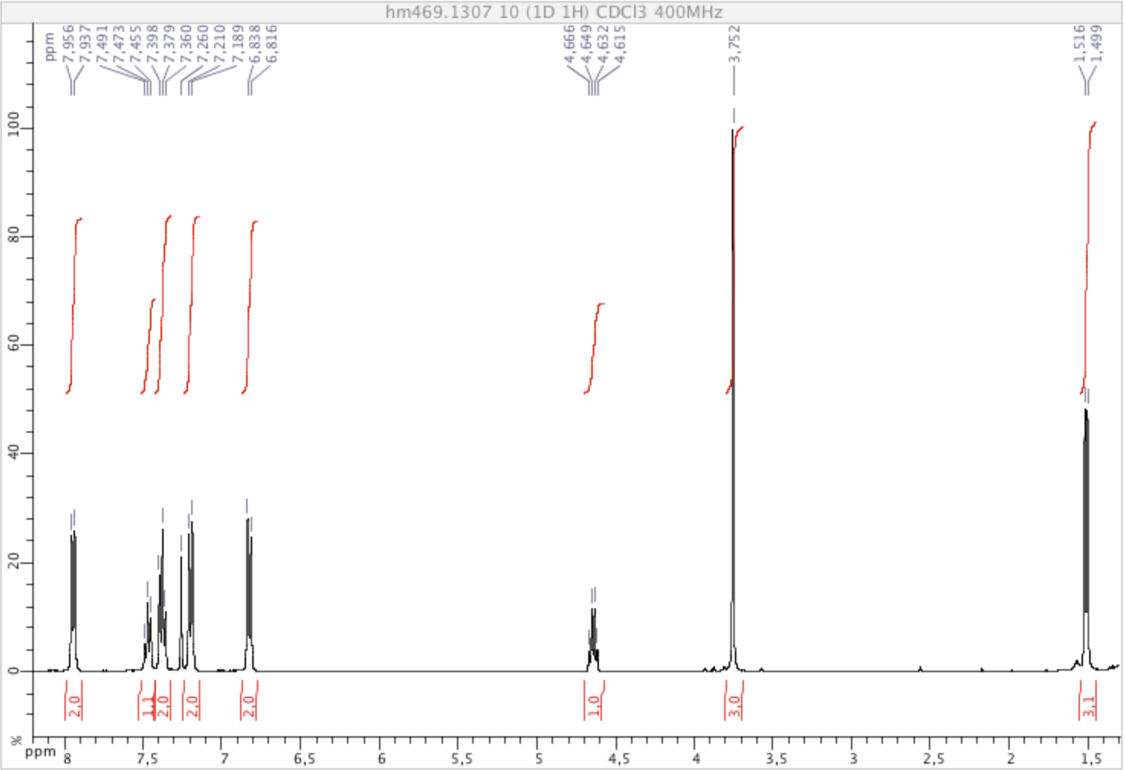


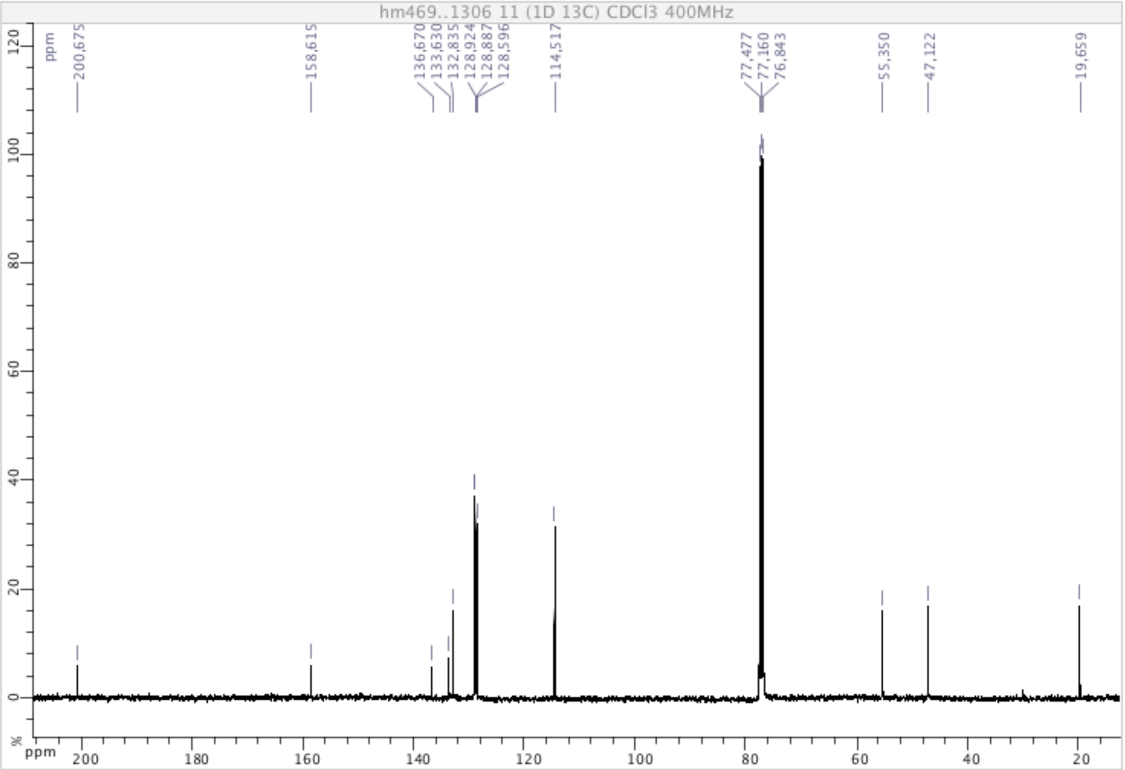
NMR spectra of 1-phenyl-2-(4-chlorophenyl)-propan-1-one (Table 2, entry 7)



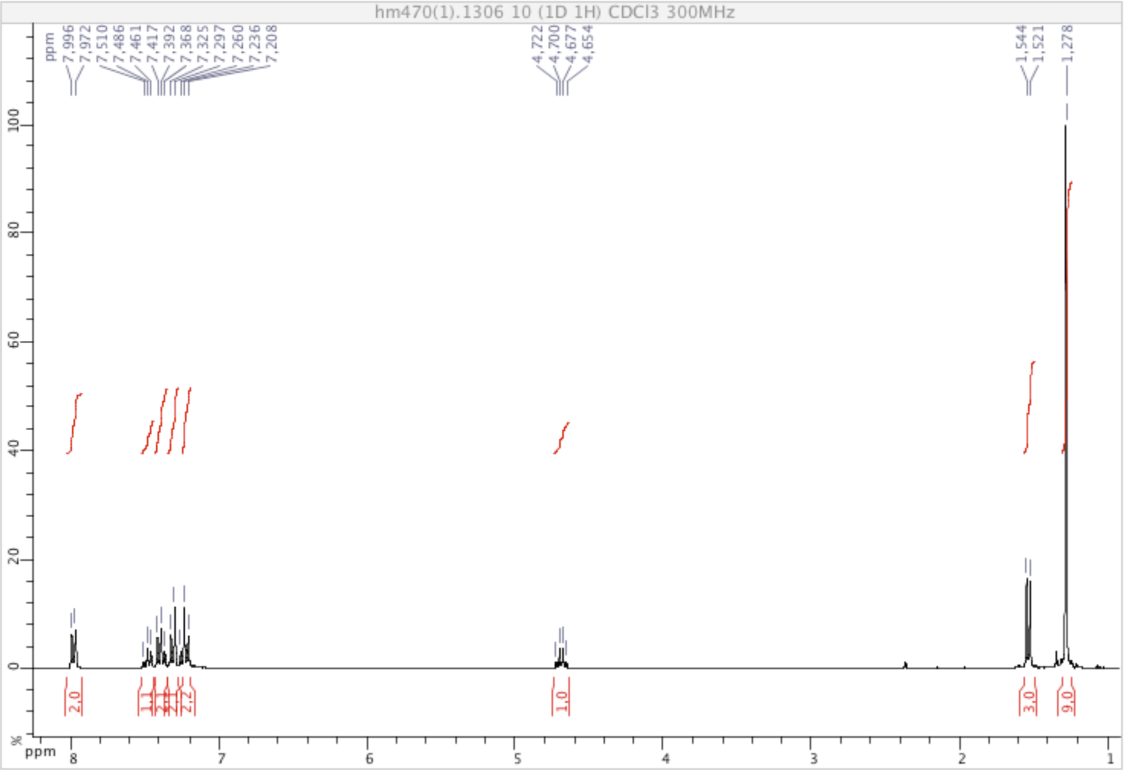


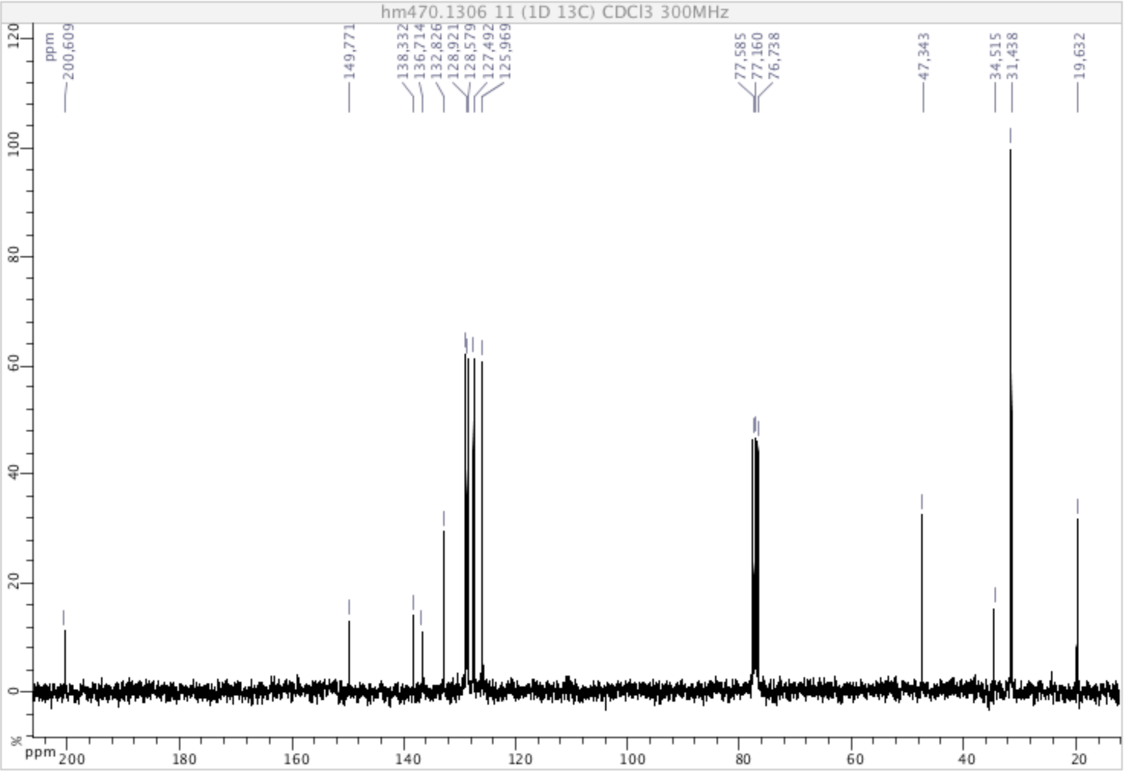
NMR spectra of 1-phenyl-2-(4-methoxyphenyl)-propan-1-one (Table 2, entries 8-9)



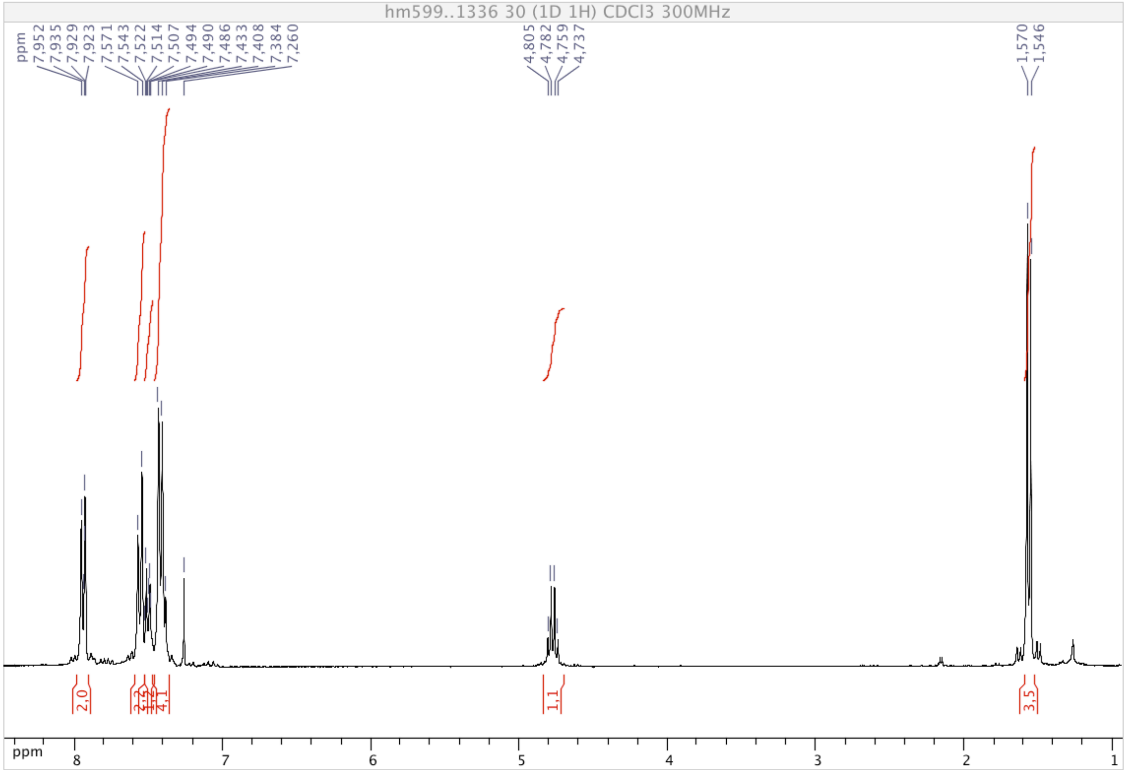


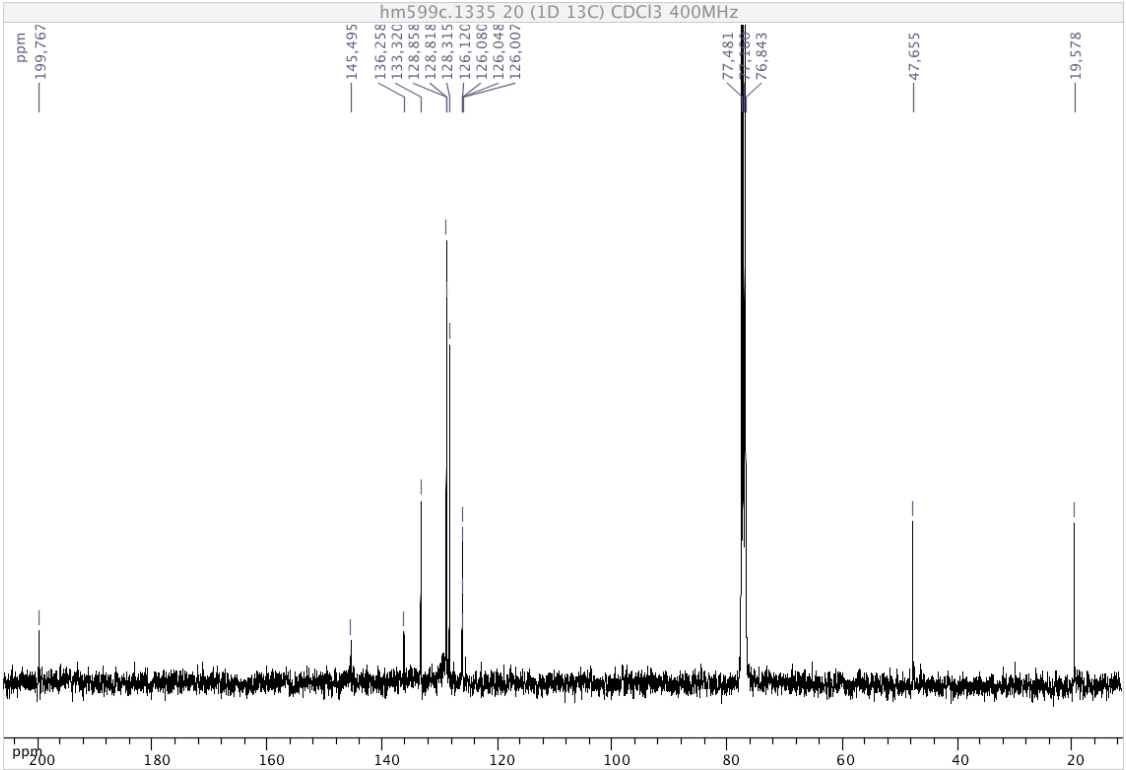
NMR spectra of 1-phenyl-2-(4-*tert*-butylphenyl)-propan-1-one (Table 2, entries 10-11)



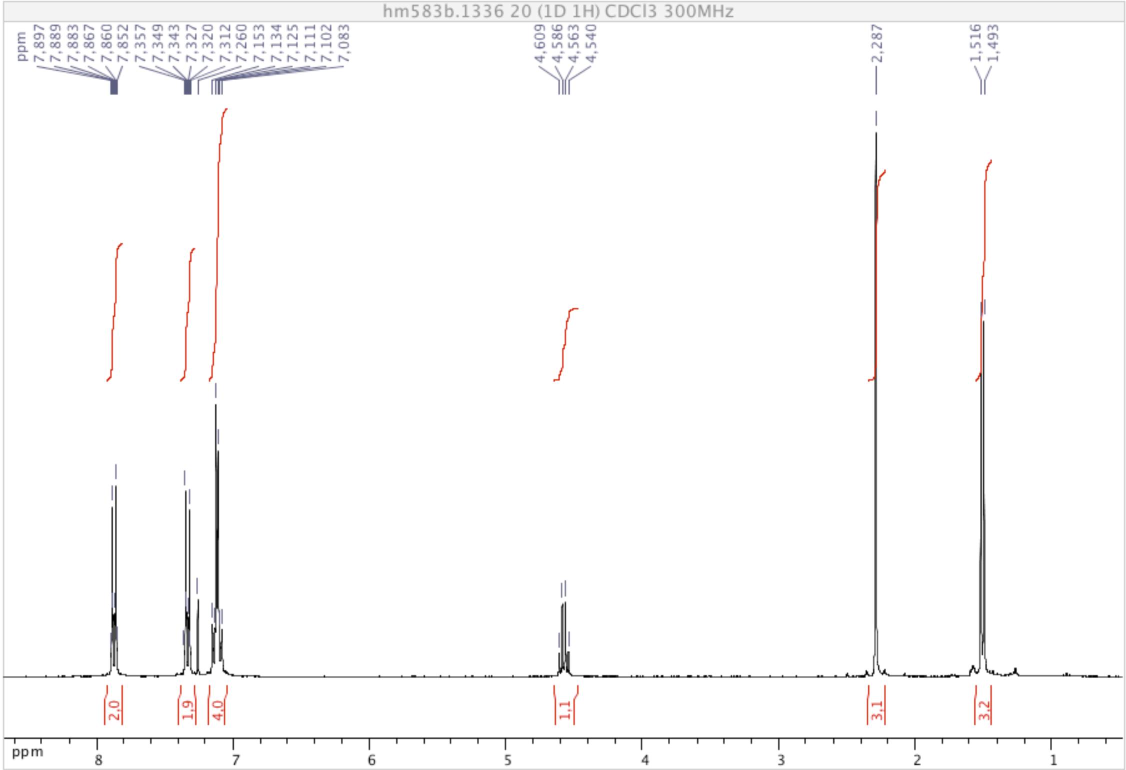


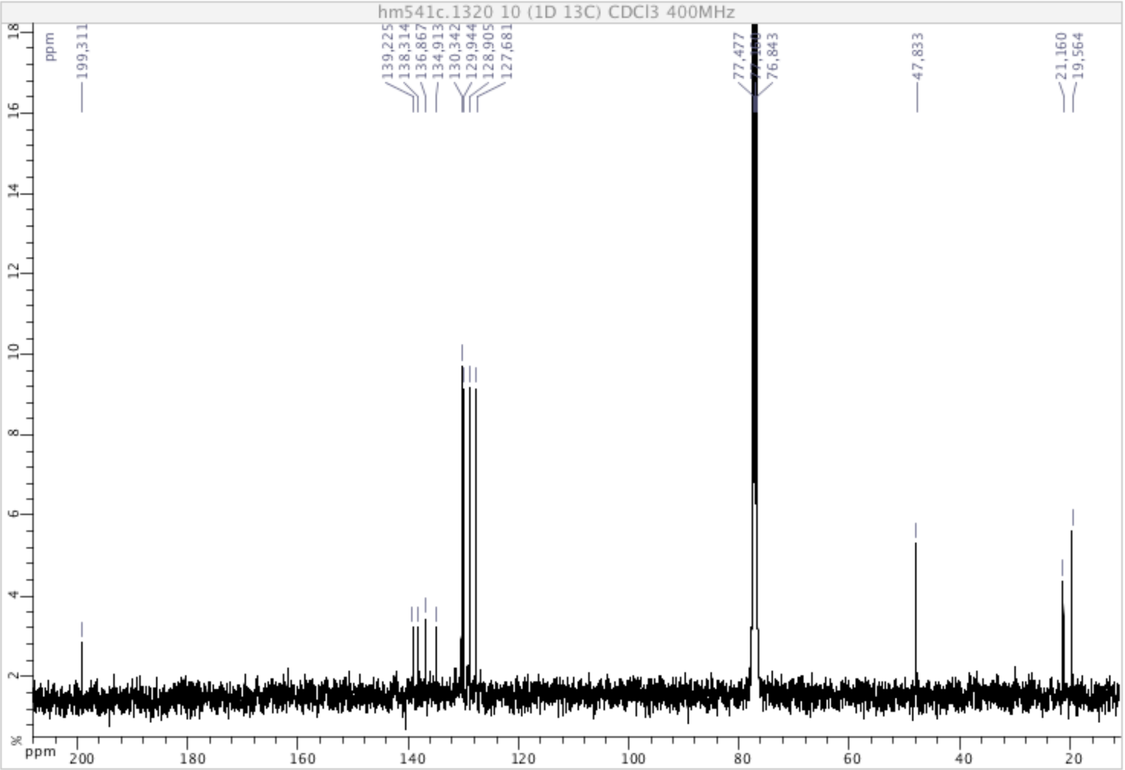
NMR spectra of 1-phenyl-2-[(4-trifluoromethyl)phenyl]-propan-1-one (Table 2, entry 12)



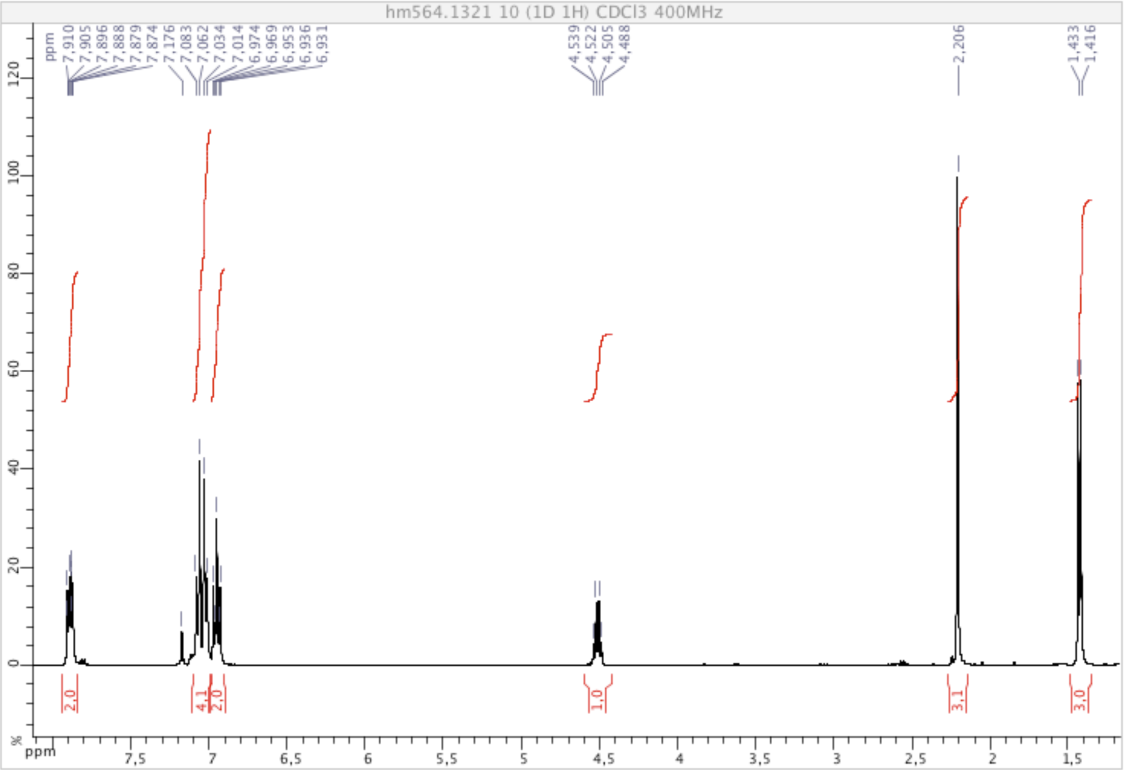


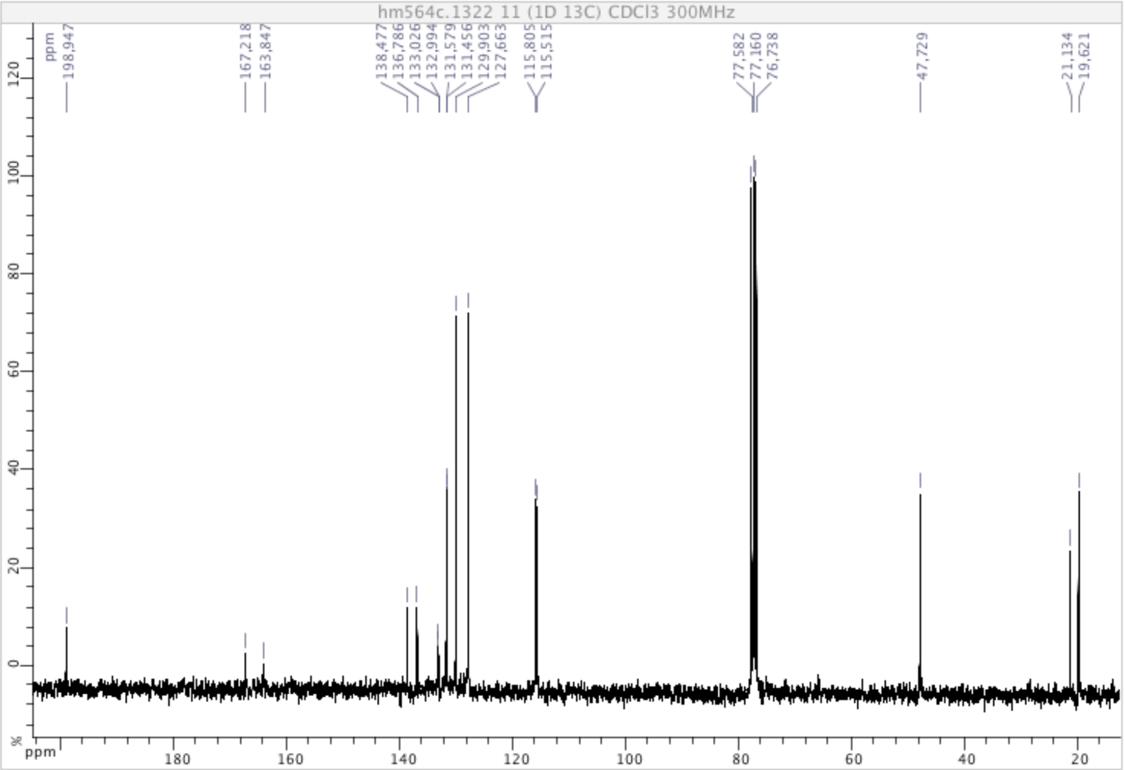
NMR spectra of 1-(4-chlorophenyl)-2-(4-methylphenyl)-propan-1-one (Table 2, entries 13-14)



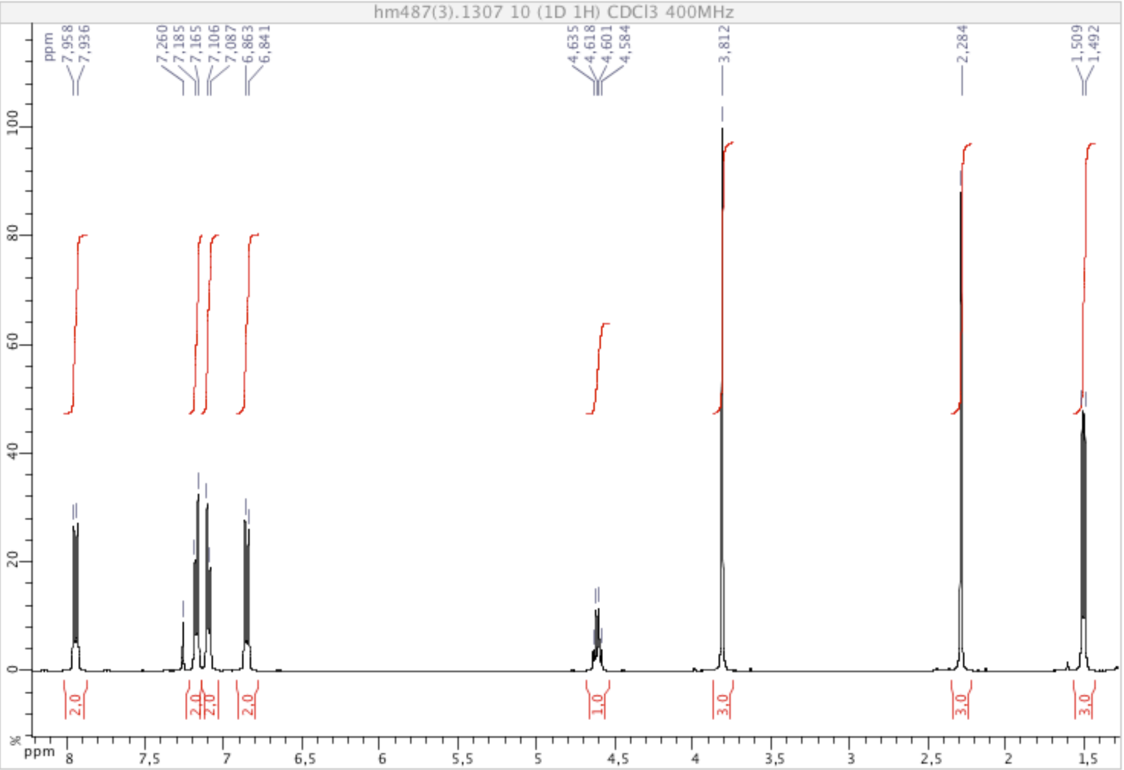


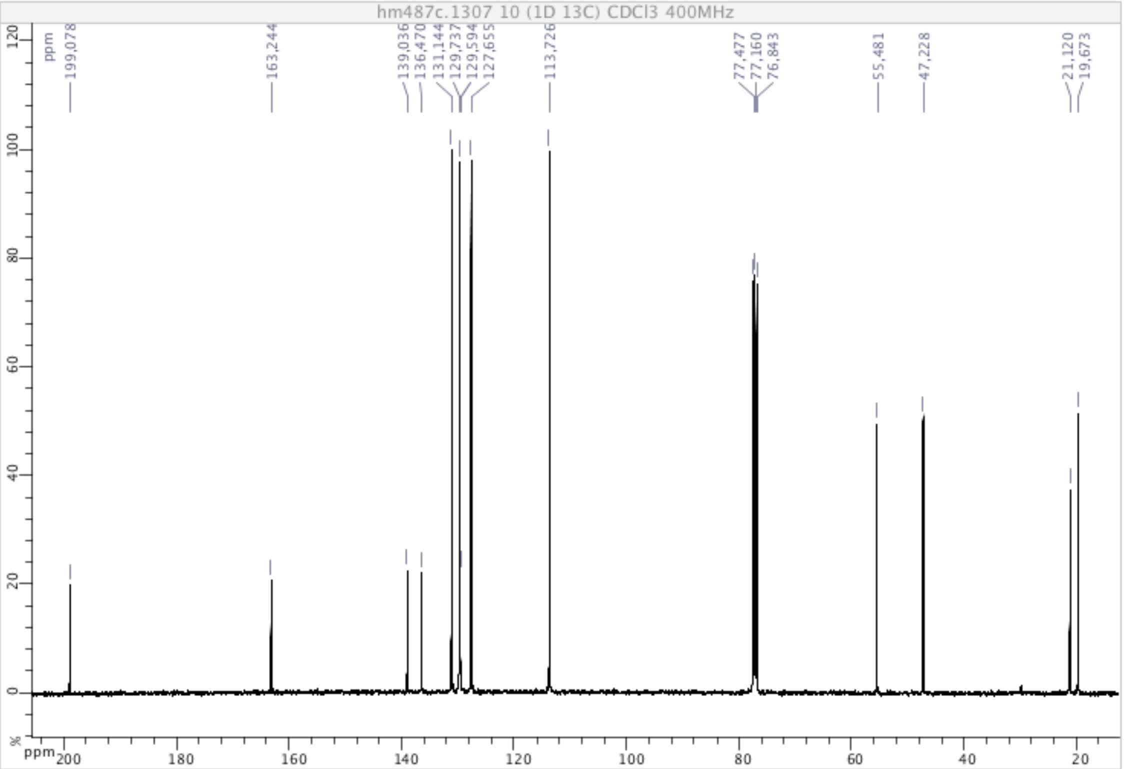
NMR spectra of 1-(4-fluorophenyl)-2-(4-methylphenyl)-propan-1-one (Table 2, entry 15)



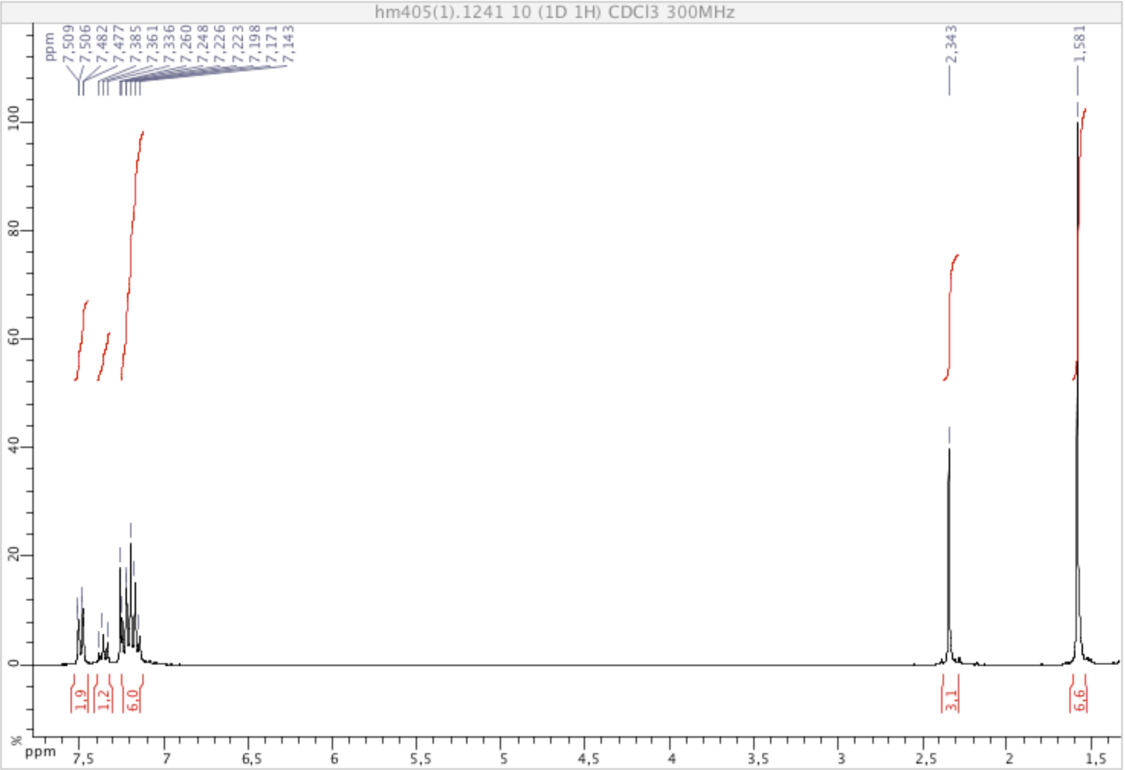


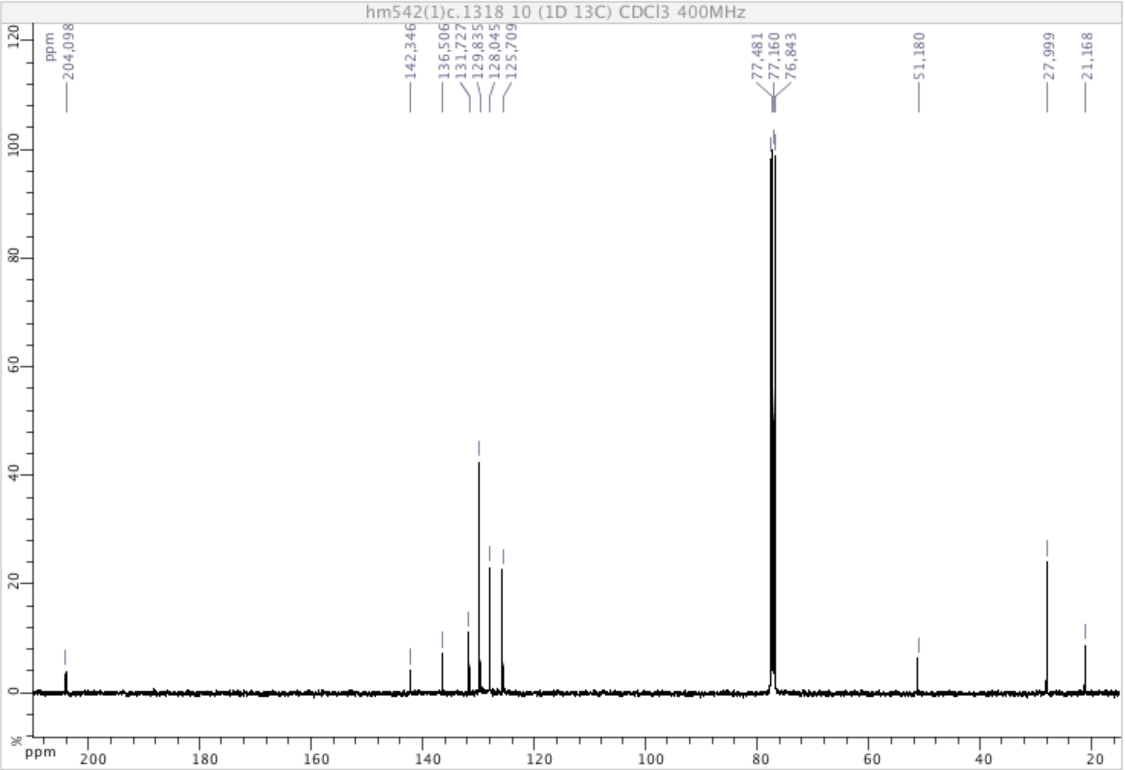
NMR spectra of 1-(4-methoxyphenyl)-2-(4-methylphenyl)-propan-1-one (Table 2, entries 16-17)



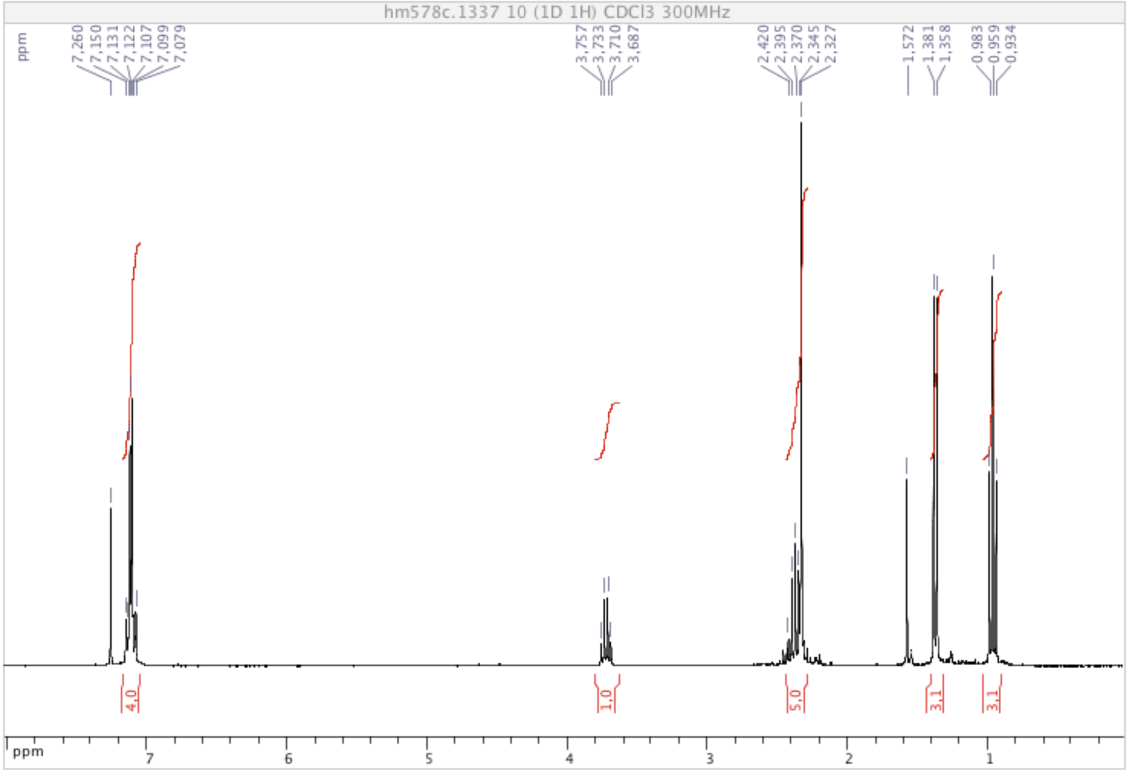


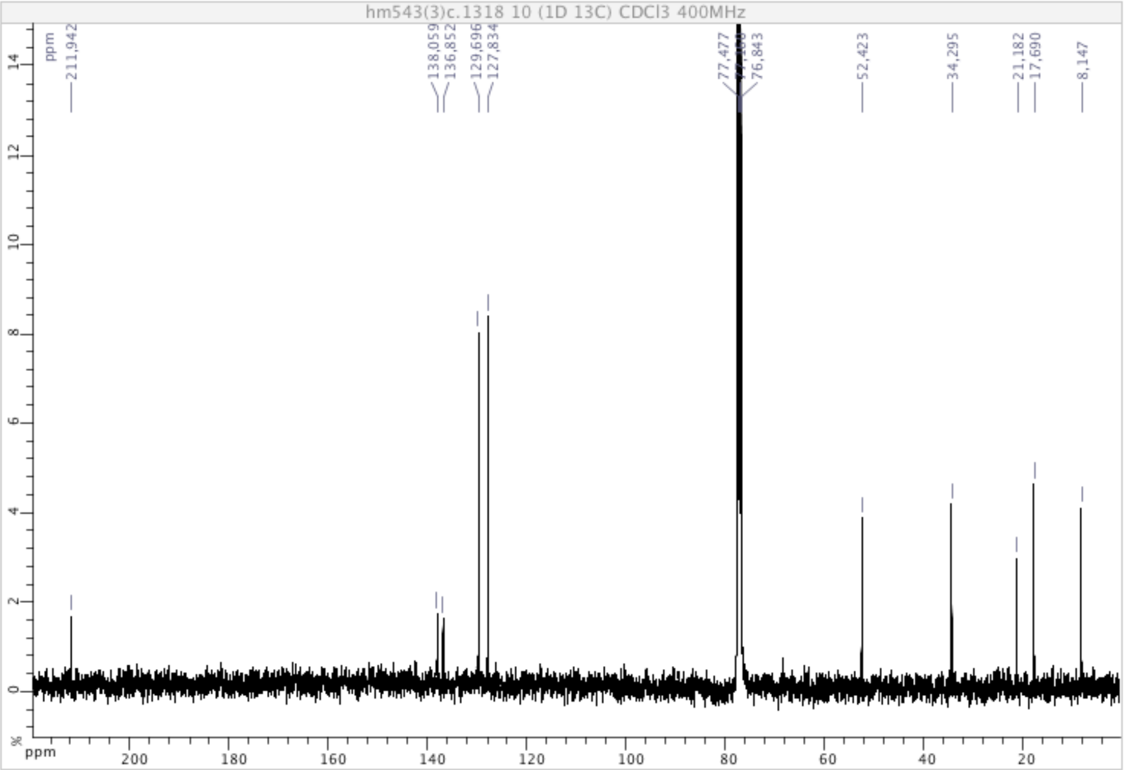
NMR spectra of 1-phenyl-2-methyl-2-(4-methylphenyl)-propan-1-one (Table 2, entries 18-19)



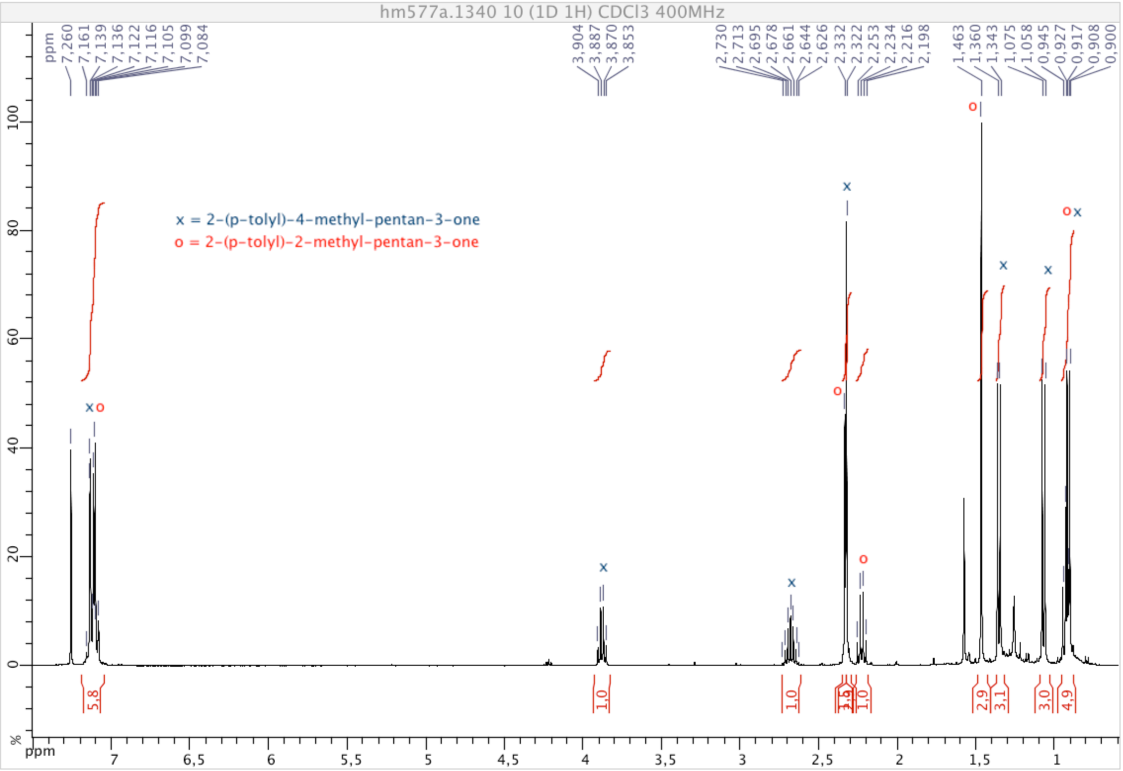


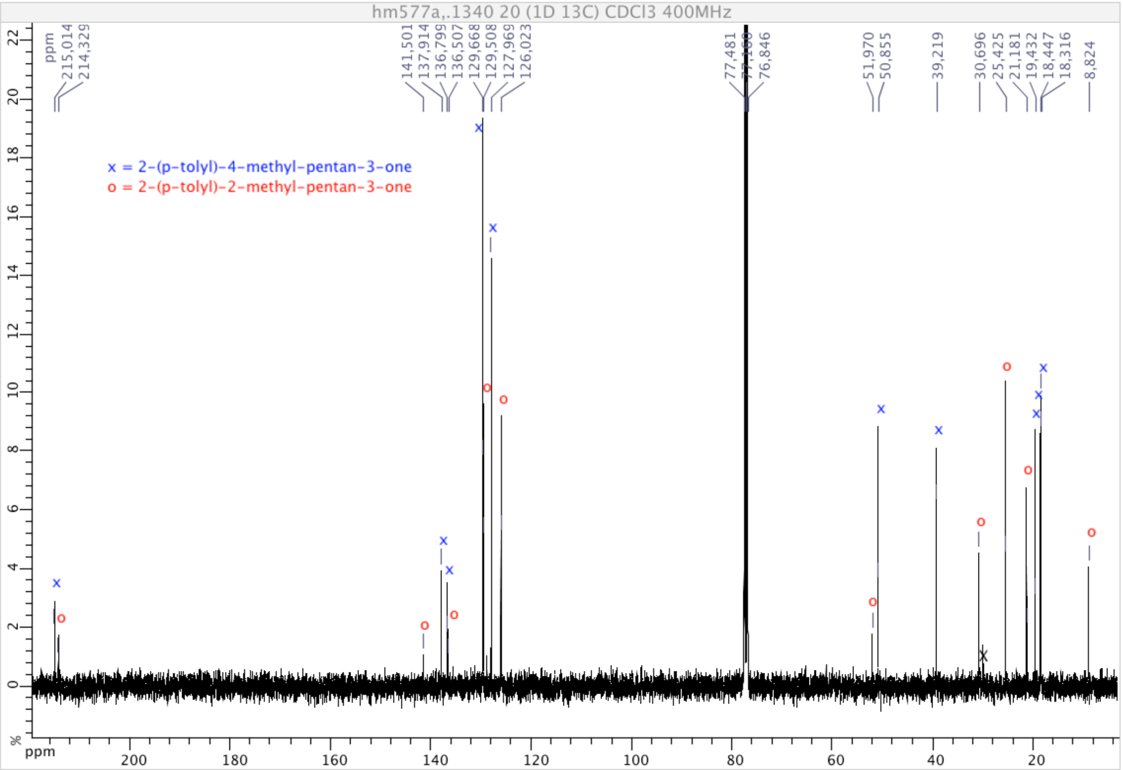
NMR spectra of 2-(4-methylphenyl)-pentan-3-one (Table 2, entries 21-22)





NMR spectra of 2-(4-methylphenyl)-4-methyl-pentan-3-one and of 2-(4-methylphenyl)-2-methyl-pentan-3-one (Table 2, entry 23)





XII. References

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