Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

An Umpolung Approach to the Hydroboration of Pyridines: A Novel and Efficient Synthesis of *N*-H 1,4-Dihydropyridines

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Contents

1. General Information

Experimental. Air- and moisture-sensitive reactions were carried out in oven-dried Schlenk flasks sealed with rubber septa under a positive pressure of dry argon, or oven-dried glass tubes sealed with Teflon screw caps. Air- and moisture-sensitive liquids and solutions were transferred by a syringe or a double-headed needle. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump or concentrated under vacuum using standard Schlenk techniques. Analytical TLC was performed on silica gel GF_{254} plates. The TLC plates were visualized by either ultraviolet light (λ = 254 nm). Purification of 1,4-dihydropyridine products was done by flash column chromatography on basic alumina (80-160 mesh, pH = 9-10) under argon. Purification of other products was accomplished by flash column chromatography on silica gel (Innochem SilicaFlashP60, 230-400 mesh).

Chemicals. Anhydrous solvents (H_2O <30 ppm), ethylene dimethyl ether, and methanol were purchased from J&K Scientific. Tetrahydrofuran and acetonitrile were purified by PureSolv MD-5 solvent purification system, and were deoxygenated by three freeze-pump-thaw cycles before use. Methanol-d_1 (MeOD) was purchased from J&K Scientific and was dried over 4Å molecular sieves and deoxygenated by three freeze-pump-thaw cycles before use. B_2pin_2, B_2neo_2, and pyridine derivatives were purchased from TCI and used without further purification. MeOK and MeONa were purchased from Sigma-Aldrich and dried under vacuum before use. Cs_2CO_3 was purchased from J&K Scientific and dried under vacuum before use. 18-crown-6 was purified by recrystallization before use. Other chemicals were purchased from various commercial sources and were used as received. B_2eg_2 was synthesized following the published procedure.

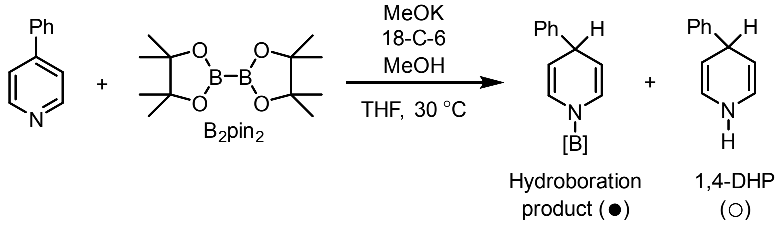
Analytical. NMR spectra were recorded on a Bruker AVANCE III HD 400 (^1H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometer. The ^1H NMR spectra were calibrated against the peak of tetramethylsilane (TMS, 0 ppm) and the ^{13}C NMR spectra were calibrated against the peak of $CDCl_3$ (77.16 ppm). GC-MS analysis was performed on a Shimadzu GCMS-QO2010SE instrument equipped with an EIS detector using helium as the carrier gas (EI ionization, 70 eV). Enantiomeric excess (e.e.) were determined by analytical high-performance liquid chromatography (HPLC) analysis using a Daicel chiral column Chirapak IC (4.6 × 250 mm). The X-ray single crystal structure analysis was performed on a SuperNova X-ray Diffraction System equipped with Atlas CCD detector and 4-circle kappa goniometer. Structure solution and refinement were accomplished with OLEX2.

2. Study on the Inversed Hydroboration of 4-Phenylpyridine

2.1 General

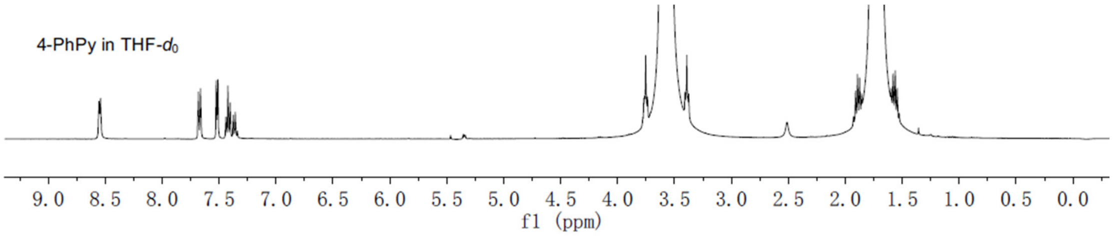
The reactions were conducted in normal THF solvent and were monitored by ^1H NMR of the crude reaction solution. The NMR spectra were recorded after ^1H gradient shimming without applying the ^2H-lock, and the undesired solvent signals were suppressed by the WET solvent suppression method (No-D NMR). The chemical shifts of the solvent utilized in the NMR experiments were calibrated against TMS (1.77 and 3.61 ppm for THF and 1.93 ppm for MeCN), and for other NMR spectra, the chemical shifts was calibrated against the solvent peaks. All measurements were performed under argon atmosphere.

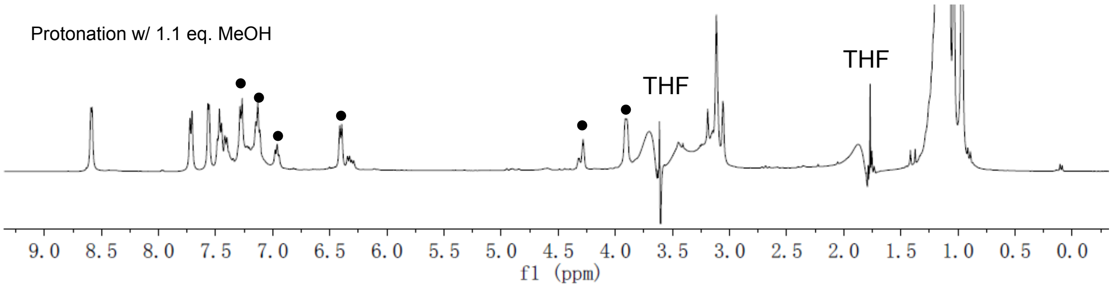
2.2 The reaction between 4-PhPy, B_2pin_2, and MeOK in the presence of MeOH

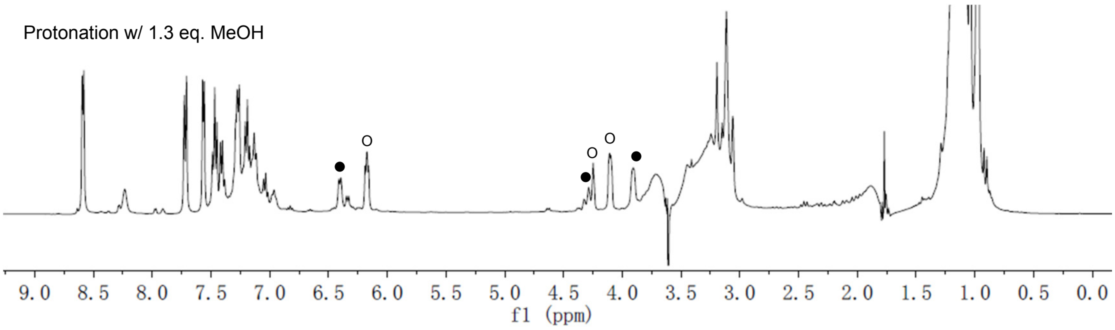


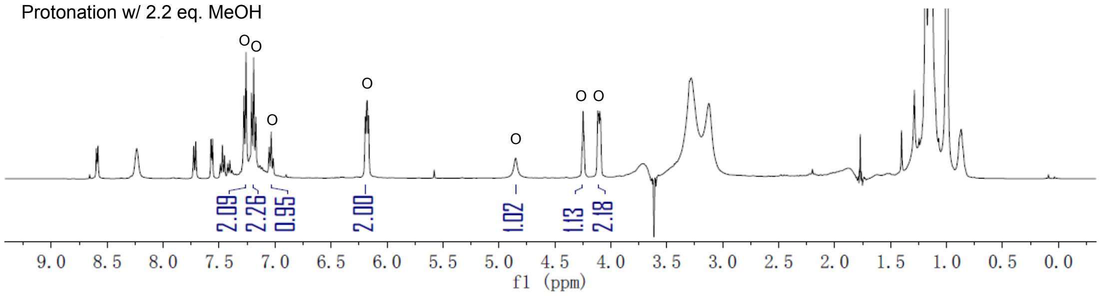
In a glove box, a 15 mL oven-dried reaction tube was charged with 4-PhPy (56.5 mg, 0.36 mmol), B_2pin_2 (102 mg, 0.40 mmol), MeOK (28.0 mg, 0.40 mmol), 18-crown-6 (106 mg, 0.40 mmol), and anhydrous THF (2 mL). An indicated amount of MeOH (0.4 mmol for 1.1 equiv., 0.48 mmol for 1.3 equiv., and 0.8 mmol for 2.2 equiv.) was added by a microsyringe. The resulting mixture was allowed to react at 30 °C for 12 h before submission to ^1H NMR analysis. The reaction mixture with 2.2 equiv. of MeOH was determined by GC-MS analysis.

^1H NMR spectra of the crude reaction mixture are shown below, which were used to construct Figure 1 in the main text:

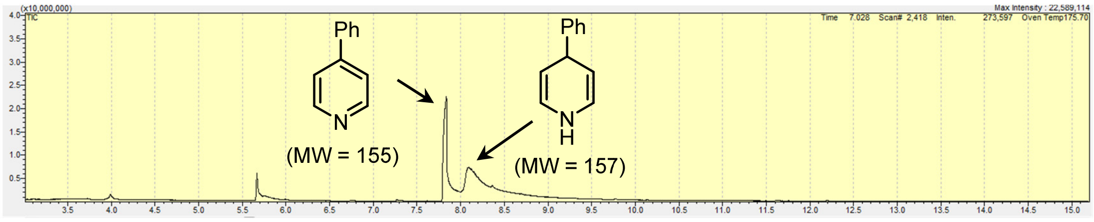




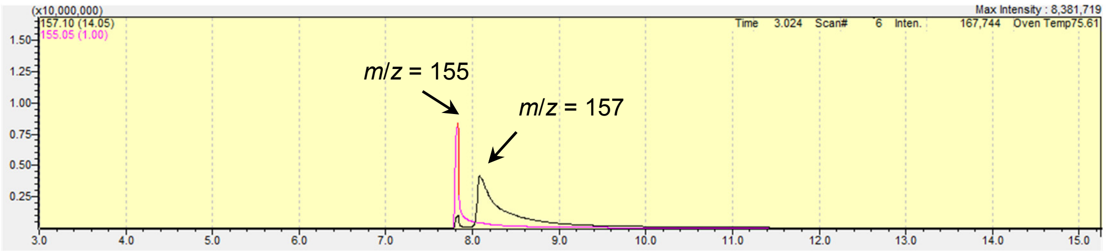

Protonation w/ 1.3 eq. MeOH


Protonation w/ 2.2 eq. MeOH

GC-MS trace of the crude reaction mixture with 2.2 equiv. of MeOH is shown below. Conditions for GC-MS analysis: helium as the carrier gas; capillary column (0.25 mm × 30 m, SH-Rxi-5Sil MS); constant pressure mode (150.2 kPa); oven temperature program: 50 °C for 2 min, elevation rate 25 °C/min to 200 °C, keep for 6 min, elevation rate 30 °C/min to 260 °C, keep for 4 min; ion source temperature 200 °C, interface temperature 250 °C, acquisition mode: scan.

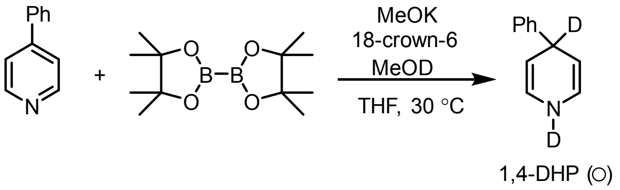


The assignment of the above peaks was confirmed by GC-MS SIM (selected ions monitoring) mode to detect ions at *m/z* = 155 and 157.



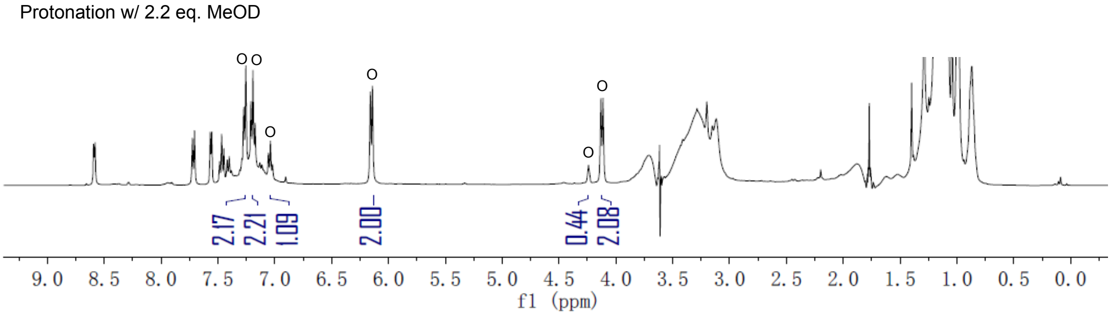
GC-MS results confirmed the formation of 1,4-DHP (MW = 157) in the reaction mixture.

2.3 The reaction between 4-PhPy, B_2pin_2, and MeOK in the presence of MeOD

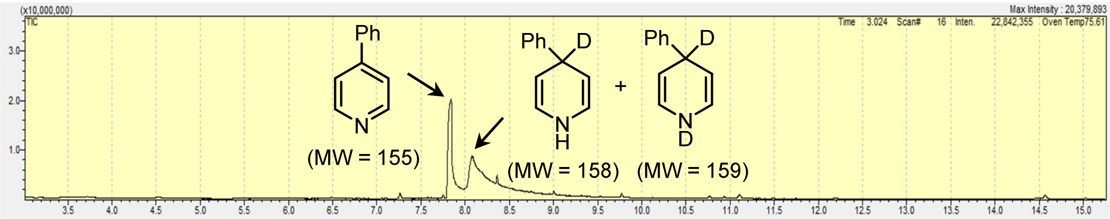


In a glove box, a 15 mL oven-dried sealed tube was charged with 4-PhPy (56.5 mg, 0.36 mmol), B_2pin_2 (102 mg, 0.40 mmol), MeOK (28.0 mg, 0.40 mmol), 18-crown-6 (106 mg, 0.40 mmol), and anhydrous THF (2 mL). Then MeOD (methanol-*d*, 26.4 mg, 0.8 mmol) was added by a microsyringe. The resulting mixture was allowed to react at 30 °C for 12 h before submission to ^1H NMR and GC-MS analysis.

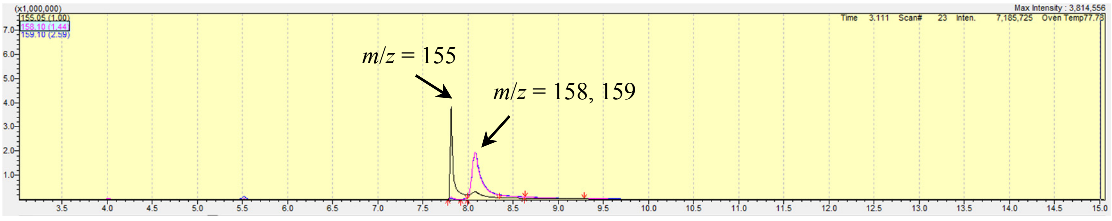
^1H NMR spectrum of the crude reaction mixture is shown below, in which the decrease of the peak at 4.25 ppm indicates deuterium incorporation at the C4-position of 1,4-DHP:



GC-MS trace of the crude reaction mixture is shown below (with identical GC-MS conditions specified in Section 2.2):



The assignment of the above peaks were confirmed by GC-MS SIM (selected ions monitoring) mode to detect ions at *m/z* = 155, 158, and 159.



Both NMR and GC-MS analyses confirmed the formation of deuterated 1,4-DHP in the presence of MeOD.

3. DFT Computational Study

3.1 General

All calculations were performed with the Gaussian 09 program.[1] Density functional theory calculations using the M06-2X functional[2] were used to locate the stationary points involved. The gas-phase structures were optimized at the M06-2X/6-31+G(d) level. NBO analysis and NAO orbital composition analysis were performed on the same level of theory.

3.2 NBO analysis on Int-A•K and TS-1•K

Cartesian coordinates of **Int-A•K**:

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          8           0        2.895648   -1.001803    0.534748
      2          5           0        1.394261   -0.928076    0.354097
      3          8           0        1.113226   -1.901059   -0.706515
      4          5           0        0.875115    0.701214   -0.031291
      5          8           0        1.165428    1.795334    0.948356
      6          8           0        1.290677    1.226822   -1.318489
      7          6           0        2.234303   -2.758618   -0.847860
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      9          6           0        1.432068    2.632578   -1.227473
     10          6           0        1.863134    2.835735    0.262331
     11          6           0        2.262002   -3.299831   -2.272617
     12          6           0        2.474646    3.077900   -2.247877
     13          6           0        1.475843    4.184720    0.856451
     14          6           0        0.096586    3.321738   -1.542573
     15          6           0        3.365586    2.596300    0.452674
     16          6           0        2.113435   -3.925134    0.141937
     17          6           0        3.819443   -0.919947   -1.677732
     18          6           0        4.667613   -2.540419    0.028430
     19          7           0       -0.807564    0.615301   -0.071429
     20          6           0       -1.591211    1.138346    0.877744
     21          6           0       -2.957993    0.905787    0.909827
     22          6           0       -3.546170    0.104534   -0.075559
     23          6           0       -2.704758   -0.426592   -1.061014
     24          6           0       -1.346109   -0.157655   -1.026431
     25          6           0       -5.002359   -0.171275   -0.076095
     26          6           0       -5.686071   -0.394368    1.125316
     27          6           0       -7.054117   -0.653285    1.123474
     28          6           0       -7.758130   -0.688648   -0.079338
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     31          8           0        0.843264   -1.381511    1.716072
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     33          1           0        3.182682   -3.865047   -2.465393
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     35          1           0        2.188317   -2.485246   -2.997554
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     37          1           0        2.734078    4.136497   -2.121204
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     47          1           0        3.639614    1.605837    0.071175
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     53          1           0        4.289873   -1.490218   -2.487365
     54          1           0        5.050403   -3.256374   -0.709433
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     58          1           0       -3.562596    1.368440    1.683590
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     60          1           0       -0.636668   -0.579275   -1.732416
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     62          1           0       -7.568668   -0.835826    2.062168
     63          1           0       -8.825081   -0.890267   -0.080888
     64          1           0       -7.629478   -0.485757   -2.220514
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     66          1           0       -0.428096   -2.673944    2.660105
     67          1           0       -1.244556   -1.387895    1.748238
     68          1           0       -0.476166   -2.738522    0.881331
     69         19           0        2.510828    0.265858    2.676980
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Summary of Natural Population Analysis:

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                                   Natural Population
             Natural  -----------------------------------------------
  Atom  No    Charge        Core      Valence    Rydberg      Total
-----------------------------------------------------------------------
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    B    2    0.86460      1.99813     2.09821    0.03906     4.13540
    O    3   -0.82472      1.99972     6.80590    0.01910     8.82472
    B    4    0.77701      1.99810     2.18774    0.03715     4.22299
    O    5   -0.86238      1.99975     6.84377    0.01887     8.86238
    O    6   -0.80280      1.99971     6.78319    0.01990     8.80280
    C    7    0.24225      1.99885     3.73398    0.02492     5.75775
    C    8    0.24797      1.99886     3.72809    0.02508     5.75203
    C    9    0.24015      1.99884     3.73489    0.02612     5.75985
    C   10    0.24146      1.99885     3.73489    0.02480     5.75854
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    C   12   -0.69395      1.99933     4.68434    0.01028     6.69395
    C   13   -0.69312      1.99932     4.68394    0.00986     6.69312
    C   14   -0.70396      1.99934     4.69435    0.01028     6.70396
    C   15   -0.70807      1.99933     4.69760    0.01114     6.70807
    C   16   -0.70789      1.99934     4.69788    0.01066     6.70789
    C   17   -0.70872      1.99933     4.69848    0.01090     6.70872
    C   18   -0.69154      1.99932     4.68268    0.00954     6.69154
    N   19   -0.47952      1.99928     5.44847    0.03177     7.47952
    C   20    0.05463      1.99910     3.92433    0.02195     5.94537
    C   21   -0.26637      1.99897     4.25447    0.01294     6.26637
    C   22   -0.00141      1.99898     3.98460    0.01783     6.00141
    C   23   -0.26076      1.99898     4.24887    0.01292     6.26076
    C   24    0.08313      1.99910     3.89563    0.02214     5.91687
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    C   28   -0.23783      1.99904     4.22349    0.01530     6.23783
    C   29   -0.23808      1.99905     4.22327    0.01576     6.23808
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    O   31   -0.88770      1.99974     6.86459    0.02338     8.88770
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    H   38    0.24941      0.00000     0.74987   0.00073     0.75059
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    H   40    0.23918      0.00000     0.76033   0.00049     0.76082
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    H   45    0.24436      0.00000     0.75512   0.00052     0.75564
    H   46    0.20523      0.00000     0.79387   0.00090     0.79477
    H   47    0.26282      0.00000     0.73591   0.00127     0.73718
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    H   49    0.22782      0.00000     0.77149   0.00069     0.77218
    H   50    0.24885      0.00000     0.74977   0.00138     0.75115
    H   51    0.27175      0.00000     0.72717   0.00108     0.72825
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    H   58    0.25932      0.00000     0.73980   0.00088     0.74068
    H   59    0.26363      0.00000     0.73557   0.00080     0.73637
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    H   61    0.24957      0.00000     0.74947   0.00096     0.75043
    H   62    0.25206      0.00000     0.74716   0.00077     0.74794
    H   63    0.25158      0.00000     0.74775   0.00067     0.74842
    H   64    0.25267      0.00000     0.74656   0.00077     0.74733
    H   65    0.25084      0.00000     0.74825   0.00091     0.74916
    H   66    0.19782      0.00000     0.80120   0.00098     0.80218
    H   67    0.16741      0.00000     0.83059   0.00200     0.83259
    H   68    0.20927      0.00000     0.78907   0.00165     0.79073
    K   69    0.98600     17.98395     0.02467   0.00537    18.01400
=======================================================================
  * Total *   -0.00000     81.95674   173.42030   0.62295   256.00000
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Cartesian coordinates of **TS-1•K**:

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Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
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     3          8           0       -0.325084    1.947220   -0.618707
     4          5           0       -0.986132   -1.061169   -0.198186
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     6          8           0       -1.807331   -1.078884   -1.350087
     7          6           0       -1.266411    3.003045   -0.854060
     8          6           0       -2.603666    2.440525   -0.246879
     9          6           0       -2.581200   -2.276793   -1.244831
    10          6           0       -2.821324   -2.394739    0.298771
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    17          6           0       -3.421951    1.647890   -1.261737
    18          6           0       -3.485942    3.499844    0.403027
    19          7           0        0.436163   -1.047537   -0.265655
    20          6           0        1.232811   -1.510176    0.796602
    21          6           0        2.588414   -1.328705    0.811152
    22          6           0        3.287485   -0.717392   -0.254508
    23          6           0        2.484145   -0.441802   -1.399137
    24          6           0        1.135503   -0.625105   -1.411385
    25          6           0        4.720951   -0.454140   -0.197117
    26          6           0        5.388851   -0.315146    1.038879
    27          6           0        6.757806   -0.080924    1.108154
    28          6           0        7.518727    0.043367   -0.054754
    29          6           0        6.876345   -0.076976   -1.288697
    30          6           0        5.510145   -0.323220   -1.360214
    31          8           0        0.043126    1.118092    1.665790
    32          6           0        1.391689    1.570357    1.598045
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    35          1           0       -1.526283    2.377335   -2.912677
    36          1           0       -3.586882   -2.067558   -3.131346
    37          1           0       -4.520356   -2.974815   -1.925642
    38          1           0       -4.383052   -1.202395   -1.808277
    39          1           0       -3.148622   -3.822559    1.884679
```

```
   40        1          0      -3.828629  -4.315755   0.324077
   41        1          0      -2.073600  -4.409955   0.606718
   42        1          0      -2.287361  -4.378187  -1.790994
   43        1          0      -1.439436  -3.193721  -2.810455
   44        1          0      -0.819016  -3.561250  -1.195275
   45        1          0      -4.955542  -1.905849   0.369212
   46        1          0      -4.080289  -1.601402   1.864458
   47        1          0      -3.863348  -0.500523   0.470760
   48        1          0       0.265238   4.447805  -0.444067
   49        1          0      -1.375567   5.114199  -0.277773
   50        1          0      -0.710657   4.043072   0.978627
   51        1          0      -2.830839   0.844755  -1.708036
   52        1          0      -4.285764   1.201960  -0.755761
   53        1          0      -3.805072   2.306703  -2.048378
   54        1          0      -3.787596   4.253661  -0.333636
   55        1          0      -4.394934   3.029853   0.793420
   56        1          0      -2.976924   4.002283   1.228655
   57        1          0       0.700244  -2.053185   1.568772
   58        1          0       3.134027  -1.727490   1.663760
   59        1          0       2.934639  -0.059583  -2.310622
   60        1          0       0.510465  -0.397417  -2.265516
   61        1          0       4.815398  -0.363053   1.961061
   62        1          0       7.231991   0.023196   2.081091
   63        1          0       8.586426   0.233324  -0.001788
   64        1          0       7.449276   0.008716  -2.208810
   65        1          0       5.049564  -0.445631  -2.336380
   66        1          0       1.938790   1.114388   2.426266
   67        1          0       1.867542   1.278351   0.658494
   68        1          0       1.418300   2.662843   1.690997
   69       19          0      -1.838654  -0.138731   2.840151
---------------------------------------------------------------------
```

Summary of Natural Population Analysis:

```
                                   Natural Population
             Natural  -----------------------------------------------
  Atom  No    Charge         Core      Valence    Rydberg      Total
-----------------------------------------------------------------------
     O    1   -0.85516      1.99971     6.83855    0.01691     8.85516
     B    2    1.24467      1.99896     1.70666    0.04971     3.75533
     O    3   -0.80524      1.99967     6.77989    0.02568     8.80524
     B    4    1.05651      1.99886     1.90346    0.04117     3.94349
     O    5   -0.84572      1.99973     6.82848    0.01751     8.84572
     O    6   -0.79270      1.99970     6.77375    0.01924     8.79270
```

C	7	0.24142	1.99885	3.73721	0.02251	5.75858
C	8	0.24594	1.99884	3.73185	0.02336	5.75406
C	9	0.23885	1.99885	3.73734	0.02497	5.76115
C	10	0.23959	1.99885	3.73698	0.02459	5.76041
C	11	-0.69841	1.99932	4.68858	0.01051	6.69841
C	12	-0.69735	1.99932	4.68779	0.01024	6.69735
C	13	-0.69743	1.99932	4.68787	0.01024	6.69743
C	14	-0.71168	1.99934	4.70085	0.01148	6.71168
C	15	-0.70740	1.99932	4.69697	0.01112	6.70740
C	16	-0.70656	1.99934	4.69640	0.01083	6.70656
C	17	-0.71446	1.99931	4.70386	0.01129	6.71446
C	18	-0.69719	1.99932	4.68767	0.01020	6.69719
N	19	-0.66107	1.99909	5.64140	0.02058	7.66107
C	20	-0.13233	1.99906	4.10376	0.02952	6.13233
C	21	-0.22597	1.99900	4.21291	0.01407	6.22597
C	22	-0.21349	1.99899	4.19381	0.02069	6.21349
C	23	-0.23234	1.99901	4.21999	0.01335	6.23234
C	24	-0.07746	1.99904	4.05369	0.02473	6.07746
C	25	-0.03872	1.99900	4.02342	0.01629	6.03872
C	26	-0.25628	1.99902	4.24249	0.01477	6.25628
C	27	-0.24192	1.99905	4.22645	0.01642	6.24192
C	28	-0.29027	1.99903	4.27300	0.01824	6.29027
C	29	-0.24043	1.99905	4.22509	0.01628	6.24043
C	30	-0.25024	1.99901	4.23664	0.01458	6.25024
O	31	-0.86376	1.99965	6.84549	0.01861	8.86376
C	32	-0.30424	1.99934	4.28910	0.01579	6.30424
H	33	0.23627	0.00000	0.76332	0.00041	0.76373
H	34	0.25402	0.00000	0.74523	0.00076	0.74598
H	35	0.25653	0.00000	0.74279	0.00068	0.74347
H	36	0.25488	0.00000	0.74434	0.00078	0.74512
H	37	0.23795	0.00000	0.76165	0.00040	0.76205
H	38	0.24439	0.00000	0.75486	0.00076	0.75561
H	39	0.23468	0.00000	0.76452	0.00080	0.76532
H	40	0.24261	0.00000	0.75694	0.00045	0.75739
H	41	0.25860	0.00000	0.74075	0.00065	0.74140
H	42	0.23675	0.00000	0.76267	0.00057	0.76325
H	43	0.25692	0.00000	0.74232	0.00076	0.74308
H	44	0.25363	0.00000	0.74537	0.00100	0.74637
H	45	0.25257	0.00000	0.74696	0.00047	0.74743
H	46	0.20892	0.00000	0.79021	0.00087	0.79108
H	47	0.25290	0.00000	0.74579	0.00130	0.74710
H	48	0.25727	0.00000	0.74191	0.00082	0.74273
H	49	0.24005	0.00000	0.75935	0.00059	0.75995
H	50	0.23782	0.00000	0.76147	0.00071	0.76218

```
    H   51    0.27902     0.00000    0.71978    0.00121    0.72098
    H   52    0.22899     0.00000    0.77031    0.00070    0.77101
    H   53    0.24115     0.00000    0.75838    0.00047    0.75885
    H   54    0.24387     0.00000    0.75569    0.00044    0.75613
    H   55    0.24157     0.00000    0.75759    0.00085    0.75843
    H   56    0.24572     0.00000    0.75362    0.00066    0.75428
    H   57    0.22903     0.00000    0.77003    0.00094    0.77097
    H   58    0.24316     0.00000    0.75577    0.00107    0.75684
    H   59    0.24568     0.00000    0.75350    0.00081    0.75432
    H   60    0.24994     0.00000    0.74914    0.00092    0.75006
    H   61    0.23088     0.00000    0.76801    0.00111    0.76912
    H   62    0.23804     0.00000    0.76109    0.00087    0.76196
    H   63    0.23924     0.00000    0.75998    0.00078    0.76076
    H   64    0.23945     0.00000    0.75971    0.00084    0.76055
    H   65    0.23540     0.00000    0.76365    0.00095    0.76460
    H   66    0.21581     0.00000    0.78346    0.00073    0.78419
    H   67    0.23683     0.00000    0.76124    0.00192    0.76317
    H   68    0.20126     0.00000    0.79773    0.00100    0.79874
    K   69    0.98903    17.98719    0.01946    0.00431   18.01097
=======================================================================
  * Total *   0.00000    81.96112   173.40002   0.63886   256.00000
```

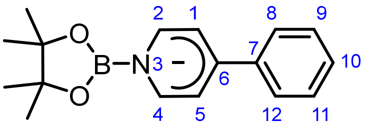
3.3 DFT calculated HOMO and NAO orbital composition of Int-B

Cartesian coordinates of **Int-B:**

```
---------------------------------------------------------------------
Center    Atomic     Atomic           Coordinates (Angstroms)
Number    Number      Type           X         Y         Z
---------------------------------------------------------------------
    1        6          0      -1.691014    1.168859  -0.364006
    2        6          0      -0.341956    1.170027  -0.414371
    3        7          0       0.423579   -0.020200  -0.194879
    4        6          0      -0.340693   -1.230641  -0.164869
    5        6          0      -1.689712   -1.220823  -0.116148
    6        6          0      -2.487888   -0.015101  -0.131547
    7        6          0      -3.901202   -0.003194  -0.010758
    8        6          0      -4.680235    1.201953  -0.060790
    9        6          0      -6.061478    1.202962   0.043365
   10        6          0      -6.793190    0.018993   0.213260
   11        6          0      -6.061162   -1.174908   0.282500
   12        6          0      -4.679944   -1.194358   0.179993
   13        5          0       1.810421   -0.007542  -0.079284
   14        8          0       2.606880    1.142296  -0.196796
   15        6          0       3.917351    0.778087   0.239170
```

```
    16          6           0        3.956209   -0.755965   -0.065941
    17          8           0        2.599431   -1.145237    0.151979
    18          6           0        4.860219   -1.564807    0.853747
    19          6           0        4.297269   -1.047922   -1.529587
    20          6           0        4.943642    1.604758   -0.522744
    21          6           0        4.010231    1.074231    1.738284
    22          1           0       -2.174618    2.124666   -0.549157
    23          1           0        0.246901    2.056032   -0.621844
    24          1           0        0.249599   -2.139548   -0.182505
    25          1           0       -2.171912   -2.194888   -0.099514
    26          1           0       -4.176584    2.157276   -0.177055
    27          1           0       -6.585982    2.157367   -0.004845
    28          1           0       -7.876076    0.027317    0.297569
    29          1           0       -6.585497   -2.119957    0.424912
    30          1           0       -4.176272   -2.153772    0.255140
    31          1           0        5.897660   -1.214769    0.786820
    32          1           0        4.527894   -1.495103    1.892045
    33          1           0        4.832313   -2.618567    0.558202
    34          1           0        4.102719   -2.106247   -1.728119
    35          1           0        3.666225   -0.454190   -2.199069
    36          1           0        5.349013   -0.835415   -1.752652
    37          1           0        5.962683    1.273325   -0.288216
    38          1           0        4.785542    1.531173   -1.601192
    39          1           0        4.849222    2.657213   -0.236453
    40          1           0        3.766229    2.128438    1.900547
    41          1           0        3.289323    0.468500    2.297104
    42          1           0        5.015293    0.880882    2.130058
 ---------------------------------------------------------------------
```

The HOMO of **Int-B** was plotted using the softwares Multiwfn[3] and VMD,[4] with isovalue = 0.07. The result of the NAO orbital composition analysis was listed below.

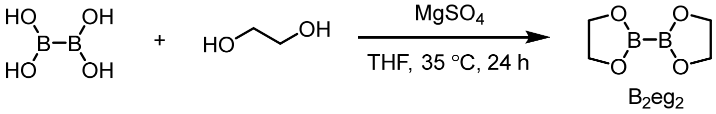


```
  NAO#   Center   Label     Type      Composition
    1    1(C )     S       Cor(1S)     0.000036%
    2    1(C )     S       Val(2S)     0.009409%
    6    1(C )     px      Val(2p)     0.003600%
    9    1(C )     py      Val(2p)     0.029929%
   12    1(C )     pz      Val(2p)     0.765625%
   20    2(C )     S       Cor(1S)     0.000025%
   21    2(C )     S       Val(2S)     0.008649%
   25    2(C )     px      Val(2p)     0.015376%
```

```
      28    2(C )    py      Val(2p)      0.439569%
      31    2(C )    pz      Val(2p)     12.110400%
      39    3(N )    S       Cor(1S)      0.000004%
      40    3(N )    S       Val(2S)      0.001369%
      44    3(N )    px      Val(2p)      0.041616%
      47    3(N )    py      Val(2p)      0.074529%
      50    3(N )    pz      Val(2p)      7.054336%
      58    4(C )    S       Cor(1S)      0.000025%
      59    4(C )    S       Val(2S)      0.010000%
      63    4(C )    px      Val(2p)      0.015376%
      66    4(C )    py      Val(2p)      0.004761%
      69    4(C )    pz      Val(2p)     12.517444%
      77    5(C )    S       Cor(1S)      0.000036%
      78    5(C )    S       Val(2S)      0.008464%
      82    5(C )    px      Val(2p)      0.003136%
      85    5(C )    py      Val(2p)      0.000169%
      88    5(C )    pz      Val(2p)      0.808201%
      96    6(C )    S       Cor(1S)      0.000049%
      97    6(C )    S       Val(2S)      0.002809%
     101    6(C )    px      Val(2p)      0.304704%
     104    6(C )    py      Val(2p)      0.297025%
     107    6(C )    pz      Val(2p)     27.510025%
Condensed above result to atoms:
1(C )    0.808599%
2(C )   12.574019%
3(N )    7.171854%
4(C )   12.547606%
5(C )    0.820006%
6(C )   28.114612%
```

4. Optimization of Reaction Conditions

4.1 The synthesis of bis(ethyleneglycolato)diboron (B_2eg_2)



B_2eg_2 was prepared according to a published procedure[5] with some modification. A 125 mL round-bottom flask was charged with a magnetic stir bar, $B_2(OH)_4$ (2.0 g, 22.4 mmol), anhydrous $MgSO_4$ (3.22 g, 26.8 mmol) and 40 mL THF. Then freshly distilled ethylene glycol (2.9 g, 46.8 mmol) was added to the flask. The flask was sealed with a rubber stopper and the reaction mixture was stirred at 35 °C for 24 h. The reaction mixture was filtered, and the residue was washed by THF. The combined filtrate was concentrated, and the residue was further purified by sublimation at reduced pressure (150 °C, 2.5 Pa) to get a white solid (1.8 g, 58% yield). The spectroscopic data was consistent with those reported in literature.[5]

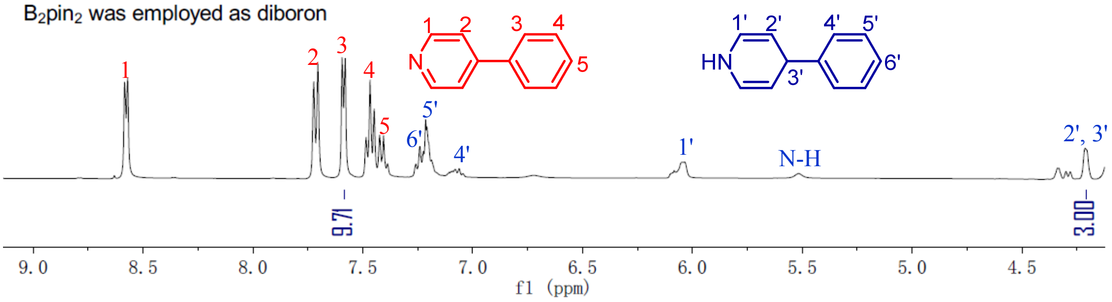
4.2 Experimental procedure for the optimization study

In a glove box, a 15 mL oven-dried glass vial was charged with 4-PhPy (56.5 mg, 0.36 mmol), diboron(4) (0.40 mmol), base (0.40 mmol), and 2 mL of anhydrous solvent. Then MeOH (128 mg, 4.0 mmol) was added by a microsyringe. The vial was sealed and the resulting mixture was allowed to react at 30 °C for 4.5 h. The crude reaction solution was transferred to an NMR tube in a glove box, and then ^1H NMR analysis (No-D NMR) of the reaction solution was performed.

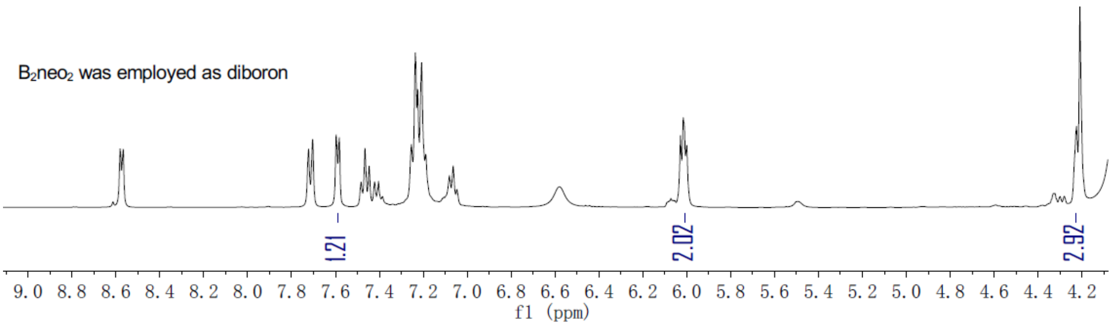
4.3 ^1H NMR spectra of the optimization experiments

^1H NMR spectra of the crude reaction mixtures of optimization experiments are shown below, which were used to calculate the conversions listed in Table 1 of the main text. The integrals of the 1,4-DHP product (6.04 ppm) and the unreacted 4-phenylpyridine (7.59 ppm) were used to calculate the NMR conversion, assuming that 1,4-DHP was the only product of the converted 4-phenylpyridine.

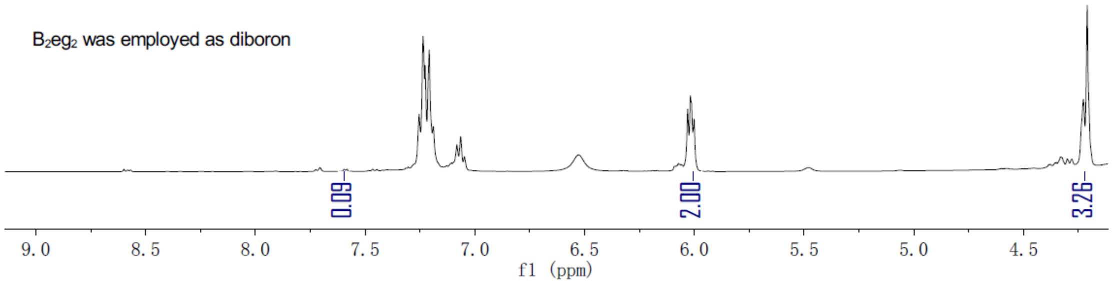
Entry 1: B_2pin_2, MeOK in THF (17% conversion)



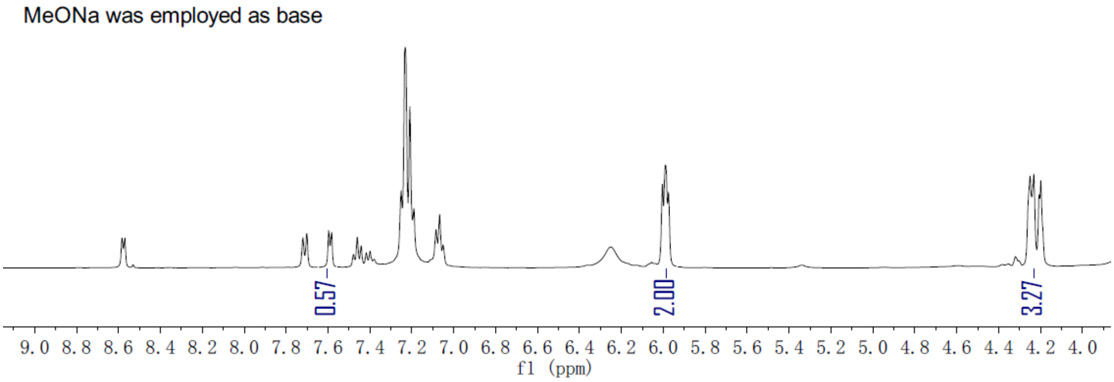
Entry 2: B_2neo_2, MeOK in THF (63% conversion)



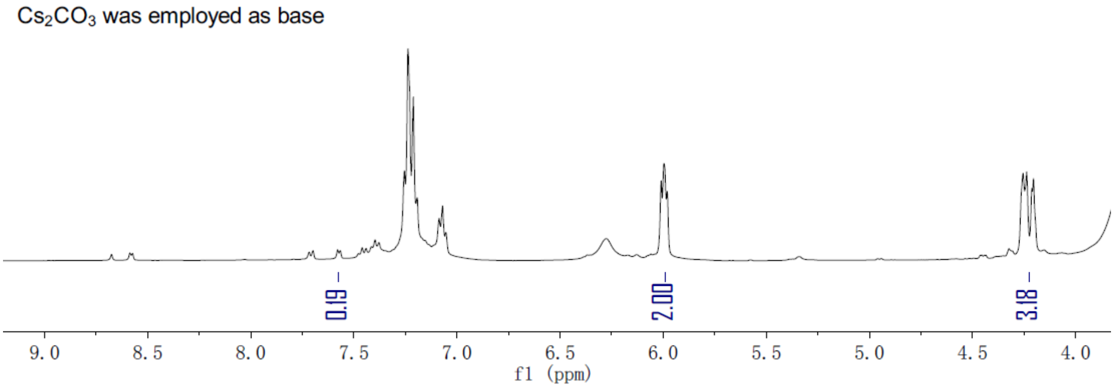
Entry 3: B_2eg_2, MeOK in THF (96% conversion)



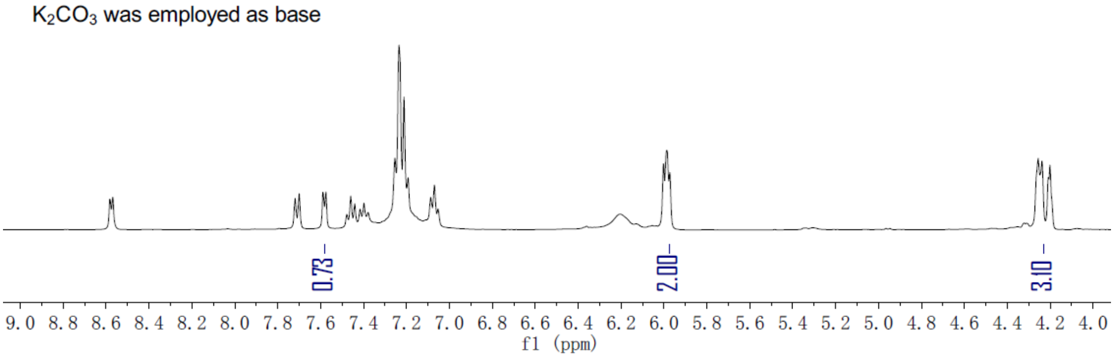
Entry 4: B_2eg_2, MeONa in THF (78% conversion)



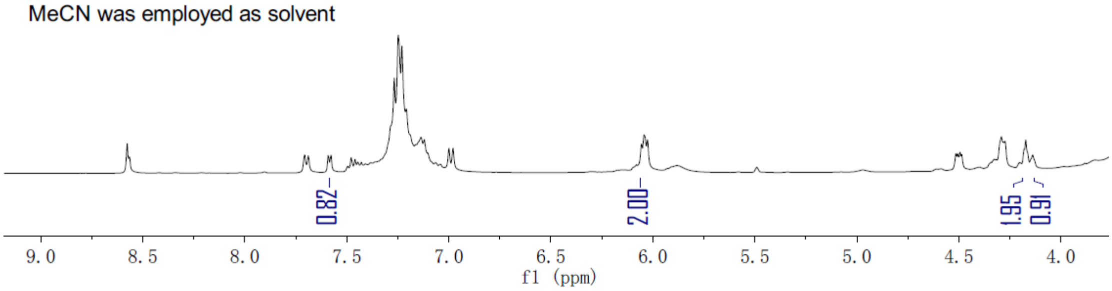
Entry 5: B_2eg_2, Cs_2CO_3 in THF (91% conversion)



Entry 6: B_2eg_2, K_2CO_3 in THF (73% conversion)



Entry 7: B_2eg_2, Cs_2CO_3 in MeCN (71% conversion)



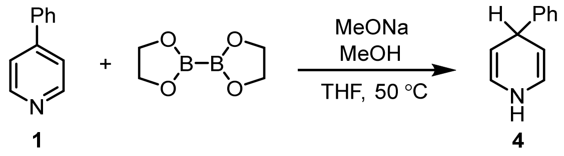
Note: the NMR shifts of the peaks of the 1,4-DHP product in the crude reaction mixture were slightly different from those obtained in the preliminary experiments (Section 2.2). This was due to the excess MeOH (11 equiv.) added in the optimization experiments, which may form hydrogen bonds with the 1,4-DHP product. This was confirmed by the observation that addition of excess MeOH to the previous reaction mixtures caused the shift of the product peaks.

5. Substrate Scope and Characterization Data

General procedure (GP-A) for determination of the NMR yield: In a glove box, a 15 mL oven-dried reaction vail was charged with pyridine substrate (0.18 mmol), B_2eg_2 (28.4 mg, 0.20 mmol), base (0.20 mmol), and anhydrous THF (2 mL). MeOH (64.0 mg, 2.00 mmol) or MeOD (134 mg, 4.00 mmol) was then added by a microsyringe. The vial was sealed by a screw cap and the resulting mixture was then allowed to react at 50 °C for 14 h. The reaction mixture was cooled to room temperature, and a standard solution of DMSO in THF was added as the internal standard under an argon atmosphere. The crude reaction solution was transferred to an NMR tube in a glove box, and then ^1H NMR analysis (No-D NMR) of the reaction solution was performed to determine the NMR yield of the 1,4-DHP product.

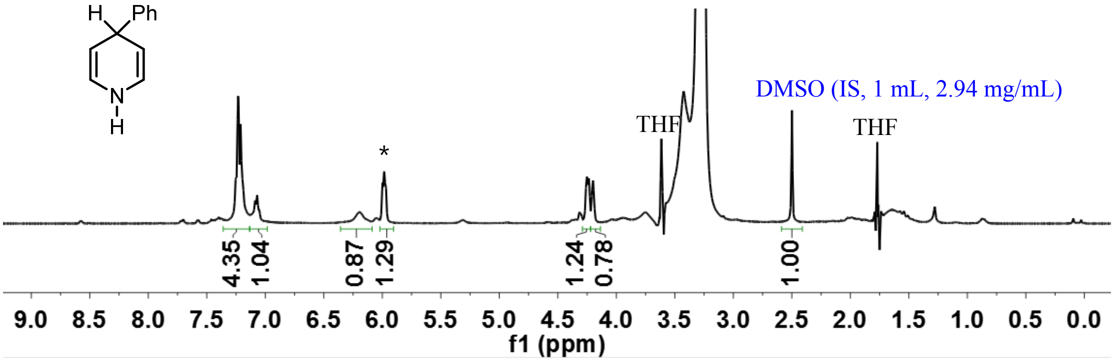
General procedure (GP-B) for obtaining the pure 1,4-DHP product: In a glove box, a 25 mL Schlenk tube was charged with the pyridine substrate (0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), Cs_2CO_3 (130 mg, 0.40 mmol) and anhydrous MeCN (2 mL). MeOH (128 mg, 4.00 mmol) or MeOD (264 mg, 8.00 mmol) was added by a microsyringe. The tube was sealed by a rubber septum and the resulting mixture was allowed to react at 50 °C for 14 h. The reaction solution was cooled to room temperature and was transferred to a column packed with a pad of basic alumina (6 g, dried in the oven prior to use) using degassed anhydrous diethyl ether. A positive pressure of argon was applied to drive the solution pass through the column, and then the column was washed by 3 × 20 mL degassed diethyl ether. The combined organic solution was concentrated under vacuum under an argon atmosphere to obtain the 1,4-dihydropyridine product.

4-Phenyl-1,4-dihydropyridine (4)



Determination of the NMR yield. Following the general procedure GP-A, starting from **1** (28.0 mg, 0.18 mmol), B_2eg_2 (28.4 mg, 0.20 mmol), and MeOH (64.0 mg, 2.00 mmol), and using MeONa (10.8 mg, 0.20 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **4** was generated in 81% NMR yield.

^1H NMR of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



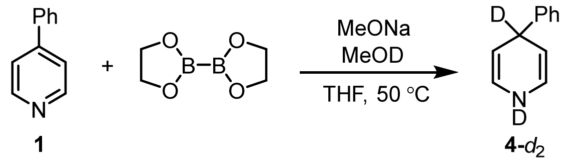
Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

^{1}H NMR (400 MHz, THF-d_0): δ 7.24 (m, 4H), 7.07 (m, 1H), 6.17 (br s, 1H), 5.99 (m, 2H), 4.26 (d, J = 6.8 Hz, 2H), 4.20 (m, 1H).

^{13}C NMR (100 MHz, THF-d_0): δ 150.5, 127.8, 127.4, 125.8, 125.3, 100.0, 39.9.

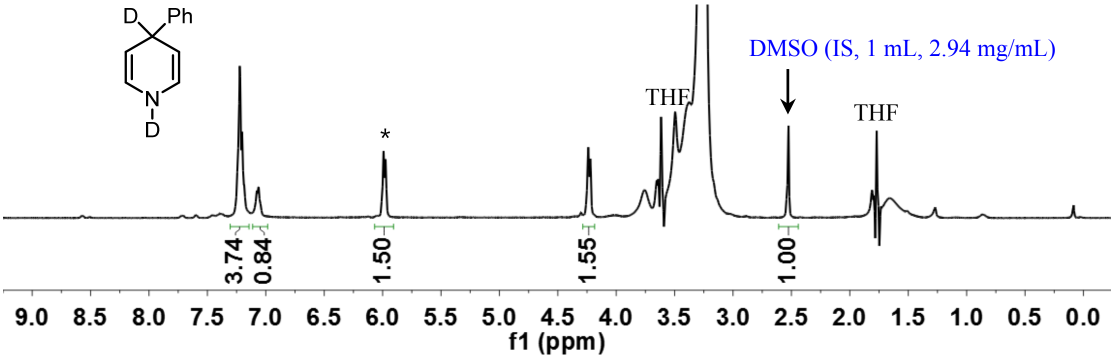
GC-MS: $C_{11}H_{11}N$ (m/z = 157, M$^{\cdot+}$).

4-Phenyl-1,4-dideuteropyridine (4-d_2)



Determination of the NMR yield. Following the general procedure GP-A, starting from **1** (28.0 mg, 0.18 mmol), B_2eg_2 (28.4 mg, 0.20 mmol), and MeOD (132 mg, 4.00 mmol), and using MeONa (10.8 mg, 0.20 mmol) as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **4**-d_2 was generated in 94% NMR yield (>98% 4-D).

^{1}H NMR of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

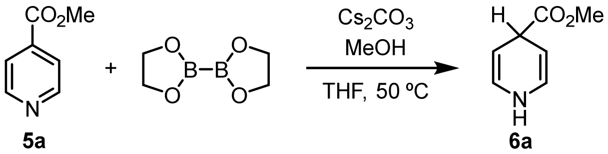
^{1}H NMR (400 MHz, THF-d_0): δ 7.24 (m, 4H), 7.06 (m, 1H), 5.99 (d, J = 7.6 Hz, 2H), 4.26 (d, J = 7.6 Hz, 2H).

^{2}H NMR (61 MHz, THF-d_0): δ 6.24, 4.17.

^{13}C NMR (100 MHz, THF-d_0): δ 150.5, 127.8, 127.4, 125.7, 125.3, 99.8, 39.4 (t, J = 20.1 Hz).

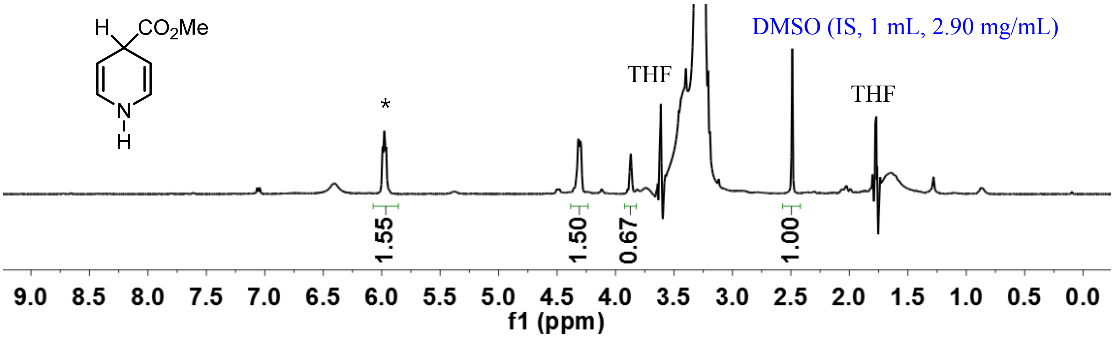
GC-MS: $C_{11}H_9ND_2$ [m/z = 159, (M-d_2)$^{\cdot+}$].

Methyl 1,4-dihydropyridine-4-carboxylate (6a)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5a** (25.0 mg, 0.18 mmol), B_2eg_2 (28.4 mg, 0.20 mmol), and MeOH (64.0 mg, 2.00 mmol), and using Cs_2CO_3 (65.2 mg, 0.20 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6a** was generated in 96% NMR yield.

^1H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



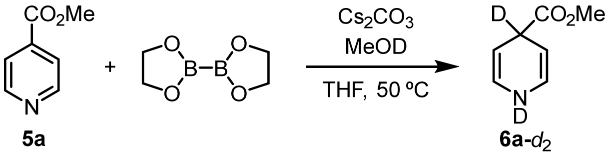
Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

^1H NMR (400 MHz, THF-d_0): δ 6.34 (br s, 1H), 5.97 (dd, J = 7.5, 4.9 Hz, 2H), 4.31 (dd, J = 7.5, 3.7 Hz, 2H), 3.87 (t, J = 3.7 Hz, 1H).

^{13}C NMR (100 MHz, THF-d_0): δ 173.4, 127.3, 93.7, 50.5, 39.2.

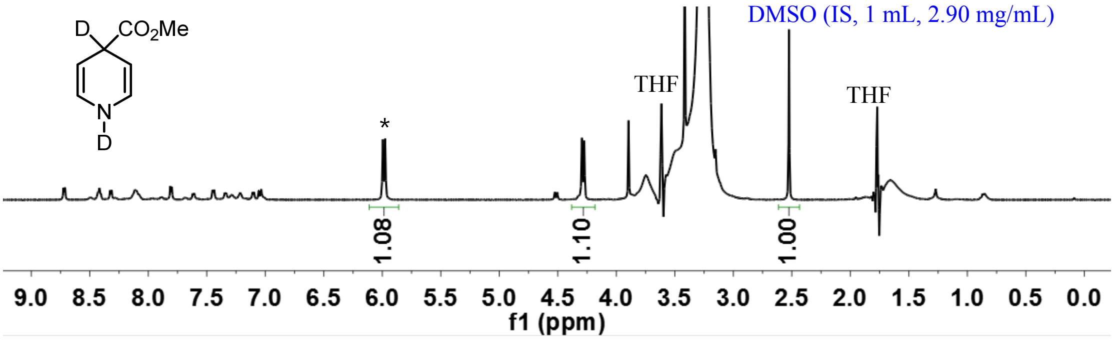
GC-MS: $C_7H_9NO_2$ [m/z = 139, ($M^{\cdot+}$)].

Methyl 1,4-dideuteropyridine-4-carboxylate (6a-d_2)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5a** (25.0 mg, 0.18 mmol), B_2eg_2 (28.4 mg, 0.20 mmol), and MeOD (132 mg, 4.00 mmol), and using Cs_2CO_3 (65.2 mg, 0.20 mmol) as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **6a-d_2** was generated in 67% NMR yield (>98% 4-D).

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

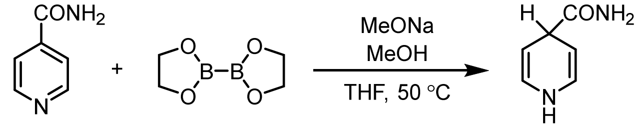
^{1}H NMR (400 MHz, THF-d_0): δ 5.99 (d, J = 7.6 Hz, 2H), 4.29 (d, J = 7.6 Hz, 2H).

^{2}H NMR (61 MHz, THF-d_0): δ 6.52, 3.84.

^{13}C NMR (100 MHz, THF-d_0): δ 173.7, 127.4, 93.5, 50.6, 38.9 (t, J = 19.8 Hz).

GC-MS: $C_7H_7NO_2D_2$ [m/z = 141, $(M\text{-}d_2)^{\cdot+}$].

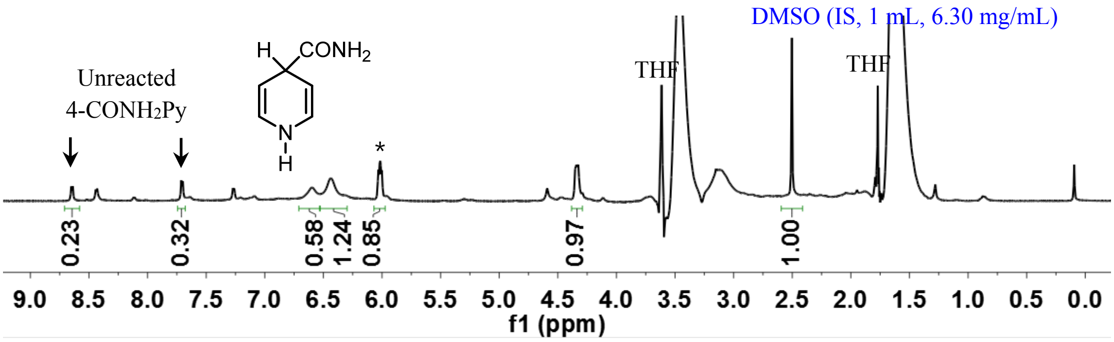
1,4-Dihydropyridine-4-carboxamide (6b)



5b **6b**

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5b** (45.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using MeONa (21.6 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6b** was generated in 57% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



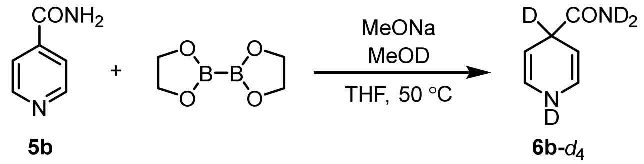
Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

^{1}H NMR (400 MHz, THF-d_0): δ 6.48 (br s, 1H), 6.40 (br s, 2H), 6.01 (m, 2H), 4.34 (m, 2H). The peak of C4-H overlapped with the THF peak at 3.61 ppm.

^{13}C NMR (100 MHz, THF-d_0): δ 177.0, 127.4, 95.7, 41.6.

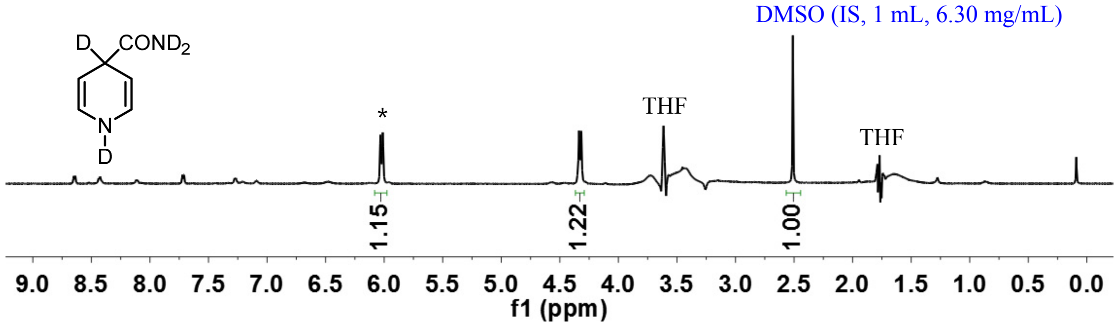
GC-MS: $C_6H_8N_2O$ [m/z = 124, (M$^{\cdot+}$)].

1,4-Dideuteropyridine-4-carboxamide (6b-d_4)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5b** (45.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 7.99 mmol), and using MeONa (21.6 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **6b-d_4** was generated in 77% NMR yield (ratio of deuterium incorporation at the C4-position was not calculated due to overlap of the residue C4-H peak with other peaks).

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

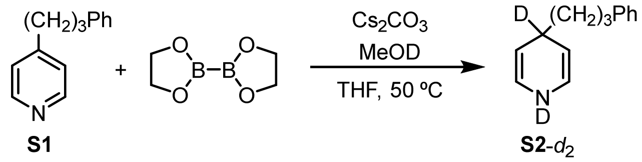
^{1}H NMR (400 MHz, THF-d_0): δ 6.02 (d, J = 7.6 Hz, 2H), 4.33 (d, J = 7.6 Hz, 2H).

^{2}H NMR (61 MHz, THF-d_0): δ 6.63, 6.50, 3.61.

^{13}C NMR (100 MHz, THF-d_0): δ 177.3, 127.5, 95.3, 41.1 (t, J = 21.0 Hz).

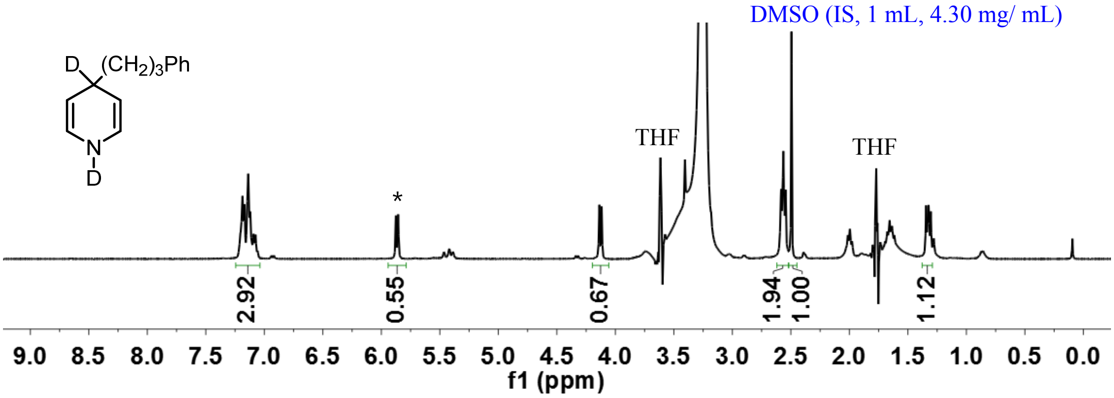
GC-MS: $C_6H_4N_2OD_4$ [m/z = 128, (M-d_4)$^{\cdot+}$].

4-(3-Phenylpropyl)-1,4-dideuteropyridine (S2-*d*2)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **S1** (35.9 mg, 0.18 mmol), B_2eg_2 (28.4 mg, 0.20 mmol), and MeOD (132 mg, 4.00 mmol), and using Cs_2CO_3 (65.2 mg, 0.20 mmol) as the base in 4 mL of anhydrous THF, 1,4-dideuteropyridine product **S2-***d*2 was generated in 50% NMR yield (98% 4-D).

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

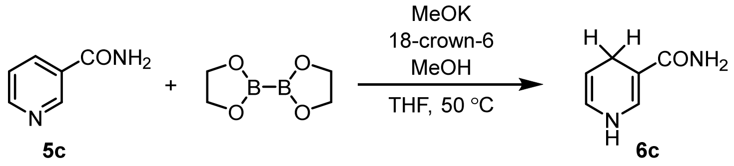
^{1}H NMR (400 MHz, THF-d_0): δ 7.16 (m, 5H), 5.87 (d, J = 7.7 Hz, 2H), 4.13 (d, J = 7.7 Hz, 2H), 2.57 (t, J = 7.8 Hz, 2H), 1.65 (m, 2H), 1.32 (m, 2H).

^{2}H NMR (61 MHz, THF-d_0): δ 5.98, 2.98.

^{13}C NMR (100 MHz, THF-d_0): δ 142.9, 128.1, 127.9, 126.5, 125.2, 99.6, 40.5, 36.2, 29.3 (t, J = 48.1 Hz), 27.3.

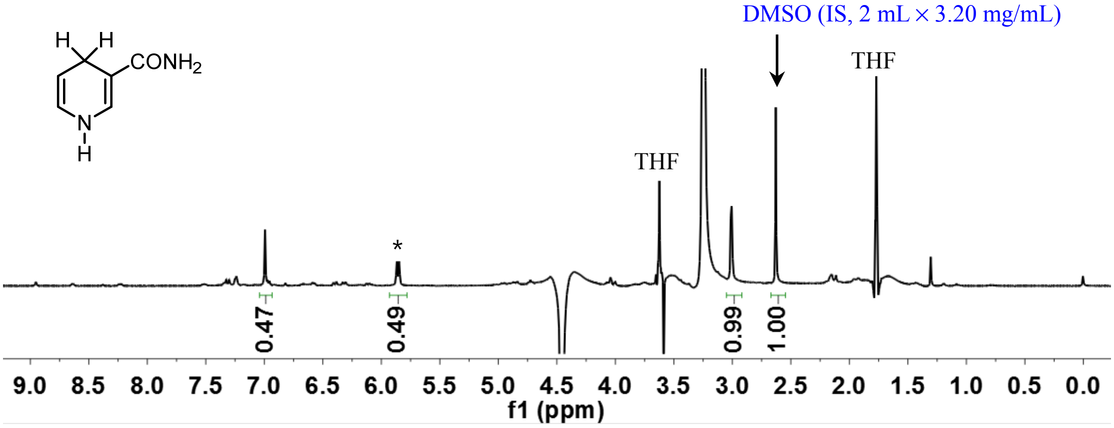
The formation of 1,4-DHP product **S2**-*d*2 from pyridine **S1** indicated that the present hydroboration process is compatible with pyridine substrate with electron-neutral substituents and is not limited to activated pyridines.

1,4-Dihydropyridine-3-carboxamide (6c)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5c** (44.5 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using the combination of MeOK (28 mg, 0.40 mmol) and 18-crown-6 (106 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6c** was generated in 67% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



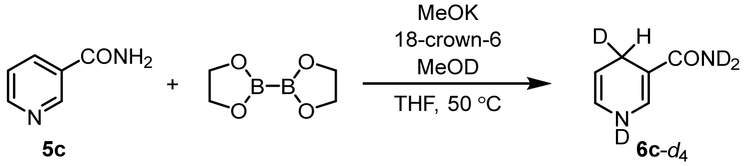
Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

^{1}H NMR (400 MHz, THF-d_0): δ 6.96 (m, 1H), 6.08 (br s, 3H), 5.84 (m, 1H), 4.50 (dt, J = 7.7, 3.5 Hz, 1H), 3.08 (m, 2H).

^{13}C NMR (100 MHz, THF-d_0): δ 170.3, 135.1, 125.4, 100.2, 99.0, 22.7.

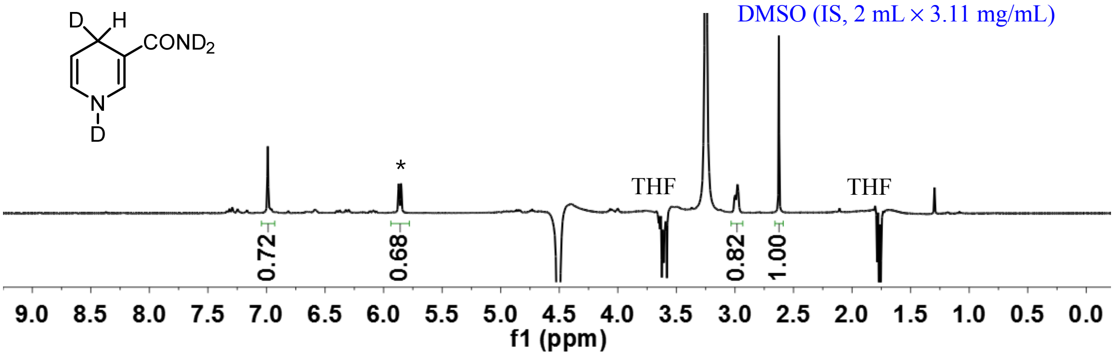
GC-MS: $C_6H_8N_2O$ [m/z = 124, $(M^{\cdot+})$].

1,4-Dideuteropyridine-3-carboxamide (6c-d_4)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5c** (45.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 7.99 mmol), and using the combination of MeOK (28 mg, 0.40 mmol) and 18-crown-6 (106 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **6c-**d_4 was generated in 90% NMR yield (86% 4-D).

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Note: This 1,4-DHP product was rather oxygen-labile, and attempts to obtain its pure form following general procedure GP-B failed. The NMR data were acquired using the No-D NMR technique from the above reaction mixture.

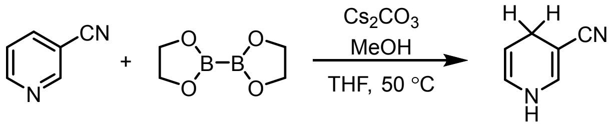
^{1}H NMR (400 MHz, THF-d_0): δ 7.01 (s, 1H), 5.85 (d, J = 7.9 Hz, 1H), 4.50 (dd, J = 7.9, 3.4 Hz, 1H), 3.06 (m, 1H).

^{2}H NMR (61 MHz, THF-d_0): δ 7.15, 6.29, 3.06.

^{13}C NMR (100 MHz, THF-d_0): δ 170.8, 135.5, 125.3, 100.1, 98.4, 22.2 (t, J = 19.8 Hz).

GC-MS: $C_6H_4N_2OD_4$ [m/z = 128, (M-d_4)$^{\cdot+}$].

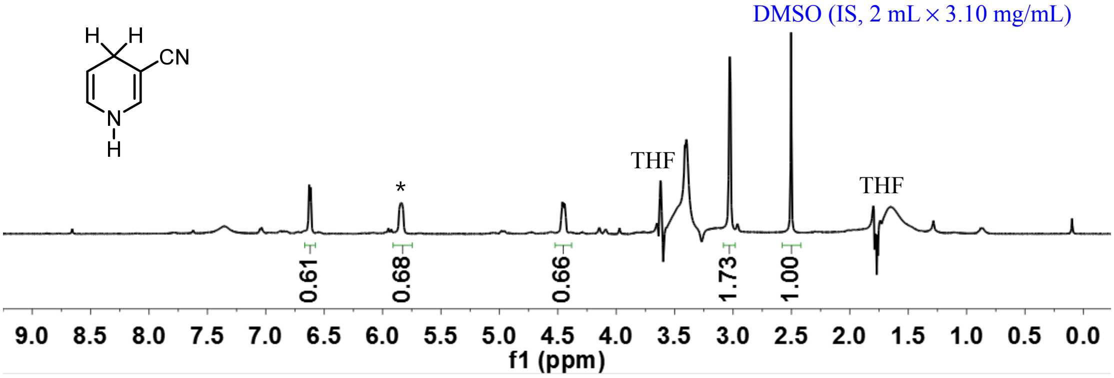
1,4-Dihydropyridine-3-carbonitrile (6d)



5d 6d

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5d** (36.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6d** was generated in 90% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



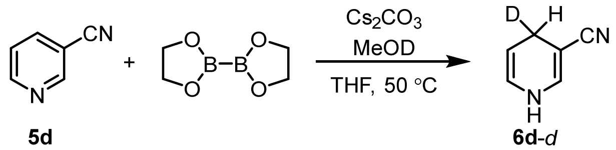
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5d** (473 mg, 4.55 mmol), the 1,4-DHP product **6d** (321 mg, 67% yield) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.61 (d, *J* = 4.7 Hz, 1H), 5.84 (m, 1H), 5.40 (br s, 1H), 4.60 (ddt, *J* = 8.2, 1.6, 3.5 Hz, 1H), 3.10 (dd, *J* = 3.5, 1.6 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 140.0, 124.3, 121.6, 100.7, 78.4, 23.4.

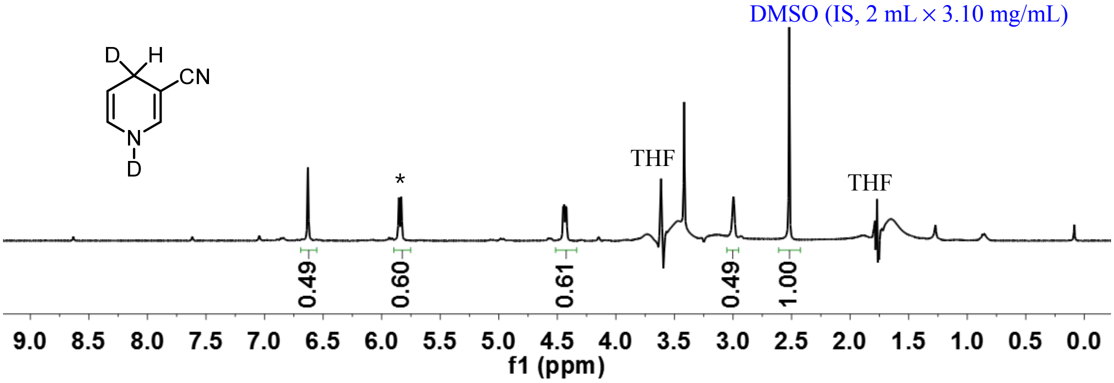
HRMS Calcd for $C_6H_6N_2$ (M+H)$^+$: 107.0609, Found: 107.0604.

4-Deutero-1-hydropyridine-3-carbonitrile (6d-*d*)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5d** (36.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 8.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **6d**-*d*$_2$ was generated in 79% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the gerenal procedure GP-B, starting from pyridine **5d** (473 mg, 4.55 mmol), the 1,4-DHP product **6d**-*d* (300 mg, 62% yield, >98% 4-D) was obtained. **Note:** In the crude mixture **6d**-*d*$_2$ was produced, which became **6d**-*d* during purification due to H/D exchange at the nitrogen atom.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.61 (dt, *J* = 5.6, 0.9 Hz, 1H), 5.84 (ddt, *J* = 8.1, 4.4, 6.5 Hz, 1H), 5.31 (br s, 1H), 4.60 (ddd, *J* = 8.1, 3.4, 1.5 Hz, 1H), 3.08 (m, 1H).

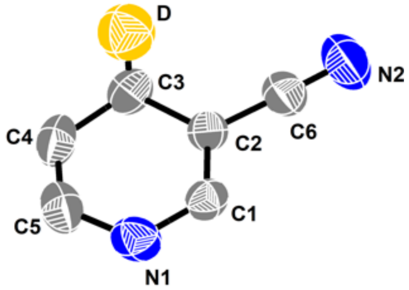
^{2}H NMR (61 MHz, CDCl$_3$): δ 3.08.

^{13}C NMR (100 MHz, CDCl$_3$): δ 140.2, 124.3, 121.6, 100.7, 78.6, 23.0 (t, *J* = 20.7 Hz).

HRMS Calcd for $C_6H_5N_2D$ (M+H)$^+$: 108.0672, Found: 108.0670.

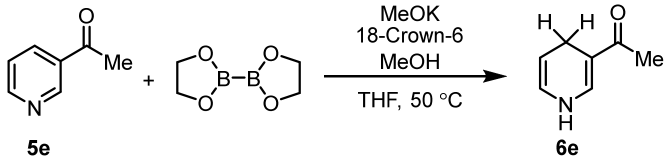
Sample for X-Ray single crystal diffraction analysis was prepared by recrystallization in CH_2Cl_2/*n*-hexane.

Data for XRD analysis of 6d-*d* (CCDC1935576)



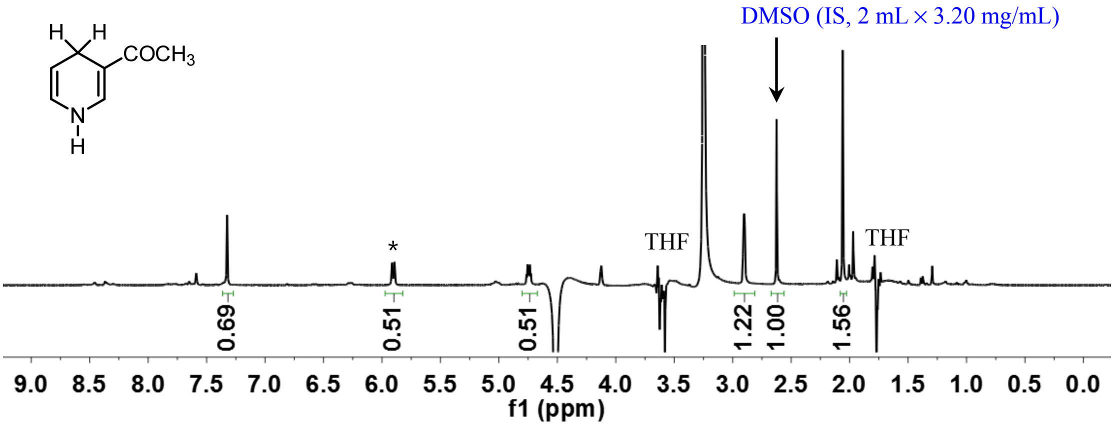
Empirical formula	$C_6H_5DN_2$
Formula weight	107.13
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	6.0431(2)
b/Å	13.3857(4)
c/Å	14.3592(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1161.53(6)
Z	8
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.613
F(000)	448.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	12.328 to 153.394
Index ranges	$-7 \le h \le 5$, $-16 \le k \le 16$, $-17 \le l \le 12$
Reflections collected	2497
Independent reflections	1181 [R_{int} = 0.0169, R_{sigma} = 0.0209]
Data/restraints/parameters	1181/0/81
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0667, wR_2 = 0.1497
Final R indexes [all data]	R_1 = 0.0746, wR_2 = 0.1598
Largest diff. peak/hole / e Å^{-3}	0.36/-0.56

3-Acetyl-1,4-dihydropyridine (6e)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5e** (45.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using the combination of MeOK (28.0 mg, 0.40 mmol) and 18-crown-6 (106 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6e** was generated in 70% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



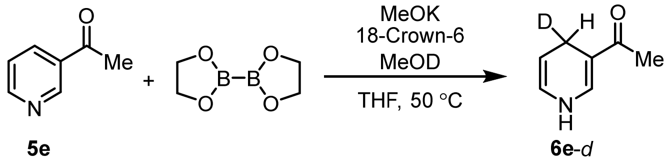
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5e** (605 mg, 5.00 mmol), the 1,4-DHP product **6e** (259 mg, 42% yield) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 5.8 Hz, 1H), 5.98 (br s, 1H), 5.88 (m, 1H), 4.83 (ddt, *J* = 6.7, 3.6, 1.8 Hz, 1H), 3.07 (dd, *J* = 3.6, 1.8 Hz, 2H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 140.0, 123.7, 109.5, 105.3, 24.1, 21.7.

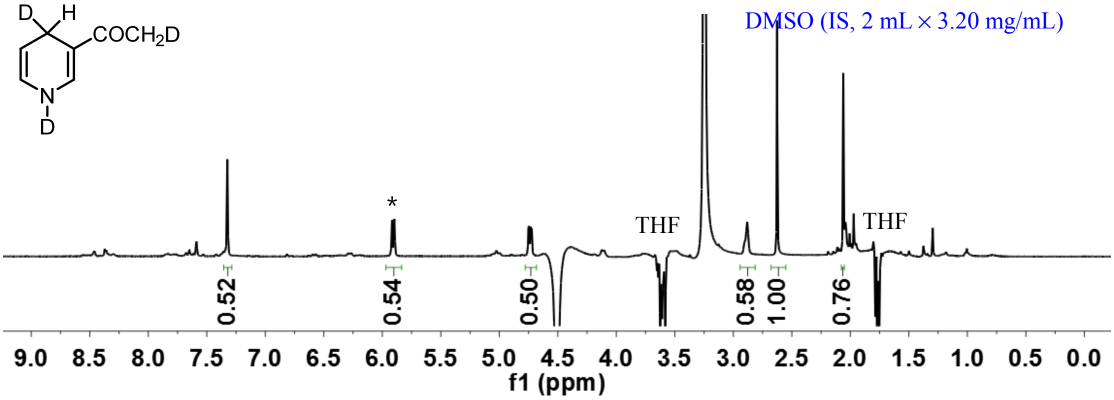
HRMS Calcd for C_7H_9NO $(M+H)^+$: 124.0762, Found: 124.0754.

3-Acetyl-4-deutero-1-hydropyridine (6e-*d*)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5e** (45.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (132 mg, 4.00 mmol), and using the combination of MeOK (28.0 mg, 0.40 mmol) and 18-crown-6 (106 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **6e**-d_2 was generated in 74% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5e** (44.0 mg, 0.36 mmol), the 1,4-DHP product **6e**-*d* (20.8 mg, 46% yield) was obtained. **Note:** In the crude mixture **6e**-d_2 was produced, which became **6e**-*d* during purification due to H/D exchange at the nitrogen atom. Both ^{1}H and ^{2}H NMR analysis also showed a minor extent of deuterium incorporation (20% D) at the methyl group.

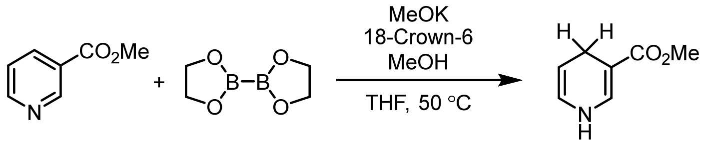
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J = 5.4 Hz, 1H), 5.89 (dd, J = 8.3, 3.8 Hz, 1H), 5.79 (br s, 1H), 4.83 (m, 1H), 3.05 (t, J = 2.6 Hz, 1H), 2.15 (s, 3H).

^{2}H NMR (61 MHz, $CDCl_3$): δ 3.07, 2.16 (t, J = 1.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 139.8, 123.7, 109.6, 105.2, 24.1, 21.3 (t, J = 20.2 Hz).

HRMS Calcd for C_7H_8NOD $(M+H)^+$: 125.0825, Found: 125.0815.

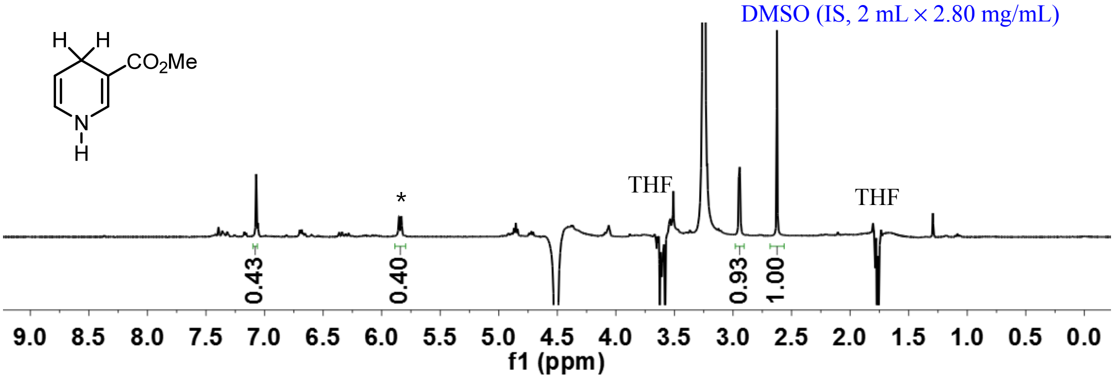
Methyl 1,4-dihydropyridine-3-carboxylate (6f)



5f **6f**

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5f** (50.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using the combination of MeOK (28.0 mg, 0.40 mmol) and 18-crown-6 (106 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6f** was generated in 48% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



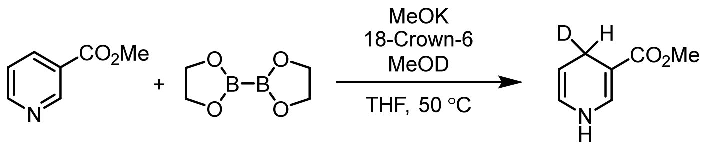
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5f** (625 mg, 4.56 mmol), the 1,4-DHP product **6f** (260 mg, 41% yield) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.12 (d, *J* = 5.6 Hz, 1H), 5.86 (m, 1H), 5.27 (br s, 1H), 4.72 (m, 1H), 3.68 (s, 3H), 3.11 (dd, *J* = 3.5, 1.7 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 168.9, 137.9, 124.2, 103.5, 98.2, 51.1, 22.2.

HRMS Calcd for $C_7H_9NO_2$ $(M+H)^+$: 140.0712, Found: 140.0702.

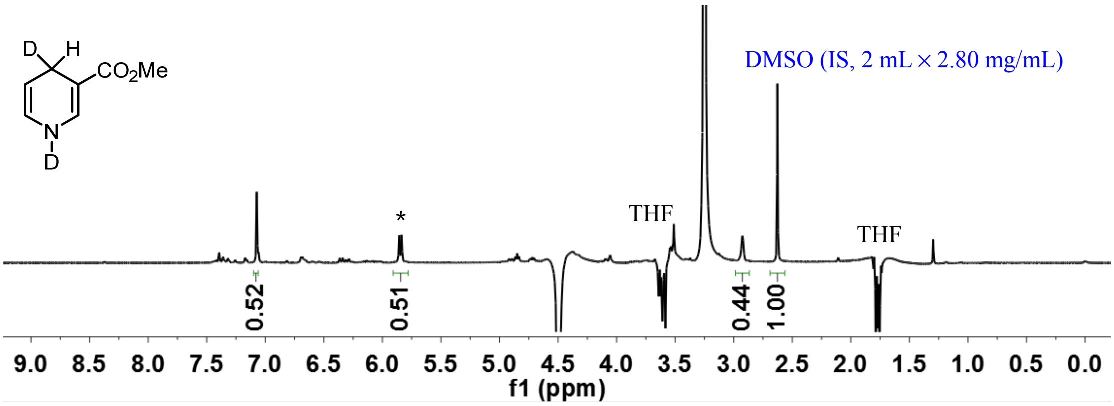
Methyl 4-deutero-1-hydropyridine-3-carboxylate (6f-*d*)



5f **6f**-*d*

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5f** (50.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (132 mg, 4.00 mmol), and using the combination of MeOK (28.0 mg, 0.40 mmol) and 18-crown-6 (106 mg, 0.40 mmol) as the base in 2 mL of anhydrous THF, 1,4-DHP product **6f**-*d*$_2$ was generated in 61% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5f** (625 mg, 4.56 mmol), the 1,4-DHP product **6f**-*d* (250 mg, 39% yield) was obtained. **Note:** In the crude mixture **6f**-d_2 was produced, which became **6f**-*d* during purification due to H/D exchange at the nitrogen atom.

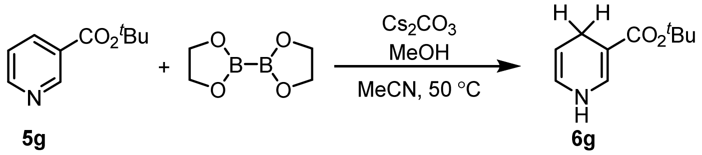
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.13 (d, *J* = 5.6 Hz, 1H), 5.86 (m, 1H), 5.27 (br s, 1H), 4.71 (ddd, *J* = 8.1, 3.6, 1.6 Hz, 1H), 3.68 (s, 3H), 3.09 (m, 1H).

^{2}H NMR (61 MHz, $CDCl_3$): *δ* 3.10

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.9, 137.9, 124.2, 103.5, 98.2, 51.1, 21.8 (t, *J* = 20.2 Hz).

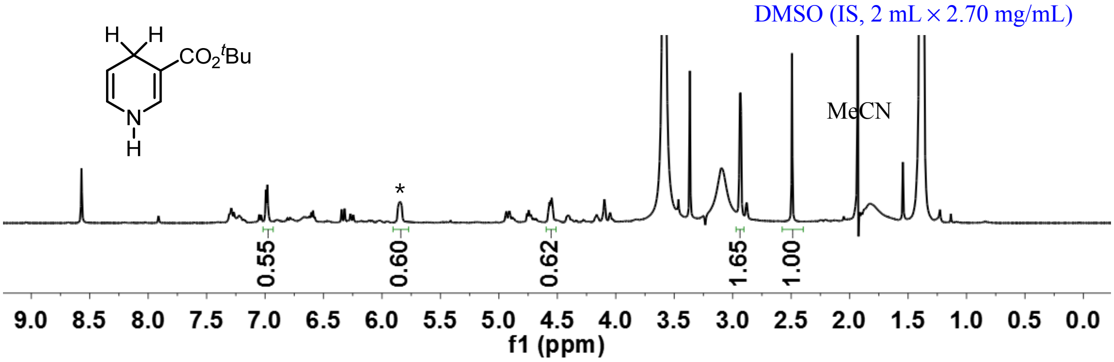
HRMS Calcd for $C_7H_8NO_2D$ $(M+H)^+$: 141.0774, Found: 141.0768.

tert-Butyl 1,4-dihydropyridine-3-carboxylate (6g)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5g** (65.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-DHP product **6g** was generated in 69% NMR yield.

^{1}H NMR spectra of the reaction mixture (⋆ denotes the peak used to calculate the NMR yield):



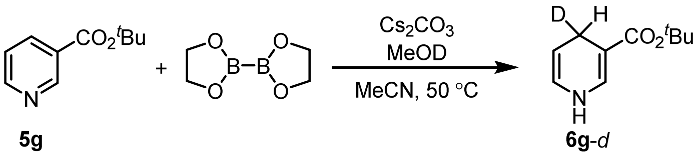
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5g** (65.0 mg, 0.36 mmol), the 1,4-DHP product **6g** (33.2 mg, 51% yield) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 5.5 Hz, 1H), 5.86 (m, 1H), 5.19 (br s, 1H), 4.70 (m, 1H), 3.06 (dd, *J* = 3.5, 1.7 Hz, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 137.1, 124.3, 103.2, 100.0, 28.5, 22.3.

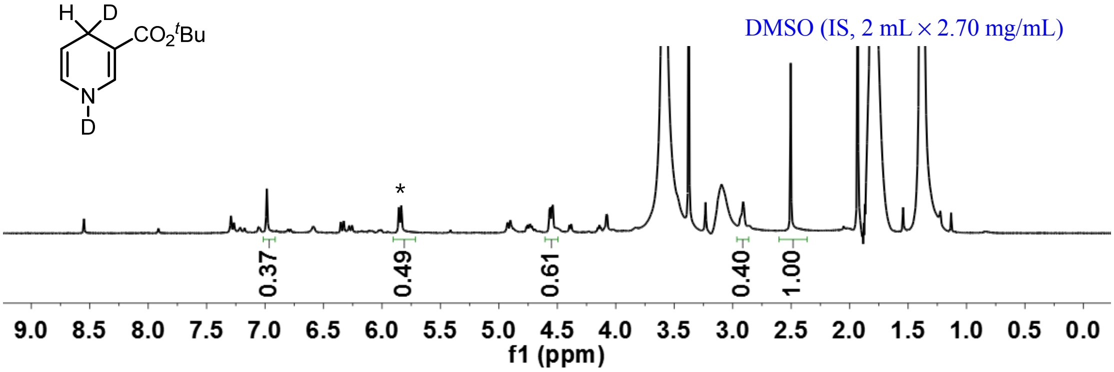
HRMS Calcd for $C_{10}H_{15}NO_2$ $(M+H)^+$: 182.1181, Found: 182.1174.

tert-Butyl 4-Deutero-1-hydropyridine-3-carboxylate (6g-*d*)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5g** (65.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 8.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-dihydrodeuteropyridine product **6g**-*d*$_2$ was generated in 57% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5g** (65.0 mg, 0.36 mmol), the 1,4-DHP product **6g**-*d* (25.5 mg, 39% yield) was obtained. **Note:** In the crude mixture **6g**-*d*$_2$ was produced, which became **6g**-*d* during purification due to H/D exchange at the nitrogen atom.

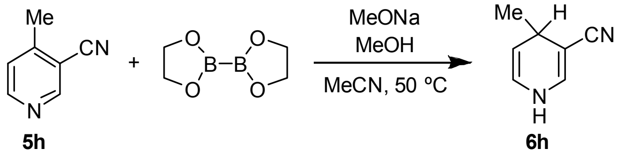
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 5.5 Hz, 1H), 5.85 (m, 1H), 5.11 (br s, 1H), 4.68 (ddd, *J* = 8.0, 3.5, 1.1 Hz, 1H), 3.04 (m, 1H), 1.46 (s, 9H).

^{2}H NMR (61 MHz, $CDCl_3$): δ 3.05

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 136.9, 124.3, 103.1, 99.9, 78.9, 28.5, 21.9 (t, *J* = 20.6 Hz).

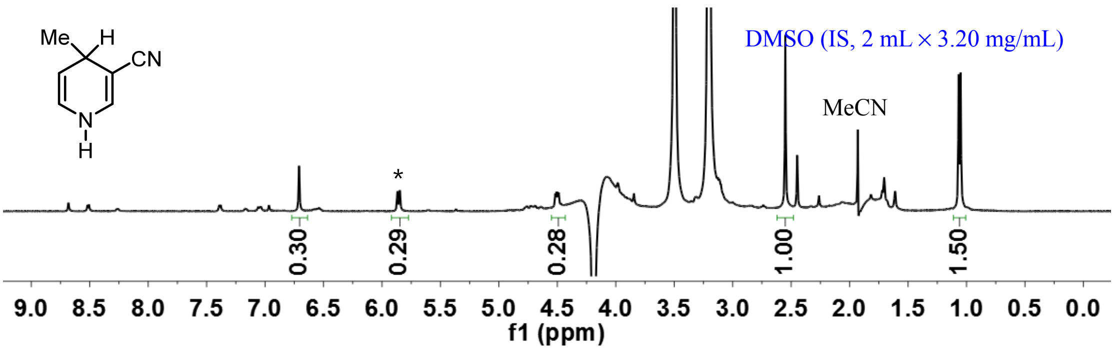
HRMS Calcd for $C_{10}H_{14}NO_2D$ $(M+H)^+$: 183.1244, Found: 183.1235.

3-Cyano-4-methyl-1,4-dihydropyridine (6h)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5h** (43.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using MeONa (21.6 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-dihydrodeuteropyridine product **6h** was generated in 40% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



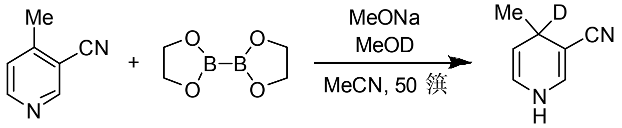
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5h** (540 mg, 4.57 mmol), the 1,4-DHP product **6h** (273 mg, 50% yield) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (dd, *J* = 5.6, 1.2 Hz, 1H), 5.87 (dd, *J* = 8.0, 4.4 Hz, 1H), 5.58 (br s, 1H), 4.59 (ddd, *J* = 8.1, 3.8, 1.5 Hz, 1H), 3.25 (ddd, *J* = 6.7, 3.8, 1.1 Hz, 1H), 1.23 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 122.8, 121.4, 106.7, 84.6, 28.3, 24.8.

HRMS Calcd for C_7H_8N $(M+H)^+$: 121.0766, Found: 121.0762.

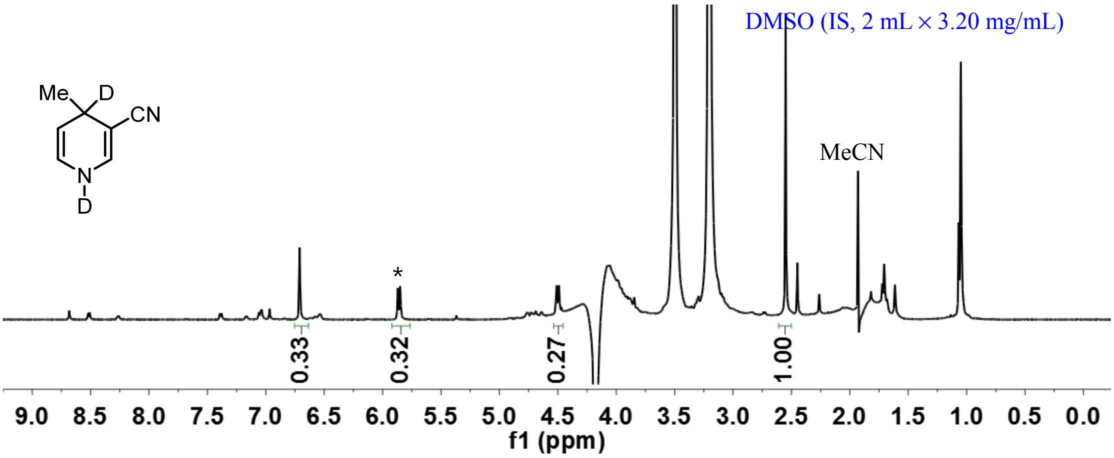
3-Cyano-4-methyl-4-deutero-1-hydropyridine (6h-*d*)



5h **6h**-*d*

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5h** (43.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (132 mg, 4.00 mmol), and using MeONa (21.6 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-dihydrodeuteropyridine product **6h-*d*₂** was generated in 44% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5h** (540 mg,4.57 mmol), the 1,4-DHP product **6h**-*d* (291 mg, 53% yield, 93% 4-D) was obtained. **Note:** In the crude mixture **6h**-d_2 was produced, which became **6h**-*d* during purification due to H/D exchange at the nitrogen atom.

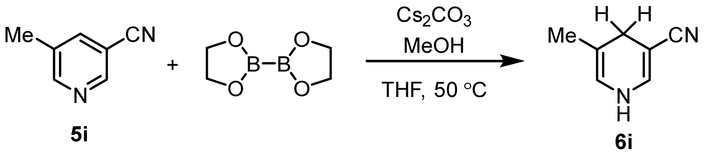
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (dd, *J* = 5.6, 1.2 Hz, 1H), 5.88 (ddd, *J* = 8.0, 4.4, 1.3 Hz, 1H), 5.50 (br s, 1H), 4.60 (dd, *J* = 8.1, 1.5 Hz, 1H), 1.23 (s, 3H).

^{2}H NMR (61 MHz, $CDCl_3$): δ 3.22

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 122.8, 121.3, 106.6, 84.7, 27.9 (t, *J* = 20.4 Hz), 24.7.

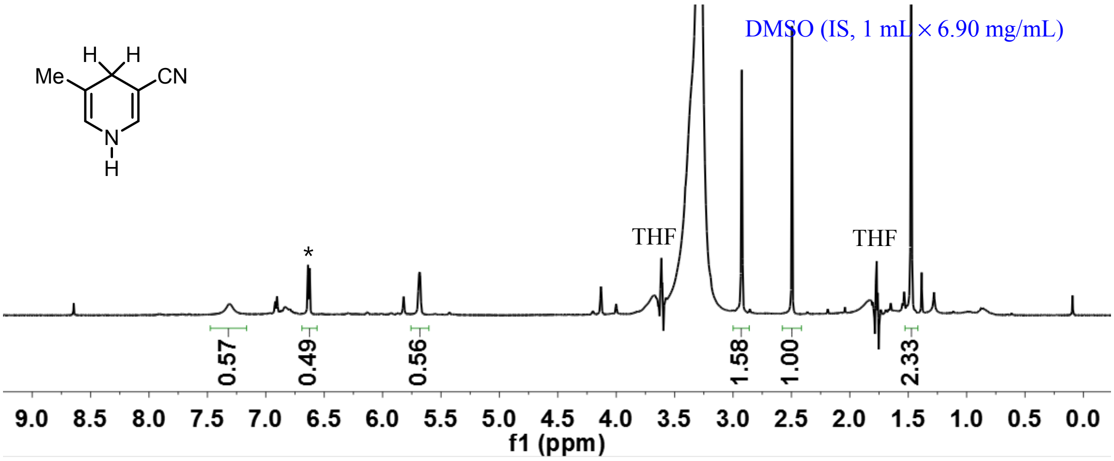
HRMS Calcd for C_7H_7ND $(M+H)^+$: 122.0828, Found: 122.0823.

3-Cyano-5-methyl-1,4-dihydropyridine (6i)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5i** (43.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous THF, 1,4-DHP product **6i** was generated in 72% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



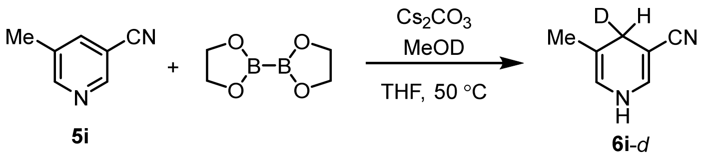
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5i** (43.0 mg, 0.36 mmol), the 1,4-DHP product **6i** (20.6 mg, 47% yield) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.62 (d, *J* = 5.6 Hz, 1H), 5.66 (d, *J* = 2.0 Hz, 1H), 5.50 (br s, 1H), 2.97 (s, 2H), 1.53 (m, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 139.5, 122.1, 118.6, 109.9, 76.9, 28.8, 20.1.

HRMS Calcd for C_7H_8N $(M+H)^+$: 121.0766, Found: 121.0762.

3-Cyano-5-methyl-4-deutero-1hydropyridine (6i-*d*)

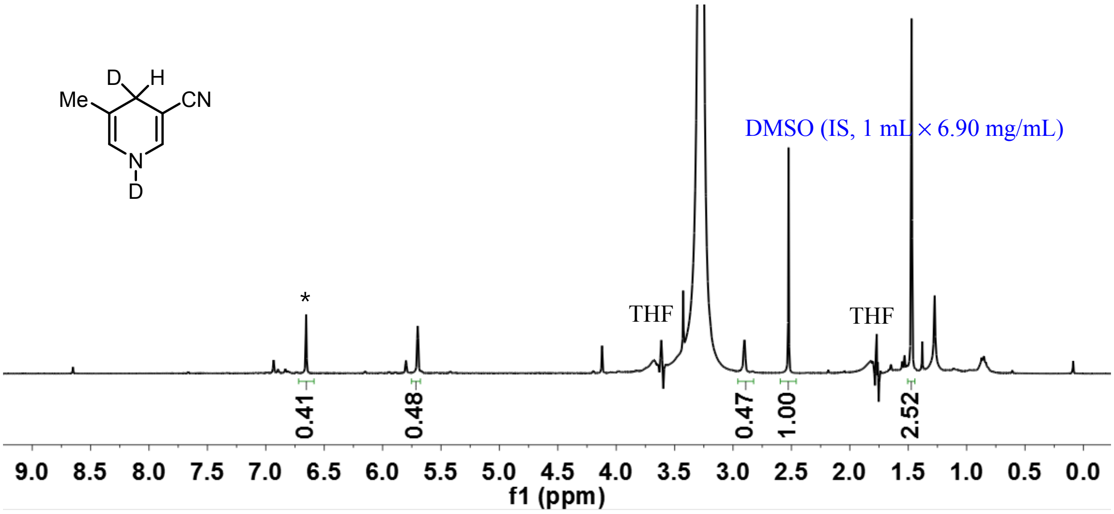


5i

6i-*d*

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5i** (43.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 8.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous THF, 1,4-dideuteropyridine product **6i**-*d*$_2$ was generated in 60% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5i** (43.0 mg, 0.36 mmol), the 1,4-DHP product **6i**-*d* (26.9 mg, 61% yield, >98% D) was obtained (in this experiment THF was used as the solvent in place of MeCN). **Note:** In the crude mixture **6i**-d_2 was produced, which became **6i**-*d* during purification due to H/D exchange at the nitrogen atom.

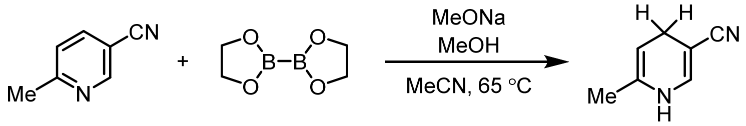
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (m, 1H), 5.68 (dq, J = 4.4, 1.4 Hz, 1H), 5.63 (br s, 1H), 2.97 (m, 1H), 1.53 (s, 3H).

^{2}H NMR (61 MHz, $CDCl_3$): δ 2.95

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 122.2, 118.6, 109.7, 76.8, 28.3 (t, J = 20.6 Hz), 20.1.

HRMS Calcd for C_7H_7ND $(M+H)^+$: 122.0828, Found: 122.0814.

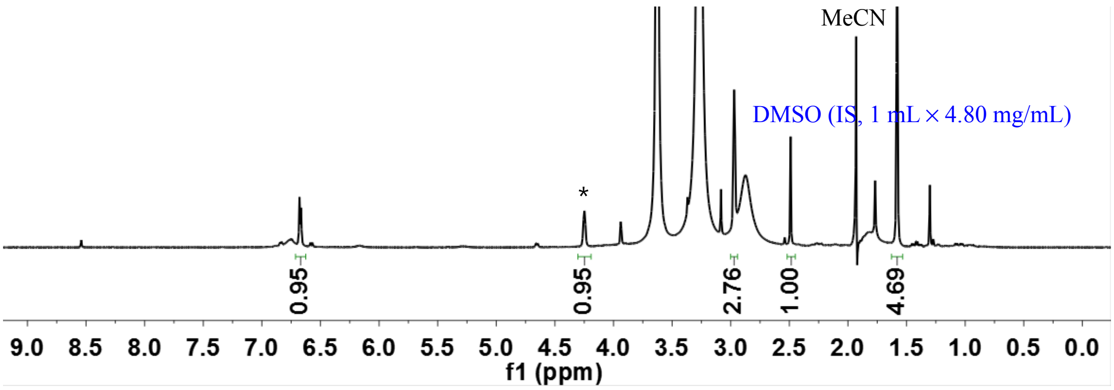
2-Methyl-5-cyano-1,4-dihydropyridine (6j)



5j **6j**

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5j** (43.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using MeONa (21.6 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-DHP product **6j** was generated in 97% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



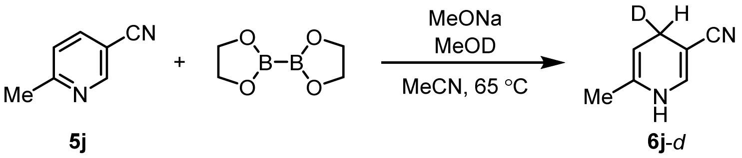
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5j** (43.0 mg, 0.36 mmol), the 1,4-DHP product **6j** (27.1 mg, 62% yield) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (d, *J* = 5.7 Hz, 1H), 5.11 (br s, 1H), 4.34 (dt, *J* = 3.3, 1.7 Hz, 1H), 3.06 (m, 2H), 1.66 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 131.6, 121.6, 96.8, 78.5, 24.2, 19.2.

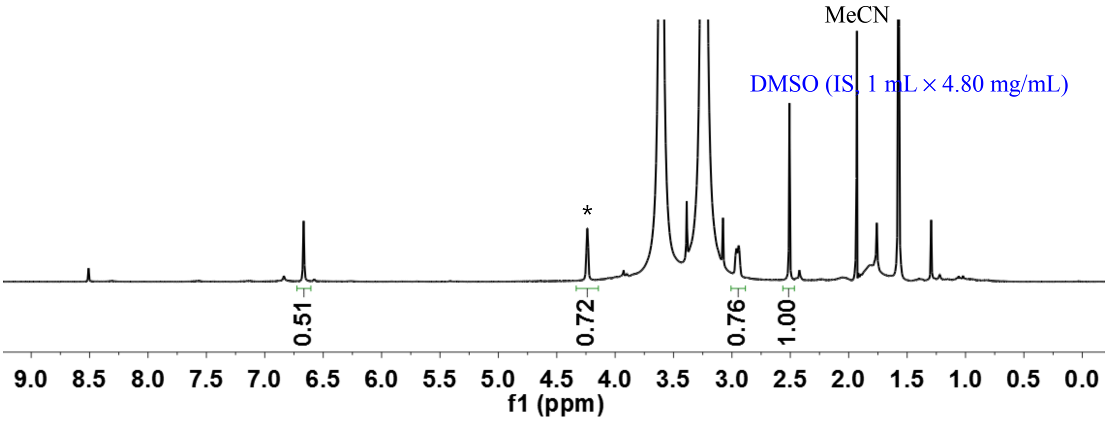
HRMS Calcd for C_7H_8N $(M+H)^+$: 121.0766, Found: 121.0762.

2-Methyl-5-cyano-4-deutero-1-hydropyridine (6j-*d*)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5j** (43.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 8.00 mmol), and using MeONa (21.6 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-dideuteropyridine product **6j**-d_2 was generated in 74% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5j** (43.0 mg, 0.36 mmol), the 1,4-DHP product **6j**-*d* (21.1 mg, 48% yield, 86% 4-D) was obtained. **Note:** In the crude mixture **6j**-*d*$_2$ was produced, which became **6j**-*d* during purification due to H/D exchange at the nitrogen atom.

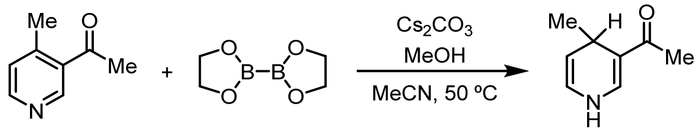
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.62 (d, *J* = 5.6 Hz, 1H), 5.11 (br s, 1H), 4.34 (dt, *J* = 3.3, 1.7 Hz, 1H), 3.06 (m, 1.06H), 1.67 (t, *J* =1.4 Hz, 3H).

^{2}H NMR (61 MHz, CDCl$_3$): δ 3.04.

^{13}C NMR (100 MHz, CDCl$_3$): δ 140.3, 131.6, 121.7, 96.7, 78.5, 23.7 (t, *J* = 20.8 Hz), 19.2.

HRMS Calcd for C_7H_7ND (M+H)$^+$: 122.0828, Found: 122.0823.

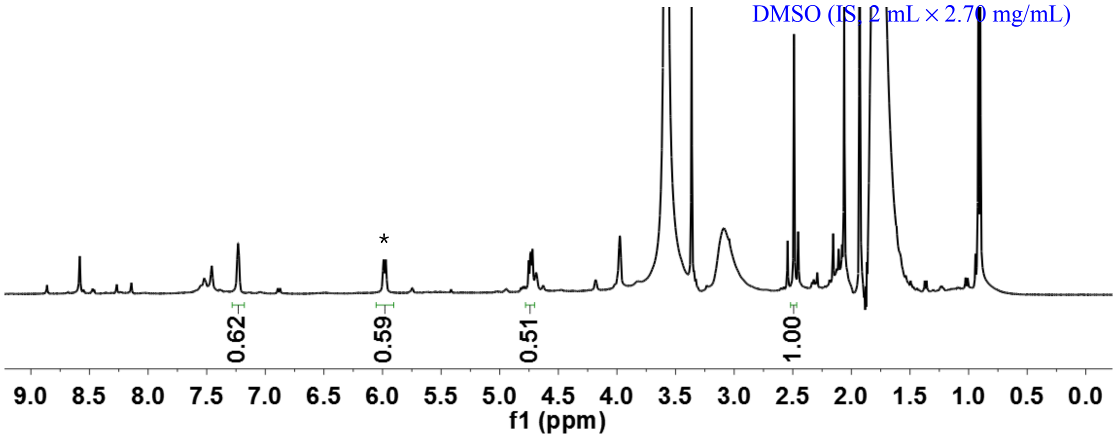
3-Acetyl-4-methyl-1,4-dihydropyridine (6k)



5k **6k**

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5k** (49.2 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-DHP product **6k** was generated in 68% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



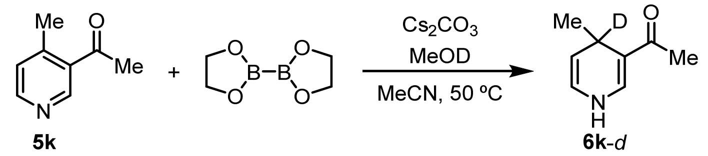
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5k** (49.2 mg, 0.36 mmol), the 1,4-DHP product **6k** (16.8 mg, 34% yield) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15 (d, *J* = 5.8 Hz, 1H), 6.10 (br s, 1H), 5.96 (m, 1H), 4.85 (ddd, *J* = 7.7, 5.1, 1.1 Hz, 1H), 3.48 (dd, *J* = 6.7, 5.5 Hz, 2H), 2.17 (s, 3H), 1.04 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 195.9, 139.0, 122.5, 115.2, 110.3, 26.1, 24.6, 24.5.

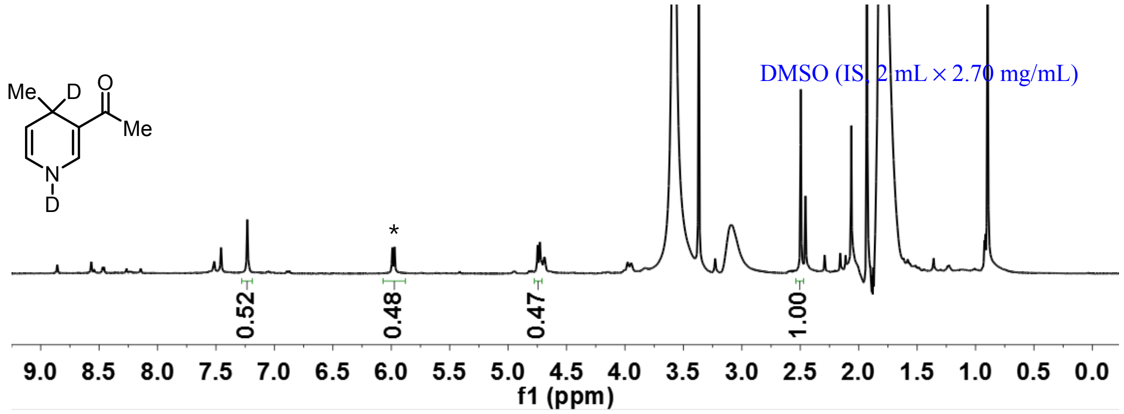
HRMS Calcd for $C_8H_{11}NO$ (M+H)$^+$: 138.0919, Found: 138.0913.

3-Acetyl-4-methyl-4-deutero-1-hydropyridine (6k-*d*)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5k** (49.2 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 8.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-dideuteropyridine product **6k-**d_2 was generated in 55% NMR yield.

^1H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5k** (49.2 mg, 0.36 mmol), the 1,4-DHP product **6k**-*d* (21.0 mg, 42% yield, 94% 4-D) was obtained. **Note:** In the crude mixture **6k**-d_2 was produced, which became **6k**-*d* during purification due to H/D exchange at the nitrogen atom. Both ^1H and ^2H NMR analysis also showed a minor extent of deuterium incorporation (9% D) at the methyl group.

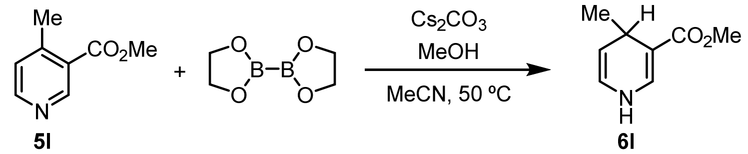
^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 5.8, 1.1 Hz, 1H), 5.99 (ddd, *J* = 7.7, 4.3, 1.1 Hz, 1H), 5.90 (br s, 1H), 4.86 (dd, *J* = 7.6, 1.7 Hz 1H), 2.19 (s, 2.74H), 1.04 (s, 3H).

^2H NMR (61 MHz, $CDCl_3$): δ 3.48, 2.18 (t, *J* = 0.73 Hz)

^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 138.8, 122.5, 115.2, 110.2, 25.7 (t, *J* = 21.3 Hz), 24.6, 24.3.

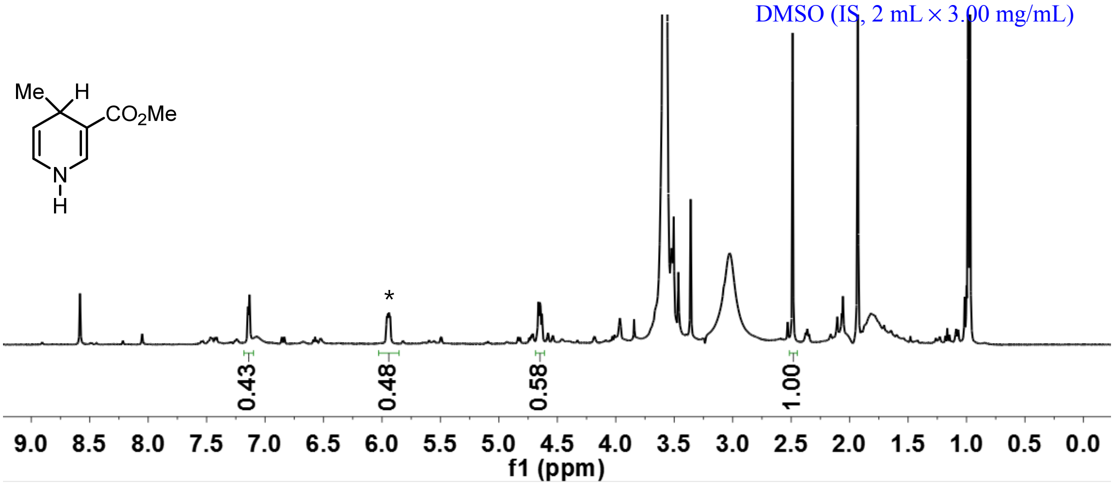
HRMS Calcd for $C_8H_{10}NOD$ $(M+H)^+$: 139.0982, Found: 139.0975.

Methyl 4-methyl-1,4-dihydropyridine-3-carboxylate (6l)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5l** (55.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOH (128 mg, 4.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-DHP product **6l** was generated in 62% NMR yield.

^{1}H NMR spectra of the reaction mixture (* denotes the peak used to calculate the NMR yield):



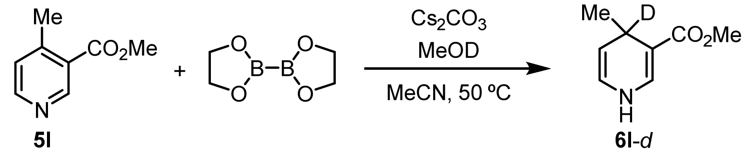
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5l** (412 mg, 2.73 mmol), the 1,4-DHP product **6l** (154 mg, 37% yield) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, *J* = 5.7, 1.2 Hz, 1H), 5.91 (ddd, *J* = 7.8, 4.3, 1.2 Hz, 1H), 5.74 (br s, 1H), 4.74 (ddd, *J* = 7.8, 4.8, 1.7 Hz, 1H), 3.67 (s, 3H), 3.34 (m, 2H), 1.08 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 137.1, 122.9, 108.7, 103.4, 50.9, 26.9, 25.1.

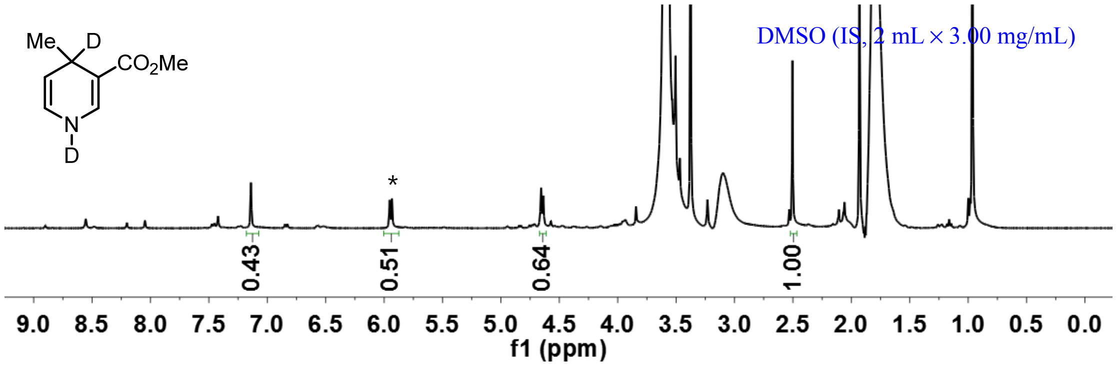
HRMS Calcd for $C_8H_{11}NO_2$ $(M+H)^+$: 154.0868, Found: 154.0860.

Methyl 4-methyl-4-deutero-1-hydropyridine-3-carboxylate (6l-*d*)



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5l** (55.0 mg, 0.36 mmol), B_2eg_2 (56.8 mg, 0.40 mmol), and MeOD (264 mg, 8.00 mmol), and using Cs_2CO_3 (131 mg, 0.40 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-dideuteropyridine product **6l**-d_2 was generated in 65% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5l** (412 mg, 2.73 mmol), the 1,4-DHP product **6l**-*d* (151 mg, 36% yield, 94% 4-D) was obtained. **Note:** In the crude mixture **6l**-*d*2 was produced, which became **6l**-*d* during purification due to H/D exchange at the nitrogen atom.

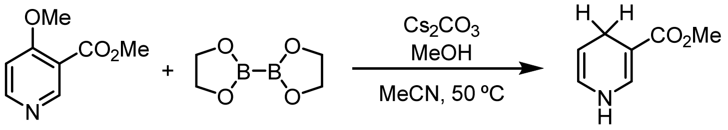
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 5.7, 1.2 Hz, 1H), 5.95 (ddd, *J* = 7.8, 4.3, 1.2 Hz, 1H), 5.55 (br s, 1H), 4.77 (dd, *J* = 7.7, 1.6 Hz, 1H), 3.69 (s, 3H), 1.09 (s, 3H).

^{2}H NMR (61 MHz, $CDCl_3$): δ 3.34.

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 136.9, 122.9, 108.7, 103.7, 51.0, 26.6 (t, *J* = 20.7 Hz), 25.0.

HRMS Calcd for $C_8H_{10}NO_2D$ $(M+H)^+$: 155.0931, Found: 155.0922.

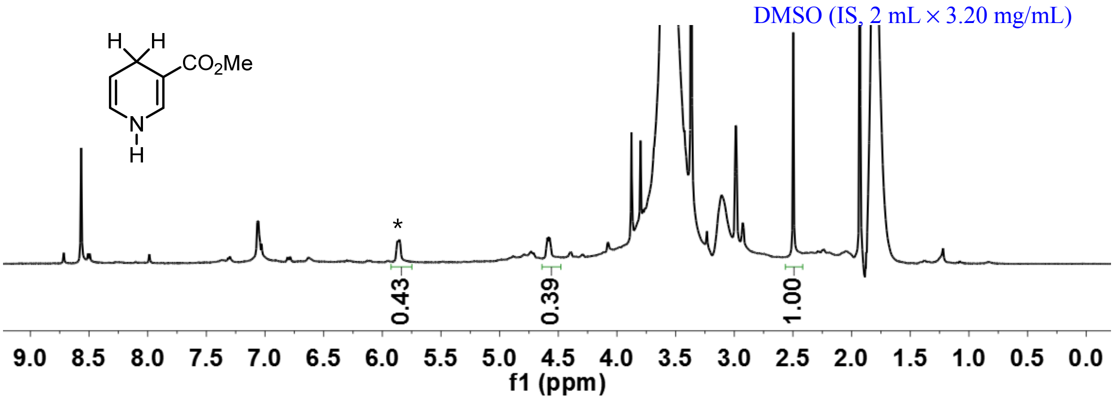
1,4-DHP 6f from double hydroboration reaction of pyridine 5m



5m **6f**

Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5m** (66.8 mg, 0.36 mmol), B_2eg_2 (114 mg, 0.80 mmol), and MeOH (264 mg, 8.25 mmol), and using Cs_2CO_3 (261 mg, 0.80 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4-DHP product **6f** was generated in 59% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



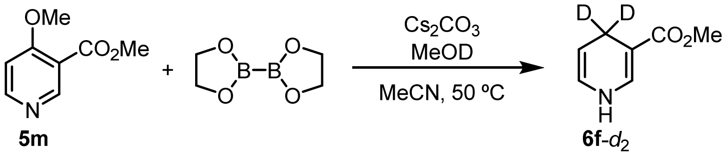
Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5m** (49.8 mg, 0.30 mmol), B_2eg_2 (78.6 mg, 0.60 mmol), and Cs_2CO_3 (196 mg, 0.60 mmol), the 1,4-DHP product **6f** (12.6 mg, 30% yield) was obtained.

^{1}H NMR (400MHz, $CDCl_3$): δ 7.05 (dd, *J* = 5.6 Hz, 1H), 5.79 (m, 1H), 5.26 (br s, 1H), 4.64 (m, 1H), 3.61 (s, 3H), 3.04 (dd, *J* = 3.5, 1.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 137.9, 124.2, 103.5, 98.1, 51.1, 22.2.

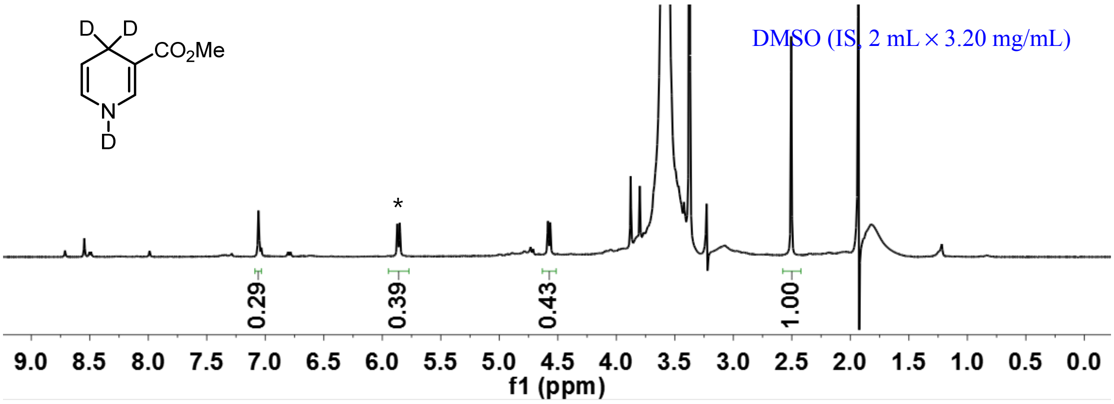
HRMS: Calcd for $C_7H_9NO_2$ (M+H): 140.07115, Found: 140.07065.

Methyl 1,4-dideuteropyridine-3-carboxylate (6f-*d*$_2$) from double hydroboration reaction of pyridine 5m



Determination of the NMR yield. Following the general procedure GP-A, starting from pyridine **5m** (66.8 mg, 0.36 mmol), B_2eg_2 (114 mg, 0.80 mmol), and MeOD (528 mg, 16.0 mmol), and using Cs_2CO_3 (261 mg, 0.80 mmol) the as the base in 2 mL of anhydrous MeCN, 1,4,4-trideuteropyridine product **6f**-*d*$_3$ was generated in 53% NMR yield.

^{1}H NMR spectra of the reaction mixture (⁎ denotes the peak used to calculate the NMR yield):



Determination of the yield after isolation. Following the general procedure GP-B, starting from pyridine **5m** (403 mg, 2.41 mmol), B_2eg_2 (747 mg, 5.27 mmol), and Cs_2CO_3 (1.73 g, 5.31 mmol), the 1,4-DHP product **6f**-*d*$_2$ (89.3 mg, 26% yield) was obtained. **Note:** In the crude mixture **6f**-*d*$_3$ was produced, which became **6f**-*d*$_2$ during purification due to H/D exchange at the nitrogen atom.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, *J* = 5.6, 1.2 Hz, 1H), 5.88 (ddd, *J* = 8.1, 4.2, 1.2 Hz, 1H), 5.26 (br s, 1H), 4.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.70 (s, 3H), 3.09 (m, 0.05H).

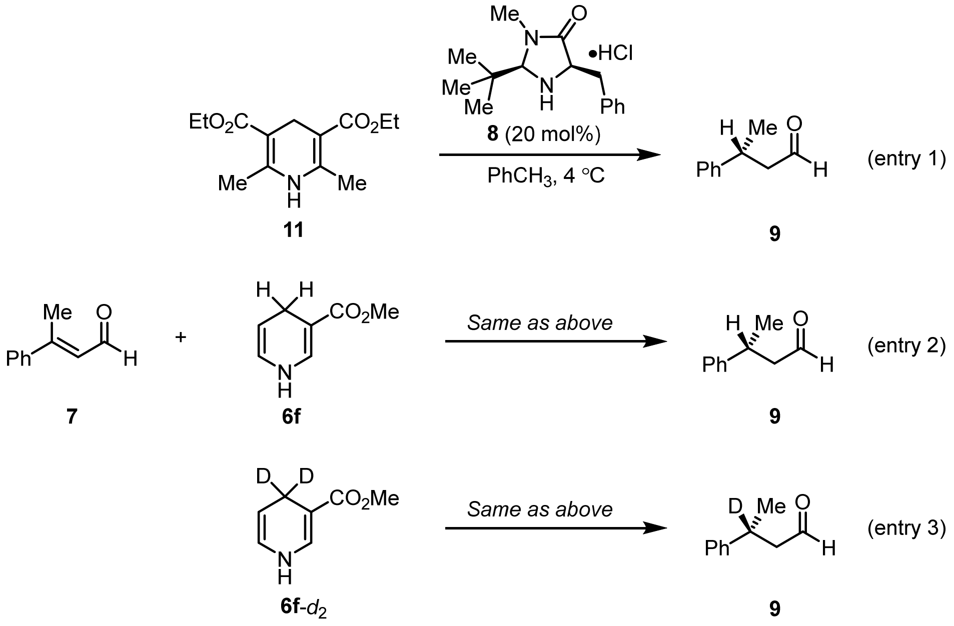
^{2}H NMR (61 MHz, $CDCl_3$): δ 3.07

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 137.7, 124.1, 103.2, 98.0, 51.1.

HRMS Calcd for $C_7H_7NO_2D_2$ $(M+H)^+$: 142.0837, Found: 142.0827.

6. The Asymmetric Hydrogen Transfer Reactions

6.1 General procedure



General procedure: In a glove box, a 15 mL oven-dried sealed tube was charged with α,β-unsaturated aldehyde **7** (1 equiv.), catalyst **8** (20 mol%), and anhydrous toluene as the solvent (to make a 0.4 M solution of substrate **7**). Then the 1,4-DHP derivative (1.2 equiv.) was added. The resulting mixture was allowed to react at 4 °C for 12 h. The reaction solution was diluted by ether, and then filtered through a pad of diatomite. The residue was washed by ether. The combined ether solution was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 80:1 V/V) to afford the desired product **9**. The enantiomeric excess (e.e.) was determined by HPLC using a Chiralpak IC column (column temperature 24 °C).

6.2 Results

Entry 1: HEH 11 was employed as the hydride donor.

Following the general procedure, starting from **7** (146 mg, 1.00 mmol), **8** (56.6 mg, 0.20 mmol), and **11** (304 mg, 1.2 mmol), in 5 mL of anhydrous toluene, product **9** (72.3 mg, 49% yield, 83% e.e.) was obtained.

Entry 2: 1,4-DHP 6f was employed as the hydride donor.

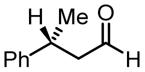
Following the general procedure, starting from **7** (74 mg, 0.50 mmol), **8** (28.3 mg, 0.10 mmol), and **6f** (83.4 mg, 0.6 mmol), in 2.5 mL of anhydrous toluene, product **9** (28.5 mg, 38% yield, 75% e.e.) was obtained.

Entry 3: 6f-*d*$_2$ was employed as the hydride donor.

Following the general procedure, starting from **7** (70 mg, 0.48 mmol), **8** (28.3 mg, 0.10 mmol), and **6f**-*d*$_2$ (67 mg, 0.5 mmol), in 2.5 mL of anhydrous toluene, product **9** (35 mg, 49% yield, 80% e.e.) was obtained.

5.3 Spectroscopic data of the product[6]

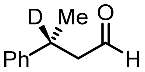
(*R*)-3-Phenylbutanal (9)



^{1}H NMR (400 MHz, CDCl$_3$): δ 9.71 (t, *J* = 2.0 Hz, 1H), 7.32 (m, 2H), 7.22 (m, 3H), 3.39 (q, 1H), 2.73 (m, 2H), 1.32 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 202.0, 145.6, 128.8, 126.9, 126.7, 51.9, 42.0, 34.4, 22.3.

(*R*)-1-Deutero-3-phenylbutanal (9-*d*)



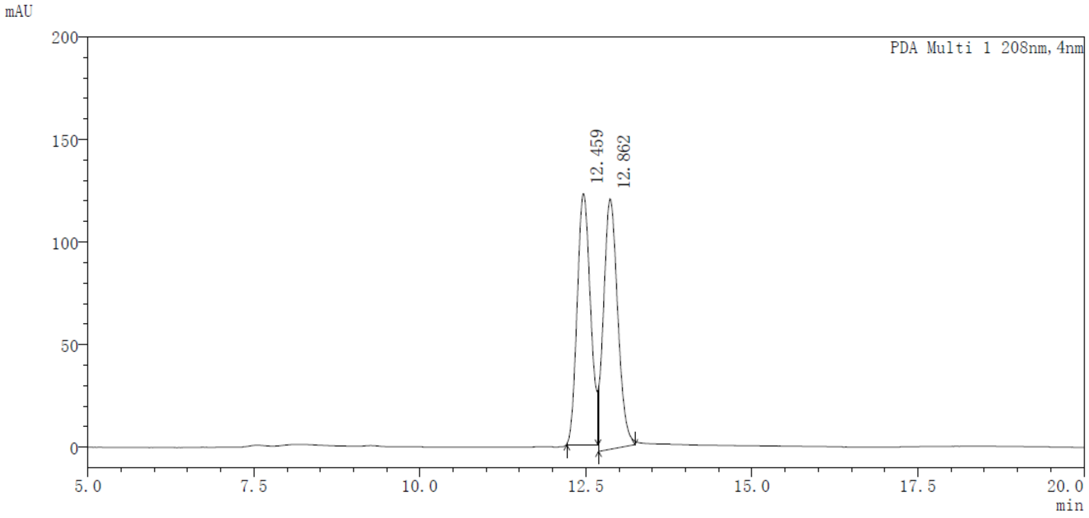
^{1}H NMR (400 MHz, CDCl$_3$): δ 9.71 (d, *J* = 1.9 Hz, 1H), 7.31 (m, 2H), 7.22 (m, 3H), 3.36 (q, 0.1H), 2.67 (m, 2H), 1.32 (q, 3H).

^{2}H NMR (61 MHz, CDCl$_3$): δ 3.36

^{13}C NMR (100 MHz, CDCl$_3$): δ 202.0, 145.6, 128.8, 126.9, 126.7, 51.9, 42.1, 34.4, 22.2 (t, *J* = 25.3 Hz).

5.4 Copies of HPLC traces for the determination of e.e.

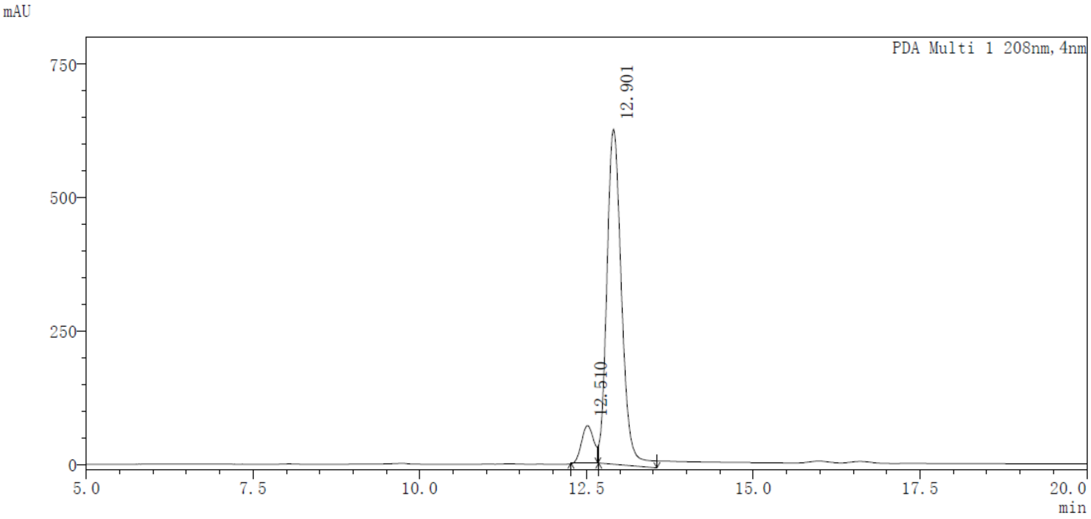
(±)-**9**:



PDA Ch1 208nm

#	Ret. time	FWHM	Height	Area	Area (%)
1	12.459	0.219	122553	1717049	48.813
2	12.862	0.233	122200	1800559	51.187

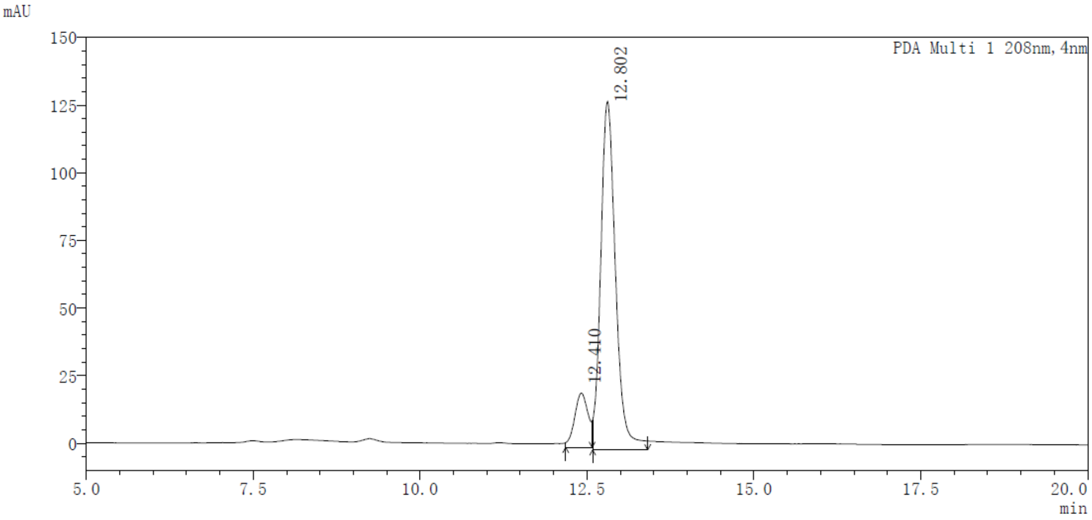
(*R*)-**9** obtained in entry 1 (83% e.e.):



PDA Ch1 208nm

#	Ret. time	FWHM	Height	Area	Area (%)
1	12.510	0.212	69759	887877	8.462
2	12.901	0.231	627290	9604162	91.538

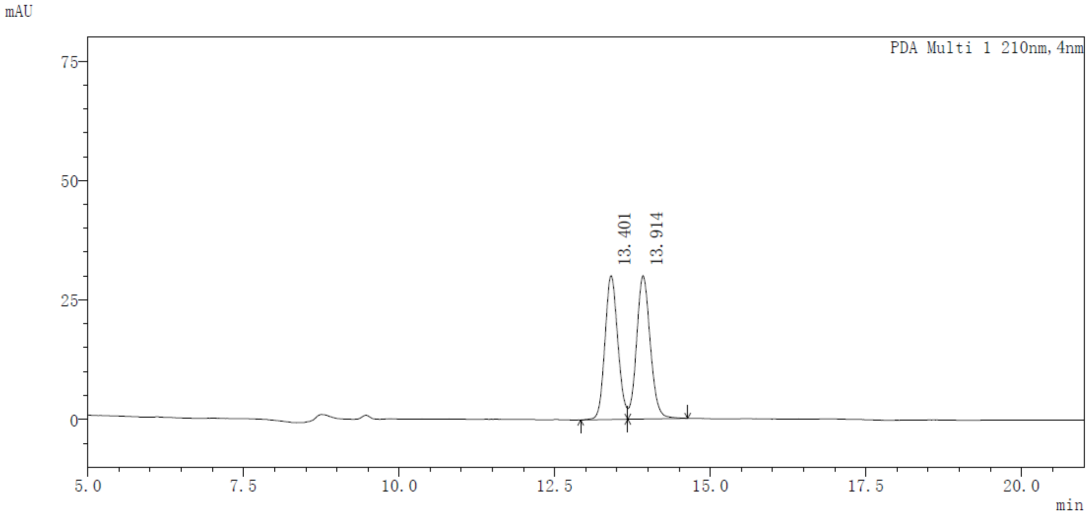
(*R*)-**9** obtained in entry 2 (75% e.e.):



PDA Ch1 208nm

#	Ret. time	FWHM	Height	Area	Area (%)
1	12.410	0.240	20085	283539	12.463
2	12.802	0.230	128737	1991464	87.537

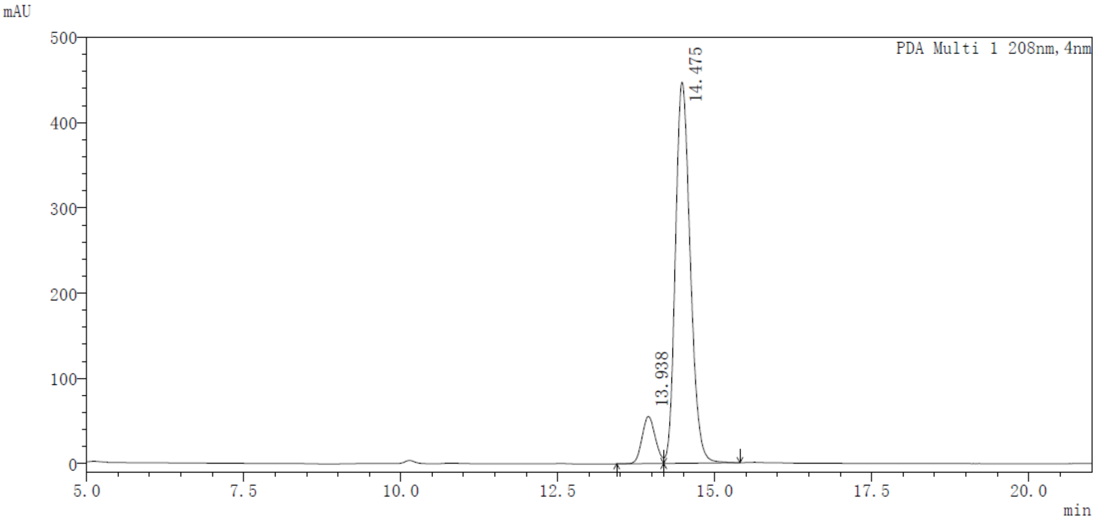
(±)-**9**-*d*:



PDA Ch1 210nm

#	Ret. time	FWHM	Height	Area	Area (%)
1	13.401	0.222	30078	433223	48.578
2	13.914	0.233	29994	458582	51.422

(*R*)-**9**-*d* obtained in entry 3 (80% e.e.):

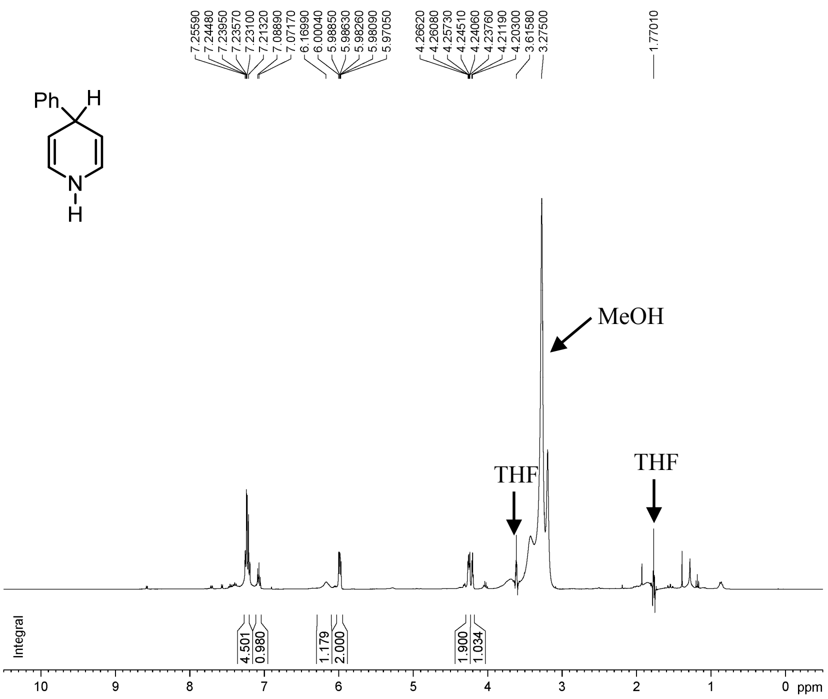


PDA Ch1 208nm

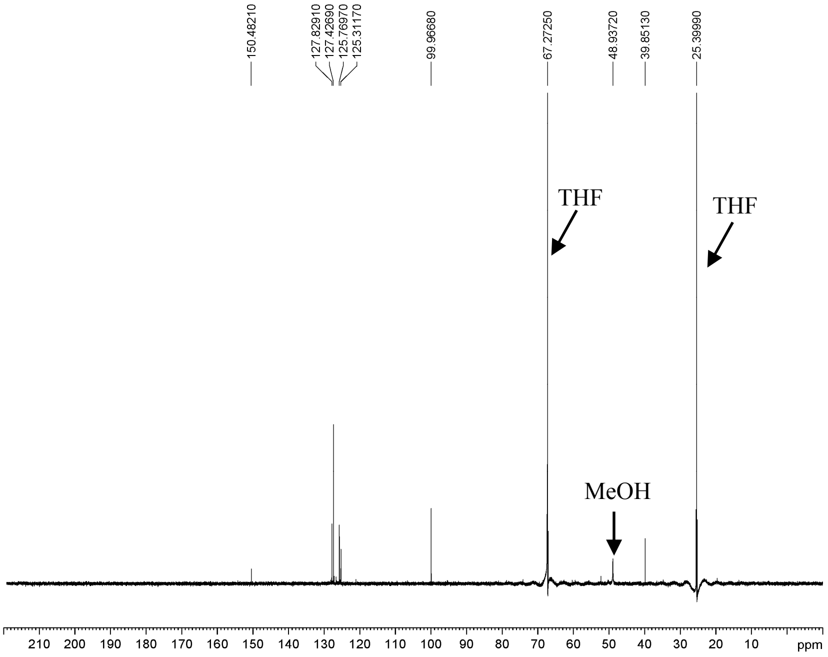
#	Ret. time	FWHM	Height	Area	Area (%)
1	13.938	0.230	55221	810221	9.919
2	14.475	0.254	447191	7358232	90.081

7. Copies of the NMR Spectra of Products

^{1}H and ^{13}C NMR of **4** (in THF-d_0, No-D NMR)

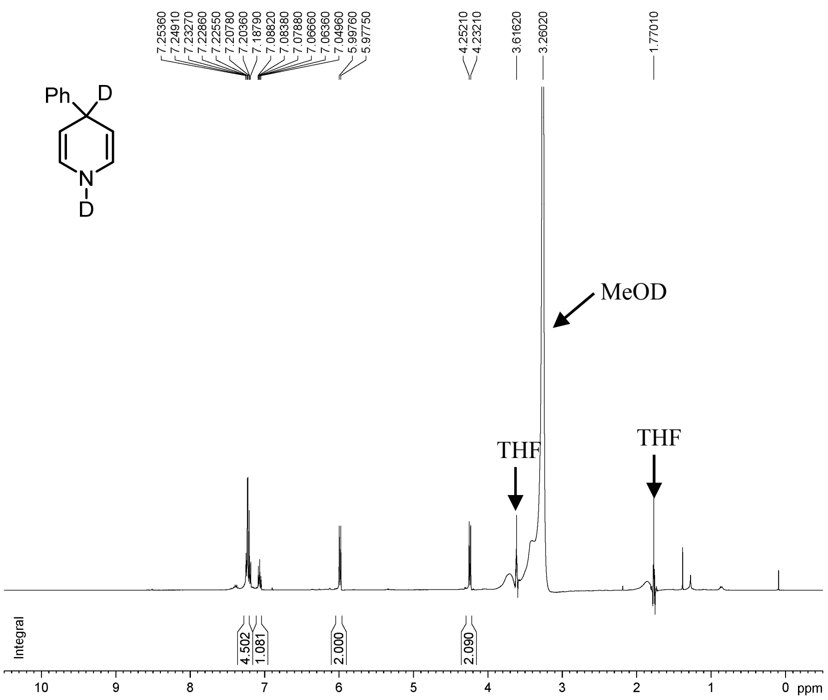


```
NAME       YH1364-F-4-PhPy-MeOH-in THF
EXPNO                   12
PROCNO                   1
Date_             20190502
Time                 16.05
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              wetdc
TD                   16384
SOLVENT               None
NS                      32
DS                      24
SWH               8000.000 Hz
FIDRES            0.488281 Hz
AQ               1.0240500 sec
RG                   21.03
DW                  62.500 usec
DE                   12.84 usec
TE                     0.0 K
D1              3.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00200000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1308389 MHz
NUC1                    1H
P1                    9.67 usec
P11               20000.00 usec
SI                   32768
SF             400.1301311 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

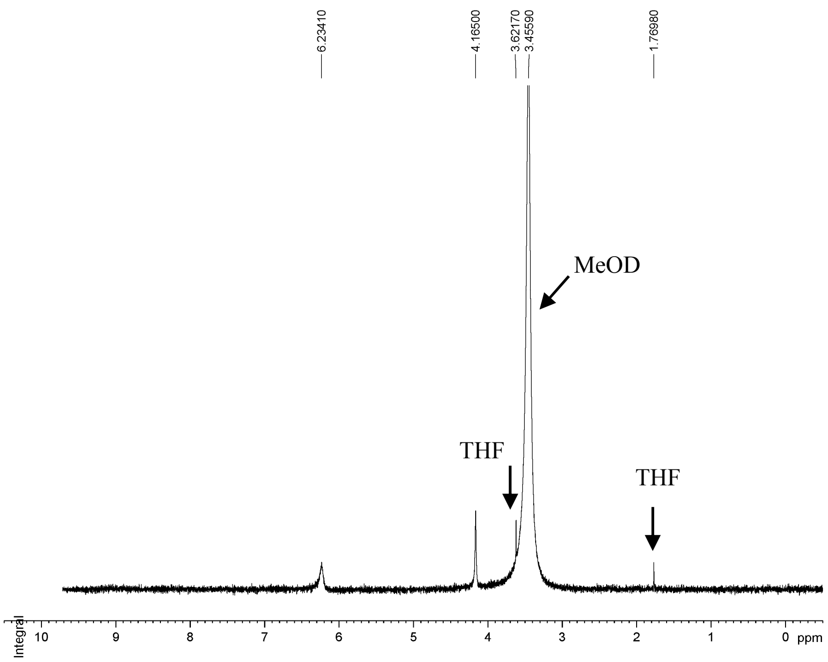


```
NAME       YH1364-F-4-PhPy-MeOH-in THF
EXPNO                   11
PROCNO                   1
Date_             20190502
Time                 15.40
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT               None
NS                     773
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                     0.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127971 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```

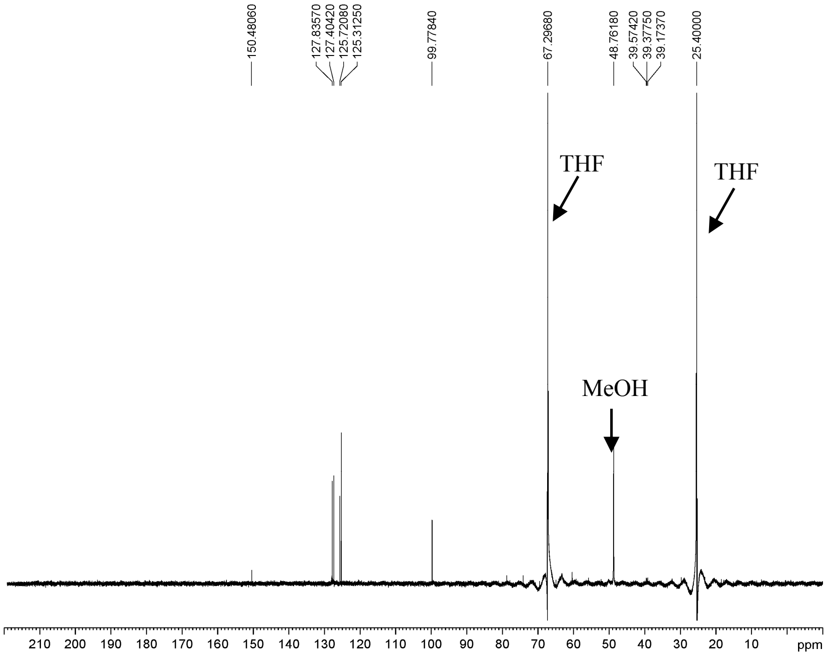
^{1}H, ^{2}H, and ^{13}C NMR of **4-d_2** (in THF-d_0, No-D NMR)



```
NAME     YH1365-A-4-PhPy-MeOD-in THF
EXPNO                    12
PROCNO                    1
Date_              20190507
Time                  10.59
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG               wetdc
TD                    16384
SOLVENT                None
NS                       32
DS                       24
SWH                8000.000 Hz
FIDRES             0.488281 Hz
AQ                1.0240500 sec
RG                    11.21
DW                   62.500 usec
DE                    12.79 usec
TE                    300.6 K
D1               3.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00200000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1308363 MHz
NUC1                     1H
P1                     9.70 usec
P11                20000.00 usec
SI                    32768
SF              400.1301284 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

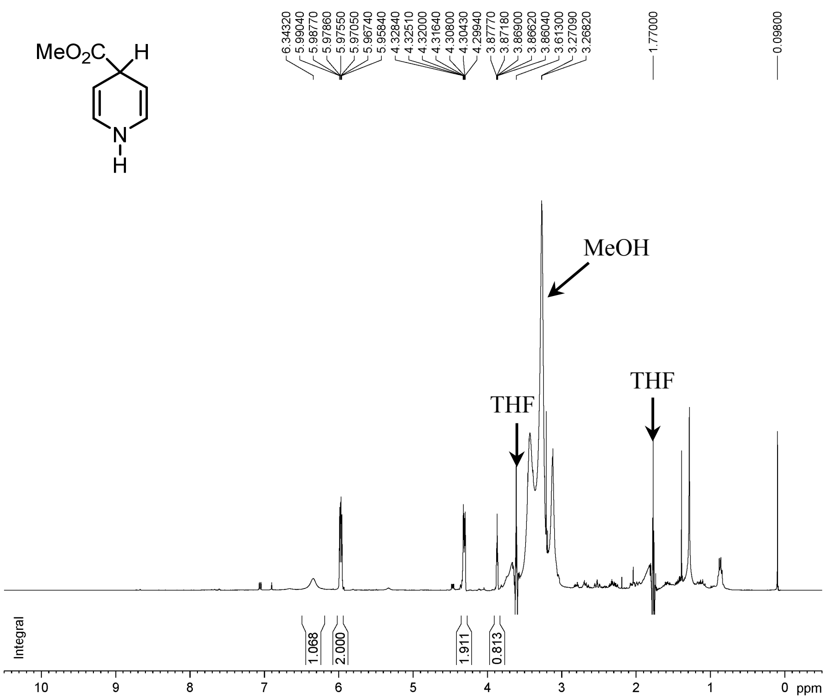


```
NAME     YH1365-A-4-PhPy-MeOD-in THF
EXPNO                    13
PROCNO                    1
Date_              20190507
Time                  11.05
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG              zgig2h
TD                    16384
SOLVENT                None
NS                       32
DS                        2
SWH                1228.501 Hz
FIDRES             0.074982 Hz
AQ                6.6683378 sec
RG                   208.17
DW                  407.000 usec
DE                    50.00 usec
TE                    300.7 K
D1               4.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             61.4223910 MHz
NUC1                     2H
P1                   356.50 usec
SI                    65536
SF               61.4224086 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

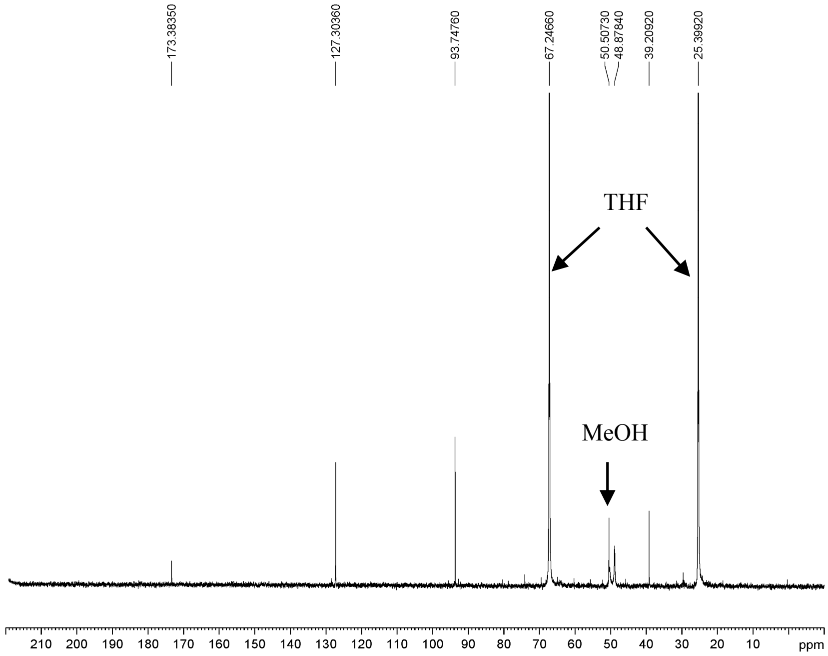


```
NAME     YH1365-A-4-PhPy-MeOD-in THF
EXPNO                   11
PROCNO                   1
Date_             20190507
Time                  9.42
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT               None
NS                    1280
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   300.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127949 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of **6a** (in THF-d_0, No-D NMR)

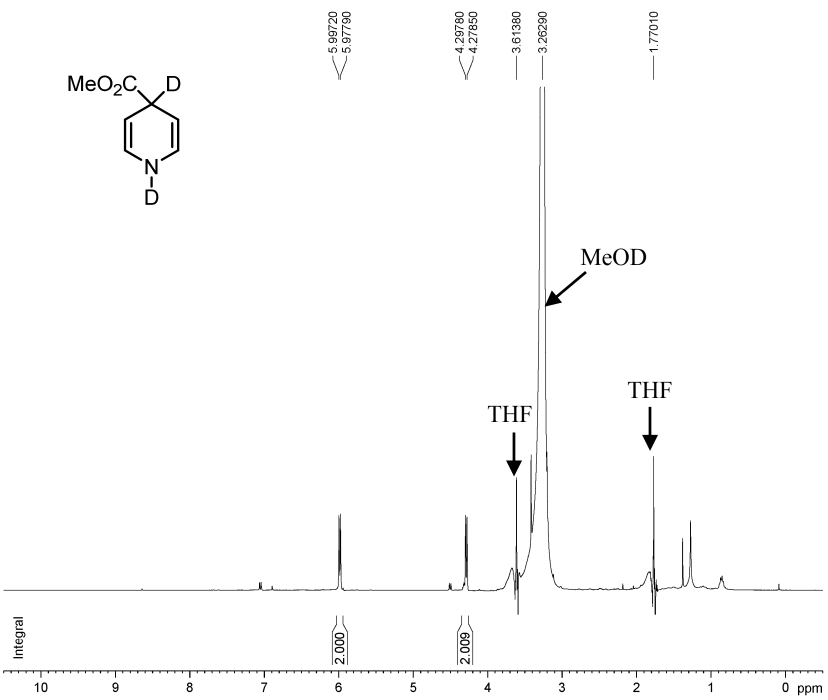


```
NAME       YH1361-B-4-CO2MePy-in THF
EXPNO                    20
PROCNO                    1
Date_              20190424
Time                   9.53
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG               wetdc
TD                    16384
SOLVENT                None
NS                       32
DS                       24
SWH                8000.000 Hz
FIDRES             0.488281 Hz
AQ                1.0240500 sec
RG                    29.41
DW                   62.500 usec
DE                    12.65 usec
TE                    300.2 K
D1               3.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00200000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1306138 MHz
NUC1                     1H
P1                     9.77 usec
P11                20000.00 usec
SI                    32768
SF              400.1299059 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

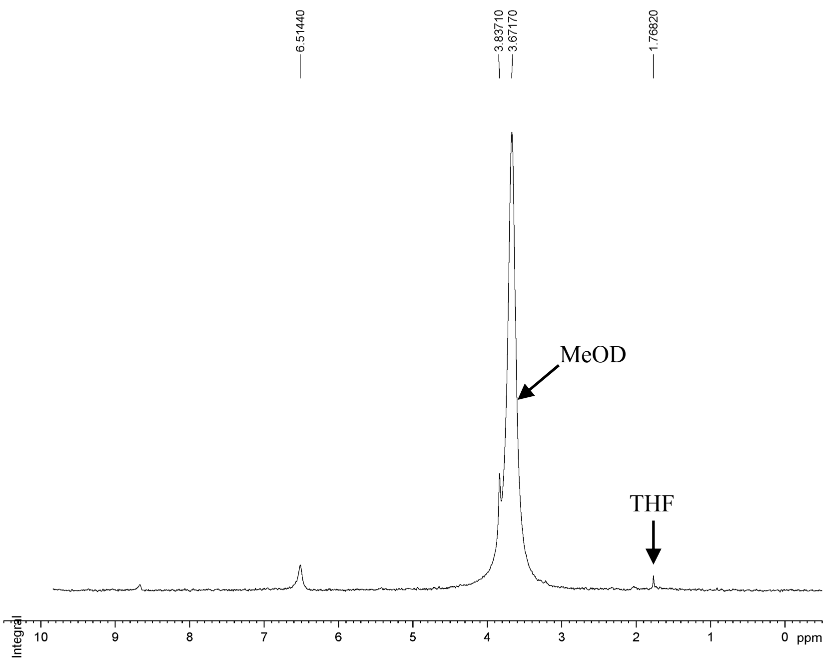


```
NAME       YH1361-B-4-CO2MePy-in THF
EXPNO                    12
PROCNO                    1
Date_              20190424
Time                   9.03
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT                None
NS                      640
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                   208.17
DW                   20.800 usec
DE                     6.50 usec
TE                    300.3 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                    13C
P1                     9.95 usec
SI                    32768
SF              100.6127993 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.40
```

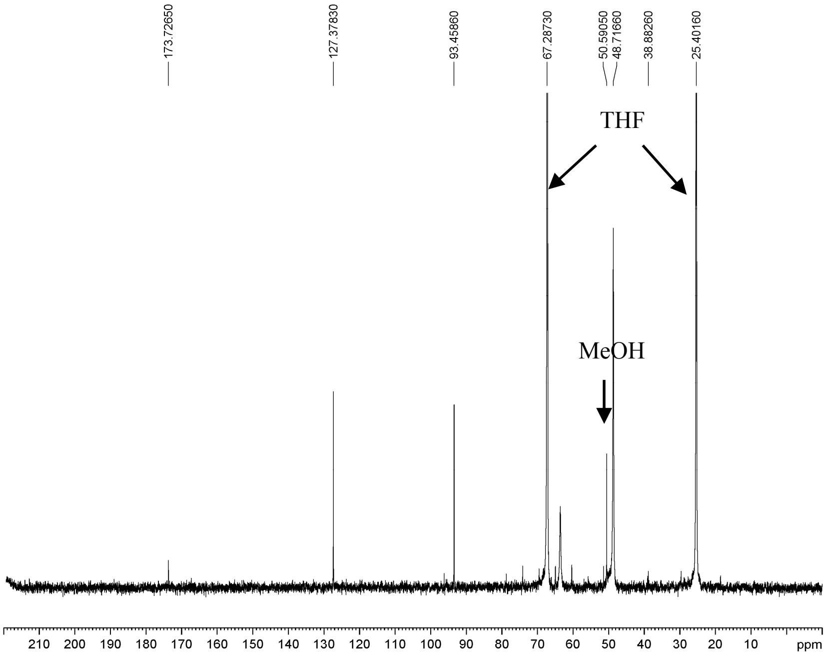
^{1}H, ^{2}H, and ^{13}C NMR of **6a-d_2** (in THF-d_0, No-D NMR)



```
NAME       YH1361-C-4-CO2MePy-MeOD-in THF
EXPNO                     12
PROCNO                     1
Date_               20190425
Time                    9.08
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                wetdc
TD                     16384
SOLVENT                 None
NS                        32
DS                        24
SWH                 8000.000 Hz
FIDRES              0.488281 Hz
AQ                 1.0240500 sec
RG                     11.21
DW                    62.500 usec
DE                     12.71 usec
TE                     298.9 K
D1                3.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
D13               0.00000400 sec
D16               0.00200000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1307858 MHz
NUC1                      1H
P1                      9.74 usec
P11                 20000.00 usec
SI                     32768
SF               400.1300784 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

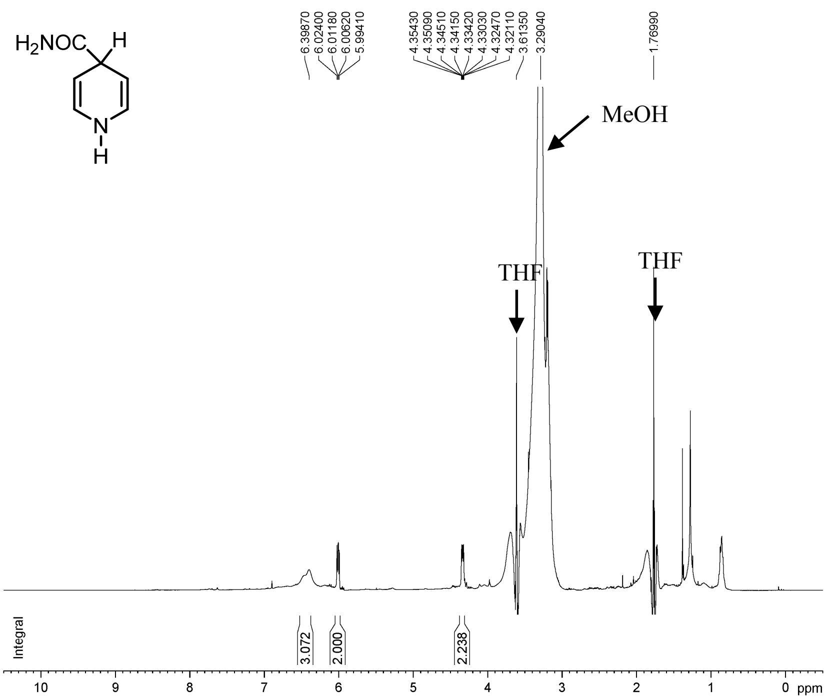


```
NAME       YH1361-C-4-CO2MePy-MeOD-in THF
EXPNO                     13
PROCNO                     1
Date_               20190425
Time                    9.12
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG               zgig2h
TD                     16384
SOLVENT                 None
NS                        32
DS                         2
SWH                 1228.501 Hz
FIDRES              0.074982 Hz
AQ                 6.6683378 sec
RG                    208.17
DW                   407.000 usec
DE                     50.00 usec
TE                     299.0 K
D1                4.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              61.4223910 MHz
NUC1                      2H
P1                    356.50 usec
SI                     65536
SF                61.4224010 MHz
WDW                       EM
SSB                        0
LB                      0.50 Hz
GB                         0
PC                      1.00
```

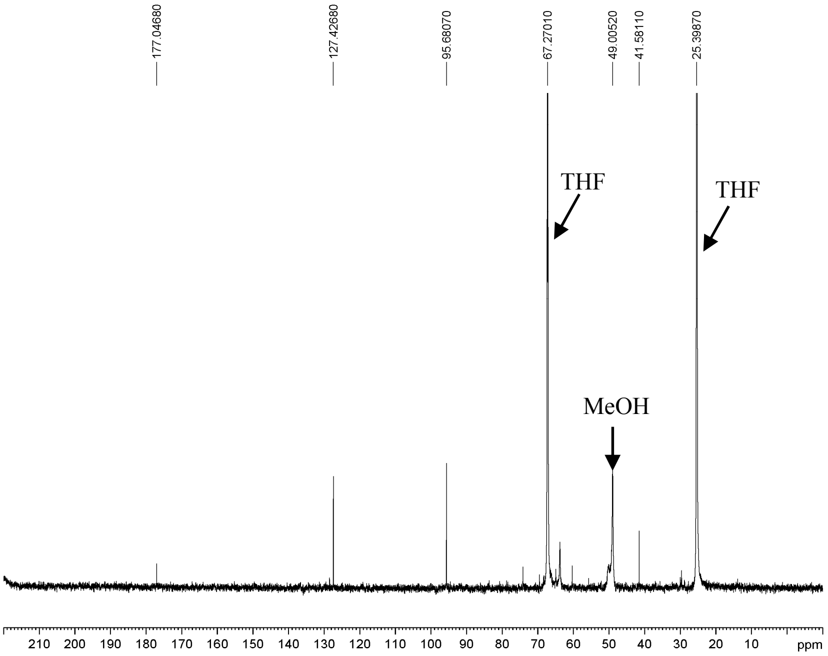


```
NAME     YH1361-C-4-CO2MePy-MeOD-in THF
EXPNO                    11
PROCNO                    1
Date_              20190425
Time                   8.30
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT                None
NS                      640
DS                        2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                   208.17
DW                   20.800 usec
DE                     6.50 usec
TE                    299.2 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                    13C
P1                     9.95 usec
SI                    32768
SF             100.6127824 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.40
```

^{1}H and ^{13}C NMR of **6b** (in THF-*d*$_0$, No-D NMR)

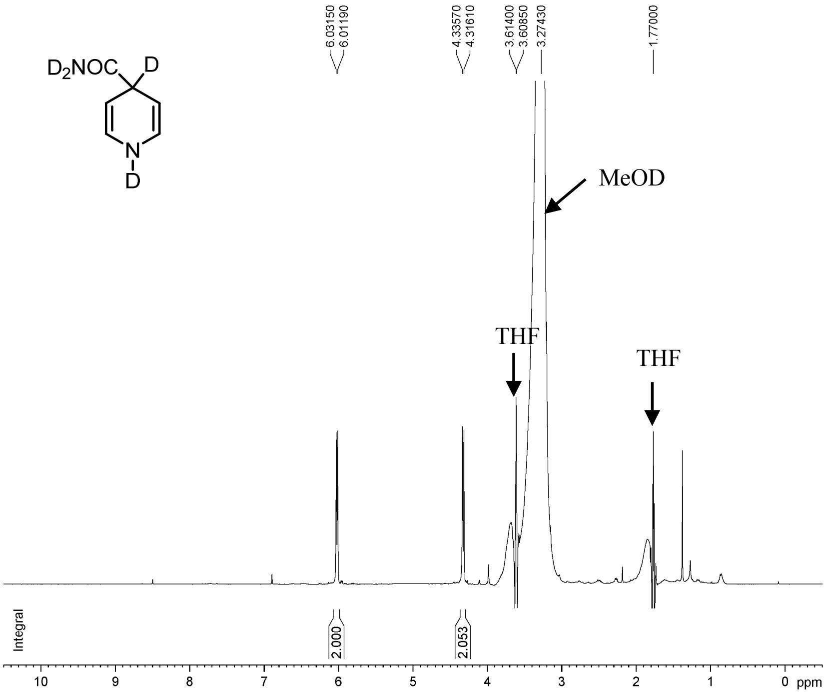


```
NAME      YH1361-F-4-CONH2-MeOH-in THF
EXPNO                   12
PROCNO                   1
Date_             20190426
Time                  9.24
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              wetdc
TD                   16384
SOLVENT               None
NS                      32
DS                      24
SWH               8000.000 Hz
FIDRES            0.488281 Hz
AQ               1.0240500 sec
RG                   21.03
DW                  62.500 usec
DE                   12.54 usec
TE                   299.3 K
D1              3.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00200000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1305050 MHz
NUC1                    1H
P1                    9.83 usec
P11               20000.00 usec
SI                   32768
SF             400.1297975 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

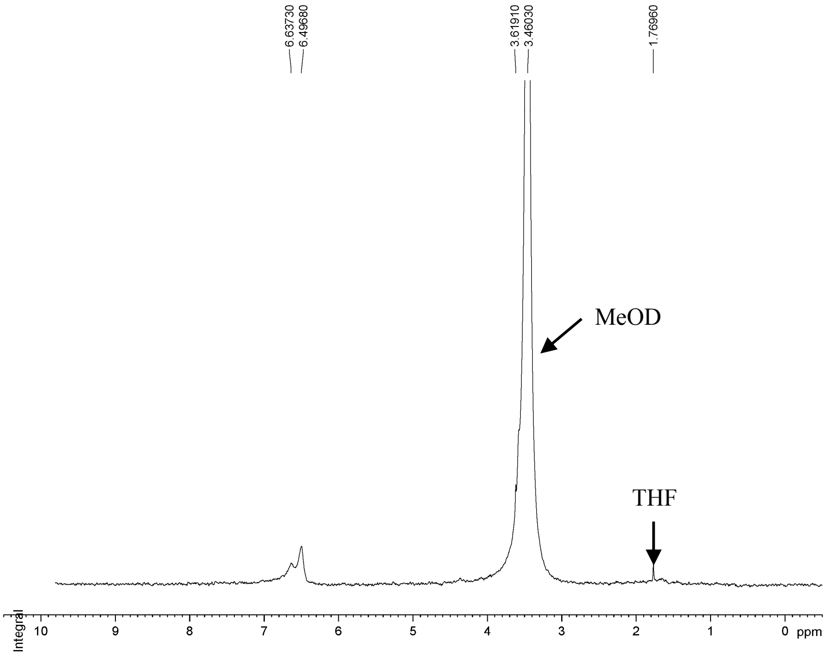


```
NAME      YH1361-F-4-CONH2-MeOH-in THF
EXPNO                   11
PROCNO                   1
Date_             20190426
Time                  8.40
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT               None
NS                    1024
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   299.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127126 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

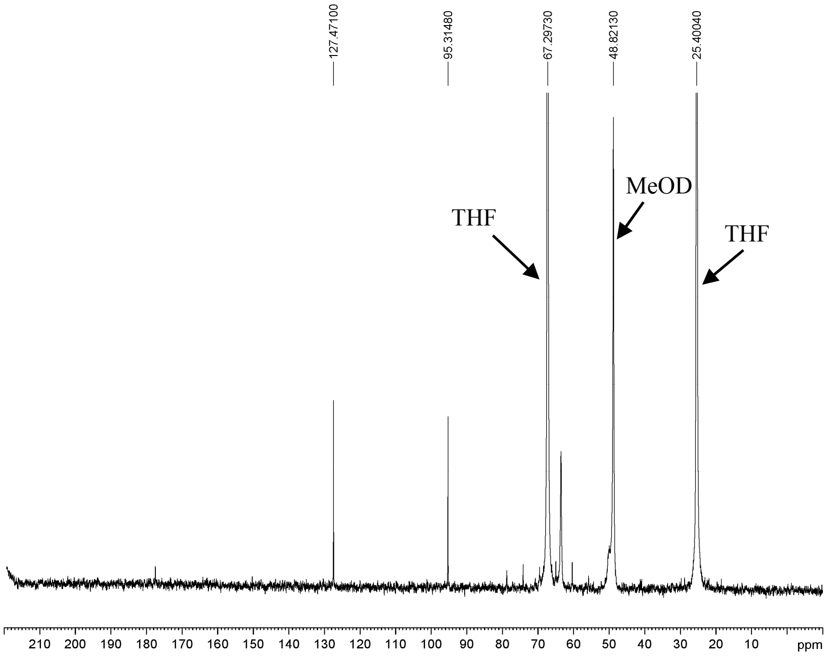
^{1}H, ^{2}H, and ^{13}C NMR of **6b-d_4** (in THF-d_0, No-D NMR)



```
NAME      YH1363-B-4-COND2Py-MeOD-in THF
EXPNO                 12
PROCNO                 1
Date_           20190501
Time                9.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            wetdc
TD                 16384
SOLVENT             None
NS                    32
DS                    24
SWH             8000.000 Hz
FIDRES          0.488281 Hz
AQ             1.0240500 sec
RG                 21.03
DW                62.500 usec
DE                 12.96 usec
TE                   0.0 K
D1            3.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00200000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1307985 MHz
NUC1                  1H
P1                  9.61 usec
P11             20000.00 usec
SI                 32768
SF           400.1300904 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

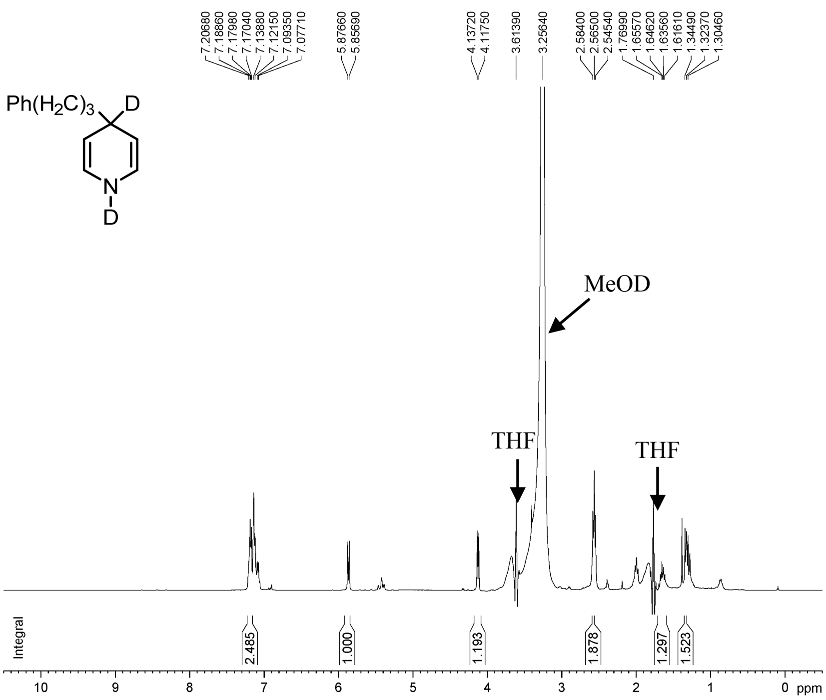


```
NAME      YH1363-B-4-COND2Py-MeOD-in THF
EXPNO                 13
PROCNO                 1
Date_           20190501
Time                9.51
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT             None
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                   0.0 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4224028 MHz
WDW                   EM
SSB                    0
LB                  0.50 Hz
GB                     0
PC                  1.00
```

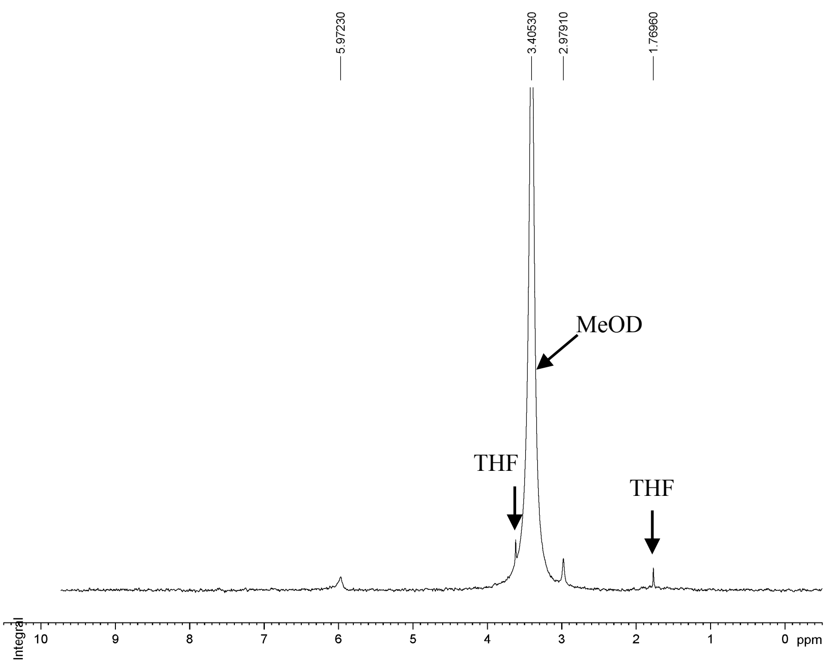


```
NAME      YH1363-B-4-COND2Py-MeOD-in THF
EXPNO                 11
PROCNO                 1
Date_           20190501
Time                8.26
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             None
NS                  1280
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                   0.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127850 MHz
WDW                   EM
SSB                    0
LB                  4.00 Hz
GB                     0
PC                  1.40
```

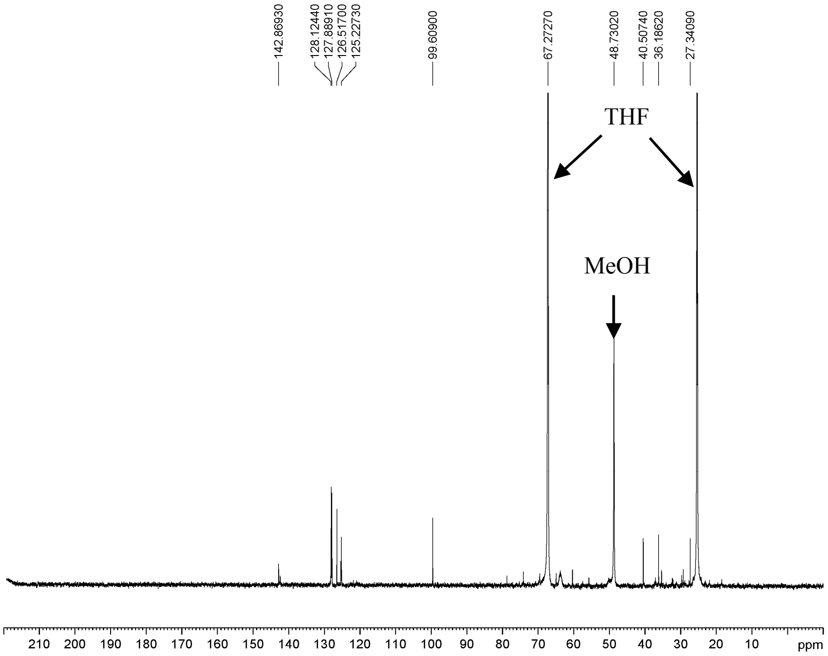
^{1}H, ^{2}H, and ^{13}C NMR of **S2**-d_2 (in THF-d_0, No-D NMR)



```
NAME     YH1361-G-4-(CH2)3PhPy-MeOD-in THF
EXPNO                 12
PROCNO                 1
Date_           20190428
Time                3.33
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            wetdc
TD                 16384
SOLVENT             None
NS                    32
DS                    24
SWH             8000.000 Hz
FIDRES          0.488281 Hz
AQ             1.0240500 sec
RG                 24.86
DW                62.500 usec
DE                 13.07 usec
TE                 297.2 K
D1            3.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00200000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1308303 MHz
NUC1                  1H
P1                  9.55 usec
P11             20000.00 usec
SI                 32768
SF           400.1301221 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

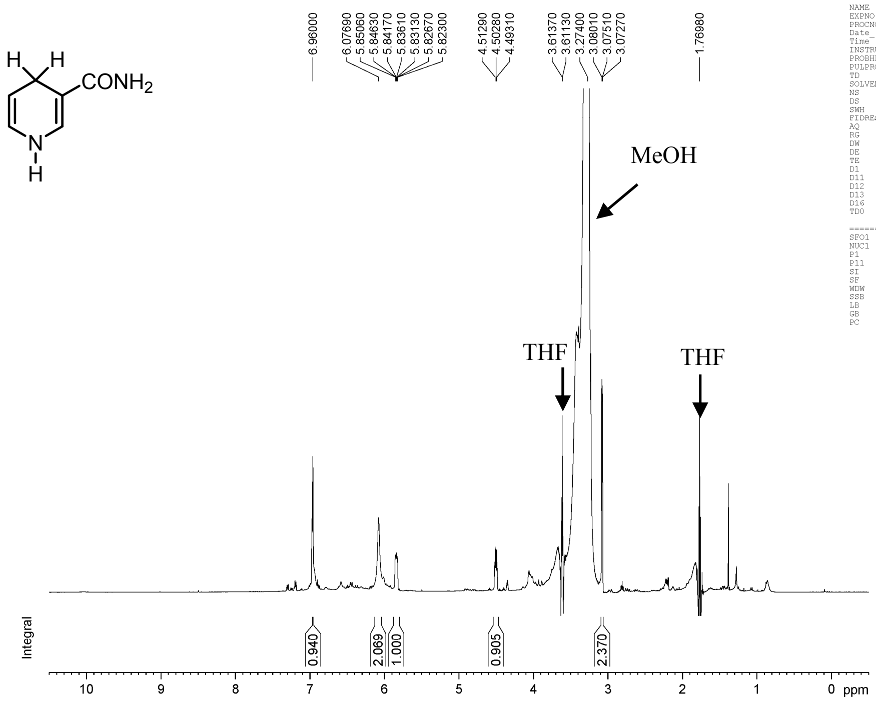


```
NAME     YH1361-G-4-(CH2)3PhPy-MeOD-in THF
EXPNO                 13
PROCNO                 1
Date_           20190428
Time                3.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT             None
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 297.3 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4224076 MHz
WDW                   EM
SSB                    0
LB                  0.50 Hz
GB                     0
PC                  1.00
```

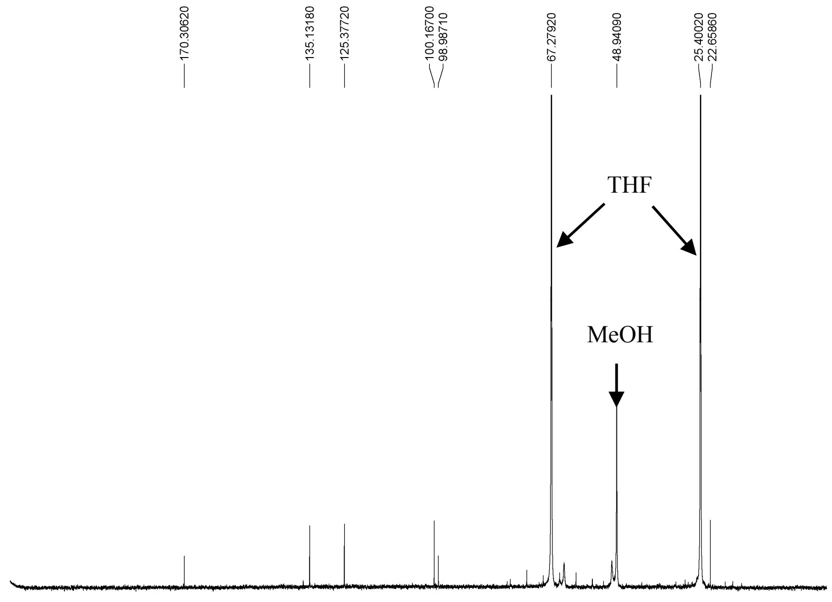


```
NAME      YH1361-G-4-(CH2)3PhPy-MeOD-in THF
EXPNO                  11
PROCNO                  1
Date_            20190428
Time                 3.25
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT              None
NS                   1920
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127948 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of **6c** (in THF-d_0, No-D NMR)

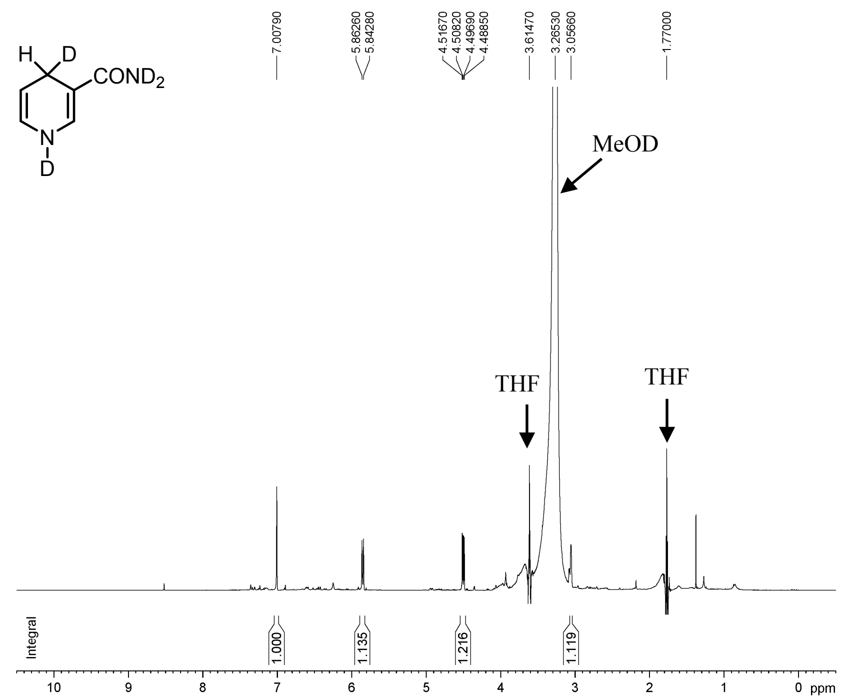


```
NAME      YH1361-J-3-CONH2Py-MeOH-in THF
EXPNO                   22
PROCNO                   1
Date_             20190428
Time                 18.35
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              wetdc
TD                   16384
SOLVENT               None
NS                      32
DS                      24
SWH               8000.000 Hz
FIDRES            0.488281 Hz
AQ               1.0240500 sec
RG                   17.91
DW                  62.500 usec
DE                   12.86 usec
TE                   298.3 K
D1              3.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00200000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1308491 MHz
NUC1                    1H
P1                    9.66 usec
P11               20000.00 usec
SI                   32768
SF             400.1301413 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

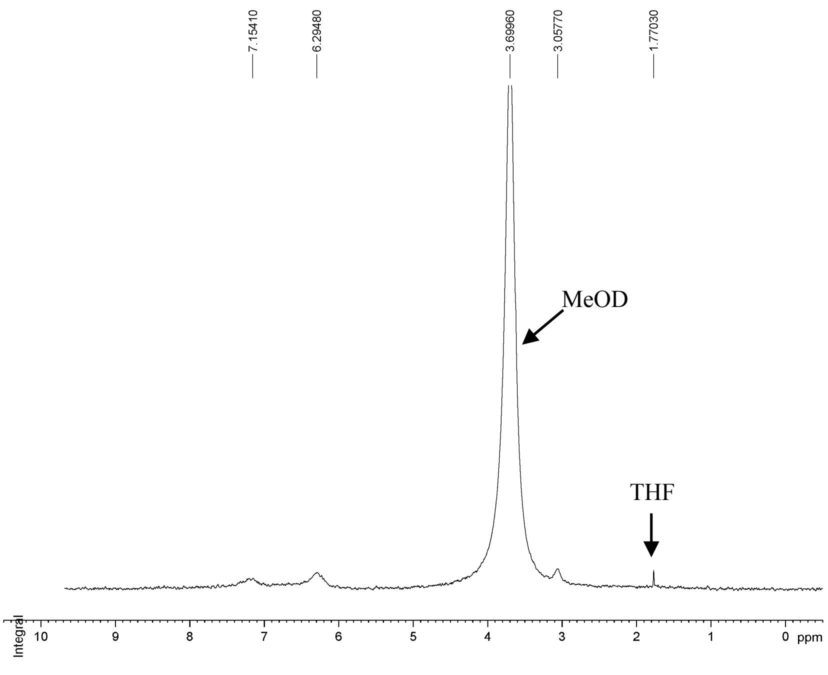


```
NAME      YH1361-J-3-CONH2Py-MeOH-in THF
EXPNO                   21
PROCNO                   1
Date_             20190428
Time                 16.53
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT               None
NS                    1920
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   298.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127985 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

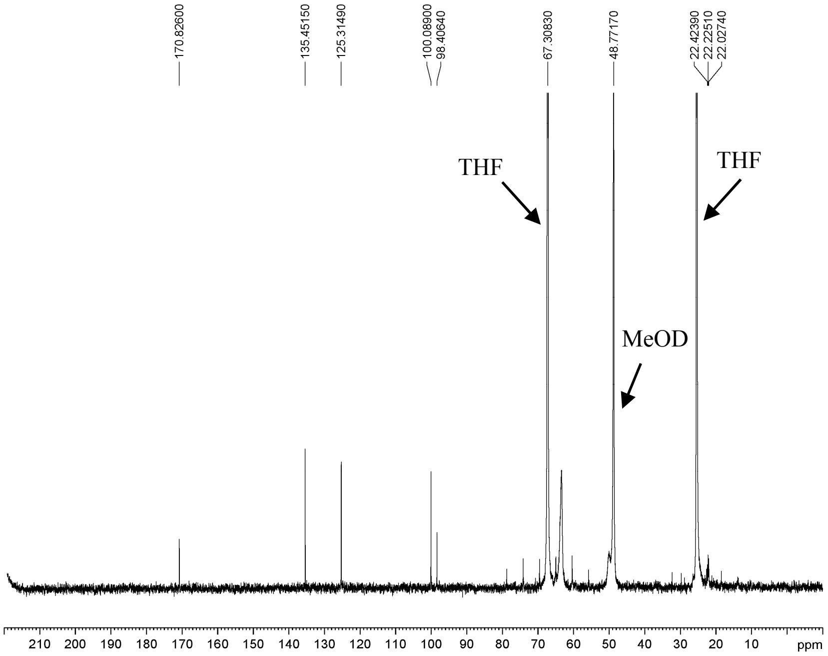
^{1}H, ^{2}H, and ^{13}C NMR of **6c-*d*₄** (in THF-*d*$_0$, No-D NMR)



```
NAME      YH1361-K-3-CONH2Py-MeOD-in THF
EXPNO                   12
PROCNO                   1
Date_             20190428
Time                 12.48
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              wetdc
TD                   16384
SOLVENT               None
NS                      32
DS                      24
SWH               8000.000 Hz
FIDRES            0.488281 Hz
AQ               1.0240500 sec
RG                    8.98
DW                  62.500 usec
DE                   12.73 usec
TE                   298.3 K
D1              3.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00200000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1308488 MHz
NUC1                    1H
P1                    9.73 usec
P11               20000.00 usec
SI                   32768
SF             400.1301406 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

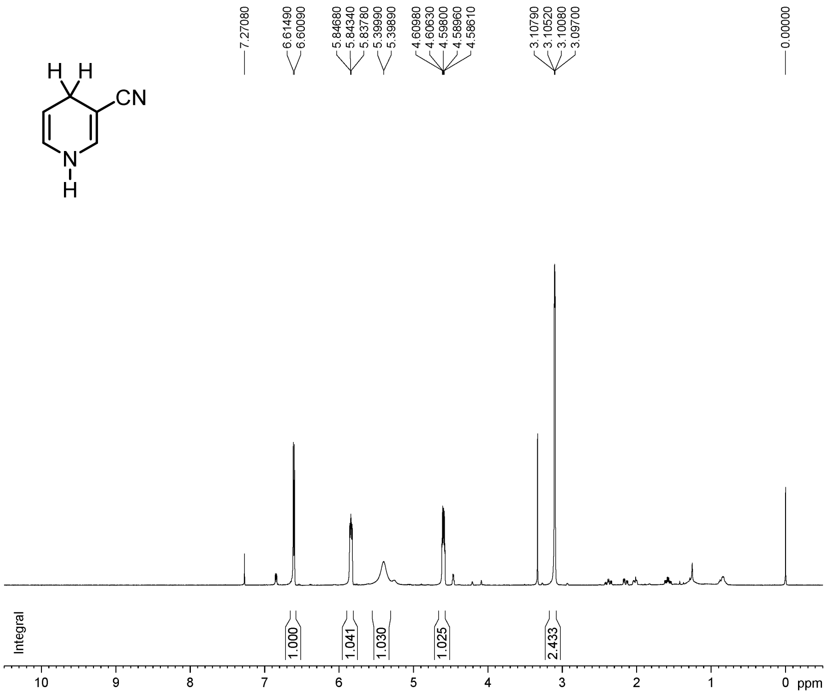


```
NAME      YH1361-K-3-CONH2Py-MeOD-in THF
EXPNO                   13
PROCNO                   1
Date_             20190428
Time                 12.54
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig2h
TD                   16384
SOLVENT               None
NS                      32
DS                       2
SWH               1228.501 Hz
FIDRES            0.074982 Hz
AQ               6.6683378 sec
RG                  208.17
DW                 407.000 usec
DE                   50.00 usec
TE                   298.4 K
D1              4.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            61.4223910 MHz
NUC1                    2H
P1                  356.50 usec
SI                   65536
SF              61.4224105 MHz
WDW                     EM
SSB                      0
LB                    0.50 Hz
GB                       0
PC                    1.00
```

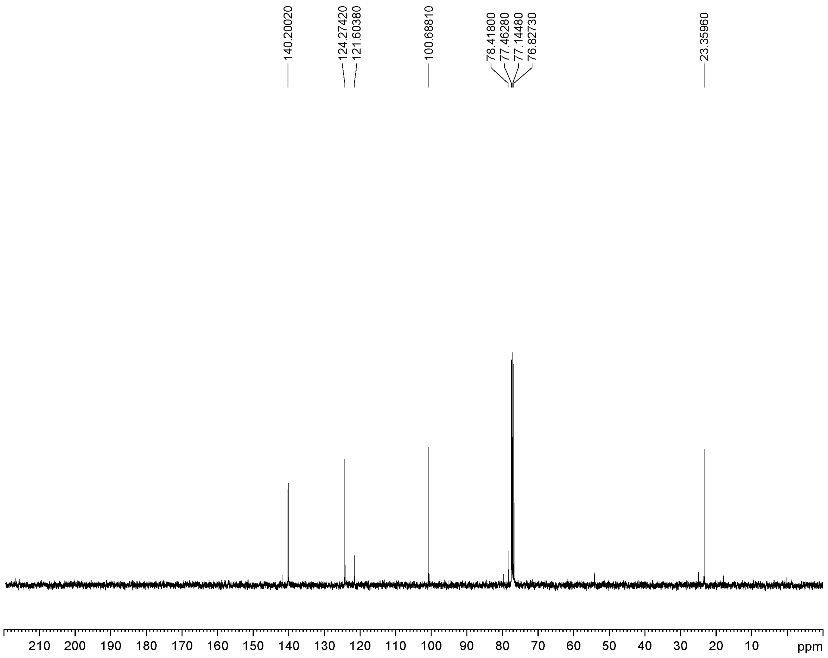


```
NAME      YH1361-K-3-CONH2Py-MeOD-in THF
EXPNO                   11
PROCNO                   1
Date_             20190428
Time                 12.40
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT               None
NS                    1920
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   298.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127971 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of **6d**:

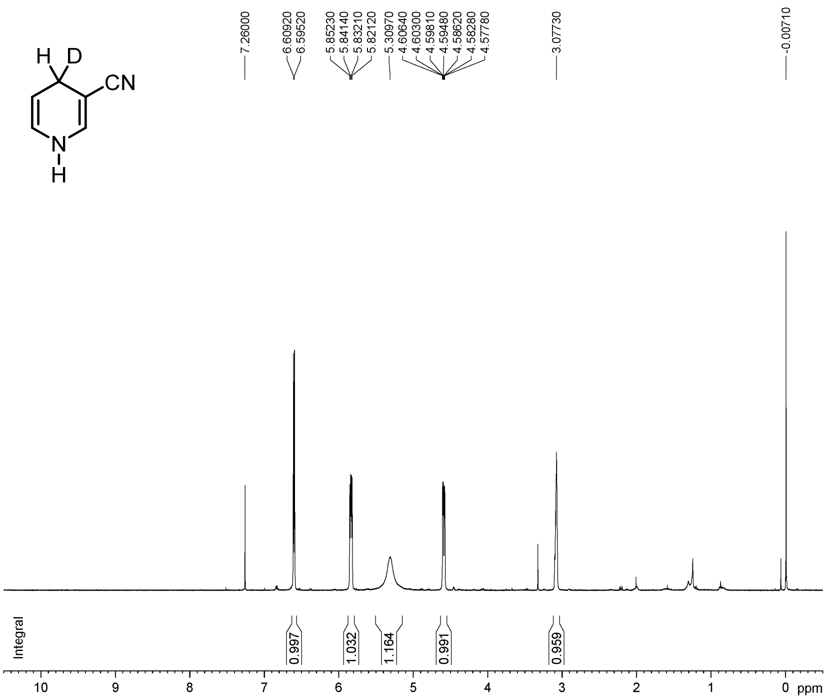


```
NAME      YH1270-3-CNPy-Et2O-phase-in CDCl3
EXPNO                   10
PROCNO                   1
Date_             20181026
Time                 15.08
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                  115.32
DW                  62.400 usec
DE                    6.50 usec
TE                   296.5 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                    9.68 usec
SI                   65536
SF             400.1300063 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

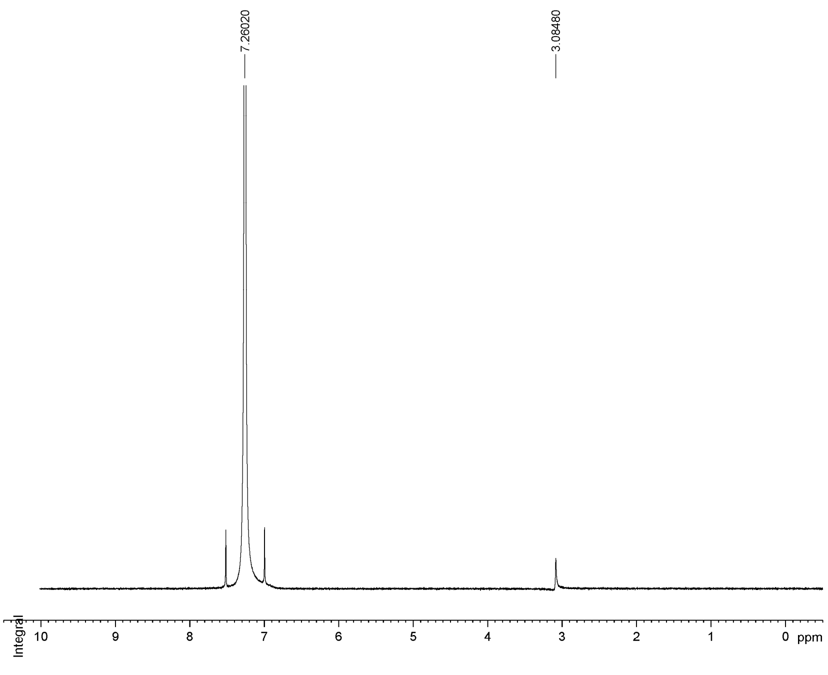


```
NAME      YH1270-3-CNPy-Et2O-phase-in CDCl3
EXPNO                   11
PROCNO                   1
Date_             20181026
Time                 16.25
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     200
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   296.8 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127584 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

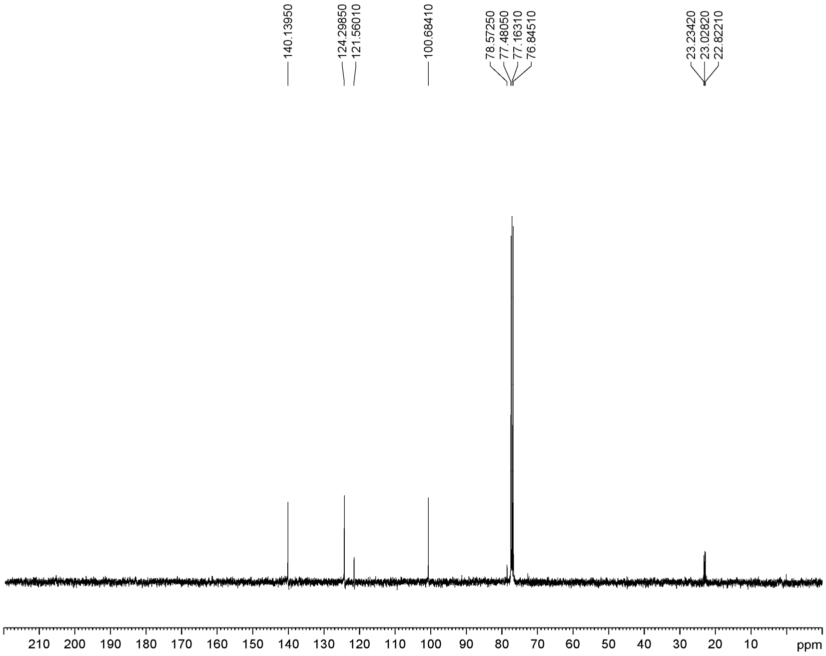
^{1}H, ^{2}H, and ^{13}C NMR of **6d**-*d*:



```
NAME      YH1277-3-CNPy-MeOD-Et2O-phase-in CDCl3
EXPNO                   10
PROCNO                   1
Date_             20181105
Time                 16.14
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                     130
DW                  62.400 usec
DE                    6.50 usec
TE                   295.3 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                    9.68 usec
SI                   65536
SF             400.1300097 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

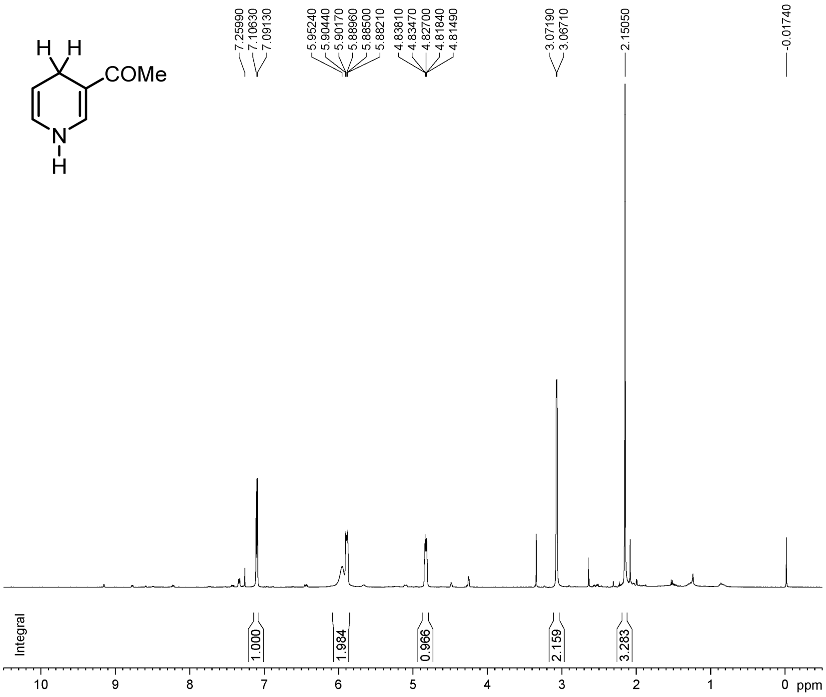


```
NAME      YH1277-3-CNPy-MeOD-Et2O-phase-in CDCl3
EXPNO                   11
PROCNO                   1
Date_             20181105
Time                 16.22
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig2h
TD                   16384
SOLVENT               None
NS                      32
DS                       2
SWH               1228.501 Hz
FIDRES            0.074982 Hz
AQ               6.6683378 sec
RG                  208.17
DW                 407.000 usec
DE                   50.00 usec
TE                   295.7 K
D1              4.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            61.4223910 MHz
NUC1                    2H
P1                  356.50 usec
SI                   65536
SF              61.4223899 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

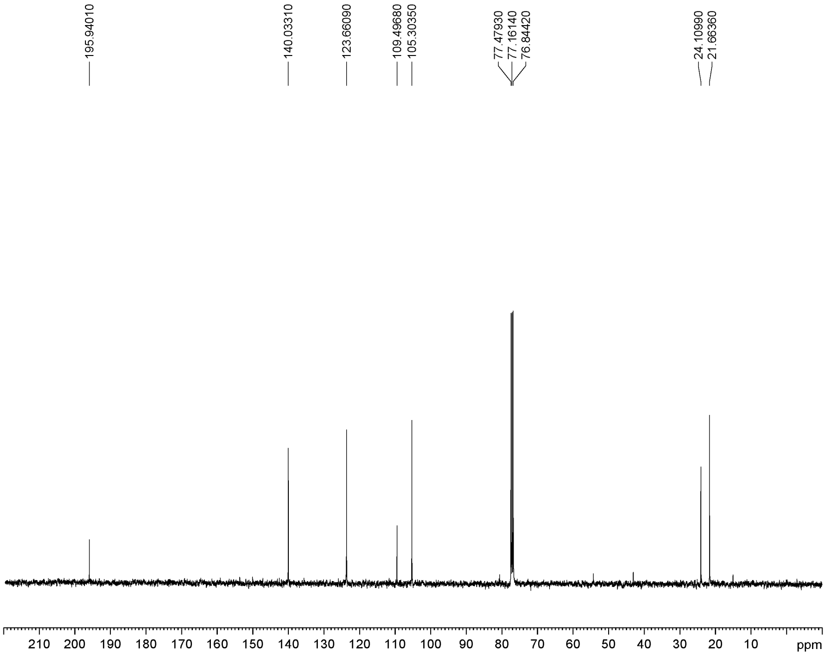


```
NAME      YH1277-3-CNPy-MeOD-Et2O-phase-in CDCl3
EXPNO                  12
PROCNO                  1
Date_            20181105
Time                16.58
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    300
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  295.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127550 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of **6e**:

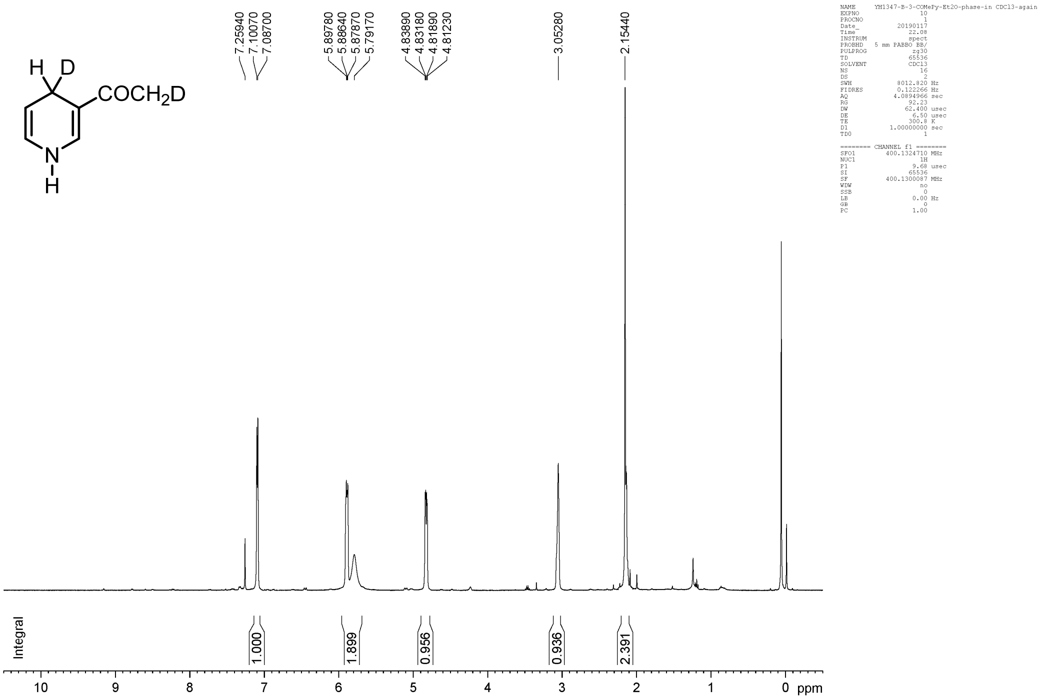


```
NAME     YH1251-3-COMePy-Et2O-phase-in CDCl3
EXPNO               10
PROCNO               1
Date_         20181011
Time             14.50
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG               69.28
DW              62.400 usec
DE                6.50 usec
TE               298.5 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       400.1324710 MHz
NUC1                1H
P1                9.68 usec
SI               65536
SF         400.1300109 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00
```

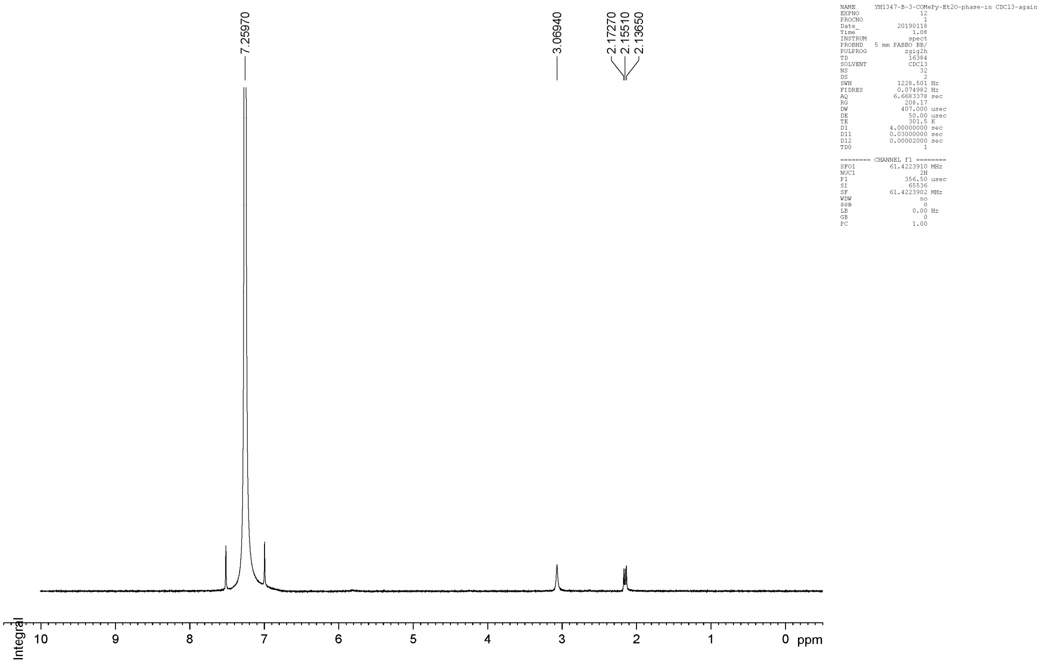


```
NAME     YH1251-3-COMePy-Et2O-phase-in CDCl3
EXPNO               11
PROCNO               1
Date_         20181011
Time             15.24
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 300
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG              208.17
DW              20.800 usec
DE                6.50 usec
TE               299.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       100.6228298 MHz
NUC1               13C
P1                9.95 usec
SI               32768
SF         100.6127562 MHz
WDW                 EM
SSB                  0
LB                3.00 Hz
GB                   0
PC                1.40
```

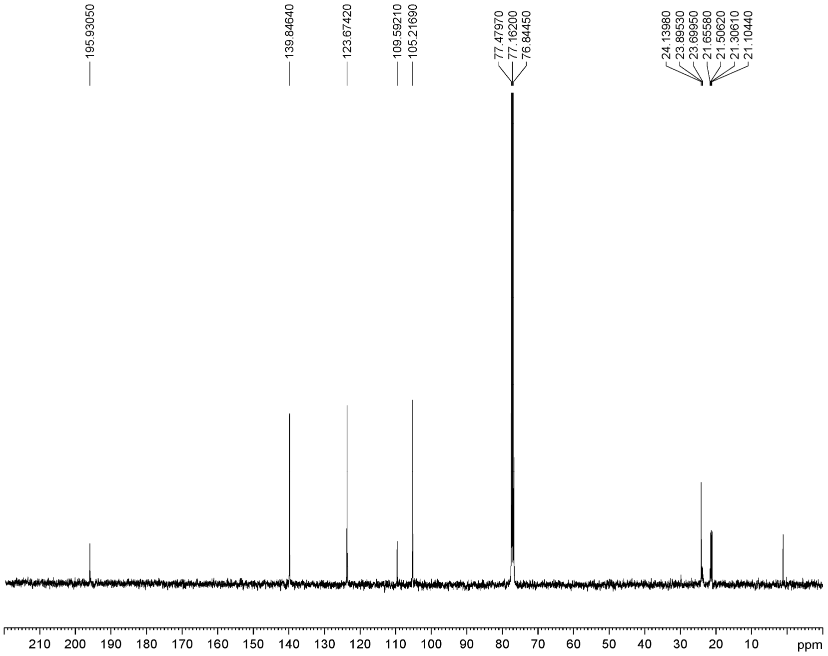
^{1}H, ^{2}H, and ^{13}C NMR of **6e**-*d*:



```
NAME      YH1347-B-3-COMePy-Et2O-phase-in CDCl3-again
EXPNO                 10
PROCNO                 1
Date_           20190117
Time               22.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 92.23
DW                62.400 usec
DE                  6.50 usec
TE                 300.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300087 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

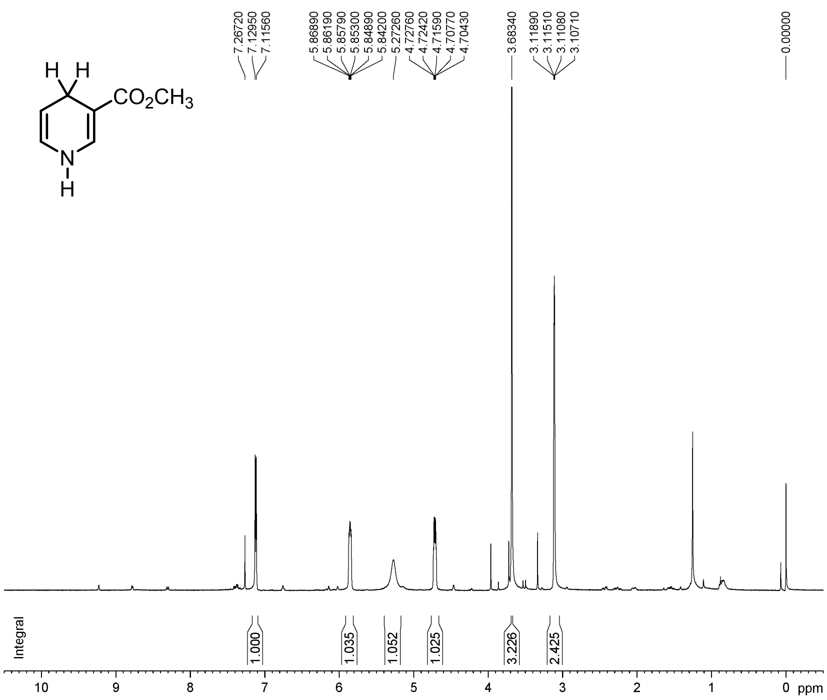


```
NAME      YH1347-B-3-COMePy-Et2O-phase-in CDCl3-again
EXPNO                 12
PROCNO                 1
Date_           20190118
Time                1.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 301.5 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4223902 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

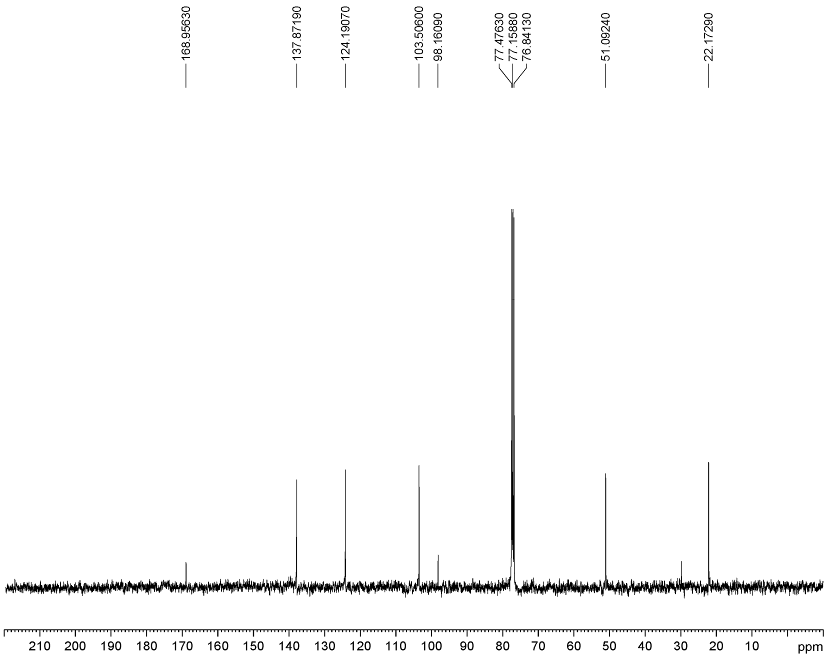


```
NAME      YH1347-B-3-COMePy-Et2O-phase-in CDCl3-again
EXPNO                 13
PROCNO                 1
Date_           20190118
Time                1.38
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 302.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127538 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of **6f**:

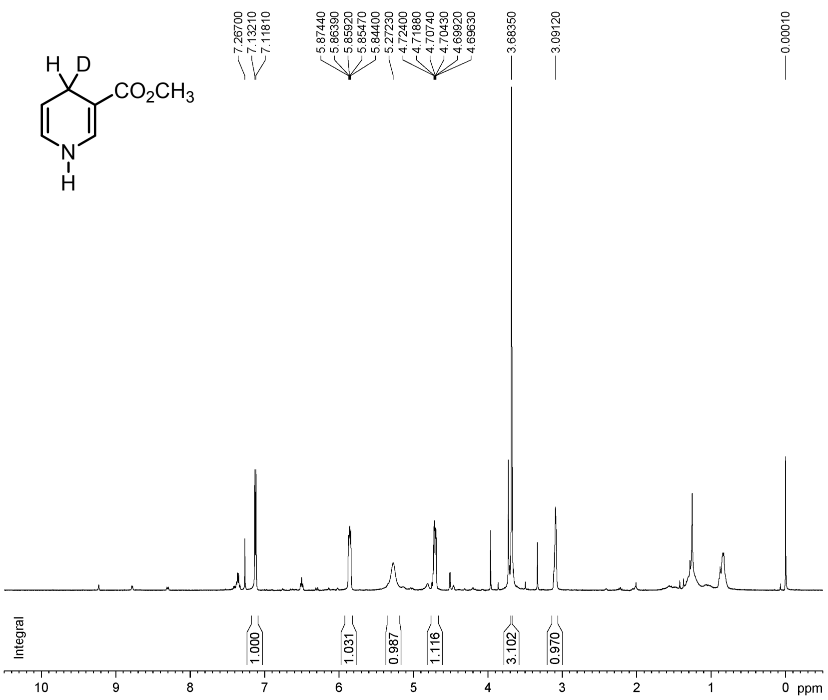


```
NAME     YH1245-3-Et2O-phase-inCDCl3-1st
EXPNO                 10
PROCNO                 1
Date_           20181005
Time               14.00
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                101.33
DW                62.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300085 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

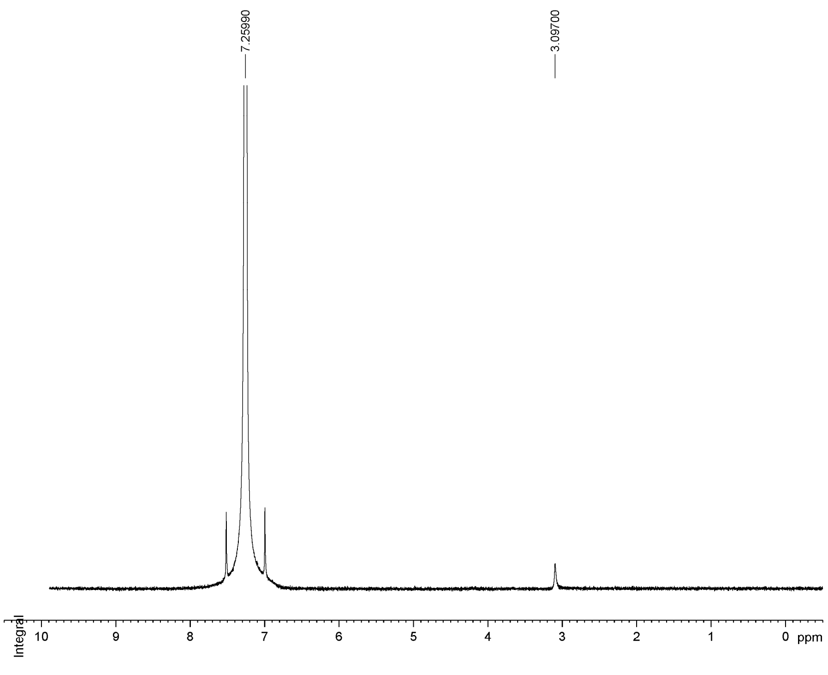


```
NAME     YH1245-3-Et2O-phase-inCDCl3-1st
EXPNO                 12
PROCNO                 1
Date_           20181005
Time               14.13
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   300
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 298.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127546 MHz
WDW                   EM
SSB                    0
LB                  4.00 Hz
GB                     0
PC                  1.40
```

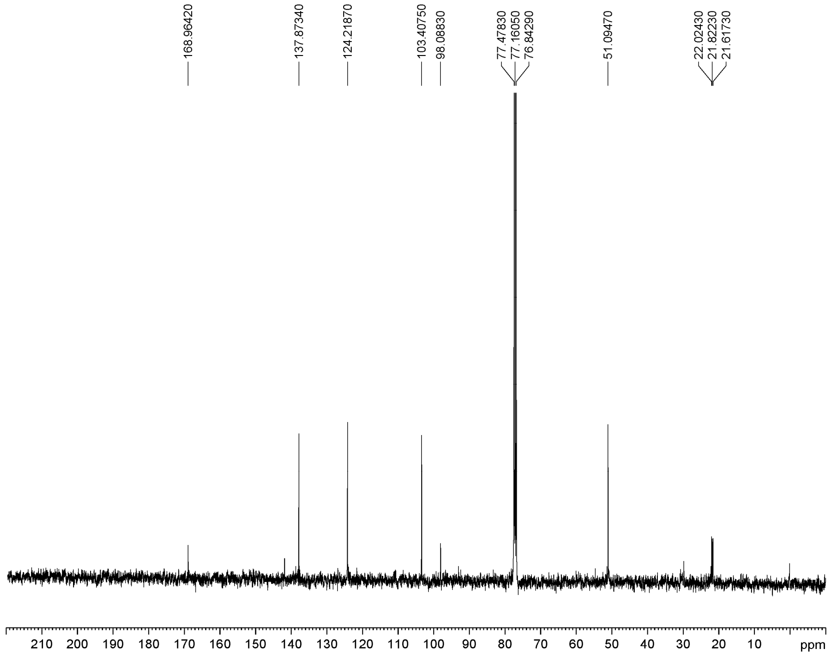
^1H, ^2H, and ^{13}C NMR of **6f**-*d*:



```
NAME      YH1297-3-CO2MePy-Et2O-phase-in CDCl3
EXPNO                 10
PROCNO                 1
Date_           20181121
Time               12.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                115.32
DW                62.400 usec
DE                  6.50 usec
TE                 297.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300070 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

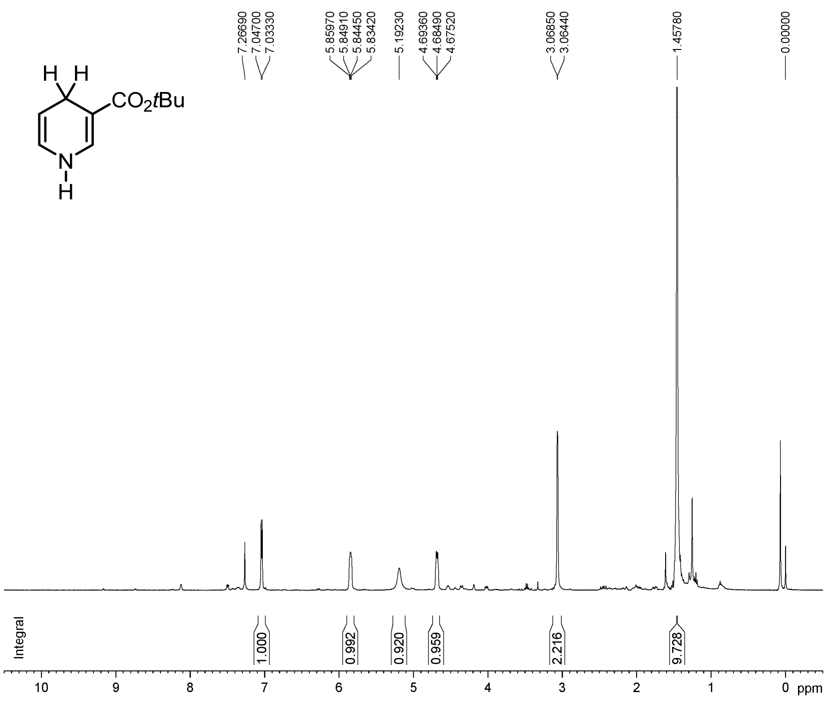


```
NAME      YH1297-3-CO2MePy-Et2O-phase-in CDCl3
EXPNO                 11
PROCNO                 1
Date_           20181121
Time               12.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 298.1 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4223975 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

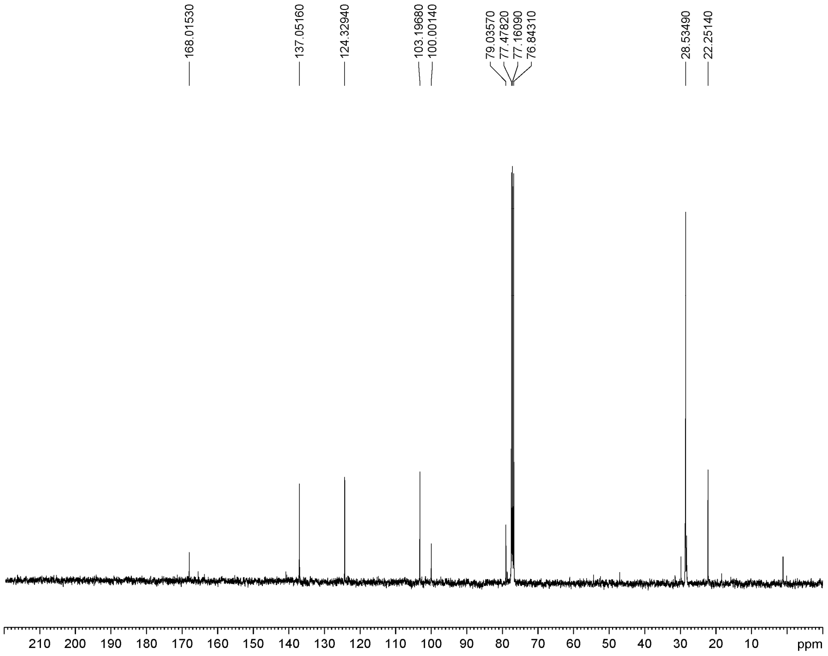


```
NAME       YH1297-3-CO2MePy-Et2O-phase-in CDCl3
EXPNO                12
PROCNO                1
Date_          20181121
Time              13.17
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  400
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               208.17
DW               20.800 usec
DE                 6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TDO                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                 9.95 usec
SI                32768
SF          100.6127538 MHz
WDW                  EM
SSB                   0
LB                 3.00 Hz
GB                    0
PC                 1.40
```

^{1}H and ^{13}C NMR of **6g**:

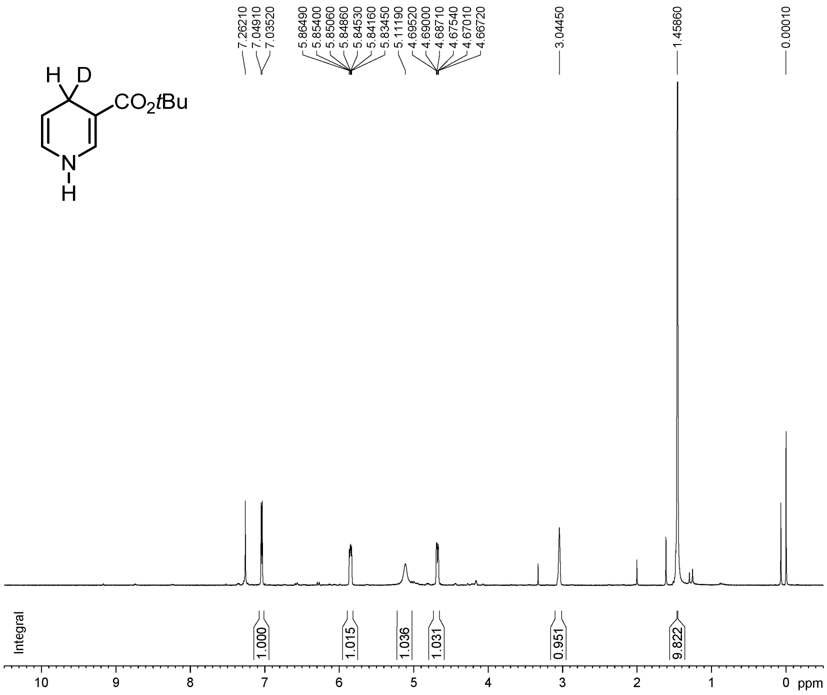


```
NAME       YH1302-3-CO2tBuPy-Et2O-phase-in CDCl3-again
EXPNO                    10
PROCNO                    1
Date_              20181218
Time                  10.17
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0894966 sec
RG                    69.28
DW                   62.400 usec
DE                     6.50 usec
TE                    301.3 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                     1H
P1                     9.68 usec
SI                    65536
SF              400.1300061 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

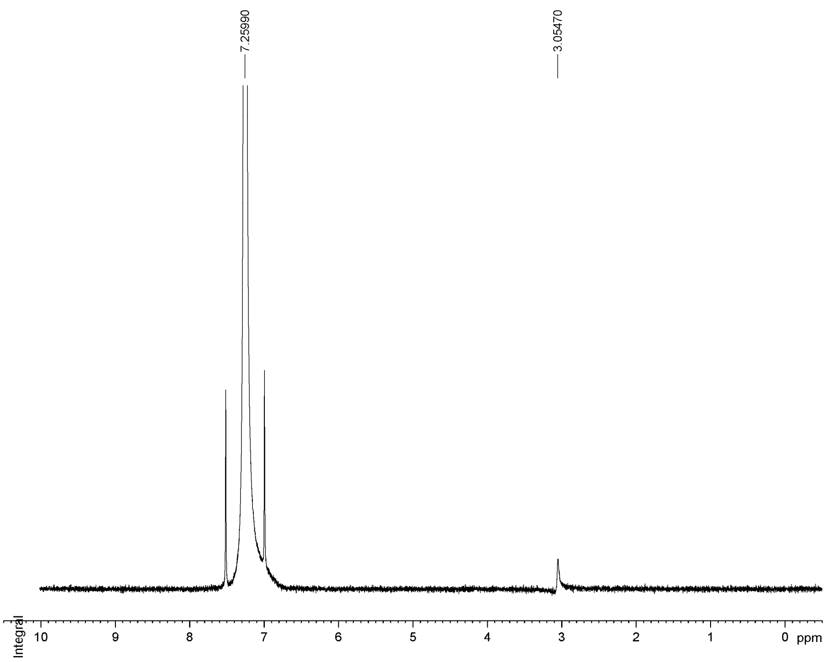


```
NAME       YH1302-3-CO2tBuPy-Et2O-phase-in CDCl3-again
EXPNO                    11
PROCNO                    1
Date_              20181218
Time                  11.49
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      500
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                   208.17
DW                   20.800 usec
DE                     6.50 usec
TE                    302.5 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                    13C
P1                     9.95 usec
SI                    32768
SF              100.6127522 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     1.40
```

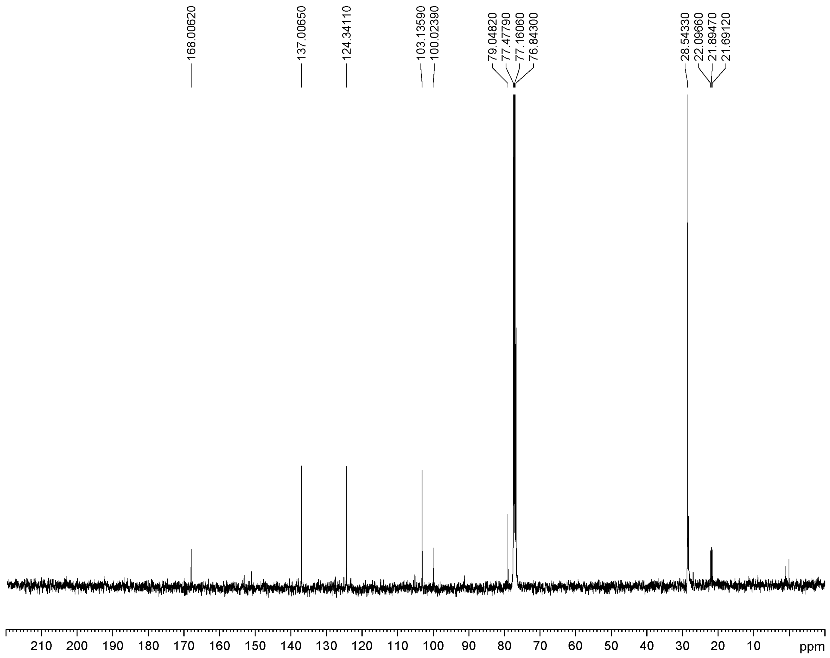
^{1}H, ^{2}H, and ^{13}C NMR of **6g**-*d*:



```
NAME      YH1347-A-3-CO2tBuPy-Et2O-phase-in CDCl3
EXPNO                  10
PROCNO                  1
Date_            20190114
Time                12.45
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                 101.33
DW                 62.400 usec
DE                   6.50 usec
TE                  302.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.68 usec
SI                  65536
SF            400.1300081 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

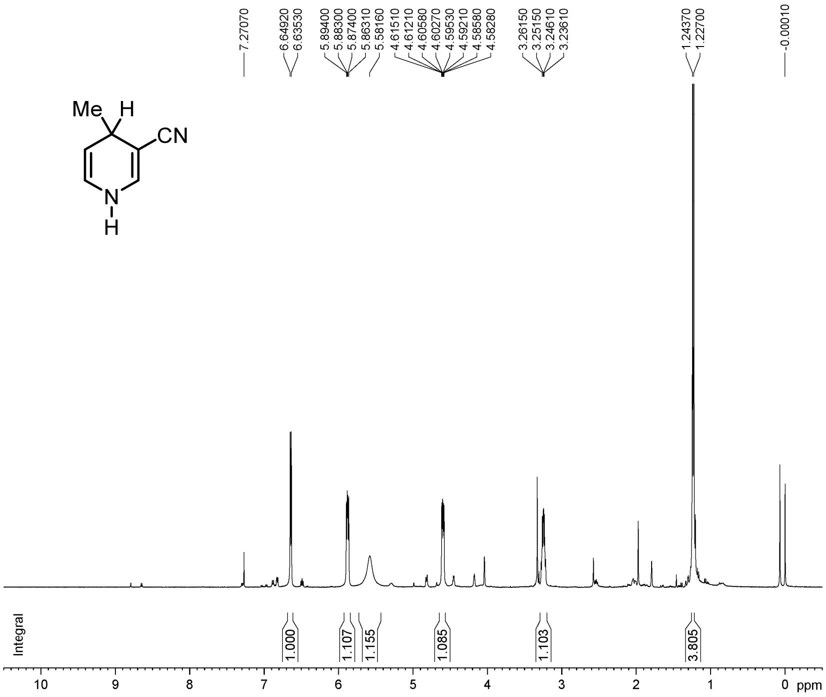


```
NAME      YH1347-A-3-CO2tBuPy-Et2O-phase-in CDCl3
EXPNO                  11
PROCNO                  1
Date_            20190114
Time                12.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgig2h
TD                  16384
SOLVENT              None
NS                     64
DS                      2
SWH              1228.501 Hz
FIDRES           0.074982 Hz
AQ              6.6683378 sec
RG                 208.17
DW                407.000 usec
DE                  50.00 usec
TE                  302.8 K
D1             4.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1           61.4223910 MHz
NUC1                   2H
P1                 356.50 usec
SI                  65536
SF             61.4223898 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

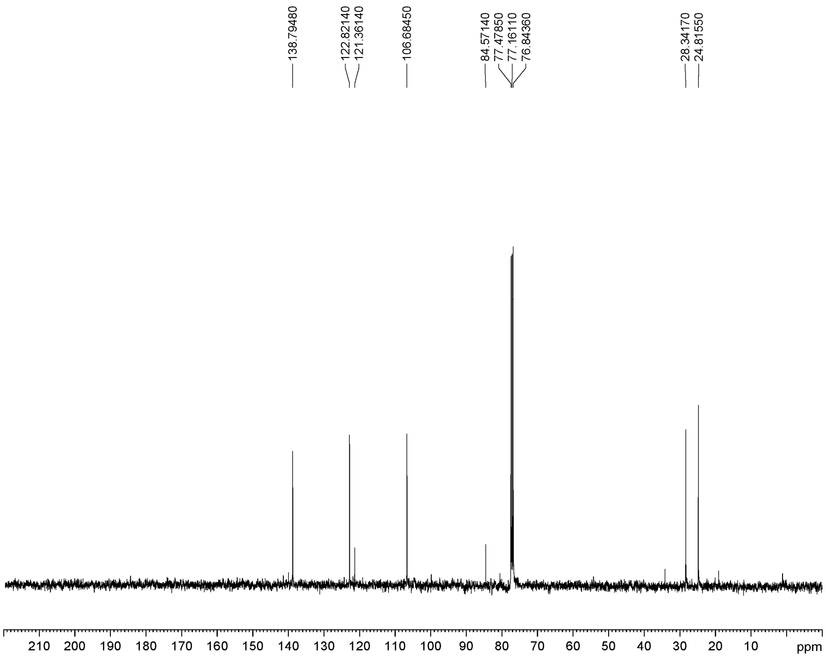


```
NAME     YH1347-A-3-CO2tBuPy-Et2O-phase-in CDCl3
EXPNO               13
PROCNO               1
Date_         20190115
Time              3.28
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                1526
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG              208.17
DW              20.800 usec
DE                6.50 usec
TE               302.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       100.6228293 MHz
NUC1               13C
P1                9.95 usec
SI               32768
SF         100.6127516 MHz
WDW                 EM
SSB                  0
LB                3.00 Hz
GB                   0
PC                1.40
```

^{1}H and ^{13}C NMR of **6h**:

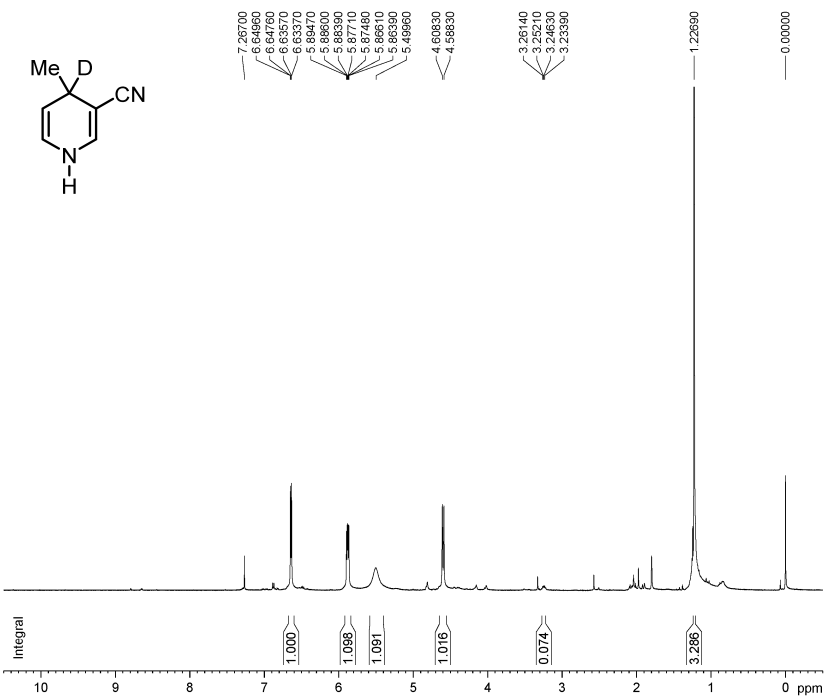


```
NAME      YH1287-3-CN-4-MePy-Et2O-phase-inCDCl3
EXPNO                 10
PROCNO                 1
Date_           20181109
Time               21.34
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 82.47
DW                62.400 usec
DE                  6.50 usec
TE                 295.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300052 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

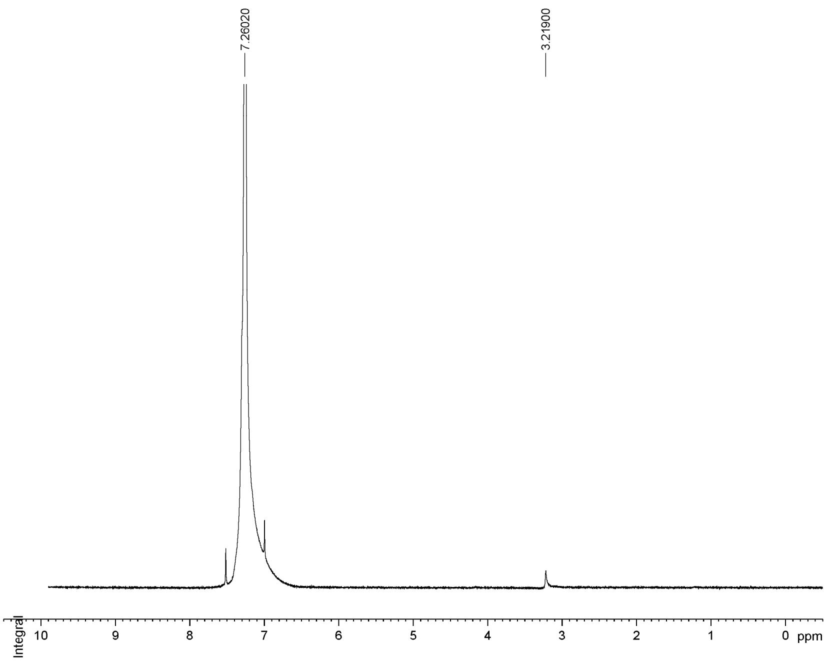


```
NAME      YH1287-3-CN-4-MePy-Et2O-phase-inCDCl3
EXPNO                 11
PROCNO                 1
Date_           20181109
Time               22.01
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127562 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40
```

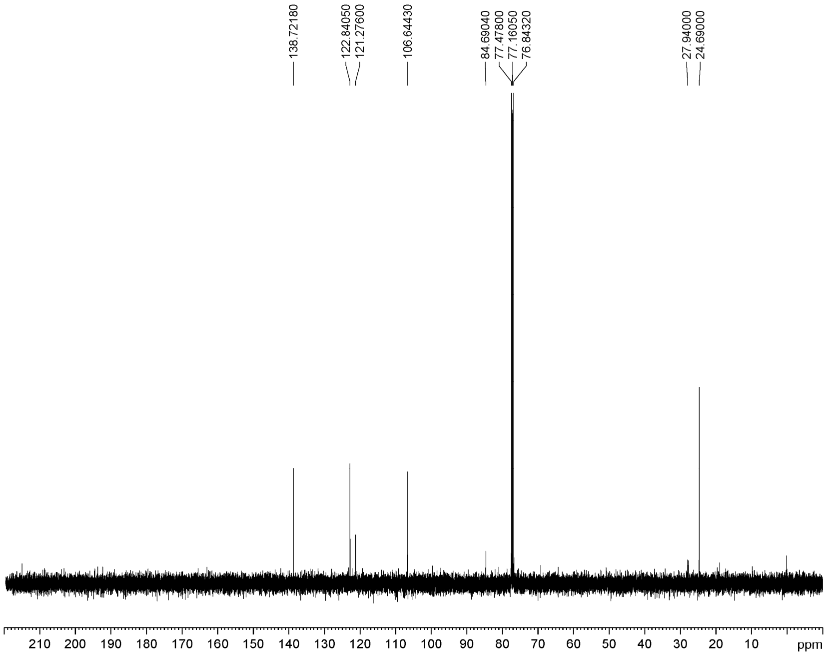
^{1}H, ^{2}H, and ^{13}C NMR of **6h-*d***:



```
NAME     YH1272-3-CN-4-MePy-Et2O-phase-inCDCl3
EXPNO                 10
PROCNO                 1
Date_           20181030
Time               12.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                115.32
DW                62.400 usec
DE                  6.50 usec
TE                 297.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300083 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

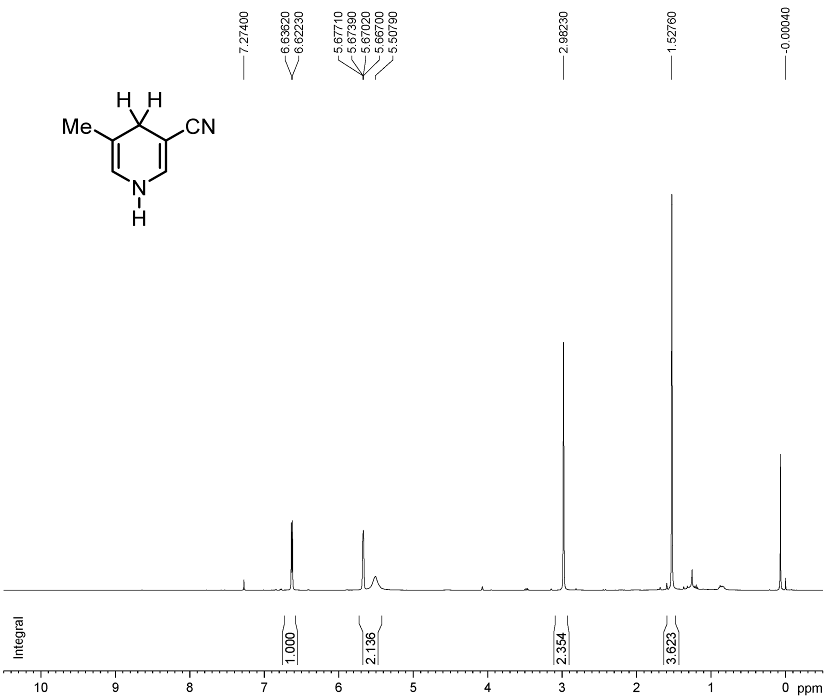


```
NAME     YH1272-3-CN-4-MePy-Et2O-phase-inCDCl3
EXPNO                 11
PROCNO                 1
Date_           20181030
Time               12.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 297.6 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4223970 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

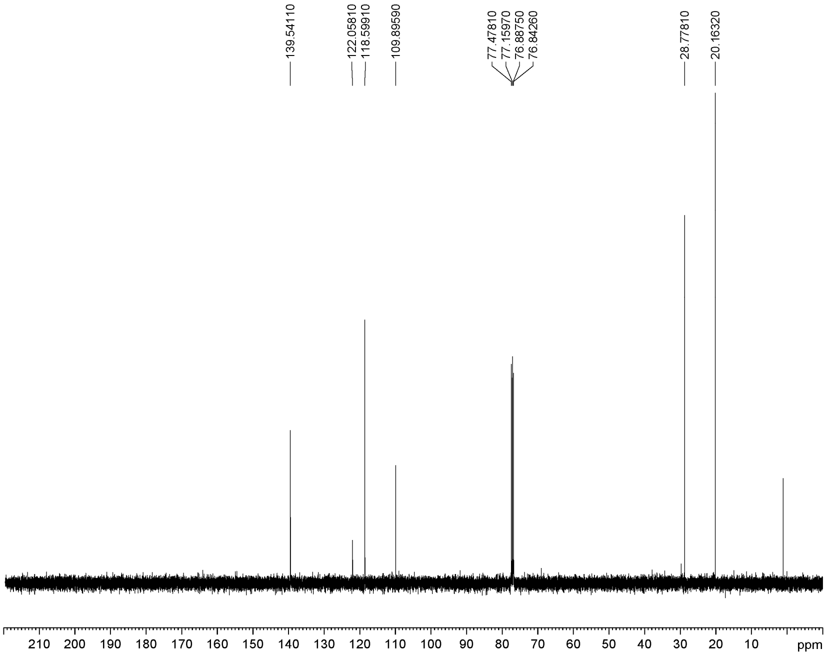


```
NAME     YH1272-3-CN-4-MePy-Et2O-phase-inCDCl3
EXPNO                  20
PROCNO                  1
Date_            20181030
Time                13.41
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    500
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127549 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of **6i**:

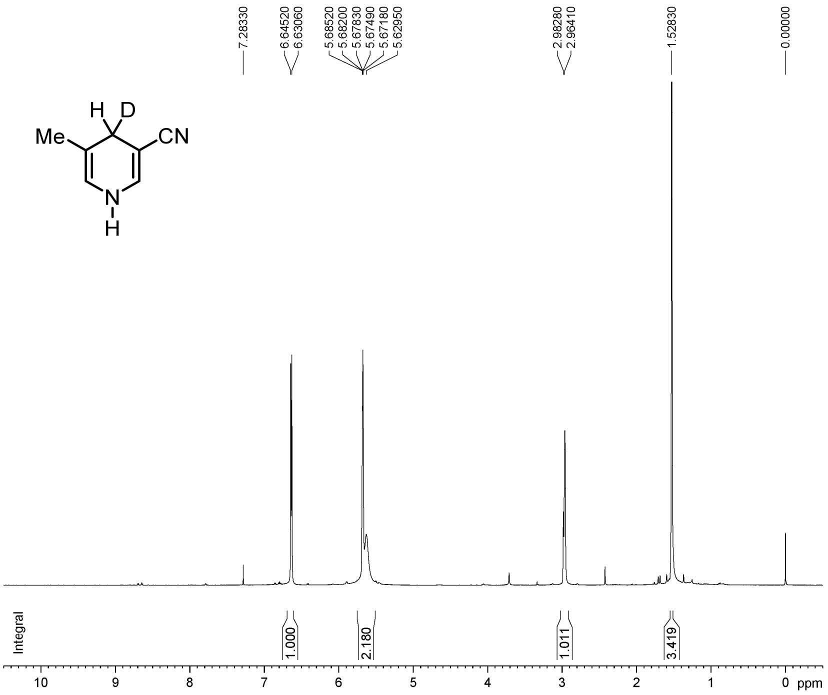


```
NAME     YH1323-3-CN-4-MePy-Et2O-phase-in CDCl3-again
EXPNO                10
PROCNO                1
Date_          20181221
Time              12.01
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                57.49
DW               62.400 usec
DE                 6.50 usec
TE                302.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                 9.68 usec
SI                65536
SF          400.1300035 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

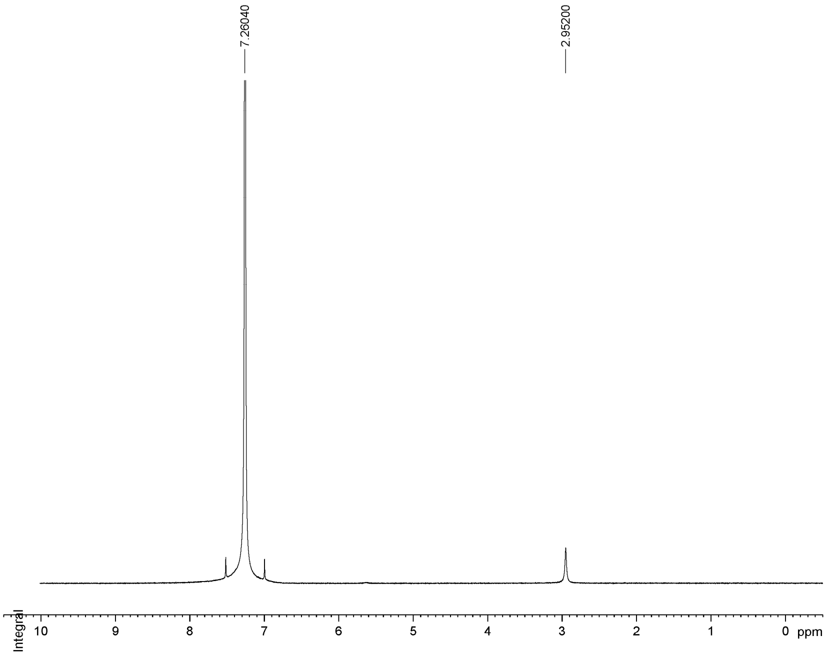


```
NAME     YH1323-3-CN-4-MePy-Et2O-phase-in CDCl3-again
EXPNO                11
PROCNO                1
Date_          20181221
Time              12.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  300
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               208.17
DW               20.800 usec
DE                 6.50 usec
TE                303.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                 9.95 usec
SI                32768
SF          100.6127569 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```

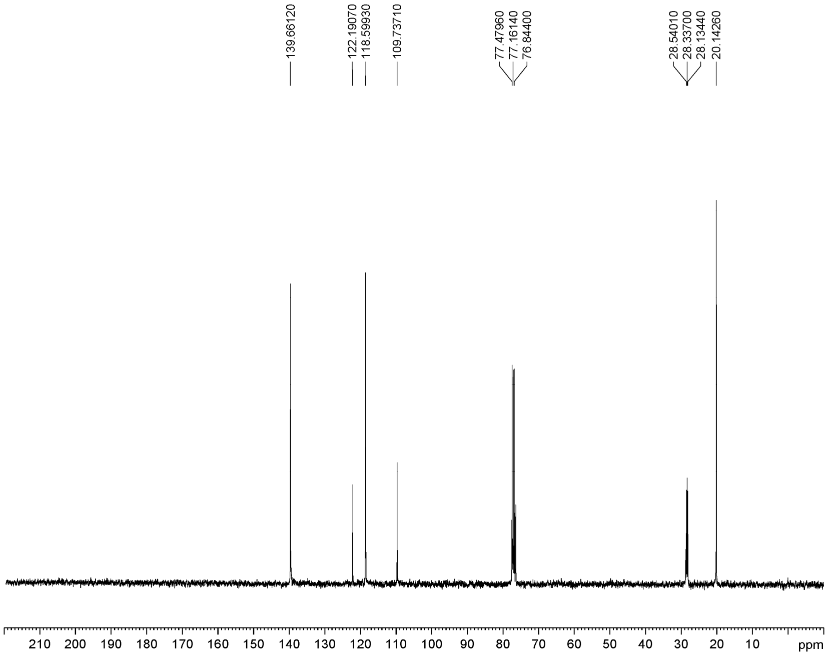
^{1}H, ^{2}H, and ^{13}C NMR of **6i**-*d*:



```
NAME      YH1228-solid-in CDCl3
EXPNO                   10
PROCNO                   1
Date_             20181004
Time                 14.57
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    31.2
DW                  62.400 usec
DE                    6.50 usec
TE                   298.3 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                    9.68 usec
SI                   65536
SF             400.1300017 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

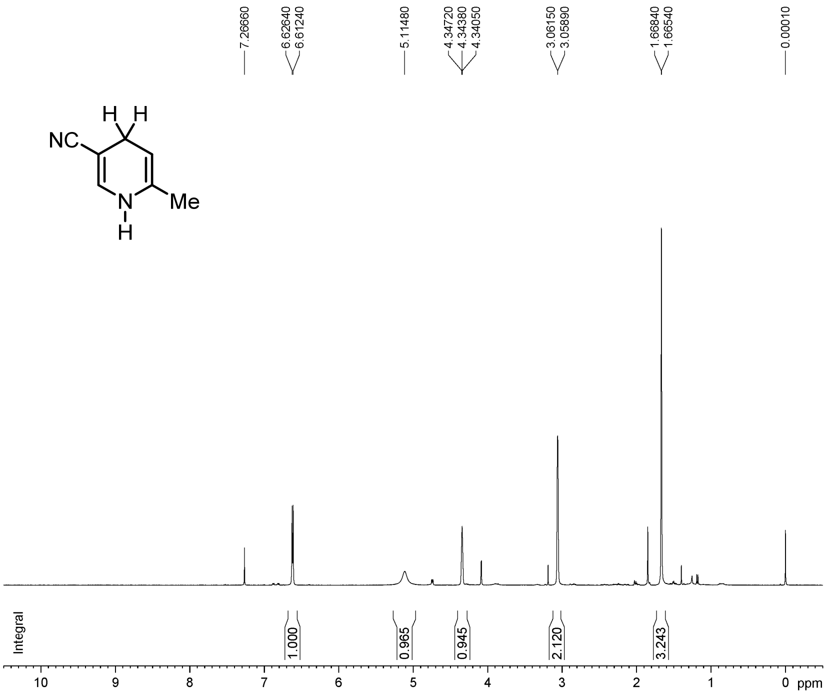


```
NAME      YH1228-solid-in CDCl3
EXPNO                   12
PROCNO                   1
Date_             20181004
Time                 15.36
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig2h
TD                   16384
SOLVENT               None
NS                      32
DS                       2
SWH               1228.501 Hz
FIDRES            0.074982 Hz
AQ               6.6683378 sec
RG                  208.17
DW                 407.000 usec
DE                   50.00 usec
TE                   298.4 K
D1              4.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            61.4223910 MHz
NUC1                    2H
P1                  356.50 usec
SI                   65536
SF              61.4223901 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

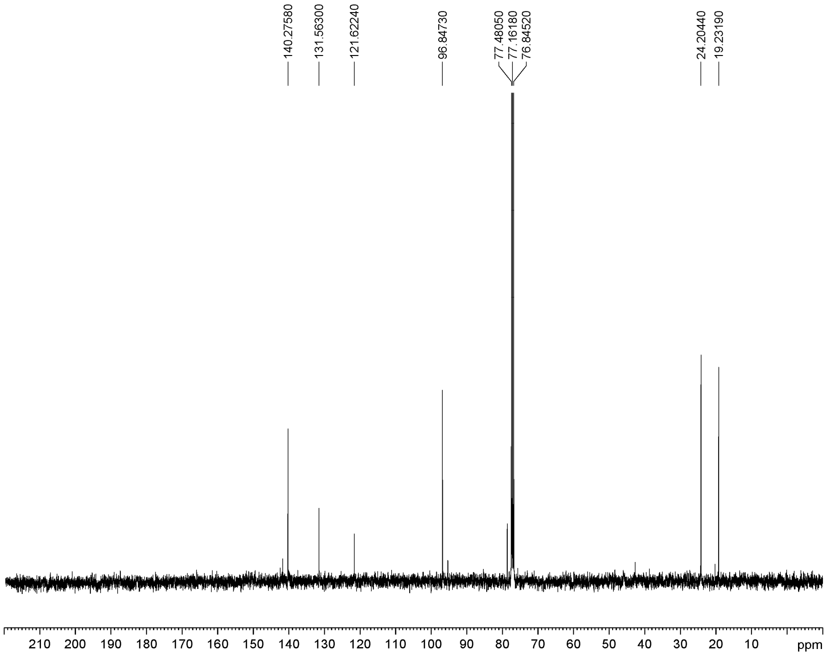


```
NAME     YH1228-solid-in CDCl3
EXPNO                 13
PROCNO                 1
Date_           20181004
Time               15.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   300
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 298.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127613 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of **6j**:

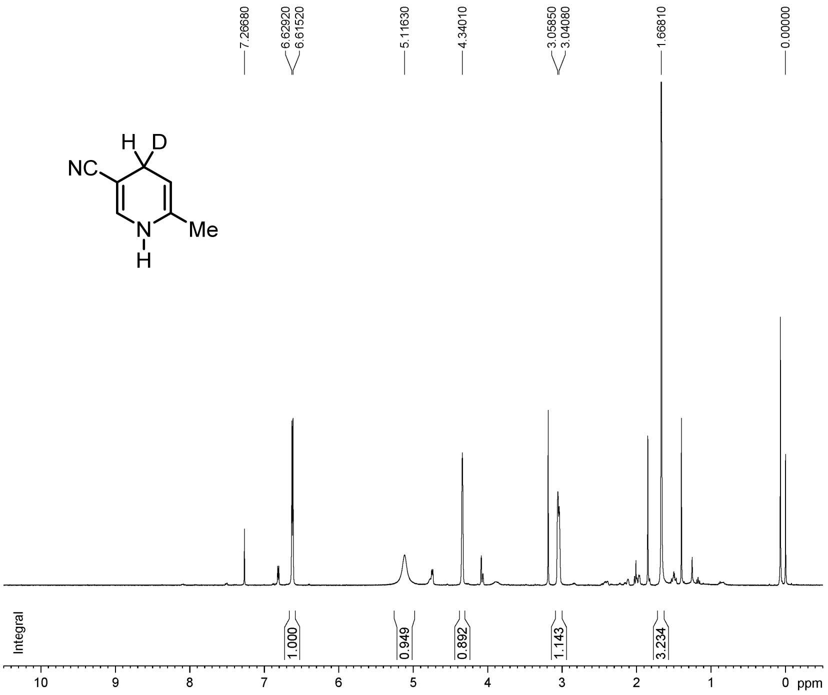


```
NAME       YH1358-A-2-Me-5-CNPy-in CDCl3
EXPNO                    10
PROCNO                    1
Date_              20190423
Time                  16.07
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0894966 sec
RG                   101.33
DW                   62.400 usec
DE                     6.50 usec
TE                    300.3 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                     1H
P1                     9.68 usec
SI                    65536
SF              400.1300059 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

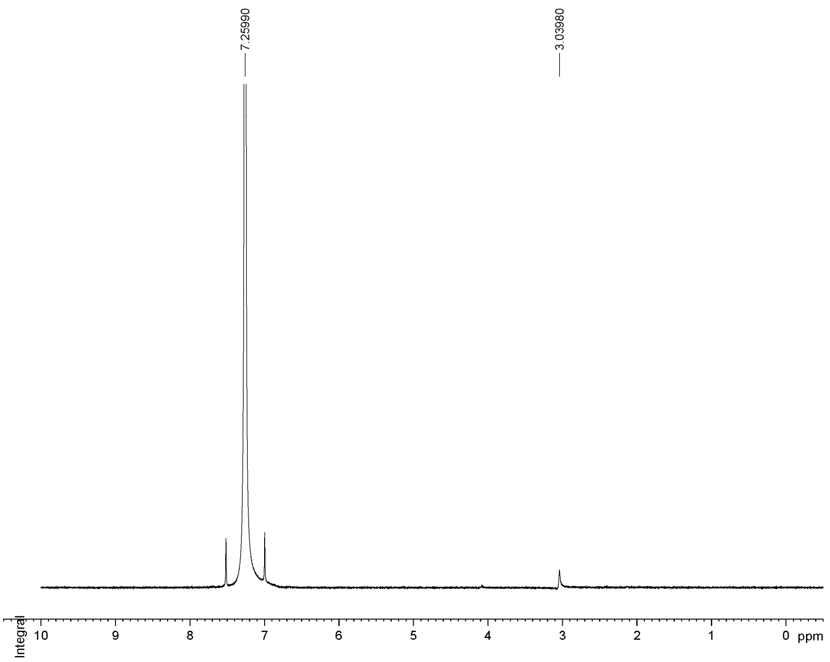


```
NAME       YH1358-A-2-Me-5-CNPy-in CDCl3
EXPNO                    11
PROCNO                    1
Date_              20190423
Time                  17.25
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      210
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                   208.17
DW                   20.800 usec
DE                     6.50 usec
TE                    300.9 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                    13C
P1                     9.95 usec
SI                    32768
SF              100.6127538 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.40
```

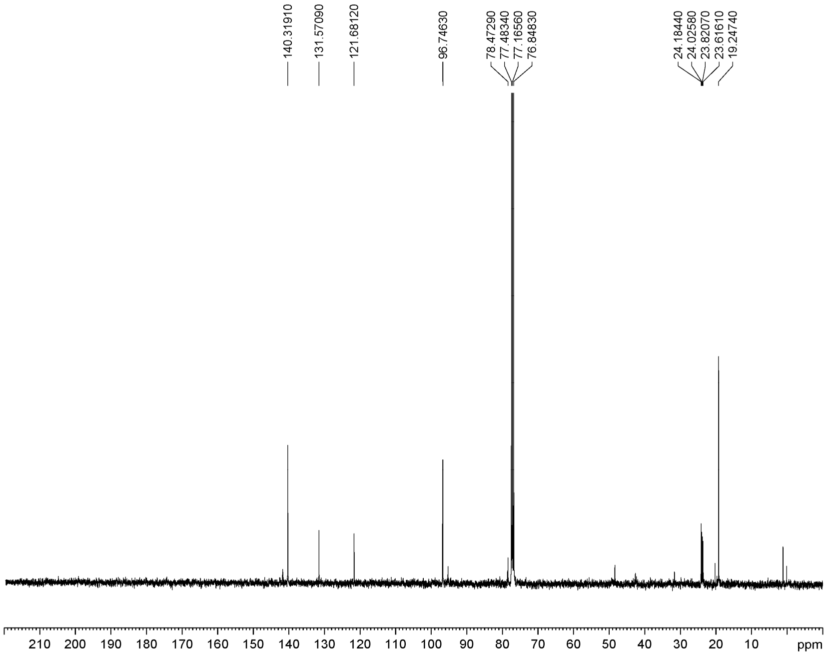
^{1}H, ^{2}H, and ^{13}C NMR of **6j**-*d*:



```
NAME     YH1312-2-Me-5-CNPy-Et2O-phase-in CDCl3
EXPNO                  10
PROCNO                  1
Date_            20181207
Time                15.10
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                 115.32
DW                 62.400 usec
DE                   6.50 usec
TE                  299.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.68 usec
SI                  65536
SF            400.1300069 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

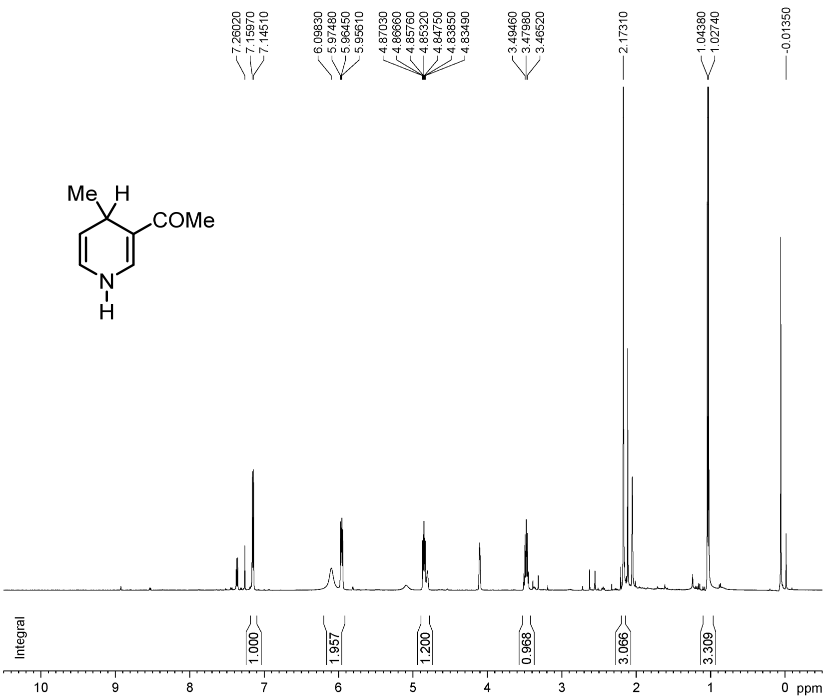


```
NAME     YH1312-2-Me-5-CNPy-Et2O-phase-in CDCl3
EXPNO                  11
PROCNO                  1
Date_            20181207
Time                15.17
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgig2h
TD                  16384
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              1228.501 Hz
FIDRES           0.074982 Hz
AQ              6.6683378 sec
RG                 208.17
DW                407.000 usec
DE                  50.00 usec
TE                  299.7 K
D1             4.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1           61.4223910 MHz
NUC1                   2H
P1                 356.50 usec
SI                  65536
SF             61.4223909 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

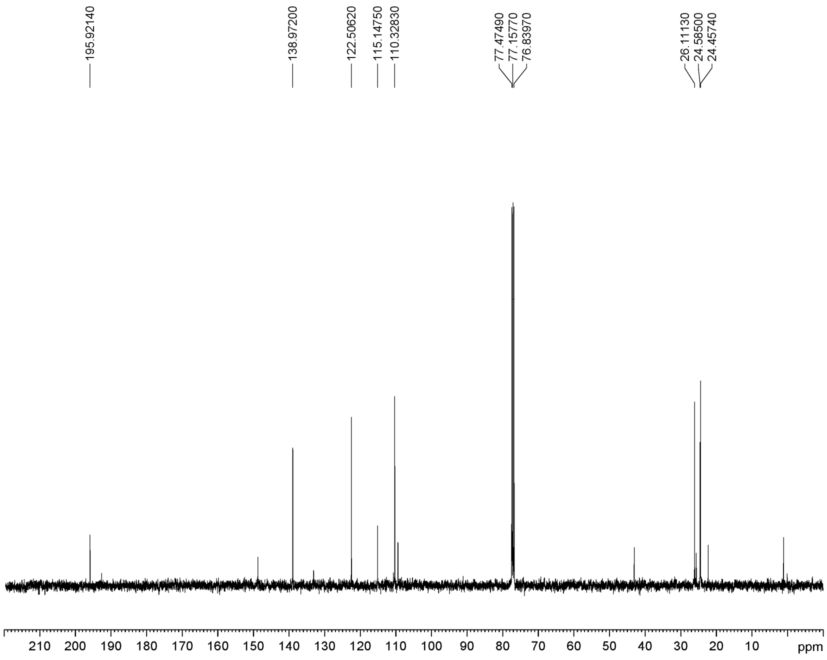


```
NAME     YH1312-2-Me-5-CNPy-Et2O-phase-in CDCl3
EXPNO                 20
PROCNO                 1
Date_           20181209
Time                1.00
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 295.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127553 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of **6k**:

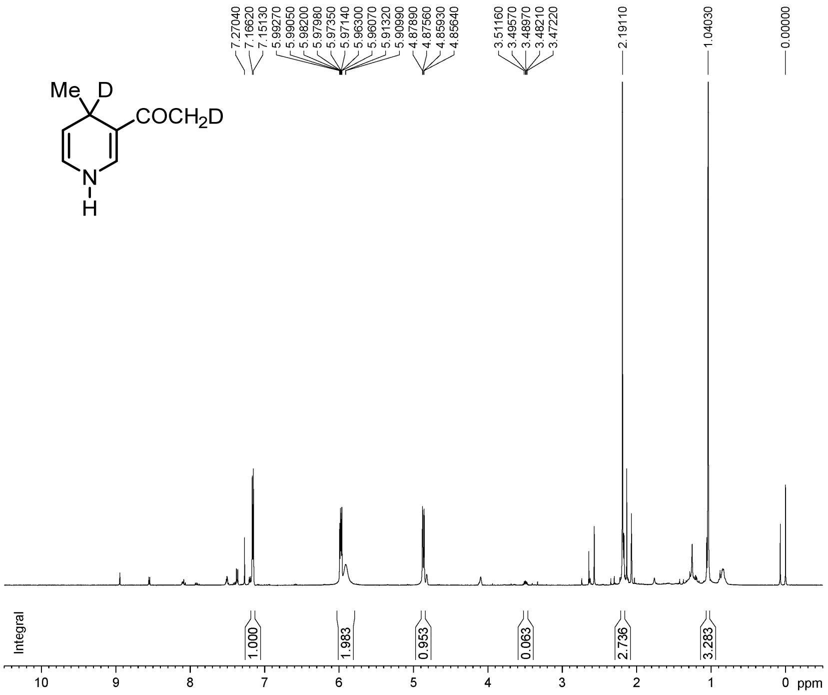


```
NAME      YH1345-3-COMe-4-MePy-Et2O-phase-in CDCl3
EXPNO                  10
PROCNO                  1
Date_            20190112
Time                15.22
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  57.49
DW                 62.400 usec
DE                   6.50 usec
TE                  301.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.68 usec
SI                  65536
SF            400.1300087 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

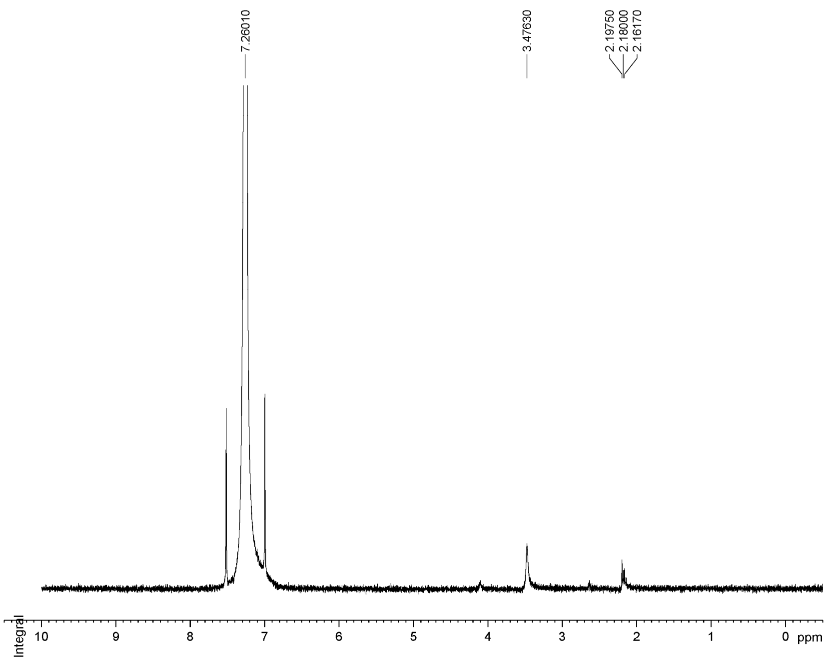


```
NAME      YH1345-3-COMe-4-MePy-Et2O-phase-in CDCl3
EXPNO                  11
PROCNO                  1
Date_            20190112
Time                15.28
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    500
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  301.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127547 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

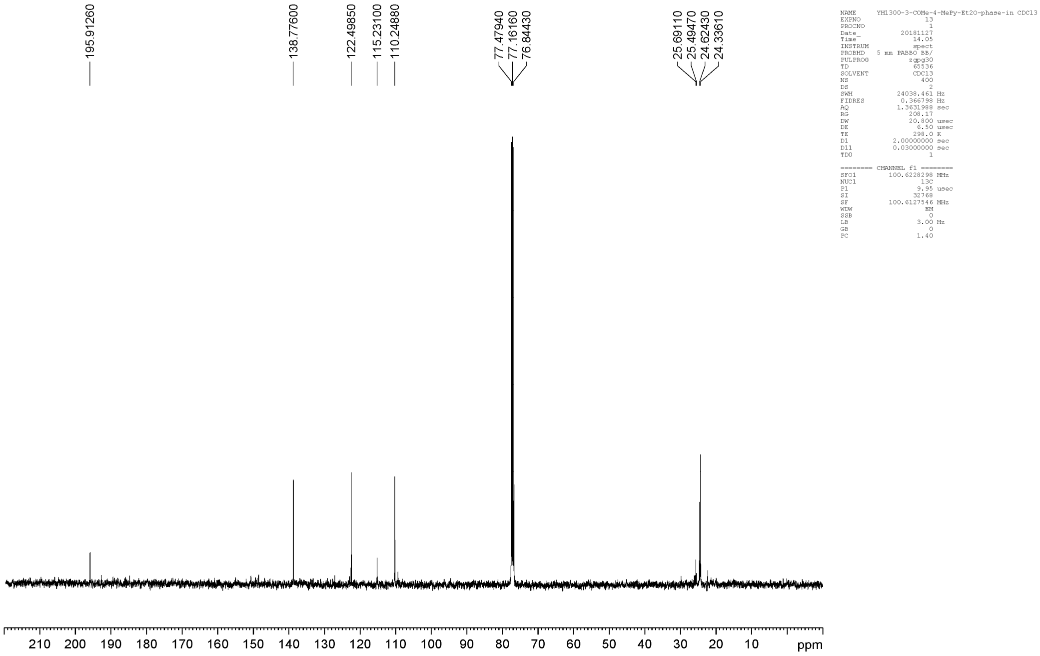
^{1}H, ^{2}H, and ^{13}C NMR of **6k**-*d*:



```
NAME     YH1300-3-COMe-4-MePy-Et2O-phase-in CDCl3
EXPNO                 10
PROCNO                 1
Date_           20181127
Time               13.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 92.23
DW                62.400 usec
DE                  6.50 usec
TE                 297.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300055 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

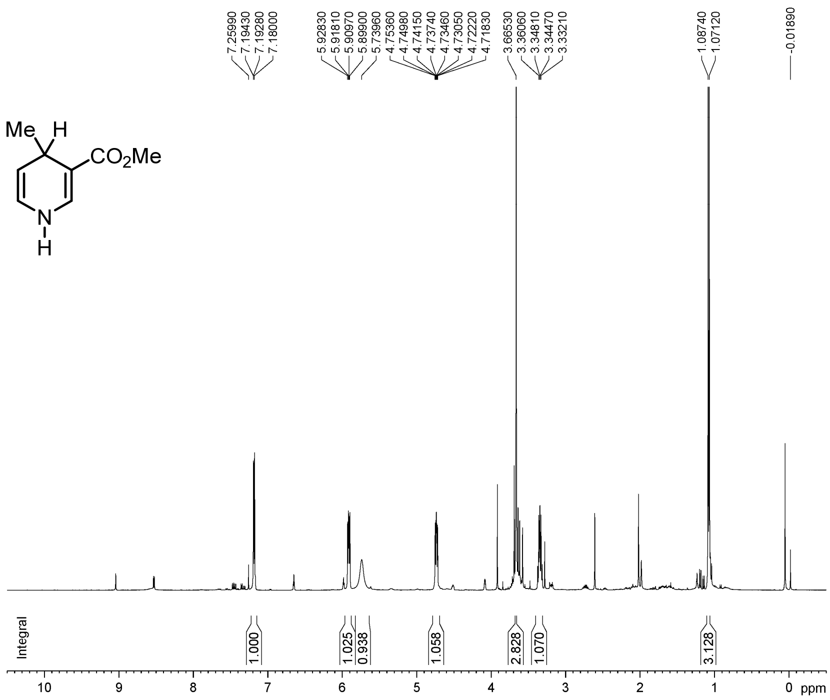


```
NAME     YH1300-3-COMe-4-MePy-Et2O-phase-in CDCl3
EXPNO                 11
PROCNO                 1
Date_           20181127
Time               13.34
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 297.4 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4223912 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

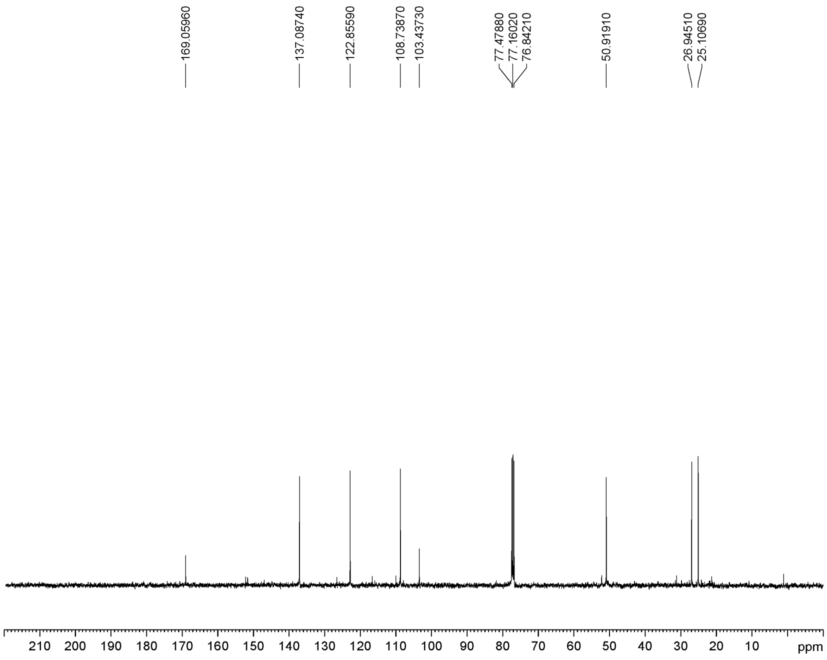


```
NAME     YH1300-3-COMe-4-MePy-Et2O-phase-in CDCl3
EXPNO                13
PROCNO                1
Date_          20181127
Time              14.05
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  400
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               208.17
DW               20.800 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                 9.95 usec
SI                32768
SF          100.6127546 MHz
WDW                  EM
SSB                   0
LB                 3.00 Hz
GB                    0
PC                 1.40
```

^{1}H and ^{13}C NMR of **6l**:

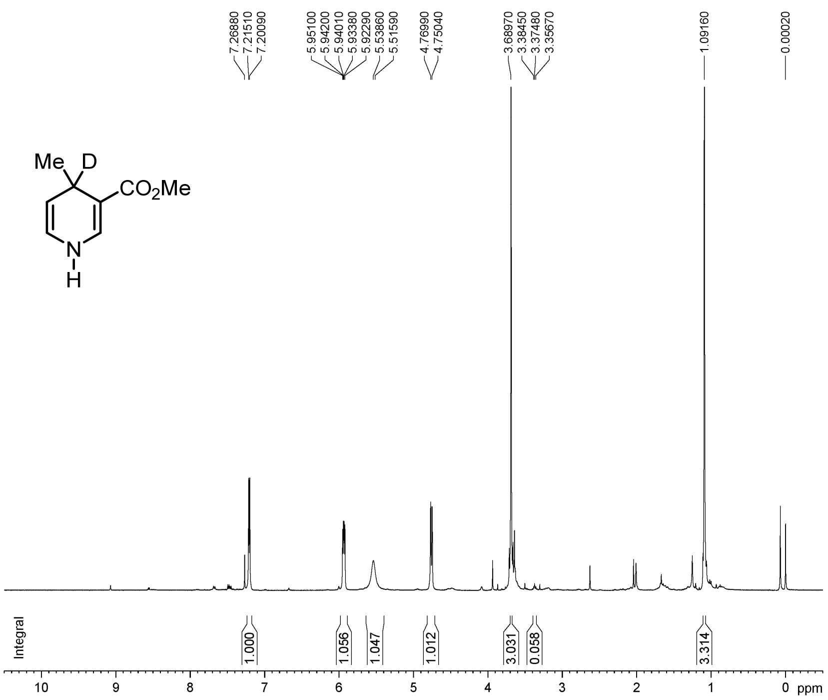


```
NAME     YH1308-3-CO2Me-4MePy-Et2O-phase-in CDCl3
EXPNO                 10
PROCNO                 1
Date_           20181204
Time               17.04
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  31.2
DW                62.400 usec
DE                  6.50 usec
TE                 296.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300095 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

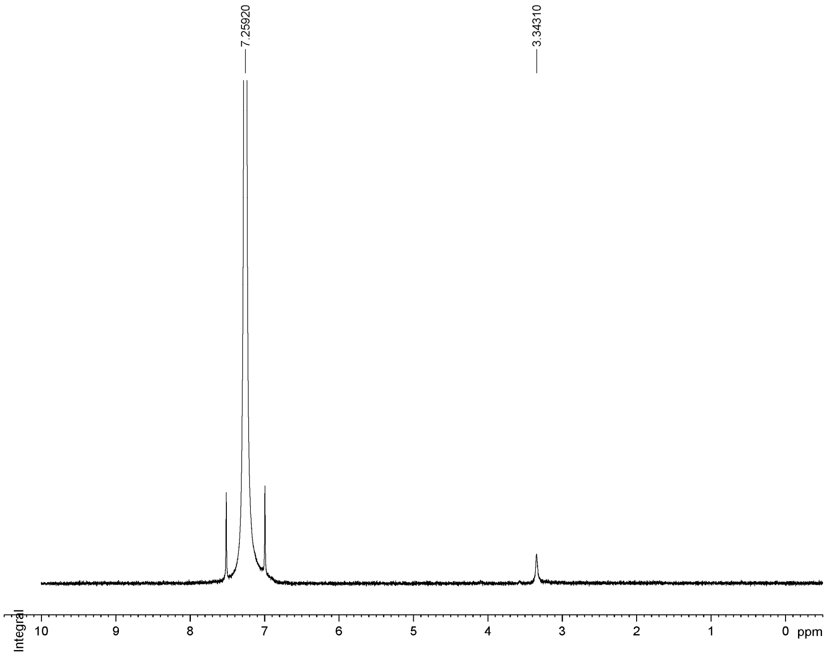


```
NAME     YH1308-3-CO2Me-4MePy-Et2O-phase-in CDCl3
EXPNO                 11
PROCNO                 1
Date_           20181204
Time               17.18
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   120
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 296.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127575 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40
```

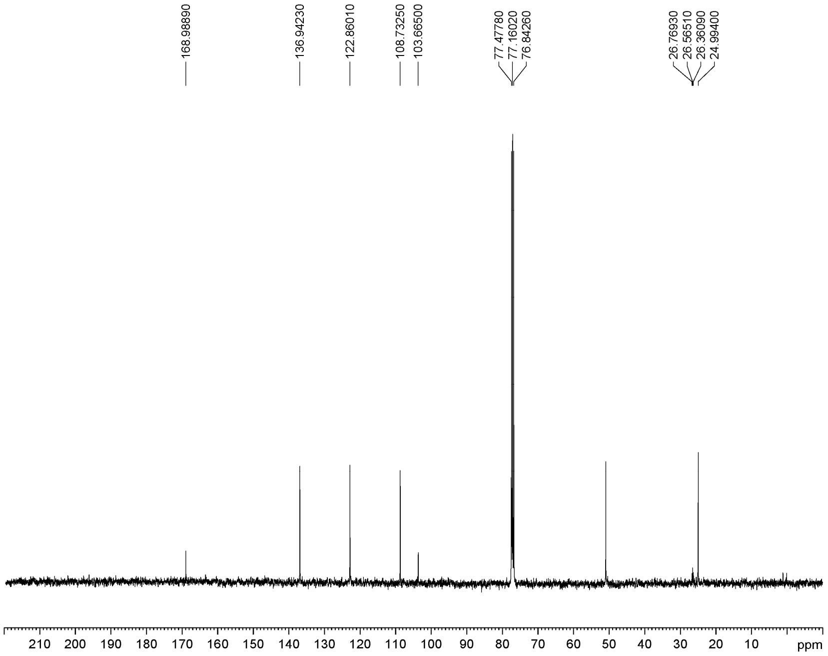
^{1}H, ^{2}H, and ^{13}C NMR of **6l-*d***:



```
NAME      YH1298-3-CO2Me-4-MePy-Et2O-phase-inCDCl3-again
EXPNO                 11
PROCNO                 1
Date_           20181123
Time               10.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 92.23
DW                62.400 usec
DE                  6.50 usec
TE                 295.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300060 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

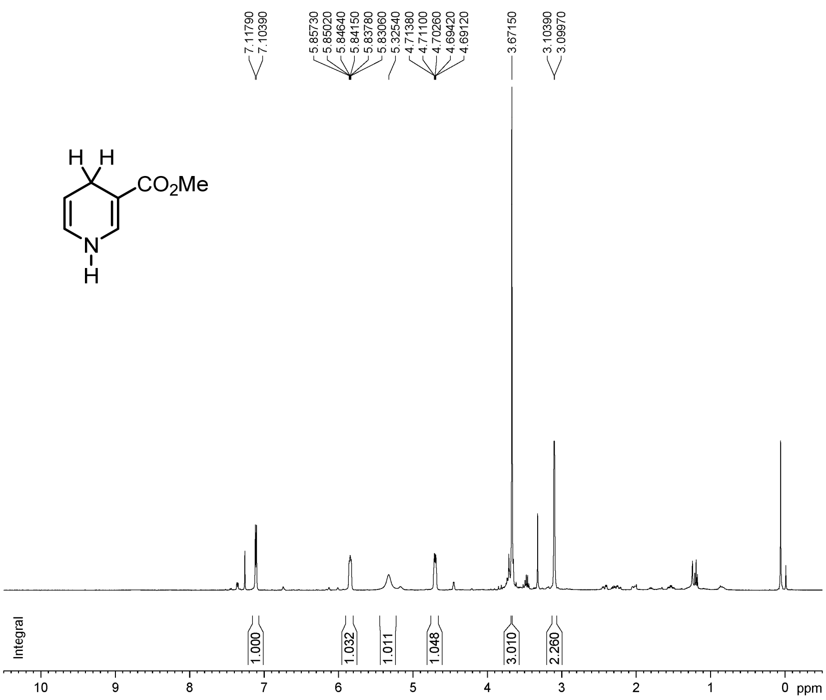


```
NAME      YH1298-3-CO2Me-4-MePy-Et2O-phase-inCDCl3-again
EXPNO                 12
PROCNO                 1
Date_           20181123
Time               10.51
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 296.1 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4223907 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

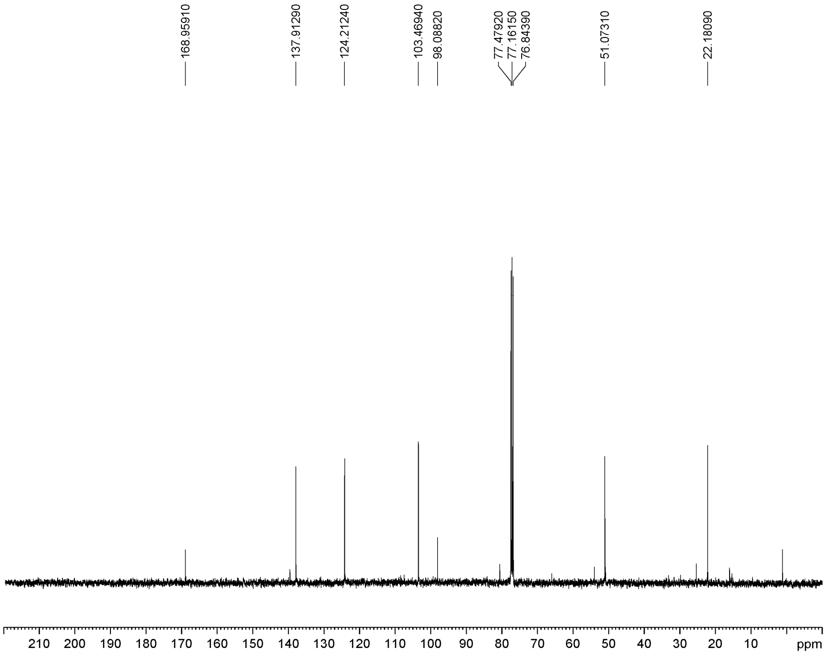


```
NAME      YH1298-3-CO2Me-4-MePy-Et2O-phase-inCDCl3-again
EXPNO                 13
PROCNO                 1
Date_           20181123
Time               19.15
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   400
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 296.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127546 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of 1,4-DHP **6f** from double hydroboration reaction of pyridine **5m**:

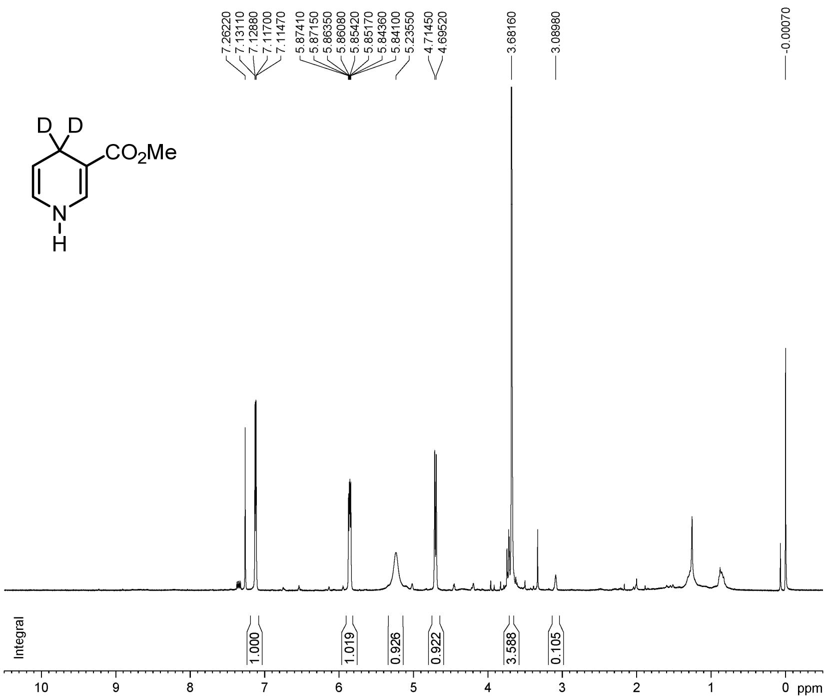


```
NAME     YH1358-B-4-OMe-3-CO2MePy-in CDCl3
EXPNO                   10
PROCNO                   1
Date_             20190423
Time                 16.09
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                   82.47
DW                  62.400 usec
DE                    6.50 usec
TE                   300.3 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                    9.68 usec
SI                   65536
SF             400.1300087 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

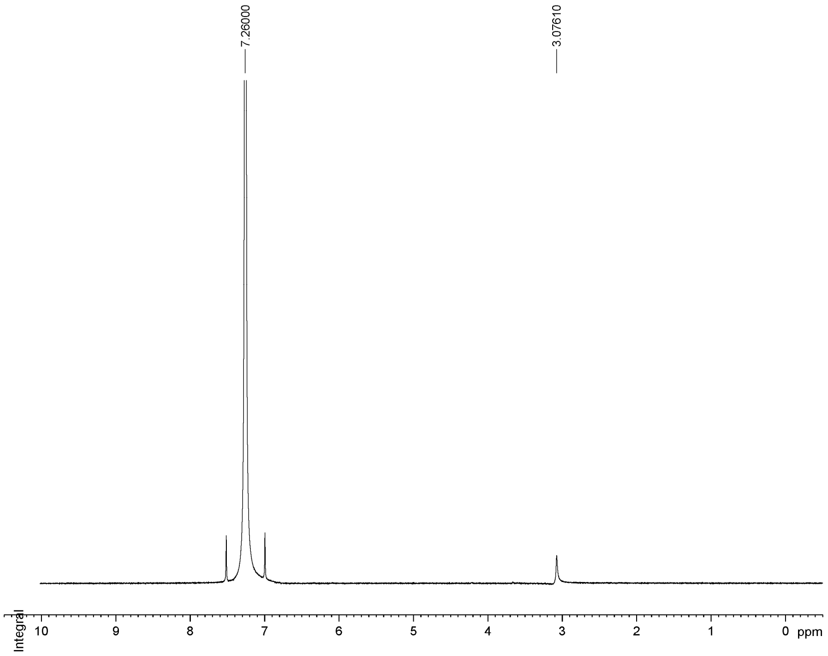


```
NAME     YH1358-B-4-OMe-3-CO2MePy-in CDCl3
EXPNO                   11
PROCNO                   1
Date_             20190423
Time                 17.54
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     300
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   301.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127537 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

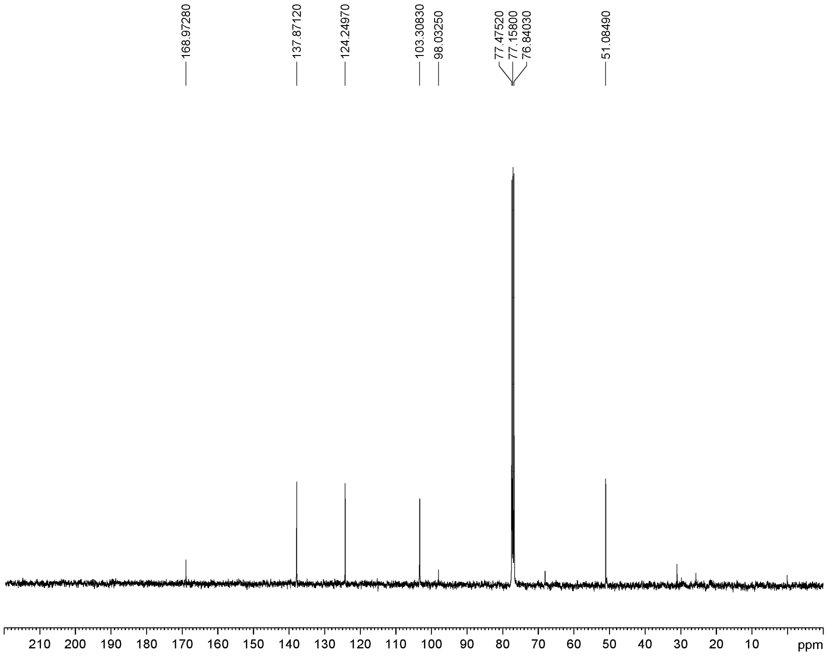
^1H, ^2H, and ^{13}C NMR of **6f**-d_2 from double hydroboration reaction of pyridine **5m**:



```
NAME     YH1336-3-CO2Me-4-MePy-Et2O-phase-in CDCl3
EXPNO                 10
PROCNO                 1
Date_           20190103
Time               12.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                    24
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 92.23
DW                62.400 usec
DE                  6.50 usec
TE                 298.9 K
D1            5.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300080 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



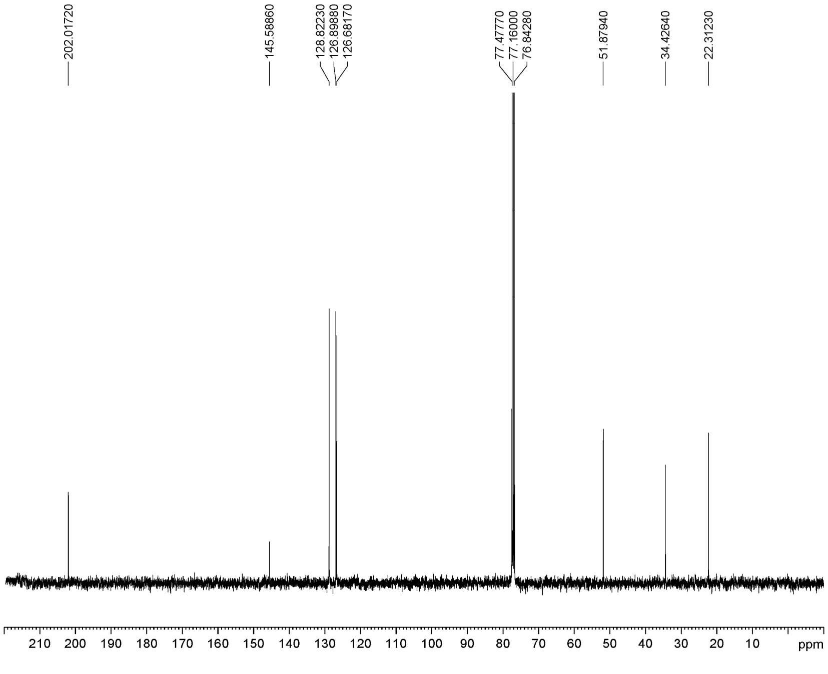
```
NAME     YH1336-3-CO2Me-4-MePy-Et2O-phase-in CDCl3
EXPNO                 12
PROCNO                 1
Date_           20190103
Time               13.18
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig2h
TD                 16384
SOLVENT             None
NS                    64
DS                     2
SWH             1228.501 Hz
FIDRES          0.074982 Hz
AQ             6.6683378 sec
RG                208.17
DW               407.000 usec
DE                 50.00 usec
TE                 297.5 K
D1            4.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          61.4223910 MHz
NUC1                  2H
P1                356.50 usec
SI                 65536
SF            61.4223898 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



```
NAME     YH1336-3-CO2Me-4-MePy-Et2O-phase-in CDCl3
EXPNO               13
PROCNO               1
Date_         20190104
Time              4.10
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                1024
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG              208.17
DW              20.800 usec
DE                6.50 usec
TE               299.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       100.6228293 MHz
NUC1               13C
P1                9.95 usec
SI               32768
SF         100.6127534 MHz
WDW                 EM
SSB                  0
LB                3.00 Hz
GB                   0
PC                1.40
```

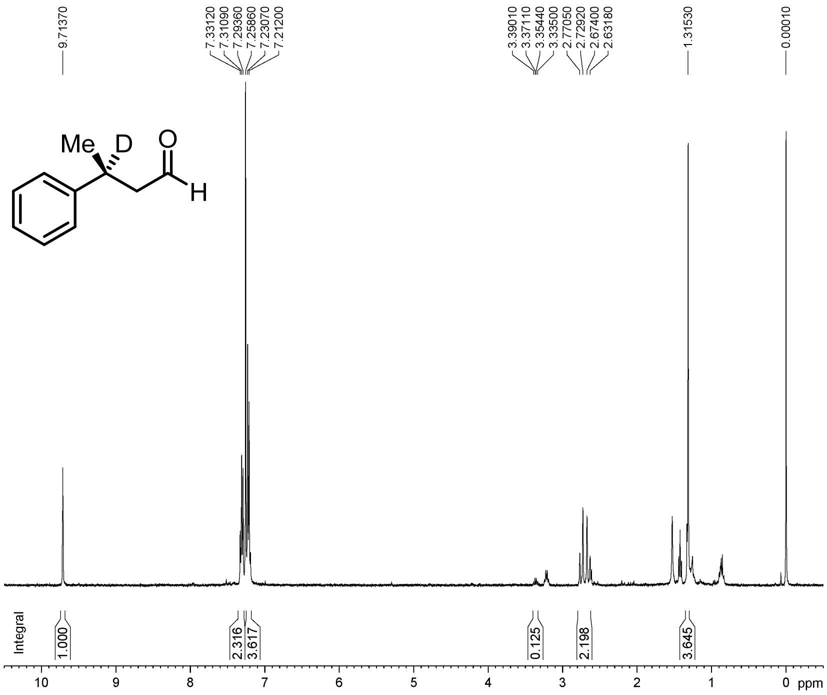
^{1}H and ^{13}C NMR of **9**:

```
NAME       YH1282-1-point
EXPNO                  10
PROCNO                  1
Date_            20181107
Time                11.04
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  92.23
DW                 62.400 usec
DE                   6.50 usec
TE                  294.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.68 usec
SI                  65536
SF            400.1300104 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

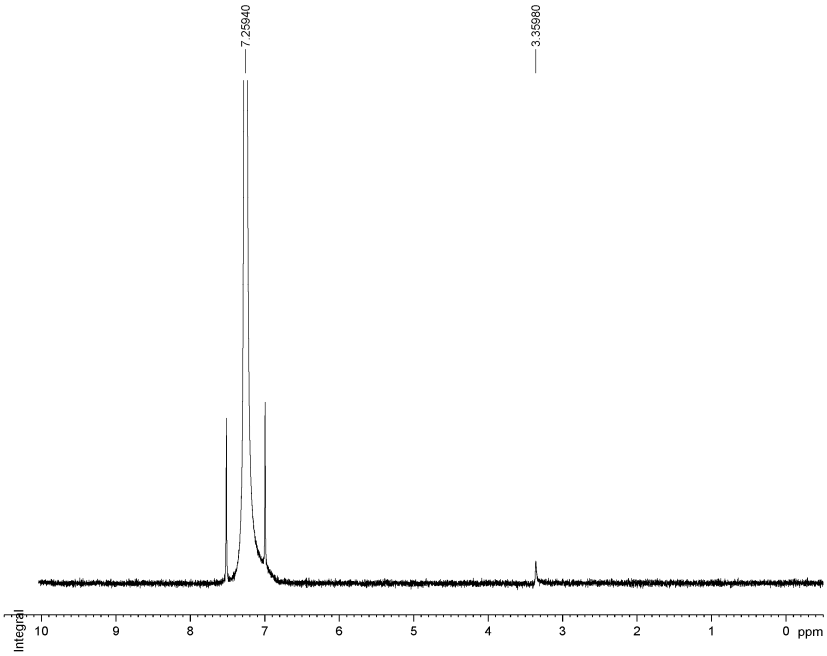


```
NAME       YH1282-1-point
EXPNO                  11
PROCNO                  1
Date_            20181107
Time                11.40
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    200
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  295.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127564 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

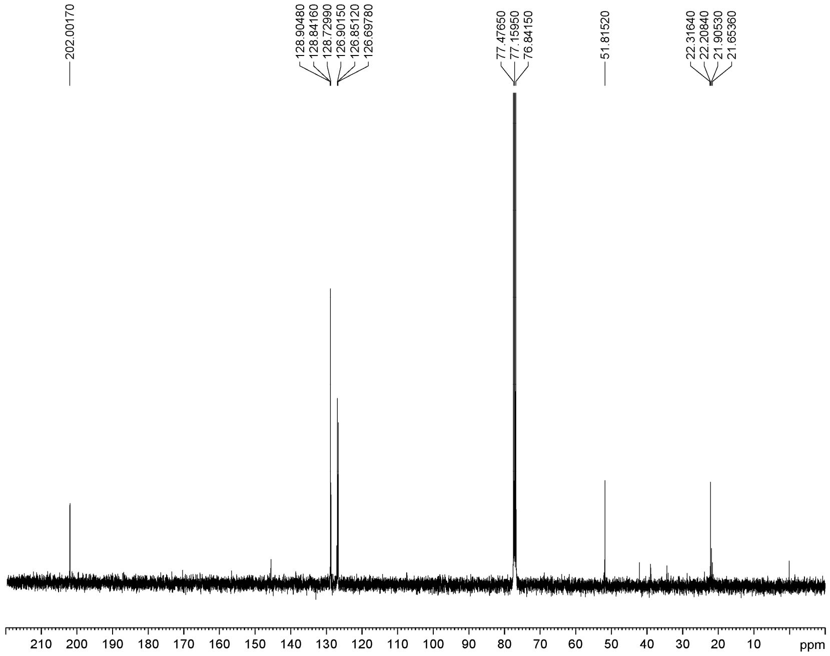
^{1}H, ^{2}H, and ^{13}C NMR of **9**-*d*:



```
NAME      YH1337-1-point-again
EXPNO                   10
PROCNO                   1
Date_             20190108
Time                 15.46
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                  160.46
DW                  62.400 usec
DE                    6.50 usec
TE                   301.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                    9.68 usec
SI                   65536
SF             400.1300094 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
NAME      YH1337-1-point-again
EXPNO                   12
PROCNO                   1
Date_             20190108
Time                 17.00
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zgig2h
TD                   16384
SOLVENT               None
NS                      32
DS                       2
SWH               1228.501 Hz
FIDRES            0.074982 Hz
AQ               6.6683378 sec
RG                  208.17
DW                 407.000 usec
DE                   50.00 usec
TE                   301.3 K
D1              4.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            61.4223910 MHz
NUC1                    2H
P1                  356.50 usec
SI                   65536
SF              61.4223886 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```



```
NAME     YH1337-1-point-again
EXPNO                  20
PROCNO                  1
Date_            20190110
Time                 1.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 299.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127526 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

References

[1] Full citation of Gaussian 09: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; *Gaussian 09, revision B.01*; Gaussian Inc.: Wallingford, CT, 2010.

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