Electronic Supporting Information

Sun Light Assisted Direct Amide Formation via a Charge-transfer Complex

Materials

All the reagents and solvents described in the manuscript were purchased from Sigma-Aldrich and used as received unless noted. Amines were purified by distillation over CaH_2 and kept in the dark over KOH.

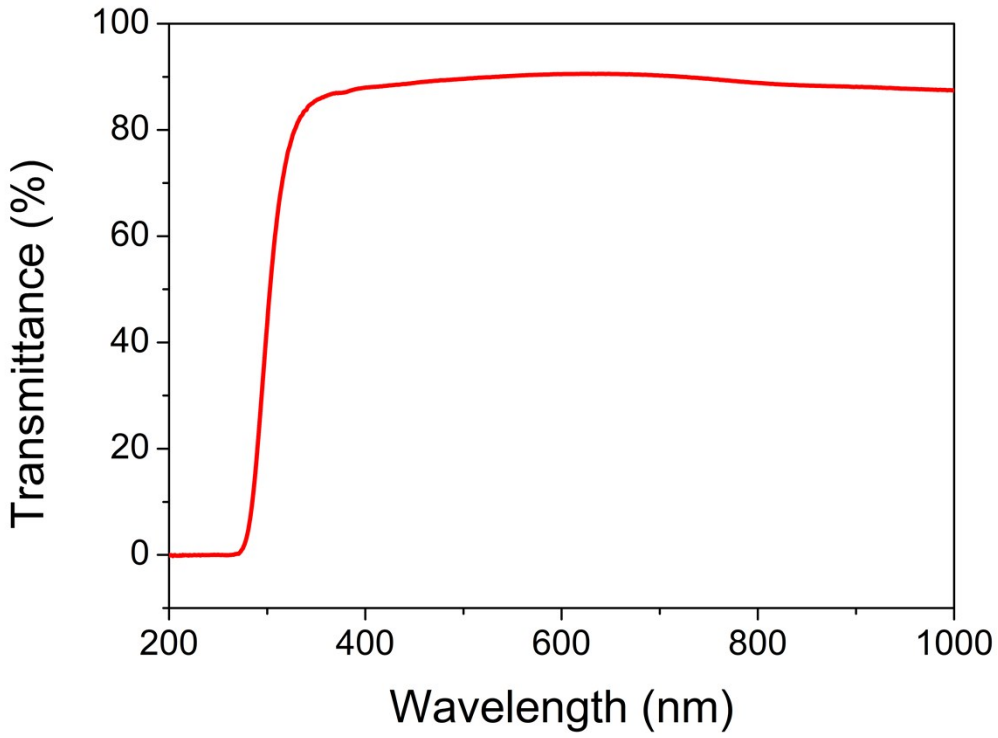
Apparatus

NMR spectra were recorded on Bruker-AM-300, Bruker-AM-400 and Bruker-AM-500 spectrometers. High-resolution mass spectra were recorded using a Waters LCT Premier (TOF) ESI (APCI) instrument. Absorption spectra were recorded on a Shimadzu UV-1601 spectrometer equipped with themperature controlled cell holders. Light intensity was measured using a Nova II- Laser power meter, Ophir. Photo amidation experiments were performed at room temperature in a Pyrex (boro-silicate) glass cell equipped with a magnetic stirrer. All experiments were performed under nitrogen atmosphere. Three different light sources were used for photo amidation experiments: a) a medium-pressure mercury lamp equipped with a 400 nm cutoff filter (light flux at the front side of the cuvette was 49 mW/cm^2); b) a blue LED, λ_{max}=450 nm (light flux at the front side of the cuvette was 55-65 mW/cm^2); the sun, using the boro-silicate vessel wall as the optical

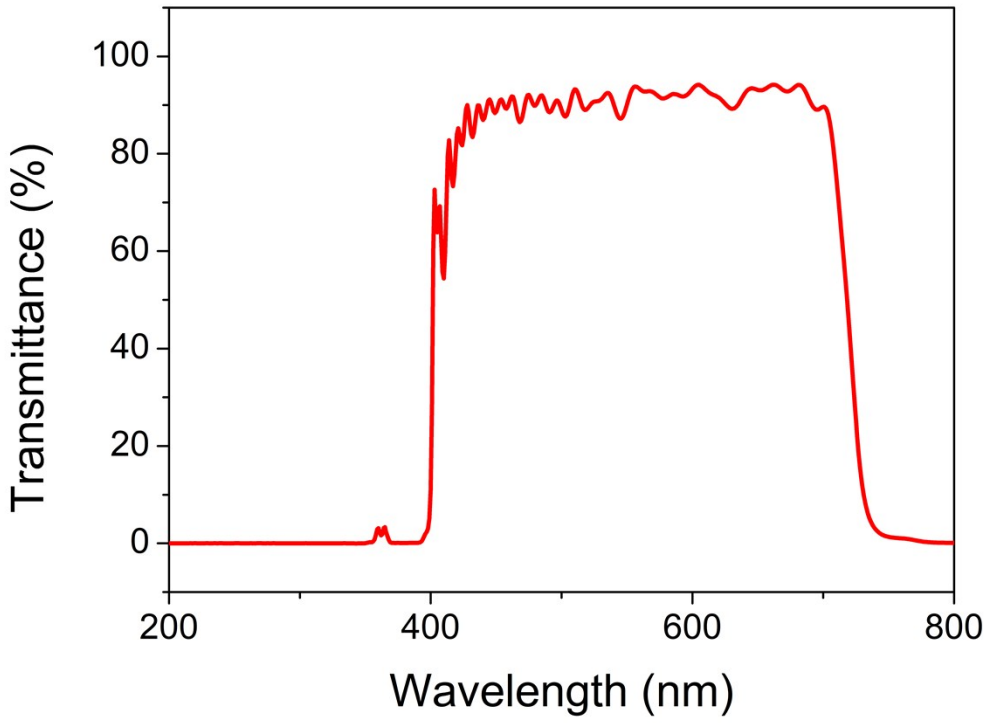
filter (light flux at the front side of the cuvette was 0.2 (early morning, late evening)-59 (at noon) mW/cm^2). The progress of the reaction was followed by analyzing aliquots of the solution at different times after the beginning of the irradiation either by TLC or HPLC. G4 calculations were carried also out using Gaussian 09.[1]

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

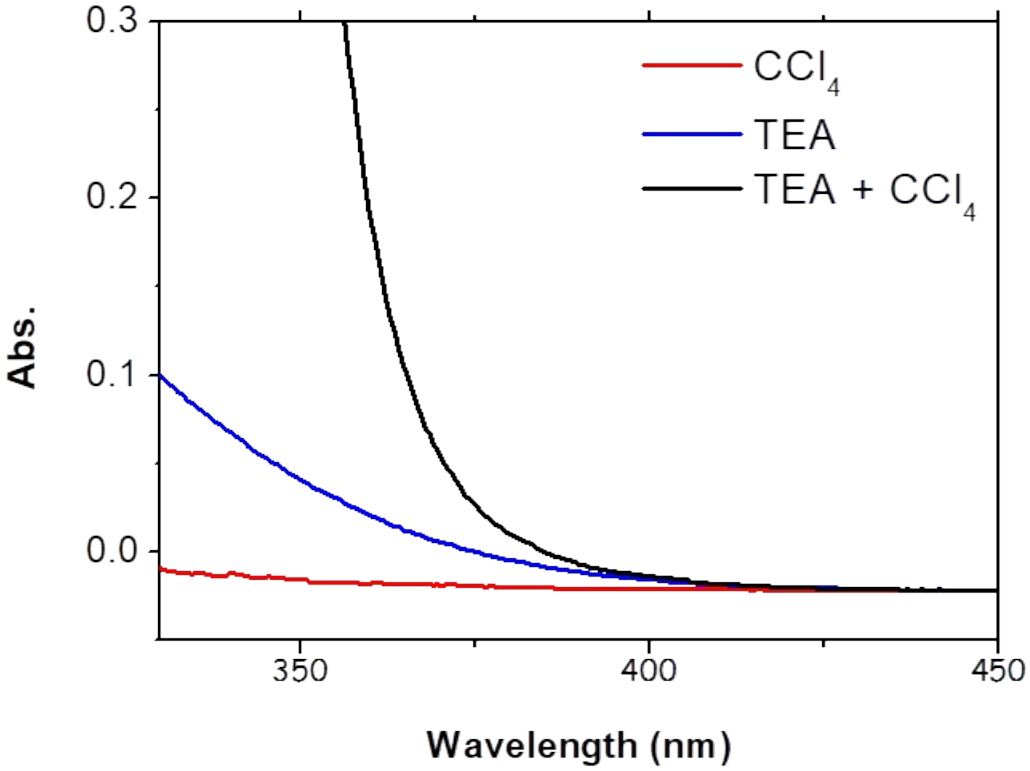
Transmission Spectrum of borosilicate glass



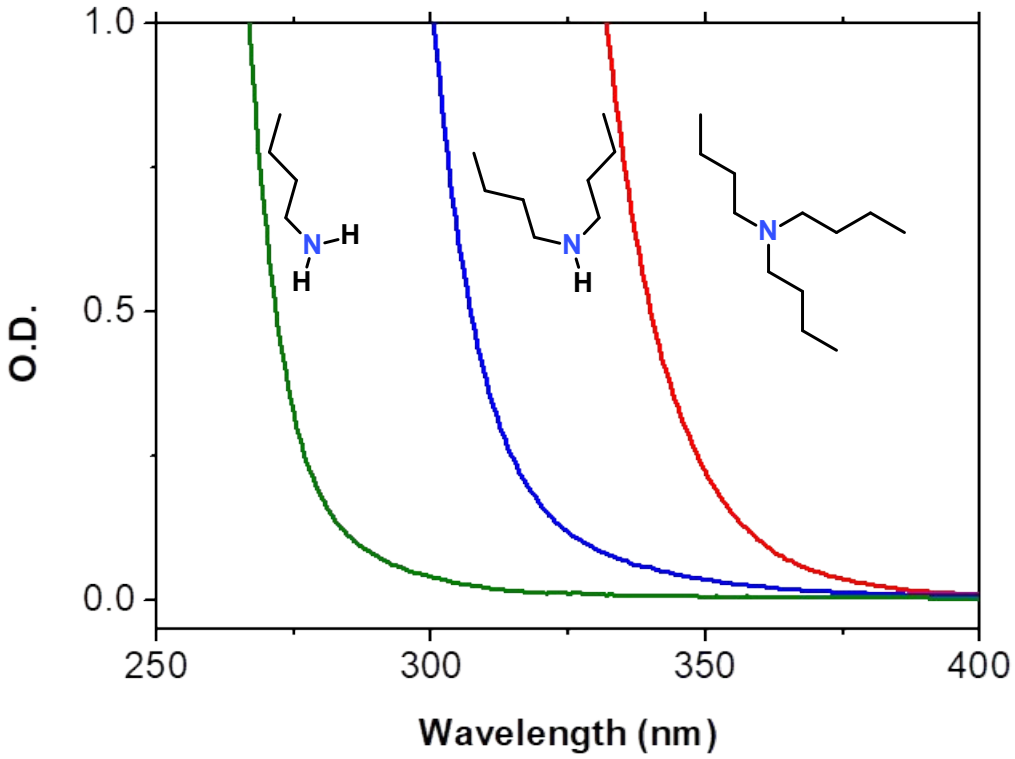
Filter used for arc-lamp



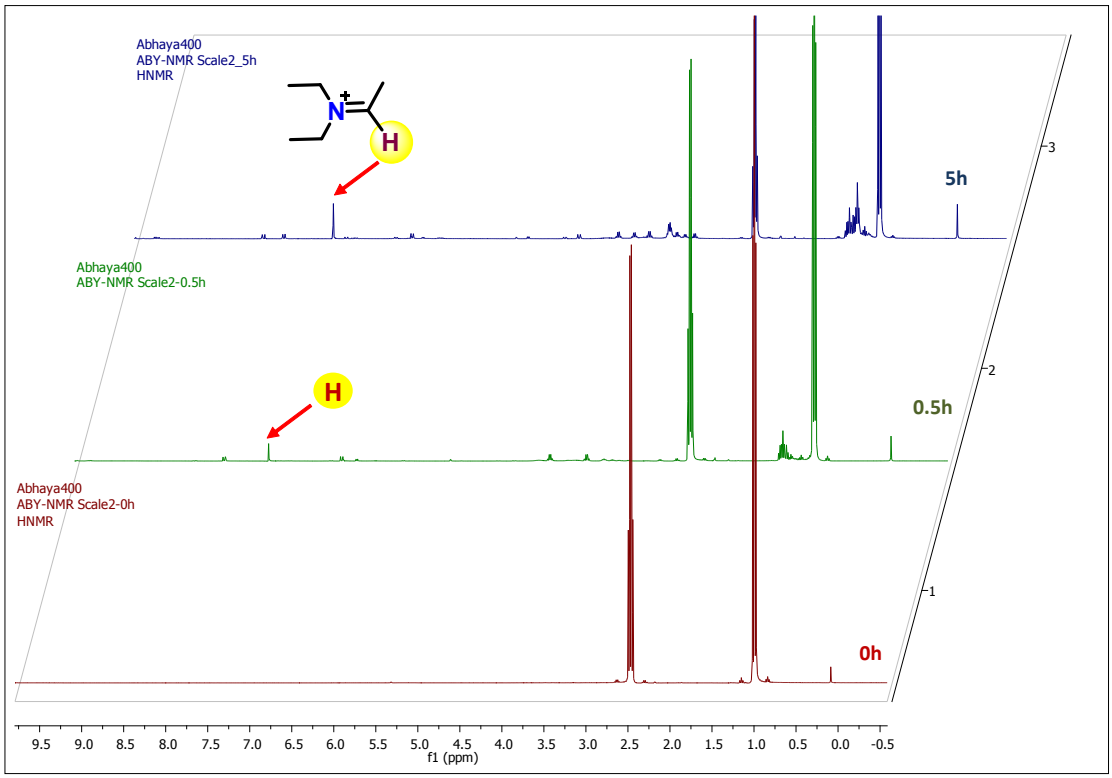
Triethylamine – CCl_4 1:1 charge transfer complex absorption in the UV-VIS spectrum.

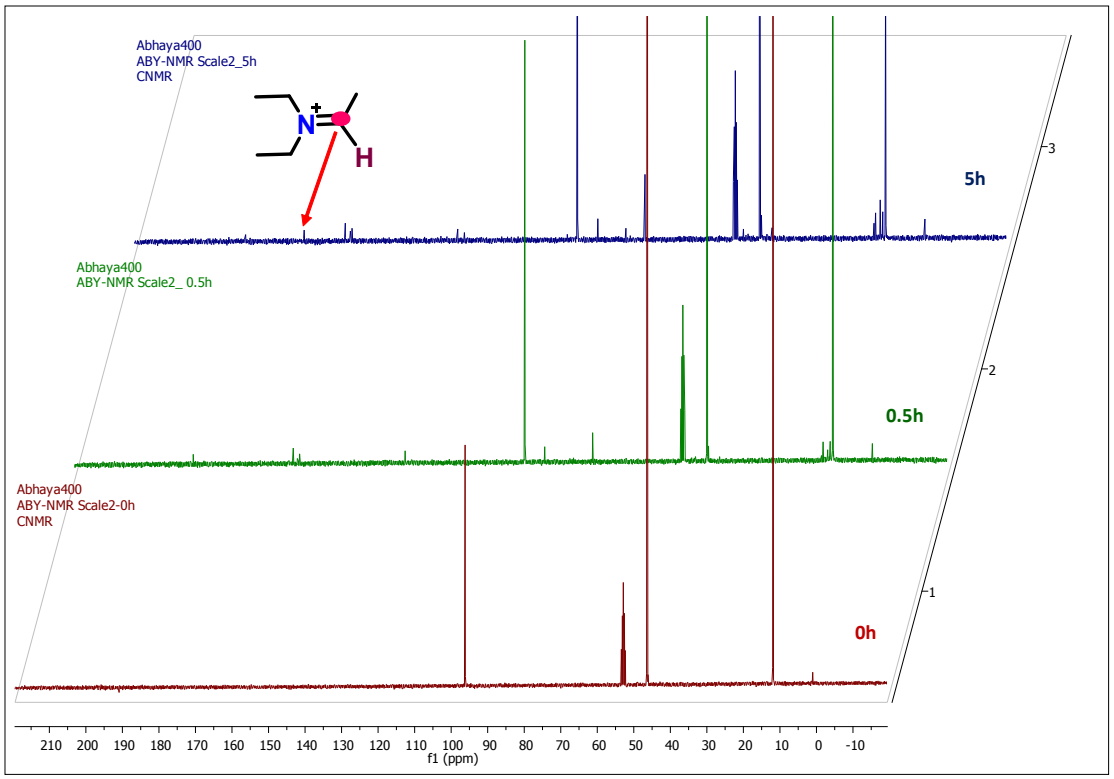


UV-VIS spectra of Butyl-amine, dibutylamine and tribulty amine complexes with CCl_4.

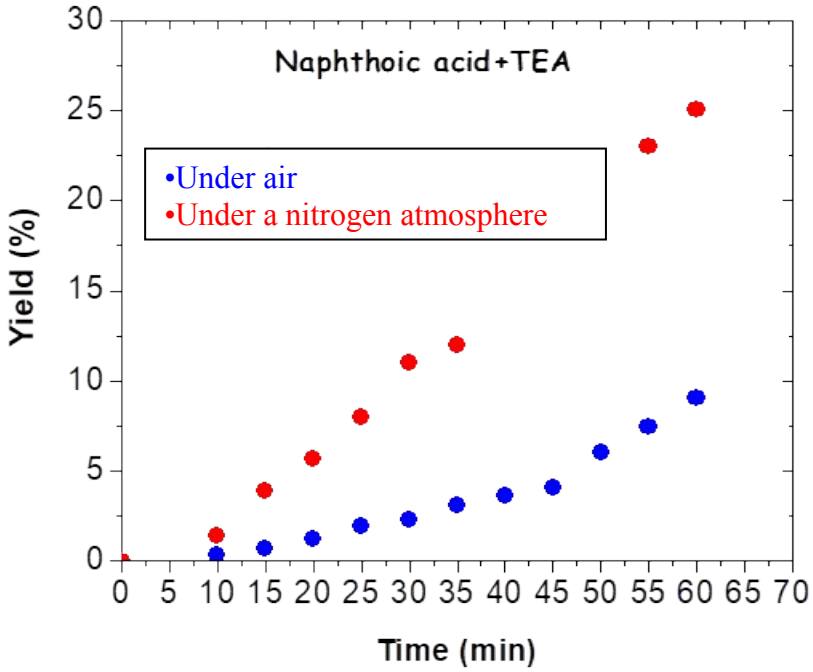


NMR study of triethylamine in $3CCl_4 + 1CD_2Cl_2$ revealing the formation of iminium ion: ^{1}H and ^{13}C NMR spectra were recorded at the noted time intervals.





Oxygen Inhibition of the reaction of 2-napthoic acid with triethylamine (yield determined by HPLC)



Determination of K_{eq}

The value of the equilibrium constant, K, was determined by the iterative process of calculating the concentration of the CCl_4-TEA complex and its molar absorbance via equations 1 and 2.

Equation 1

$$K = \frac{[Complex]}{([TEA]_0 - [Complex])([CCl_4]_0 - [Complex])}$$

Equation 2

$$A = \varepsilon_{complex} \cdot l \cdot [Complex] + \varepsilon_{TEA} \cdot l \cdot ([TEA]_0 - [Complex])$$

Were

$[TEA]_0$ is the concentration of TEA calculated by the mass of TEA added divided by the volume of the solution.
$[CCl4]_0$ is the concentration of CCl_4 calculated by the mass of CCl_4 added divided by the volume of the solution.
$[Complex]$ is the concentration of the complex.
l is the optical pathway
$\varepsilon_{complex}$ is the molar absorption of the complex
ε_{TEA} is the molar absorption of TEA

The following experiment was conducted. 6 solutions where prepared, for each one the concentration of the CCl4 was kept constant and high relatively to the TEA for maintaining the ratio of CCL4:TEA in the complex low.
The TEA was added to the solutions in different amounts. The absorbance of the solutions was measured as well as the absorbance of TEA and CCl4 in separate.

The values were calculated for the values measured at 330 nm

ε_{TEA} was obtained by measuring the absorbance of neat TEA in certain concentrations.

The same experiment wasz performed in different temperatures to learn about the nature of the equilibrium constant, K.

The procedure commenced with completing the calculations for values of K ranging from 0.01 to 100.01 in steps of 1, then plotting calculated complex concentration as a function of CCl_4 concentration.
In order to discover the correct solution these plots where compared to the plot of the absorbance of the solution as a function of CCl_4 concentration. The RSS (Residual Sum of Squares) was calculated for each one of the calculated plots with reference to the empiric plot. The K was selected as the one with the minimal RSS.
The calculations where then refined to a range of K of 0.01 to 1 in 0.01 steps. The same procedure for selecting the K was made.

General procedure for the preparation of amides 10a–q

The relevant carboxylic acid (1 equiv., 0.1M), amine (7.5 equiv., 0.717M) and K_2CO_3 (6.8 equiv., 0.687M) were added to a mixture of CCl_4 (6.9M) and DCM (3.6M) in a borosilicate vessel equipped with a rubber stopper and the combined mixture degassed using N_2 or argon. The oxygen-free reaction mixture was then stirred under sun light for the indicated time. The progress of the reaction was monitored by thin layer chromatogrophy. After acidification of the TLC sample with 1M HCl and extraction with DCM. Upon completion the reactions were acidified with 1M solution of HCl and extracted with DCM. The organic extracts were dried over anhydrous Na_2SO_4 and the solvent removed using a rotary evaporator under reduced pressure. The residue were subjected to column chromatography to isolate the amides as a pure product.

Procedure for the large scale (10g) reaction

2-Naphthoic acid (10 g, 58.14 mmol), triethylamine (61.27 mL, 436.05 mmol) and K_2CO_3 (26.07 g, 188.95 mmol) were added to a mixture of CCl_4 (450 mL) and DCM (150 mL) in a borosilicate 2L round bottom flask with a rubber stopper and the combined mixture degassed using N_2. The oxygen-free reaction mixture was then stirred under sun light for 24 h. The reaction was found to incomplete by thin layer chromatogrophy (TLC). TLC was performed after acidification of the TLC sample with 1M HCl and extraction with DCM. The reaction mixture was filtered over whatman filter paper to removed K_2CO_3 that had been finely crushed by the magnet during reaction. Fresh K_2CO_3 (26.07 g) was added to reaction mixture which was degassed with N_2. The reaction mixture was allowed to stir exposed to sunlight sun light further 16 h. Again reaction was found to incomplete by TLC. Filtration was repeated and fresh K_2CO_3 (26.07 g) added to the solution. The reaction was found to be complete after additional 16 h of sunlight exposure. Upon completion the reaction was acidified with 1M solution of HCl and extracted with DCM. The organic extract was dried over anhydrous Na_2SO_4 and the solvent removed using a rotary evaporator under reduced pressure. The residue was subjected to column chromatography to isolate the pure *N*-*N*-diethyl-2-naphthamide (**10k**) with 91% yield (12.02 g).

Procedure for the large scale (10g) reaction with mechanical stirring

2-Naphthoic acid (10 g, 58.14 mmol), triethylamine (61.27 mL, 436.05 mmol) and K_2CO_3 (52.14 g, 377.91 mmol) were added to a mixture of CCl_4 (450 mL) and DCM (150 mL) in a borosilicate 2L round bottom flask with a rubber stopper and the combined mixture degassed using N_2. The oxygen-free reaction mixture was then stirred using mechanical stirrer under sun light. After 65 h of stirring the proton NMR of reaction mixture shown about 85% conversion. The reaction was acidified with 1M HCl and extracted with DCM. The organic extract was dried over anhydrous Na_2SO_4 and the solvent removed using a rotary evaporator under reduced pressure. The residue was subjected to column chromatography to isolate the pure *N*-*N*-diethyl-2-naphthamide (**10k**) with 80% yield (10.52 g).

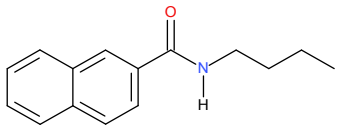
Procedure for synthesis of *N*-butyl-2-naphthamide using mixture of amines (DABCO (1,4-diazabicyclo[2.2.2]octane) and *n*-butylamine)

The relevant 2-naphthoic acid (0.50 g, 2.90 mmol), *n*-butylamineamine (0.43 mL, 4.35 mmol), DABCO (2.44 g, 21.75 mmol) and K_2CO_3 (2.60 g, 18.89) were added to a mixture of CCl_4 (20 mL) and DCM (10 mL) in a borosilicate vessel equipped with a rubber stopper and the combined mixture degassed using N_2. The oxygen-free reaction mixture was then stirred under sun light exposure for 62 h. The starting material was shown to have undergone 80% conversion into product by NMR of the reaction mixture. The reaction was acidified with 1M solution of HCl and extracted with DCM. The organic extract was dried over anhydrous Na_2SO_4 and the solvent removed using a rotary evaporator under reduced pressure. The residue was subjected to column chromatography to isolate the *N*-butyl-2-naphthamide in 65% yield (0.430 g) as a pure product.

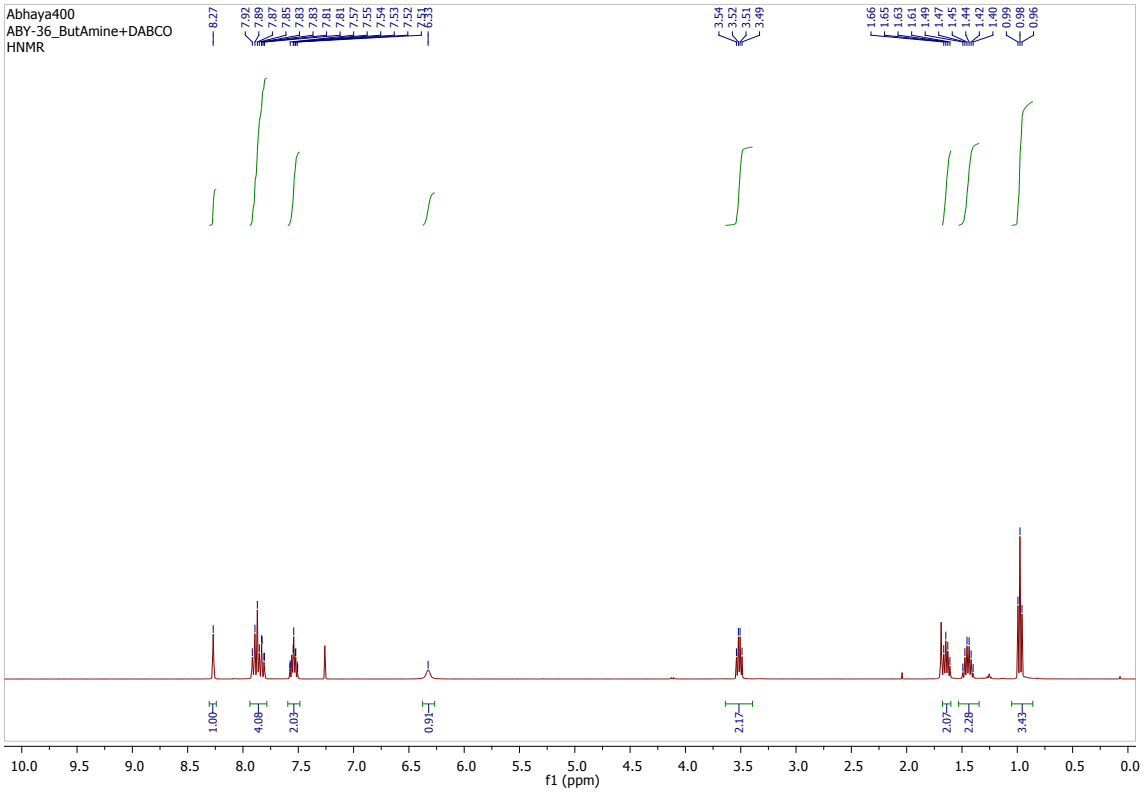
When this reaction is carried out in the absence of butylamine the anhydride of napthoic acid can be ioslated from the reaction . In reactions carried out under the general proced (without DABCO) the anhydride cannot be observed. These reactions are also faster.

Characterization Data

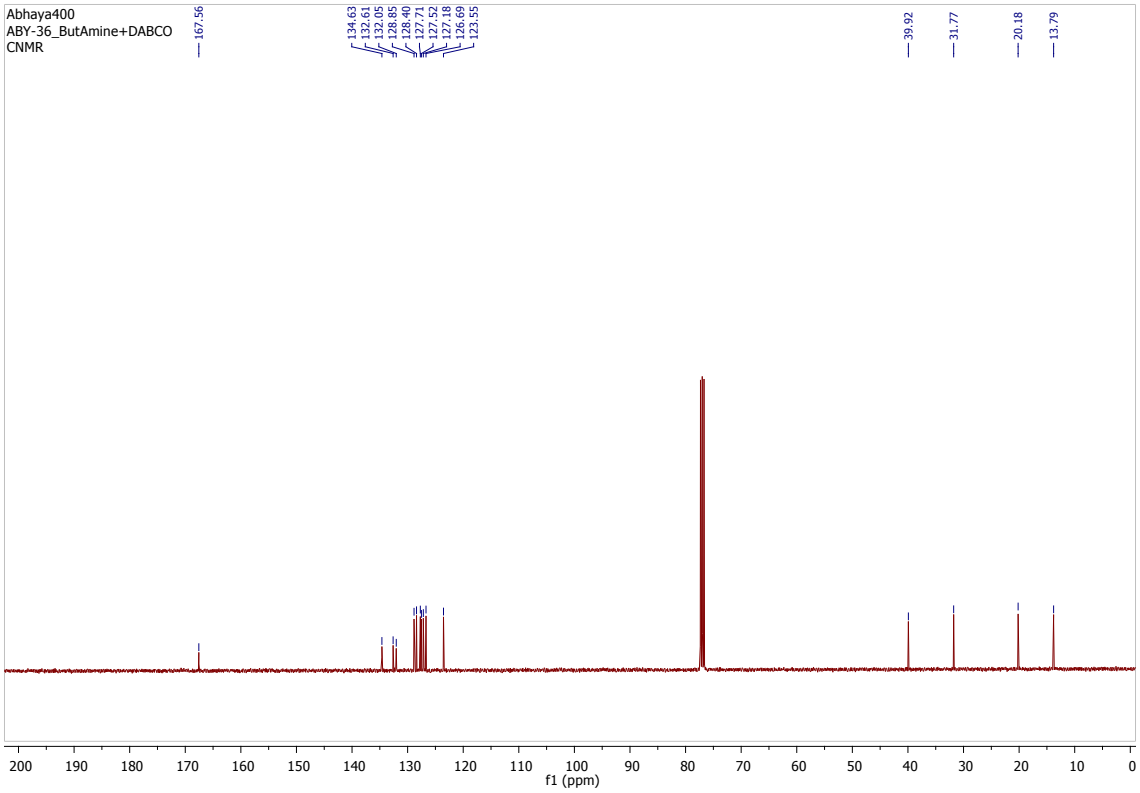
N-Butyl-2-naphthamide (11)[2]



Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.95 – 7.76 (m, 4H), 7.62 – 7.45 (m, 2H), 6.33 (br, 1H), 3.51 (dd, *J* = 13.0, 7.1 Hz, 2H), 1.64 (dd, *J* = 14.8, 7.6 Hz, 2H), 1.45 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 134.63, 132.61, 132.05, 128.85, 128.40, 127.71, 127.52, 127.18, 126.69, 123.55, 39.92, 31.77, 20.18, 13.79; HRMS (ESI^+) *m/z*: Calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388, found 228.1383.

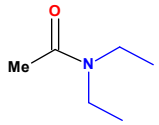


[2] A. Correa and R. Martin, *J. Am. Chem. Soc.*, 2014, 136, 7253.

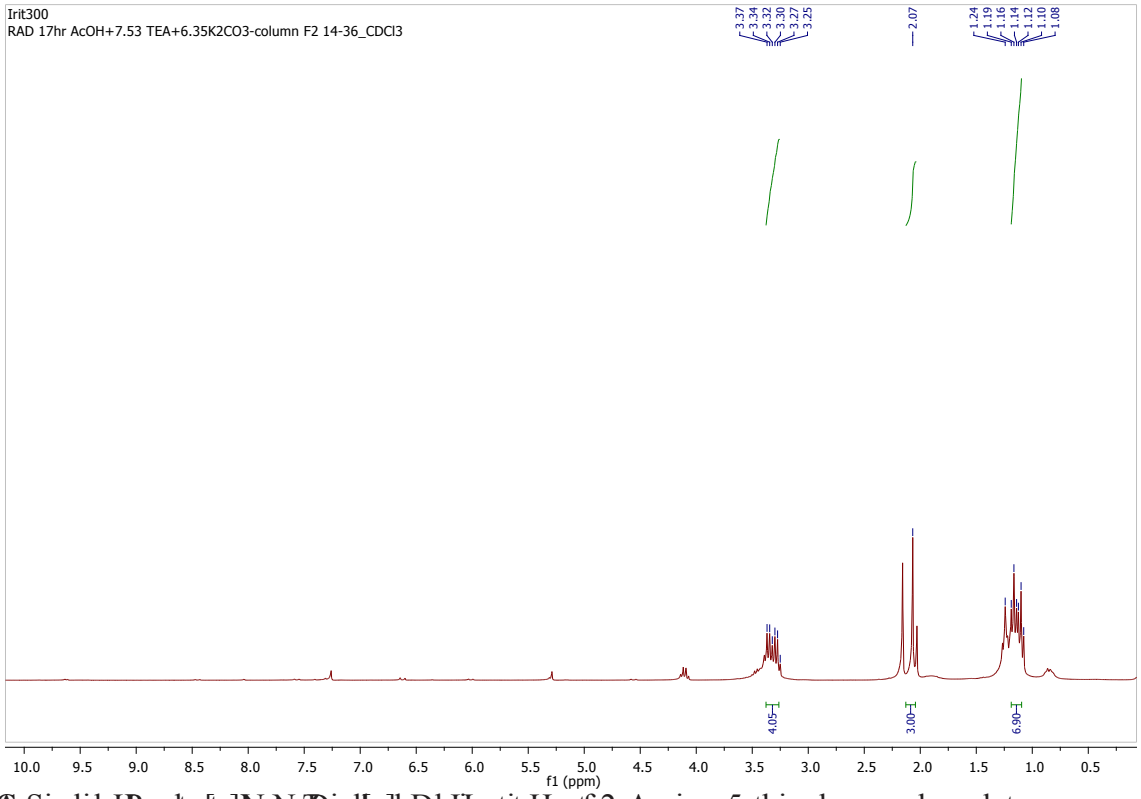


N,*N*-Diethylacetamide (10a)[3]

[3] C. Heyde, I. Zug and H. Hartmann, *Eur. J. Org. Chem*., 2000, 3273.



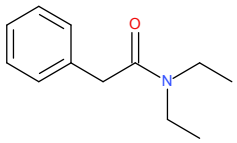
Colorless liquid, yield quantitative (Based on HPLC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38 - 3.25 (m, 4H), 2.07 (s, 3H), 1.24 - 1.08 (m, 6H).



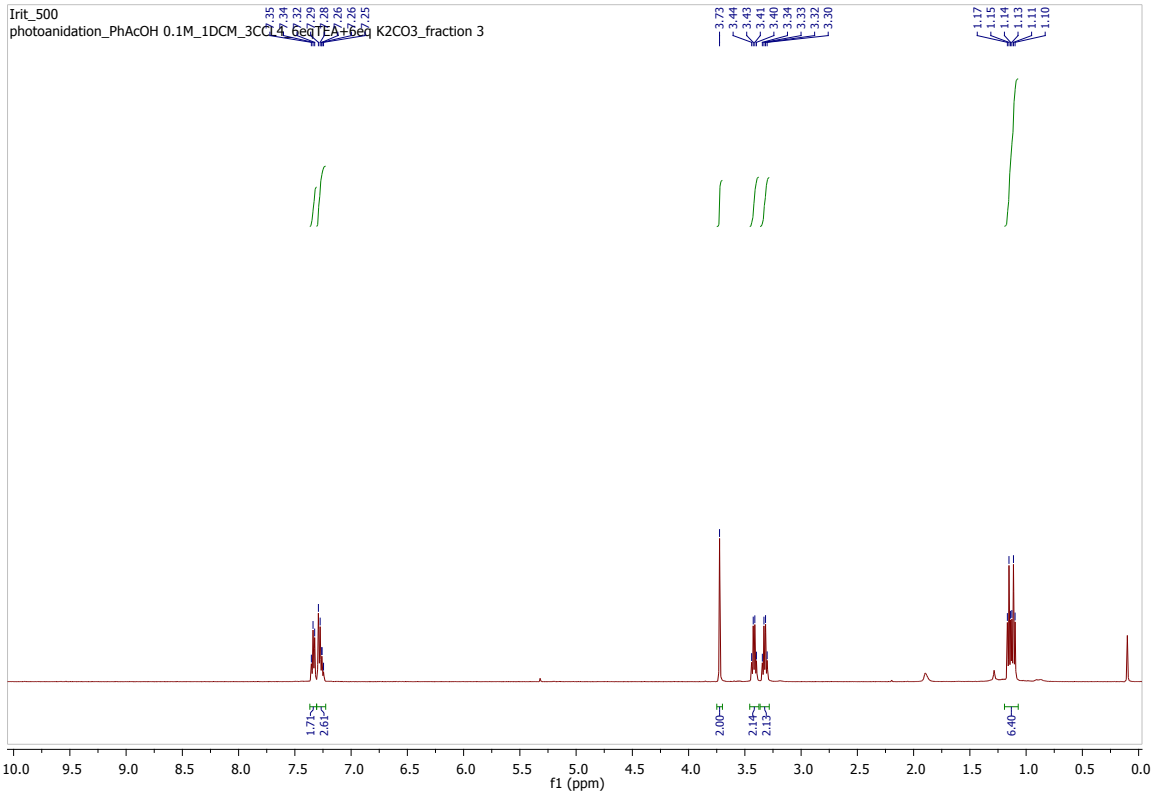
A Simple Route to N,N-Dialkyl Derivatives of 2-Amino-5-thiophenecarboxylates

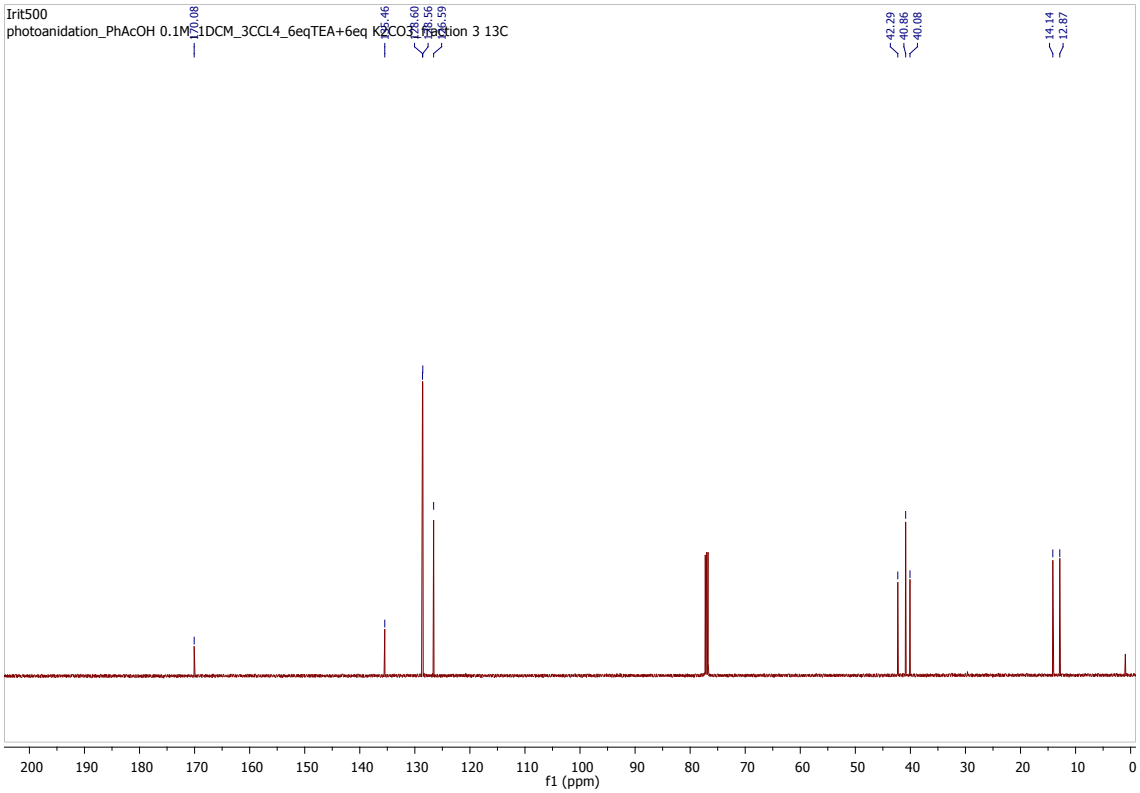
_N_,_N_-Diethyl-2-phenylacetamide (10b)[4]

[4] M. S. Carle, G. K. Shimokura and G. K. Murphy, *Eur. J. Org. Chem*., 2016, 3930.



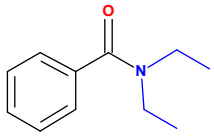
Yellow liquid, yield 79% (0.274g); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, J = 7.4 Hz, 2H), 7.30 – 7.24 (m, 3H), 3.73 (s, 2H), 3.42 (q, J = 7.1 Hz, 1H), 3.32 (q, J = 7.1 Hz, 1H), 1.18 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.08, 135.46, 128.60, 128.56, 126.59, 42.29, 40.86, 40.08, 14.14, 12.87; HRMS (ESI^{+}) *m/z*: Calcd for $C_{12}H_{18}NO$ $[M+H]^{+}$ 192.1388, found 192.1336.



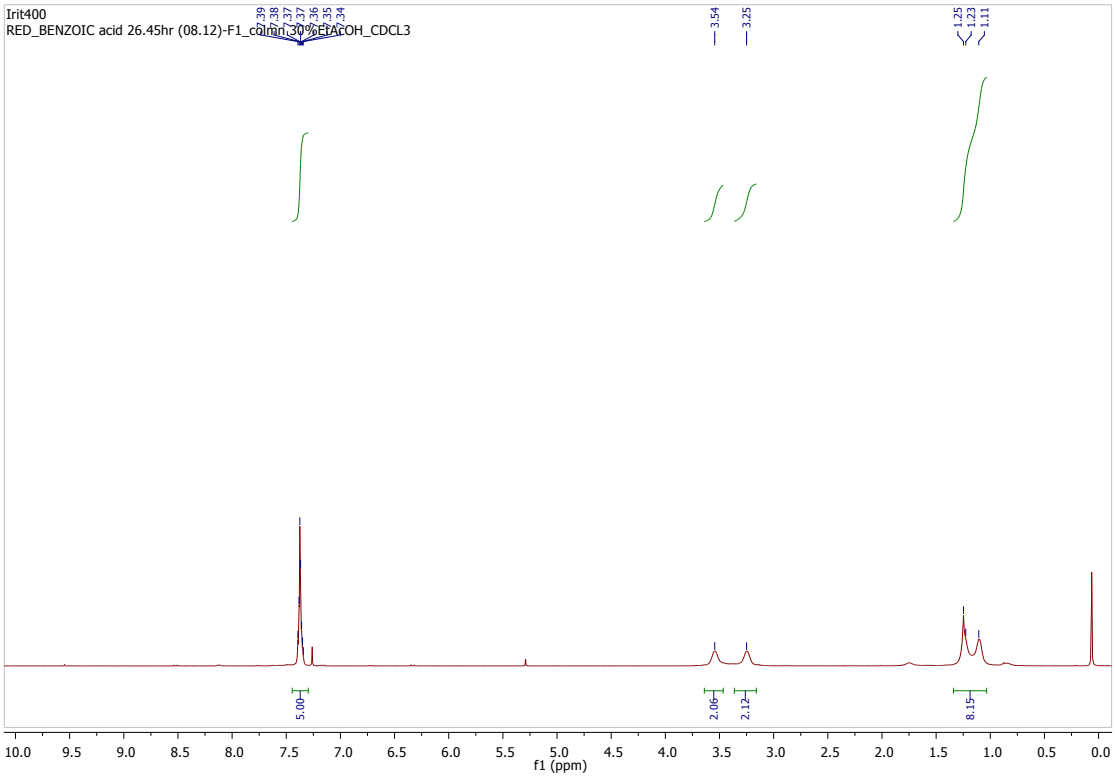


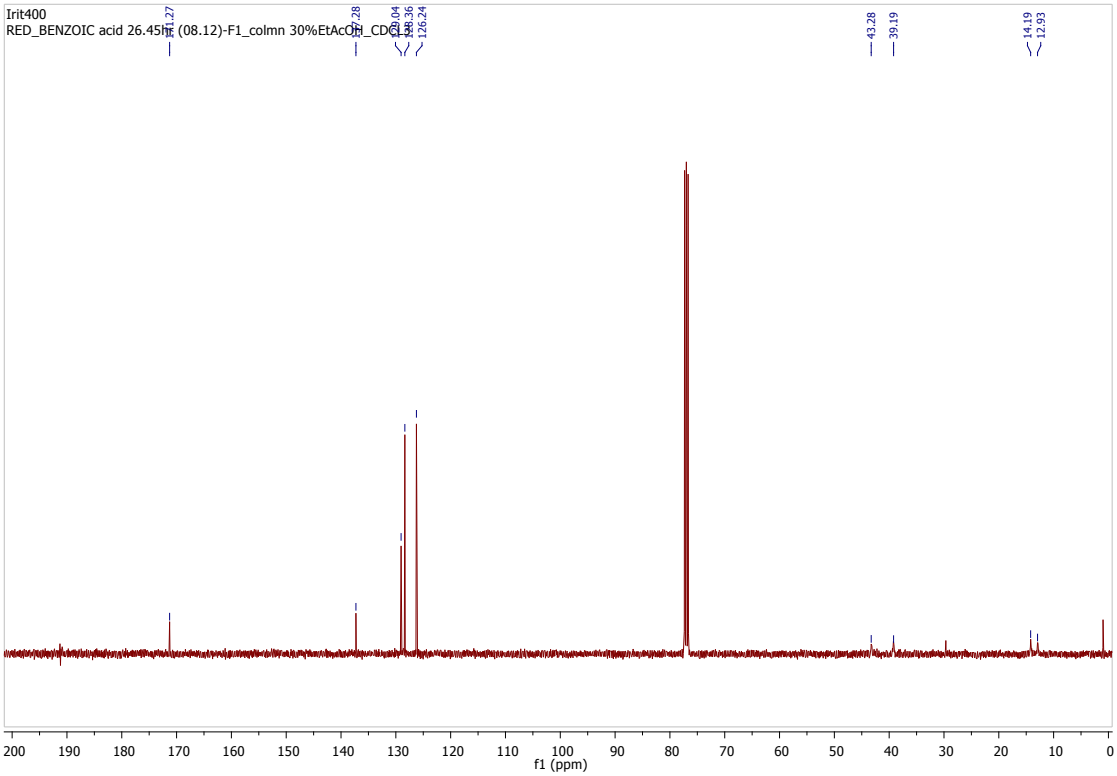
[5] Z. Yin, Z. Wang, W. Li and X.-F. Wu, *Eur. J. Org. Chem*., 2017, 1769.

_N_,_N_-Diethylbenzamide (10c)[5]

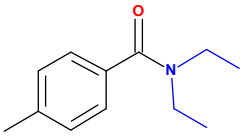


Viscous liquid, yield 83% (0.240 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.34 (m, 5H), 3.54 (br, 2H), 3.25 (br, 2H), 1.27 - 1.09 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.27, 137.28, 129.04, 128.36, 126.24, 43.28, 39.09,14.19, 12.93; HRMS (ESI^+) *m/z*: Calcd for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1231, found 178.1261.

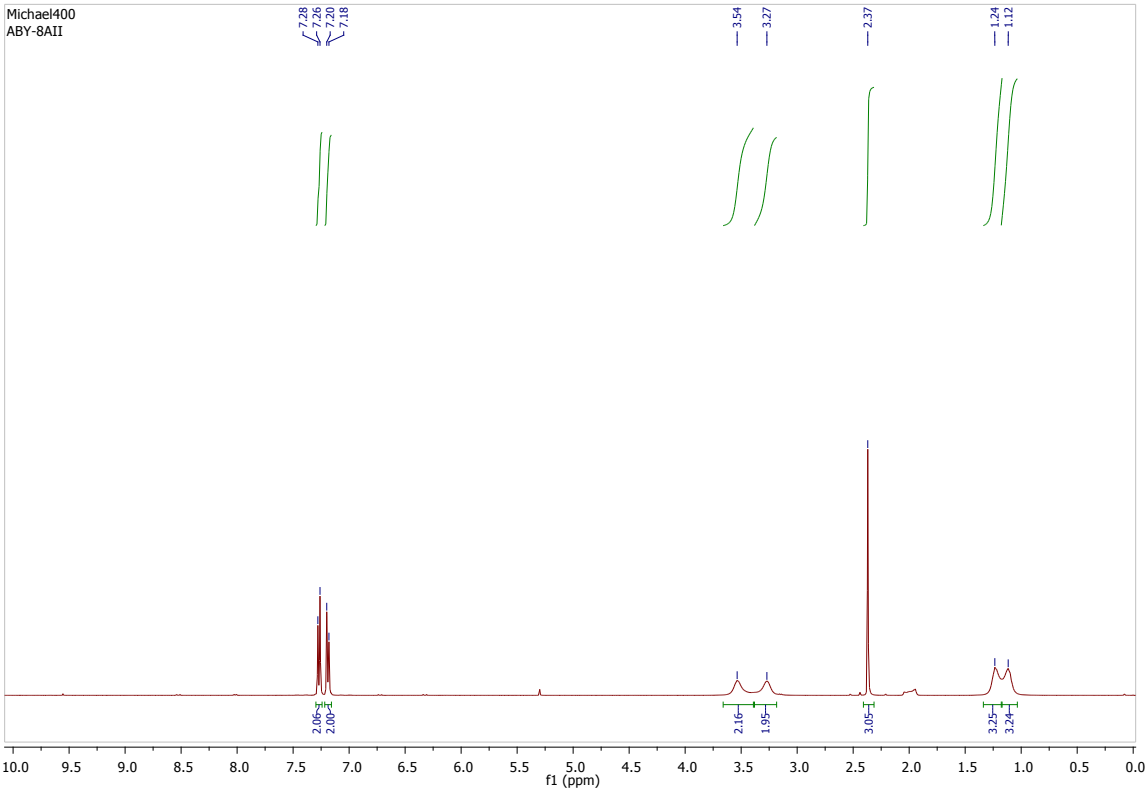



Irit400
RED_BENZOIC acid 26.45mg (08.12)-F1_colmn 30%EtAcOH_CDCl3
171.27
137.28
129.04
128.36
126.24
43.28
39.19
14.19
12.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

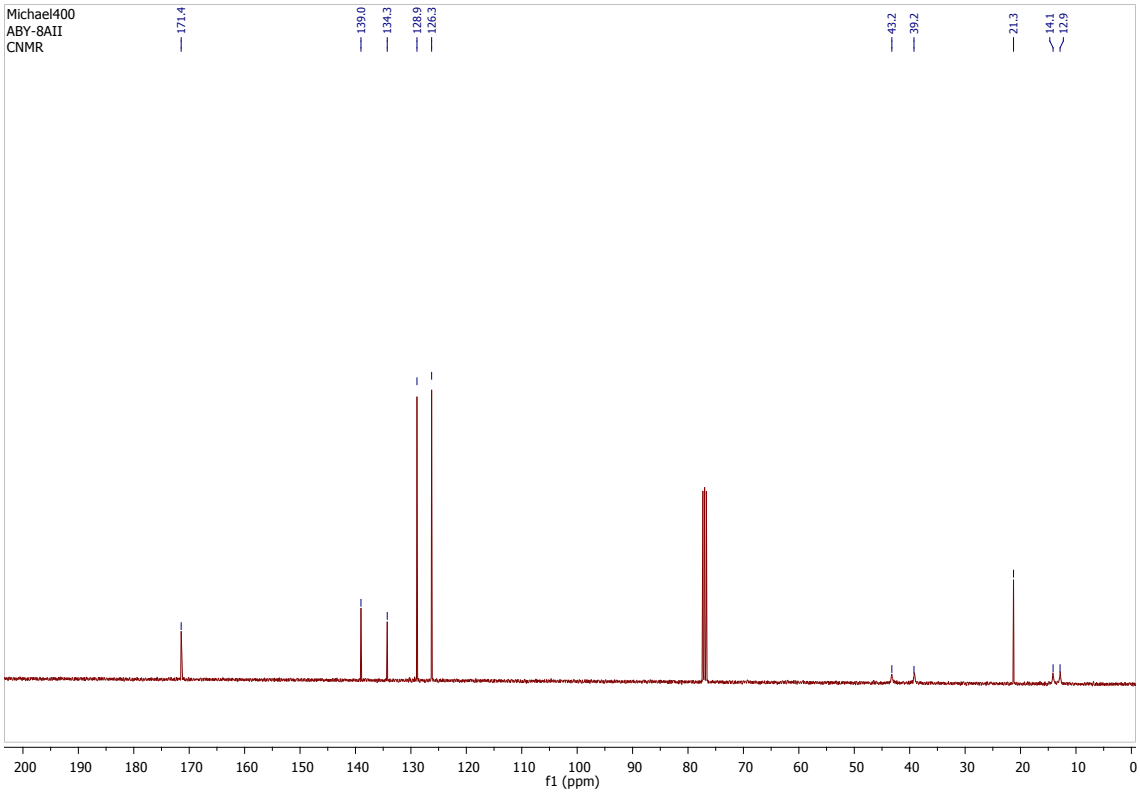
_N_,_N_-Diethyl-4-methylbenzamide (10d)[6]



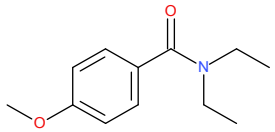
Viscous liquid, yield 63% (0.176 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 3.54 (br, 2H) 3.27 (br, 2H), 2.37 (s, 3H), 1.22 (br, 3H), 1.10 (br, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.45, 139.01, 134.27, 128.90, 126.18, 43.20, 39.16, 21.27, 14.16, 12.70; HRMS (ESI$^+$) *m/z*: Calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1388, found 192.1373.



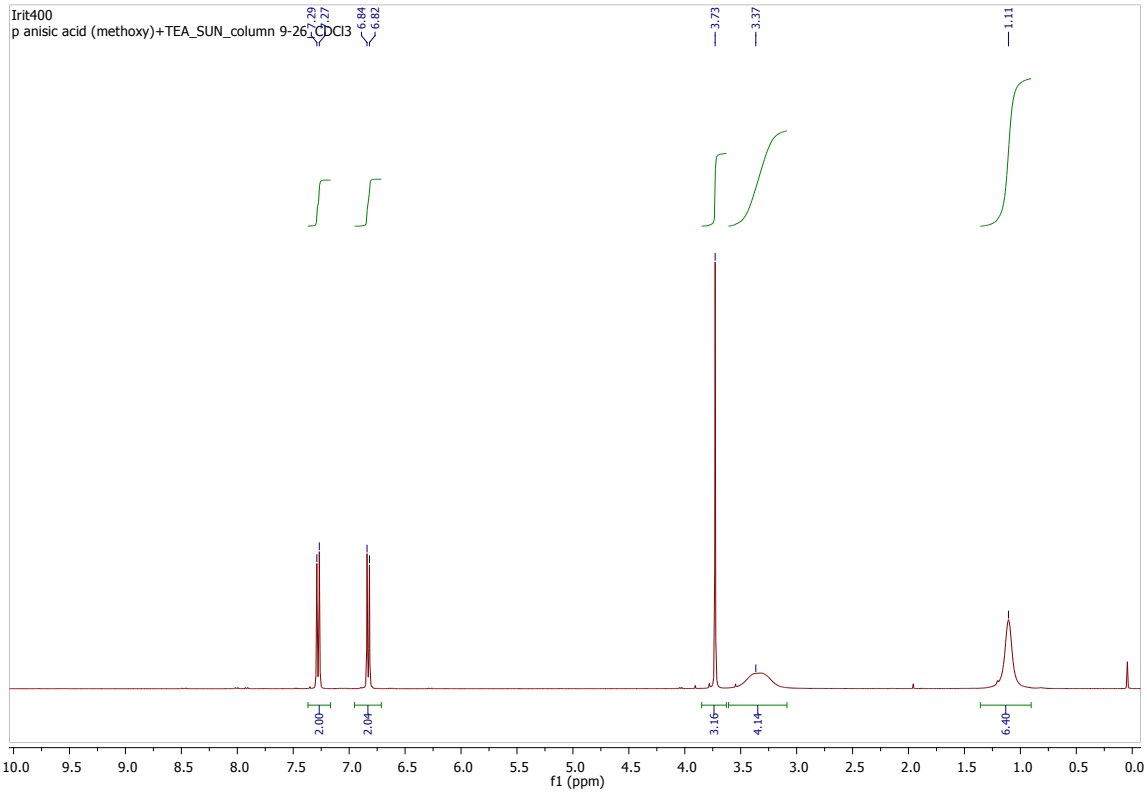
[6] S. L. Zultanski, J. Zhao and S. S. Stahl, *J. Am. Chem. Soc*., 2016, **138**, 6416.


Michael400
ABY-8AII
CNMR
171.4
139.0
134.3
128.9
126.3
43.2
39.2
21.3
14.1
12.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

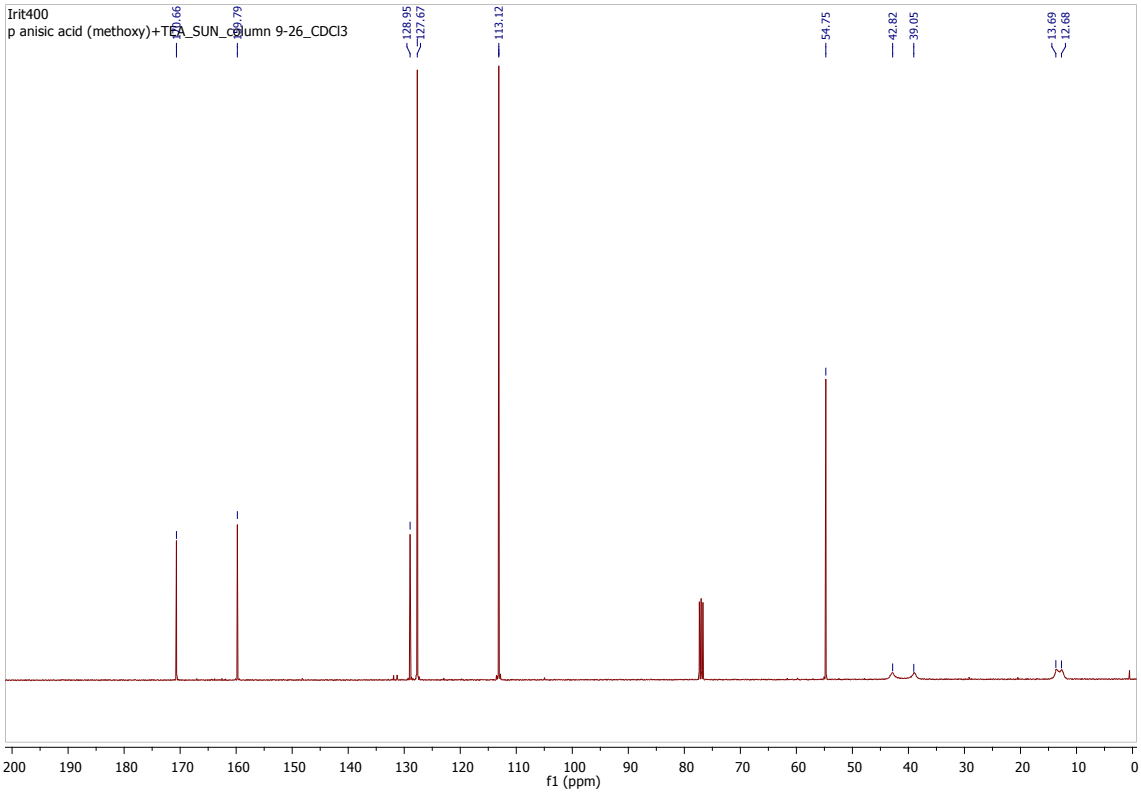
_N_,_N_-Diethyl-4-methoxybenzamide (10e)[7]



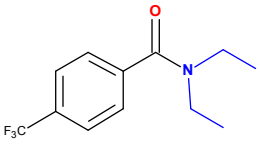
Yellow liquid, yield 45% (0.2632 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 3.33 (br, 4H), 1.17 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.66, 159.79, 128.95, 127.67, 113.12, 54.75, 42.88, 38.82, 13.48, 12.78; HRMS (ESI$^+$) *m/z*: Calcd for $C_{12}H_{18}NO_2$ $[M+H]^+$ 208.1337, found 208.1363.



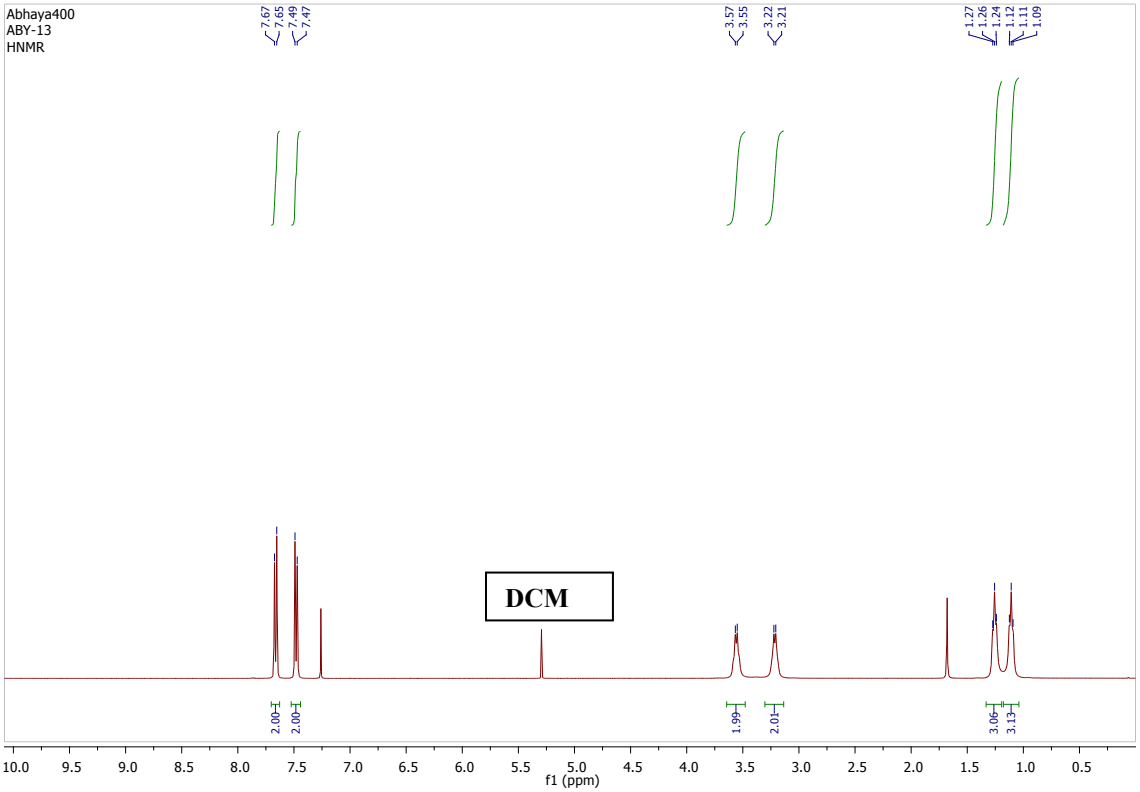
[7] P. Nareddy, F. Jordan, S. E. Brenner-Moyer and M. Szostak *ACS Catal*., 2016, **6**, 4755.


Irit400
p anisic acid (methoxy)+TEA_SUN_column 9-26_CDCl3
169.66
159.79
128.95
127.67
113.12
54.75
42.82
39.05
13.69
12.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

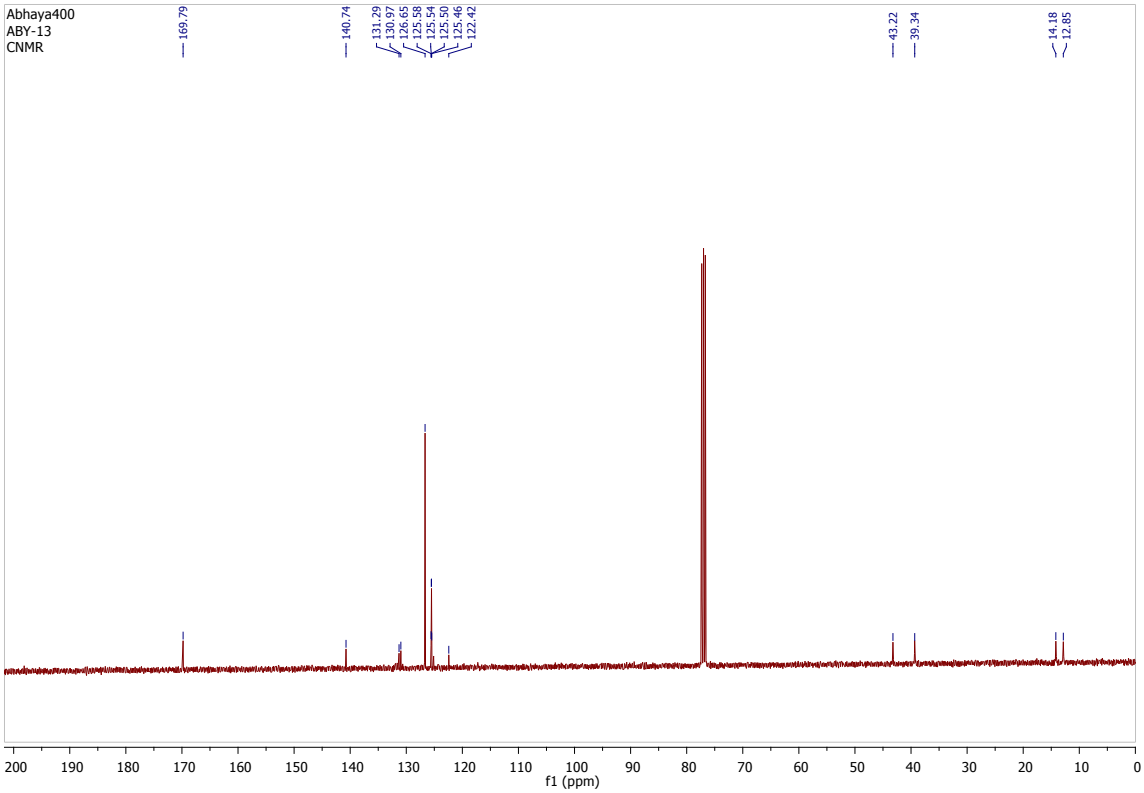
***N*,*N*-Diethyl-4-(trifluoromethyl)benzamide (10f)[8]**



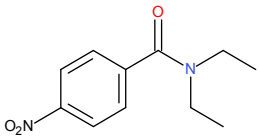
Yellow liquid, yield 88% (0.231 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 3.56 (q, *J* = 6.8 Hz, 2H), 3.21 (q, *J* = 6.7 Hz, 2H), 1.26 (t, *J* = 6.5 Hz, 3H), 1.11 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.79, 140.74, 131.29, 130.97, 126.65, 125.50, 122.42, 43.22, 39.35, 14.18, 12.85; HRMS (ESI^{+}) *m/z*: Calcd for $C_{12}H_{15}F_3NO$ $[M+H]^{+}$ 246.1105, found 246.1096.



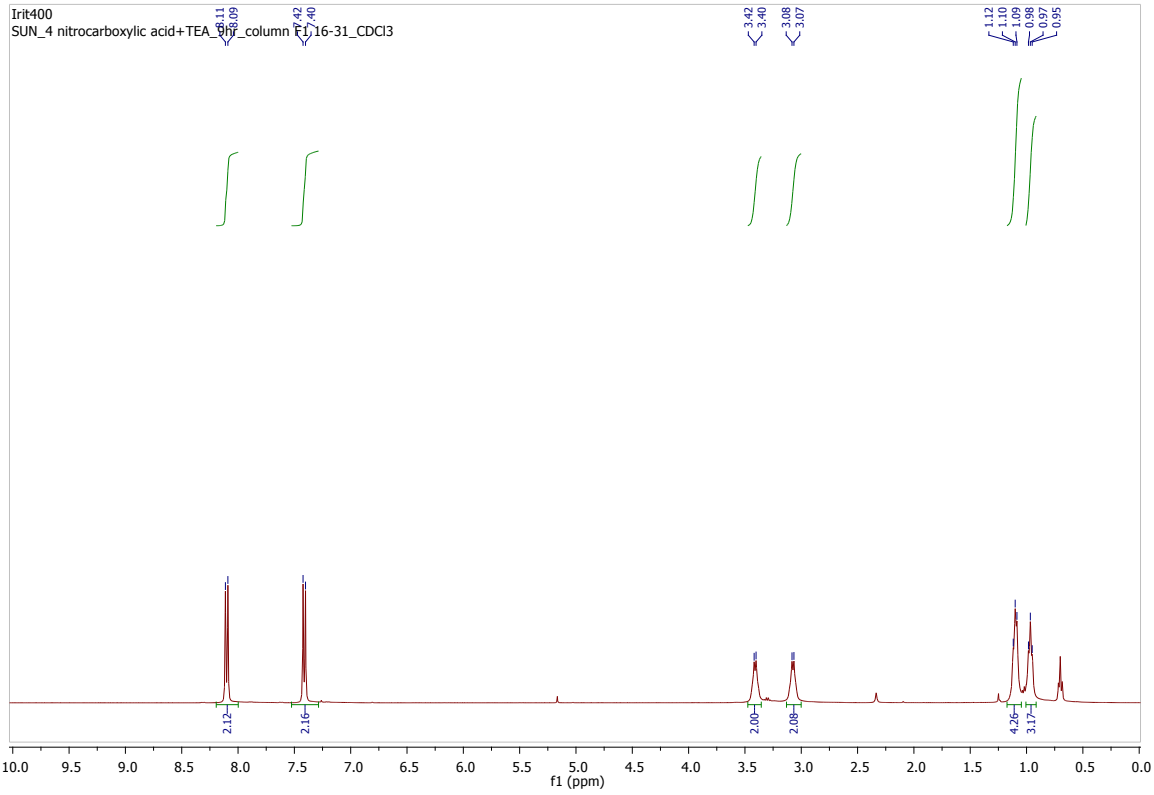
[8] W. Li and X.-F. Wu, *Org. Lett*. 2015, **17**, 1910.


Abhaya400
ABY-13
CNMR
169.79
140.74
131.29
130.97
126.65
125.58
125.54
125.50
125.46
122.42
43.22
39.34
14.18
12.85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

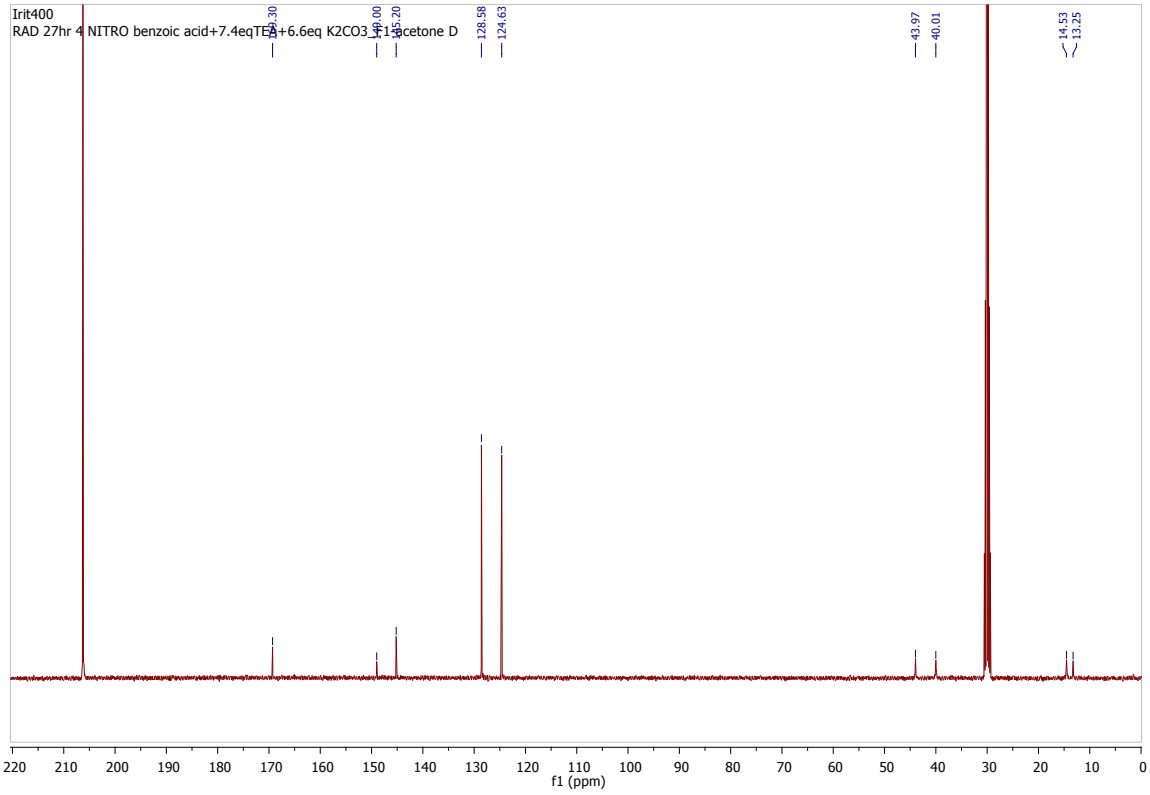
_N_,_N_-Diethyl-4-nitrobenzamide (10g)[9]



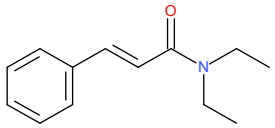
Viscpous liquid, yield 72% (0.4651g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 3.41 (q, J = 6.8 Hz, 2H), 3.07 (q, J = 6.8 Hz, 2H), 1.09 (t, J = 6.2 Hz, 3H), 0.97 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, Acetone) δ 169.30, 148.95, 145.23, 128.64, 124.63, 43.90, 39.95, 14.55, 13.25; HRMS (ESI^{+}) *m/z*: Calcd for $C_{11}H_{15}N_2O_3$ $[M+H]^{+}$ 223.1082, found 223.1060.



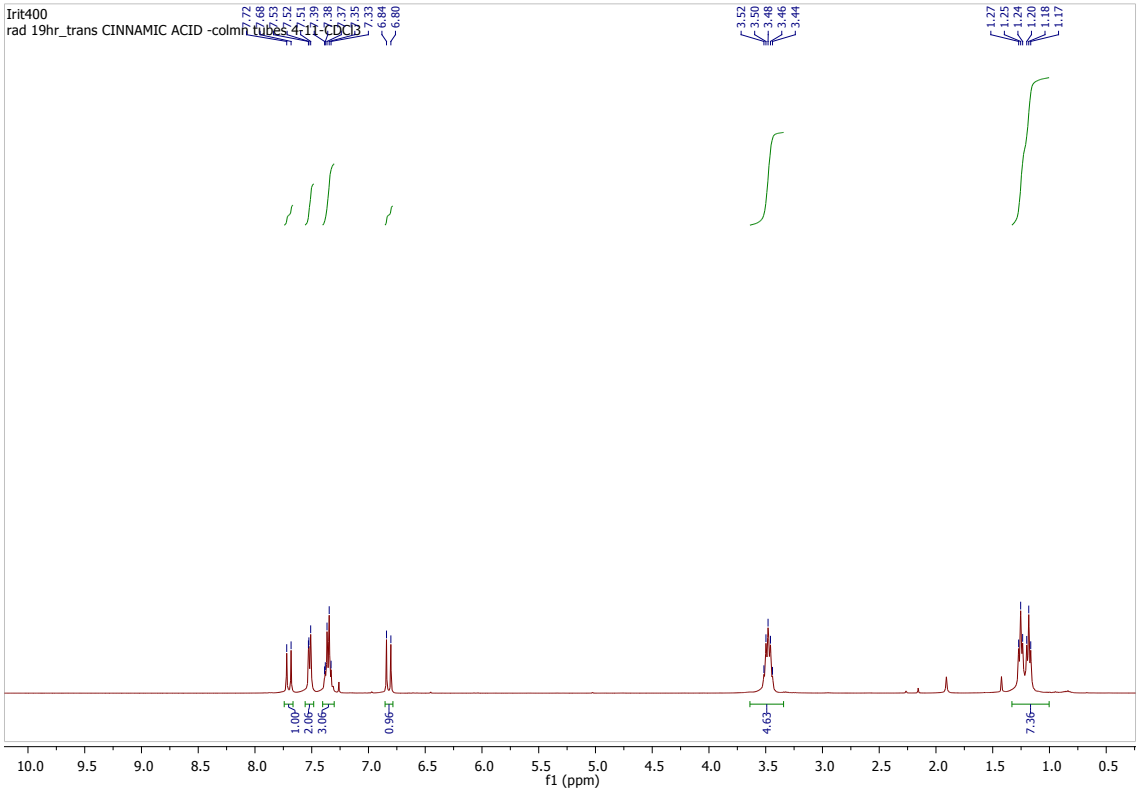
[9] N. Iranpoor, F. Panahi, F. Roozbin, S. Erfan and S. Rahimi *Eur. J. Org. Chem*. 2016, 1781.



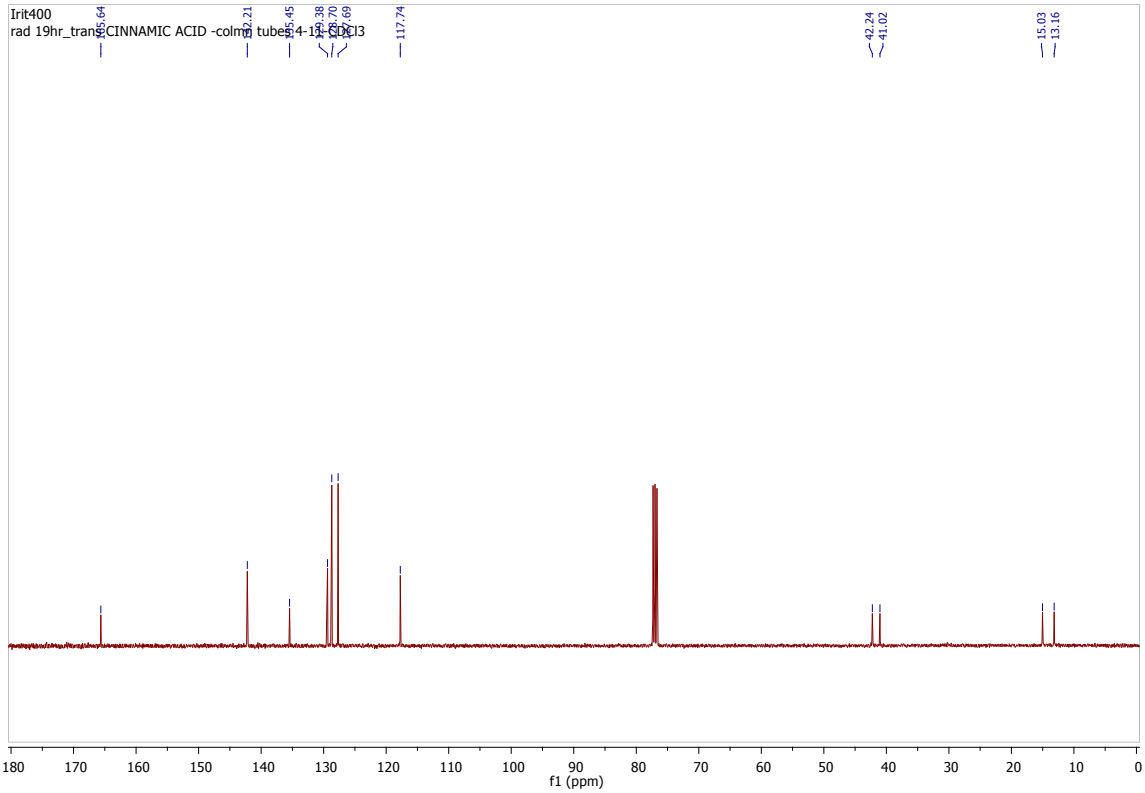
N,*N*-Diethylcinnamamide (10h)[10]



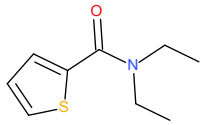
Viscous liquid, yield 65% (0.2359 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 15.4 Hz, 1H), 7.59 - 7.46 (m, 2H), 7.44 - 7.30 (m, 3H), 6.82 (d, *J* = 15.4 Hz, 1H), 3.72 - 3.33 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.64, 142.21, 135.45, 129.38, 128.70, 127.69, 117.74, 42.24, 41.02, 15.03, 13.16; HRMS (ESI^+) *m/z*: Calcd for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1388, found 204.1340.



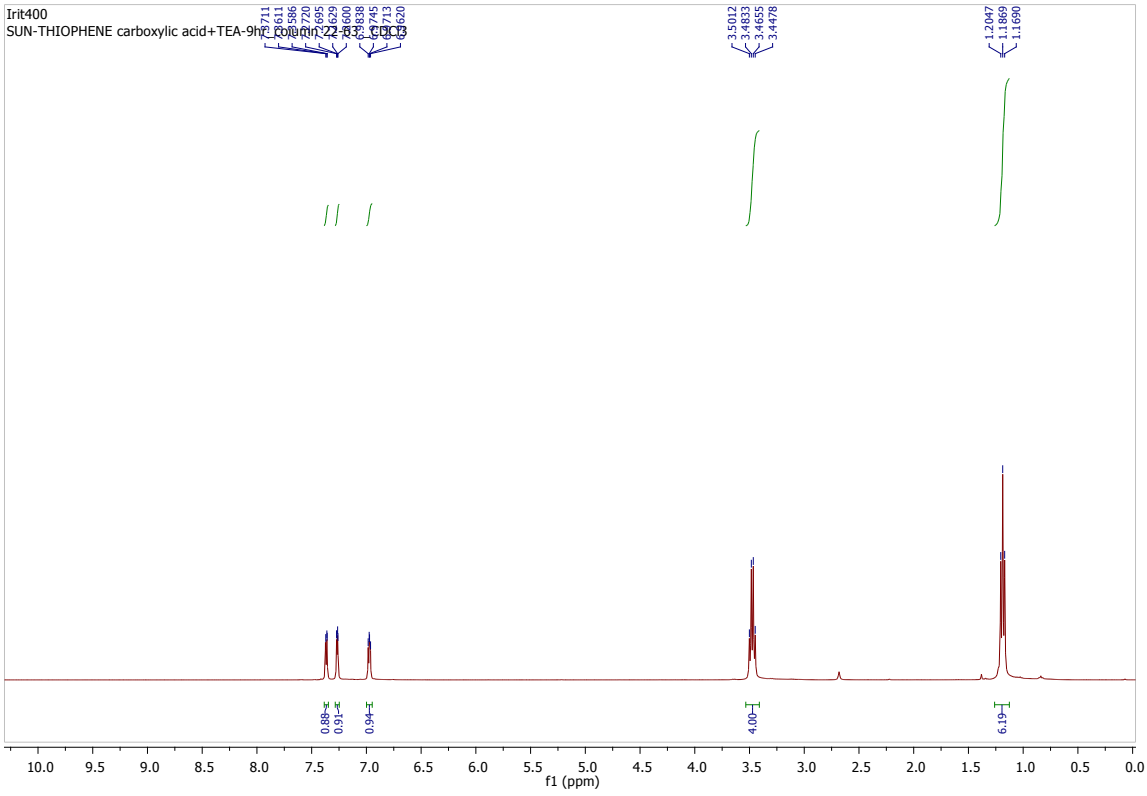
[10] Y. Kim and S. Chang, *Angew. Chem. Int. Ed.*, 2016, **55**, 218.


Irit400
rad 19hr_trans-CINNAMIC ACID -colmar tubes-4-12-CDCl3
165.64
142.21
135.45
129.38
128.70
127.69
117.74
42.24
41.02
15.03
13.16
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

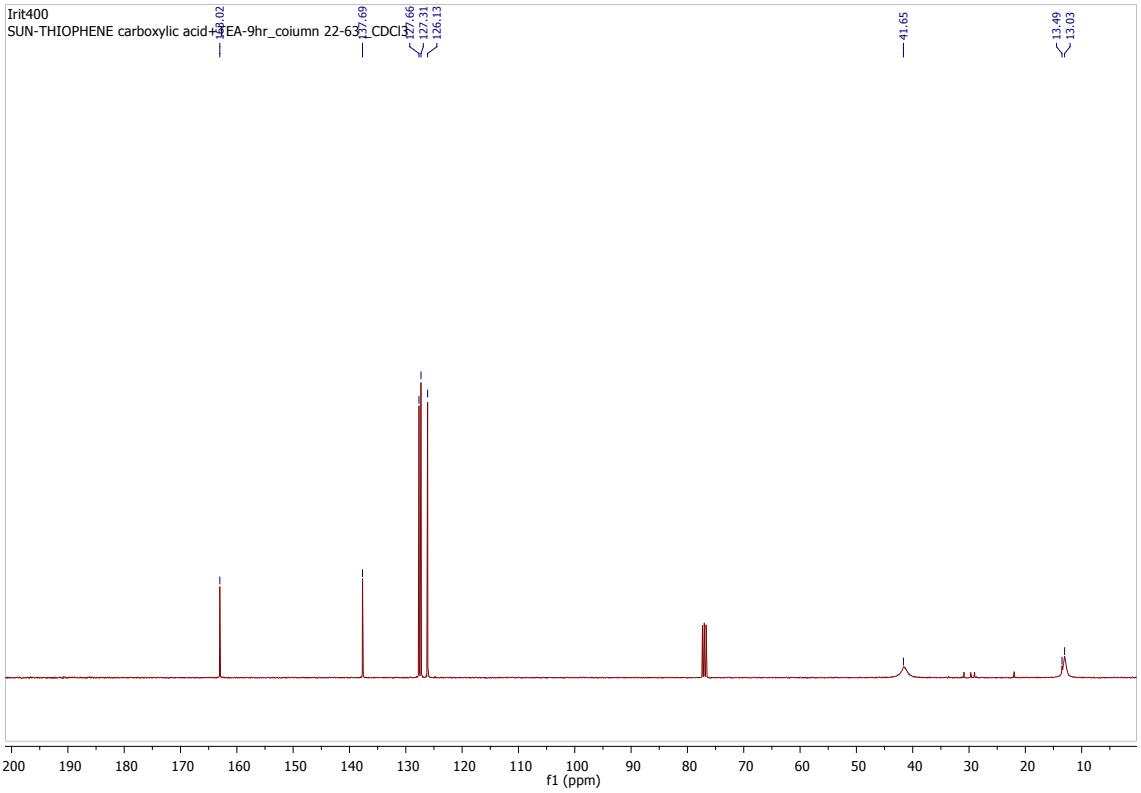
_N_,_N_-Diethyl-2-thiophenecarboxamide (10i)[11]



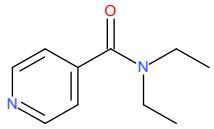
Viscous solid, yield 52% (0.3652 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 5.0, 1.0 Hz, 1H), 7.27 (dd, J = 3.7, 1.1 Hz, 1H), 7.00 – 6.95 (m, 1H), 3.51 - 3.43 (q, 4H), 1.21 - 1.15 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.02, 137.69, 127.66, 127.31, 126.13, 41.65 (bs), 13.49, 13.03; HRMS (ESI$^+$) *m/z*: Calcd for $C_9H_{14}NOS$ $[M+H]^+$ 184.0796, found 184.0782.



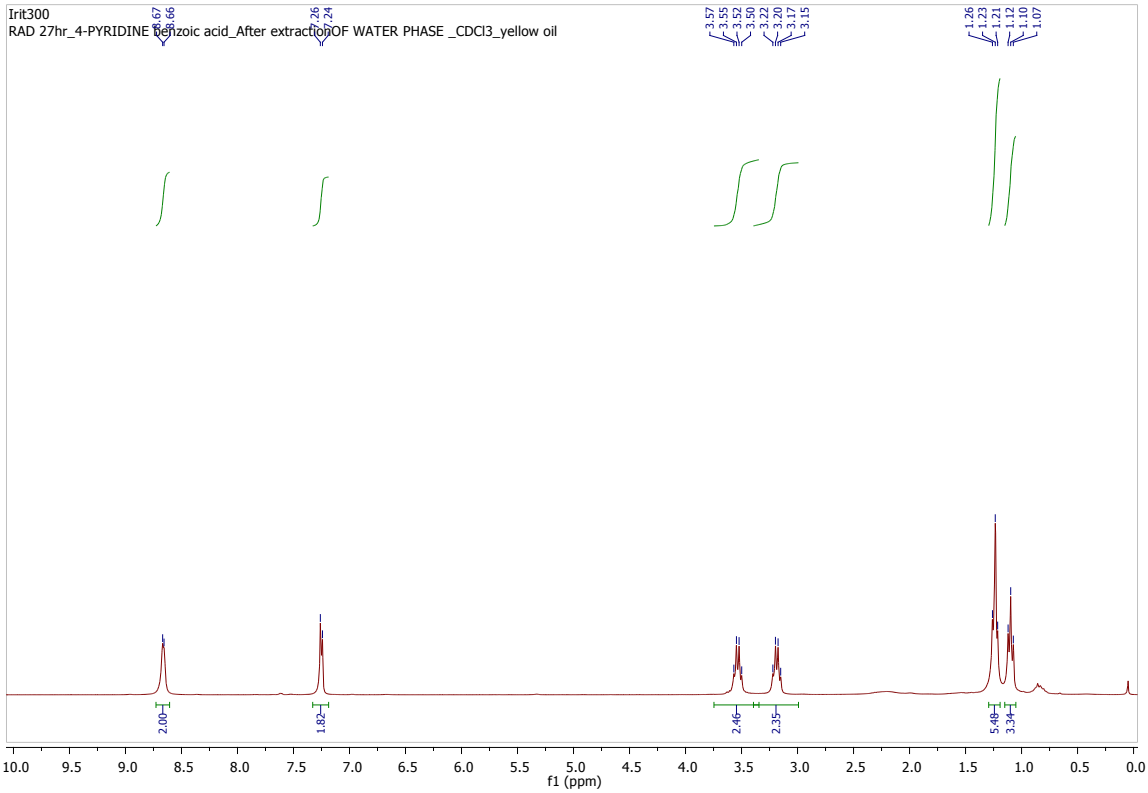
[11] K. Fukuzumi, Y. Unoh, Y. Nishii, T. Satoh, K. Hirano and M. Miura *J. Org. Chem*. 2016, **81**, 2474.


Irit400
SUN-THIOPHENE carboxylic acid+TEA-9hr_coiumn 22-63_CDCl3
138.02
137.69
127.66
127.31
126.13
41.65
13.49
13.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

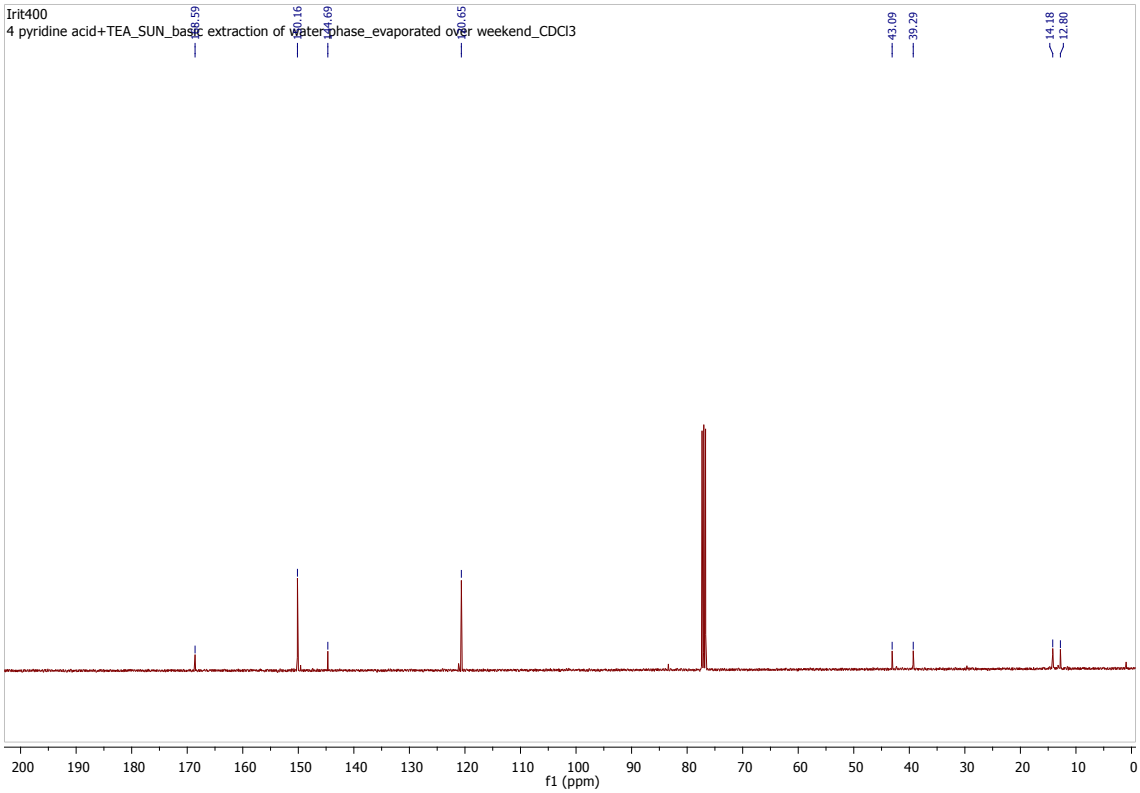
***N*,*N*-Diethylisonicotinamide (10j)[12]**



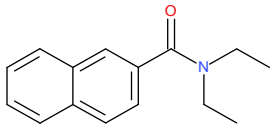
Reaction was performed as general procedure. Subsequently, reaction mixture was washed with 1M HCl, furthermore water layer was basifiy by 10% NaOH solution and extracted with DCM. The solvent was evaporated in in rotary evaporator and cound was kept under high vacume over two days. Viscous liquid, yield 69% (0.2496 g); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (br, 2H), 7.25 (d, J = 5.7 Hz, 2H), 3.51 (q, J = 9.0 Hz, 2H), 3.19 (q, J = 9.0 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 150.16, 144.69, 120.65, 43.09, 39.29, 14.18, 12.80; HRMS (ESI^+) *m/z*: Calcd for $C_{10}H_{15}N_2O$ $[M+H]^+$ 179.1184, found 179.1192.



[12] Y. Zhaoa and V. Snieckus, *Adv. Synth. Catal*., 2014, **356**, 152.


Irit400
4 pyridine acid+TEA_SUN_basic extraction of water phase_evaporated over weekend_CDCl3
168.59
150.16
144.69
120.65
43.09
39.29
14.18
12.80
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

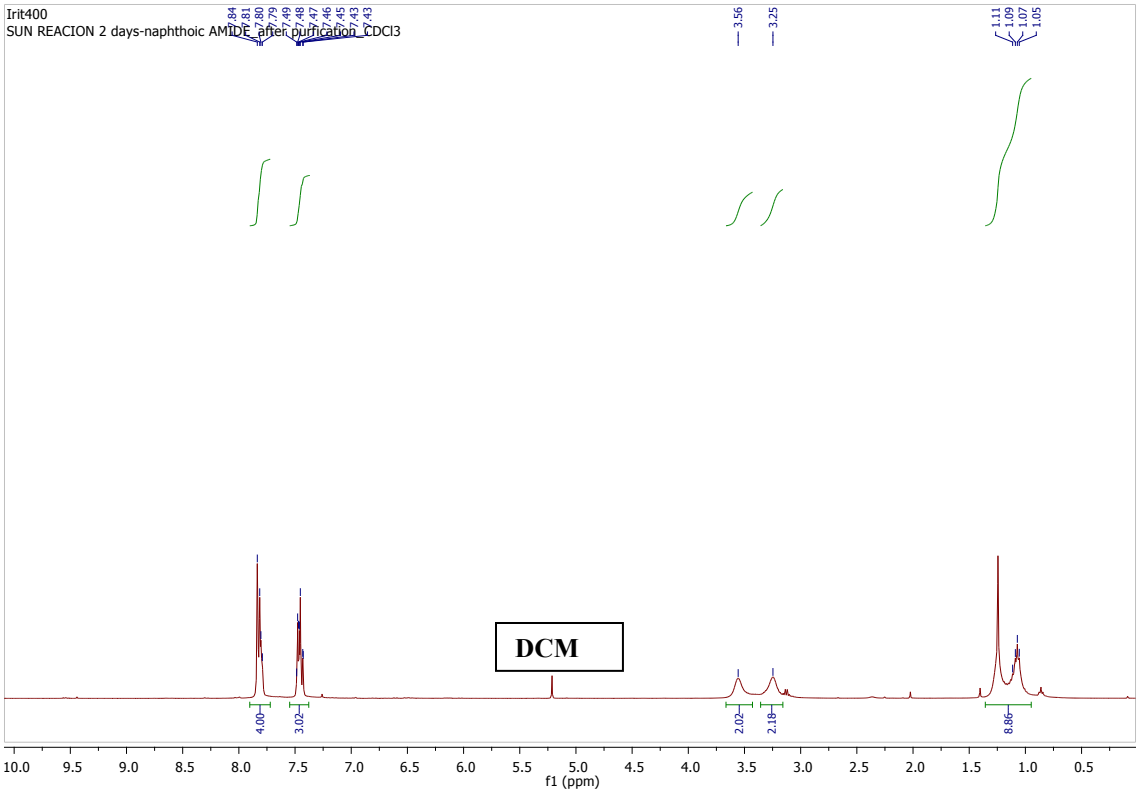
***N*-*N*-Diethyl-2-naphthamide (10k)[13]**

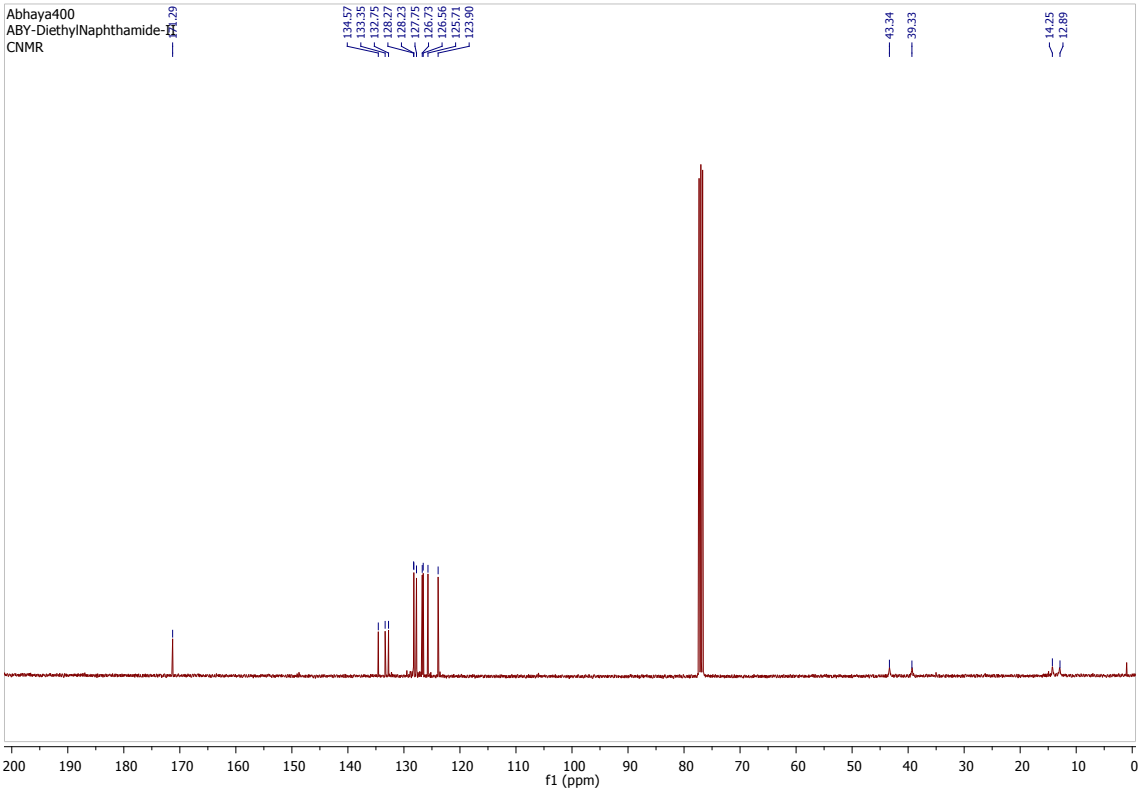


Viscous liquid, yield 96% (0.636 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.86 (m, 4H), 7.50 - 7.41 (m, 3H), 3.56 (br, 2H), 3.25 (br, 2H), 1.12 - 1.05 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.29, 134.57, 133.35, 132.75, 128.27, 128.23, 127.75, 126.73, 126.56, 125.71, 123.90, 43.34, 39.33, 14.25, 12.89. HRMS (ESI^+) *m/z*: Calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388, found 228.1395.

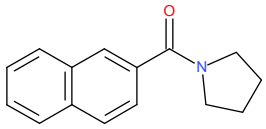
Gram-scale experiment. The 2-naphthoic acid (3.0 g, 17.44 mmol), triethylamine (18.25 mL, 130.8 mmol) and K_2CO_3 (16.60 g, 120 mmol) were added to a mixture of CCl_4 (135 mL) and DCM (45 mL) in a 2 L borosilicate vessel equipped with a rubber stopper. The combined mixture was degassed using N_2. The oxygen-free reaction mixture was then stirred under sun light for 18 hours combined over two days. Upon completion the reaction was acidified with 1M solution of HCl and extracted with DCM. The organic extracts were dried over anhydrous Na_2SO_4 and the solvent removed using a rotary evaporator under reduced pressure. The residue was subjected to column chromatography to isolate the 3.23 g (82%) *N*-*N*-diethyl-2-naphthamide.

[13] R. S. Mane and B. M. Bhanage *J. Org. Chem*., 2016, **81**, 1223.

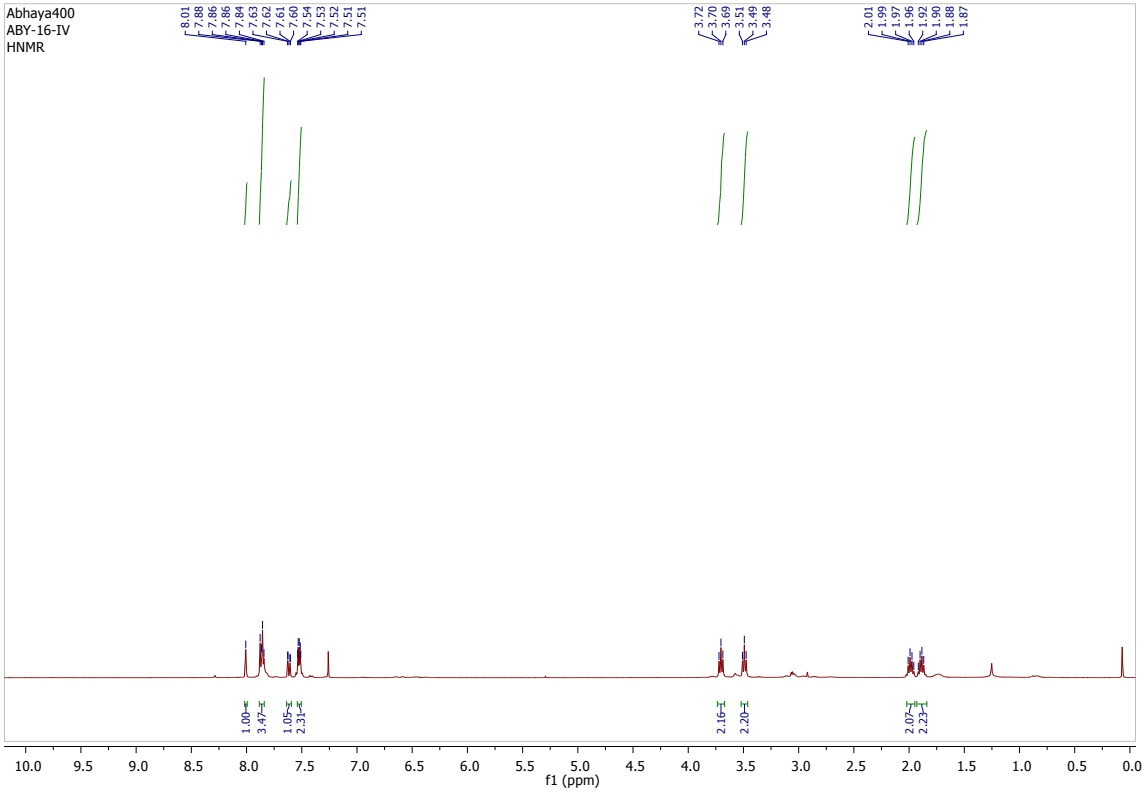

Irit400
SUN REACION 2 days-naphthoic AMIDE after purification CDCl3
7.84
7.81
7.80
7.79
7.49
7.48
7.47
7.46
7.45
7.43
3.56
3.25
1.11
1.09
1.07
1.05
DCM
4.00
3.02
2.02
2.18
8.86
f1 (ppm)


Abhaya400
ABY-DiethylNaphthamide-II
CNMR
169.29
134.57
133.35
132.75
128.27
128.23
127.75
126.73
126.56
125.71
123.90
43.34
39.33
14.25
12.89
f1 (ppm)

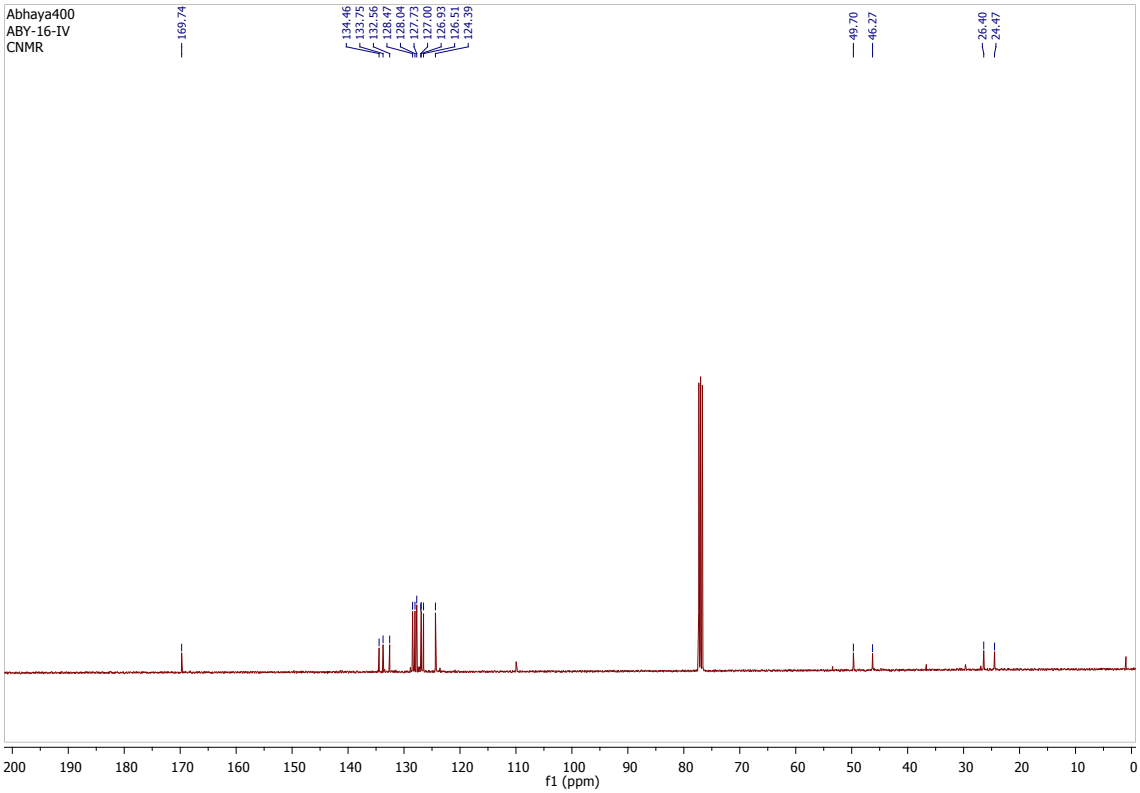
_N_-(2-Naphthoyl)pyrrolidine (10l)[14]



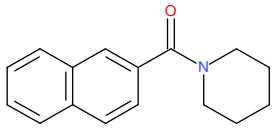
Visous liquid, yield 56% (0.148 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.83 - 7.89 (m, 3H), 7.62 (dd, J = 8.5, 1.5 Hz, 1H), 7.57 - 7.47 (m, 2H), 3.70 (t, J = 7.0 Hz, 2H), 3.49 (t, J = 6.6 Hz, 2H), 1.98 (q, J = 13.7, Hz, 2H), 1.89 (q, J = 13.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.74, 134.46, 133.75, 132.56, 128.47, 128.04, 127.73, 127.00, 126.93, 126.51, 124.39, 49.70, 46.27, 26.40, 24.47; HRMS (APCI) *m/z*: Calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1231, found 226.1249.



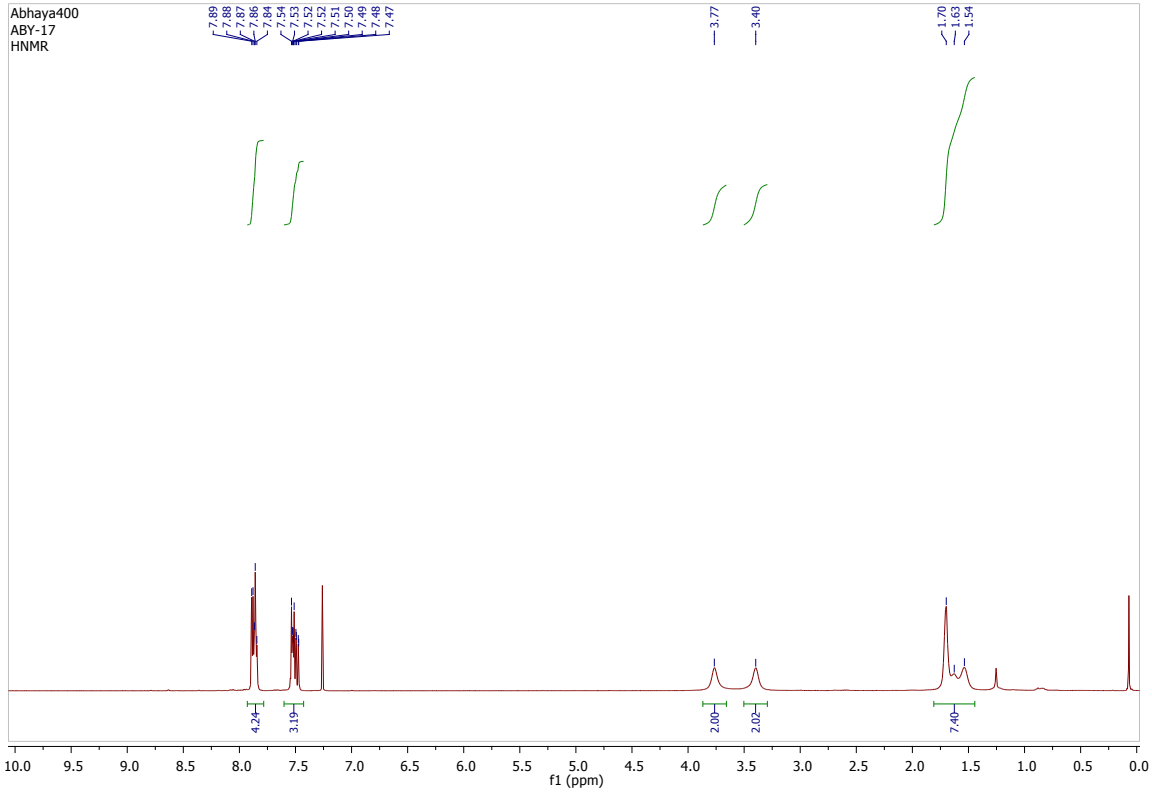
[14] P. Nareddy, F. Jordan, S. E. Brenner-Moyer and M. Szostak *ACS Catal.,* 2016, **6**, 4755.


Abhaya400
ABY-16-IV
CNMR
169.74
134.46
133.75
132.56
128.47
128.04
127.73
127.00
126.93
126.51
124.39
49.70
46.27
26.40
24.47
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

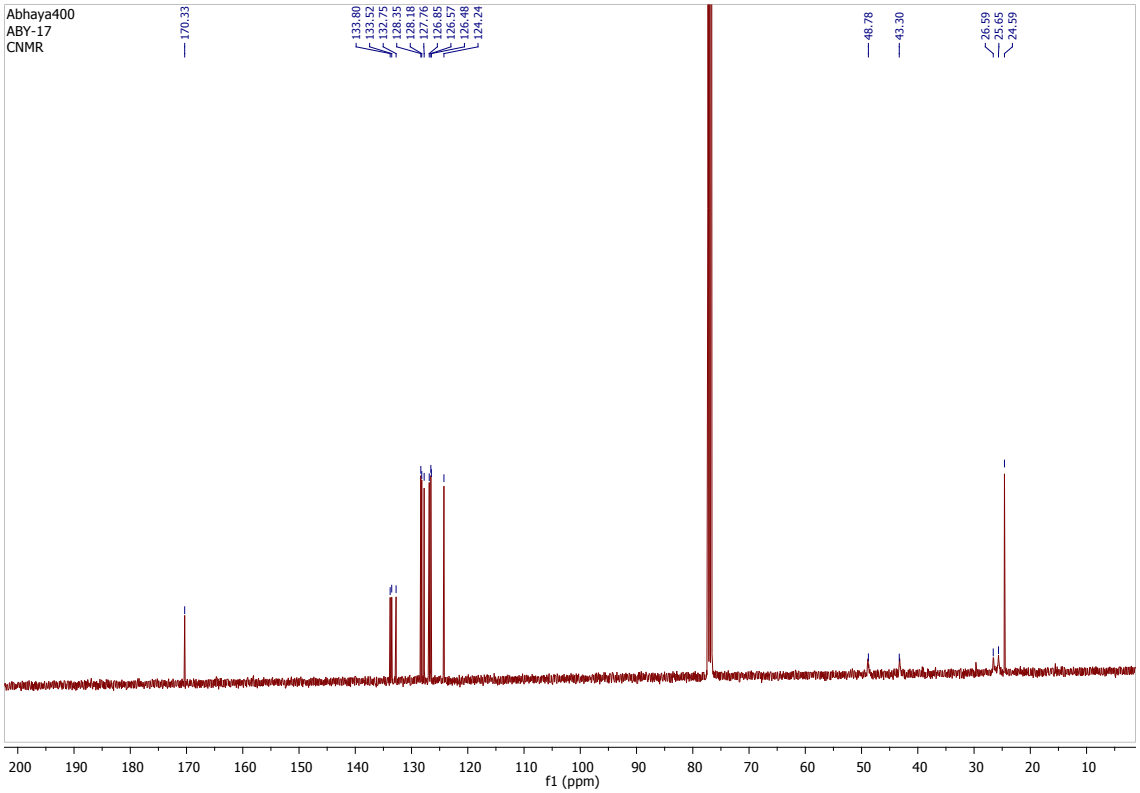
_N_-(2-Naphthoyl)piperidine (10m)[15]



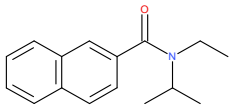
Yellow solid, yield 48% (0.142 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.68 (m, 4H), 7.64 – 7.35 (m, 3H), 3.77 (br, 2H), 3.40 (br, 2H), 1.87 – 1.38 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.33, 133.80, 133.52, 132.75, 128.35, 128.18, 127.76, 126.85, 126.57, 126.48, 124.24, 48.78, 43.30, 26.59, 25.65, 24.59. HRMS (APCI) *m/z*: Calcd for $C_{16}H_{18}NO$ [M+H$^+$ 240.1388, found 240.1397.



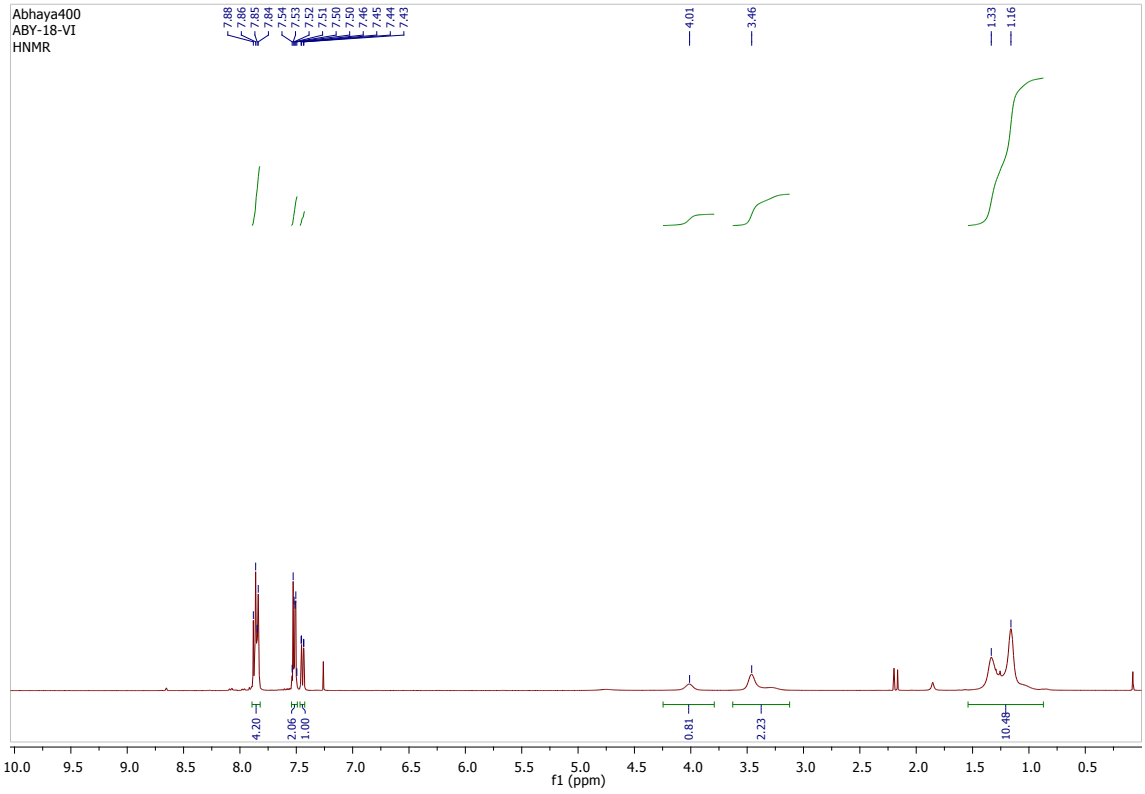
[15] S. W. Krabbe, V. S. Chan, T. S. Franczyk, S. Shekhar, J. Napolitano, C. A. Presto and J A. Simanis, *J. Org. Chem*. 2016, **81**, 10688.

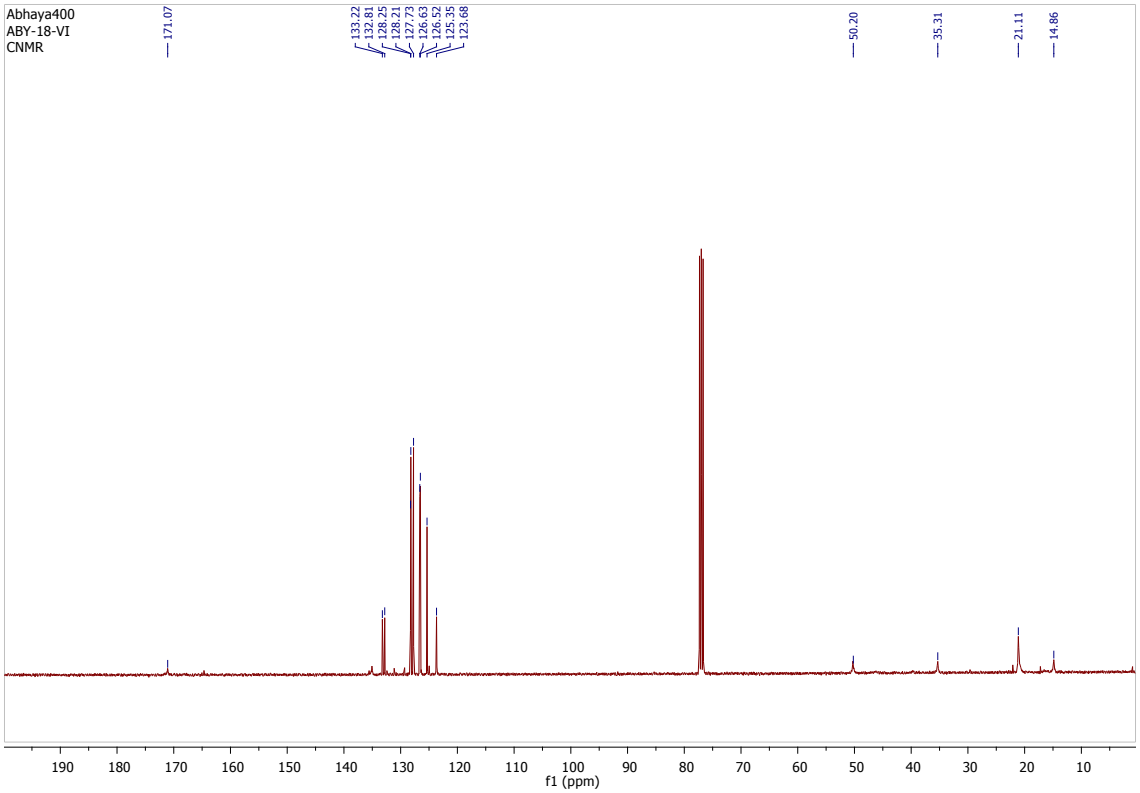

Abhaya400
ABY-17
CNMR
170.33
133.80
133.52
132.75
128.35
128.18
127.76
126.85
126.57
126.48
124.24
48.78
43.30
26.59
25.65
24.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

_N_-Ethyl-_N_-isopropyl-2-naphthamide (10n)

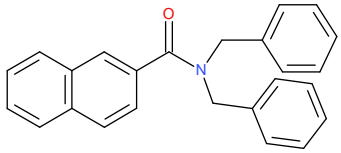


Yellowish liquid, yield 50% (0.140 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.76 (m, 4H), 7.58 – 7.46 (m, 2H), 7.44 (dd, J = 8.4, 1.5 Hz, 1H), 4.01 (br, 1H), 3.45 (br, 2H), 1.48 – 0.94 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.17, 133.33, 132.91, 128.36, 128.31, 127.83, 126.73, 126.63, 125.45, 123.78, 50.30, 35.42, 21.21, 14.96; HRMS (ESI^{+}) *m/z*: Calcd for $C_{16}H_{20}NO$ $[M+H]^{+}$ 242.1544, found 242.1540.

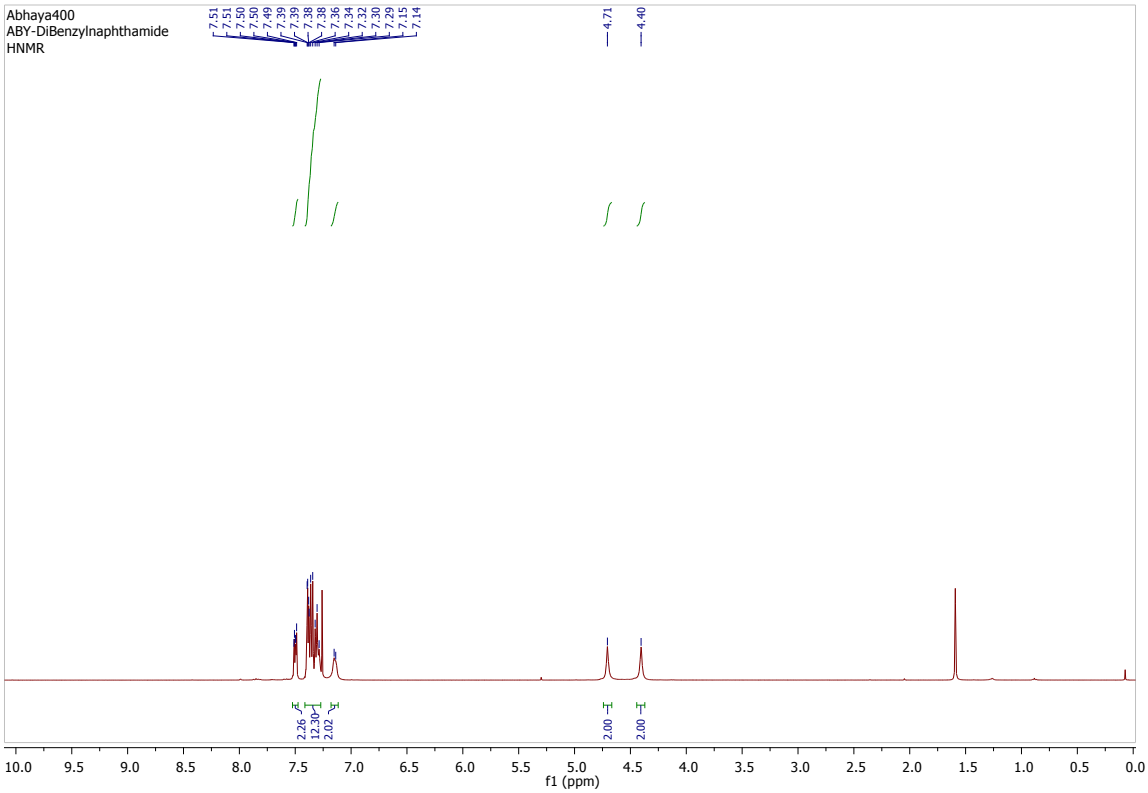



Abhaya400
ABY-18-VI
CNMR
171.07
133.22
132.81
128.25
128.21
127.73
126.63
126.52
125.35
123.68
50.20
35.31
21.11
14.86
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

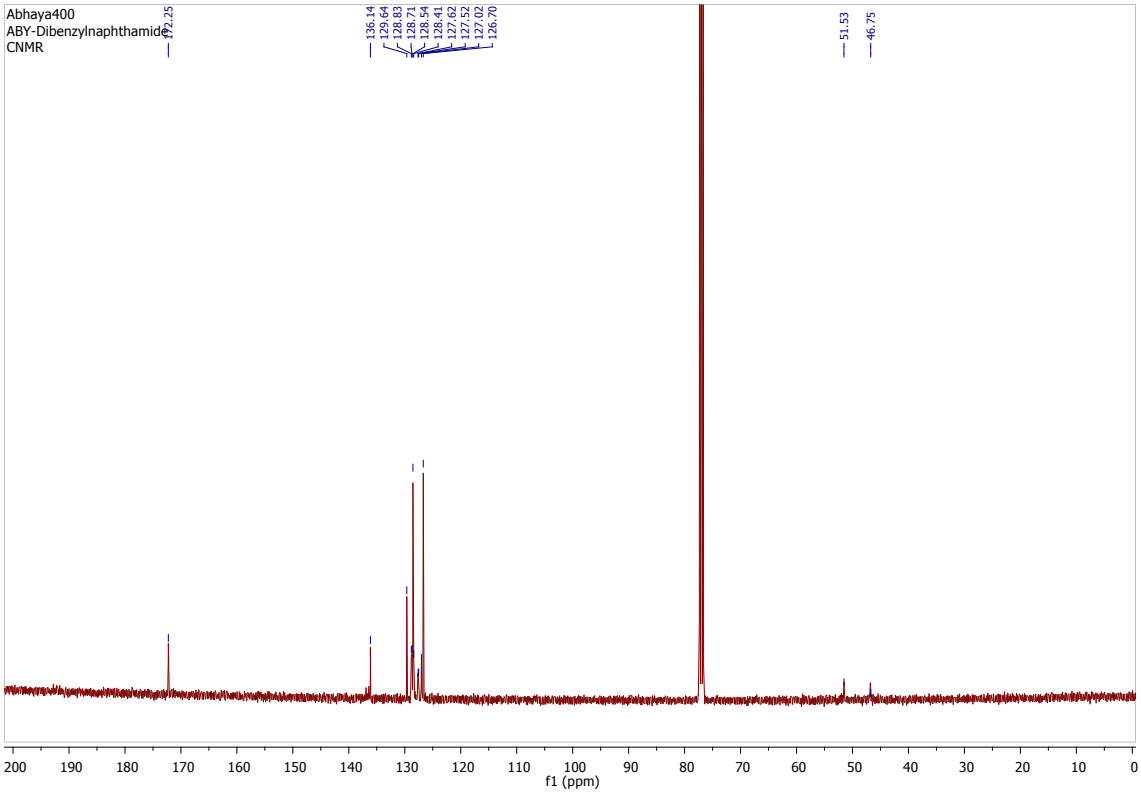
***N*,*N*-Dibenzyl-2-naphthamide (10o)[16]**



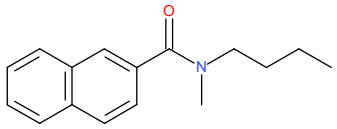
Yellow solid, yield 35% (0.214 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.41 – 7.27 (m, 12H), 7.14 (d, *J* = 5.8 Hz, 2H), 4.71 (s, 2H), 4.40 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.25, 136.14, 129.64, 128.83, 128.71, 128.54, 128.41, 127.62, 127.52, 127.02, 126.70, 51.53, 46.75.



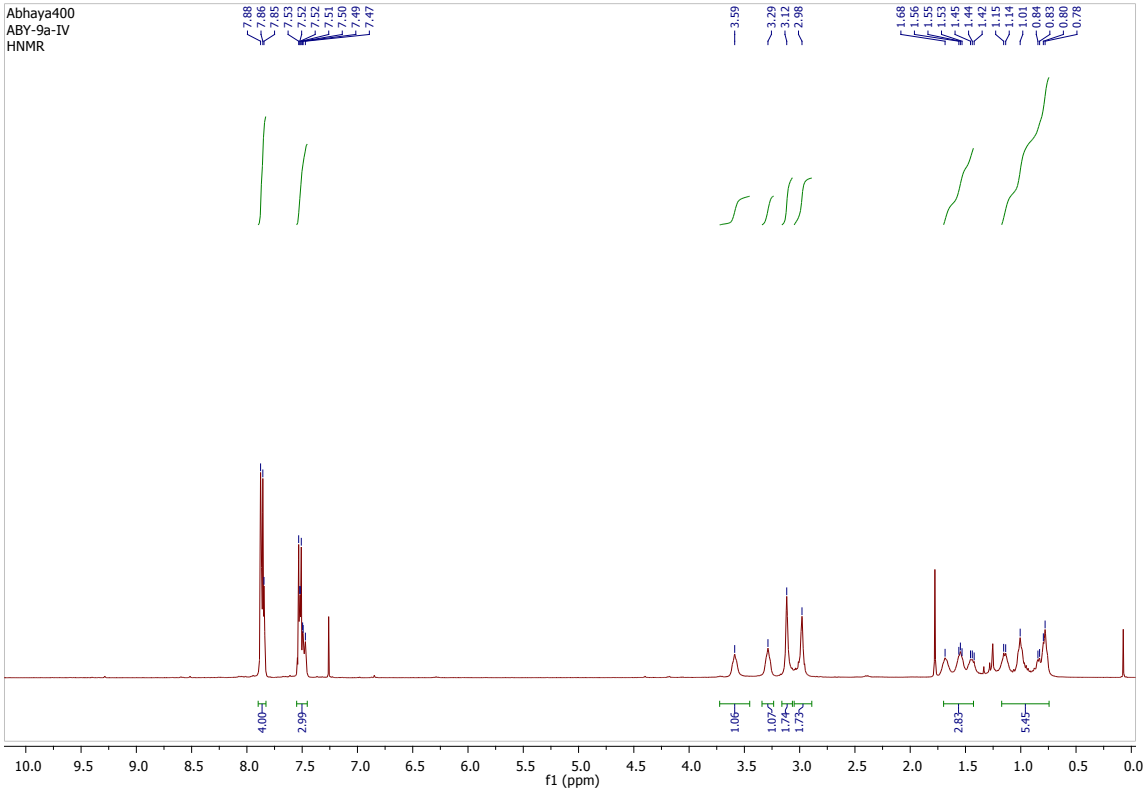
[16] X. Chen, T. Chen, Q. Li, Y. Zhou, L.-B. Han and S.-F. Yin, *Chem. Eur. J.,* 2014, **20**, 12234.

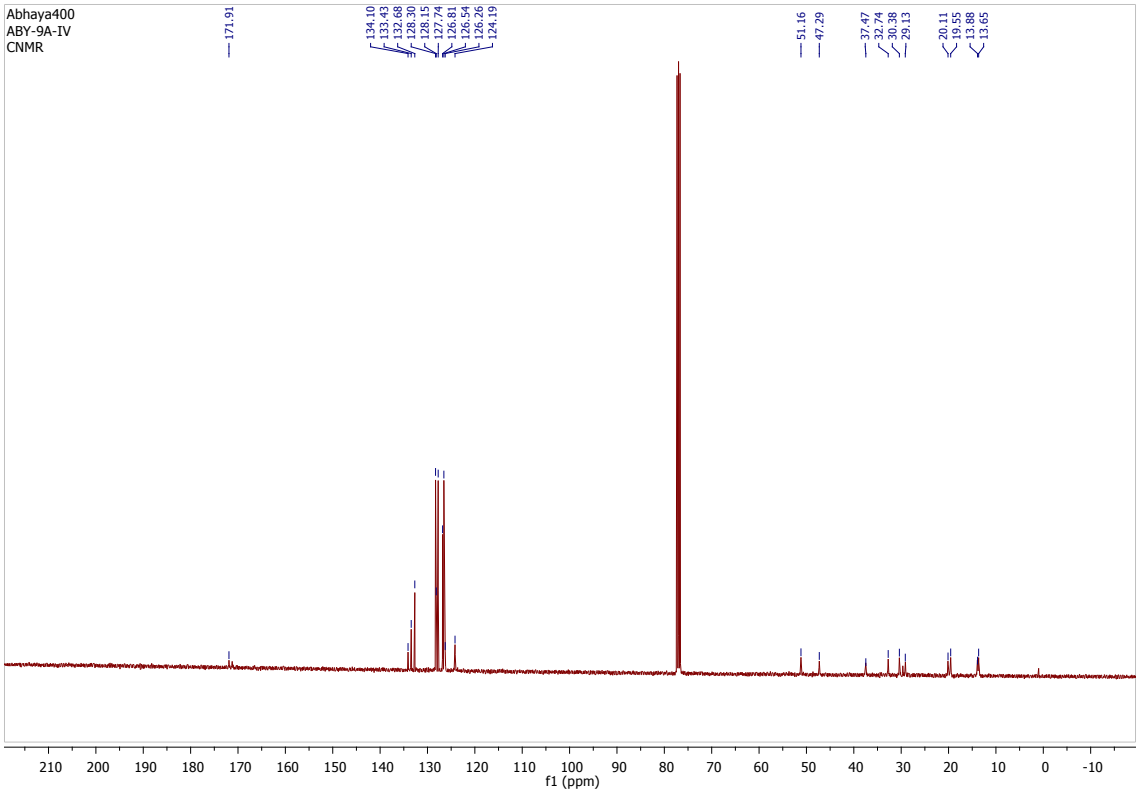

Abhaya400
ABY-Dibenzylnaphthamide
CNMR
172.25
136.14
129.64
128.83
128.71
128.54
128.41
127.62
127.52
127.02
126.70
51.53
46.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

***N*-Butyl-*N*-methyl-2-naphthamide (10p)**

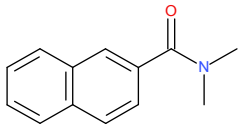


Yellowish liquid, yield 40% (0.120 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 4H), 7.55 – 7.45 (m, 3H), 3.59 (br, 1H), 3.29 (br, 1H), 3.12 (br, 3/2H), 2.98 (br, 3/2H), 1.73 – 1.29 (m, 2H), 1.22 – 0.72 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.91, 134.10, 133.43, 132.68, 128.30, 128.15, 127.74, 126.81, 126.54, 126.26, 124.19, 51.16, 47.29, 37.47, 32.74, 30.38, 29.13, 20.11, 19.55, 13.88, 13.65; HRMS (ESI^{+}) *m/z*: Calcd for $C_{16}H_{20}NO$ $[M+H]^{+}$ 242.1544, found 242.1542.

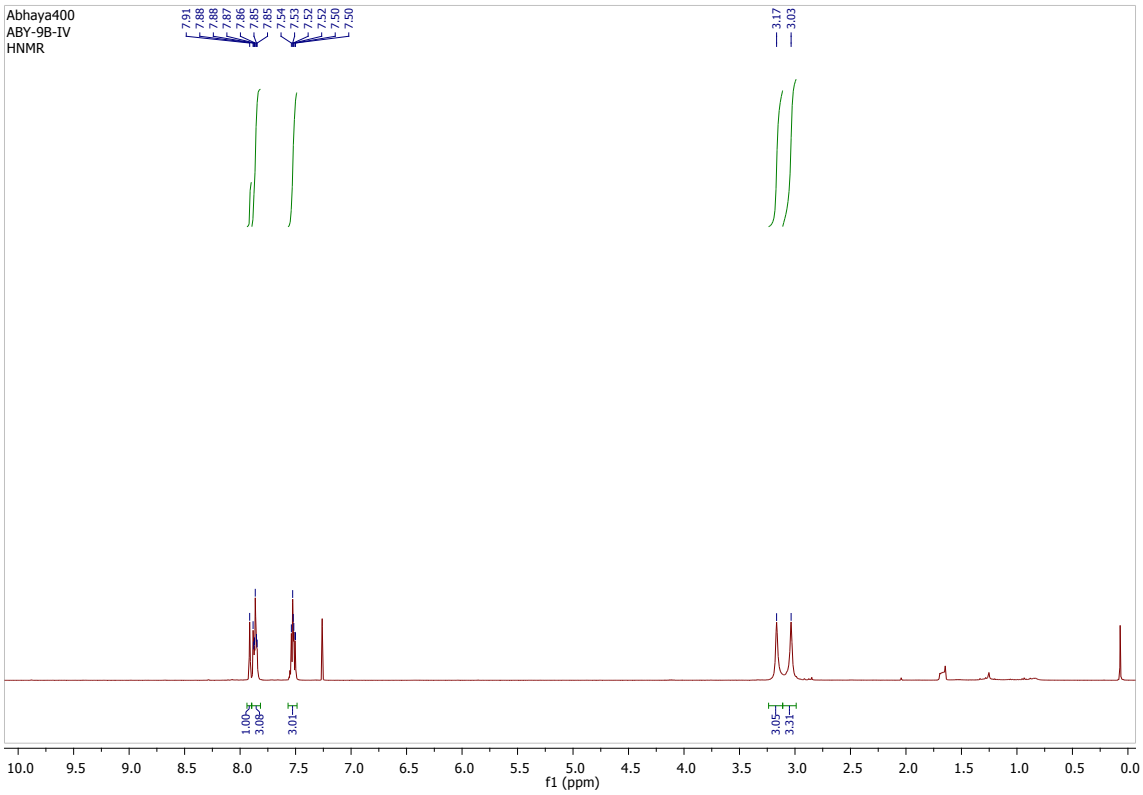



Abhaya400
ABY-9A-IV
CNMR
171.91
134.10
133.43
132.68
128.30
128.15
127.74
126.81
126.54
126.26
124.19
51.16
47.29
37.47
32.74
30.38
29.13
20.11
19.55
13.88
13.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

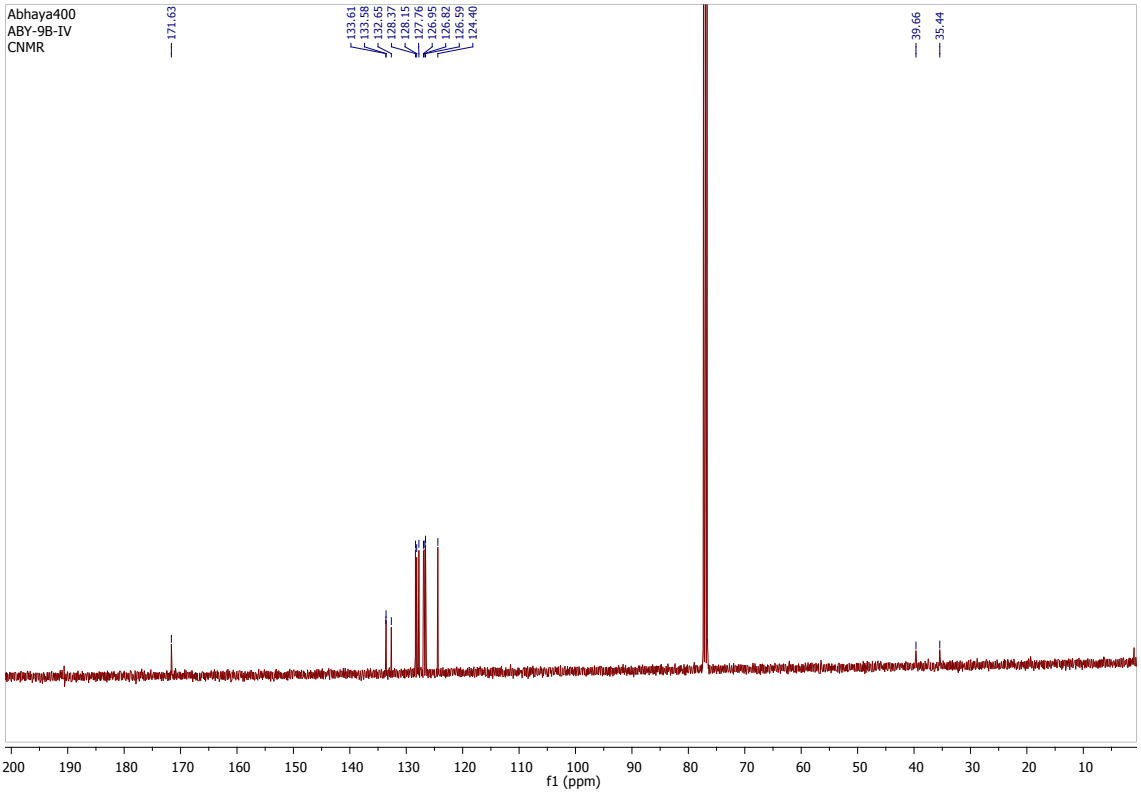
***N,N*-Dimethyl-2-naphthamide (10p')[17]**



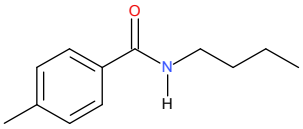
Yellowish liquid, yield 41% (0.120 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br, 1H), 7.89 – 7.83 (m, 3H), 7.56 – 7.49 (m, 3H), 3.17 (br, 3H), 3.03 (br, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.63, 133.58, 132.65, 128.37, 128.15, 127.76, 126.95, 126.82, 126.59, 124.40, 39.66, 35.44; HRMS (APCI) *m/z*: Calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1075, found 200.1091.



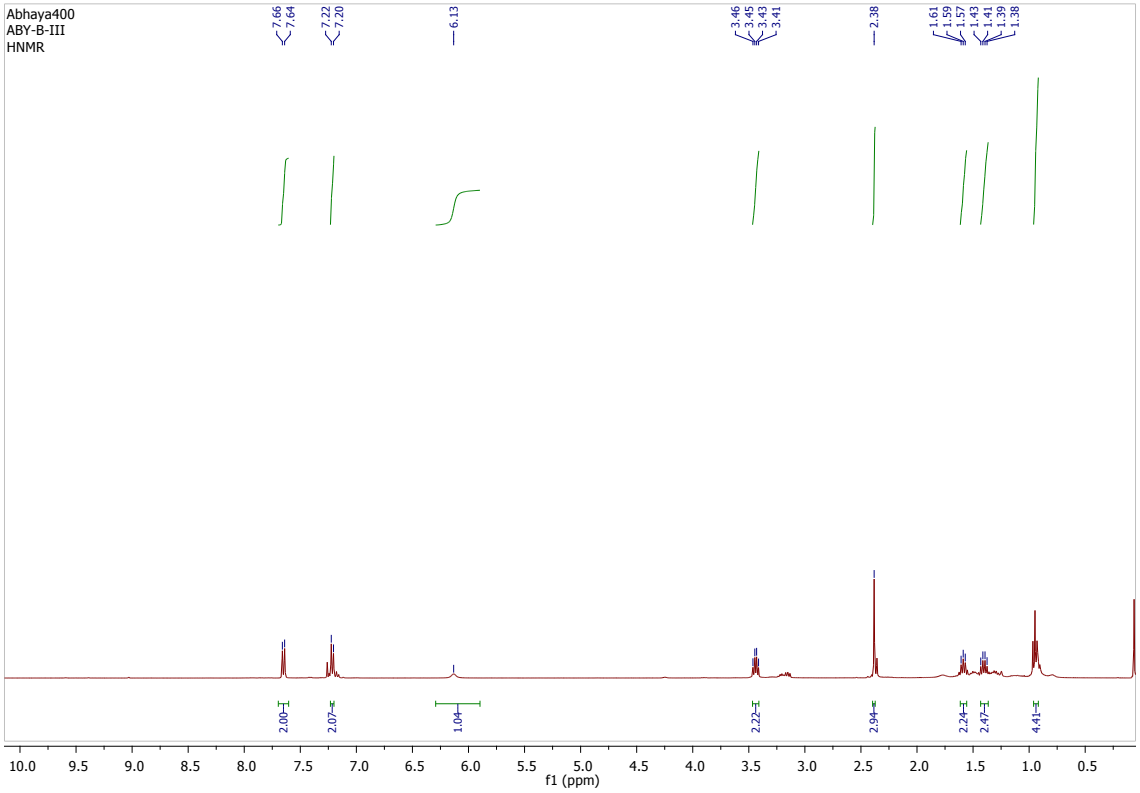
[17] M.-Z. Zhang, Q.-H. Guo, W.-B. Sheng and C.-C. Guo, *Adv. Synth. Catal*., 2015, **357**, 2855.


Abhaya400
ABY-9B-IV
CNMR
171.63
133.61
133.58
132.65
128.37
128.15
127.76
126.95
126.82
126.59
124.40
39.66
35.44
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

_N_-Butyl-_p_-toluamide (10q)[18]

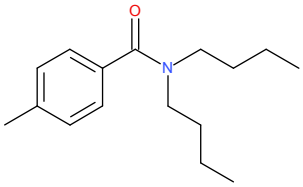


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.13 (br, 1H), 3.447 – 3.40 (m, 2H), 2.38 (s, 3H), 1.66 – 1.52 (m, 2H), 1.43 – 1.31 (m, 2H), 1.07 – 0.81 (m, 3H); HRMS (APCI) *m/z*: Calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1388, found 192.1400.

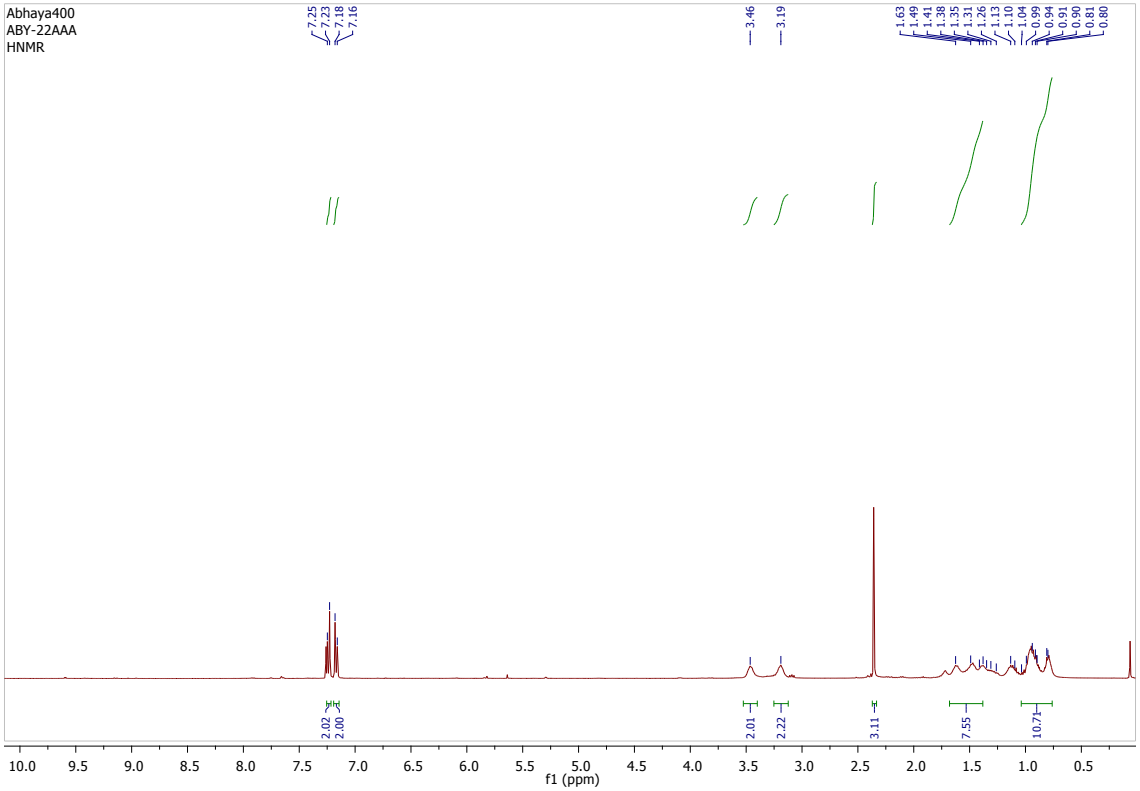


[18] Y.-L. Deng, S. Tang, G.-L. Ding, M.-W. Wang, J. Li, Z.-Z. Li, L. Yuana and R.-L. Sheng, *Org. Biomol. Chem*., 2016, **14**, 9348.

***N*,*N*-Dibutyl-*p*-toluamide (10q')[19]**



Viscous liquid, yield 6% (0.022 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.46 (br, 2H), 3.19 (br, 2H), 2.41 (s, 3H), 1.70 – 1.25 (m, 4H), 1.20 – 0.75 (m, 6H); HRMS (APCI) *m/z*: Calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.2023.



Computational Results

[19] T. Fang, X.-H. Gao, R.-Y. Tang, X.-G. Zhang and C.-L. Deng, *Chem. Commun*., 2014, **50**, 14775.

TMA-TCM-comp9-G4.log:
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.075878	-0.000051	0.001552
2	6	0	3.494041	0.334197	-1.352527
3	1	0	3.095701	-0.403701	-2.054998
4	1	0	3.101165	1.316986	-1.628847
5	1	0	4.594226	0.358826	-1.465517
6	6	0	3.510823	1.003052	0.963236
7	1	0	3.116137	1.983006	0.679322
8	1	0	3.126535	0.754178	1.956693
9	1	0	4.612287	1.081540	1.029524
10	6	0	3.507419	-1.337055	0.384149
11	1	0	3.123924	-1.578760	1.379719
12	1	0	3.109431	-2.070581	-0.323088
13	1	0	4.608623	-1.440501	0.404641
14	17	0	0.211874	-0.000685	0.005422
15	6	0	-1.574811	0.000042	0.000636
16	17	0	-2.178166	-1.030870	-1.331790
17	17	0	-2.185652	-0.636838	1.557317
18	17	0	-2.180056	1.668273	-0.228671

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.128390 E(Thermal)= 0.141760
E(CCSD(T))= -2050.377638 E(Empiric)= -0.201463
DE(Plus)= -0.026112 DE(2DF)= -0.446530
E(Delta-G3XP)= -1.724516 DE(HF)= -0.063826
G4(0 K)= -2052.711696 G4 Energy= -2052.698326
G4 Enthalpy= -2052.697382 G4 Free Energy= -2052.755796
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7269704,-1.094212953,0.8141022393\H,0,3.0769902059,-0.9740168009,1.828
7505842\H,0,3.0810713793,-2.0331170267,0.4072405397\H,0,4.5693877244,-
1.1734433811,0.8761277707\C,0,3.4551237089,-0.1411662687,-1.3999319366
\H,0,3.0667525952,-1.0827176142,-1.7991099909\H,0,3.0569157507,0.67762
69619,-2.0062159334\H,0,4.5557934139,-0.1482214138,-1.5106283938\C,0,3
.4535925158,1.2995345832,0.5328975721\H,0,3.0561671113,2.1141378152,-0
.0795763639\H,0,3.0632822315,1.4133316472,1.5484508106\H,0,4.554158623
9,1.4039968862,0.5730695095\Cl,0,0.1668029441,-0.0079535636,0.00618442
59\C,0,-1.6196491251,-0.0302460449,0.0250866247\Cl,0,-2.2076696192,-0.
0855802503,1.7142714593\Cl,0,-2.2529234792,1.4434515573,-0.7681197917\

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4\MP2/GTBas3=-2050.6453657\MP4/GTBas3=-2050.825783\HF/GTLargeXP=-2049.
2227849\MP2/GTLargeXP=-2052.393624\HF/GFHFB1=-2049.2765764\HF/GFHFB2=-
2049.2846451\G4=-2052.7116956\

TMA-G4.log

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000067	0.000087	-0.366195
2	6	0	-1.054175	0.903413	0.059683
3	1	0	-0.863450	1.908073	-0.331329
4	1	0	-2.017261	0.562478	-0.333844
5	1	0	-1.146122	0.980090	1.161612
6	6	0	-0.255400	-1.364553	0.059639
7	1	0	-1.220152	-1.702059	-0.332725
8	1	0	0.522125	-2.028129	-0.332454
9	1	0	-0.277541	-1.482160	1.161597
10	6	0	1.309529	0.461120	0.059699
11	1	0	2.084163	-0.205572	-0.332826
12	1	0	1.495410	1.466263	-0.332426
13	1	0	1.422637	0.500524	1.161632

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.118183 E(Thermal)= 0.123715
E(CCSD(T))= -173.895284 E(Empiric)= -0.090311
DE(Plus)= -0.011871 DE(2DF)= -0.177111
E(Delta-G3XP)= -0.246538 DE(HF)= -0.017355
G4(0 K)= -174.320287 G4 Energy= -174.314754
G4 Enthalpy= -174.313810 G4 Free Energy= -174.347676
1\1\GINC-N100\Mixed\G4\G4\C3H9N1\GALITPAR\24-May-2017\0\\#G4\\TMA G4\\
0,1\N,0,-0.0000948805,-0.0000743427,-0.3600421631\C,0,-0.5977897456,-1
.2531335115,0.0658669696\H,0,-1.6173109908,-1.3307528334,-0.325487597\
H,0,-0.0176284266,-2.0942474455,-0.3272939028\H,0,-0.6482573491,-1.361
6669093,1.1677993528\C,0,1.3838320612,0.1088081251,0.0662573523\H,0,1.
9611157091,-0.734806786,-0.3257420178\H,0,1.8221172924,1.0322608546,-0
.3258605214\H,0,1.5027598824,0.1182768973,1.1682549182\C,0,-0.78644064
96,1.1441829906,0.0653552709\H,0,-0.3443932086,2.0656562783,-0.3271921
015\H,0,-1.8051662822,1.0617616145,-0.3271114453\H,0,-0.8543324122,1.2
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Bas2=-173.839221\MP4/GTBas2=-173.9052922\MP2/GTBas3=-173.9945802\MP4/G

TBas3=-174.0705315\HF/GTLargeXP=-173.331101\MP2/GTLargeXP=-174.2520517
\HF/GFHFB1=-173.3446977\HF/GFHFB2=-173.3477197\G4=-174.3202866

TCM-G4.log

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	17	0	1.030084	1.030084	1.030084
3	17	0	-1.030084	-1.030084	1.030084
4	17	0	1.030084	-1.030084	-1.030084
5	17	0	-1.030084	1.030084	-1.030084

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.009118 E(Thermal)= 0.014837
E(CCSD(T))= -1876.474544 E(Empiric)= -0.111152
DE(Plus)= -0.012678 DE(2DF)= -0.268239
E(Delta-G3XP)= -1.479873 DE(HF)= -0.047008
G4(0 K)= -1878.384375 G4 Energy= -1878.378656
G4 Enthalpy= -1878.377712 G4 Free Energy= -1878.413067