Oxidative Functionalization of Alcohols and Aldehydes via the Merger of Oxoammonium Cations and Photoredox Catalysis

Jyoti Nandi,[†] John M. Ovian,[†] Christopher B. Kelly,[†] and Nicholas E. Leadbeater *,[†]

[†]*Department of Chemistry, University of Connecticut, 55 N. Eagleville Road, Storrs, Connecticut 06269, USA*

Supporting Information

Key to Abbreviated Terms:

4CzIPN – 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile
ACT – 4-Acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl
bpy – 2,2′-Bipyridyl
$CDCl_3$ − Deuterated chloroform
DMSO-d_6 – Deuterated dimethylsulfoxide
Et_2O − Diethyl ether
EtOAc − Ethyl acetate
Hex – Hexanes
LED – Light-emitting diode
$MesAcr^+BF_4^+$ − 9-Mesityl-10-methylacridinium tetrafluoroborate
TEMPO – 2,2,6,6-tetramethylpiperidine 1-oxyl
TEMPOH –2,2,6,6-tetramethylpiperidin-1-ol
THF − Tetrahydrofuran
TLC − Thin layer chromatography

General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 3- or 4-port dual-bank manifold. Nitrogen was used to provide such an atmosphere. NMR Spectra (^{1}H, ^{13}C, ^{19}F) were performed at 300 K on either a Brüker Avance Ultra Shield 300 MHz NMR, Brüker DRX-400 400 MHz NMR, or Brüker Avance 500 MHz NMR. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (7.26 ppm) in $CDCl_3$. ^{13}C NMR spectra were referenced to $CDCl_3$ (77.30 ppm). ^{19}F NMR spectra were referenced to hexafluorobenzene (-164.9 ppm).[1] High-resolution mass spectra were performed on a JEOL AccuTOF-DART SVP 100 in positive direct analysis in real time (DART) ionization method, using PEG as the internal standard. Reactions were monitored by an Agilent Technologies 7820A Gas Chromatograph attached to a 5975 Mass Spectrometer, ^{1}H NMR, and/or by TLC on silica gel plates (60Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/ethyl acetate as the eluent and visualized using permanganate stain, *p*-anisaldehyde stain, Seebach's Stain, and/or UV light. Flash chromatography and silica plugs utilized Dynamic Adsorbents Inc. Flash Silica Gel (60Å porosity, 32-63 μm).

Chemicals: Deuterated chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories and stored over 4Å molecular sieves and K_2CO_3. Deuterated DMSO-d_6 was used as purchased. Na_2SO_4, CH_2Cl_2, EtOAc, hexane, pentane, Et_2O, THF, MeCN, acetone, pyridine, $Na_2S_2O_8$ and 2,6-lutidine were purchased from Sigma-Aldrich. Molecular sieves for photochemical experiments (3Å molecular sieves, 3.2 mm pellets) were also purchased from Sigma-Aldrich. Hexafluorobenzene was purchased from Synquest Laboratories and/or Oakwood Chemicals. Aldehydes and alcohols were either purchased from commercial suppliers (and distilled/recrystallized before use), or prepared in-house. All azoles were purchased from commercial suppliers and used without further purification. The oxoammonium salt 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium ("Bobbitt's Salt") and 4-acetamido-TEMPO (ACT) was prepared according to our recently published protocol.[2] TEMPOH was purchased from Synthonix. The photocatalysts $Ru(bpy)_3(PF_6)_2$ and 4CzIPN were prepared in-house by literature procedures[3,4]

Photochemistry: Irradiation of reaction vessels was accomplished using blue LEDs. LEDs were configured as outlined in the *Photochemical Reactor Design* section of previous articles.[5] A fan was employed to ensure reactions remained at or near rt when using LEDs.

Information for LED-based Photoreactor Components:

- *Blue LEDs*: 39.4 inch strips, 470 nm blue light, 32918 mcd ft^{-1}
- *Power Supply*: 12V DC power supply - 60 Watt
- *Connectors*: LC2 Locking male connector CPS adapter cable
- *Clip Fan*: 2-Speed clip fan, 6-inch
- Pyrex crystallizing dishes (150 × 75 mm)
- Aluminum foil, duct tape

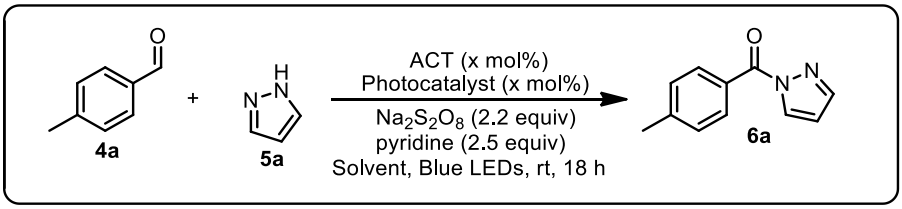
[1] Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun.* **2011** , 47, 4721.
[2] Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666.
[3] Kelly, C. B.; Patel, N. R.; Primer, D. N.; Jouffroy, M.; Tellis, J. C.; Molander, G. A. *Nat. Protoc.* **2017**, *12*, 472.
[4] Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766.
[5] For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**, *18*, 876.

Optimization & Control Studies for Photoredox Oxidative Amidation

Procedure for optimization and control studies:

To a 1 mL reaction vial equipped with a stir bar was added *p*-tolualdehyde **4a** (0.060 g, 0.0005 mol, 1 equiv), ACT (0.213 g, 0.001 mol, 0.2 equiv), pyrazole **5a** (0.051 g, 0.00075 mol, 1.5 equiv), pyridine (0.099 g, 0.1 mL, 0.00125 mol, 2.5 equiv), and the appropriate solvent. The solution was allowed to stir at room temperature for two minutes. After this time, the vial was charged with appropriate photocatalyst and $Na_2S_2O_8$ (0.261 g, 0.0011 mol, 2.2 equiv). The vial was sealed with a cap and was irradiated in the aforementioned LED reactor for 18 h. The temperature of the reaction was maintained at approximately 27 ^oC *via* a fan. Conversion was evaluated by both GCMS and ^1H NMR of the crude reaction mixture.

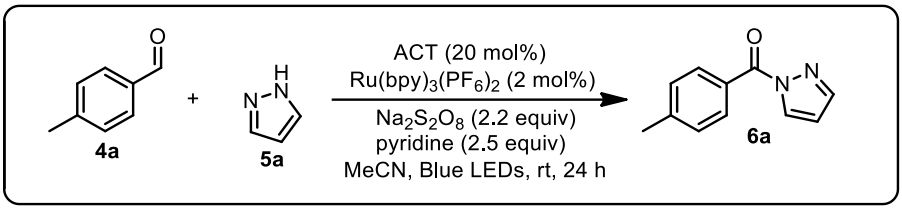
Table S1: Optimization of the ACT/Photoredox Dual Catalytic Process



Entry	Solvent (Conc. of 4a)	Photocatalyst (mol%)	ACT loading (mol%)	Conversion to 6a (%)
1[b]	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	0
2	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	98
3	THF (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	20
4	EtOAc (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	57
5	CH_2Cl_2 (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	50
6	^{t}BuOH (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	59
7	TFE (0.5 M) (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	< 5
8	DMSO (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	0
9	DMF (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	61
10	Acetone (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	10	85
11	MeCN (0.5 M)	MesAcr+ClO_4- (2 mol%)	10	trace
12	MeCN (0.5 M)	4CzIPN (2.5 mol%)	10	0
13	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (1.5 mol%)	10	90
14	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	10	98
15	MeCN (0.25 M)	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	10	46
16	MeCN (0.1 M)	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	10	26
17	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	20	100
18[c]	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	0	99
19[d]	MeCN (0.5 M)	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	0	85

[a] Percent conversion was approximated based upon relative areas from the GCMS trace of a given run and confirmed by ^1H NMR. In cases where the two values differed substantially, ^1H NMR integrations were used. Conversion = 100 × (area of oxidative amidation product **6a**)/(area of **6a** + area of **4a**). [b] No $Na_2S_2O_8$ added and reaction performed under O_2 [c] 20 mol% Bobbitt's salt used in place of ACT. [d] 20 mol% TEMPOH used in place of ACT.

Table S2: Control Studies for the ACT/Photoredox Dual Catalytic Process



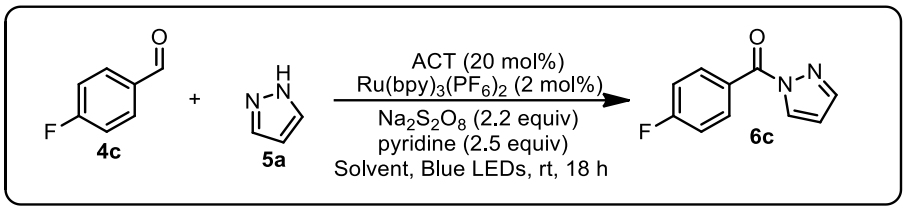
Entry	Deviation from procedure	Conversion to 6a (%)
1	*None*	>99
2	*No $Ru(bpy)_3(PF_6)_2$*	0
3	*No light*	0
4	*No ACT*	52[b]
6	*No $Na_2S_2O_8$*	0

[a] Percent conversion was approximated based upon relative areas from the GCMS trace of a given run and confirmed by ^{1}H NMR. In cases where the two values differed substantially, ^{1}H NMR integrations were used. Conversion = 100 × (area of oxidative amidation product **6a**)/(area of **6a** + area of **4a**). [b] ~10% carboxylic acid formation along with several unidentifiable products

Procedure for "light/dark" studies:

To a 20-mL vial equipped with a stir bar was added *p*-fluorobenzaldehyde (0.620 g, 0.005 mol, 1 equiv), ACT (0.213 g, 0.001 mol, 0.2 equiv), pyrazole (0.511 g, 0.0075 mol, 1.5 equiv), pyridine (0.989 g, 1.0 mL 0.0125 mol, 2.2 equiv), and MeCN (10 mL, 0.5 M). The reaction mixture was was stirred for about two minutes at room temperature. After this time, $Na_2S_2O_8$ (2.618 g, 0.011 mol, 2.2 equiv) and the photocatalyst $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.0001 mol, 0.02 equiv) were added. After the addition of the components, an aliquot was taken and kept in the dark until a ^{19}F NMR was obtained (T_0 data point). The remainder of the reaction mixture was sealed in the vial and irradiated in the aforementioned LED reactor for 30 minutes. After this time, an aliquot was taken and kept in the dark until a ^{19}F NMR was obtained (T_1 data point). The reaction mixture was removed from the irradiation zone and placed on a stir plate in complete darkness (via the aid of aluminium foil and a box) for 30 minutes. After this time an aliquot was taken and kept in the dark until a ^{19}F NMR was obtained (T_2 data point). After this time, the reaction was returned to the irradiation zone for an additional 240 minutes, at which time a final aliquot was take (T_∞ data point) By this time the reaction was essentially complete.

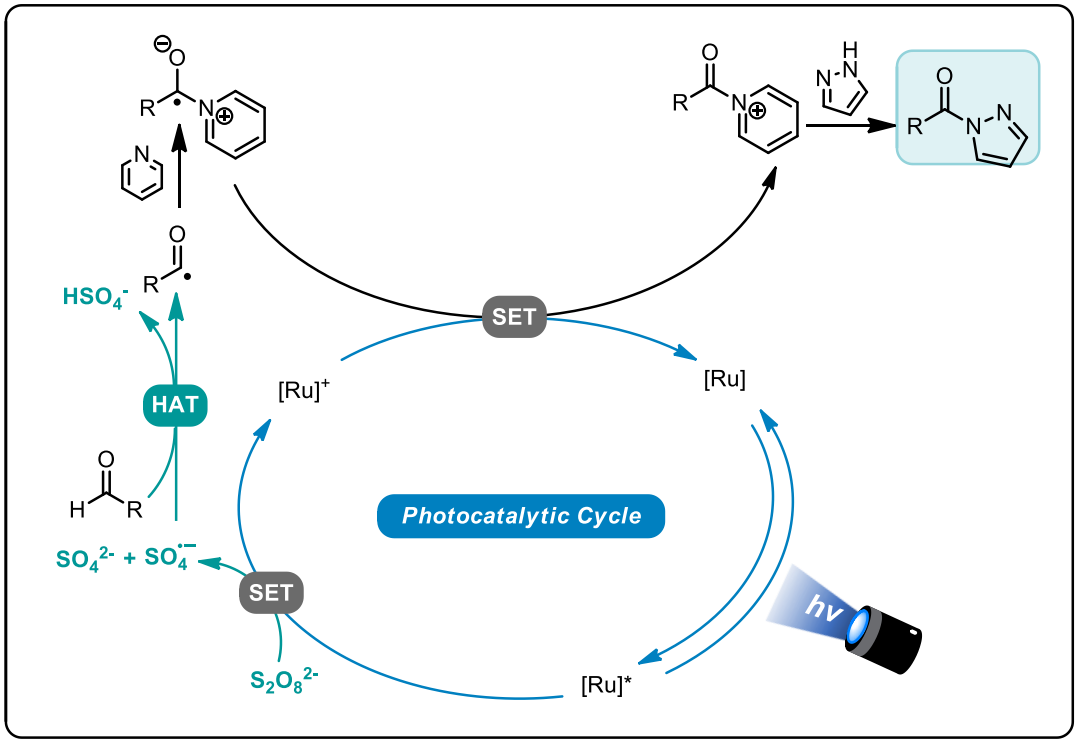
Table S3: Control Studies for the ACT/Photoredox Dual Catalytic Process



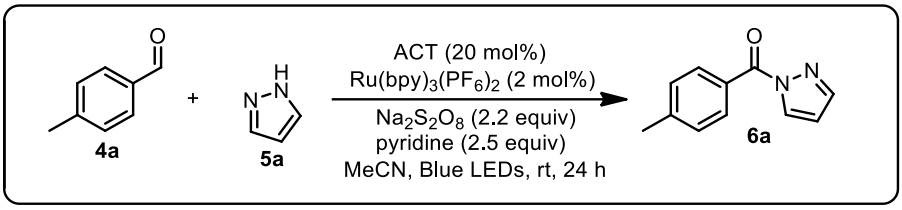
Entry	Time (min)	Conversion to 6c (%)[a]
1	*0*	0
2	*30*	13
3	*60*	14
4	*300*	97

[a] Percent conversion determined by ^{19}F NMR of the crude reaction mixture,

Figure S1: Plausible Mechanistic Rationale for Observed Oxidative Amidation in Absence of a TEMPO-based species



Representative Procedure for Photoredox Oxidative Amidation from Aldehydes

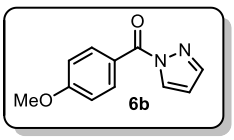


(1*H*-pyrazol-1-yl)(*p*-tolyl)methanone[6] (6a)

To a 20-mL vial equipped with a stir bar was added *p*-tolualdehyde (0.601 g, 0.005 mol, 1 equiv), ACT (0.213 g, 0.001 mol, 0.2 equiv), pyrazole (0.511 g, 0.0075 mol, 1.5 equiv), pyridine (0.989 g, 1.0 mL 0.0125 mol, 2.2 equiv), and MeCN (10 mL, 0.5 M). The reaction mixture was was stirred for about two minutes at room temperature. After this time, $Na_2S_2O_8$ (2.618 g, 0.011 mol, 2.2 equiv) and the photocatalyst $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.0001 mol, 0.02 equiv) were added. The vial was sealed with a cap and irradiated in the aforementioned LED reactor for 24 h. After this time, Et_2O (10 mL) was added and the resulting mixture was filtered through a coarse porosity fritted glass funnel. The solution was then transferred to a separatory funnel, diluted with Et_2O (50 mL) and 0.5 M aqueous HCl (75 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 75 mL). The organic layers were then combined and washed with 0.5 M aqueous HCl (3 × 50 mL), saturated aqueous sodium bicarbonate (50 mL), deionized water (50 mL), and finally brine (100 mL). The organic layer was then dried over sodium sulfate and the solvent removed *in vacuo* to afford the pure *N*-acyl pyrazole (0.801 g, 86%).

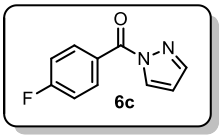
^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.44 (s, 3 H) 6.51 (dd, *J*=2.75, 1.43 Hz, 1 H) 7.31 (d, *J*=8.14 Hz, 2 H) 7.79 (d, *J*=0.66 Hz, 1 H) 8.05 (d, *J*=8.14 Hz, 2 H) 8.43 (dd, *J*=2.86, 0.44 Hz, 1 H)
^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 21.98 (CH_3) 109.50 (CH) 128.91 (C) 129.12 (CH 130.69 (CH) 131.95 (CH) 144.23 (C) 144.56 (CH) 166.57 (C)
GC-MS (EI) 186 ([M]$^+$, 23%) 158 (13%) 119 (100%) 91 (50%) 65 (19%) 63 (6%)

(4-methoxyphenyl)(1*H*-pyrazol-1-yl)methanone,[6] 6b (0.689 g, 68%) was prepared according to the general procedure from *p*-anisaldehyde, **4b** (0.681 g, 0.005 mol) ***with the following modification: with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 3 Å molecular sieves (0.190 g) were used in the reaction; 3) Further purification was accomplished by recrystallization from hexanes. The desired acyl pyrazole, **6b**, was isolated as a powdery yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 3.87 (s, 3 H) 6.49 (dd, *J*=2.64, 1.54 Hz, 1 H) 6.98 (d, *J*=9.02 Hz, 2 H) 7.78 (s, 1 H) 8.22 (d, *J*=9.02 Hz, 2 H) 8.42 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 55.70 (CH_3) 109.18 (CH) 113.73 (CH) 123.70 (C) 130.73 (CH) 134.42 (CH) 144.29 (CH) 163.82 (C) 165.58 (C) **GC-MS** (EI) 202 ([M]$^+$, 19%) 174 (6%) 135 (100%) 107 (10%) 92 (19%) 77 (23%) 64 (11%)

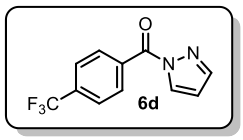


[6] Ovian, J. M.; Kelly, C. B.; Pistritto, V. A.; Leadbeater, N. E. *Org. Lett.* **2017**, *19*, 1286.

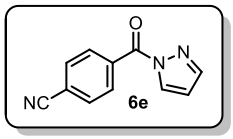
(4-fluorophenyl)(1*H*-pyrazol-1-yl)methanone, 6c (0.868 g, 90%) was prepared according to the general procedure from 4-fluorobenzaldehyde, **4c** (0.620 g, 0.005 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 3 Å molecular sieves (0.190 g) were used in the reaction. The desired acyl pyrazole, **6c**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.55 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.20 (tt, *J*=8.60, 2.90 Hz, 2 H) 7.82 (d, *J*=0.66 Hz, 1 H) 8.15 - 8.32 (m, 2 H) 8.46 (d, *J*=2.42 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 109.79 (CH) 115.67 (d, $J_{C\text{-}C\text{-}F}$ =22.01 Hz, CH) 127.85 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =3.12 Hz, C) 130.82 (CH) 134.77 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ =9.17 Hz, CH) 144.85 (CH) 165.99 (d, $J_{C\text{-}F}$ =255.29 Hz, CF) 165.34 (s, C). **^{19}F NMR** ($CDCl_3$, 377 MHz) δ ppm -107.95 – -107.82 (m, 1 F) **GC-MS** (EI) 190 ($[M]^+$, 14%) 162 (12%) 123 (100%) 95 (70%) 75 (29%) 50 (7%) **HRMS** (DART) calcd for $C_{10}H_8FN_2O$ $[M+H]^+$: 191.0621, obs. 191.0609.



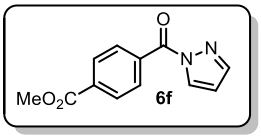
(1*H*-pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone,[6] 6d (1.01 g, 84%) was prepared according to the general procedure from was prepared according to the general procedure from 4-(trifluoromethyl)benzaldehyde, **4d** (0.871 g, 0.005 mol) ***with the following modification:*** 5 equiv of pyridine (1.98 g, 0.025 mol) was used. The desired acyl pyrazole, **6d**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.59 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.80 (d, *J*=8.14 Hz, 2 H) 7.84 (d, *J*=0.66 Hz, 1 H) 8.26 (d, *J*=8.14 Hz, 2 H) 8.49 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.25 (CH) 123.80 (q, $J_{C\text{-}F}$=272.30 Hz, CF_3) 125.28 (q, $J_{C\text{-}C\text{-}C\text{-}F}$=3.60 Hz, CH) 130.59 (CH) 132.02 (CH) 134.48 (q, $J_{C\text{-}C\text{-}F}$=32.10 Hz, C) 135.08 (C) 145.22 (CH) 165.52 (C) **^{19}F NMR** ($CDCl_3$, 377 MHz) -114.53 (s, 3 F) **GC-MS** (EI) 240 ($[M]^+$, 25%) 212 (13%) 173 (100%) 145 (89%) 125 (12%) 95 (14%) 75 (13%) 69 (5%) 50 (6%)



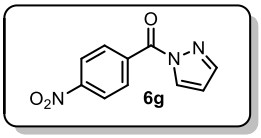
4-(1*H*-pyrazole-1-carbonyl)benzonitrile,[6] 6e (0.872 g, 88%) was prepared according to the general procedure from was prepared according to the general procedure from 4-formylbenzonitrile, **4e** (0.656 g, 0.005 mol). The desired acyl pyrazole, **6e**, was isolated as an powdery off-white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.57 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.77 - 7.83 (m, 3 H) 8.23 (d, *J*=8.58 Hz, 2 H) 8.45 (d, *J*=2.86 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.48 (CH) 116.47 (C) 118.08 (C) 130.61 (CH) 131.99 (CH) 132.16 (CH) 135.65 (C) 145.40 (CH) 165.03 (C) **GC-MS** (EI) 197 ($[M]^+$, 21%) 169 (17%) 130 (100%) 102 (71%) 76 (13%) 75 (20%) 51 (11%).



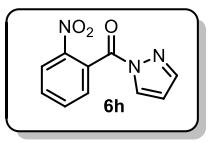
methyl 4-(1*H*-pyrazole-1-carbonyl)benzoate,[6] 6f (0.790 g, 69%) was prepared according to the general procedure from methyl 4-formylbenzoate, **4f** (0.820 g, 0.005 mol). The desired acyl pyrazole, **6f**, was isolated as a powdery off-white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 3.97 (s, 3 H) 6.56 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.82 (d, *J*=0.66 Hz, 1 H) 8.17 (s, 4 H) 8.46 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 52.71 (CH_3) 110.11 (CH) 129.37 (CH) 130.57 (CH) 131.57 (CH) 133.93 (C) 135.60 (C) 145.09 (CH) 165.94 (C) 166.35 (C) **GC-MS** (EI) 230 ($[M]^+$, 21%) 202 (10%) 171 (10%) 163 (100%) 135 (25%) 103 (24%) 76 (26%) 50 (14%).



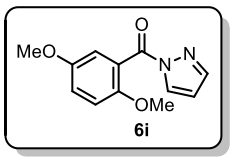
(4-nitrophenyl)(1*H*-pyrazol-1-yl)methanone, 6g (0.934 g, 86%) was prepared according to the general procedure from 4-nitrobenzaldehyde, **4g** (0.756 g, 0.005 mol). The desired acyl pyrazole, **6g**, was isolated as a powdery off-white solid. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ ppm 6.59 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.82 (d, *J*=0.66 Hz, 1 H) 8.25 - 8.38 (m, 4 H) 8.47 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.65 (CH) 123.38 (CH) 130.66 (CH) 132.80 (CH) 137.34 (C) 145.57 (CH) 150.37 (C) 164.91 (C) **GC-MS** (EI) 217 ([M]$^+$, 29%) 201 (18%) 189 (25%) 165 (25%) 150 (100%) 120 (19%) 104 (84%) 92 (50%) 76 (82%) 64 (15%) 50 (45%) **HRMS** (DART) calcd for $C_{10}H_8N_3O_3$ [M+H]$^+$: 218.0566, obs. 218.0568.



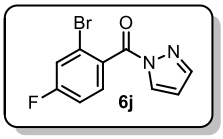
(2-nitrophenyl)(1*H*-pyrazol-1-yl)methanone,[6] 6h (1.03 g, 95%) was prepared according to the general procedure from 2-nitrobenzaldehyde, **4h** (0.756 g, 0.005 mol) ***with the following modification:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 3 Å molecular sieves (0.190 g) were used in the reaction. The desired acyl pyrazole, **6h**, was isolated as a powdery yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.52 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.63 (d, *J*=0.88 Hz, 1 H) 7.68 (dd, *J*=7.48, 1.32 Hz, 1 H) 7.72 (td, *J*=7.70, 1.32 Hz, 1 H) 7.81 (td, *J*=7.50, 1.10 Hz, 1 H) 8.24 (dd, *J*=8.14, 0.88 Hz, 1 H) 8.44 (d, *J*=2.86 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.73 (CH) 124.36 (CH) 129.19 (CH) 129.81 (CH) 130.17 (C) 131.75 (CH) 134.29 (CH) 145.47 (CH, C) 165.47 (C) **GC-MS** (EI) 217 ([M]$^+$, 0.1%) 171 (100%) 150 (74%) 104 (13%) 78 (11%) 76 (45%) 51 (43%).



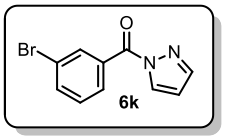
(2,5-dimethoxyphenyl)(1*H*-pyrazol-1-yl)methanone, 6i (1.02 g, 87%) was prepared according to the general procedure from 2,5-dimethoxybenzaldehyde, **4i** (0.831 g, 0.005 mol). The desired acyl pyrazole, **6i**, was isolated as a powdery yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 3.75 (s, 3 H) 3.79 (s, 3 H) 6.48 (dd, *J*=2.86, 1.32 Hz, 1 H) 6.92 - 7.09 (m, 3 H) 7.73 (d, *J*=0.66 Hz, 1 H) 8.32 (dd, *J*=2.86, 0.44 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 55.96 (CH_3) 56.66 (CH_3) 109.80 (CH) 113.29 (CH) 114.88 (CH) 118.34 (CH) 132.52 (CH) 129.56 (CH) 144.75 (C) 151.67 (C) 153.28 (C) 166.36 (C) **GC-MS** (EI) 232 ([M]$^+$, 45%) 201 (100%) 165 (100%) 150 (18%) 122 (25%) 107 (40%) 92 (13%) 79 (26%) 77 (21%) 63 (9%) 53 (9%) **HRMS** (DART) calcd for $C_{12}H_{13}N_2O_3$ [M+H]: 233.0926, obs. 233.0939.



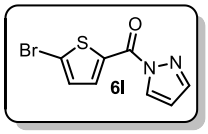
(2-bromo-4-fluorophenyl)(1*H*-pyrazol-1-yl)methanone,[6] 6j (1.27 g, 95%) was prepared according to the general procedure from 2-bromo-4-fluorobenzaldehyde, **4j** (1.02 g, 0.005 mol).The desired acyl pyrazole, **6j**, was isolated as a powdery yellow solid. **^{1}H NMR** ($CDCl_3$, 100 MHz) δ ppm 6.55 (dd, *J*=2.92, 1.41 Hz, 1 H) 7.16 (td, *J*=8.30, 2.40 Hz, 1 H) 7.42 (dd, *J*=8.10, 2.45 Hz, 1 H) 7.52 (dd, *J*=8.57, 5.75 Hz, 1 H) 7.76 (d, *J*=0.75 Hz, 1 H) 8.39 (dd, *J*=2.83, 0.57 Hz, 1 H)**^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.84 (CH) 114.80 (d, $J_{C\text{-}C\text{-}F}$=22.01 Hz, CH) 121.01 (d, $J_{C\text{-}C\text{-}F}$=24.94 Hz, CH) 121.75 (d, $J_{C\text{-}C\text{-}C\text{-}F}$=9.90 Hz, C) 129.65 (CH) 131.75 (d, $J_{C\text{-}C\text{-}C\text{-}F}$=9.17 Hz, CH) 131.64 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$=3.85 Hz, C) 145.54 (CH) 163.69 (d, $J_{C\text{-}F}$=256.03 Hz, CF) 165.77 (C) **^{19}F NMR** ($CDCl_3$, 377 MHz) -109.65 – -109.56 (m, 1 F) **GC-MS** (EI) 270 ([M]$^+$, ^{81}Br, 0.1%) 268 ([M]$^+$, ^{79}Br, 0.1%) 203 (^{81}Br, 40%) 201 (^{79}Br, 42%) 189 (100%) 175 (^{81}Br, 20%) 173 ([^{79}Br, 21%) 94 (41%) 74 (8%) 50 (6%)



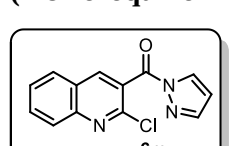
(3-bromophenyl)(1*H*-pyrazol-1-yl)methanone,[6] 6k (0.786 g, 63%) was prepared according to the general procedure from 3-bromobenzaldehyde, **4k** (0.925 g, 0.005 mol). The desired acyl pyrazole, **6k**, was isolated as a viscous, clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ ppm 6.54 (dd, *J*=2.83, 1.51 Hz, 1 H) 7.38 (t, *J*=8.01 Hz, 1 H) 7.73 (dq, *J*=7.91, 0.90 Hz, 1 H) 7.81 (d, *J*=0.70 Hz, 1 H) 8.08 (dt, *J*=7.82, 1.18 Hz, 1 H) 8.29 (t, *J*=1.79 Hz, 1 H) 8.43 (d, *J*=2.83 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 109.90 (CH) 122.18 (C) 129.69 (CH) 130.25 (CH) 130.51 (CH) 133.40 (C) 134.47 (CH) 135.95 (CH) 144.90 (CH) 164.87 (C) **GC-MS** (EI) 252 ([M]$^+$, ^{81}Br, 32%) 250 ([M]$^+$, ^{79}Br, 33%) 225 (23%, ^{81}Br) 223(23%, ^{79}Br) 185(99%, ^{81}Br) 183 (100%, ^{79}Br) 157(70%, ^{81}Br) 155(71%, ^{79}Br) 76 (58%) 50 (37%).



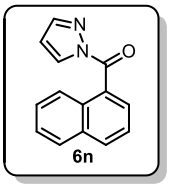
(5-bromothiophen-2-yl)(1*H*-pyrazol-1-yl)methanone,[6] 6l (1.24 g, 96%) was prepared according to the general procedure from 5-bromothiophene-2-carbaldehyde, **4l** (0.955 g, 0.005 mol) ***with the following modification:*** Further purification was accomplished by washing the crude solid with hexanes. The desired acyl pyrazole, **6l**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.52 (dd, *J*=2.75, 1.43 Hz, 1 H) 7.17 (d, *J*=4.18 Hz, 1 H) 7.80 (s, 1 H) 8.13 (d, *J*=4.18 Hz, 1 H) 8.40 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.25 (CH) 127.38 (C) 129.74 (CH) 130.44 (CH) 132.89 (C) 138.74 (CH) 144.22 (CH) 157.79 (C) **GC-MS** (EI) 258 ([M]$^+$, ^{81}Br, 38%) 256 ([M]$^+$, ^{79}Br, 37%) 230 (^{81}Br, 41%) 228 (^{79}Br, 41%) 191 (^{81}Br, 100%) 189 (^{79}Br, 99%) 163 (^{81}Br, 12%) 161 (^{79}Br, 12%) 119 (^{81}Br, 12%) 117 (^{79}Br, 12%) 82 (43%) 38 (12%).



(2-chloroquinolin-3-yl)(1*H*-pyrazol-1-yl)methanone, 4m (1.07 g, 83%) was prepared according to the general procedure from 2-chloroquinoline-3-carbaldehyde, **4m** (0.958 g, 0.005 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used 2) EtOAc was used in place of Et_2O in the workup. The desired acyl pyrazole, **6m**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.61 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.66 (ddd, *J*=8.50, 7.00, 1.30 Hz, 1 H) 7.78 (d, *J*=0.88 Hz, 1 H) 7.86 (ddd, *J*=8.47, 7.04, 1.43 Hz, 1 H) 7.91 (d, *J*=8.36 Hz, 1 H) 8.11 (d, *J*=8.58 Hz, 1 H) 8.41 (s, 1 H) 8.48 (d, *J*=2.86 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 111.06 (CH) 125.80 (C) 127.51 (C) 128.18 (CH) 128.53 (CH) 128.93 (CH) 129.54 (CH) 132.51 (CH) 139.65 (CH) 145.64 (CH) 146.57 (C) 148.35 (C) 164.57 (C) **GC-MS** (EI) 257 ([M]$^+$, 0.1%) 222 (100%) 190 (36%) 162 (40%) 127 (20%) 101 (33%) 75 (22%) 51 (11%) 40 (18%) **HRMS** (DART) calcd for $C_{13}H_9ClN_3O$ [M+H]$^+$: 258.0434, obs. 258.0438.



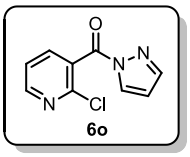
naphthalen-1-yl(1*H*-pyrazol-1-yl)methanone,[7] 6n (0.892 g, 80%) was prepared according to the general procedure from 1-naphthaldehyde, **4n** (0.781 g, 0.005 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used 2) Further purification was accomplished by washing the crude solid with hexanes. The desired acyl pyrazole, **6n**, was isolated as a powdery pale yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.58 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.52 - 7.63 (m, 3 H) 7.78 (d, *J*=0.88 Hz, 1 H) 7.84 (dd, *J*=7.15, 1.21 Hz, 1 H) 7.91 - 7.97 (m, 1 H) 7.98 - 8.05 (m, 1 H) 8.08 (d, *J*=8.36 Hz, 1 H) 8.50 (dd, *J*=2.86, 0.44 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.21 (CH) 124.50 (CH) 125.23 (CH) 126.79 (CH)



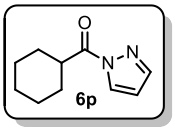
[7] Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 3231.

127.80 (CH) 128.83 (CH) 129.13 (CH) 130.02 (C) 130.34 (CH) 131.12 (C) 132.44 (CH) 133.75 (C) 145.10 (CH) 167.62 (C) **GC-MS** (EI) 222 ([M]$^+$, 27%) 194 (11%) 155 (82%) 127 (100%) 77 (12%) 51 (5%).

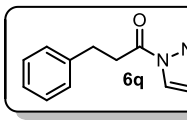
(2-chloropyridin-3-yl)(1*H*-pyrazol-1-yl)methanone,[6] 6o (0.798 g, 77%) was prepared according to the general procedure from 2-chloronicotinaldehyde, **4o** (0.707 g, 0.005 mol) ***with the following modification:*** EtOAc was used in place of Et_2O in the workup. The desired acyl pyrazole, **6o**, was isolated as a powdery yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.57 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.38 (dd, *J*=7.70, 4.84 Hz, 1 H) 7.75 (d, *J*=0.66 Hz, 1 H) 7.87 (dd, *J*=7.59, 1.87 Hz, 1 H) 8.40 (d, *J*=2.86 Hz, 1 H) 8.55 (dd, *J*=4.84, 1.76 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 111.13 (CH) 122.00 (CH) 129.46 (CH) 130.07 (C) 138.73 (CH) 145.74 (CH) 148.60 (C) 151.59 (CH) 164.45 (C) **GC-MS** (EI) 172 ([M-Cl]$^+$, 100%) 142 (16%) 140 (49%) 114 (14%) 112 (44%) 76 (28%) 50 (13%) **HRMS** (DART) calcd for $C_9H_6ClN_3O$ [M+H]: 208.0278, found: 208.0302.



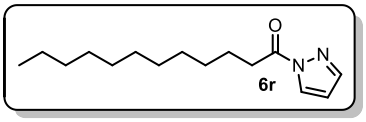
cyclohexyl(1*H*-pyrazol-1-yl)methanone,[6] 6p (0.698 g, 78%) was prepared according to the general procedure from cyclohexanecarbaldehyde, **4p** (0.561 g, 0.005 mol). The desired acyl pyrazole, **6p**, was isolated as a clear, pale brown oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.28 (tt, *J*=12.32, 3.30 Hz, 1 H) 1.41 (qt, *J*=12.64, 3.16 Hz, 2 H) 1.55 (qd, *J*=12.10, 3.08 Hz, 2 H) 1.68 - 1.77 (m, 1 H) 1.82 (dt, *J*=13.04, 3.27 Hz, 2 H) 1.93 - 2.02 (m, 2 H) 3.62 (tt, *J*=11.58, 3.49 Hz, 1 H) 6.41 (dd, *J*=2.75, 1.43 Hz, 1 H) 7.69 (s, 1 H) 8.22 (d, *J*=2.86 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 25.30 (CH_2) 25.66 (CH_2) 28.96 (CH_2) 41.40 (CH) 109.21 (CH) 128.22 (CH) 143.58 (CH) 174.88 (C) **GC-MS** (EI) 178 ([M]$^+$, 3%) 110 (10%) 83 (37%) 69 (100%) 55 (34%) 41 (23%) 39 (16%) **HRMS** (DART) calcd for $C_{10}H1_4N_2O$ [M+H]: 179.1184, found: 179.1202.



3-phenyl-1-(1*H*-pyrazol-1-yl)propan-1-one,[8] 6q (0.744 g, 74%) was prepared according to the general procedure from 2-methyl-2-phenylpropanal, **4q** (0.670 g, 0.005 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 3 Å molecular sieves (0.190 g) were used in the reaction; 3) Further purification was accomplished by SiO_2 plug, eluting with 95:5 Hex/EtOAc. The desired acyl pyrazole, **6q**, was isolated as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 3.13 (t, *J*=7.70 Hz, 2 H) 3.49 (t, *J*=7.90 Hz, 2 H) 6.44 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.18 - 7.24 (m, 1 H) 7.25 - 7.35 (m, 4 H) 7.70 (d, *J*=0.66 Hz, 1 H) 8.26 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 30.11 (CH_2) 35.54 (CH_2) 109.48 (CH) 126.25 (CH) 128.15 (CH) 128.36 (CH) 128.45 (CH) 140.23 (C) 143.86 (CH) 171.25 (C) **GC-MS** (EI) 200 ([M]$^+$, 4%) 131 (6%) 104 (100%) 91 (34%) 77 (17%) 69 (42%) 51 (8%).



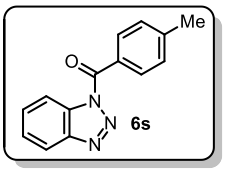
1-(1*H*-pyrazol-1-yl)dodecan-1-one,[6] 6r (0.987 g, 79%) was prepared according to the general procedure from dodecanal, **4r** (0.921 g, 0.005 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 3 Å molecular sieves (0.190 g) were used in the reaction; 3) Further purification was accomplished by SiO_2 plug, eluting with 95:5 Hex/EtOAc. The desired acyl pyrazole, **6r**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 0.88 (t, *J*=7.00 Hz, 3 H) 1.17 - 1.46 (m, 16 H) 1.78 (quin, *J*=7.48 Hz, 2 H) 3.12 (t, *J*=7.48 Hz, 2 H) 6.43 (dd, *J*=2.86, 1.54



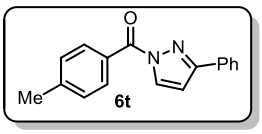
[8] Holzer, W.; Pöecher, I. *J. Heterocyclic Chem.* **1995**, 32, 189.

Hz, 1 H) 7.70 (d, *J*=0.88 Hz, 1 H) 8.26 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 14.34 (CH_3) 22.92 (CH_2) 24.63 (CH_2) 29.37 (CH_2) 29.55 (2 × CH_2) 29.69 (CH_2) 29.84 (2 × CH_2) 32.14 (CH_2) 34.19 (CH_2) 109.61 (CH) 128.42 (CH) 144.01 (CH) 172.59 (C) **GC-MS** (EI) 250 ($[M]^+$, 1%) 249 (4%) 182 (5%) 110 (34%) 98 (22%) 84 (21%) 82 (17%) 69 (100%) 57 (15%) 55 (32%) 43 (17%) 41 (29%) **HRMS** (DART) calcd for $C_{15}H_{26}N_2O$ [M+H]: 251.2123, found: 251.2127.

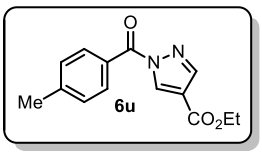
p*-toluoyl-1*H*-1,2,3-benzotriazole,[9] 6s** (0.792 g, 67%) was prepared according to the general procedure from *p*-tolualdehyde **4a** (0.601 g, 0.005 mol) and 1*H*-benzotriazole, **5b** (0.893 g, 0.0075 mol) ***with the following modifications: 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 2 M HCl was used in place of 0.5 M HCl in the work-up. The desired acyl azole, **6s**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 2.49 (s, 3 H) 7.39 (d, *J*=8.14 Hz, 2 H) 7.55 (td, *J*=7.70, 0.88 Hz, 1 H) 7.71 (td, *J*=7.70, 0.88 Hz, 1 H) 8.11 - 8.20 (m, 3 H) 8.39 (d, *J*=8.36 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 22.08 (CH_3) 115.10 (CH) 120.42 (CH) 126.51 (CH) 128.91 (C) 129.49 (CH) 130.56 (CH) 132.22 (CH) 132.74 (C) 145.14 (C) 146.03 (C) 166.86 (C) **GC-MS** (EI) 237 ($[M]^+$, 7%) 209 (72%) 180 (14%) 119 (100%) 91 (65%) 65 (30%) 39 (9%).



(3-phenyl-1*H*-pyrazol-1-yl)(*p*-tolyl)methanone,[6] 6t (1.03 g, 79%) was prepared according to the general procedure from *p*-tolualdehyde **4a** (0.601 g, 0.005 mol) and 3-phenyl-1*H*-pyrazole, **5c** (1.44 g, 0.010 mol, 2 equiv). The desired acyl azole, **6t**, was isolated as a powdery pale yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 2.47 (s, 3 H) 6.85 (d, *J*=2.86 Hz, 1 H) 7.33 (d, *J*=7.92 Hz, 2 H) 7.36 - 7.47 (m, 3 H) 7.85 - 7.92 (m, 2 H) 8.20 (d, *J*=8.36 Hz, 2 H) 8.46 (d, *J*=3.08 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 22.02 (CH_3) 107.24 (CH) 126.67 (CH) 128.93 (C) 129.02 (CH) 129.09 (CH) 129.40 (CH) 132.05 (CH) 132.23 (C) 132.39 (CH) 144.23 (C) 156.00 (C) 166.26 (C) **GC-MS** (EI) 262 ($[M]^+$, 27%) 234 (3%) 119 (100%) 91 (35%) 65 (13%) 51 (2%).

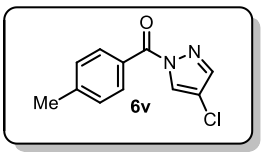


ethyl 1-(4-methylbenzoyl)-1*H*-pyrazole-4-carboxylate,[6] 6u (0.845 g, 65%) was prepared according to the general procedure from *p*-tolualdehyde **4a** (0.601 g, 0.005 mol) and ethyl 1*H*-pyrazole-4-carboxylate, **5d** (1.05 g, 0.0075 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 2 M HCl was used in place of 0.5 M HCl in the work-up. The desired acyl azole, **6u**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.38 (t, *J*=7.30 Hz, 3 H) 2.45 (s, 3 H) 4.35 (q, *J*=7.04 Hz, 2 H) 7.32 (d, *J*=7.92 Hz, 2 H) 8.06 (d, *J*=8.36 Hz, 2 H) 8.12 (s, 1 H) 8.86 (s, 1 H) **^{13}C NMR** ($CDCl_3$, 400 MHz) δ ppm 14.55 (CH_3) 22.01 (CH_3) 61.14 (CH_2) 118.30 (CH) 127.83 (C) 129.27 (CH) 132.18 (CH) 133.99 (CH) 144.27 (CH) 145.06 (C) 162.40 (C) 166.03 (C) **GC-MS** (EI) 258 ($[M]^+$, 11%) 230 (6%) 119 (100%) 91 (29%) 65 (9%).

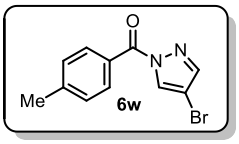


[9] Katritzky, A. R.; Huang, T.-B.; Voronkov, M. V. *J. Org. Chem.*, **2001**, *66*, 1043.

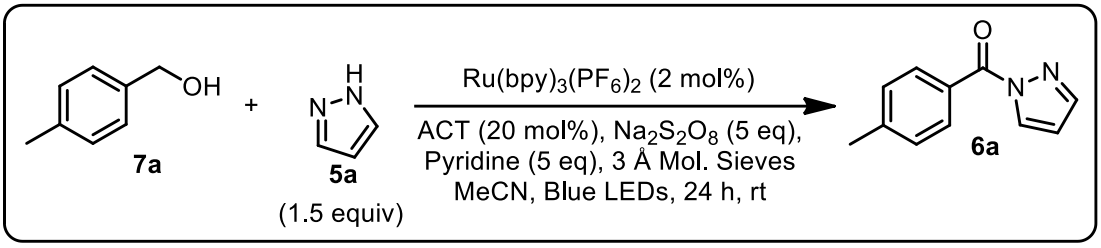
(4-chloro-1*H*-pyrazol-1-yl)(p-tolyl)methanone,[6] 6v (0.566 g, 51%) was prepared according to the general procedure from *p*-tolualdehyde **4a** (0.601 g, 0.005 mol) and 4-chloro-1*H*-pyrazole, **5e** (0.769 g, 0.0075 mol) ***with the following modifications:*** 1) 5 equiv of pyridine (1.98 g, 0.025 mol) was used; 2) 3 Å molecular sieves (0.190 g) were used in the reaction. The desired acyl azole, **6v**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 2.44 (s, 3 H) 7.31 (d, *J*=7.92 Hz, 2 H) 7.70 (s, 1 H) 8.01 (d, *J*=8.36 Hz, 2 H) 8.38 (d, *J*=0.66 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 21.99 (CH_3) 115.51 (C) 127.89 (C) 128.11 (CH) 129.20 (CH) 131.99 (CH) 143.09 (CH) 144.66 (C) 165.58 (C) **GC-MS** (EI) 220 ([M]$^+$, 17%) 119 (100%) 91 (36%) 65 (13%) 51 (2%) 39 (3%).



(4-bromo-1*H*-pyrazol-1-yl)(*p*-tolyl)methanone,[6] 6w (1.18 g, 89%) was prepared according to the general procedure from *p*-tolualdehyde, **2a** (0.601 g, 5 mmol) and 4-bromo-1*H*-pyrazole, **5f** (1.10 g, 0.0075 mol) 2) 2 M HCl was used in place of 0.5 M HCl in the work-up. The desired acyl azole, **6w**, was isolated as a powdery off-white solid. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ ppm 2.45 (s, 3 H) 7.31 (d, *J*=7.91 Hz, 2 H) 7.73 (s, 1 H) 8.01 (d, *J*=8.10 Hz, 2 H) 8.44 (s, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 22.03 (CH_3) 99.35 (C) 127.91 (C) 129.25 (CH) 130.59 (CH) 132.01 (CH) 144.73 (C) 144.97 (CH) 165.48 (C) **GC-MS** (EI) 266 ([M]$^+$, ^{81}Br, 12%) 264 ([M]$^+$, ^{79}Br, 12%) 119 (100%) 91 (46%) 65 (20%) 38 (6%).



One Pot Procedure for Photoredox Oxidative Amidation from Alcohols

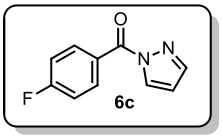


(1*H*-pyrazol-1-yl)(*p*-tolyl)methanone[6] (6a)

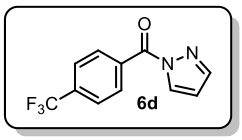
To a 20-mL vial equipped with a stir bar was added *p*-tolylcarbinol **7a** (0.610 g, 0.005 mol, 1 equiv), ACT (0.213 g, 0.001 mol, 0.2 equiv), pyrazole (0.511 g, 0.0075 mol, 1.5 equiv), 3Å molecular sieves (0.190 g), pyridine (1.98 g, 0.025 mol), and MeCN (10 mL, 0.5 M). The reaction mixture was was stirred for about two minutes at room temperature. After this time, sodium persulfate (5.95 g, 0.025 mol, 5 equiv) and the photocatalyst $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.0001 mol, 0.02 equiv) were added. The vial was sealed with a cap and the vial was irradiated in the aforementioned LED reactor for 24 h. After this time, Et_2O (10 mL) was added and the resulting mixture was filtered through a coarse porosity fritted glass funnel. The solution was then transferred to a separatory funnel, diluted with Et_2O (50 mL) and 0.5 M aqueous HCl (75 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 75 mL). The organic layers were then combined and washed with 0.5 M aqueous HCl (3 × 50 mL), saturated aqueous sodium bicarbonate (50 mL), deionized water (50 mL), and finally brine (100 mL). The organics were then dried over sodium sulfate and the solvent removed *in vacuo* to afford the crude *N*-acyl pyrazole which was further purified by recrystallization to give the pure *N*-acyl pyrazole (0.468 g, 50%) as powdery pale yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.44 (s, 3 H) 6.51 (dd, *J*=2.75, 1.43 Hz, 1 H) 7.31 (d, *J*=8.14 Hz, 2 H) 7.79 (d, *J*=0.66 Hz, 1 H) 8.05 (d, *J*=8.14 Hz, 2 H) 8.43 (dd, *J*=2.86, 0.44 Hz, 1 H)
^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 21.98 (CH_3) 109.50 (CH) 128.91 (C) 129.12 (CH 130.69 (CH) 131.95 (CH) 144.23 (C) 144.56 (CH) 166.57 (C)
GC-MS (EI) 186 ($[M]^+$, 23%) 158 (13%) 119 (100%) 91 (50%) 65 (19%) 63 (6%)

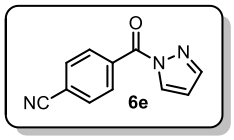
(4-fluorophenyl)(1H-pyrazol-1-yl)methanone, 6c (0.744 g, 78%) was prepared according to the general procedure from 4-fluorobenzyl alcohol, **7c** (0.630 g, 0.005 mol). The desired acyl pyrazole, **6c**, was isolated as a powdery white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.55 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.20 (tt, *J*=8.60, 2.90 Hz, 2 H) 7.82 (d, *J*=0.66 Hz, 1 H) 8.15 - 8.32 (m, 2 H) 8.46 (d, *J*=2.42 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 109.79 (CH) 115.67 (d, $J_{C\text{-}C\text{-}F}$ =22.01 Hz, CH) 127.85 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =3.12 Hz, C) 130.82 (CH) 134.77 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ =9.17 Hz, CH) 144.85 (CH) 165.99 (d, $J_{C\text{-}F}$ =255.29 Hz, CF) 165.34 (s, C). **^{19}F NMR** ($CDCl_3$, 377 MHz) δ ppm -107.95 – -107.82 (m, 1 F) **GC-MS** (EI) 190 ($[M]^+$, 14%) 162 (12%) 123 (100%) 95 (70%) 75 (29%) 50 (7%) **HRMS** (DART) calcd for $C_{10}H_8FN_2O$ $[M+H]^+$: 191.0621, obs. 191.0609.



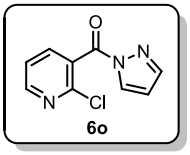
(1*H*-pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone,[6] 6d (0.793 g, 66%) was prepared according to the general procedure from was prepared according to the general procedure from 4-(trifluoromethyl)benzyl alcohol, **7d** (0.881 g, 0.005 mol). The desired acyl pyrazole, **6d**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.59 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.80 (d, *J*=8.14 Hz, 2 H) 7.84 (d, *J*=0.66 Hz, 1 H) 8.26 (d, *J*=8.14 Hz, 2 H) 8.49 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.25 (CH) 123.80 (q, $J_{C\text{-}F}$=272.30 Hz, CF_3) 125.28 (q, $J_{C\text{-}C\text{-}C\text{-}F}$=3.60 Hz, CH) 130.59 (CH) 132.02 (CH) 134.48 (q, $J_{C\text{-}C\text{-}F}$=32.10 Hz, C) 135.08 (C) 145.22 (CH) 165.52 (C) **^{19}F NMR** (CDCl3, 377 MHz) -114.53 (s, 3 F) **GC-MS** (EI) 240 ([M]$^+$, 25%) 212 (13%) 173 (100%) 145 (89%) 125 (12%) 95 (14%) 75 (13%) 69 (5%) 50 (6%)



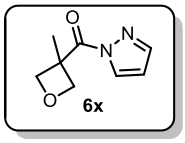
4-(1*H*-pyrazole-1-carbonyl)benzonitrile,[6] 6e (0.769 g, 78%) was prepared according to the general procedure from was prepared according to the general procedure from 4-cyanobenzyl alcohol, **7e** (0.665 g, 0.005 mol) ***with the following modification:*** No molecular sieves were used. The desired acyl pyrazole, **6e**, was isolated as a powdery off-white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.57 (dd, *J*=2.86, 1.54 Hz, 1 H) 7.77 - 7.83 (m, 3 H) 8.23 (d, *J*=8.58 Hz, 2 H) 8.45 (d, *J*=2.86 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 110.48 (CH) 116.47 (C) 118.08 (C) 130.61 (CH) 131.99 (CH) 132.16 (CH) 135.65 (C) 145.40 (CH) 165.03 (C) **GC-MS** (EI) 197 ([M]$^+$, 21%) 169 (17%) 130 (100%) 102 (71%) 76 (13%) 75 (20%) 51 (11%).



(2-chloropyridin-3-yl)(1*H*-pyrazol-1-yl)methanone,[6] 6o (0.892 g, 86%) was prepared according to the general procedure from (2-chloropyrid-3-yl)methanol, **7o** (0.717 g, 0.005 mol). The desired acyl pyrazole, **6o**, was isolated as a powdery yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 6.57 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.38 (dd, *J*=7.70, 4.84 Hz, 1 H) 7.75 (d, *J*=0.66 Hz, 1 H) 7.87 (dd, *J*=7.59, 1.87 Hz, 1 H) 8.40 (d, *J*=2.86 Hz, 1 H) 8.55 (dd, *J*=4.84, 1.76 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 111.13 (CH) 122.00 (CH) 129.46 (CH) 130.07 (C) 138.73 (CH) 145.74 (CH) 148.60 (C) 151.59 (CH) 164.45 (C) **GC-MS** (EI) 172 ([M-Cl]$^+$, 100%) 142 (16%) 140 (49%) 114 (14%) 112 (44%) 76 (28%) 50 (13%)

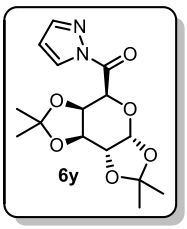


(3-methyloxetan-3-yl)(1*H*-pyrazol-1-yl)methanone, 6x (0.436 g, 52%)[10] was prepared according to the general procedure from (3-methyloxetan-3-yl)methanol, **7x** (0.510 g, 0.005 mol). The desired acyl pyrazole, **6x**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.88 (s, 3 H) 4.53 (d, *J*=6.82 Hz, 2 H) 5.10 (d, *J*=6.60 Hz, 2 H) 6.43 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.67 (d, *J*=0.66 Hz, 1 H) 8.16 - 8.23 (m, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 24.26 (CH_3) 46.86 (C) 79.76 (CH_2) 109.79 (CH) 128.83 (CH) 144.68 (CH) 173.53 (C) **GC-MS** (EI) 166 ([M]$^+$, 0.1%) 136 (10%) 108 (13%) 81 (11%) 69 (100%), 41 (74%) **HRMS** (DART) calcd for $C_8H_{11}N_2O_2$ [M+H]$^+$: 167.0821, found: 167.0807.

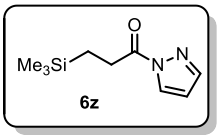


[10] This compound is quite volatile and thus care must be taken during rotary evaporation. We found a room temperature water bath (24 °C) at 450 mmHg was ideal for solvent removal.

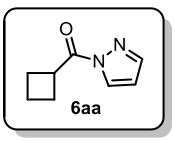
(1*H*-pyrazol-1-yl)((3*a*R,5S,5*a*R,8*a*S,8*b*R)-2,2,7,7-tetramethyltetrahydro-3*a*H-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methanone,[6] 6y (1.18 g, 73%) was prepared according to the general procedure from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, **7y** (1.30 g, 0.005 mol). The desired acyl pyrazole, **6y**, was isolated as a powdery off-white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.28 (s, 3 H) 1.37 (s, 3 H) 1.49 (s, 3 H) 1.59 (s, 3 H) 4.47 (dd, *J*=5.17, 2.75 Hz, 1 H) 4.71 (dd, *J*=7.48, 2.86 Hz, 1 H) 4.96 (dd, *J*=7.48, 2.42 Hz, 1 H) 5.59 (d, *J*=2.42 Hz, 1 H) 5.76 (d, *J*=5.06 Hz, 1 H) 6.45 (dd, *J*=2.86, 1.32 Hz, 1 H) 7.71 (s, 1 H) 8.31 (d, *J*=2.86 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 25.14 (CH_3) 25.20 (CH_3) 26.17 (CH_3) 26.29 (CH_3) 69.42 (CH) 70.62 (CH) 71.49 (CH) 72.82 (CH) 96.92 (CH) 109.58 (C) 109.82 (CH) 110.80 (C) 129.13 (CH) 144.60 (CH) 165.98 (C) **GC-MS** (EI) 309 ([M-CH_3]$^+$, 35%) 239 (6%) 199 (6%) 163 (5%) 141 (47%) 113 (29%) 100 (16%) 95 (26%) 85 (28%) 83 (17%) 71 (23%) 69 (43%) 59 (34%) 43 (100%) 41 (16%).



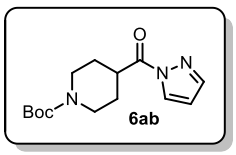
1-(1*H*-pyrazol-1-yl)-3-(trimethylsilyl)propan-1-one, 6z (0.411 g, 42%) was prepared according to the general procedure from 3-(trimethylsilyl)-1-propanol, **7z** (0.661 g, 0.005 mol) ***with the following modification:*** Further purification was accomplished by SiO_2 plug, eluting with 95:5 to 9:1 Hex/EtOAc. The desired acyl pyrazole, **6z**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 0.07 (s, 9 H) 0.84 - 1.06 (m, 2 H) 2.98 - 3.28 (m, 2 H) 6.44 (dd, *J*=2.75, 1.43 Hz, 1 H) 7.71 (d, *J*=0.66 Hz, 1 H) 8.26 (d, *J*=2.64 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm -1.60 (CH_3) 11.26 (CH_2) 29.02 (CH_2) 109.62 (CH) 128.61 (CH) 144.04 (CH) 173.89 (C) **GC-MS** (EI) 196 ([M]$^+$, 2%) 195 ([M-H]$^+$, 12%) 181 (59%) 169 (14%) 167 (12%) 153 (33%) 141 (29%) 125 (100%) 113 (13%) 98 (10%) 85 (9%) 73 (76%) 69 (19%) 43 (16%) 41 (14%) **HRMS** (DART) calcd for $C_9H_{17}N_2OSi$ [M+H]$^+$: 197.1110, obs. 197.1118.



cyclobutyl(1*H*-pyrazol-1-yl)methanone,[10] 6aa (0.246 g, 33%) was prepared according to the general procedure from cyclobutylmethanol, **7aa** (0.420 g, 0.005 mol) ***with the following modification:*** Further purification was accomplished by SiO_2 plug, eluting with 95:5 Hex/EtOAc. The desired acyl pyrazole, **6aa**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.87 - 2.18 (m, 2 H) 2.23 - 2.53 (m, 4 H) 4.27 (quind, *J*=8.57, 0.94 Hz, 1 H) 6.41 (dd, *J*=2.73, 1.41 Hz, 1 H) 7.67 (d, *J*=0.56 Hz, 1 H) 8.23 (dd, *J*=2.83, 0.38 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 18.43 (CH_2) 25.24 (CH_2) 37.68 (CH) 109.29 (CH) 128.30 (CH) 143.83 (CH) 173.56 (C) **GC-MS** (EI) 150 ([M]$^+$, 2%) 122 (21%) 94 (23%) 82 (13%) 69 (71%), 55 (100%) **HRMS** (DART) calcd for $C_8H_{11}N_2O$ [M+H]$^+$: 151.0871, found: 151.0865.

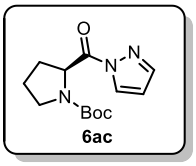


tert*-butyl 4-(1*H*-pyrazole-1-carbonyl)piperidine-1-carboxylate, 6ab** (0.876 g, 63%) was prepared according to the general procedure from *tert*-butyl 4-(hydroxymethyl)piperidine-1-carboxylate, **7ab** (1.08 g, 0.005 mol) ***with the following modification: Further purification was accomplished by SiO_2 plug, eluting with 8:2 Hex/EtOAc.The desired acyl pyrazole, **6ab**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.50 (s, 9 H), 1.79 (qd, *J*=11.9, 4.4 Hz, 2 H), 1.93 - 2.06 (m, 2 H), 2.93 (t, *J*=12.8 Hz, 2 H), 3.82 (tt, *J*=11.7, 3.7 Hz, 1 H), 4.08 - 4.32 (m, 2 H), 6.48 (dd, *J*=2.8, 1.4 Hz, 1 H), 7.75 (d, *J*=0.9 Hz, 1 H), 8.27 (d, *J*=2.9 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 28.30 (CH_2), 28.62 (CH_3), 40.02 (CH), 43.09 (CH_2), 79.79 (C), 109.89 (CH), 128.65 (CH), 144.23 (CH), 154.81 (C), 173.73 (C) **GC-MS** (EI) 279 ([M]$^+$, 0.1%) 222 (33%) 206 (12%) 178 (7%) 138 (14%) 127 (35%) 110 (5%) 95 (7%) 83 (74%)



69 (39%) 57 (100%) 41 (28%) **HRMS** (DART) calcd for $C_{10}H_{12}N_3O_3$ [M – ^{t}Bu]$^+$: 222.0879, found: 222.0889.

(*S*)-*tert*-butyl 2-(1*H*-pyrazole-1-carbonyl)pyrrolidine-1-carboxylate,[11] 6ac (0.939 g, 71%) was prepared



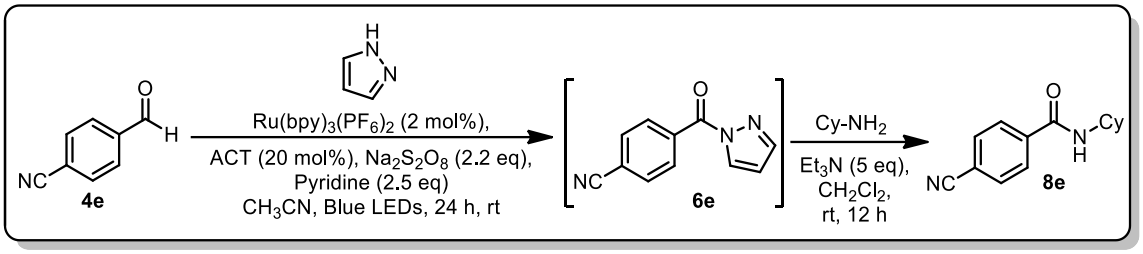
6ac

according to the general procedure from (*S*)-*tert*-butyl 2-(hydroxymethyl)pyrrolidine-1-carboxylate, **7ac** (1.06 g, 0.005 mol) ***with the following modification:*** Further purification was accomplished by SiO_2 column chromatography, eluting with 7:3 Hex/EtOAc. The desired acyl pyrazole, **6ac**, was isolated as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ ppm 1.28 & 1.49 (s, 9 H), 1.87 - 2.14 (m, 3 H), 2.34 - 2.53 (m, 1 H), 3.44 - 3.75 (m, 2 H), 5.52 - 5.63 (m, 1 H), 6.44 & 6.49 (dd, *J*=2.4, 1.3 Hz & dd, *J*=2.7, 1.4 Hz, 1 H), 7.72 & 7.75 (s, 1 H), 8.27 & 8.30 (d, *J*=2.8 Hz, & d, *J*=2.8 Hz, 1 H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ppm 24.12 & 24.64 (CH_2), 28.34 & 28.74 (CH_3), 30.74 & 31.55 (CH_2), 46.94 & 47.26 (CH_2), 58.36 & 58.64 (CH), 80.21 & 80.24 (s, 1 C), 109.80 & 110.07 (CH), 128.82 & 129.18 (CH), 144.41 (CH), 153.87 & 154.67 (C), 171.30 & 171.99 (C) **GC-MS** (EI) 266 ([M]$^+$, 0.1%) 209 (2%) 197 (8%) 192 (7%) 170 (12%) 164 (35%) 141 (47%) 114 (78%) 95 (5%) 70 (100%) 57 (86%) 41 (45%) **HRMS** (DART) calcd for $C_{13}H_{20}N_3O_3$ [M+H]$^+$: 266.1505, found: 266.1479.

[11] NMR spectra of this compound indicates significant rotameric character; values for all rotameric carbons and protons signals are given. A Coalesce study is included in spectral data section of this Supporting Information.

Sequential Reactions of *N*-Acyl Pyrazoles

From Aldehydes



4-cyano-*N*-cyclohexylbenzamide,[12] 8e

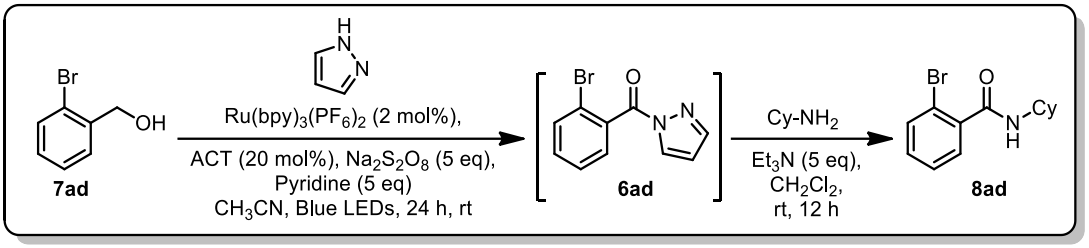
Stage One:
To a 20-mL vial equipped with a stir bar was added 4-formylbenzonitrile, **4e**, (0.656 g, 0.005 mol, 1 equiv), ACT (0.213 g, 0.001 mol, 0.2 equiv), pyrazole (0.511 g, 0.0075 mol, 1.5 equiv), pyridine (0.978 g, 0.0125 mol, 2.5 equiv), and MeCN (10 mL, 0.5 M). The reaction mixture was stirred for two minutes and, after this time, sodium persulfate (2.62 g, 0.011 mol, 2.2 equiv) and $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.0001 mol, 0.02 equiv) were added. The vial was sealed with a cap and the vial was irradiated in the aforementioned LED reactor for 24 h. After this time, Et_2O (10 mL) was added and the resulting mixture was filtered through a coarse porosity fritted glass funnel. The solvent was then removed *in vacuo* to afford the crude *N*-acyl pyrazole which was used directly in the next step.

Stage Two:
To a 50 mL round bottom flask equipped with a stir bar was added the crude acyl pyrazole in MeCN (5 mL) and allowed to stir for 5 minutes. After this time, Et_3N (2.53 g, 3.48 mL, 0.025 mol, 5 equiv) was added all at once, followed by dropwise addition of freshly distilled cyclohexylamine (1.49 g, 1.72 mL, 0.015 mol, 3 equiv). The reaction was allowed to stir for 12 h at room temperature, and after this time, Et_2O (~ 20 mL) was added. The solution was then transferred to a separatory funnel and diluted with aqueous 0.5 M HCl (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with 0.5 M HCl (3 × 50 mL), saturated aqueous $NaHCO_3$ (50 mL), deionized H_2O (50 mL), and brine (100 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo* to afford the pure amide **8e** (0.756 g, 66%) as a off-white powdery solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.20 - 1.33 (m, 3 H), 1.39 - 1.52 (m, 2 H), 1.70 (dt, *J*=13.0, 3.6 Hz, 1 H), 1.79 (dt, *J*=13.5, 3.7 Hz, 2 H), 2.01 - 2.12 (m, 2 H), 3.87 - 4.10 (m, 1 H), 5.98 (d, *J*=6.4 Hz, 1 H), 7.75 (d, *J*=8.4 Hz, 2 H), 7.87 (d, *J*=8.4 Hz, 2 H)
^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 25.14 (CH_2), 25.77 (CH_2), 33.42 (CH_2), 49.42 (CH), 115.18 (C), 118.33 (C), 127.87 (CH), 132.69 (CH), 139.31 (C), 165.08 (C)
GC-MS (EI) 228 ([M]$^+$, 11%) 185 (8%) 147 (77%) 130 (100%) 102 (61%) 82 (16%) 75 (11%) 67 (20%) 41 (13%)

From Alcohols

[12] Correa, A.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 7253.



2-bromo-*N*-cyclohexylbenzamide,[13] 8ad

Stage One:
To a 20-mL vial equipped with a stir bar was added 2-bromobenzyl alcohol, (0.935 g, 0.005 mol, 1 equiv), ACT (0.213 g, 0.001 mol, 0.2 equiv), pyrazole (0.511 g, 0.0075 mol, 1.5 equiv), pyridine (1.98 g, 0.025 mol, 5 equiv), and MeCN (10 mL, 0.5 M). The reaction mixture was stirred for two minutes and, after this time, sodium persulfate (5.95 g, 0.025 mol, 5 equiv) and $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.0001 mol, 0.02 equiv) were added. The vial was sealed with a cap and the vial was irradiated in the aforementioned LED reactor for 24 h. After this time, Et_2O (10 mL) was added and the resulting mixture was filtered through a coarse porosity fritted glass funnel. The solvent was then removed *in vacuo* to afford the crude *N*-acyl pyrazole which was used directly in the next step.

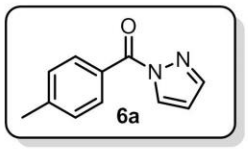
Stage Two:
To a 50 mL round bottom flask equipped with a stir bar was added the crude acyl pyrazole in MeCN (5 mL) and allowed to stir for 5 minutes. After this time, Et_3N (2.53 g, 3.48 mL, 0.025 mol, 5 equiv) was added all at once, followed by dropwise addition of freshly distilled cyclohexylamine (1.49 g, 1.72 mL, 0.015 mol, 3 equiv). The reaction was allowed to stir for 12 h at room temperature, and after this time, Et_2O (~ 20 mL) was added. The solution was then transferred to a separatory funnel and diluted with aqueous 0.5 M HCl (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with 0.5 M HCl (3 × 50 mL), saturated aqueous $NaHCO_3$ (50 mL), deionized H_2O (50 mL), and brine (100 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo* to afford the pure amide **8ad** (1.10 g, 78%) as a white powdery solid.

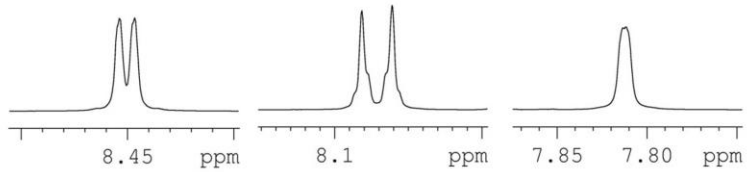
^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.17 - 1.37 (m, 3 H), 1.38 - 1.52 (m, 2 H), 1.66 (dt, *J*=12.9, 3.8 Hz, 1 H), 1.77 (dt, *J*=13.5, 3.9 Hz, 2 H), 2.02 - 2.13 (m, 2 H), 3.95 - 4.09 (m, 1 H), 5.86 (br. s., 1 H), 7.27 (td, *J*=7.5, 1.8 Hz, 1 H), 7.34 - 7.39 (m, 1 H), 7.53 (dd, *J*=7.6, 1.7 Hz, 1 H), 7.59 (dd, *J*=8.0, 1.0 Hz, 1 H)
^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 25.03 (CH_2), 25.79 (CH_2), 33.18 (CH_2), 49.18 (CH), 119.48 (C), 127.79 (CH), 129.80 (CH), 131.28 (CH), 133.52 (CH), 138.53 (C), 166.92 (C)
GC-MS (EI) 283 ($[M]^+$, ^{81}Br, 14%) 281 ($[M]^+$, ^{79}Br, 15%) 202 (^{81}Br, 74%) 200 (^{79}Br, 74%) 185 (^{81}Br, 97%) 183 (^{79}Br, 100%) 157 (^{81}Br, 37%) 155 (^{79}Br, 36%) 105 (17%) 82 (8%) 76 (38%) 67 (15%) 50 (18%) 41 (28%).

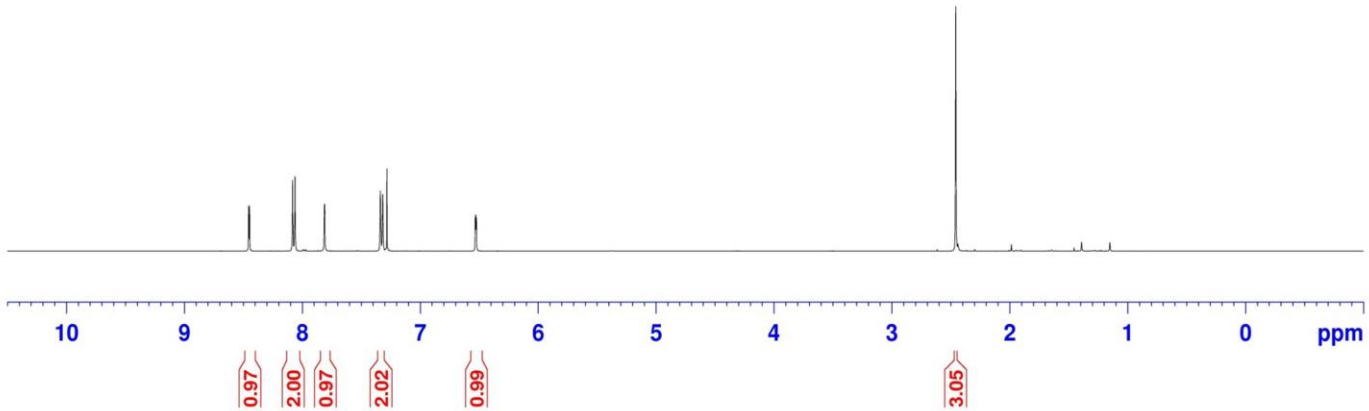
[13] Wrobel, J.; Dietrich, A. *Heterocycles* **1994**, *38*, 1823.

^{1}H NMR Spectra of Synthesized Compounds

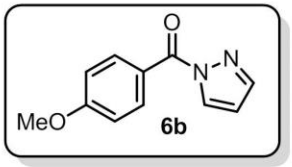
(1H−pyrazol−1−yl)(p−tolyl)methanone
400 MHz, CDCl3

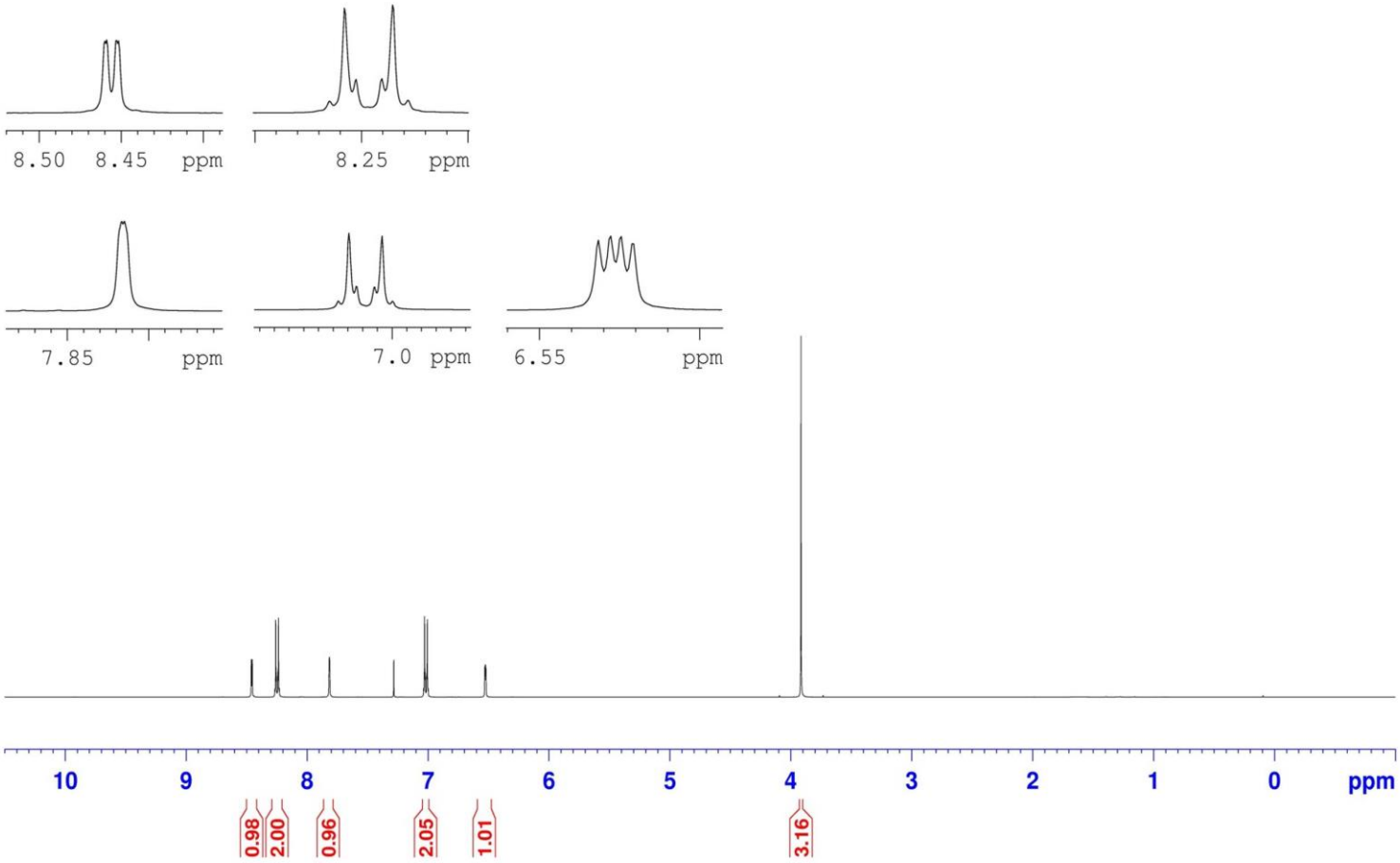




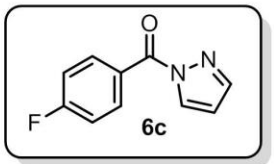


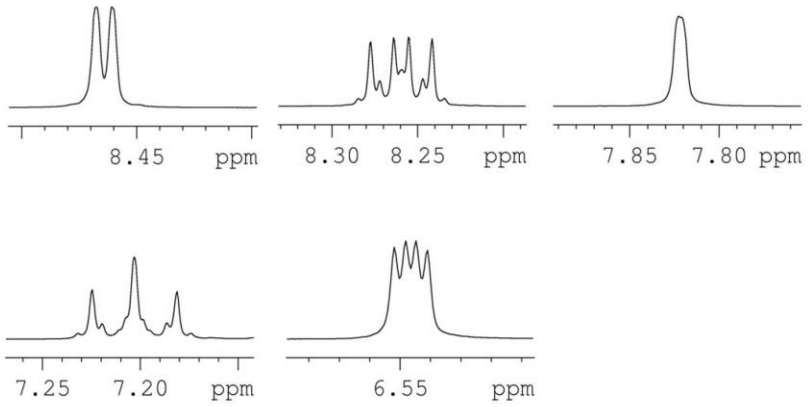
(4–methoxyphenyl)(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3

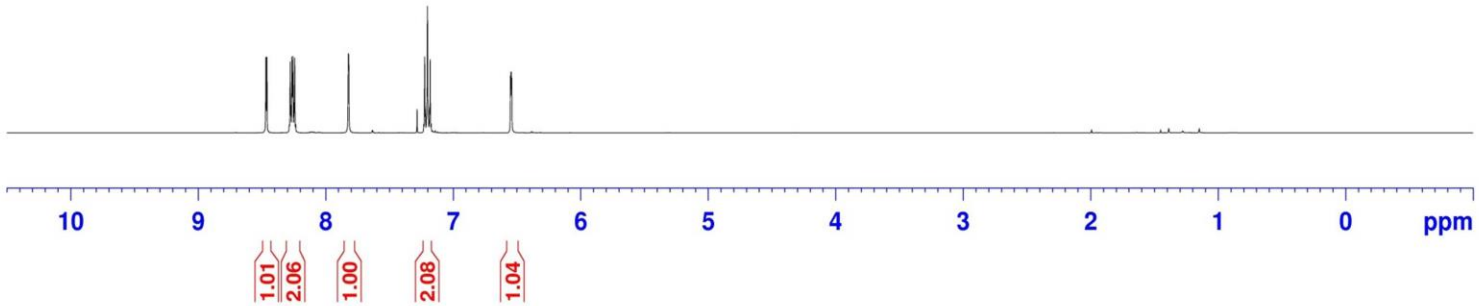




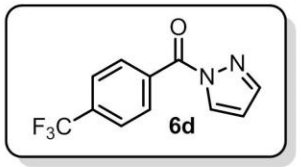
(4–fluorophenyl)(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3

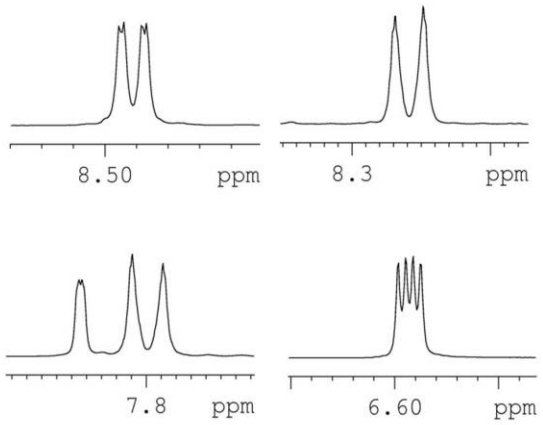


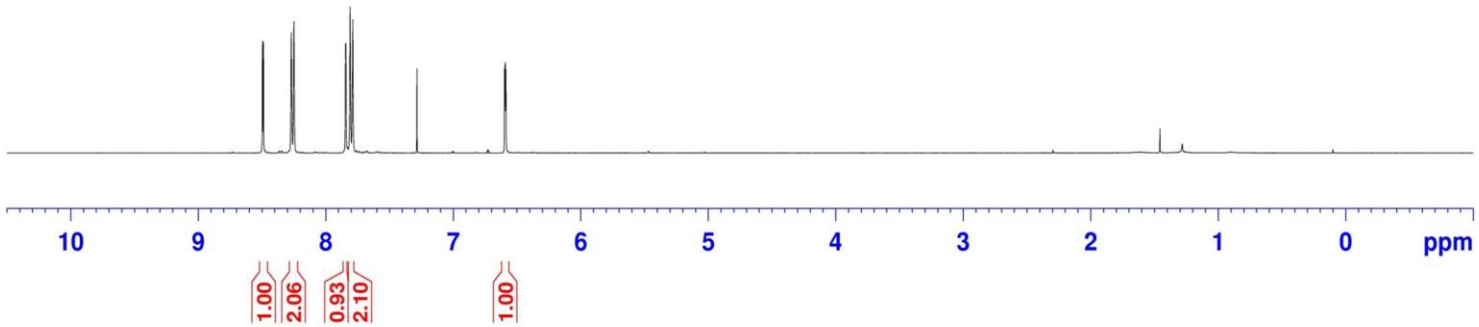




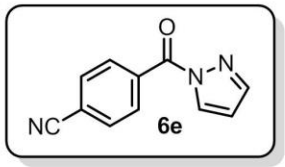
(1H−pyrazol−1−yl)(4−(trifluoromethyl)phenyl)methanone
400 MHz, CDCl3

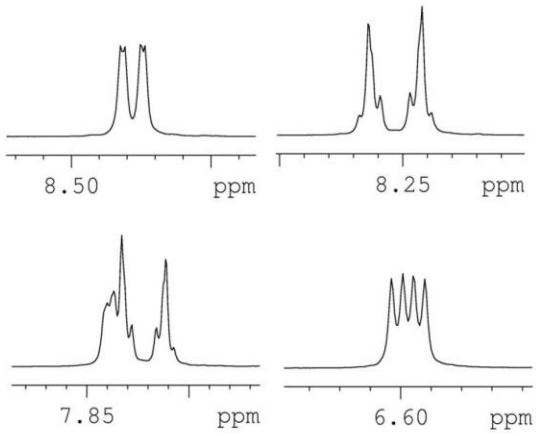


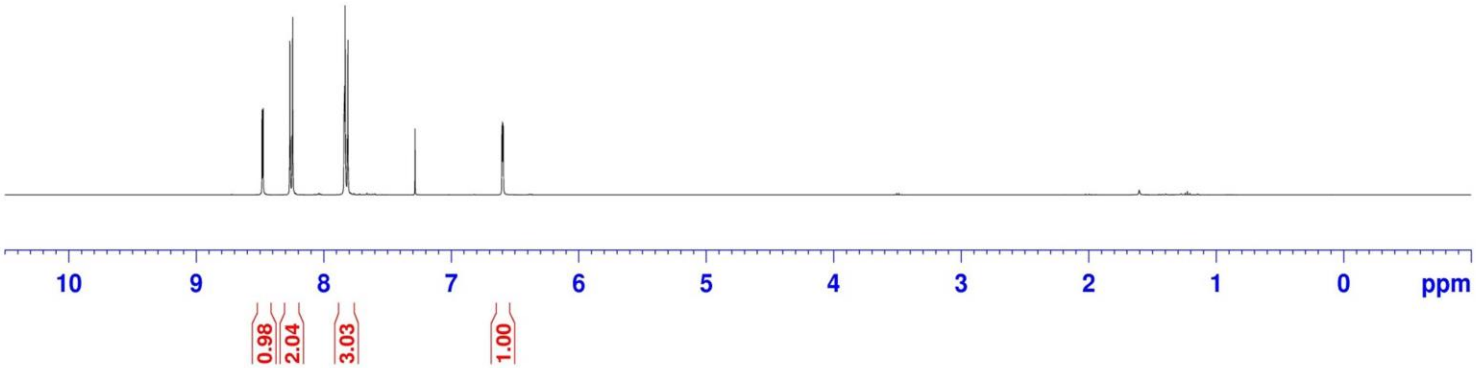




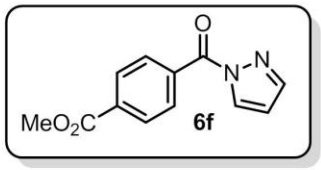
4–(1H–pyrazole–1–carbonyl)benzonitrile
400 MHz, CDCl3

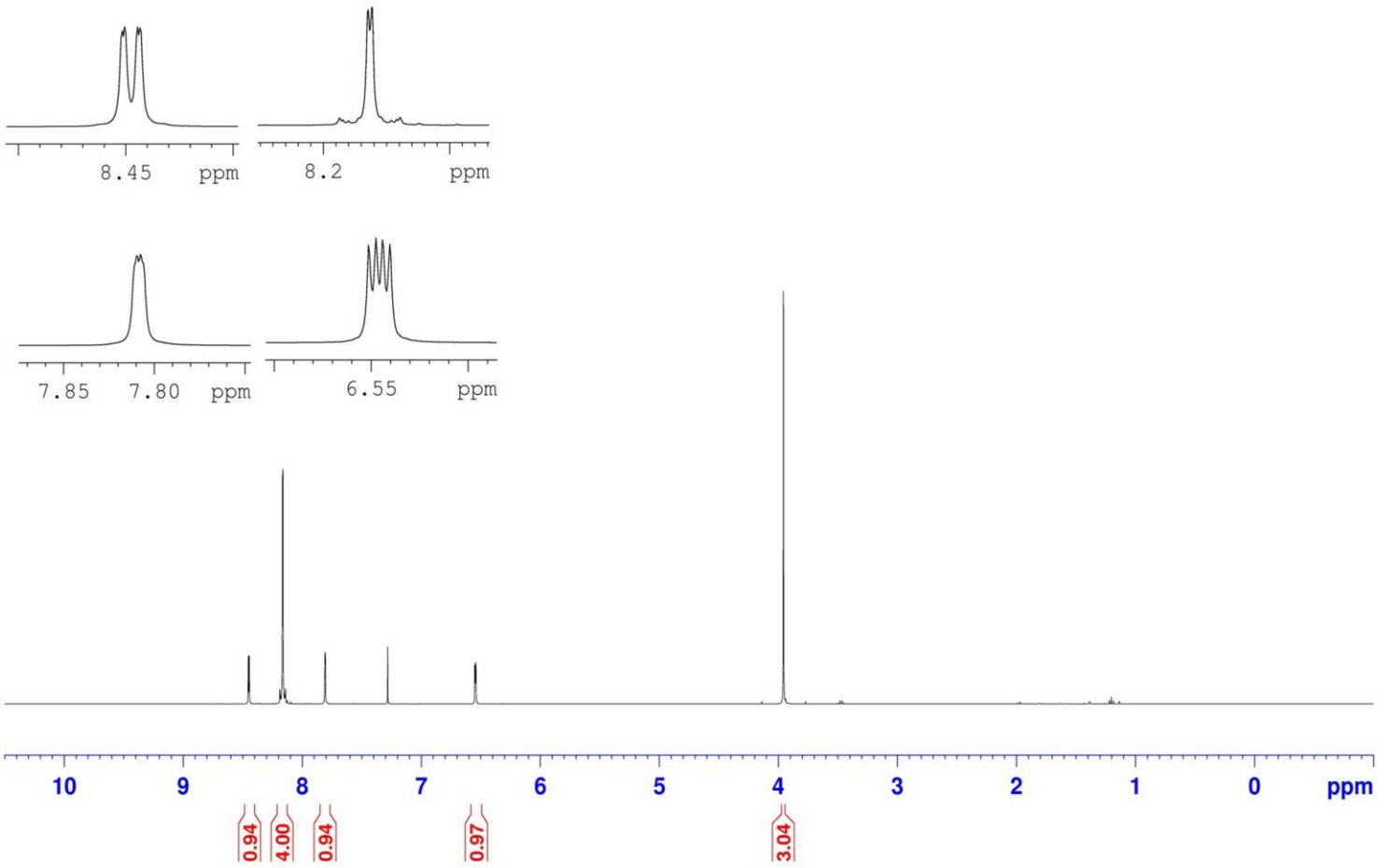




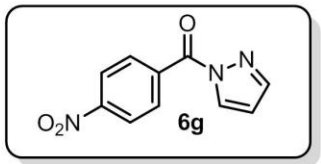


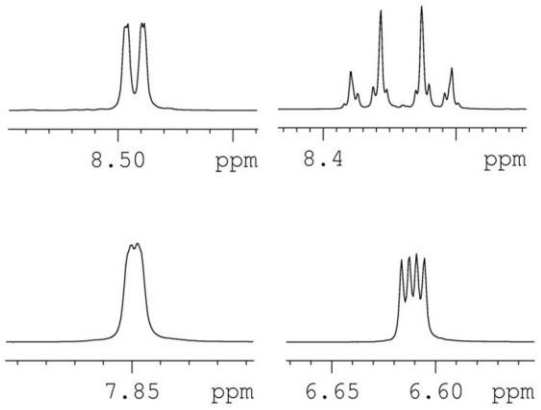
methyl 4–(1H–pyrazole–1–carbonyl)benzoate
400 MHz, CDCl3

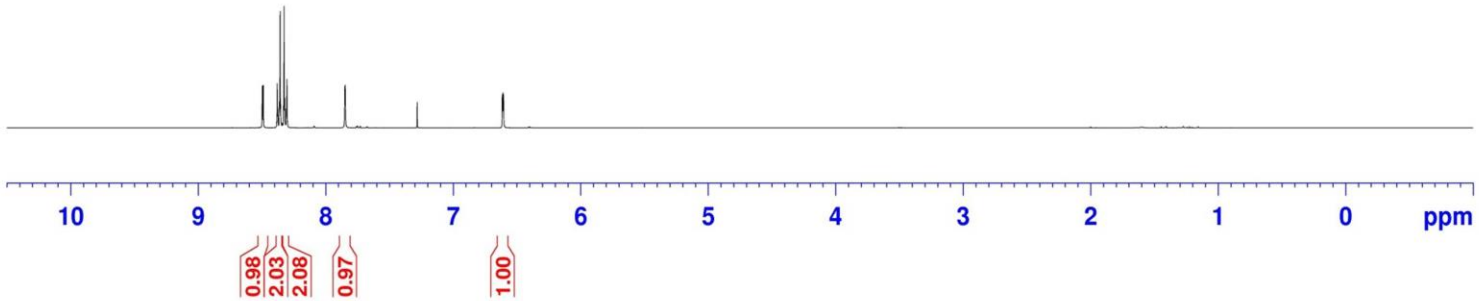




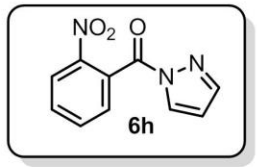
(4–nitrophenyl)(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3

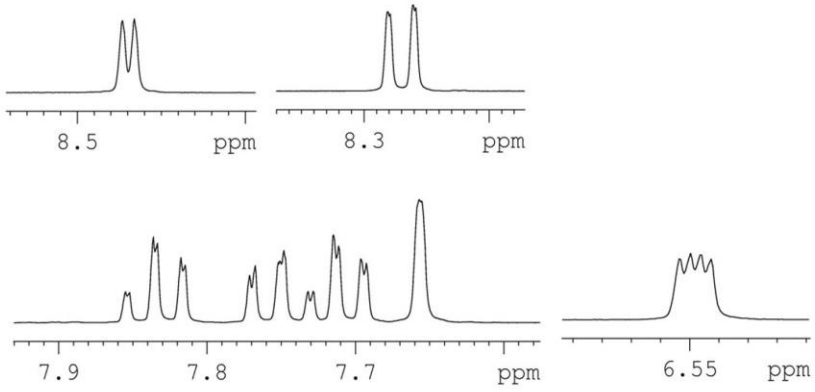


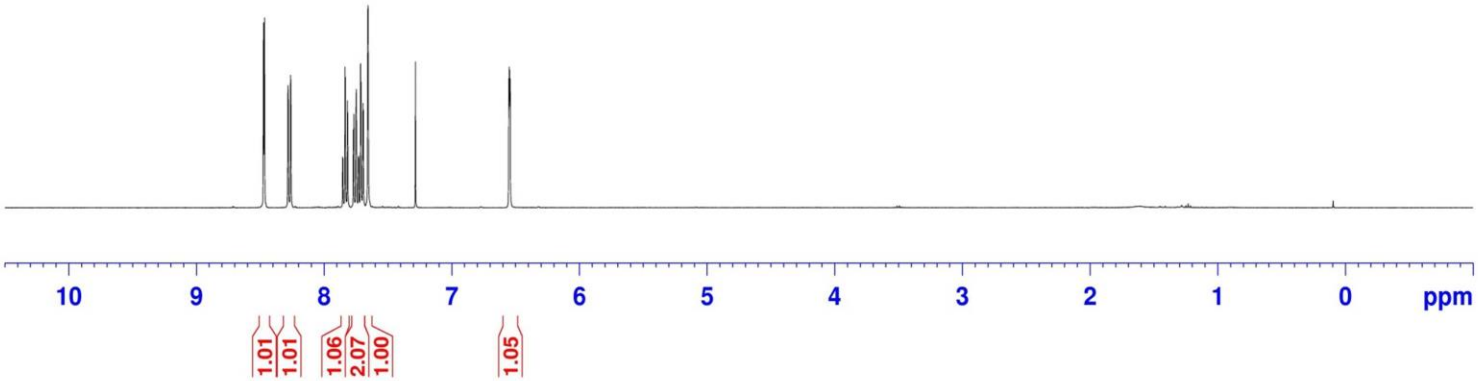




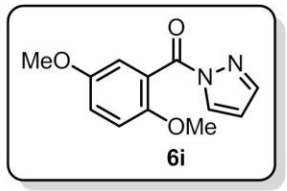
(2–nitrophenyl)(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3







(2,5−dimethoxyphenyl)(1H−pyrazol−1−yl)methanone
400 MHz, CDCl3



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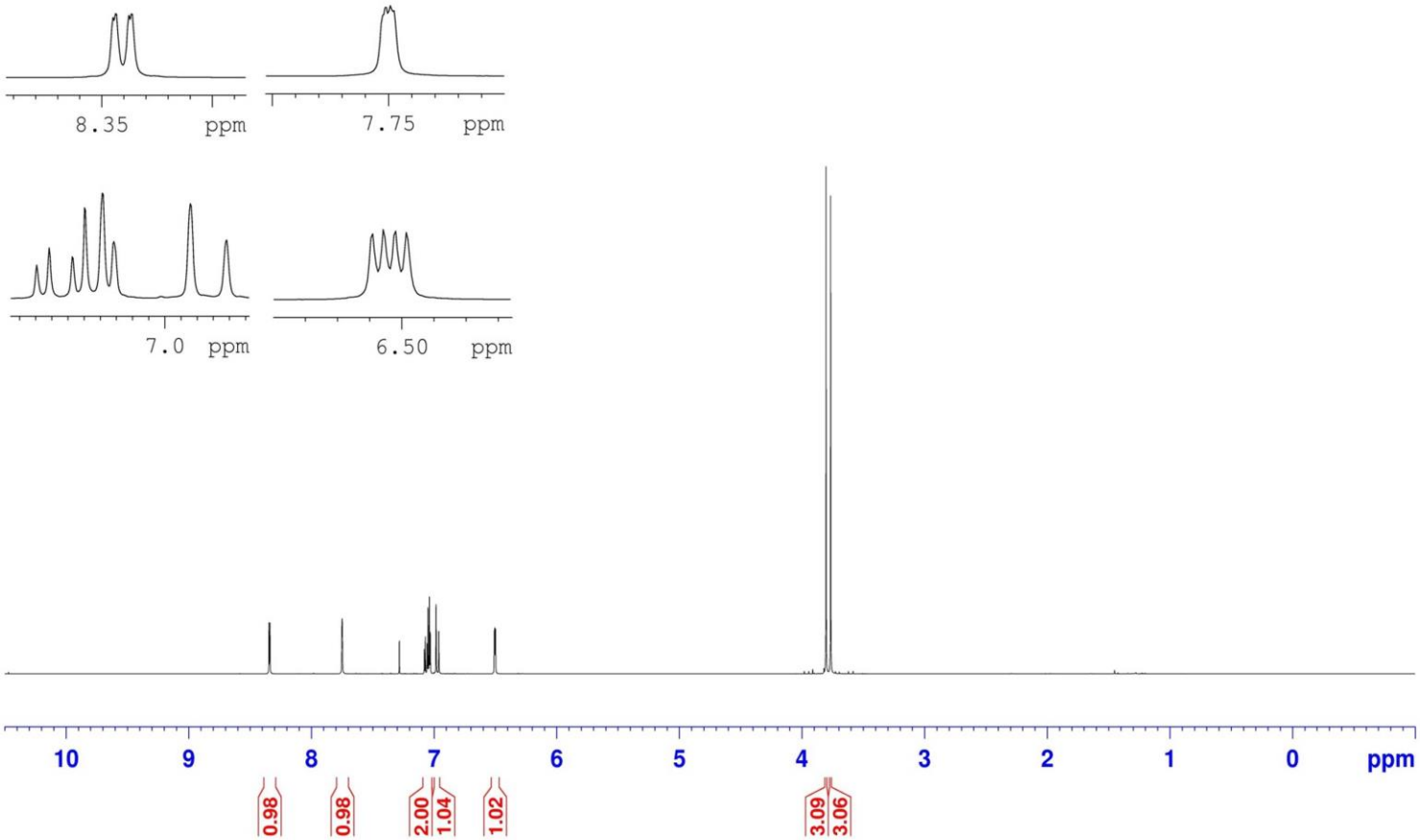
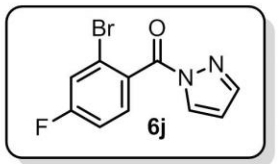
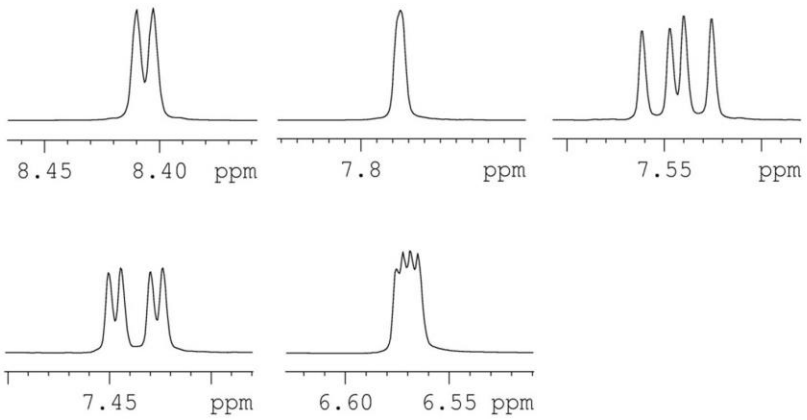
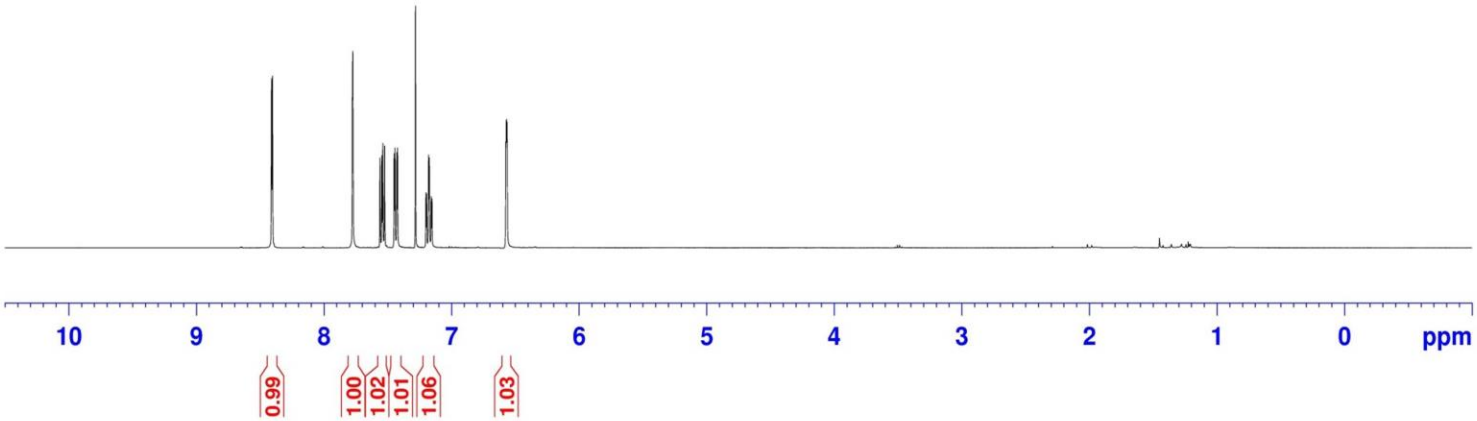


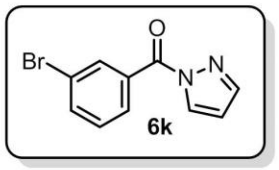
(2−bromo−4−fluorophenyl)(1H−pyrazol−1−yl)methanone
400 MHz, CDCl3

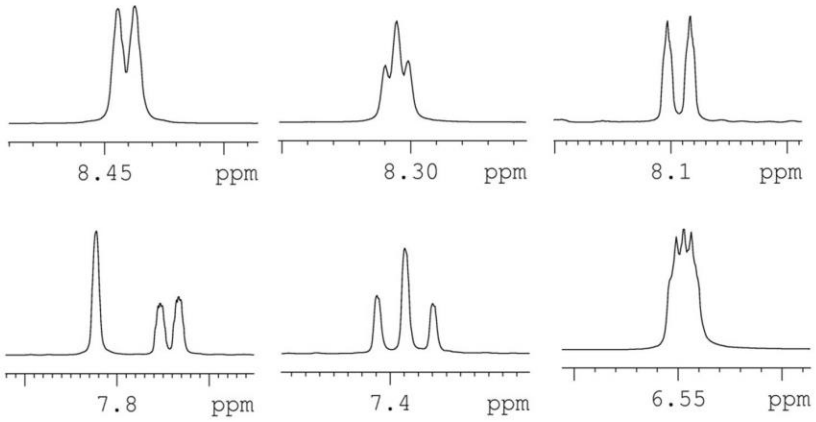


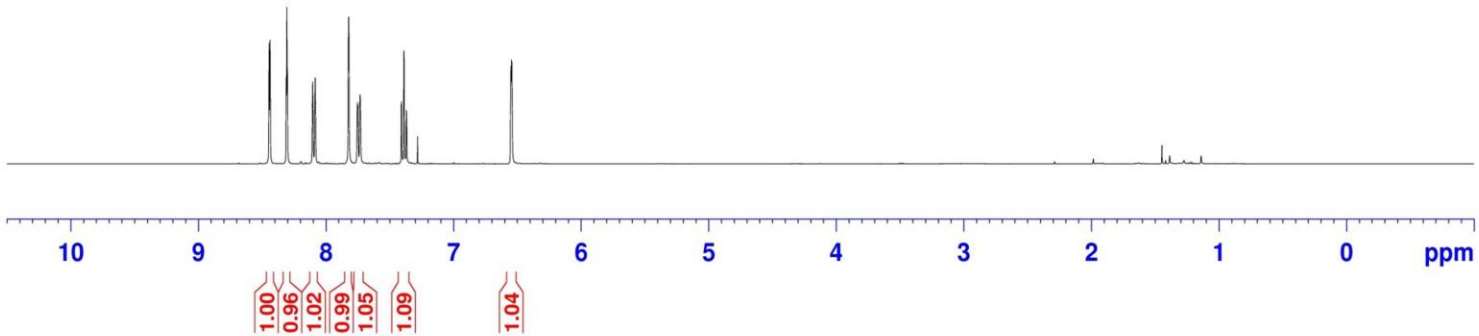




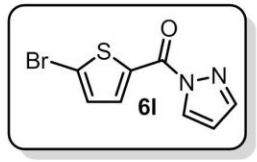
(3–bromophenyl)(1H–pyrazol–1–yl)methanone
300 MHz, CDCl3

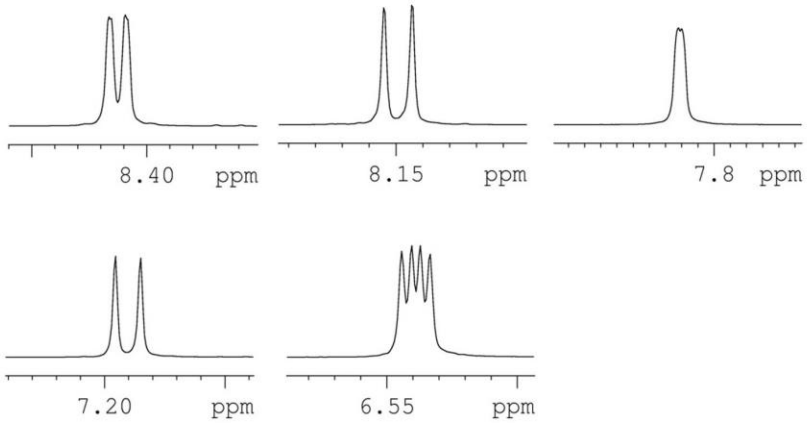


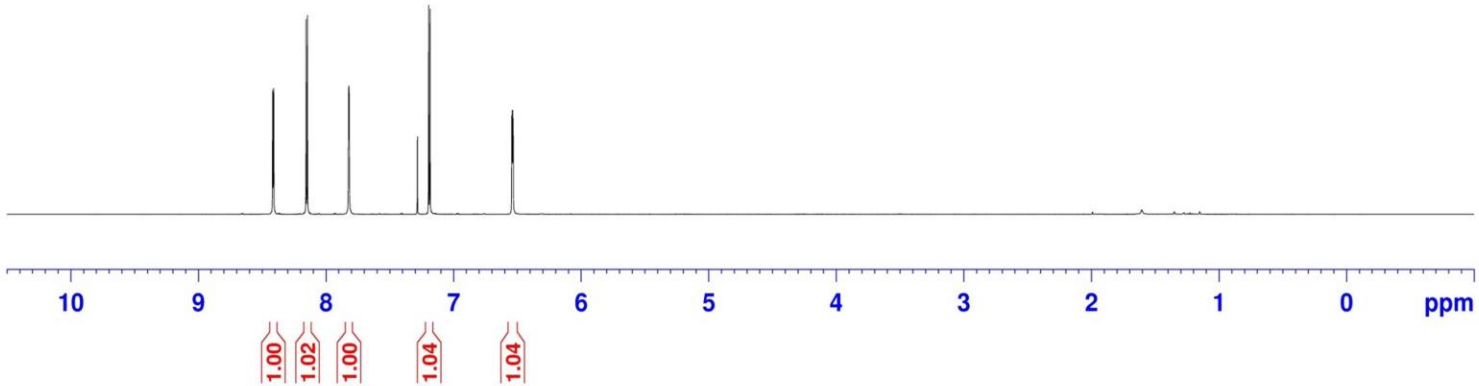




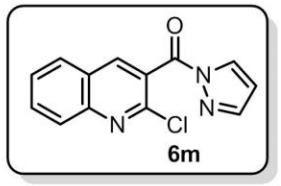
(5–bromothiophen–2–yl)(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3

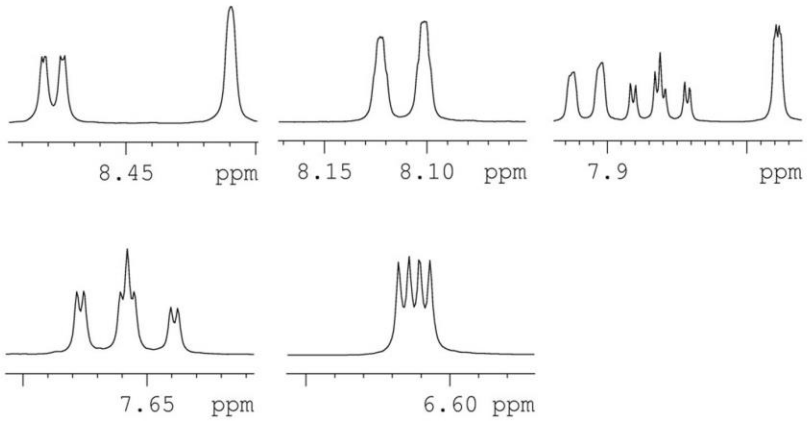


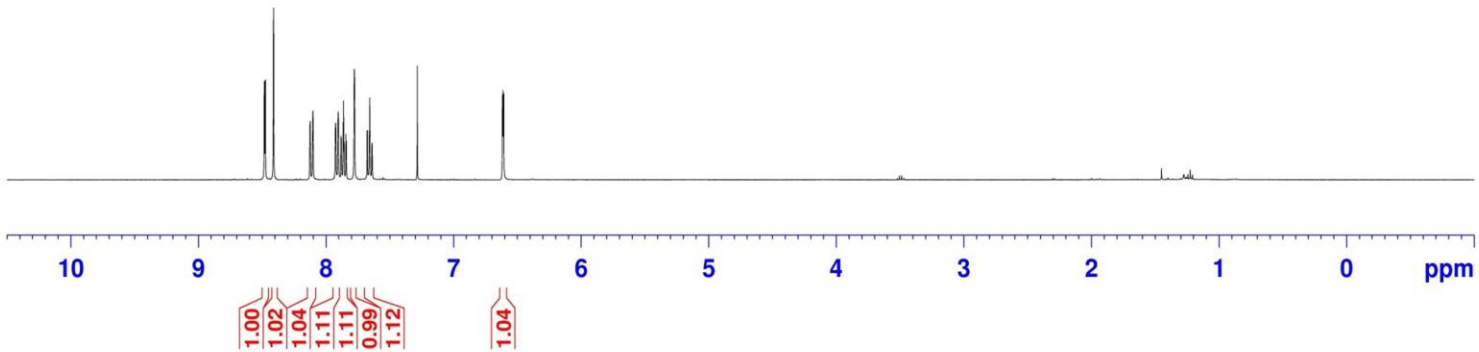




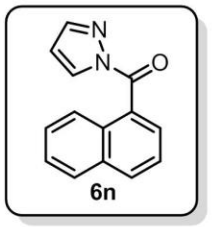
(2−chloroquinolin−3−yl)(1H−pyrazol−1−yl)methanone
400 MHz, CDCl3

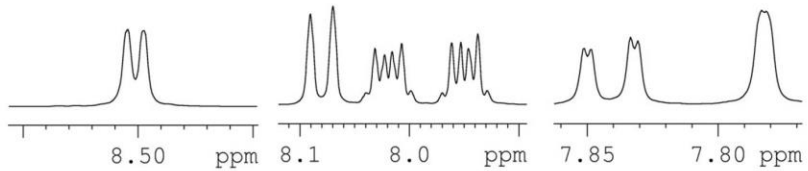


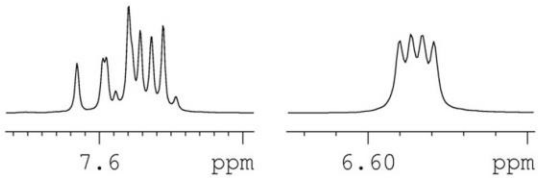


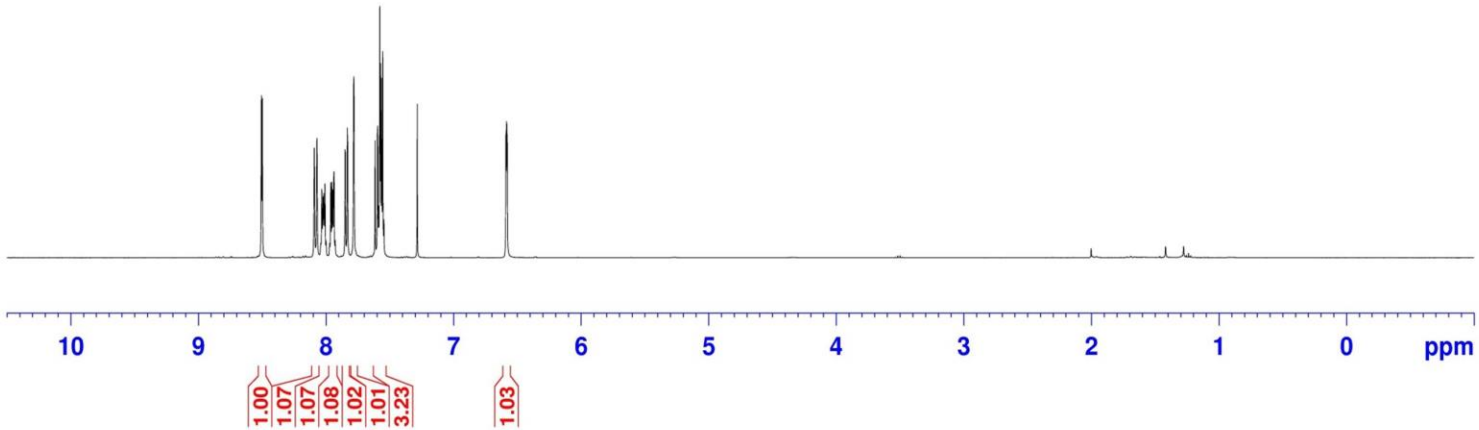


naphthalen−1−yl(1H−pyrazol−1−yl)methanone
400 MHz, CDCl3

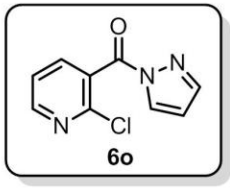




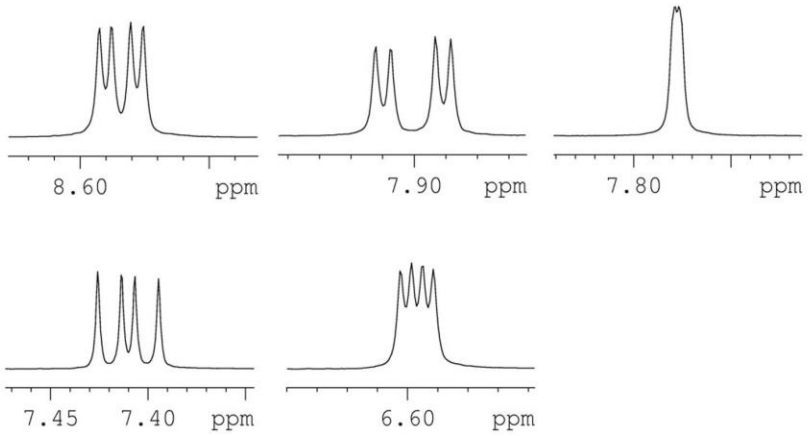


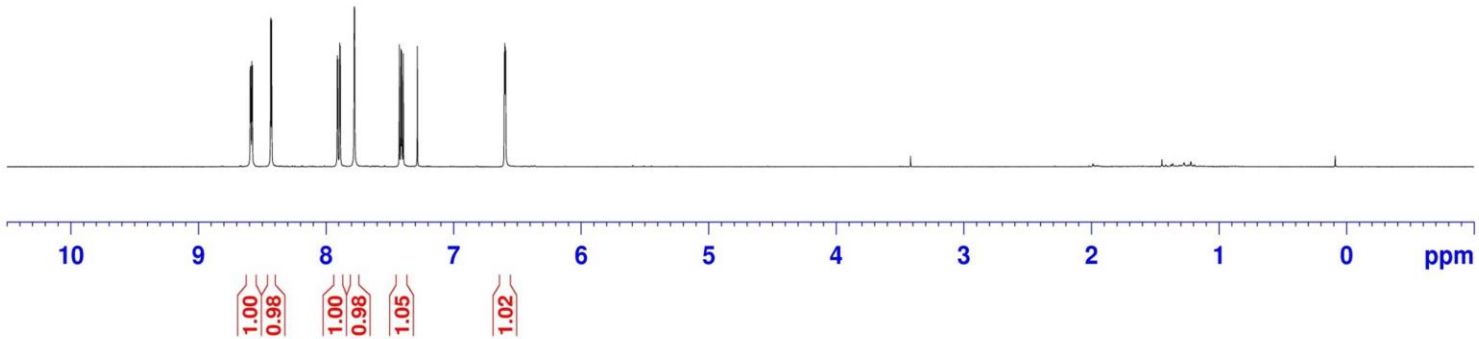


(2−chloropyridin−3−yl)(1H−pyrazol−1−yl)methanone
400 MHz, CDCl3

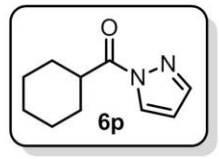


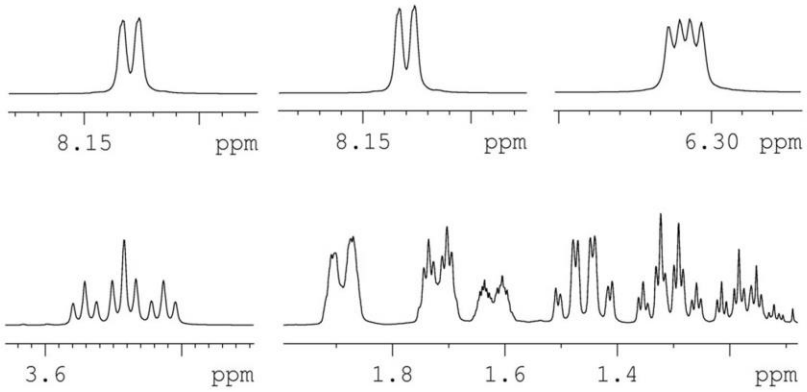
6o

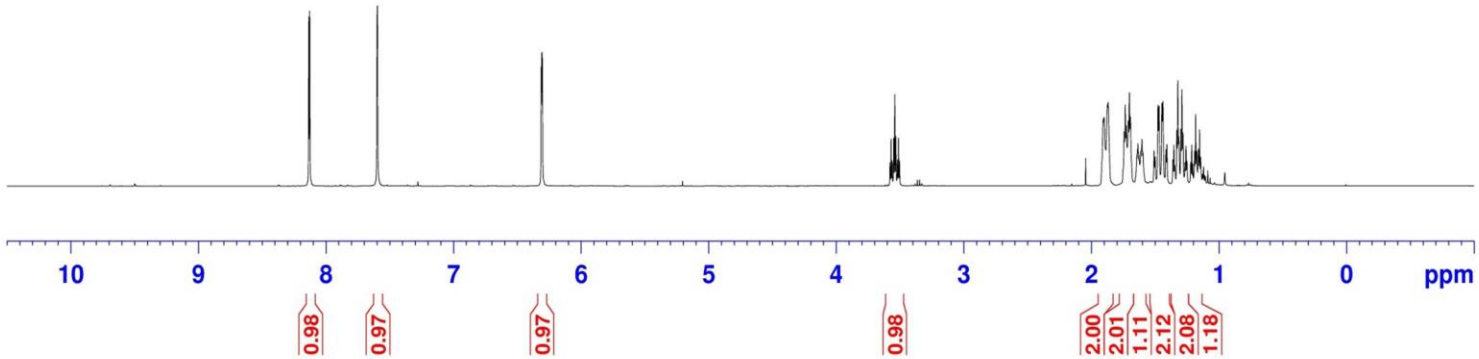




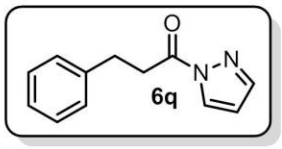
cyclohexyl(1H−pyrazol−1−yl)methanone
400 MHz, CDCl3

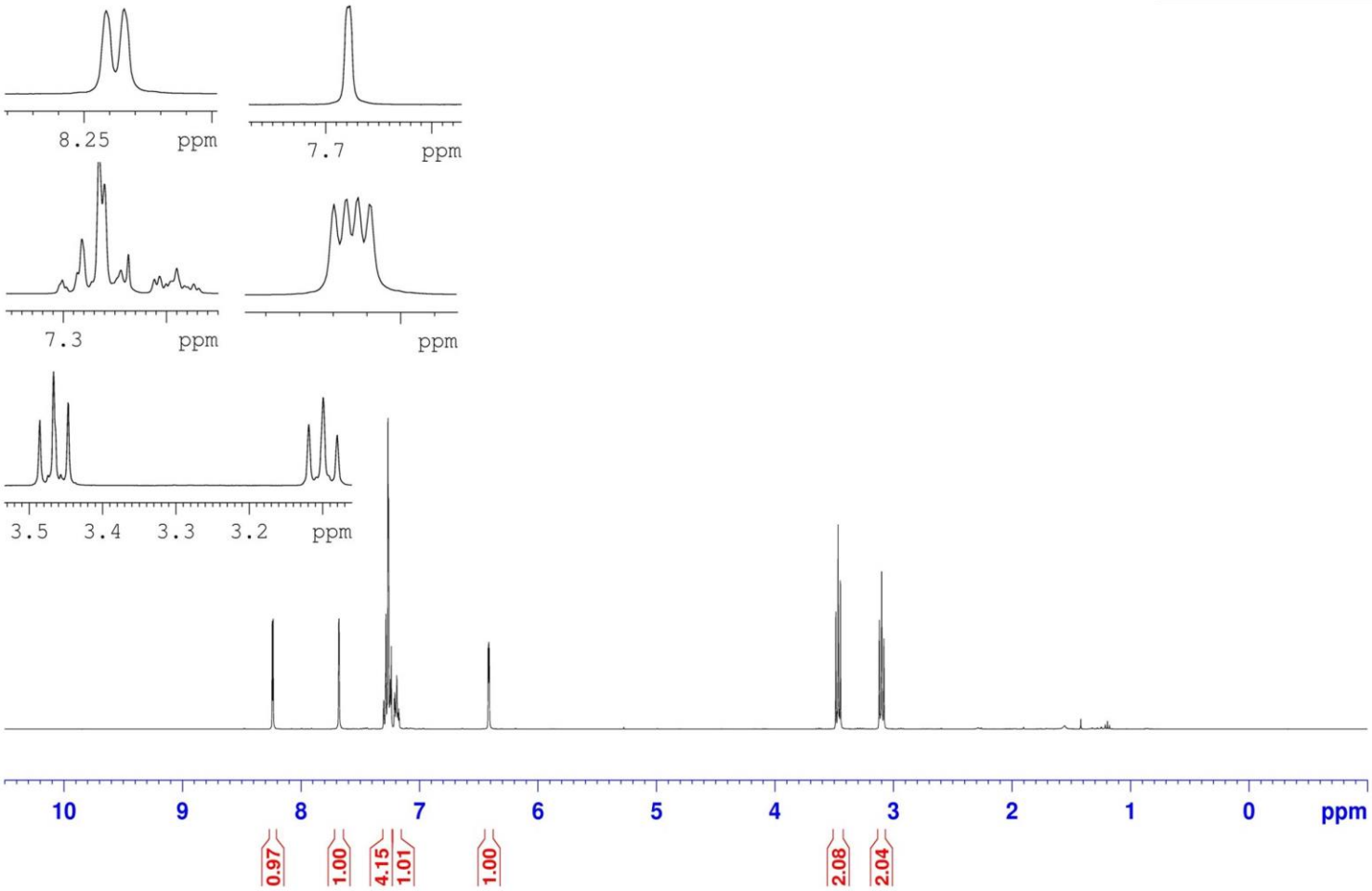




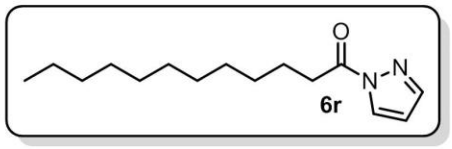


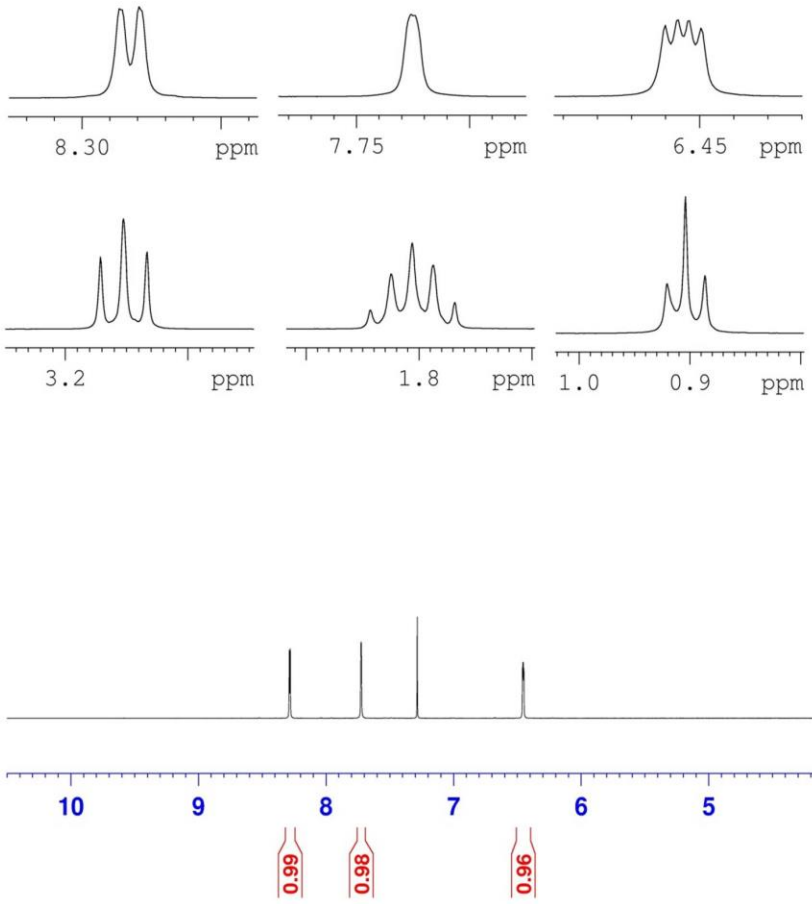
3–phenyl–1–(1H–pyrazol–1–yl)propan–1–one
400 MHz, CDCl3



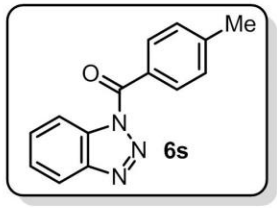


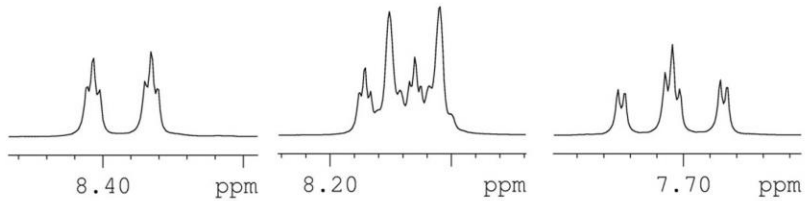
1–(1H–pyrazol–1–yl)dodecan–1–one
400 MHz, CDCl3

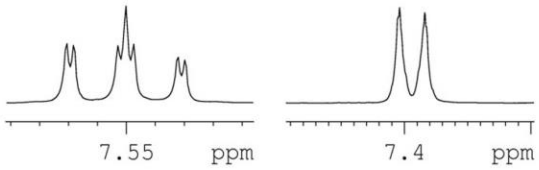




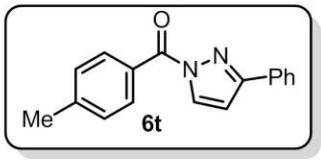
p–toluoyl–1H–1,2,3–benzotriazole
400 MHz, CDCl3

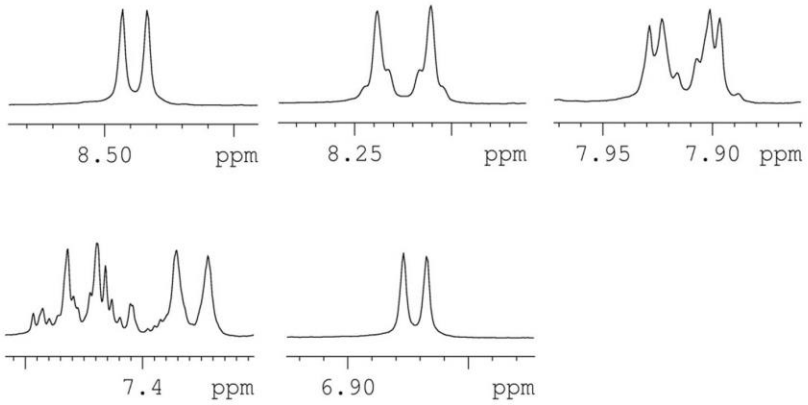


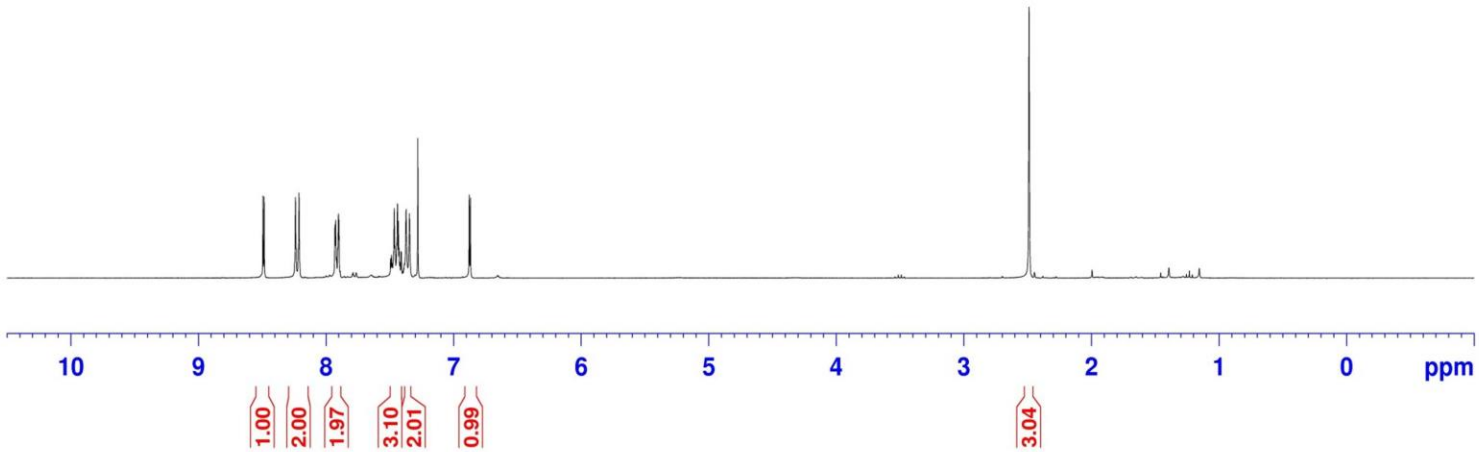




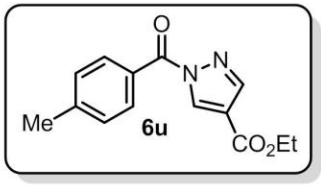
(3−phenyl−1H−pyrazol−1−yl)(p−tolyl)methanone
400 MHz, CDCl3

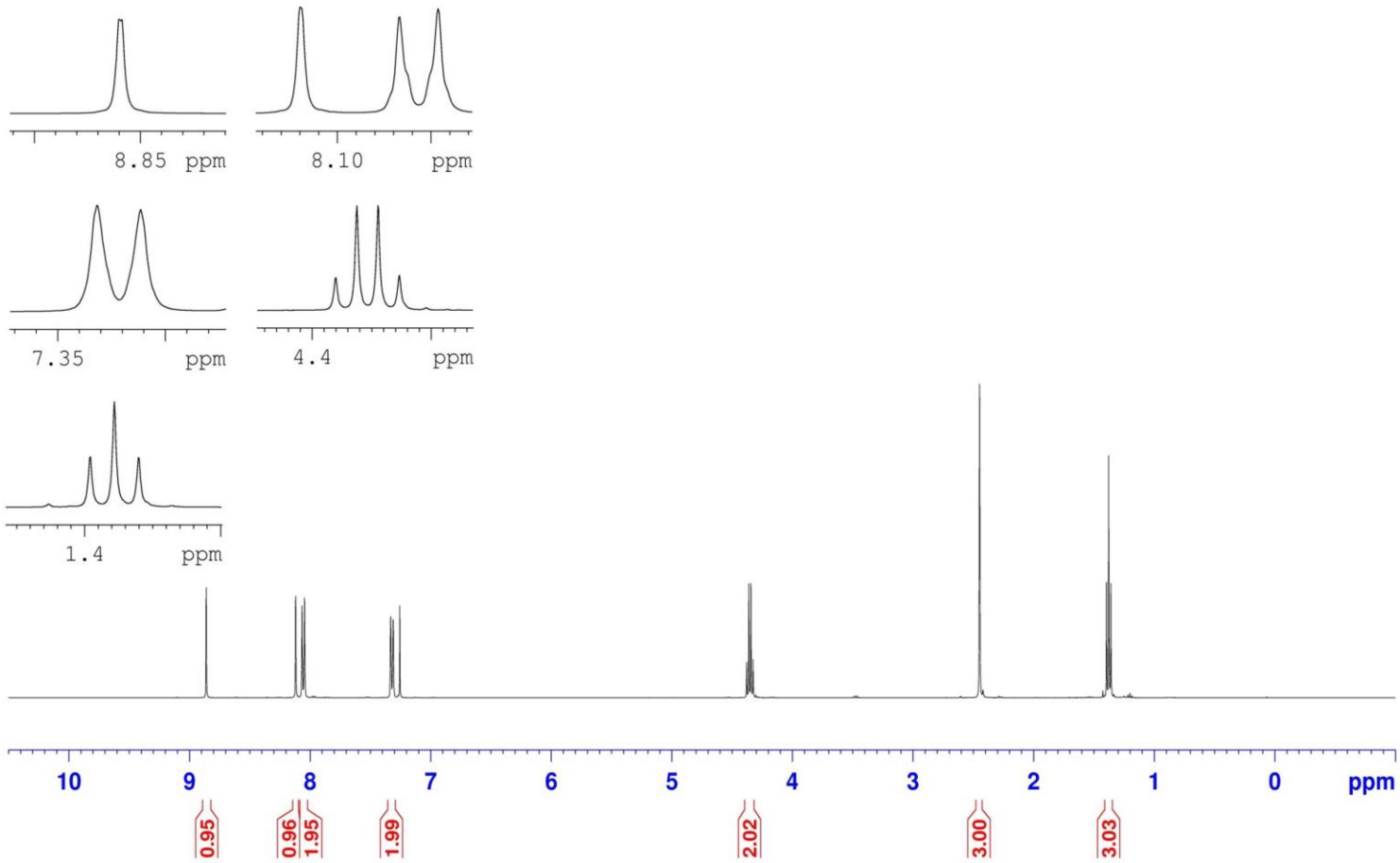




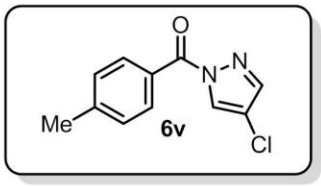


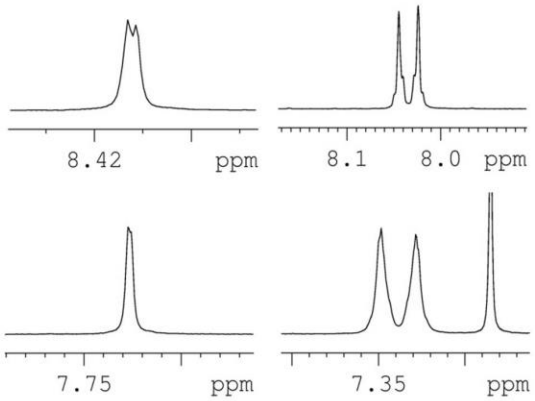
ethyl 1−(4−methylbenzoyl)−1H−pyrazole−4−carboxylate
400 MHz, CDCl3

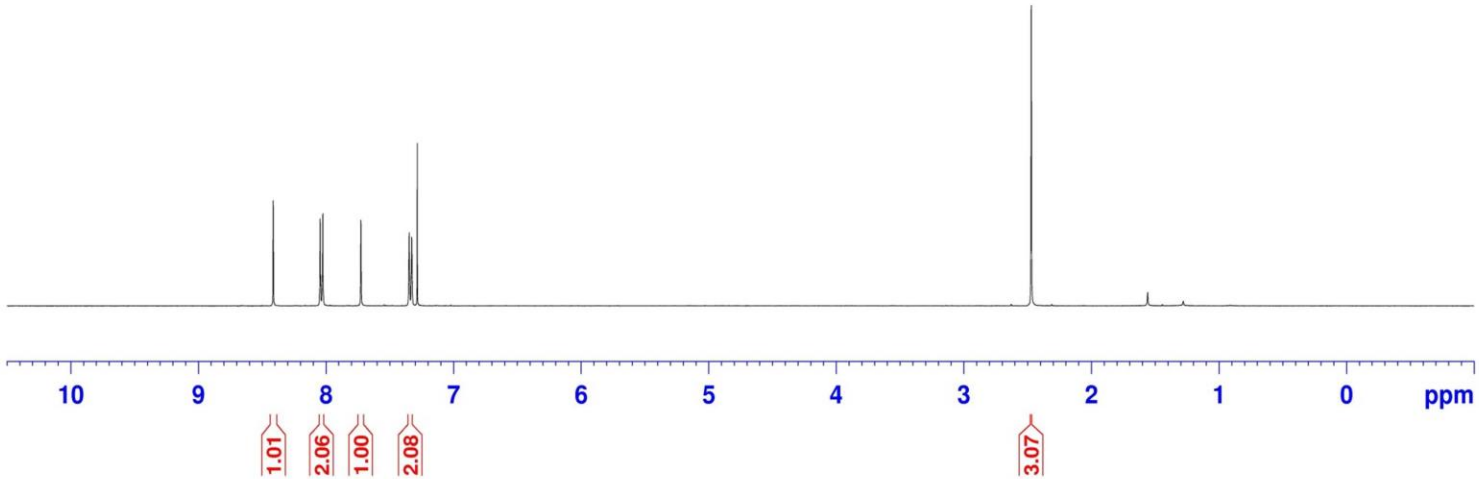




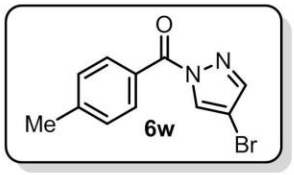
(4–chloro–1H–pyrazol–1–yl)(p–tolyl)methanone
400 MHz, CDCl3

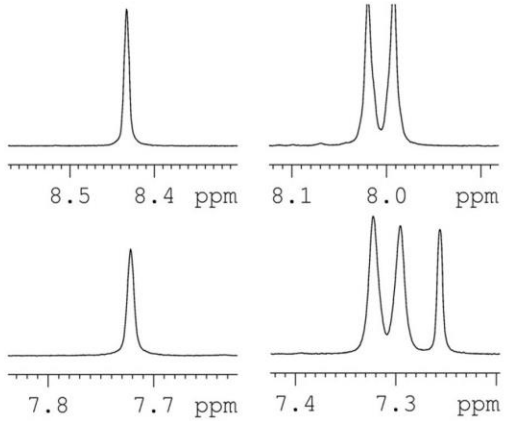


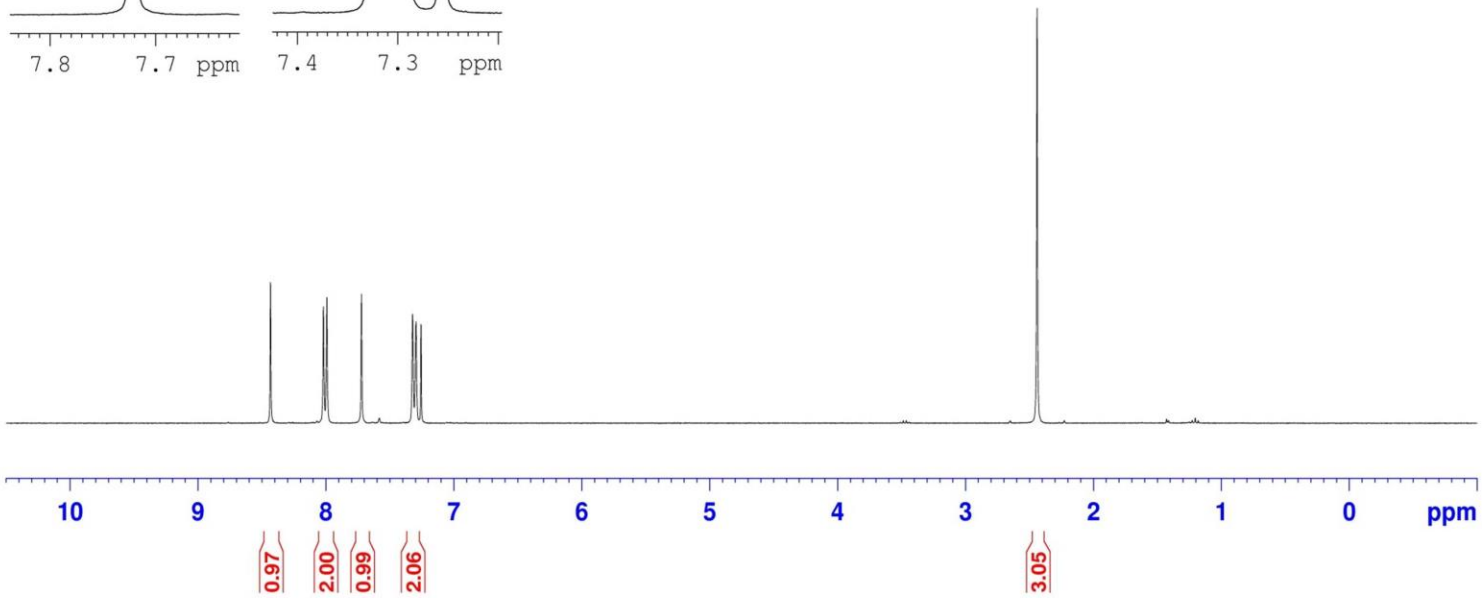




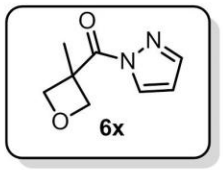
(4−bromo−1H−pyrazol−1−yl)(p−tolyl)methanone
300 MHz, CDCl3

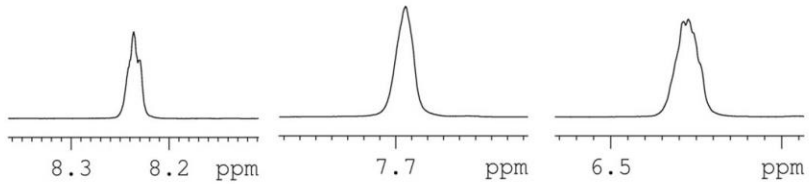


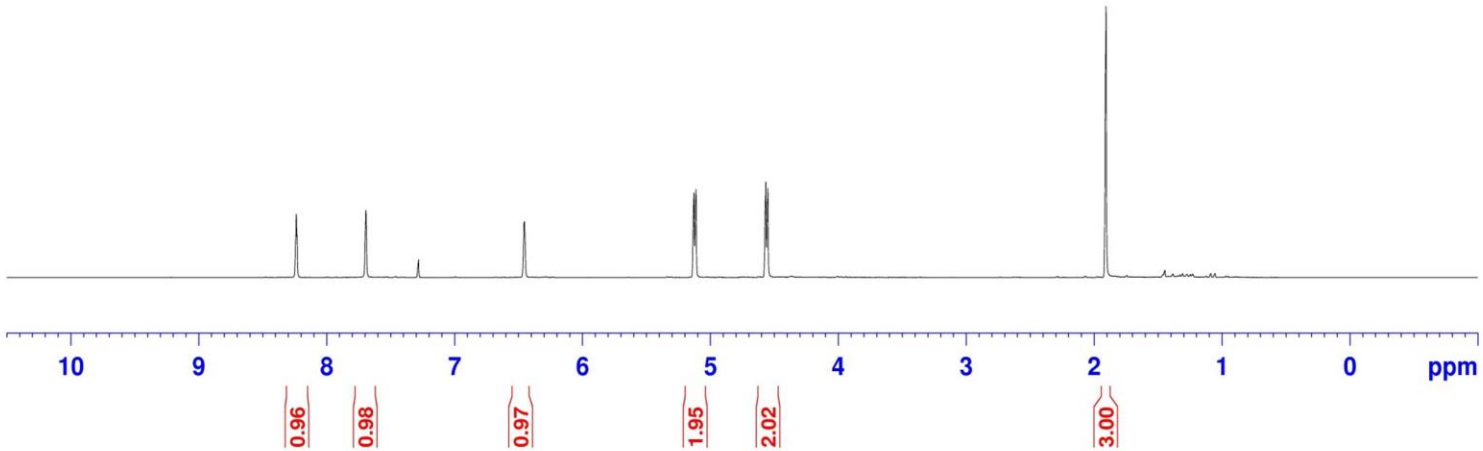




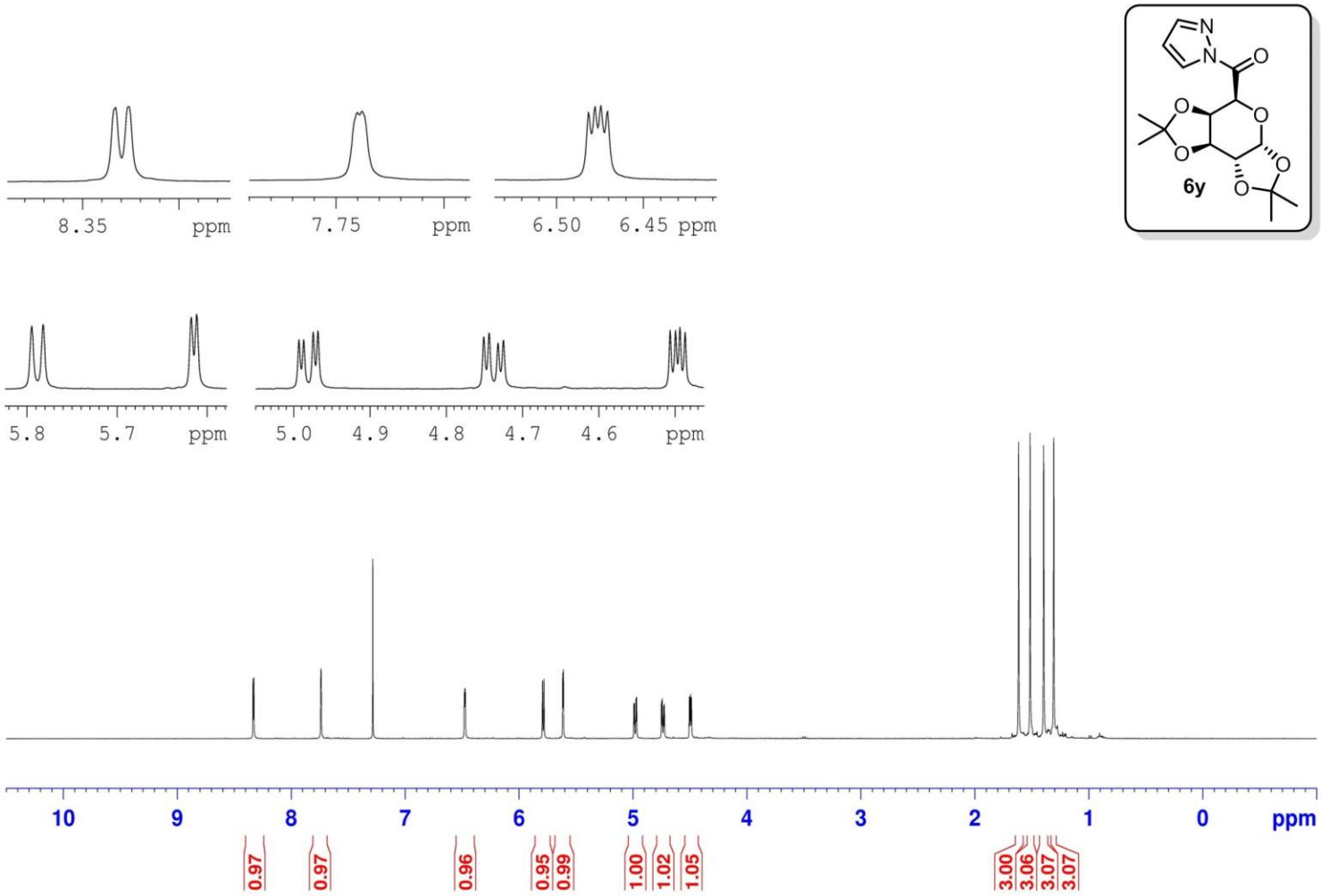
(3–methyloxetan–3–yl)(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3



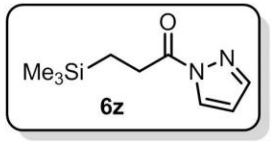


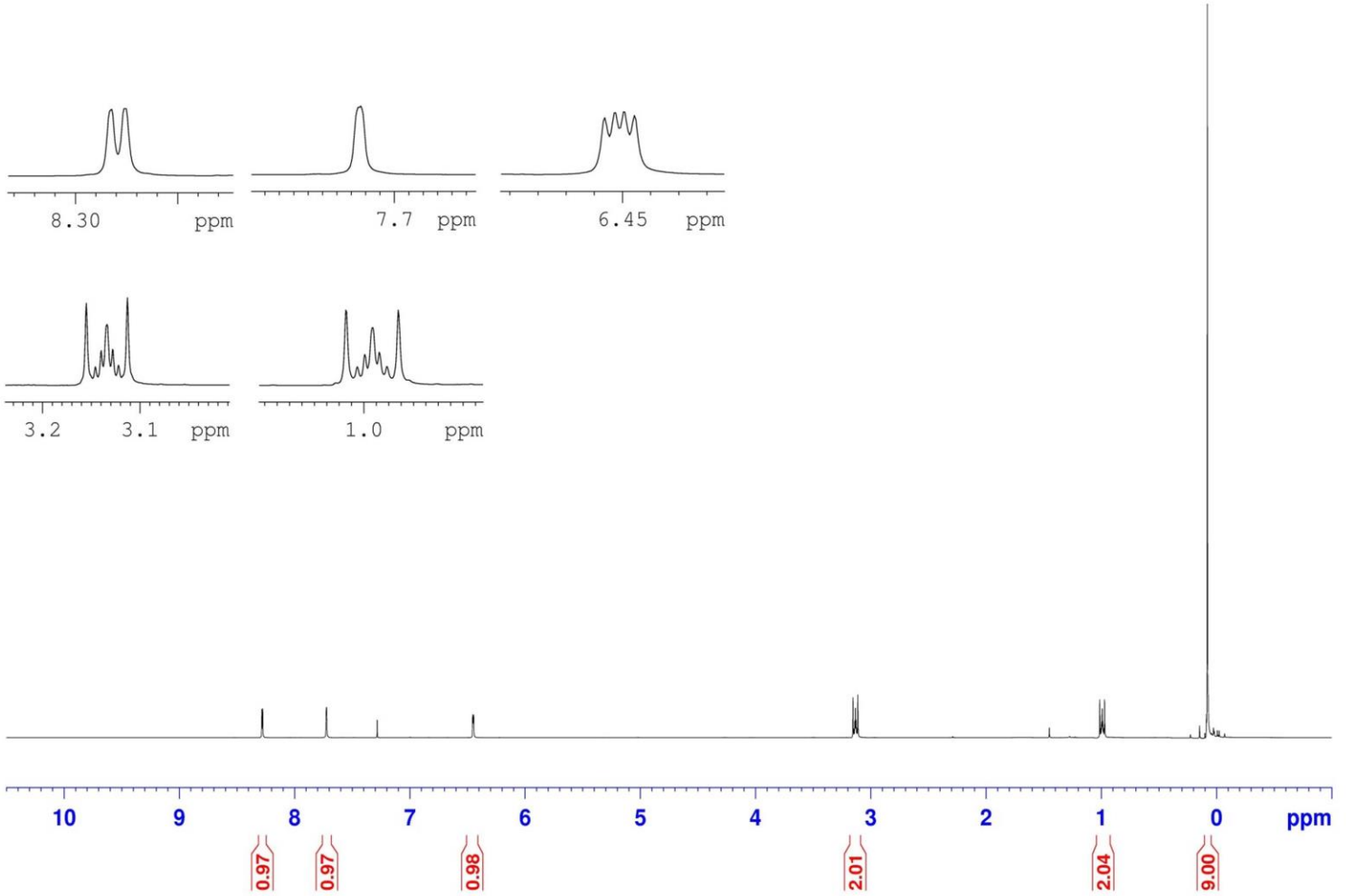


(1H−pyrazol−1−yl)((3aR,5S,5aR,8aS,8bR)−2,2,7,7−tetramethyltetrahydro−3aH−bis([1,3]dioxolo)[4,5−b:4',5'−d]pyran−5−yl)methanone
400 MHz, CDCl3

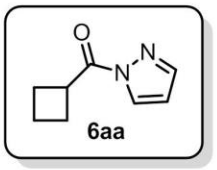


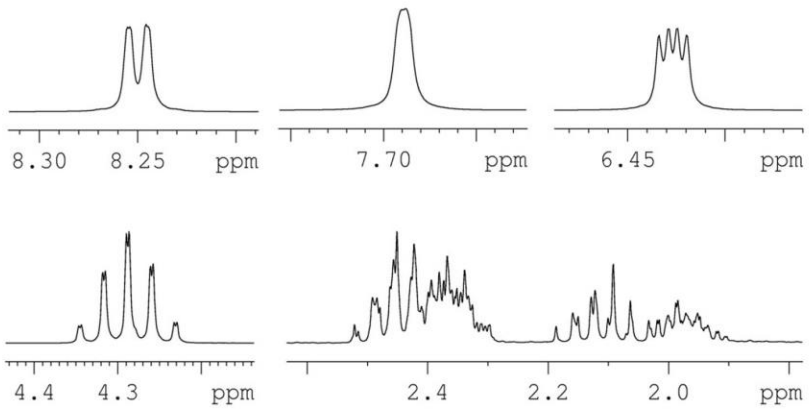
1–(1H–pyrazol–1–yl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3

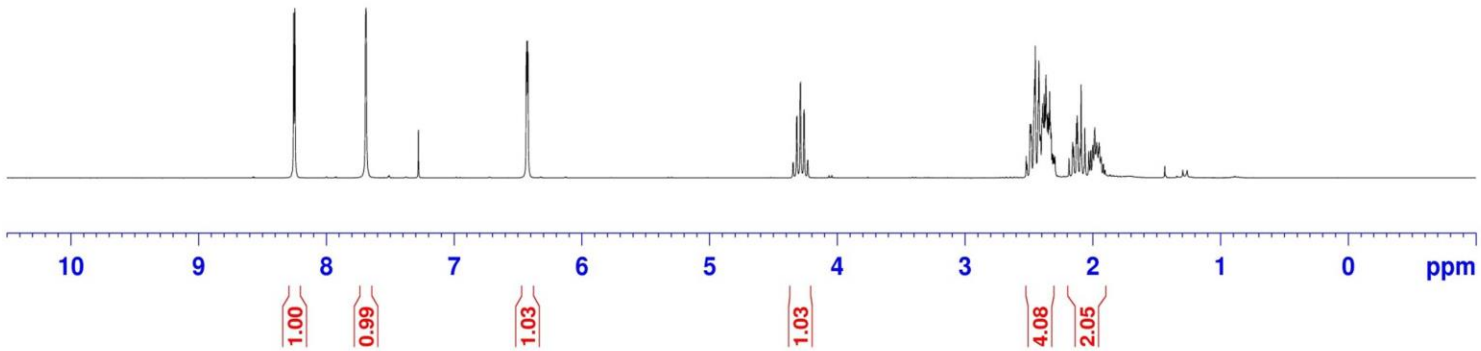




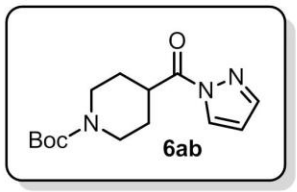
cyclobutyl(1H–pyrazol–1–yl)methanone
400 MHz, CDCl3



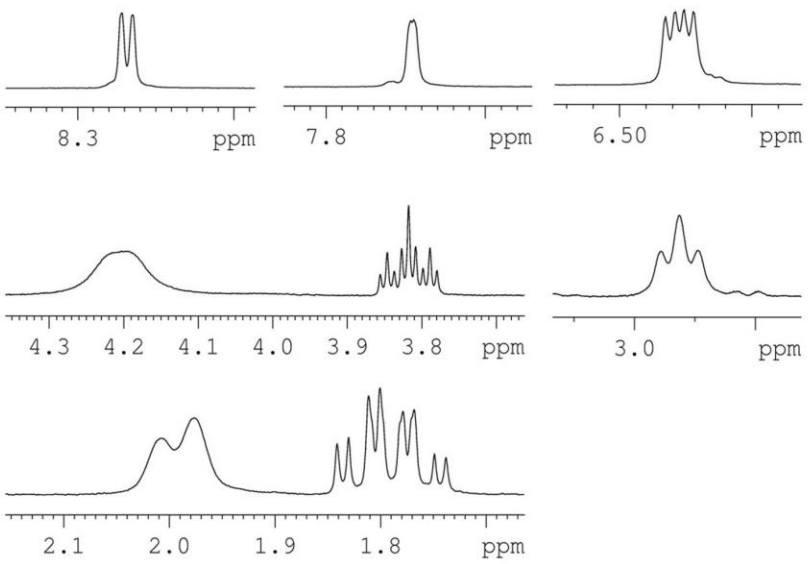


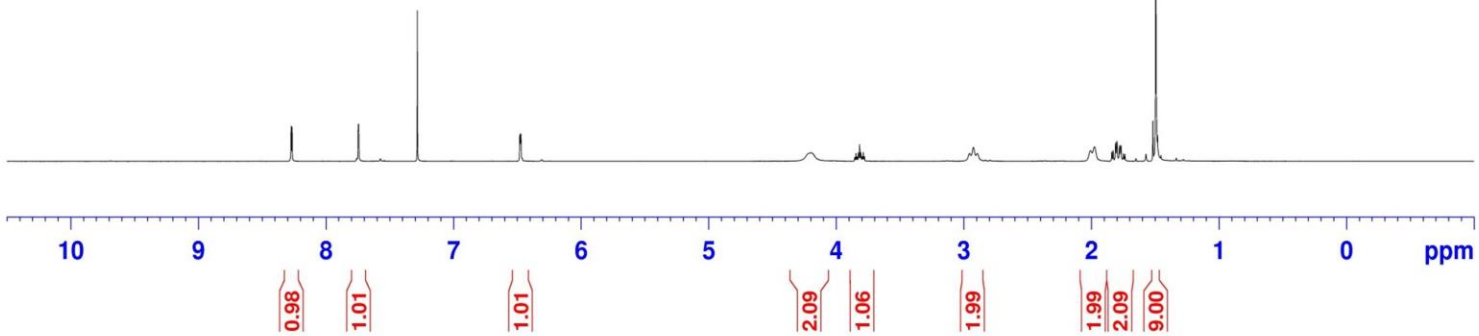


tert-butyl 4-(1H-pyrazole-1-carbonyl)piperidine-1-carboxylate
400 MHz, CDCl3

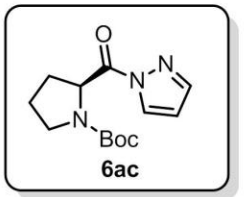


6ab

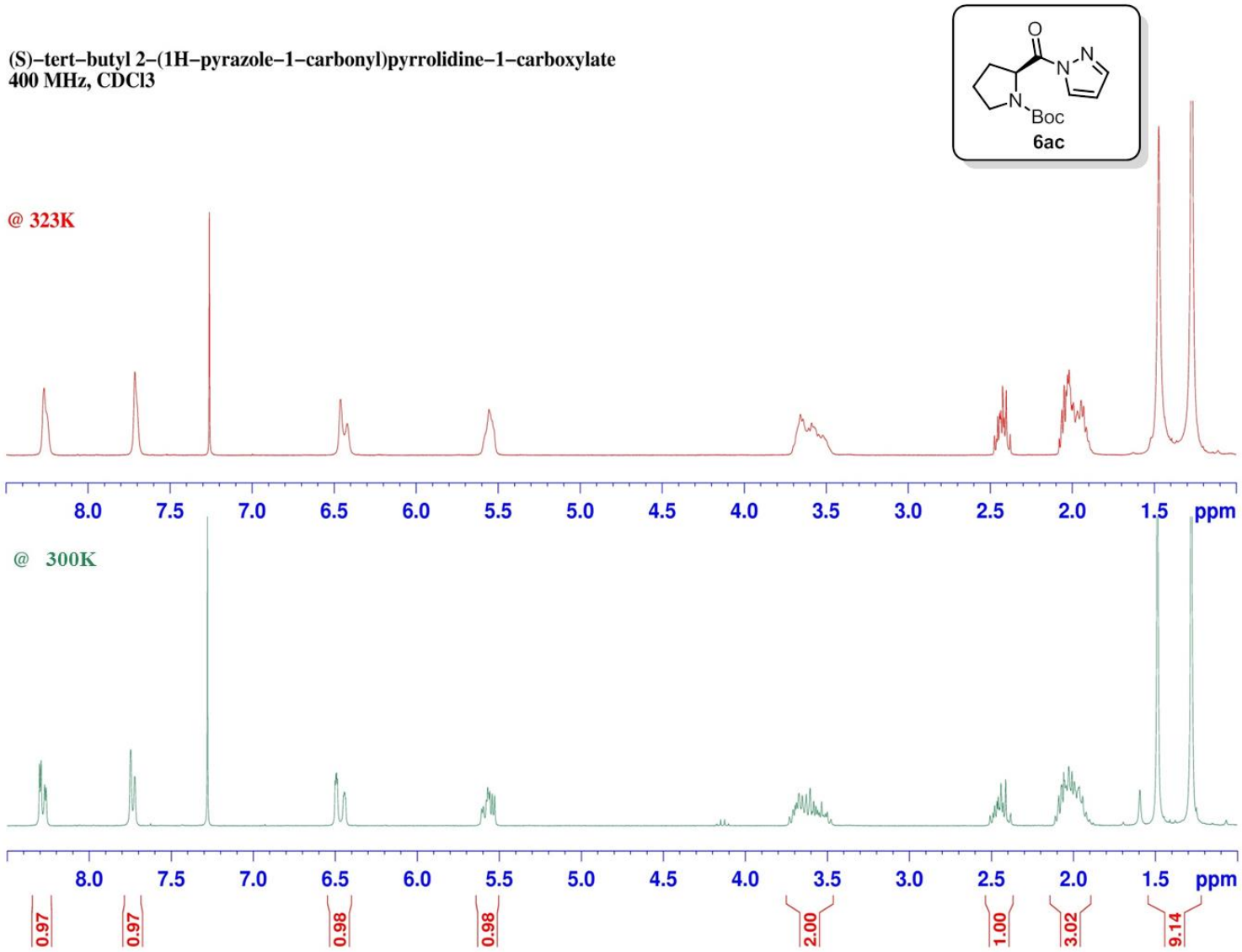




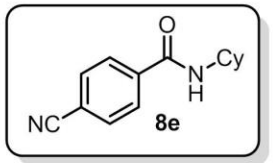
(S)–tert–butyl 2–(1H–pyrazole–1–carbonyl)pyrrolidine–1–carboxylate
400 MHz, CDCl3

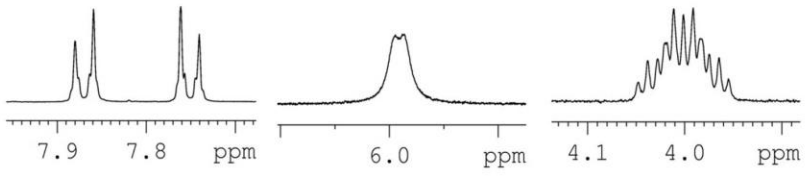


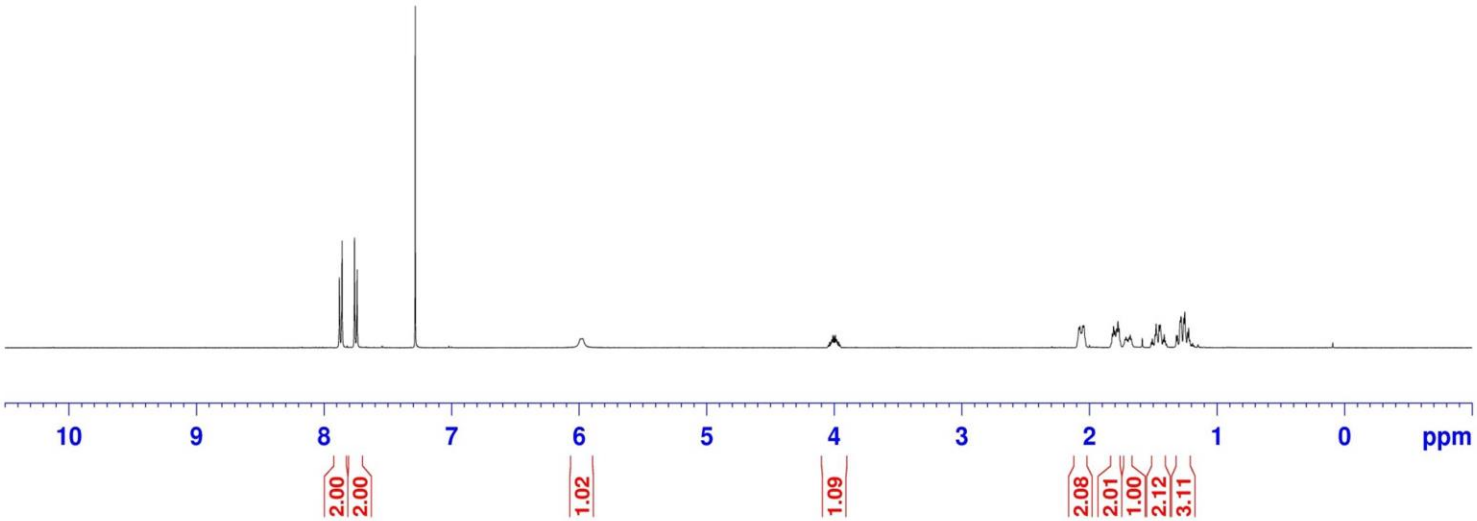
6ac


(S)–tert–butyl 2–(1H–pyrazole–1–carbonyl)pyrrolidine–1–carboxylate
400 MHz, CDCl3
Boc
6ac
@ 323K
@ 300K
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.97
0.97
0.98
0.98
2.00
1.00
3.02
9.14

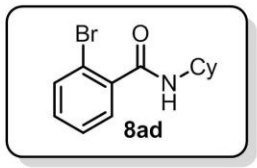
4–cyano–N–cyclohexylbenzamide
400 MHz, CDCl3

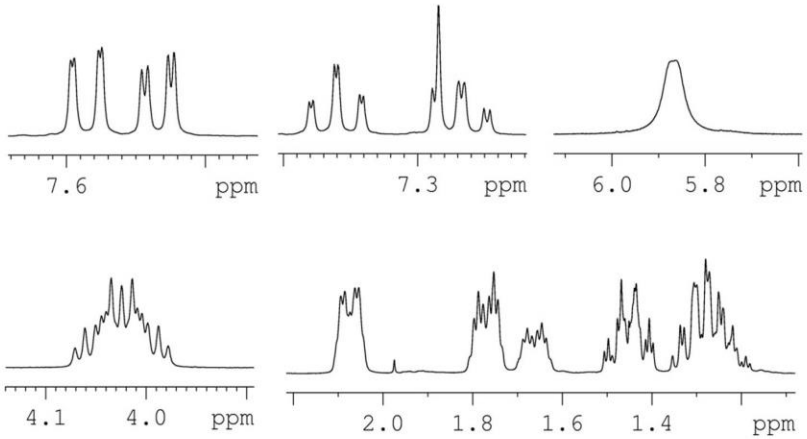


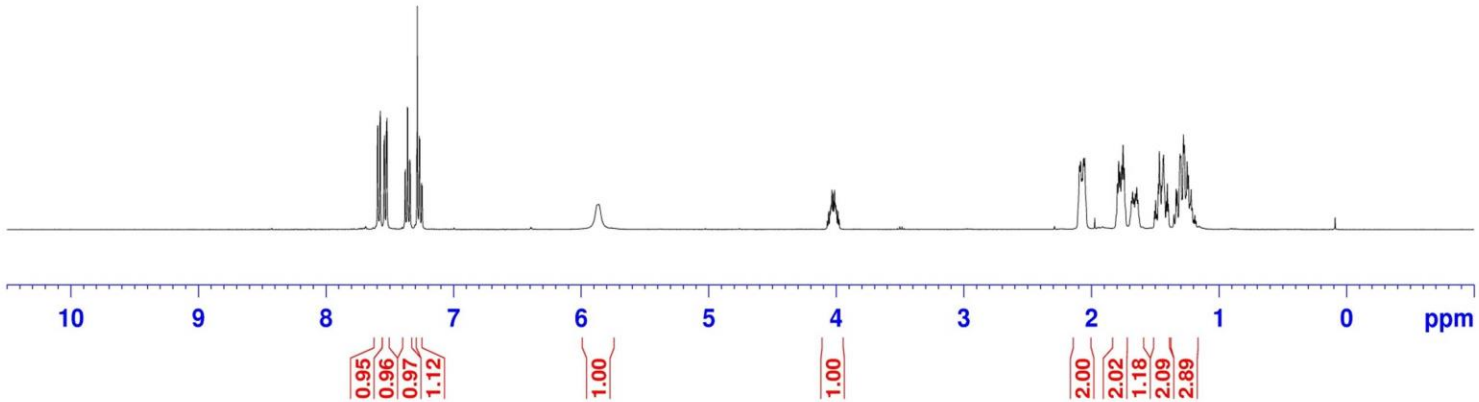




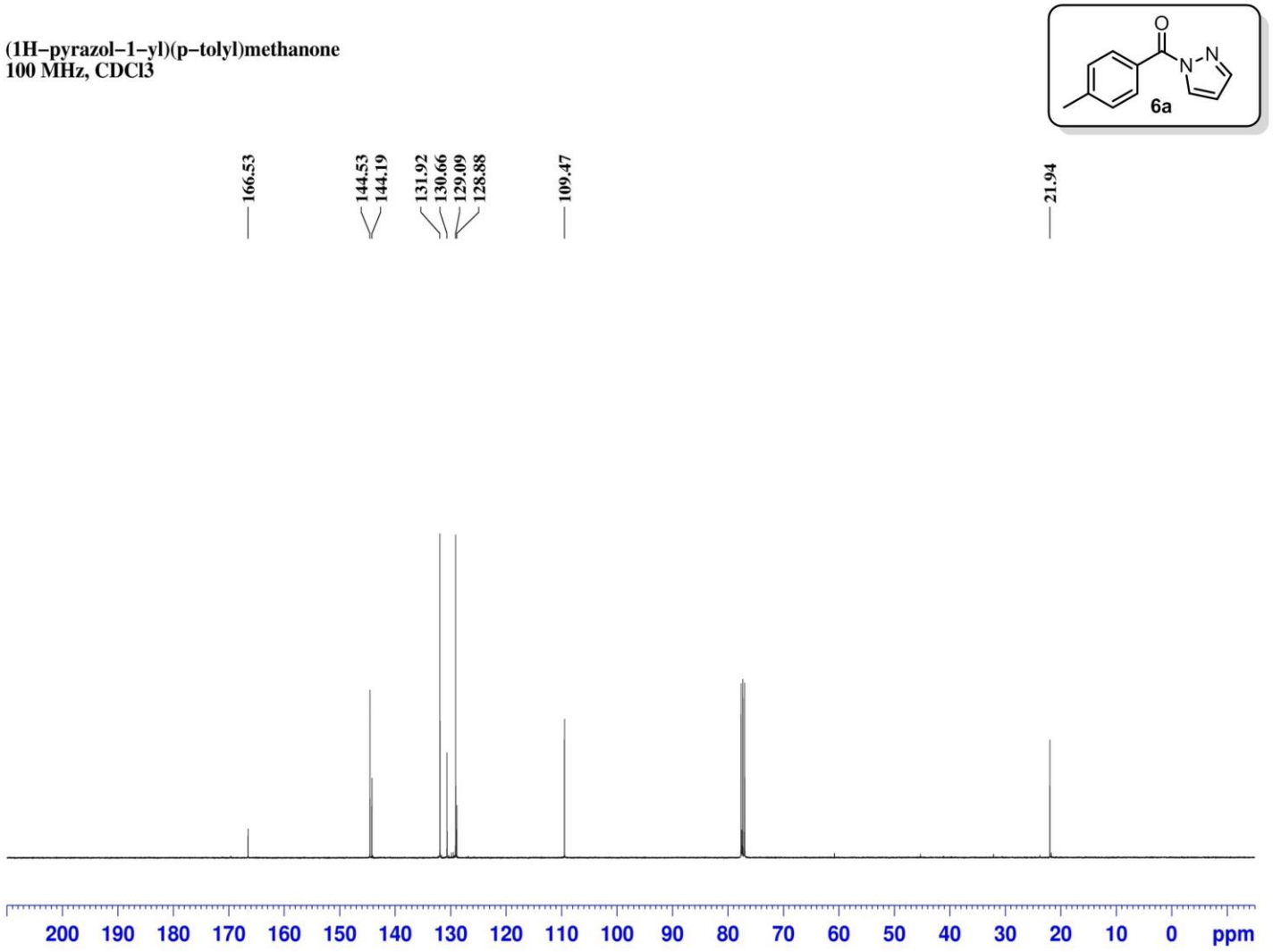
2-bromo-*N*-cyclohexylbenzamide
400 MHz, CDCl3



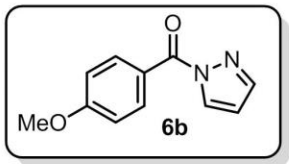


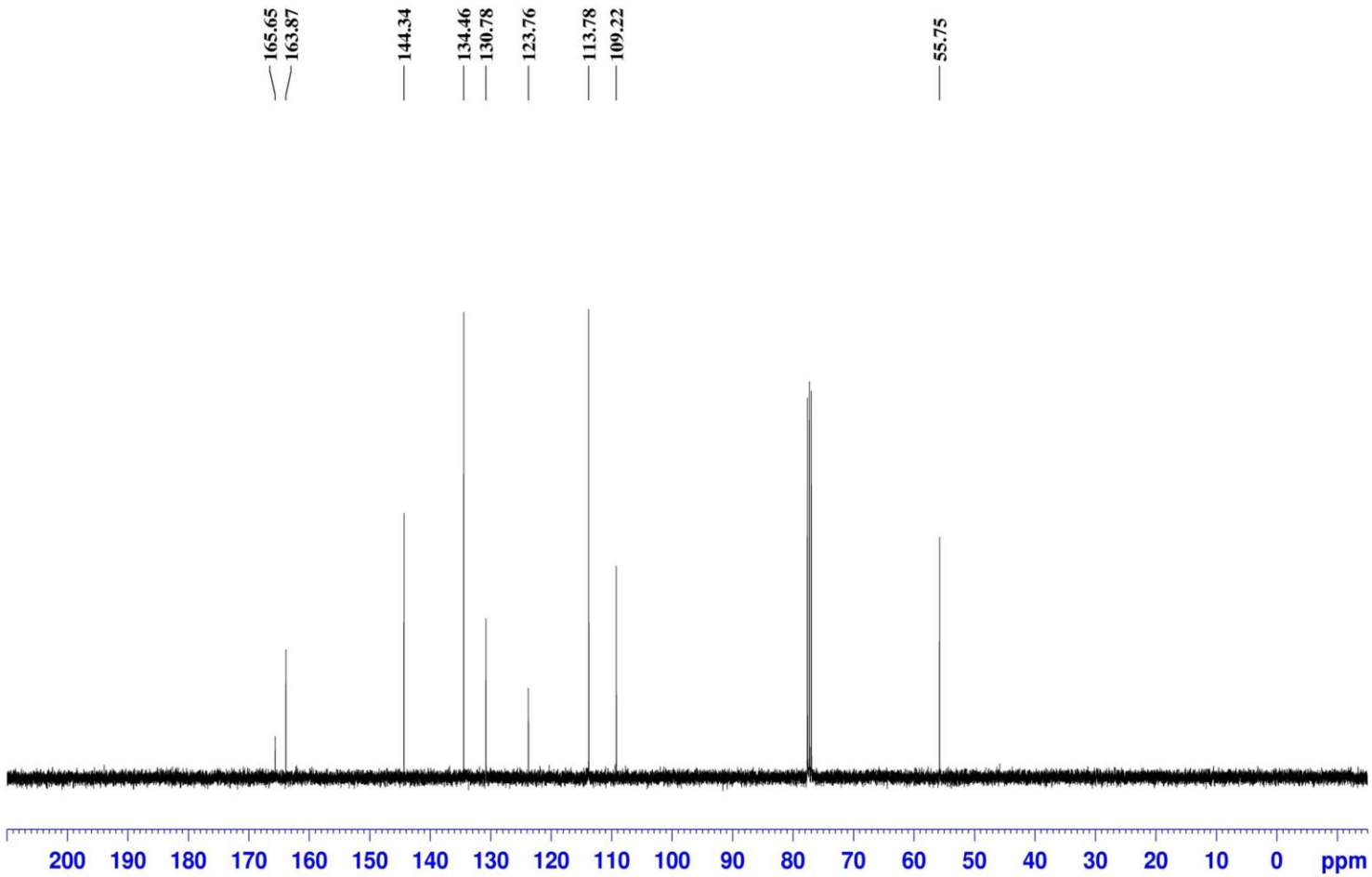


^{13}C NMR Spectra of Synthesized Compounds

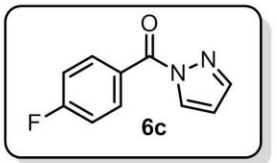


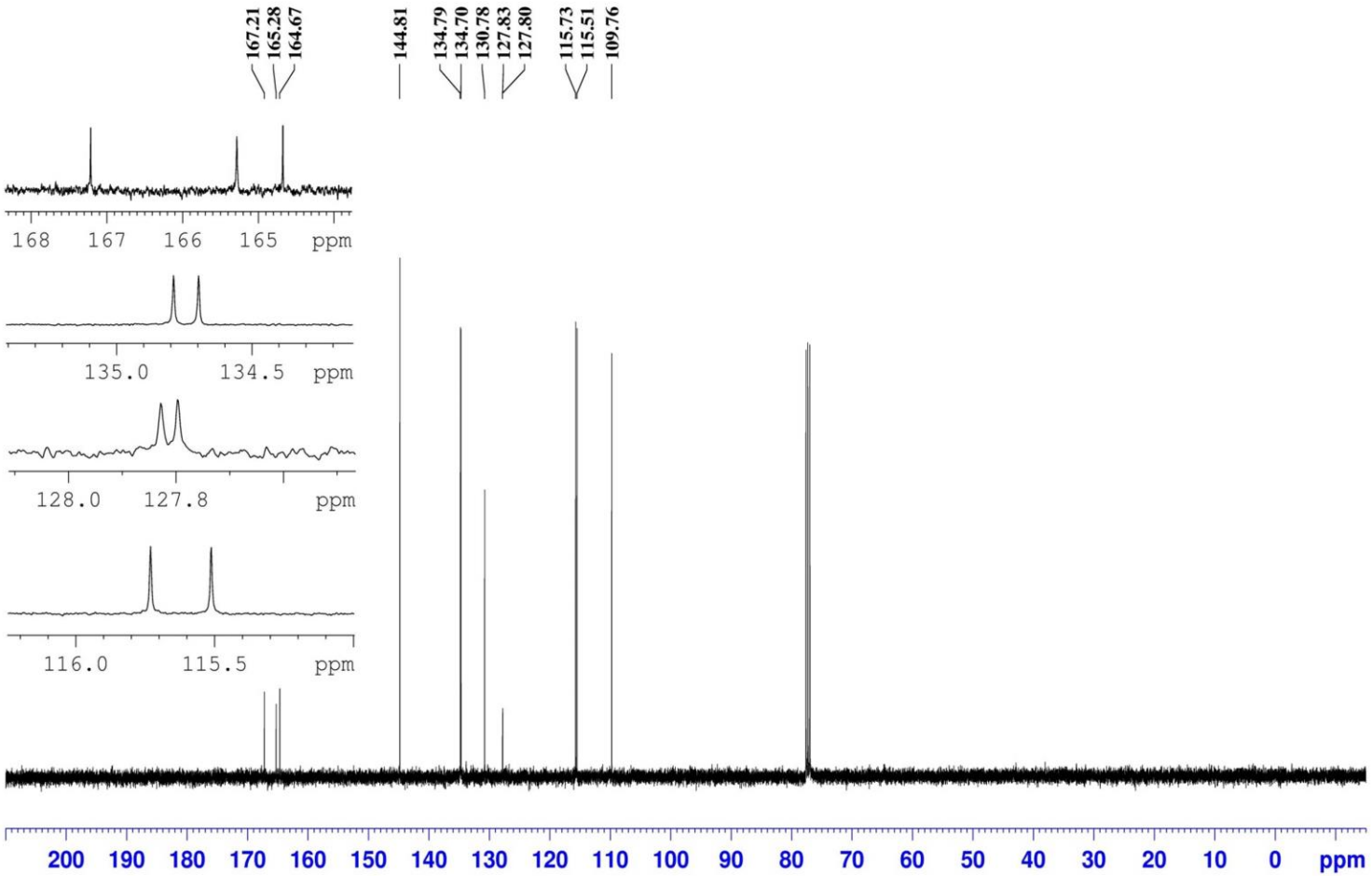
(4–methoxyphenyl)(1H–pyrazol–1–yl)methanone
100 MHz, CDCl3



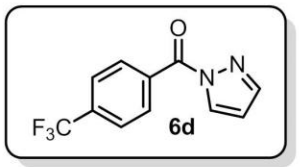


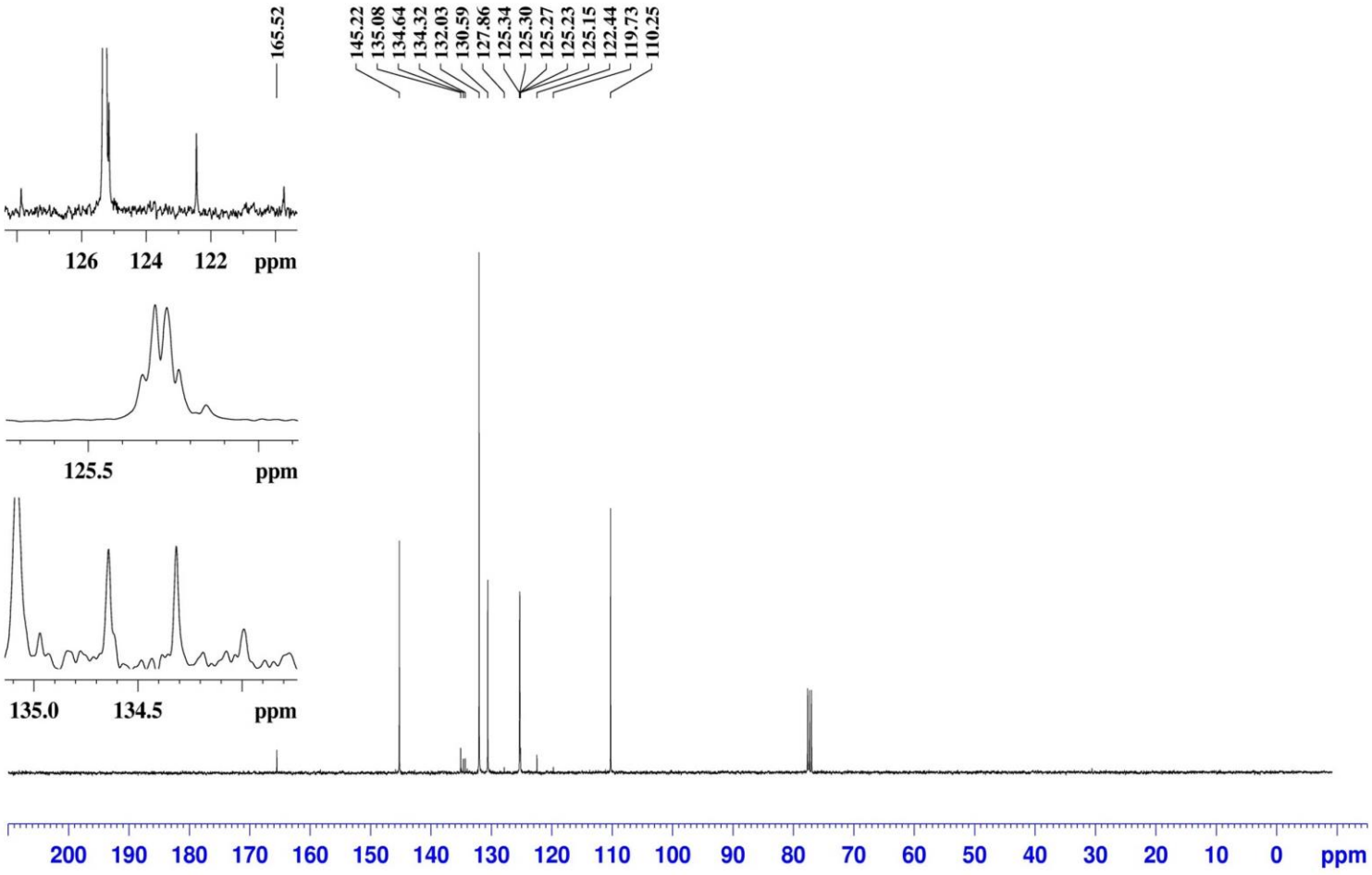
(4–fluorophenyl)(1H–pyrazol–1–yl)methanone
100 MHz, CDCl3



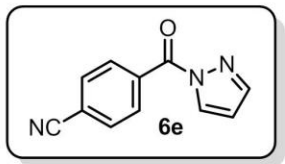


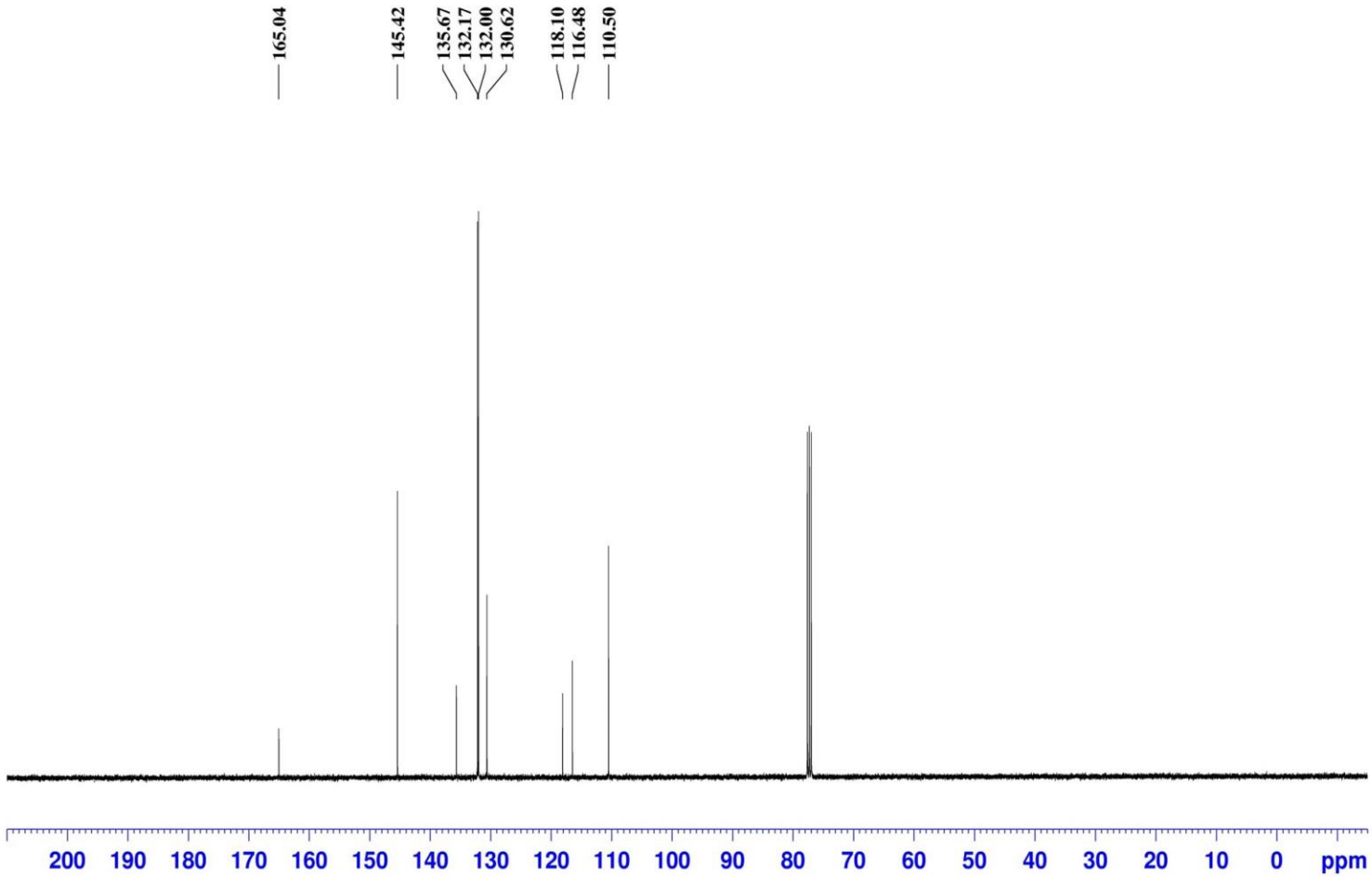
(1H−pyrazol−1−yl)(4−(trifluoromethyl)phenyl)methanone
100 MHz, CDCl3



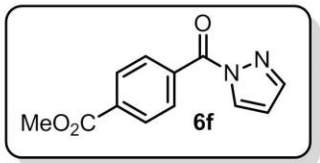


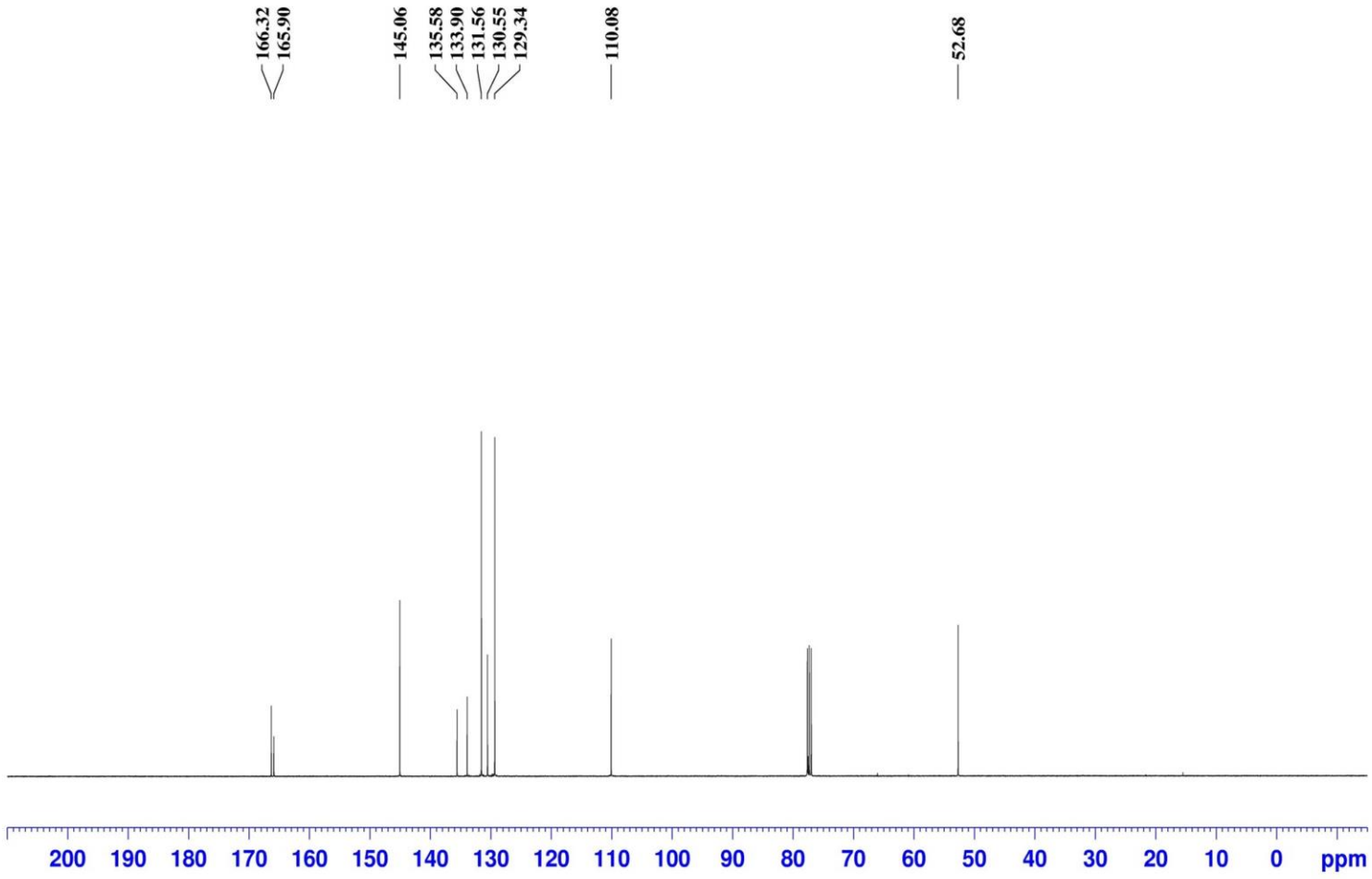
4–(1H–pyrazole–1–carbonyl)benzonitrile
100 MHz, CDCl3



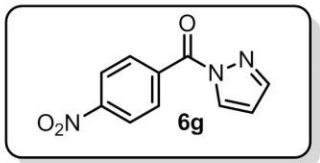


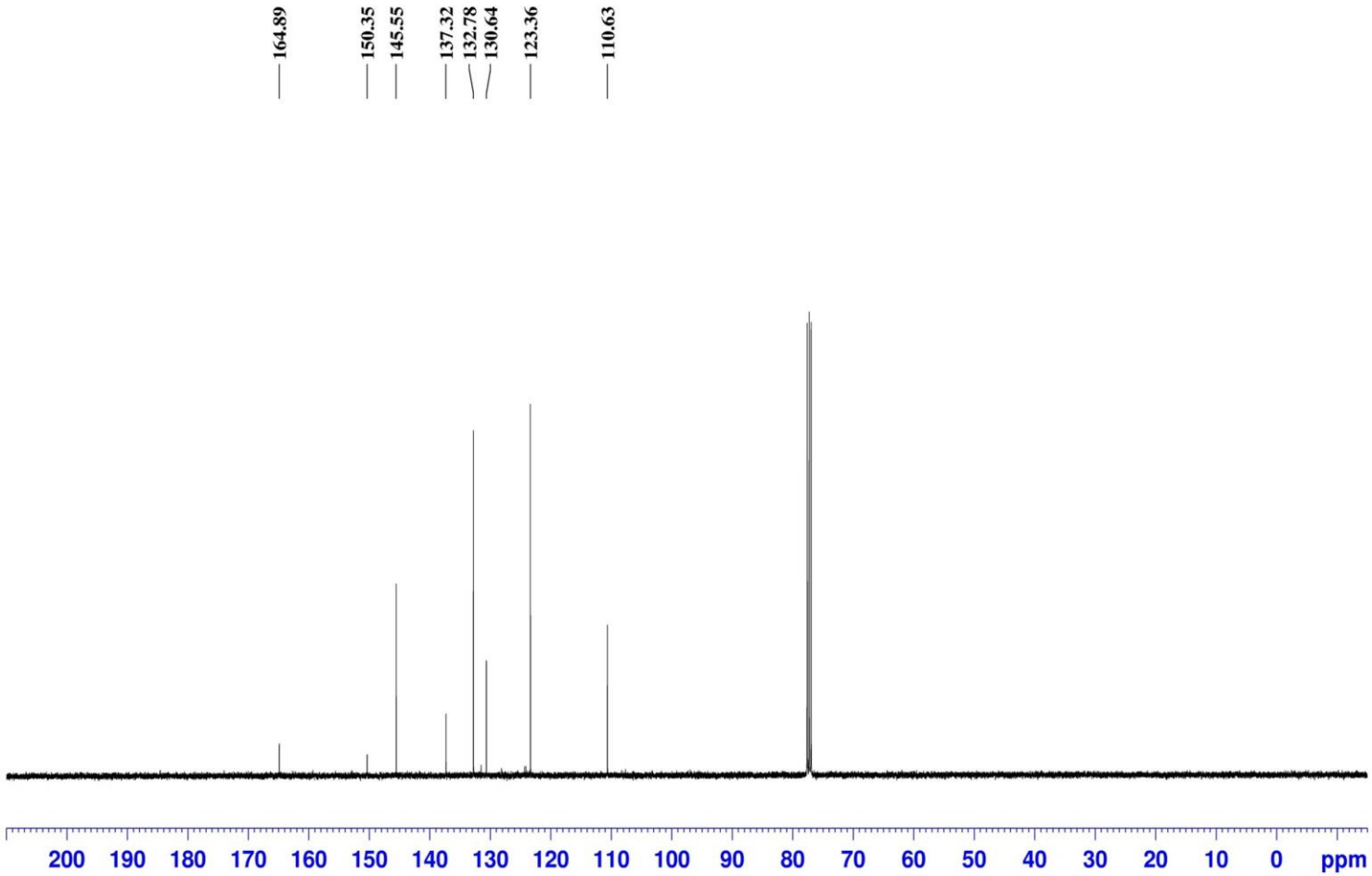
methyl 4–(1H–pyrazole–1–carbonyl)benzoate
100 MHz, CDCl3



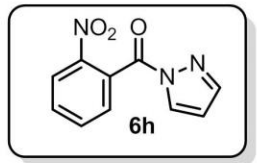


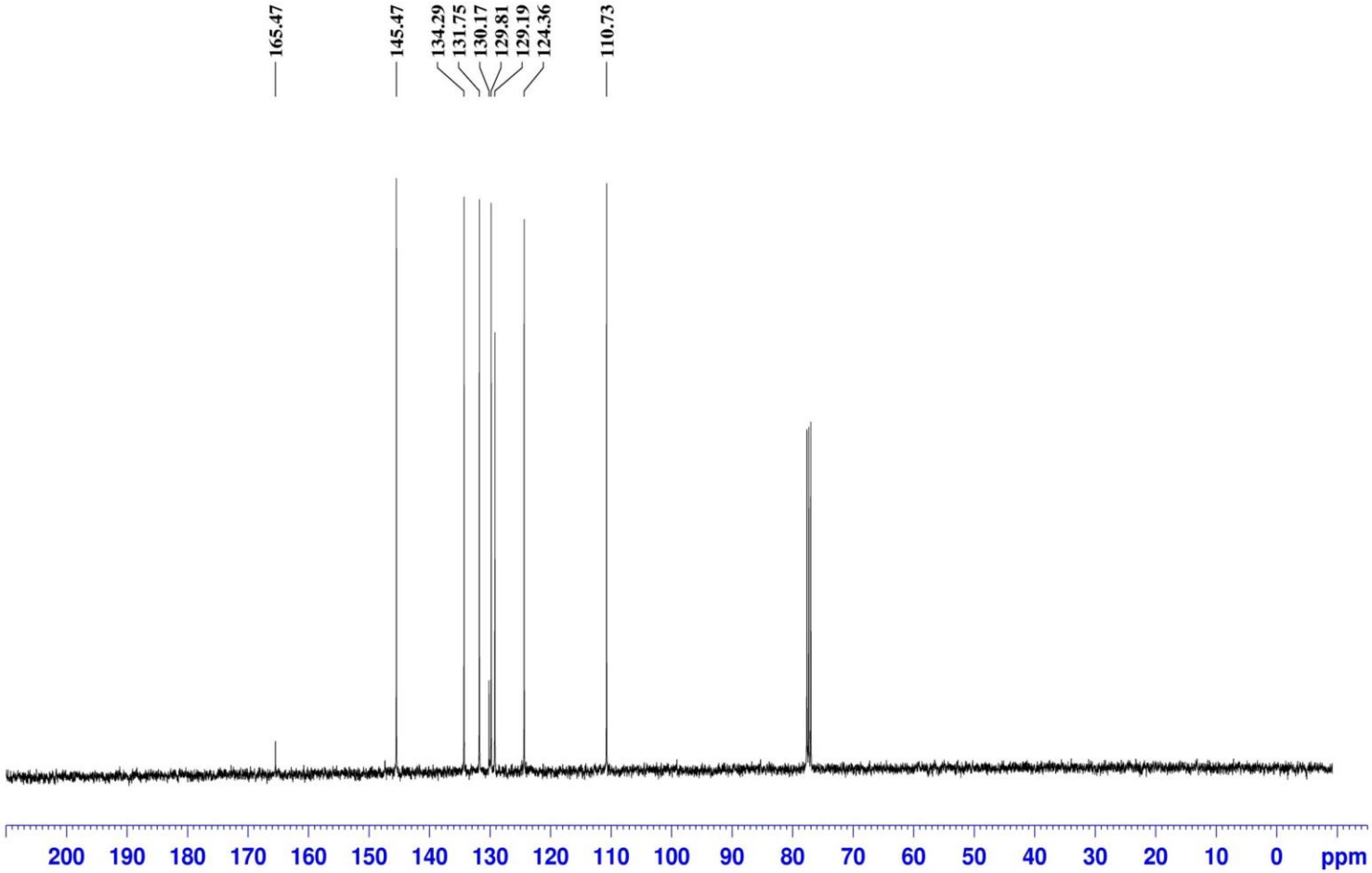
(4−nitrophenyl)(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3



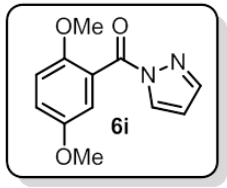


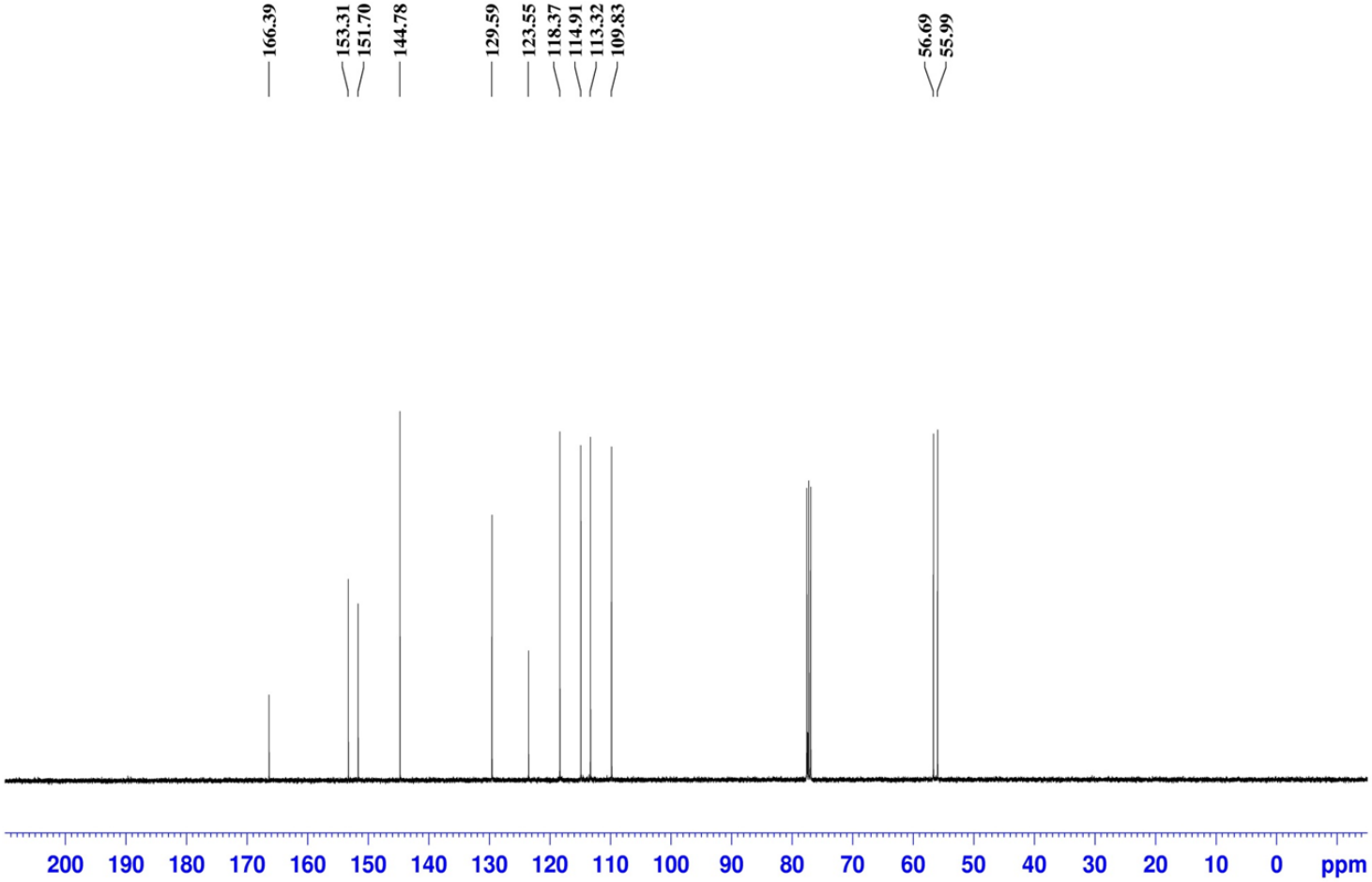
(2–nitrophenyl)(1H–pyrazol–1–yl)methanone
100 MHz, CDCl3



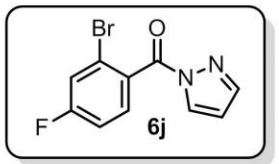


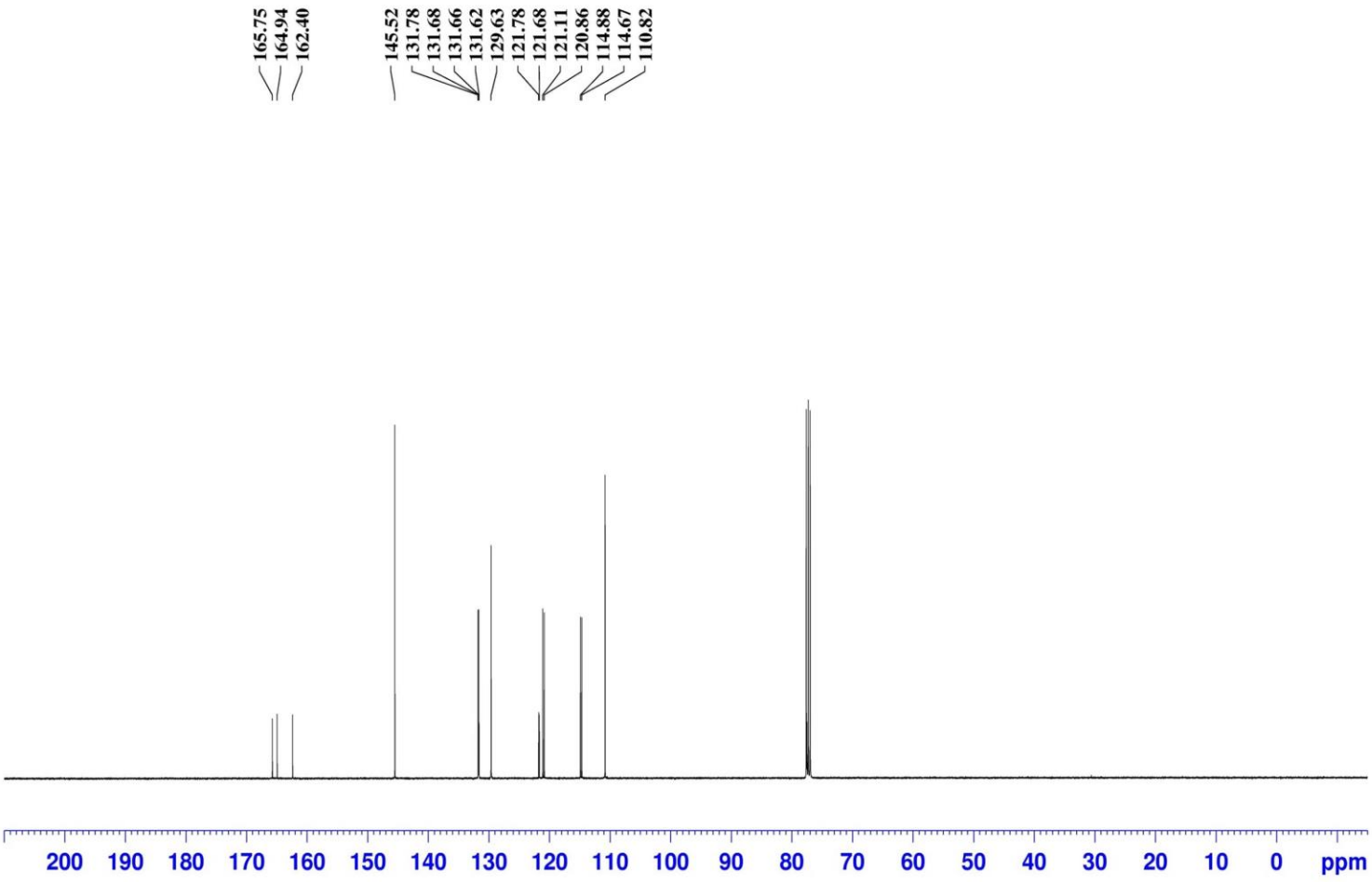
(2,5–dimethoxyphenyl)(1H–pyrazol–1–yl)methanone
100 MHz, CDCl3



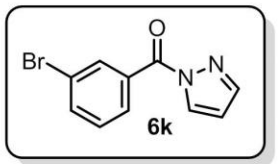


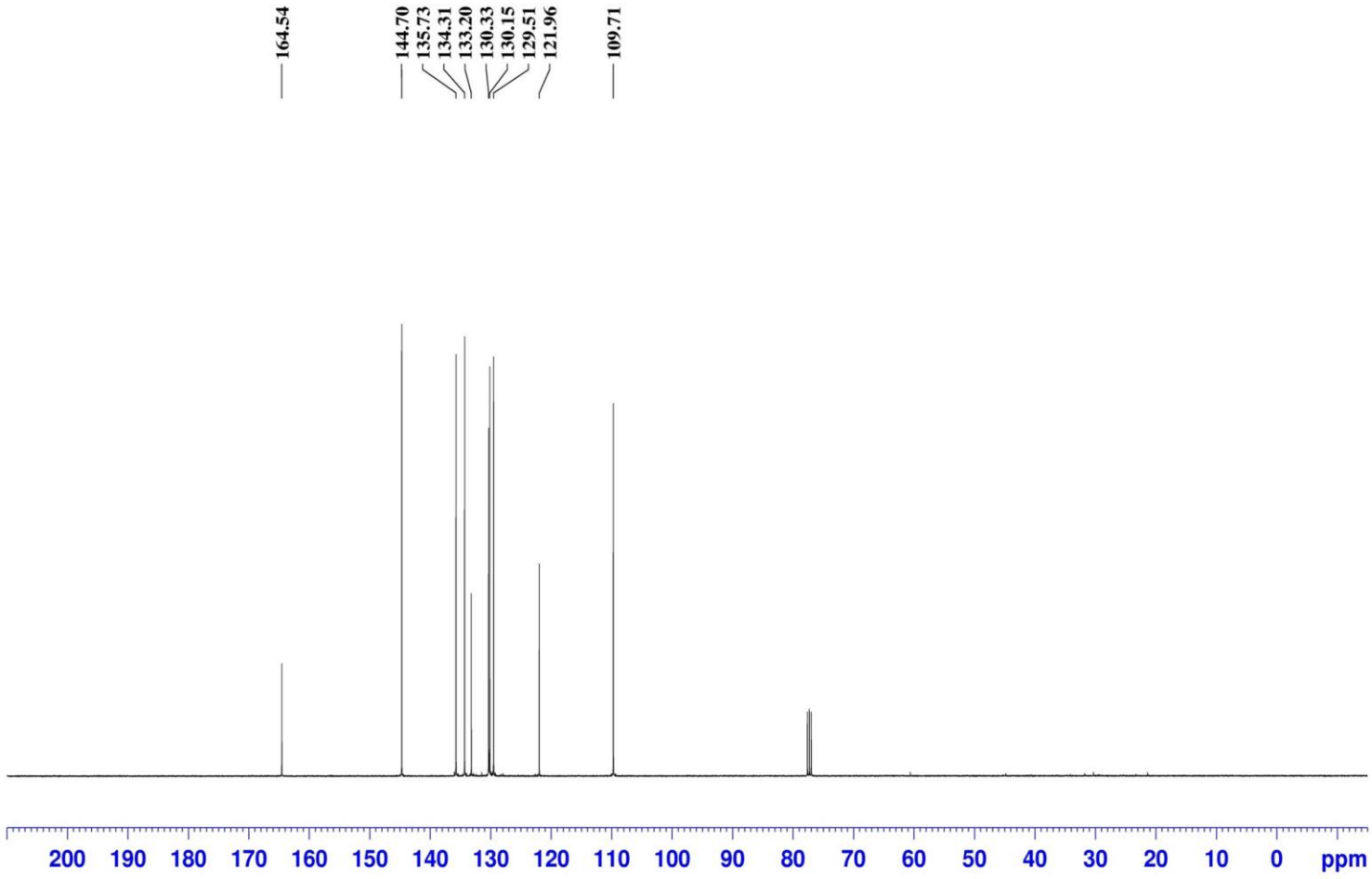
(2−bromo−4−fluorophenyl)(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3



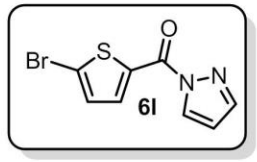


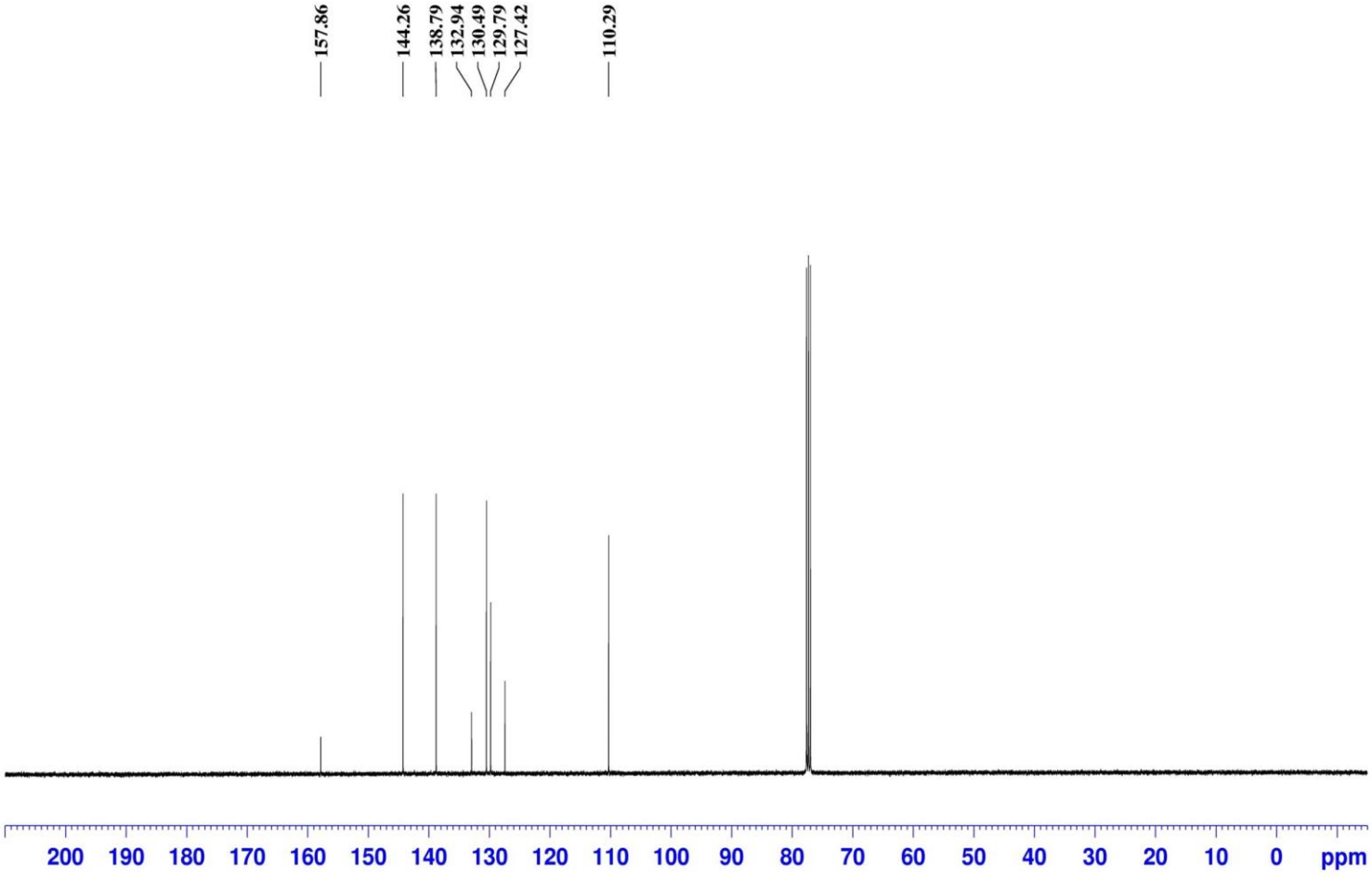
(3–bromophenyl)(1H–pyrazol–1–yl)methanone
100 MHz, CDCl3



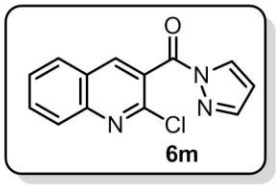


(5−bromothiophen−2−yl)(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3

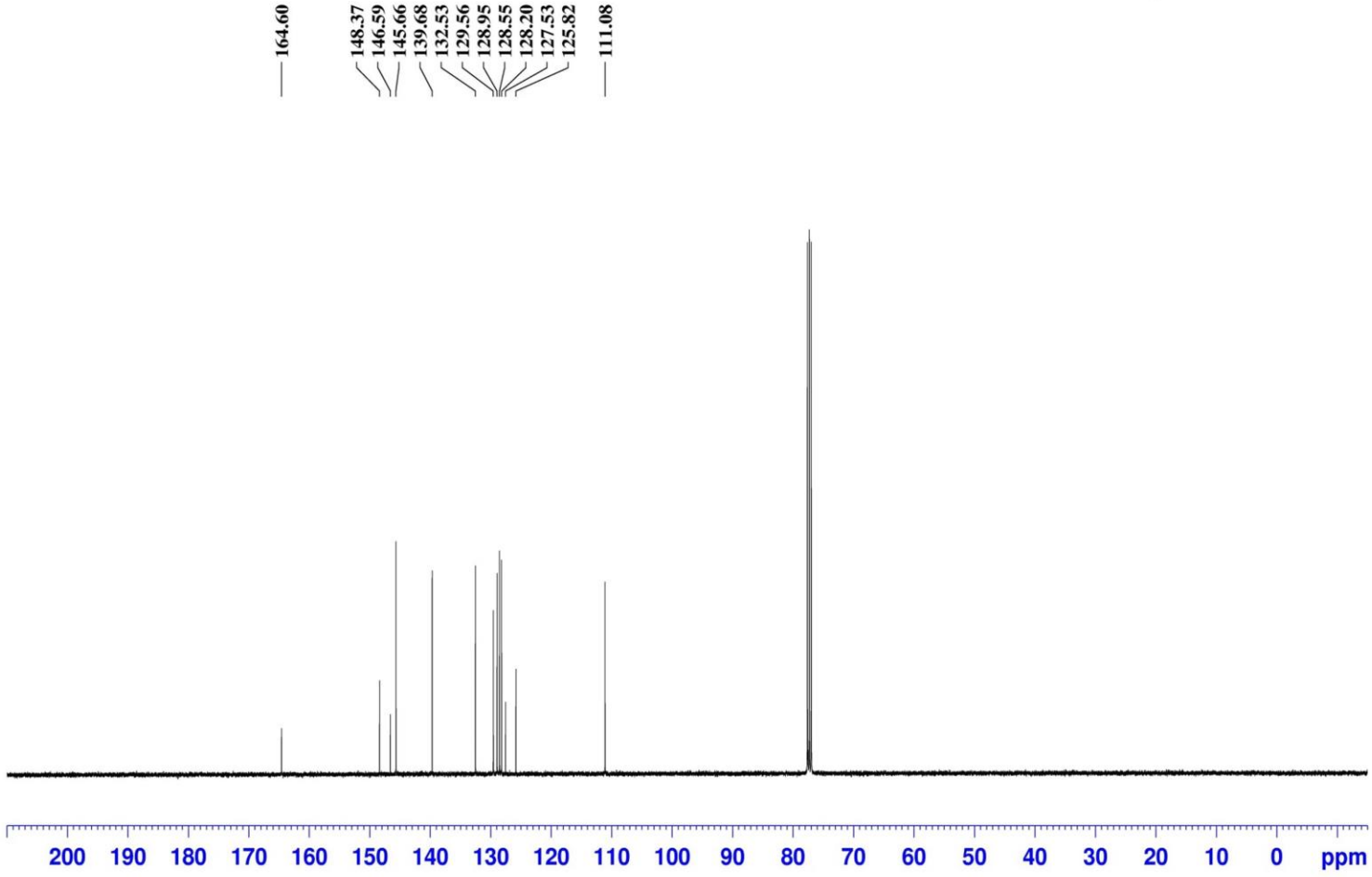




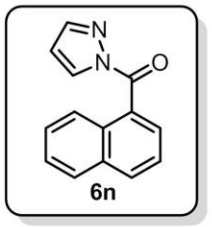
(2−chloroquinolin−3−yl)(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3

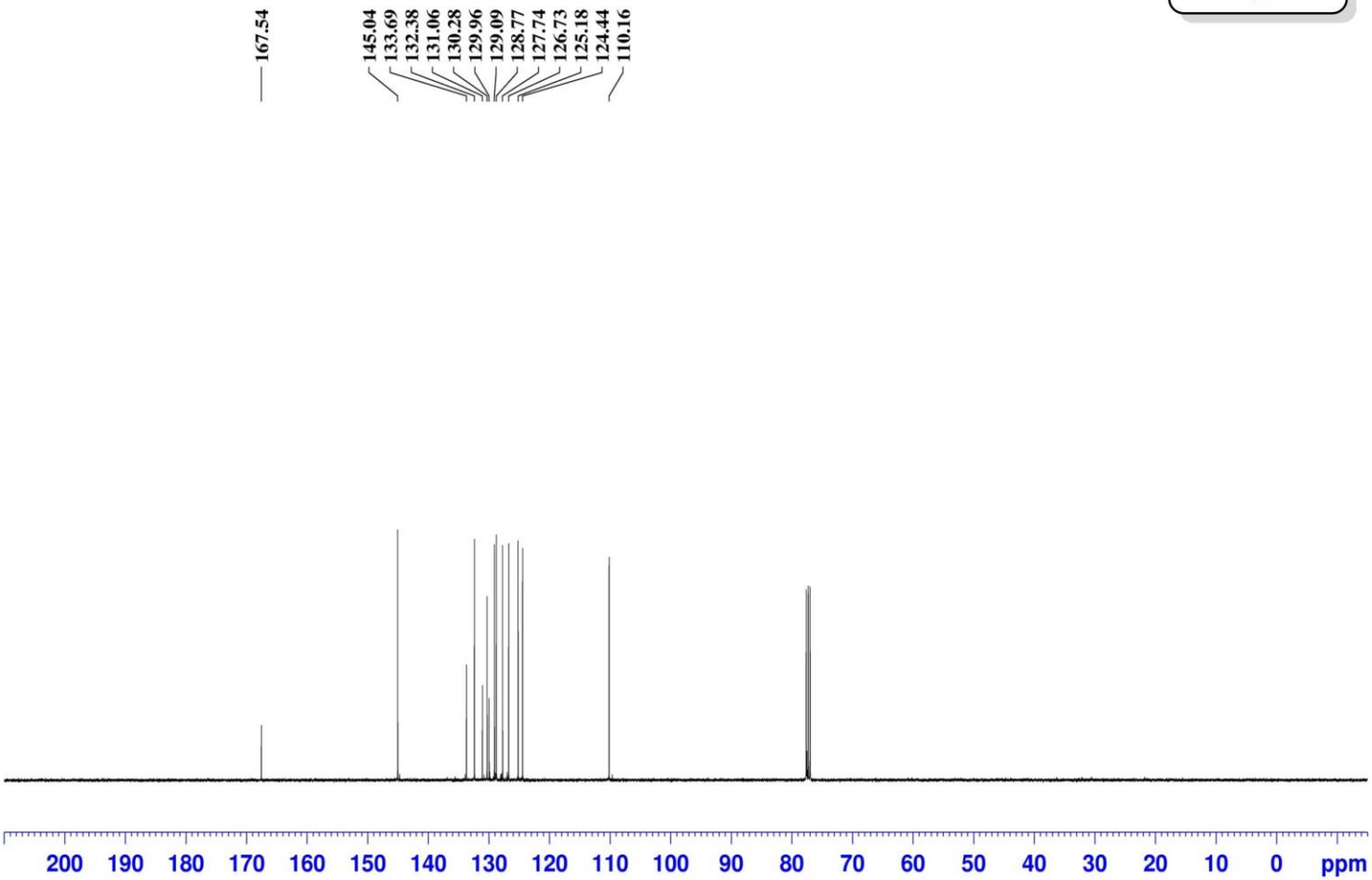


6m

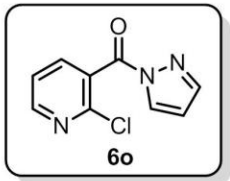


naphthalen−1−yl(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3

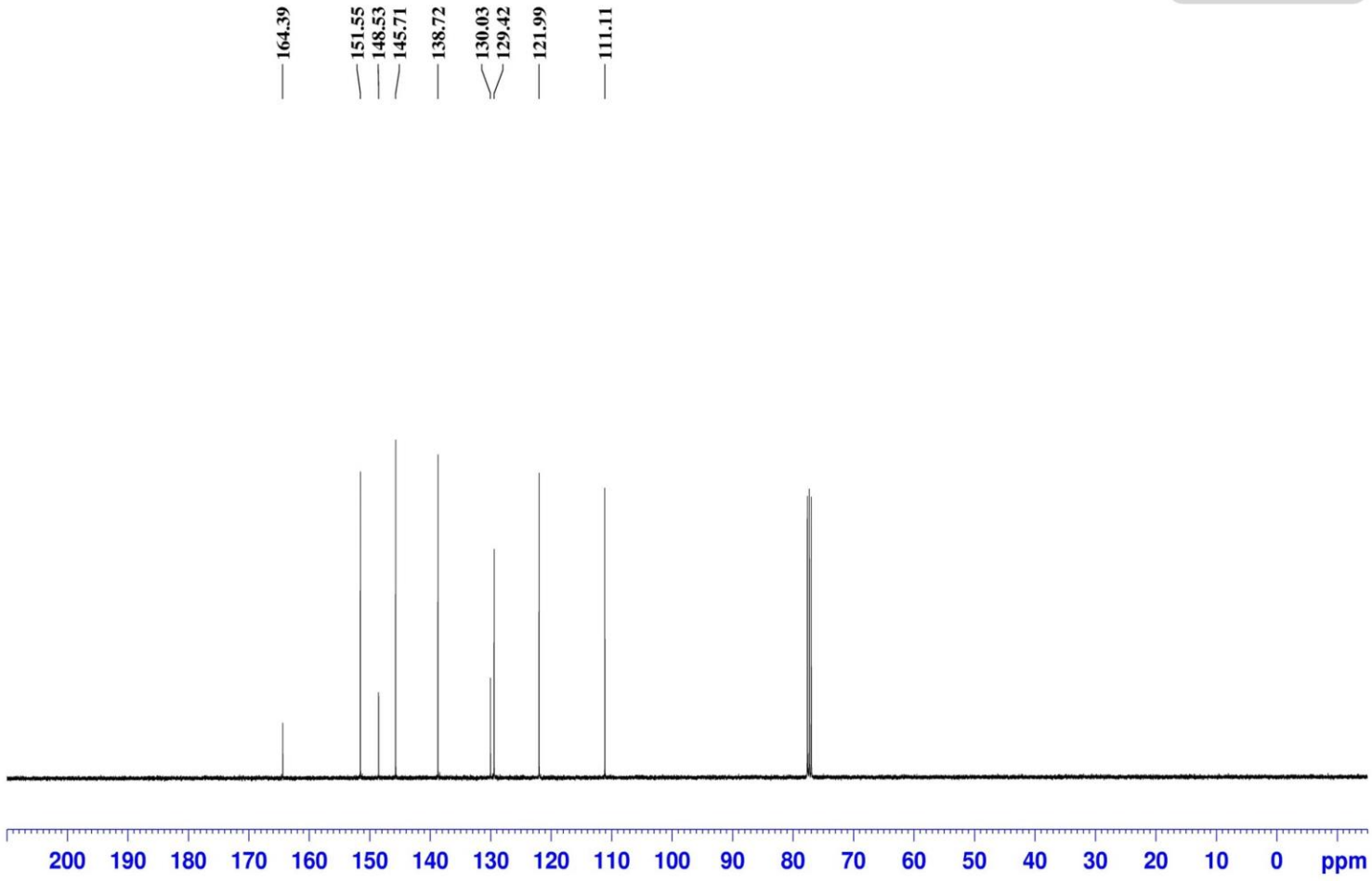




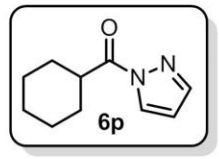
(2−chloropyridin−3−yl)(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3

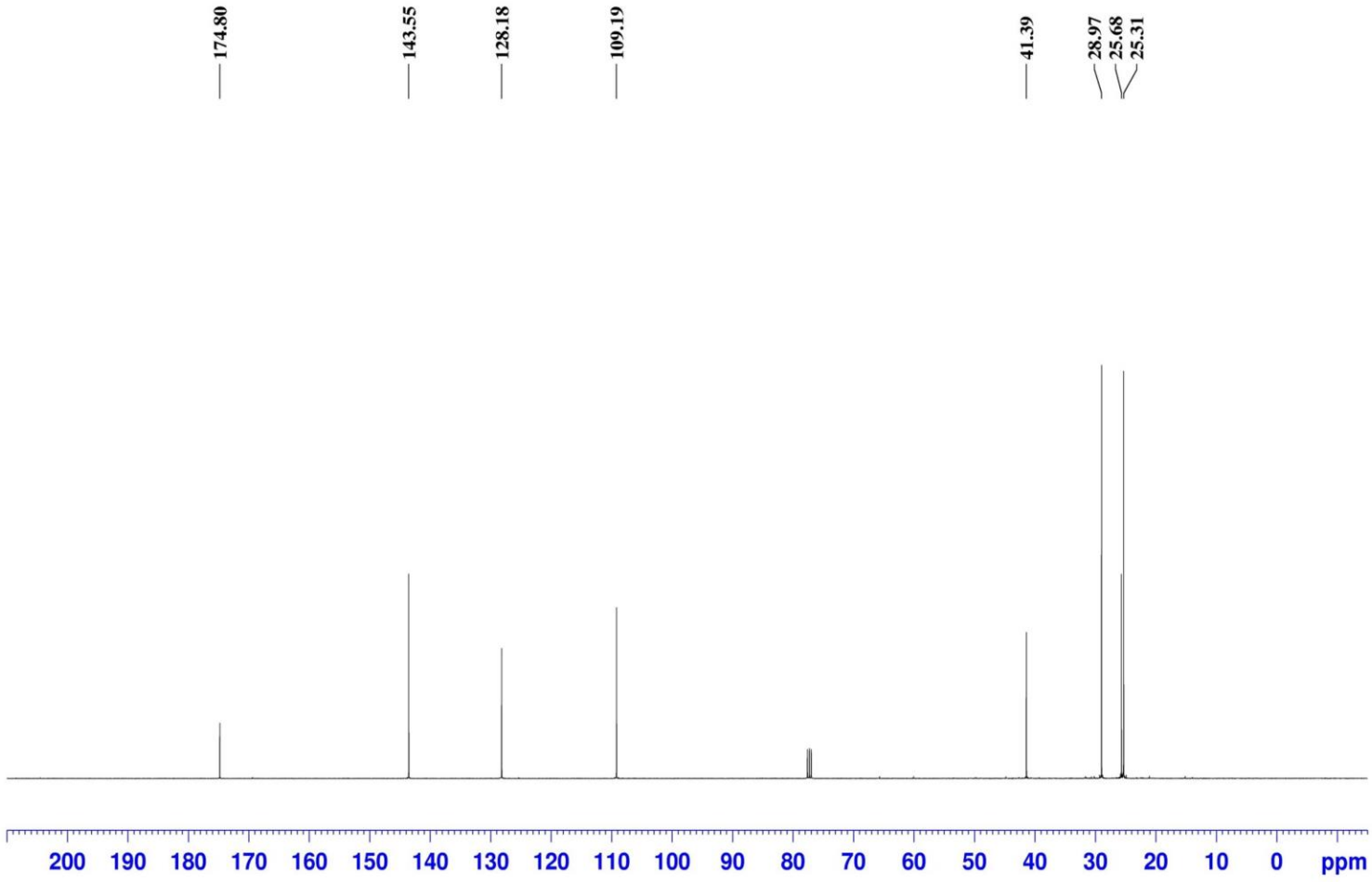


6o

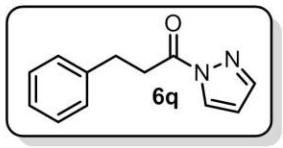


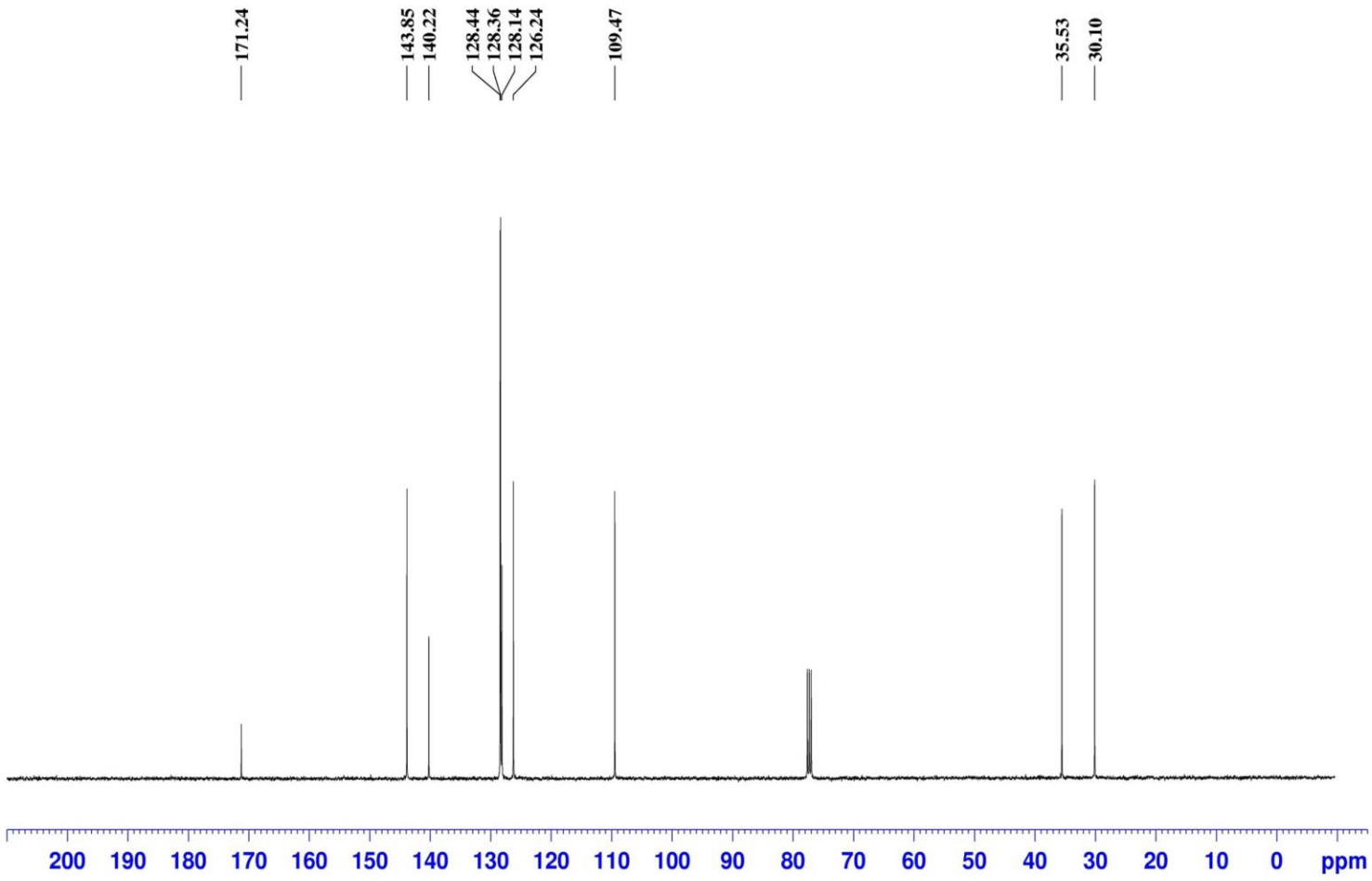
cyclohexyl(1H−pyrazol−1−yl)methanone
100 MHz, CDCl3



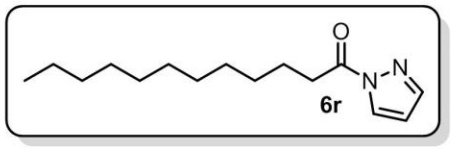


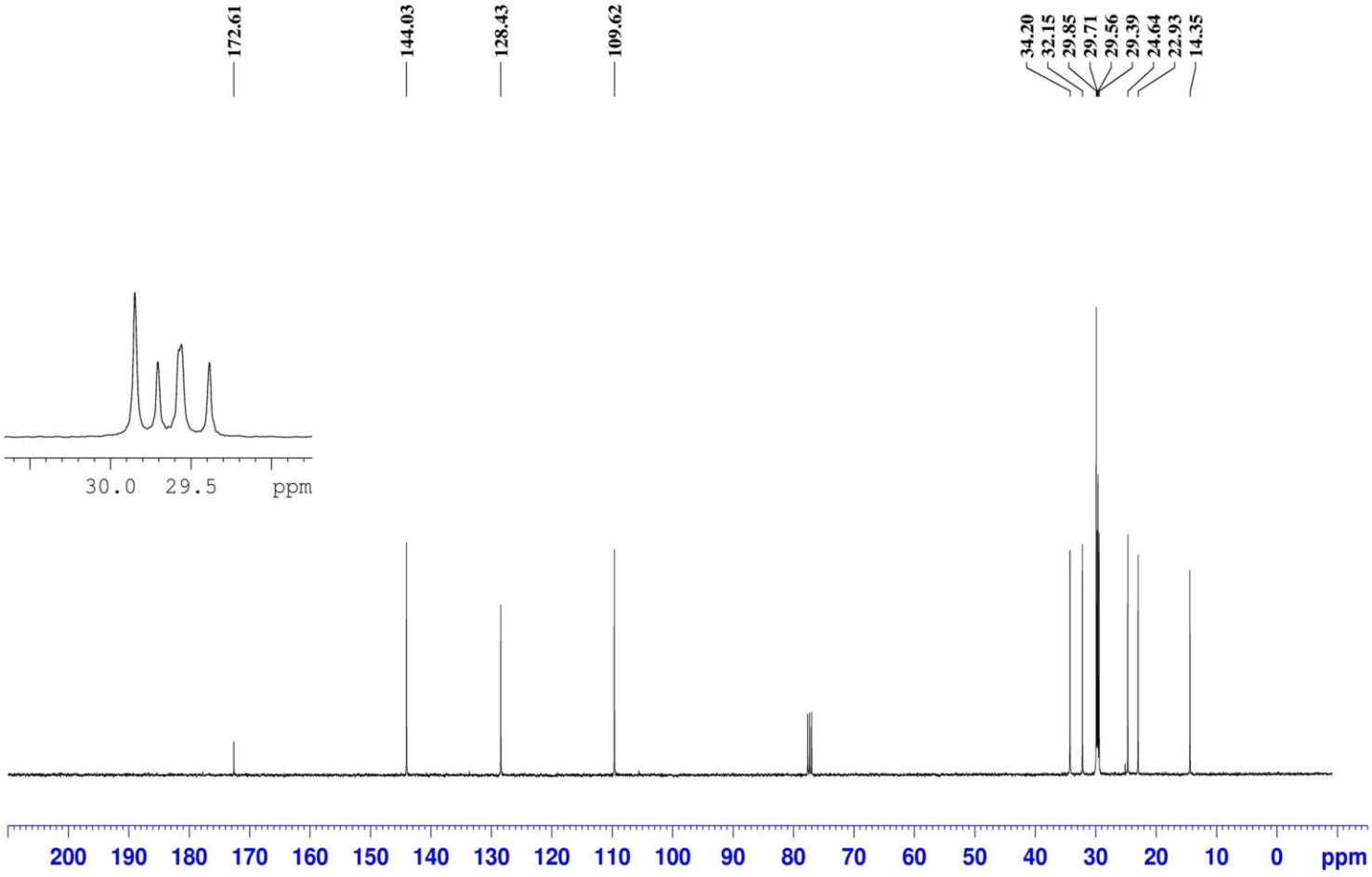
3–phenyl–1–(1H–pyrazol–1–yl)propan–1–one
100 MHz, CDCl3



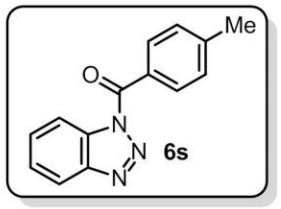


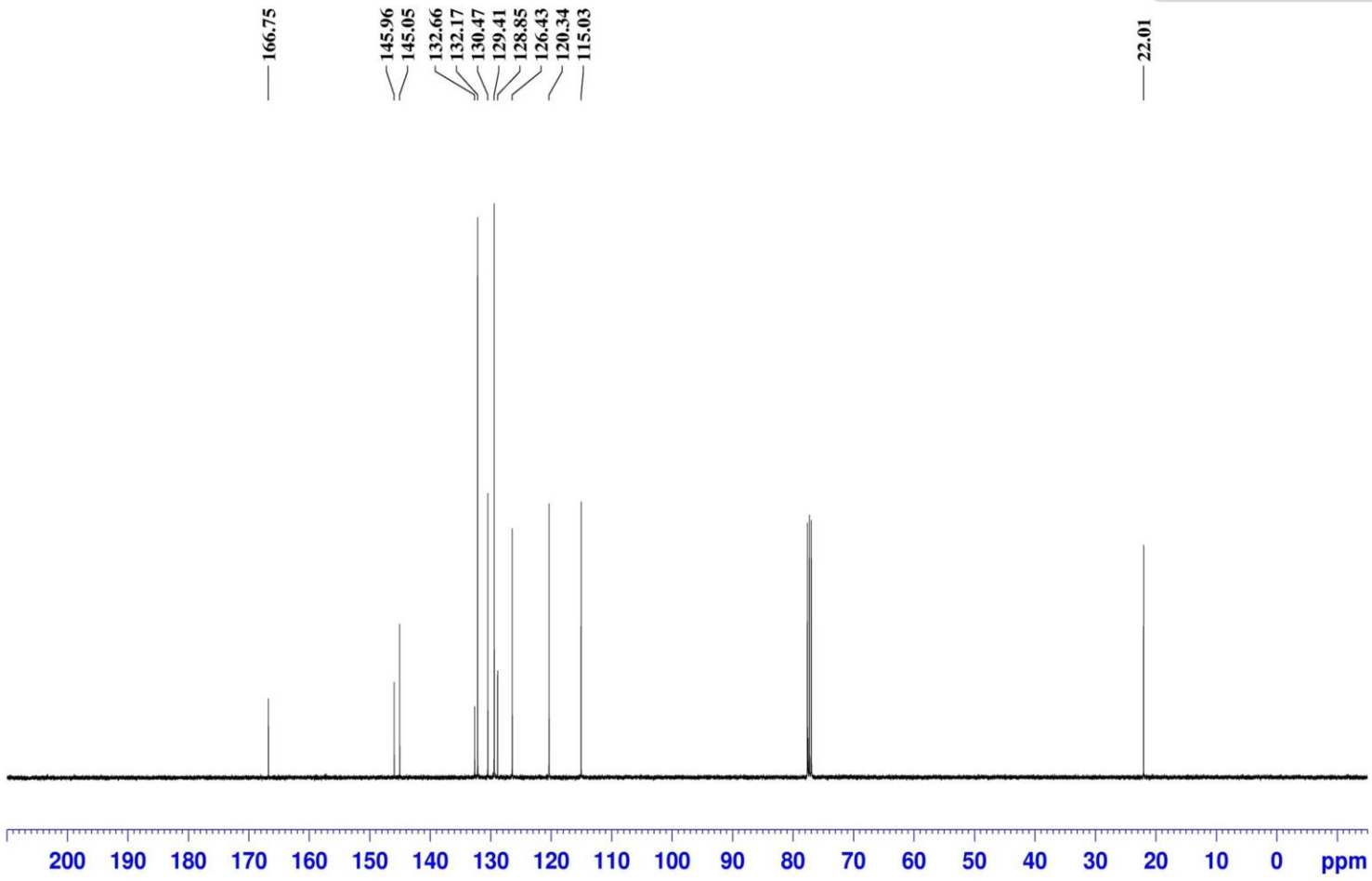
1–(1H–pyrazol–1–yl)dodecan–1–one
100 MHz, CDCl3



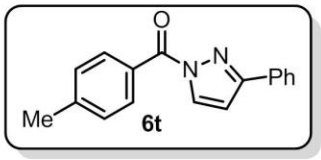


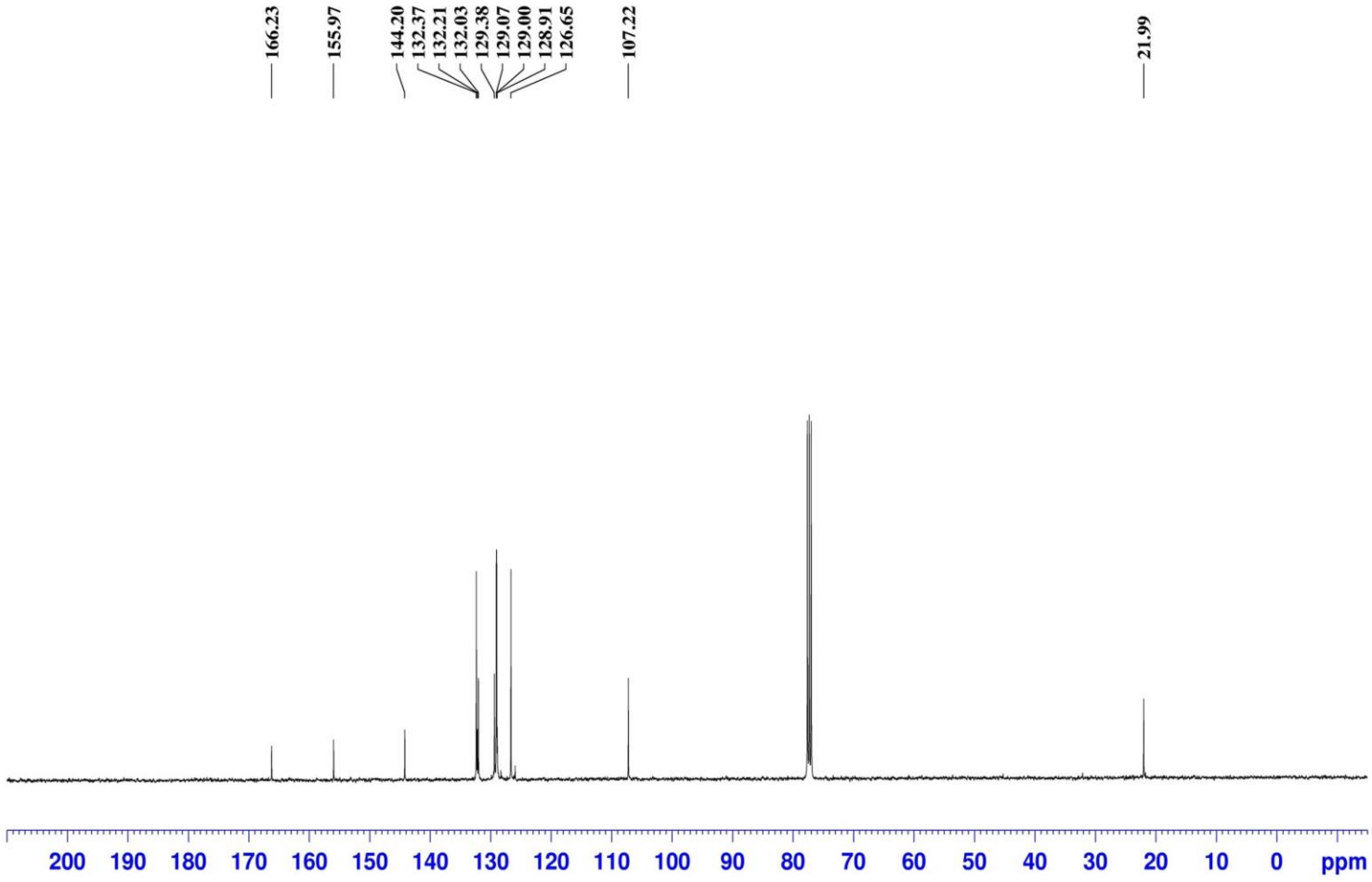
p–toluoyl–1H–1,2,3–benzotriazole
100 MHz, CDCl3



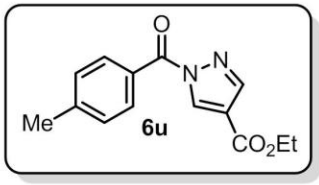


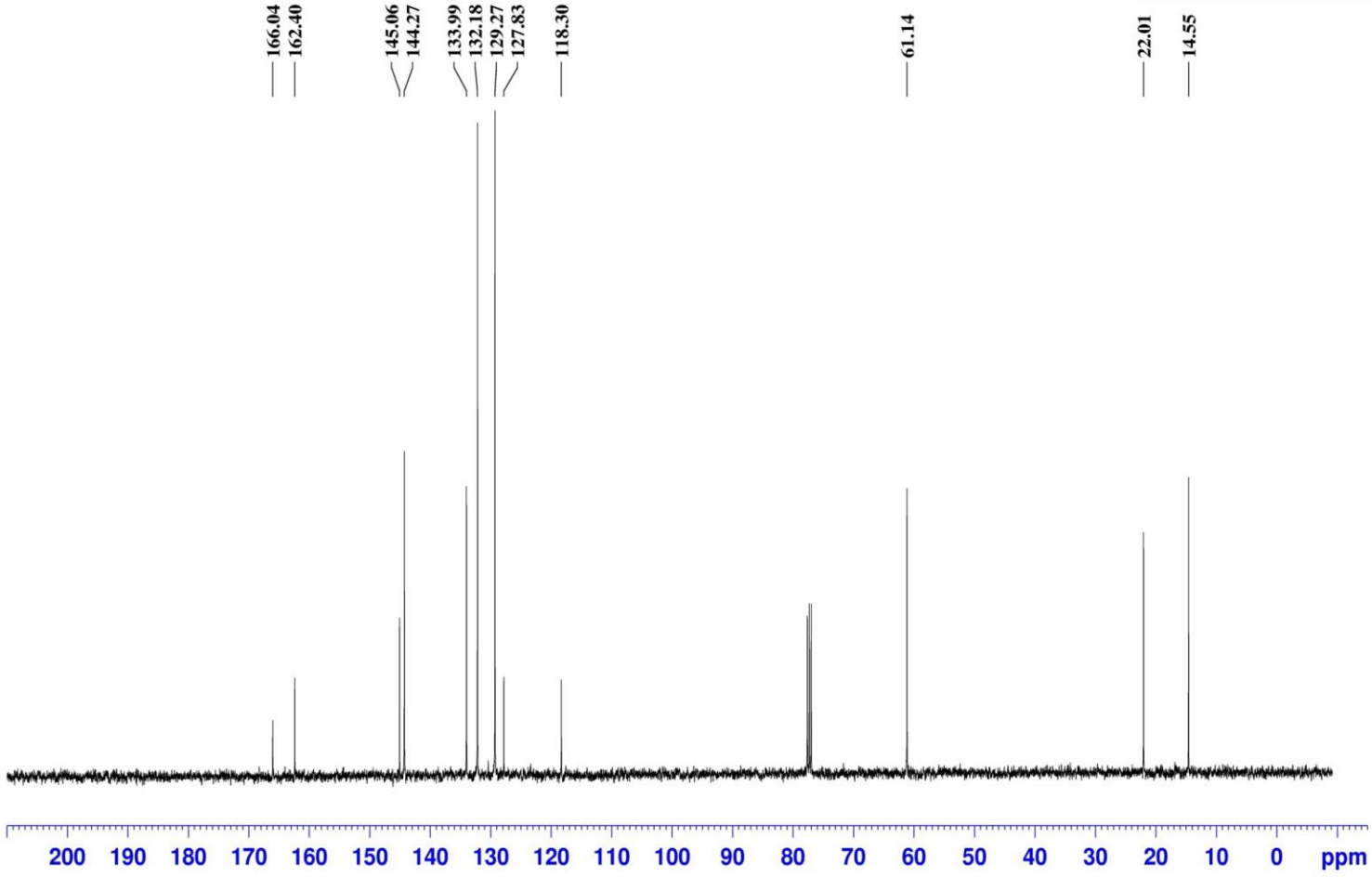
(3−phenyl−1H−pyrazol−1−yl)(p−tolyl)methanone
100 MHz, CDCl3



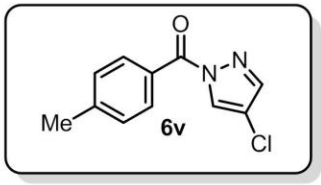


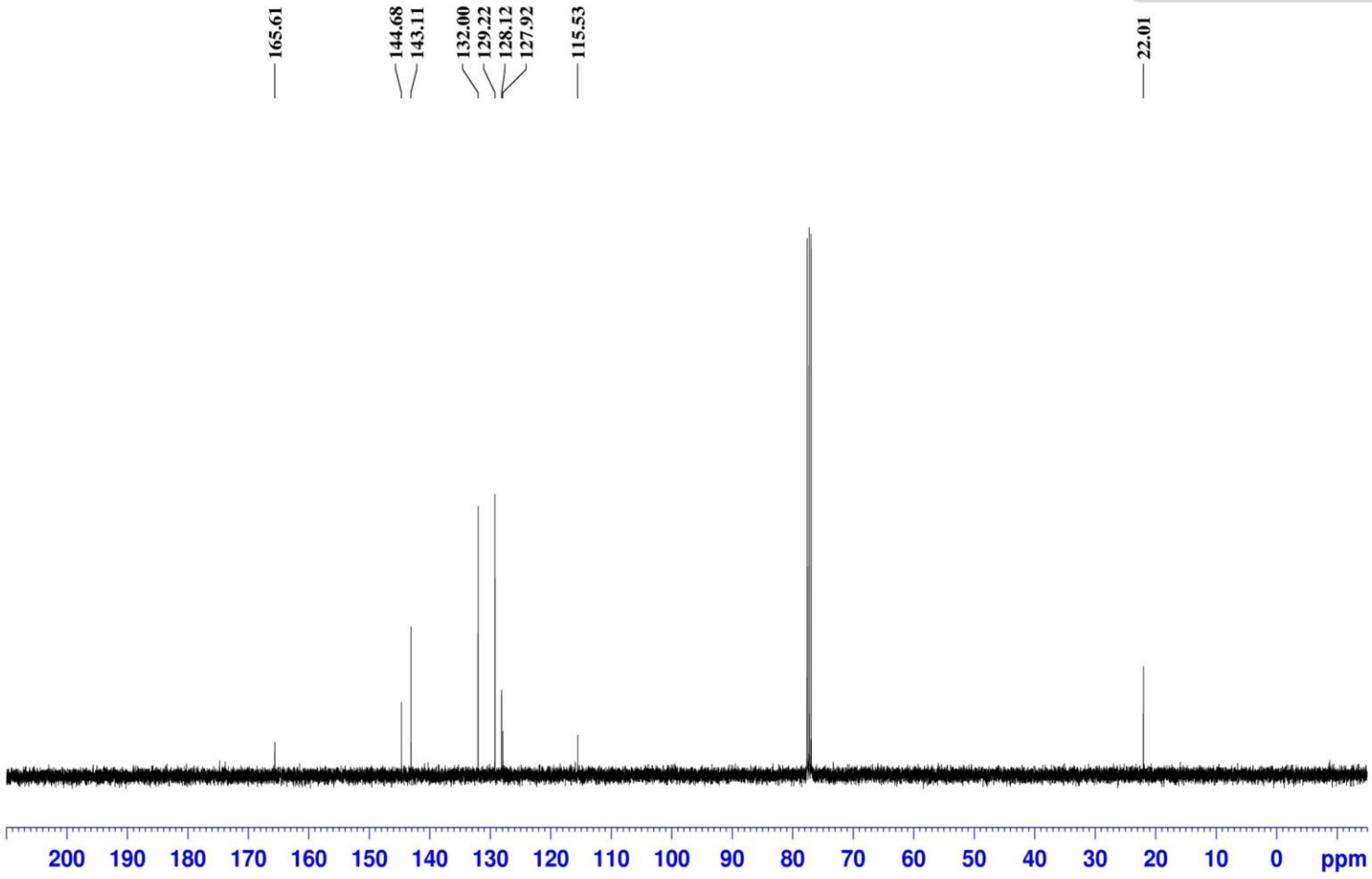
ethyl 1–(4–methylbenzoyl)–1H–pyrazole–4–carboxylate
100 MHz, CDCl3



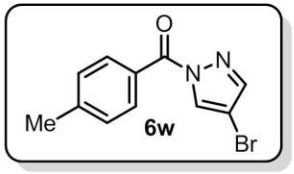


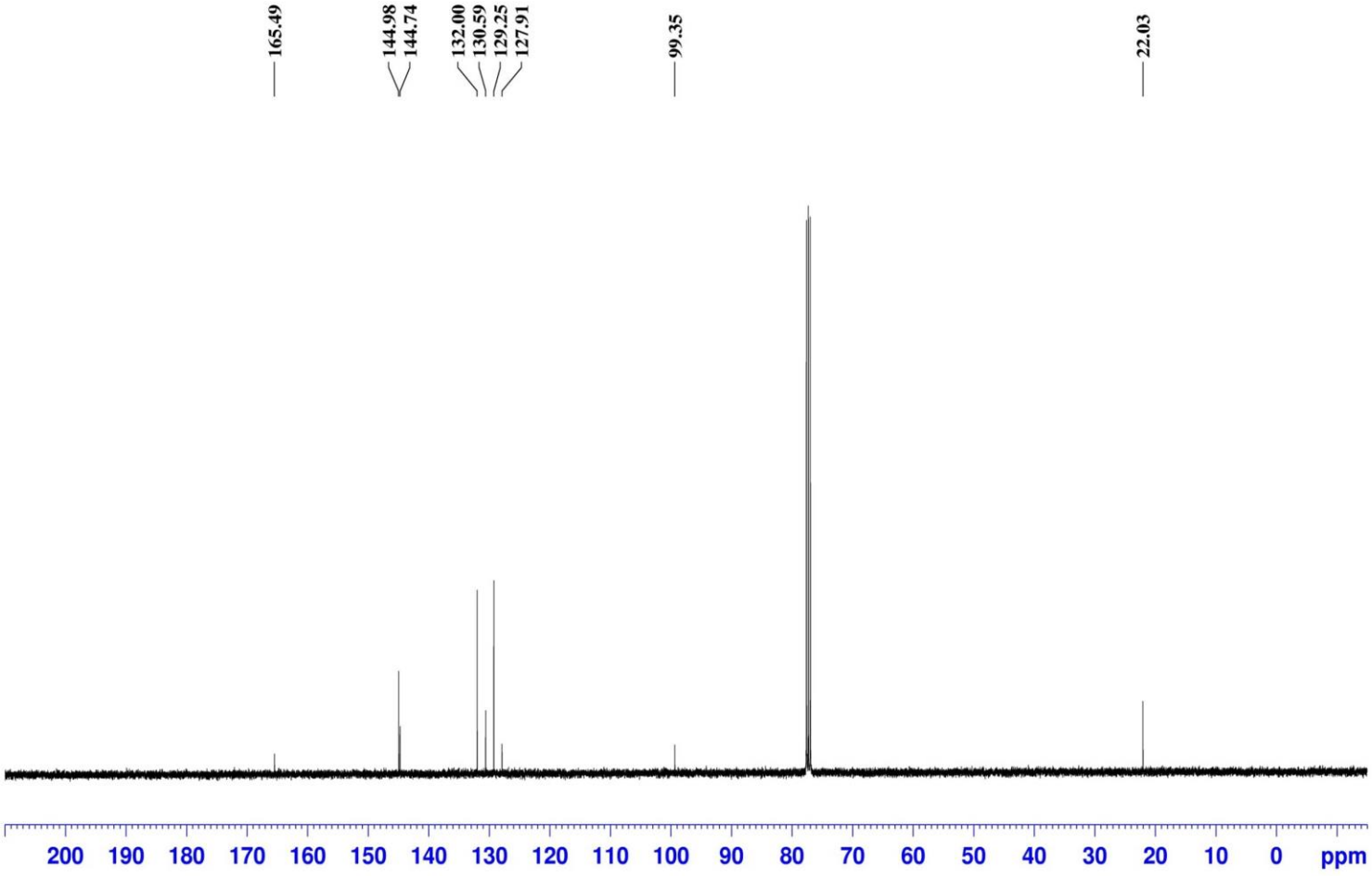
(4–chloro–1H–pyrazol–1–yl)(p–tolyl)methanone
100 MHz, CDCl3



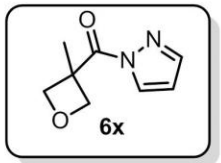


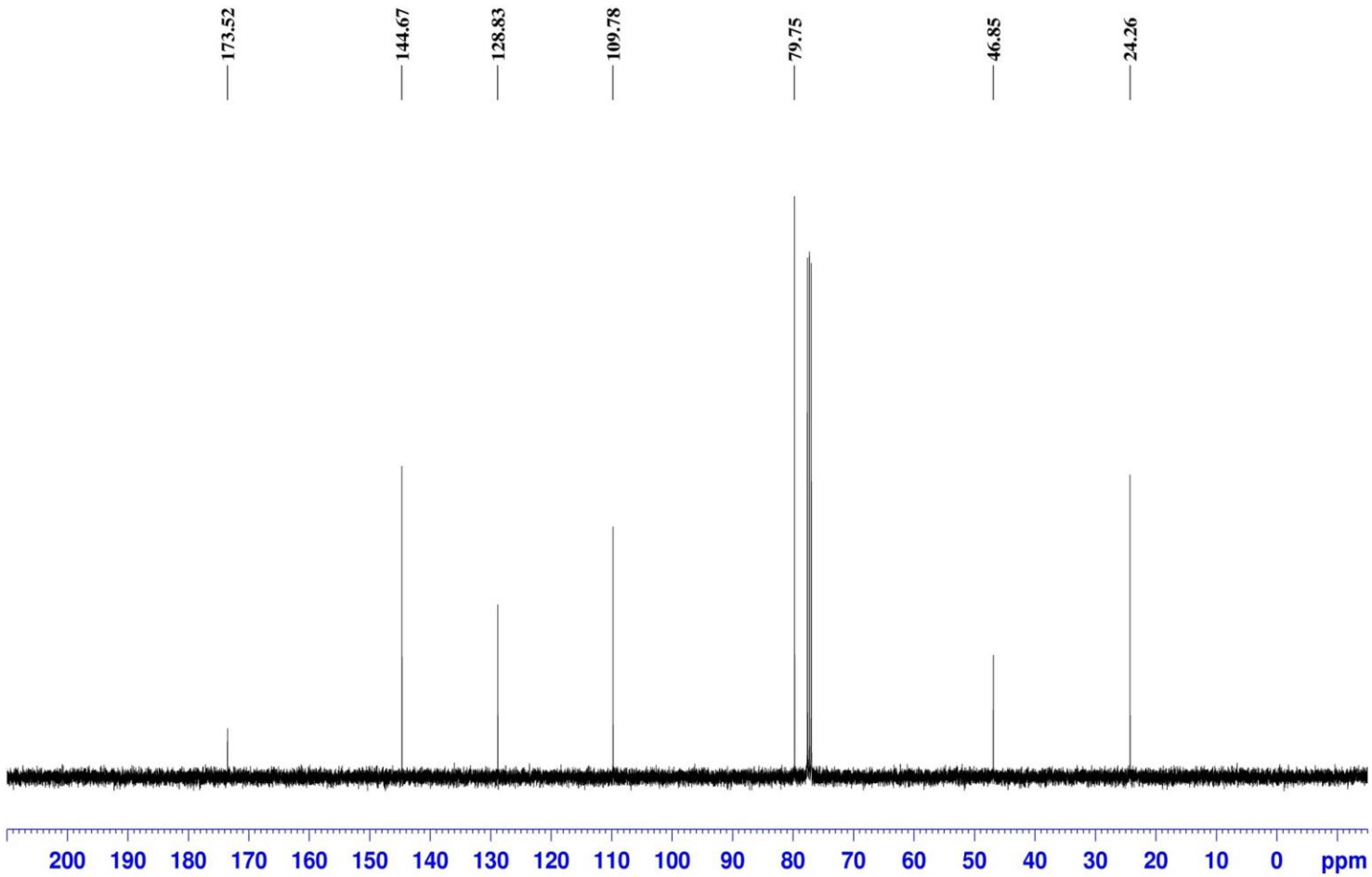
(4–bromo–1H–pyrazol–1–yl)(p–tolyl)methanone
100 MHz, CDCl3



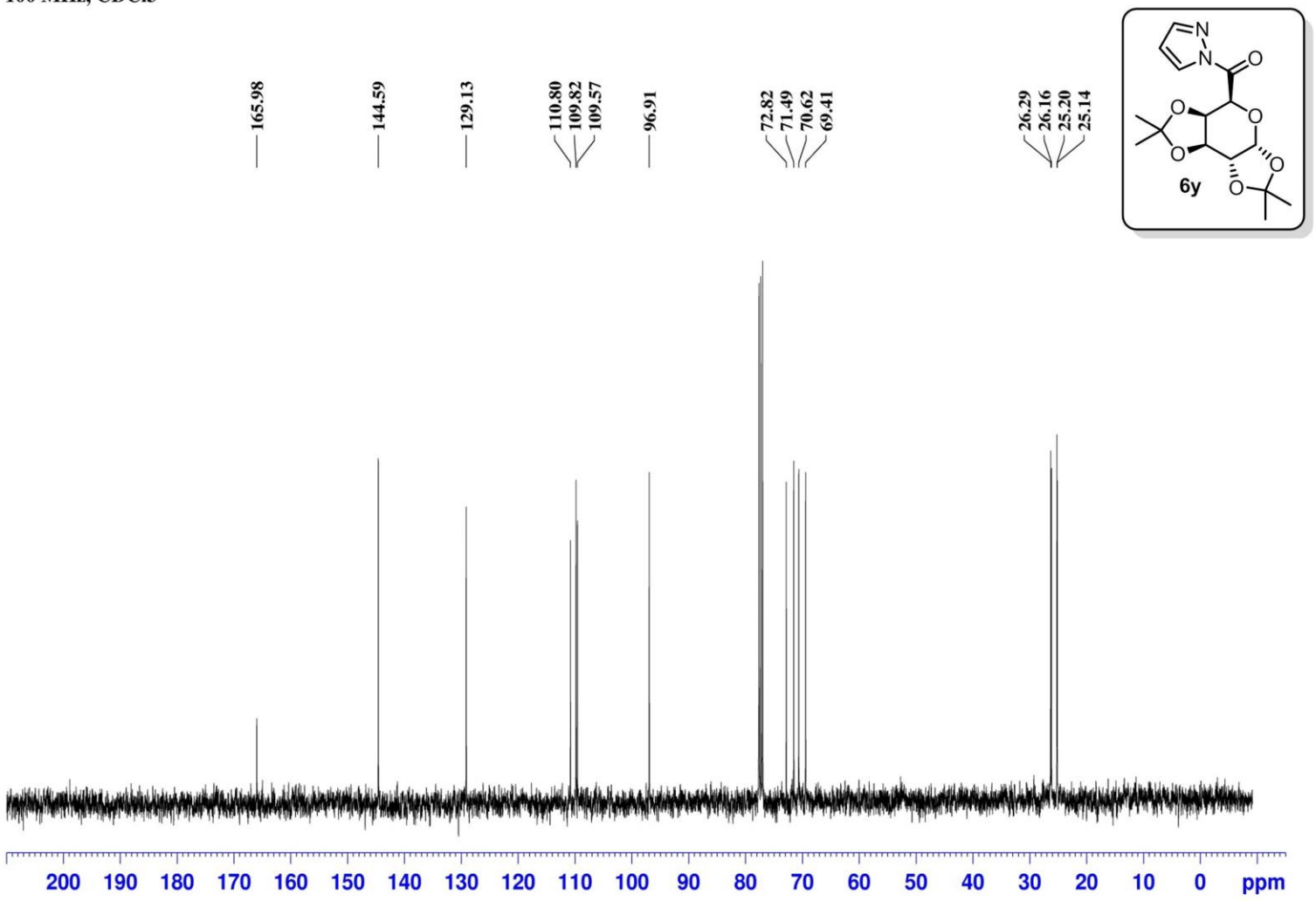


(3−methyloxetan−3−yl)(1H−pyrazol−1−yl)methanone
100 MHz. CDCl3

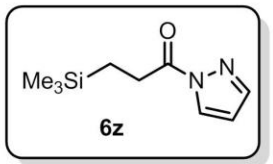




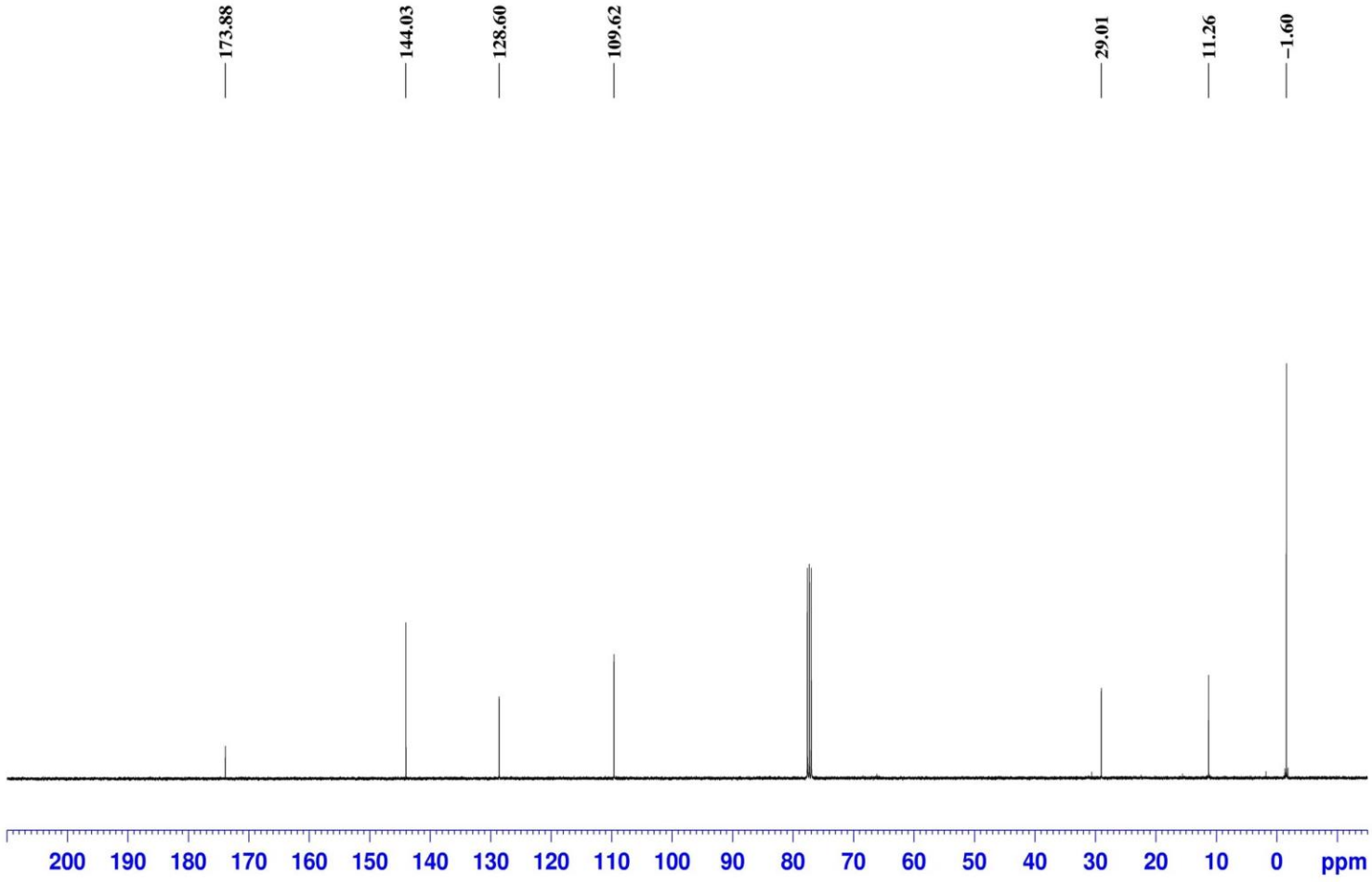
(1H−pyrazol−1−yl)((3aR,5S,5aR,8aS,8bR)−2,2,7,7−tetramethyltetrahydro−3aH−bis([1,3]dioxolo)[4,5−b:4',5'−d]pyran−5−yl)methanone
100 MHz, CDCl3



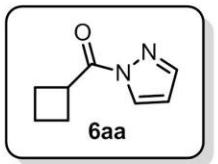
1-(1H-pyrazol-1-yl)-3-(trimethylsilyl)propan-1-one
100 MHz, CDCl3

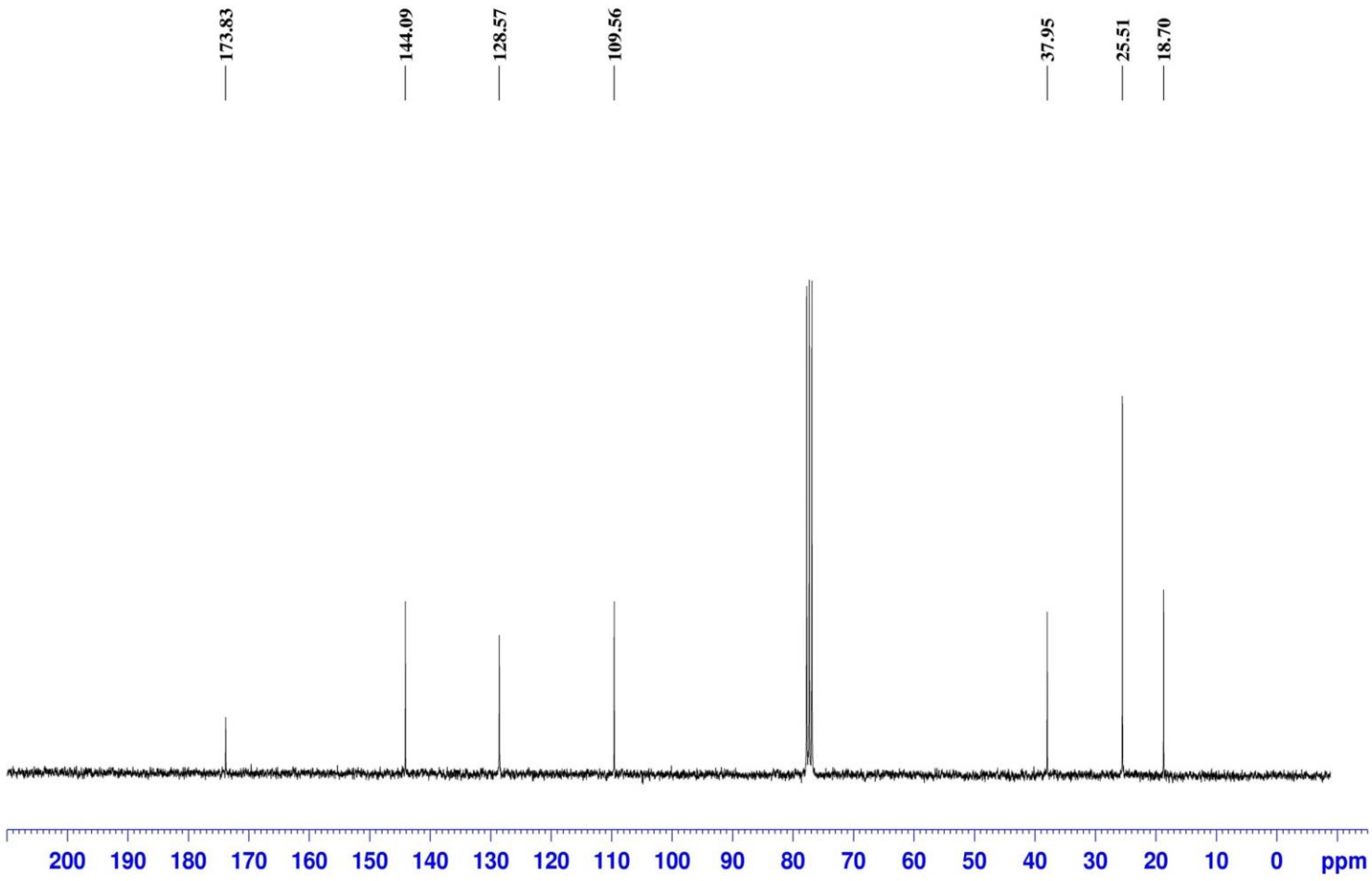


6z

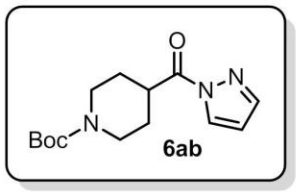


cyclobutyl(1H–pyrazol–1–yl)methanone
100 MHz, CDCl3

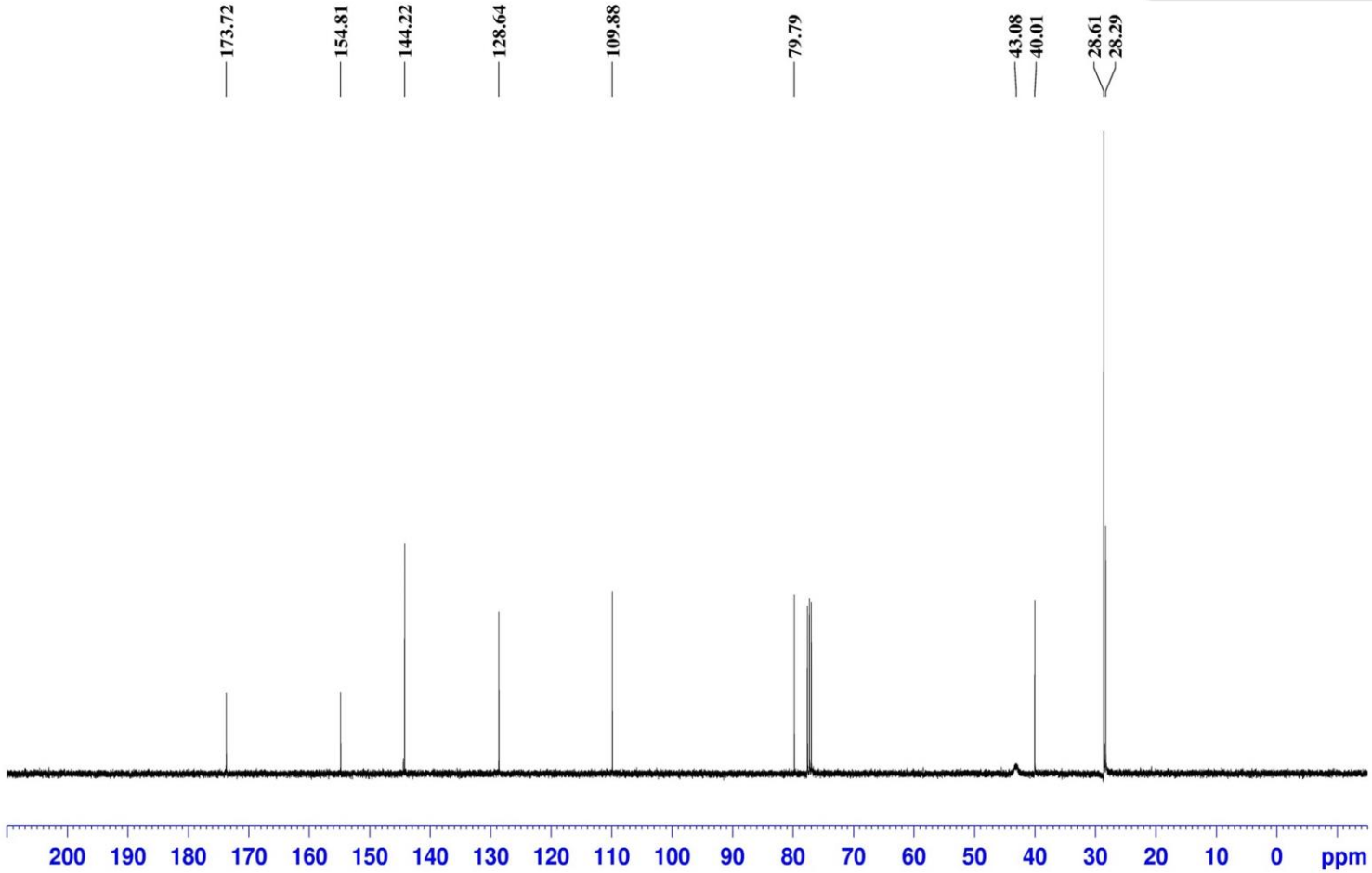




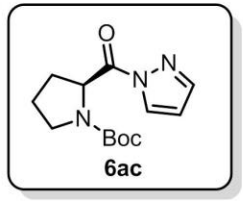
tert−butyl 4−(1H−pyrazole−1−carbonyl)piperidine−1−carboxylate
100 MHz, CDCl3



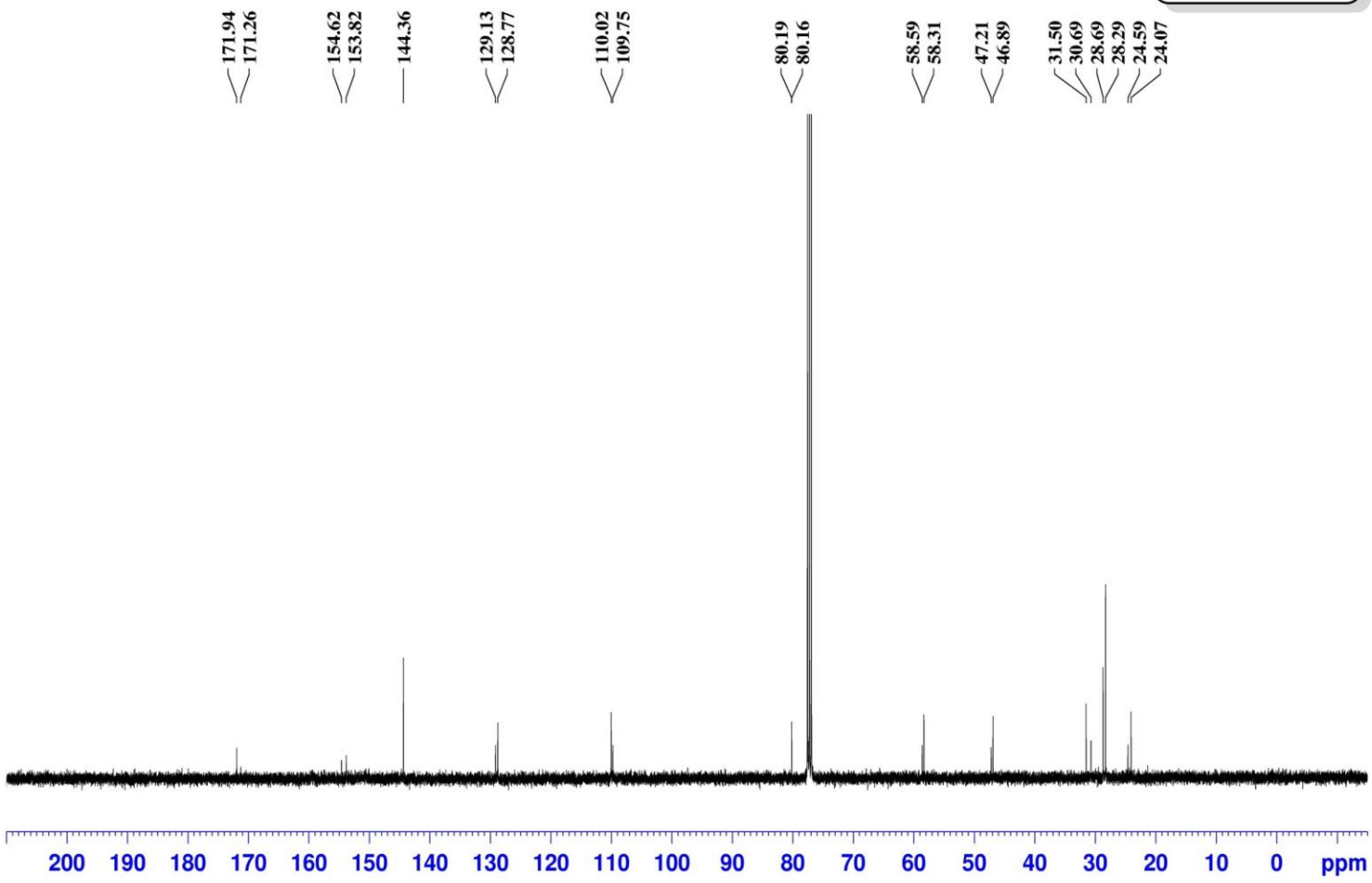
6ab



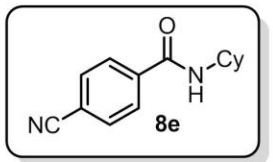
(S)–tert–butyl 2–(1H–pyrazole–1–carbonyl)pyrrolidine–1–carboxylate
100 MHz, CDCl3

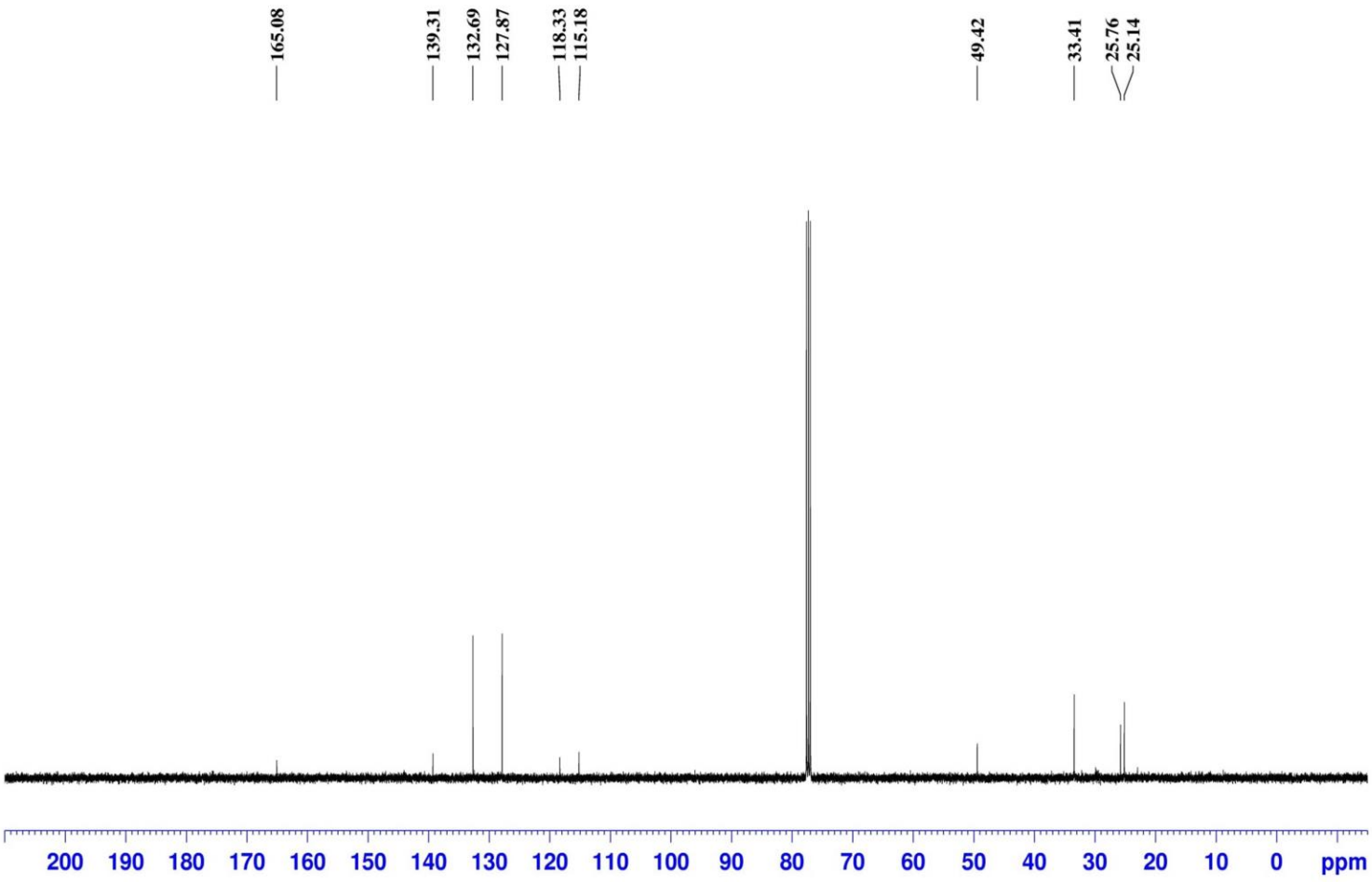


6ac

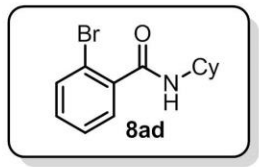


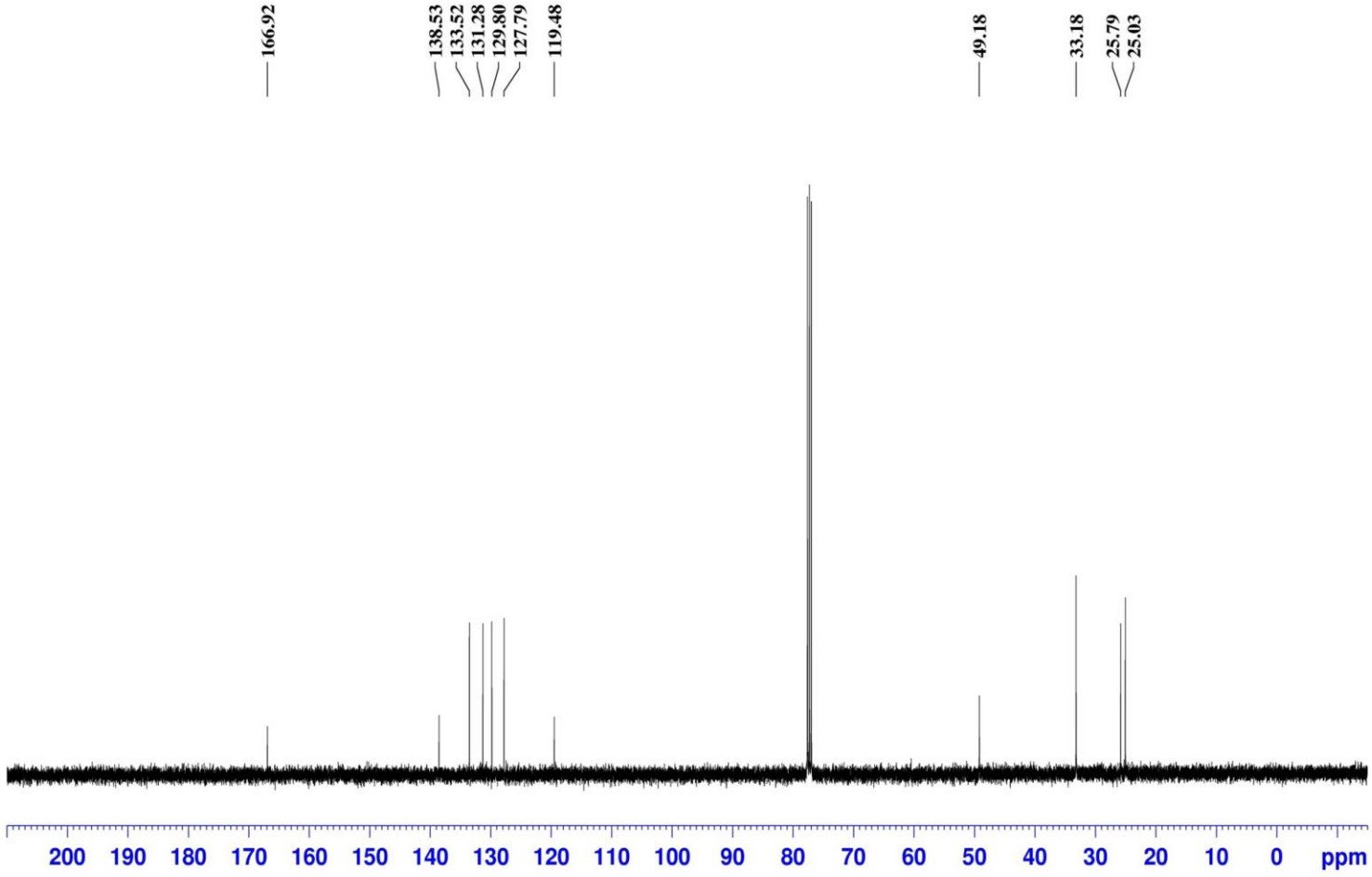
4–cyano–N–cyclohexylbenzamide
100 MHz, CDCl3





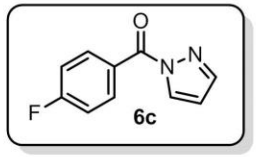
2–bromo–N–cyclohexylbenzamide
100 MHz, CDCl3

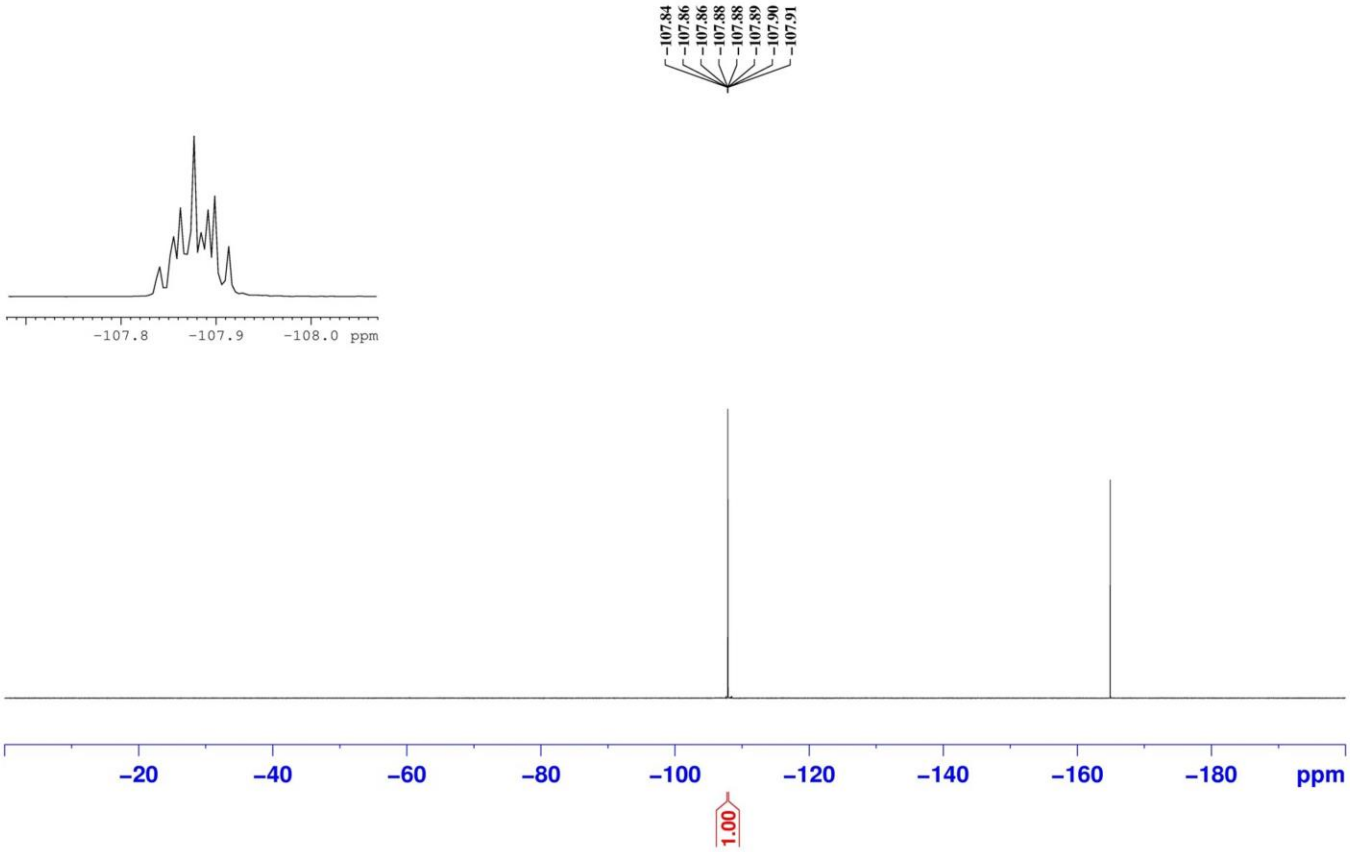




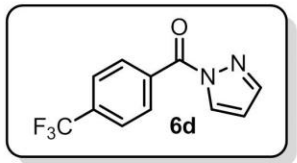
^{19}F NMR Spectra of Synthesized Compounds

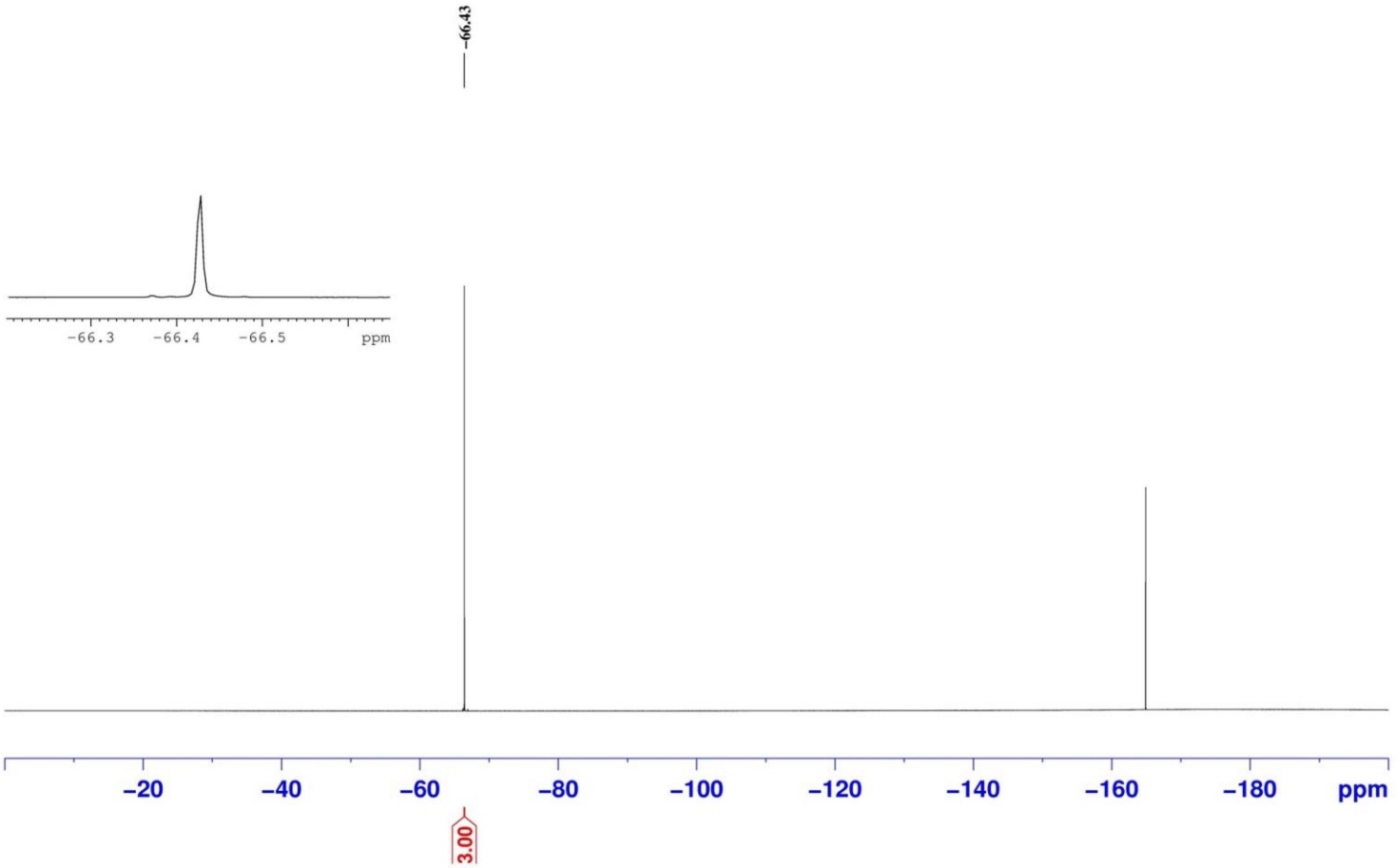
(4–fluorophenyl)(1H–pyrazol–1–yl)methanone
377 MHz, CDCl3





(1H–pyrazol–1–yl)(4–(trifluoromethyl)phenyl)methanone
377 MHz, CDCl3





(2−bromo−4−fluorophenyl)(1H−pyrazol−1−yl)methanone
377 MHz, CDCl3