# First organocatalytic asymmetric synthesis of 1-benzamido-1,4-dihydropyridine derivatives

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# Electronic Supplementary Information (ESI)

**Figure S1. $^{1}H$ and $^{13}C$-APT NMR spectra of (E)-dimethyl 2-(2-(4-nitrobenzoyl)hydrazono)succinate (7b)**

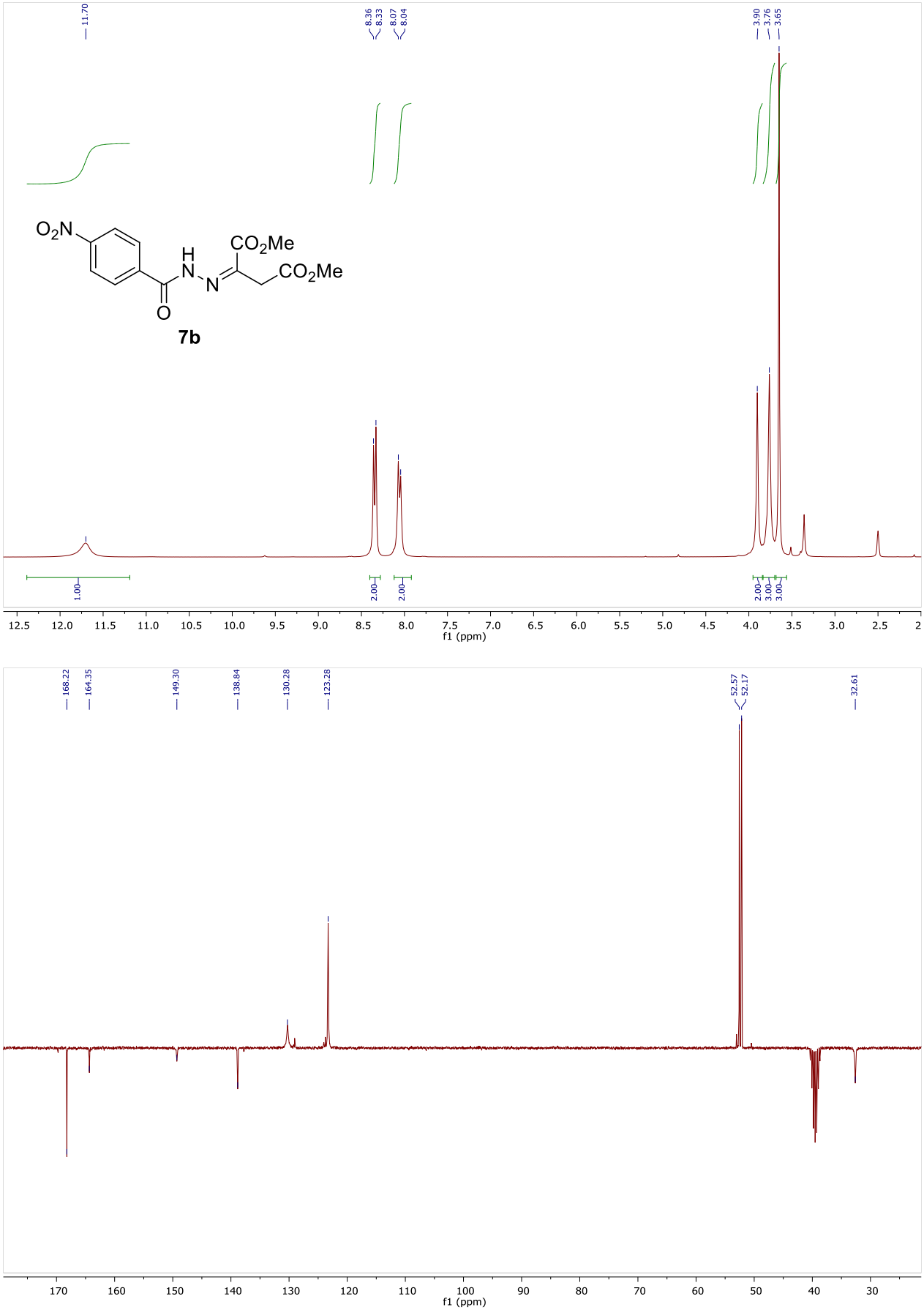
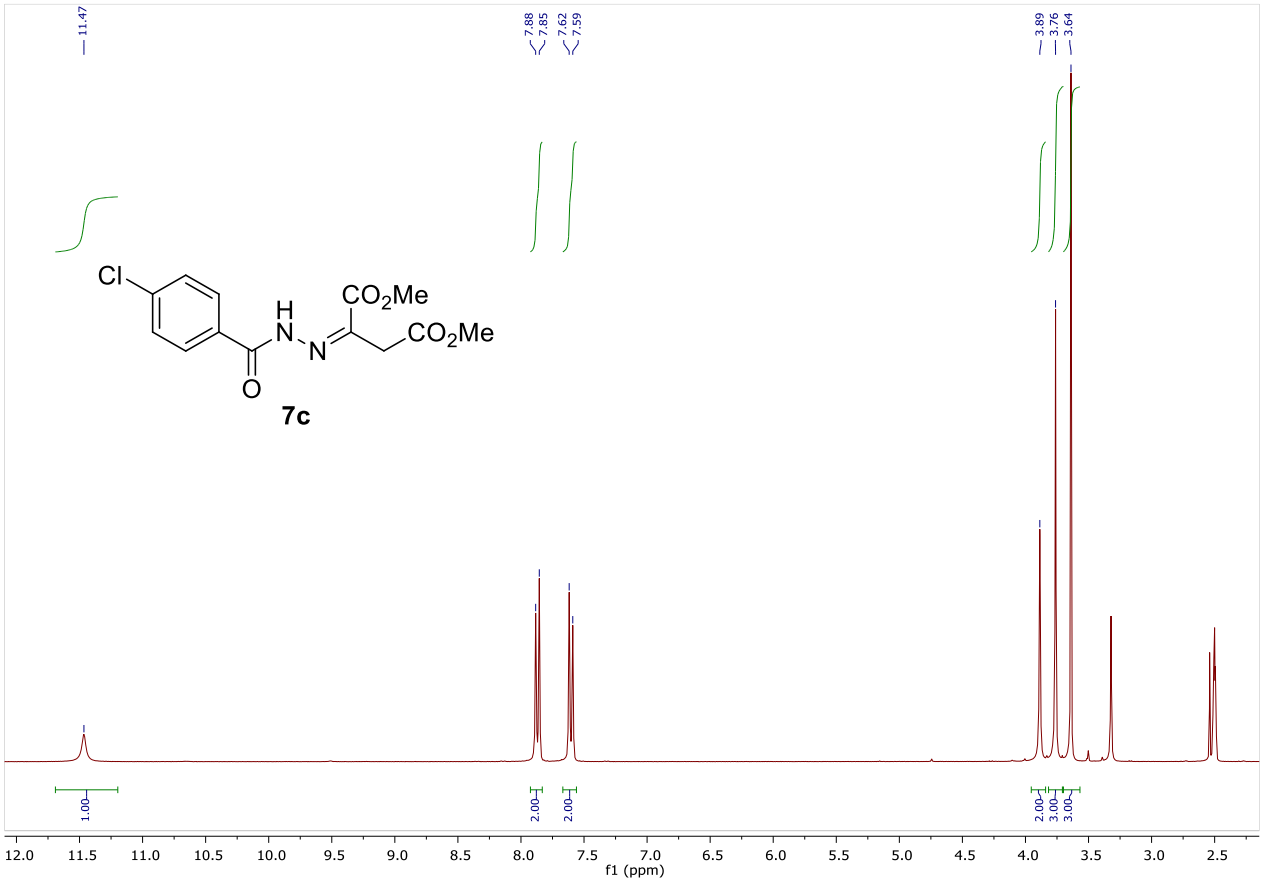


**Figure S2. $^{1}H$ and $^{13}C$-APT NMR spectra of (*E*)-dimethyl 2-(2-(4-chlorobenzoyl)hydrazono)succinate (7c)**



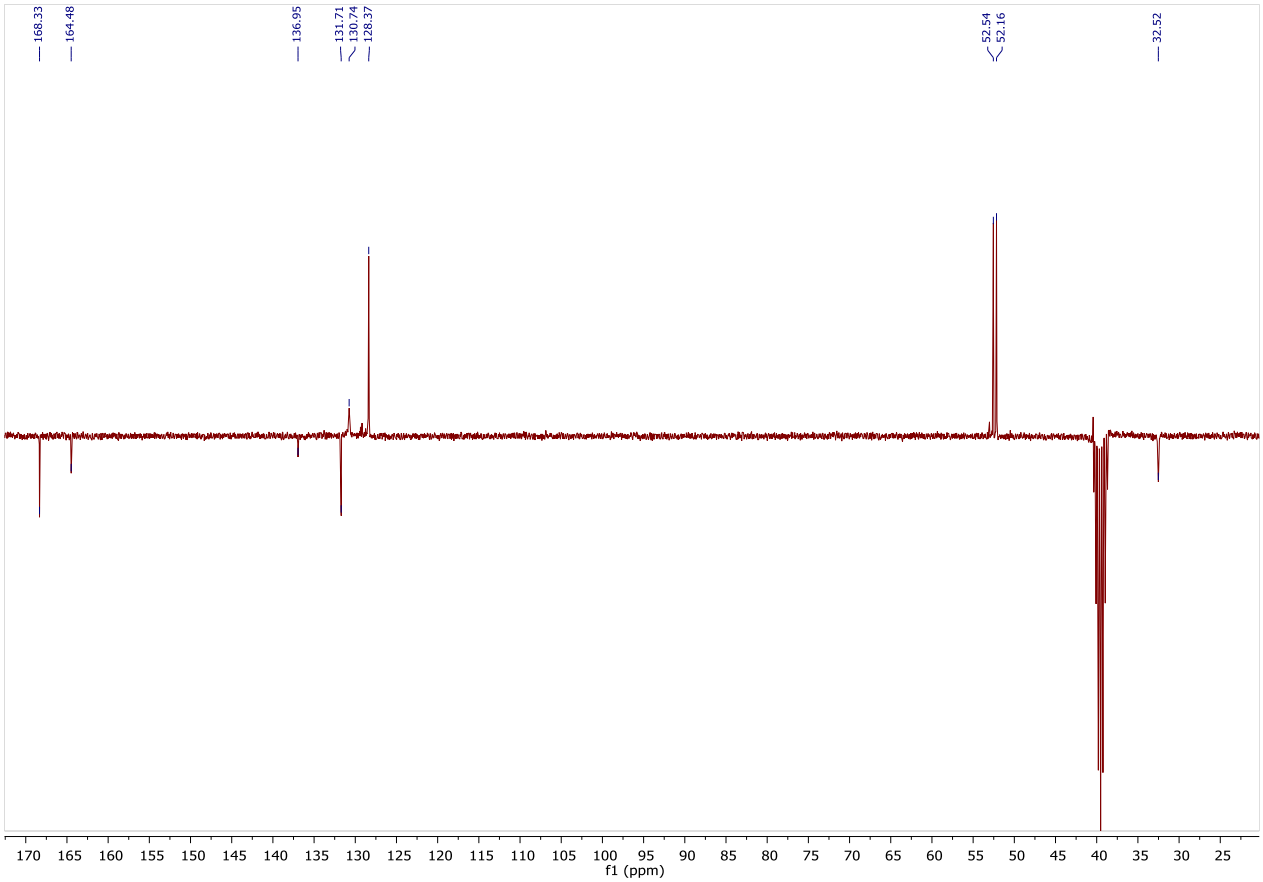



**Figure S3. $^{1}H$ and $^{13}C$-APT NMR spectra of (E)-dimethyl 2-(2-(4-bromobenzoyl)hydrazono)succinate (7d)**

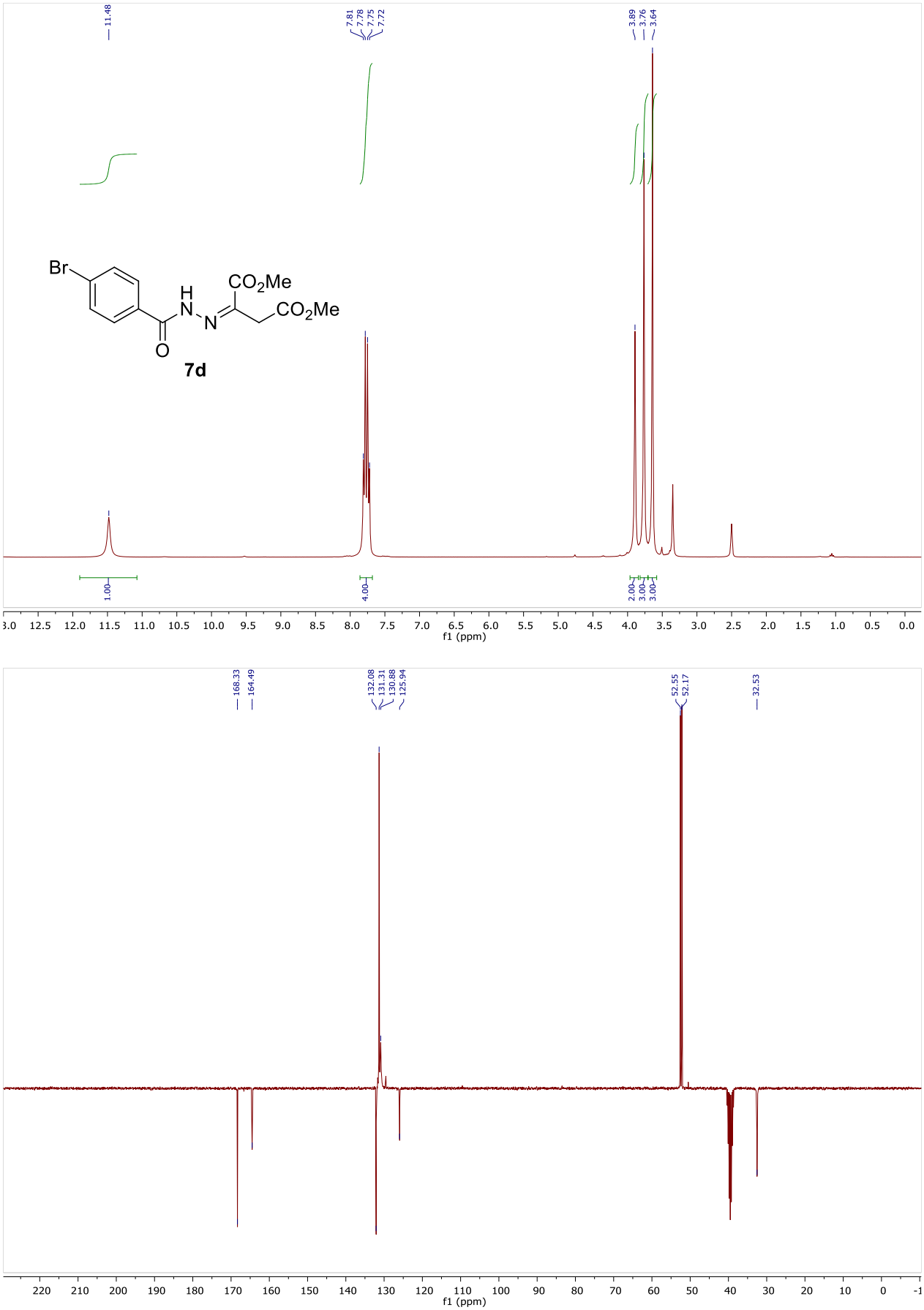
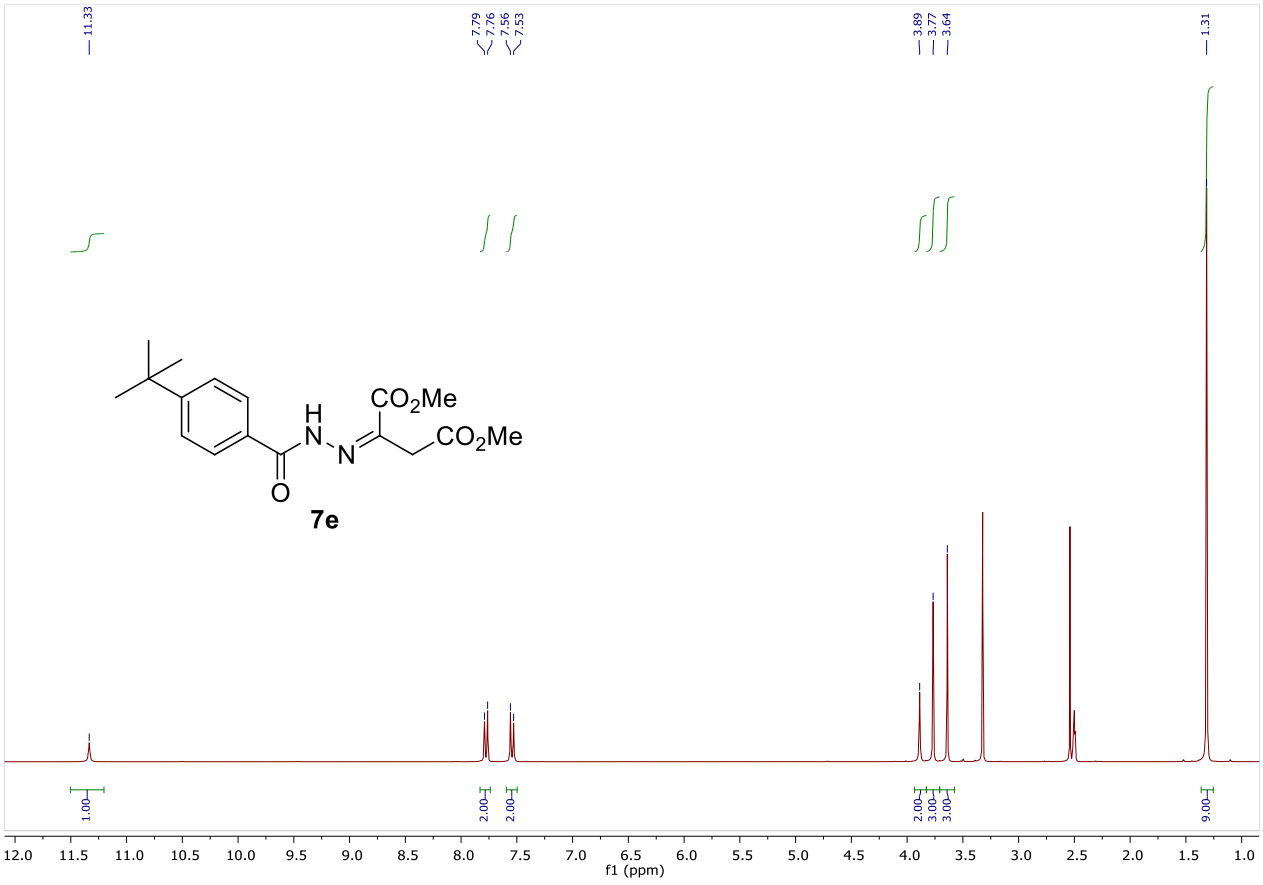


**Figure S4. $^{1}H$ and $^{13}C$-APT NMR spectra of (E)-dimethyl 2-(2-(4-tert-butylbenzoyl)hydrazono)succinate (7e)**



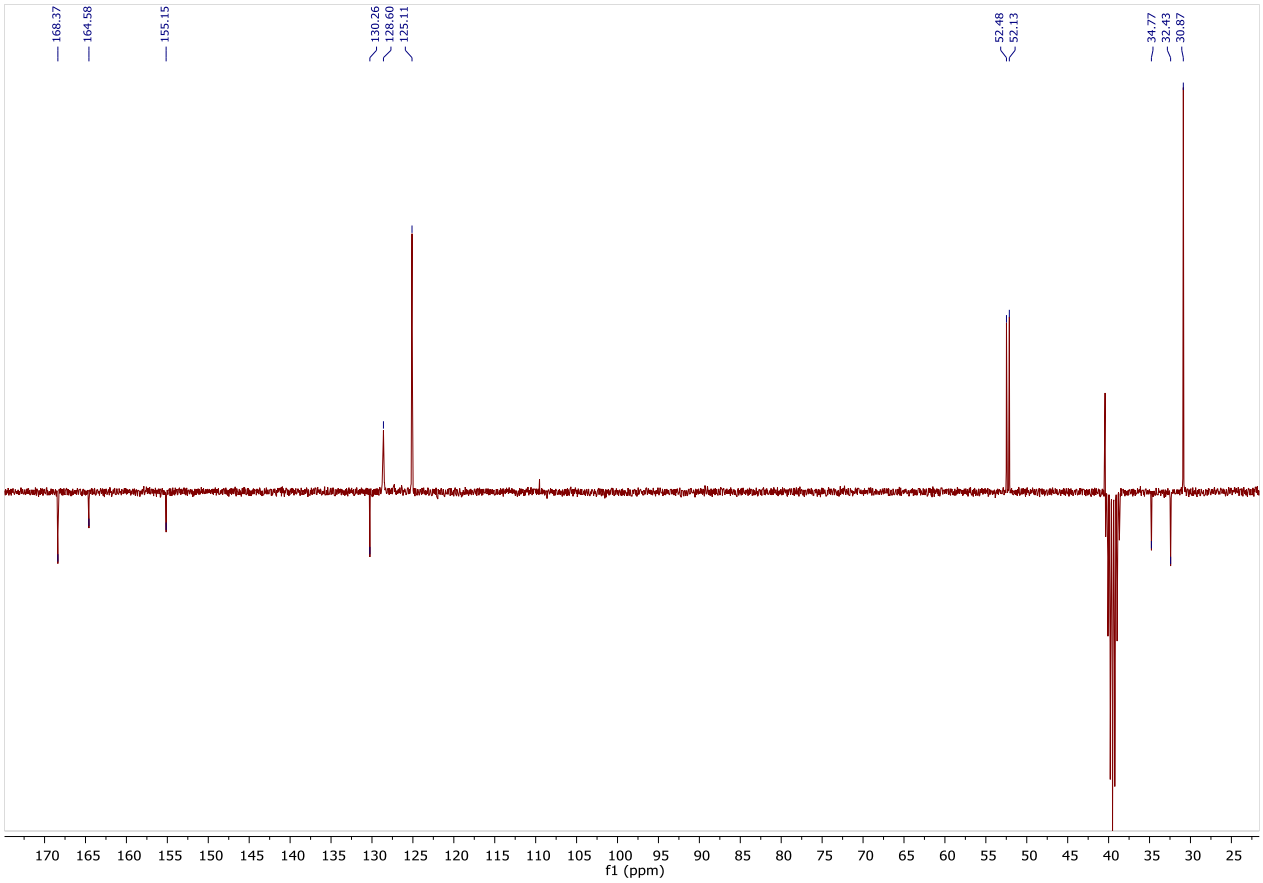



**Figure S5. $^{1}H$ and $^{13}C$-APT NMR spectra of (E)-dimethyl 2-(2-(4-methoxybenzoyl)hydrazono)succinate (7f)**

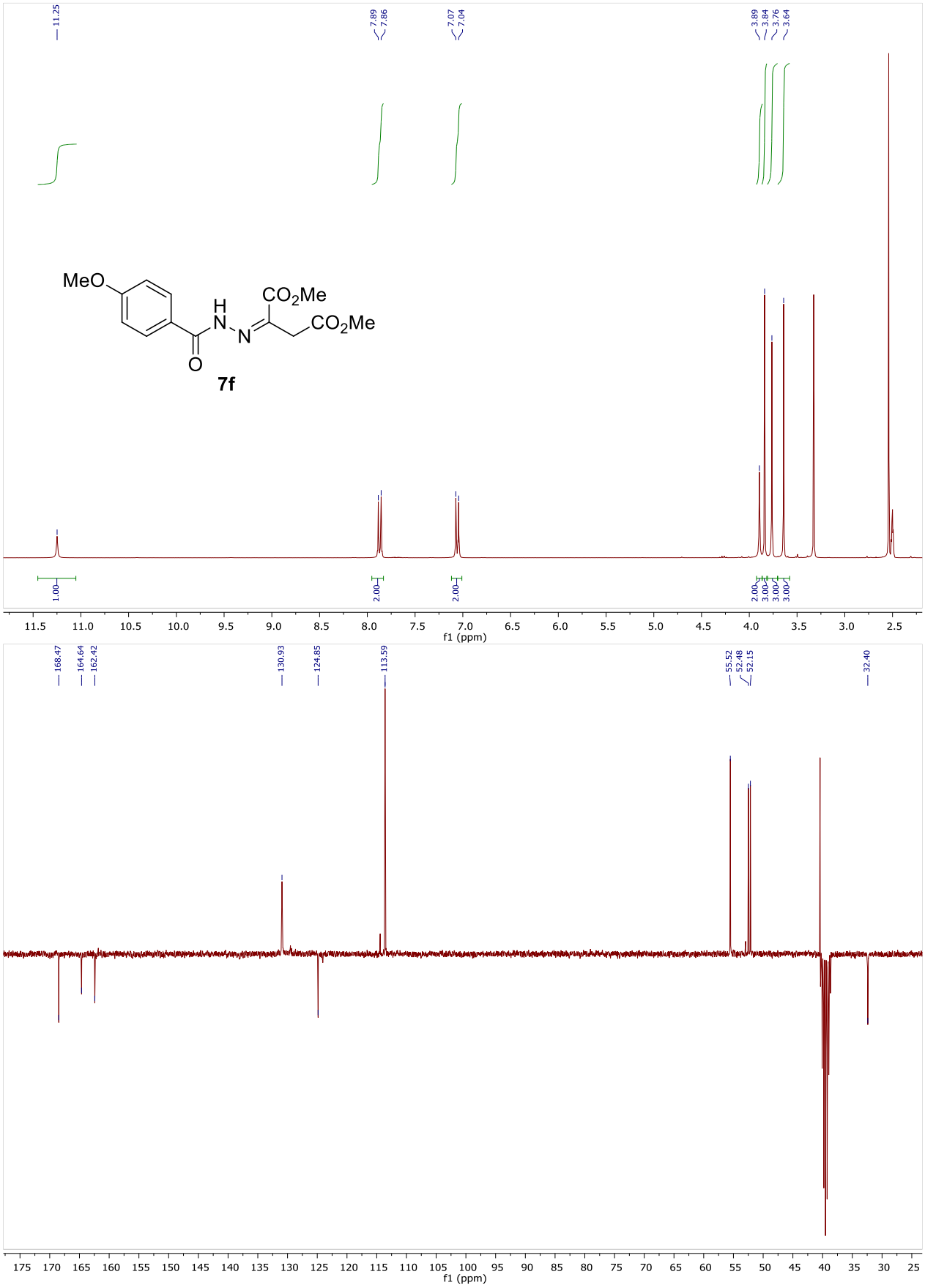


**Figure S6. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10aa)**

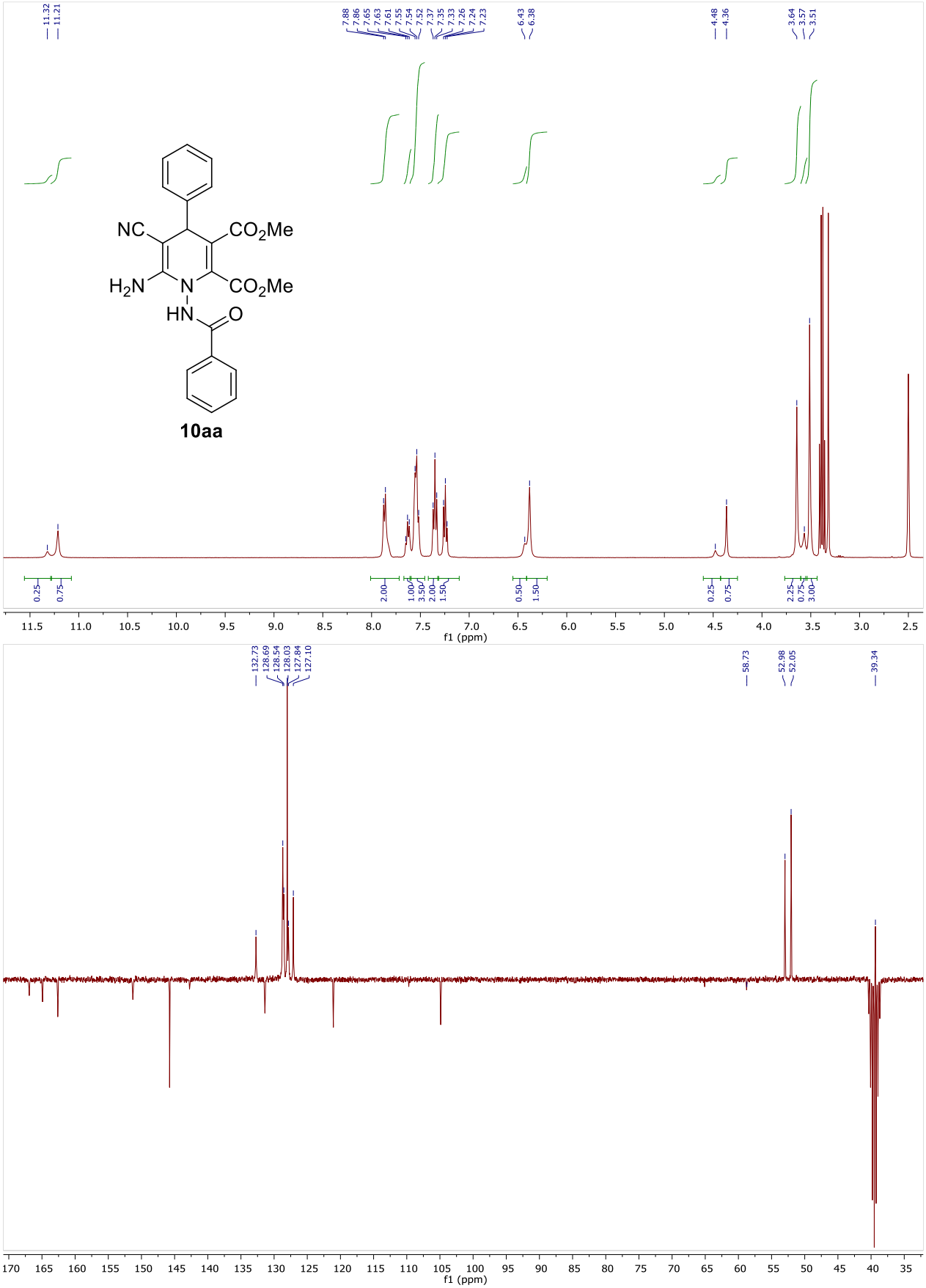


**Figure S7. $^{1}$H and $^{13}$C-APT NMR spectra of dimethyl 6-amino-5-cyano-1-(4-nitrobenzamido)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ba)**

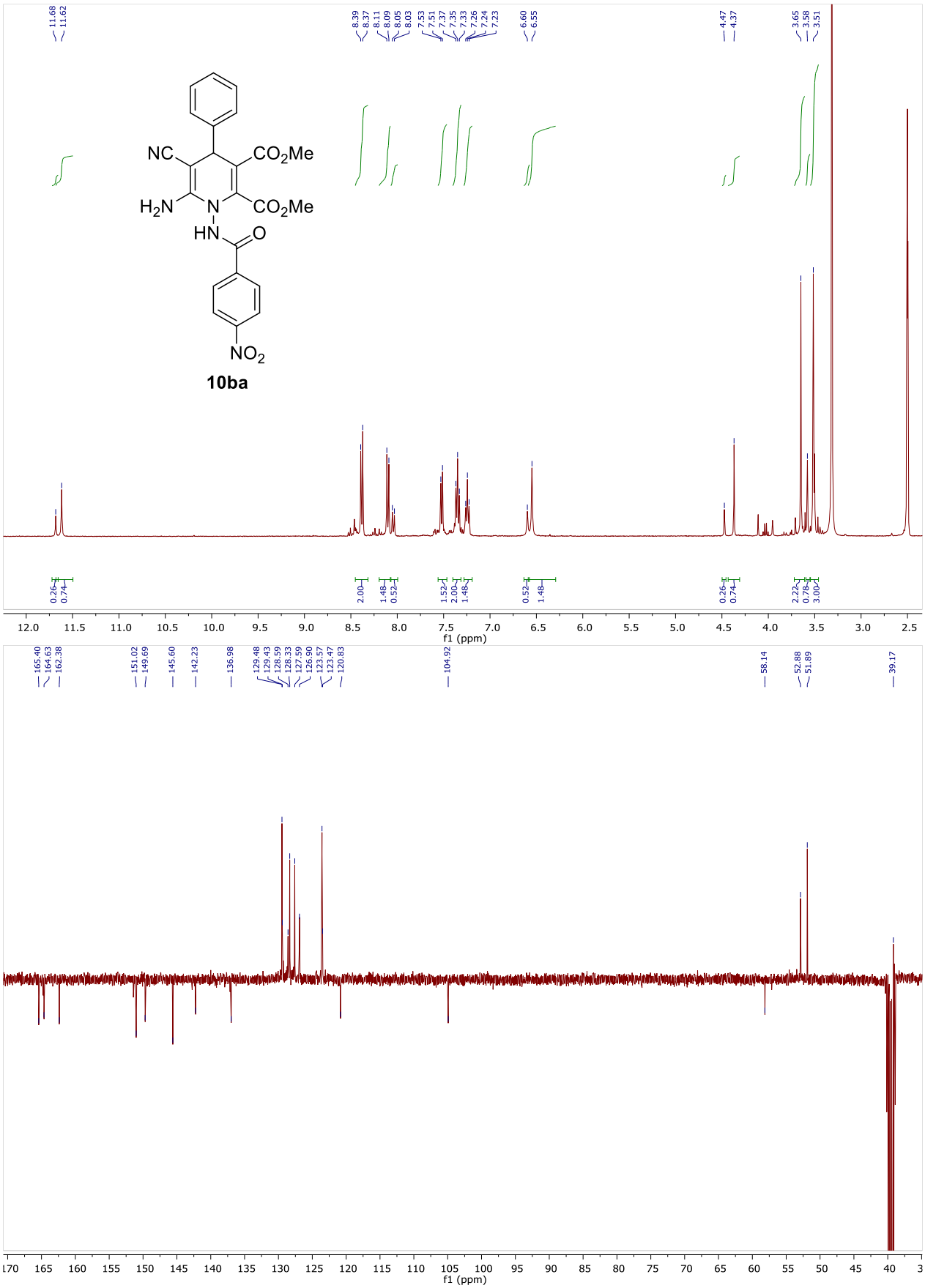


**Figure S8. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-(4-chlorobenzamido)-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ca)**

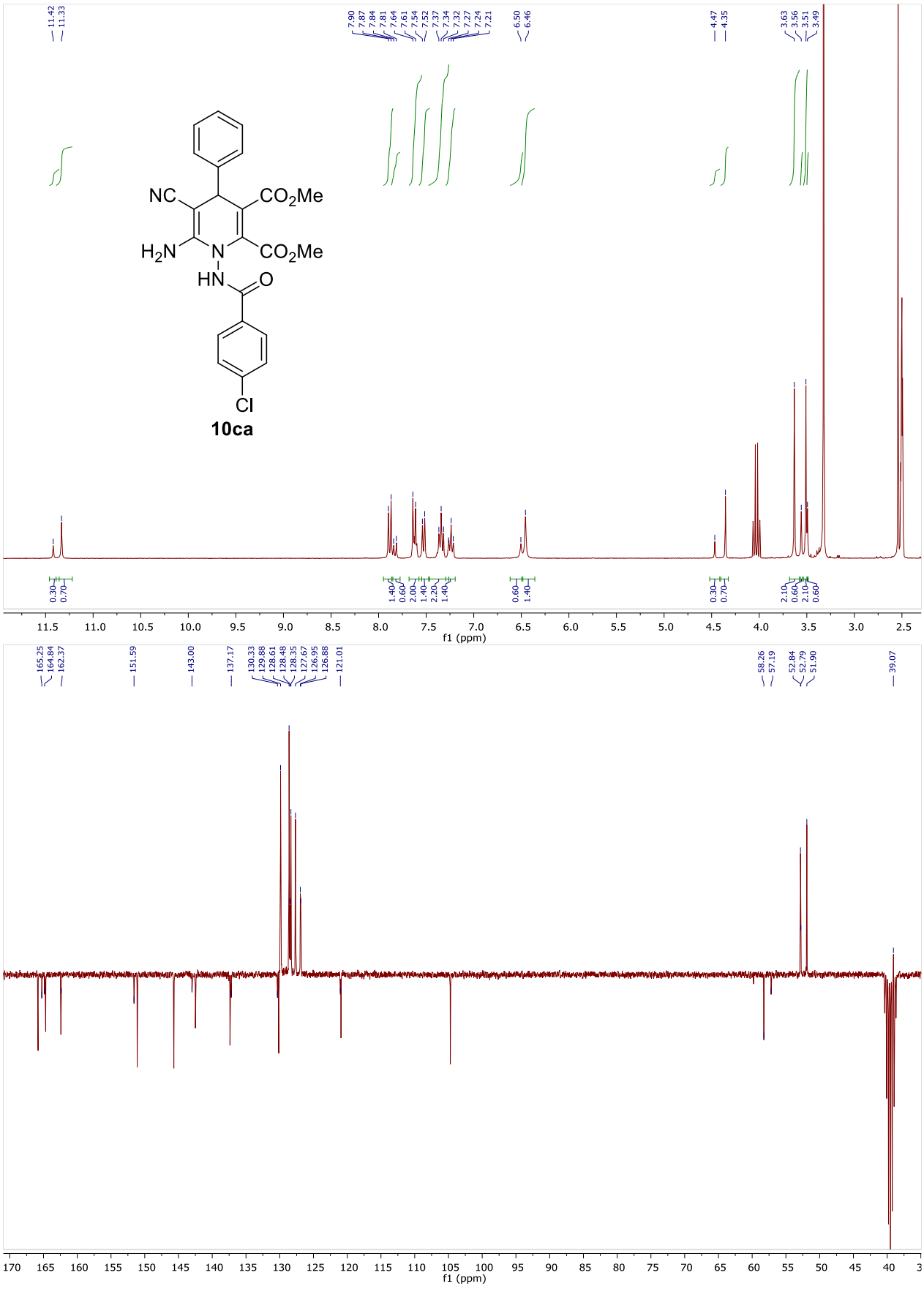


**Figure S9. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-(4-bromobenzamido)-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10da)**

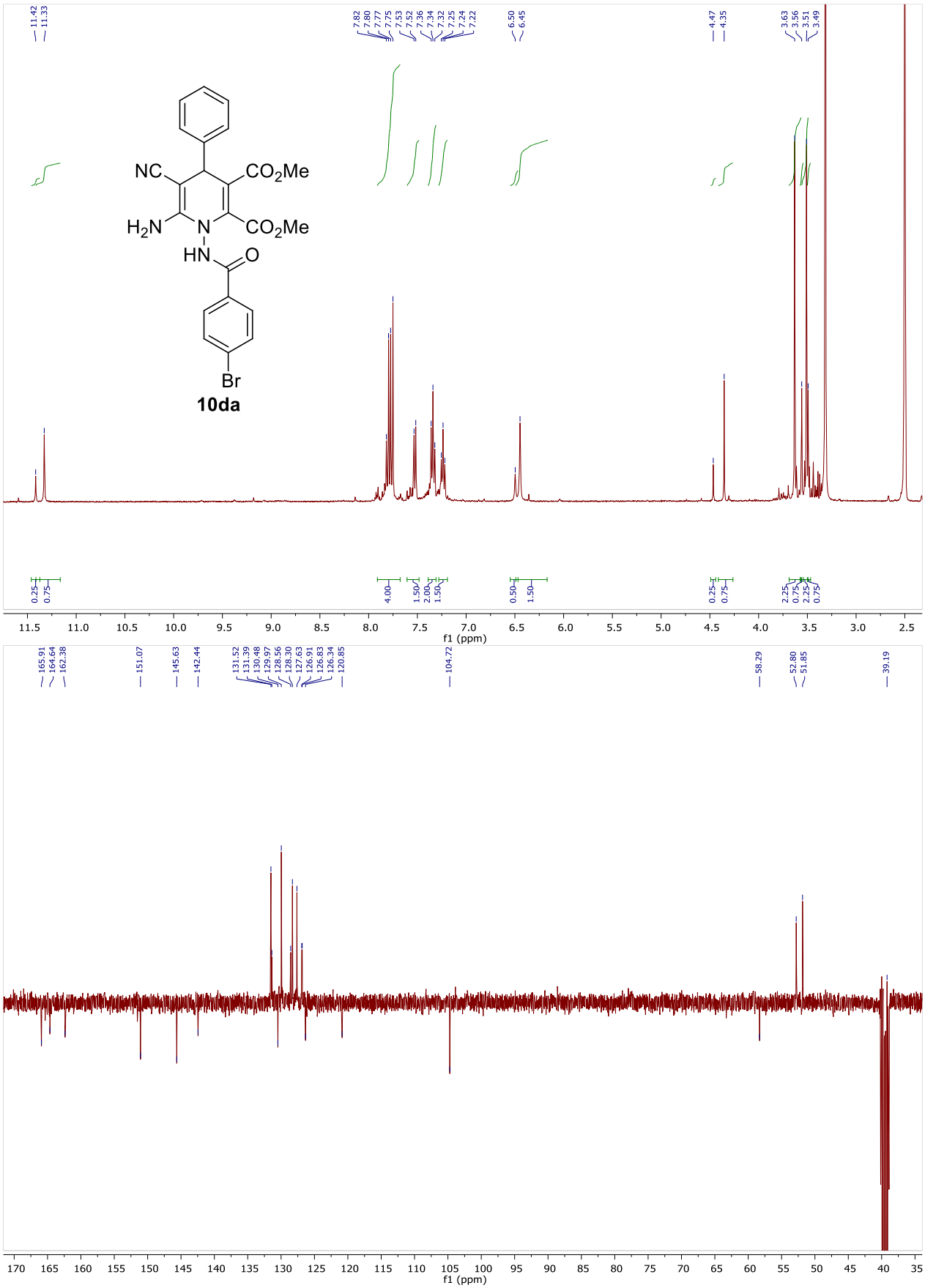


**Figure S10. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-(4-(tert-butyl)benzamido)-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ea)**

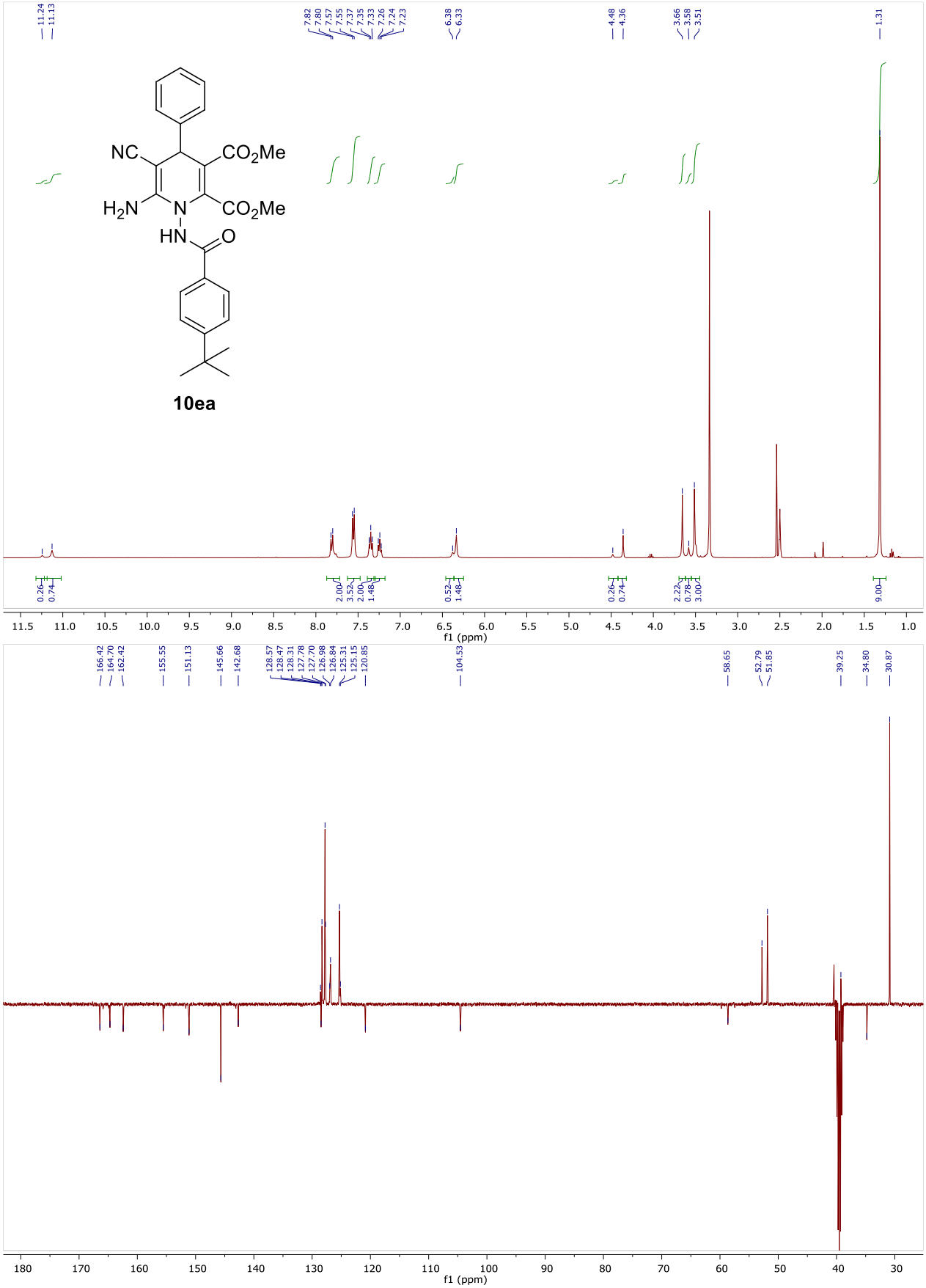


**Figure S11. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-5-cyano-1-(4-methoxybenzamido)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10fa)**

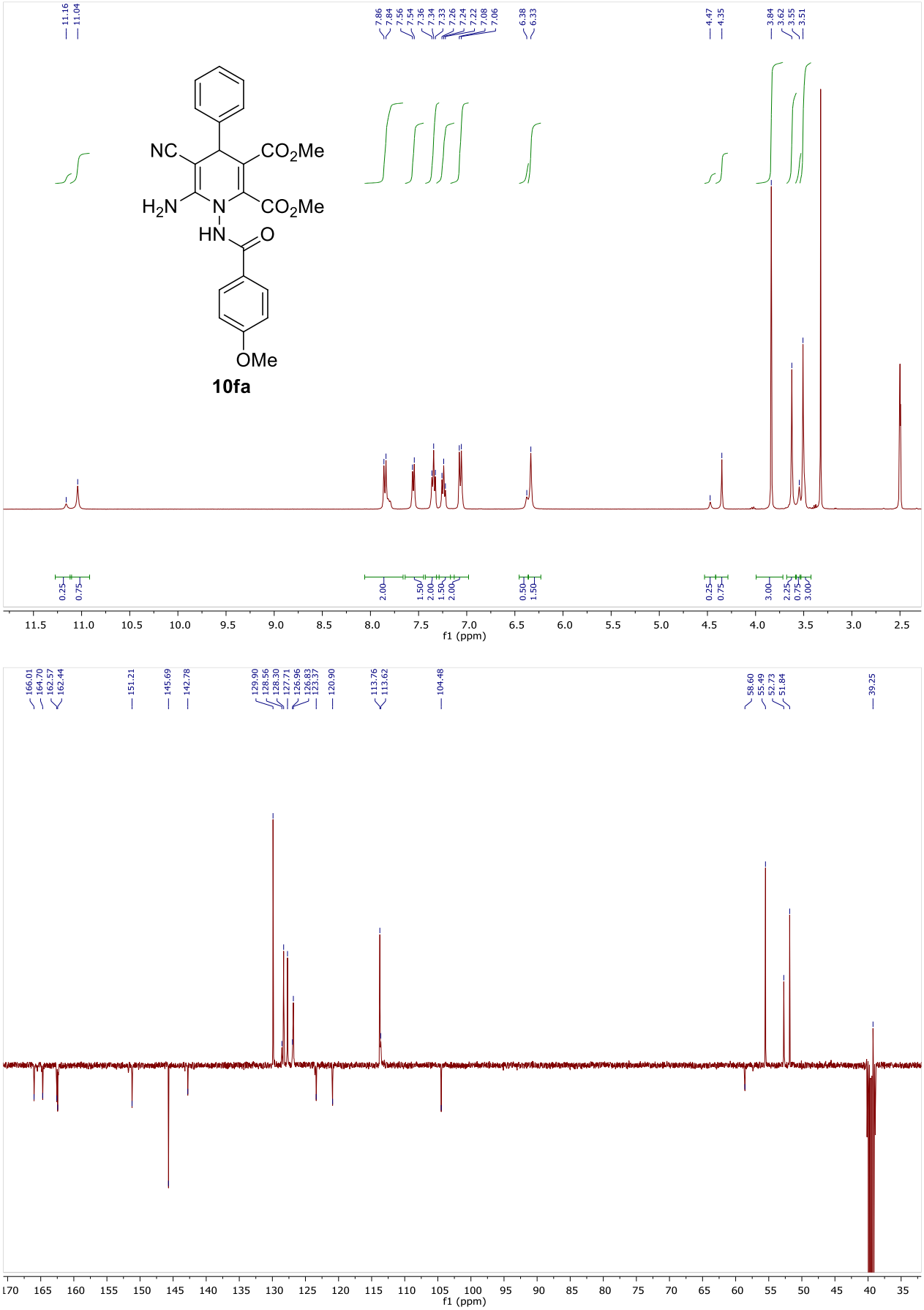


**Figure S12. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10ab)**

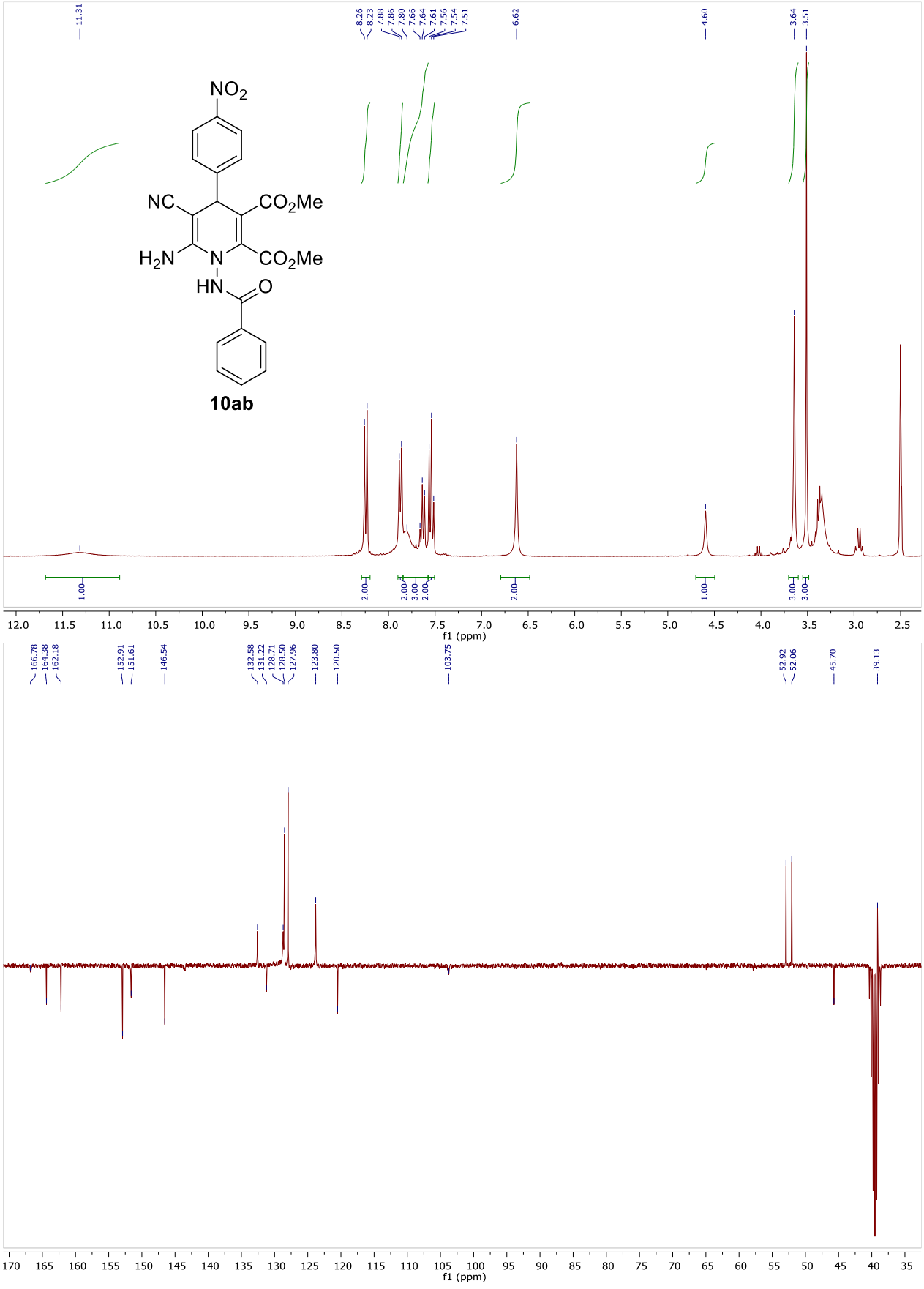


**Figure S13. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-4-(3-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (10ad)**

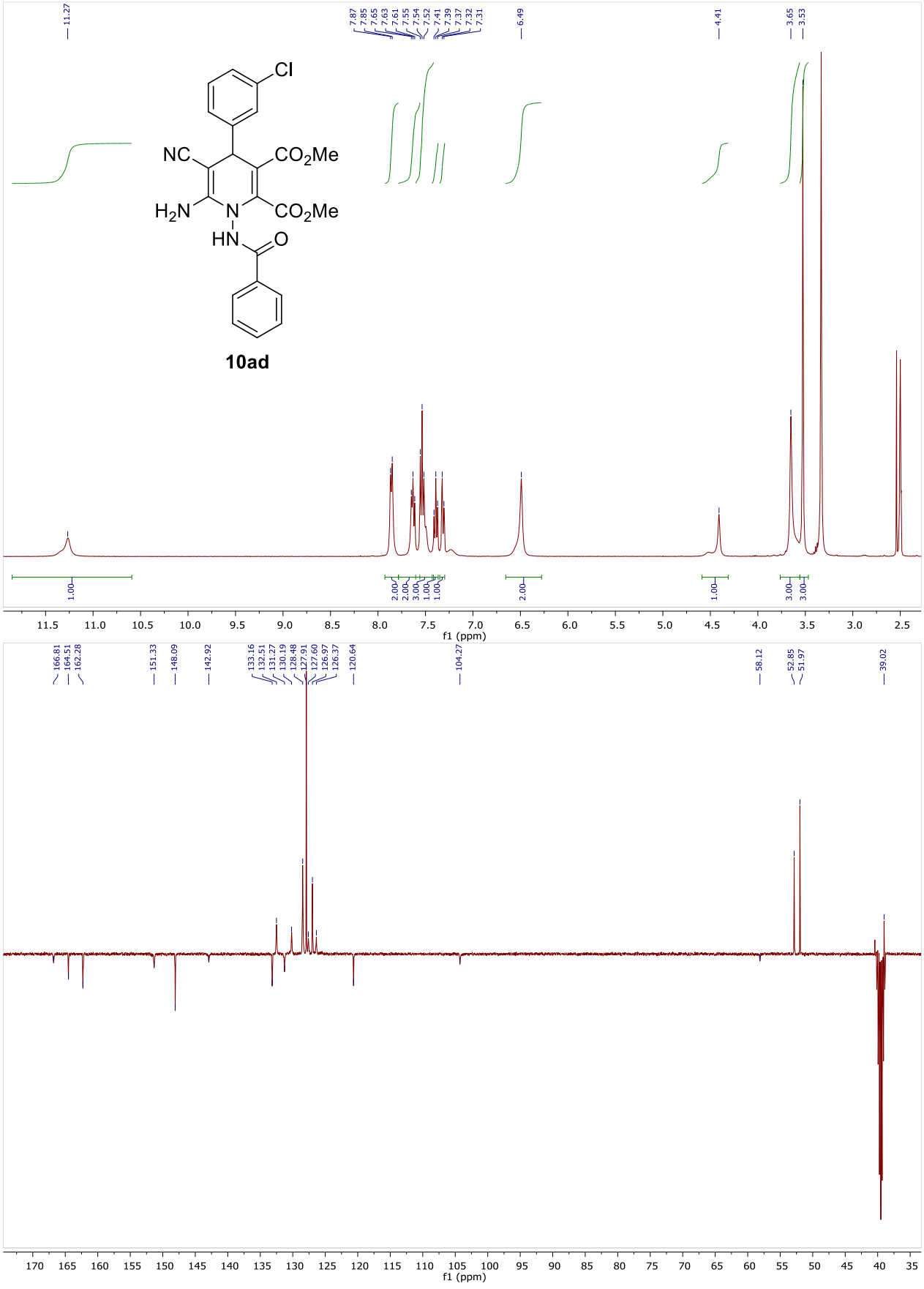


**Figure S14. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-(4-cyanophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10ag)**

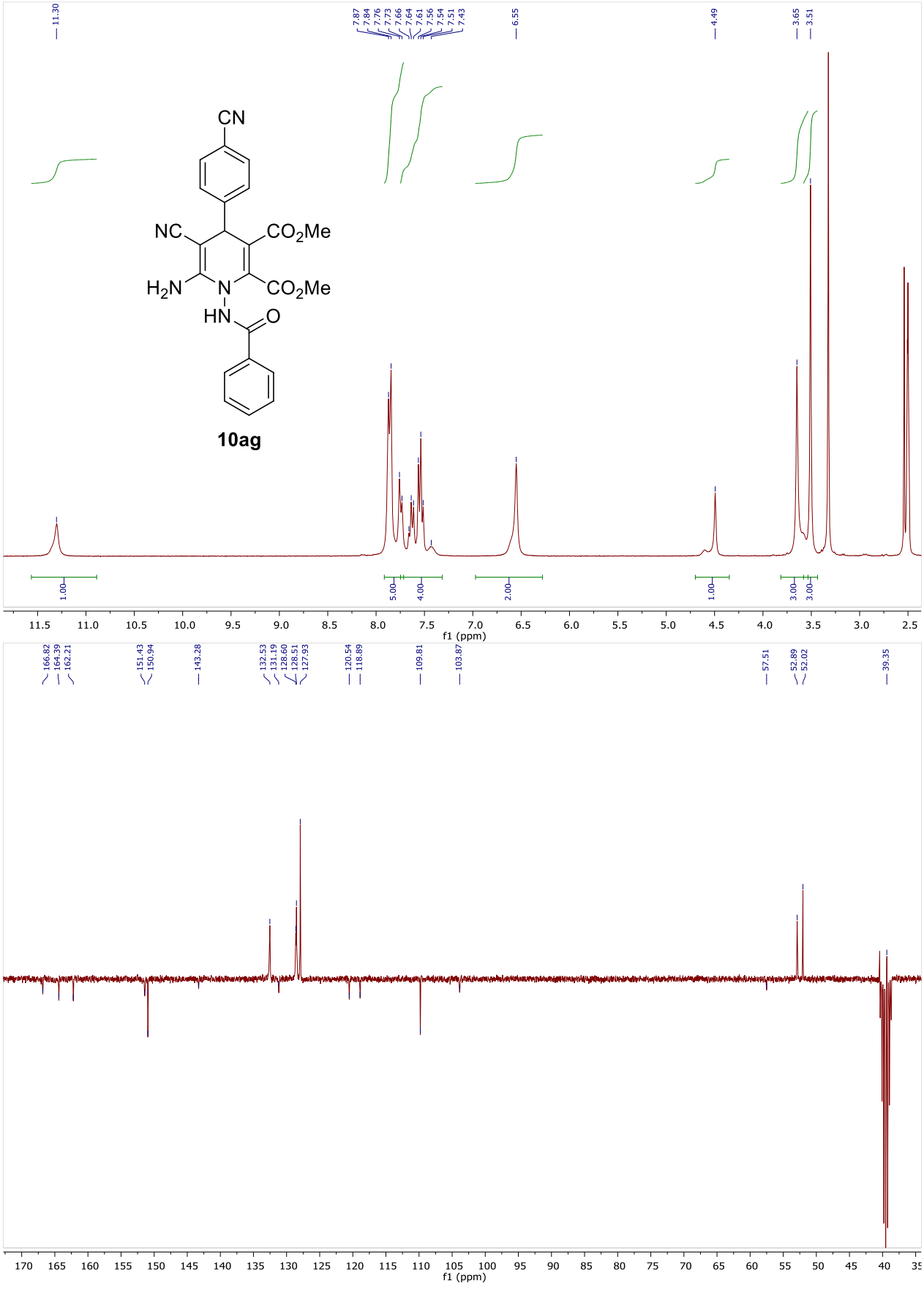
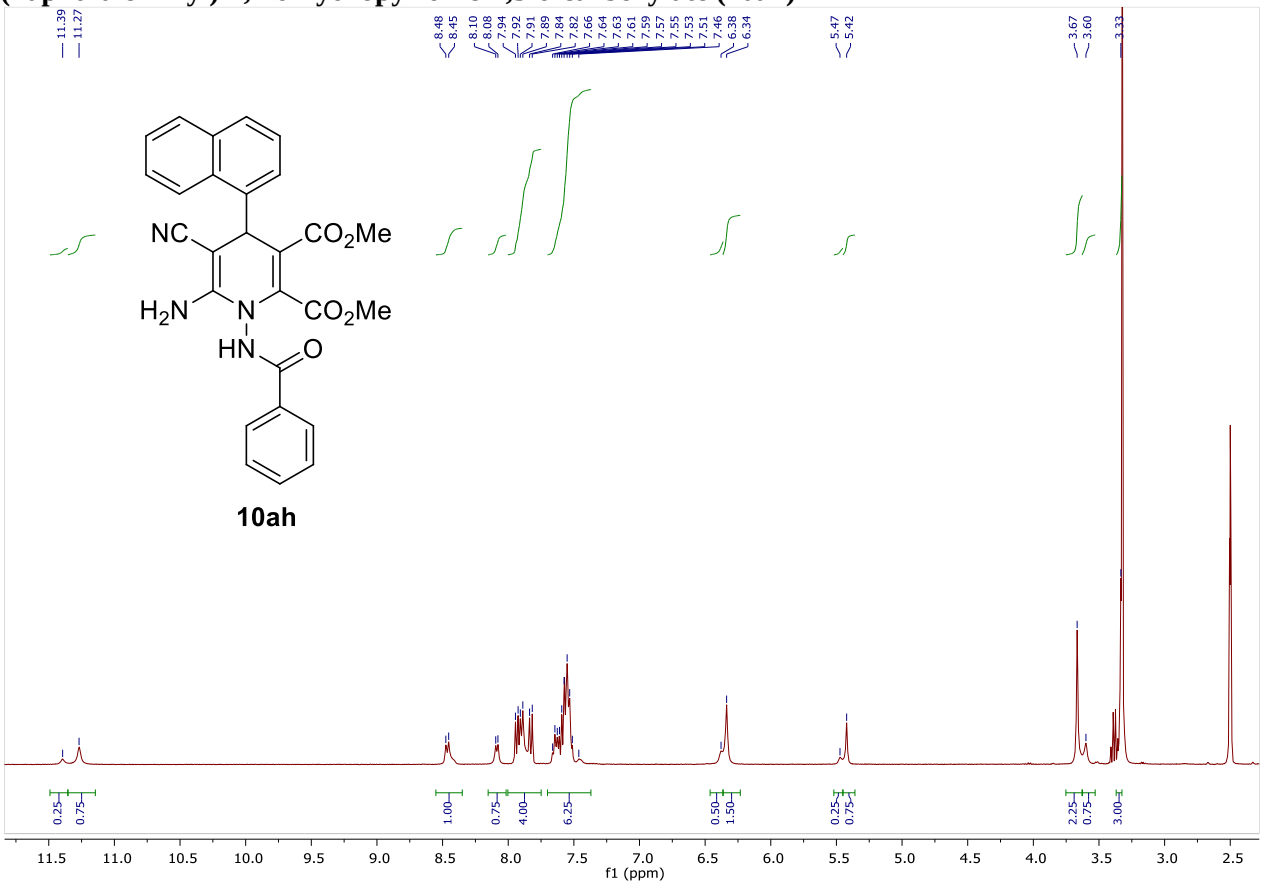


**Figure S15. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-(naphthalen-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate (10ah)**



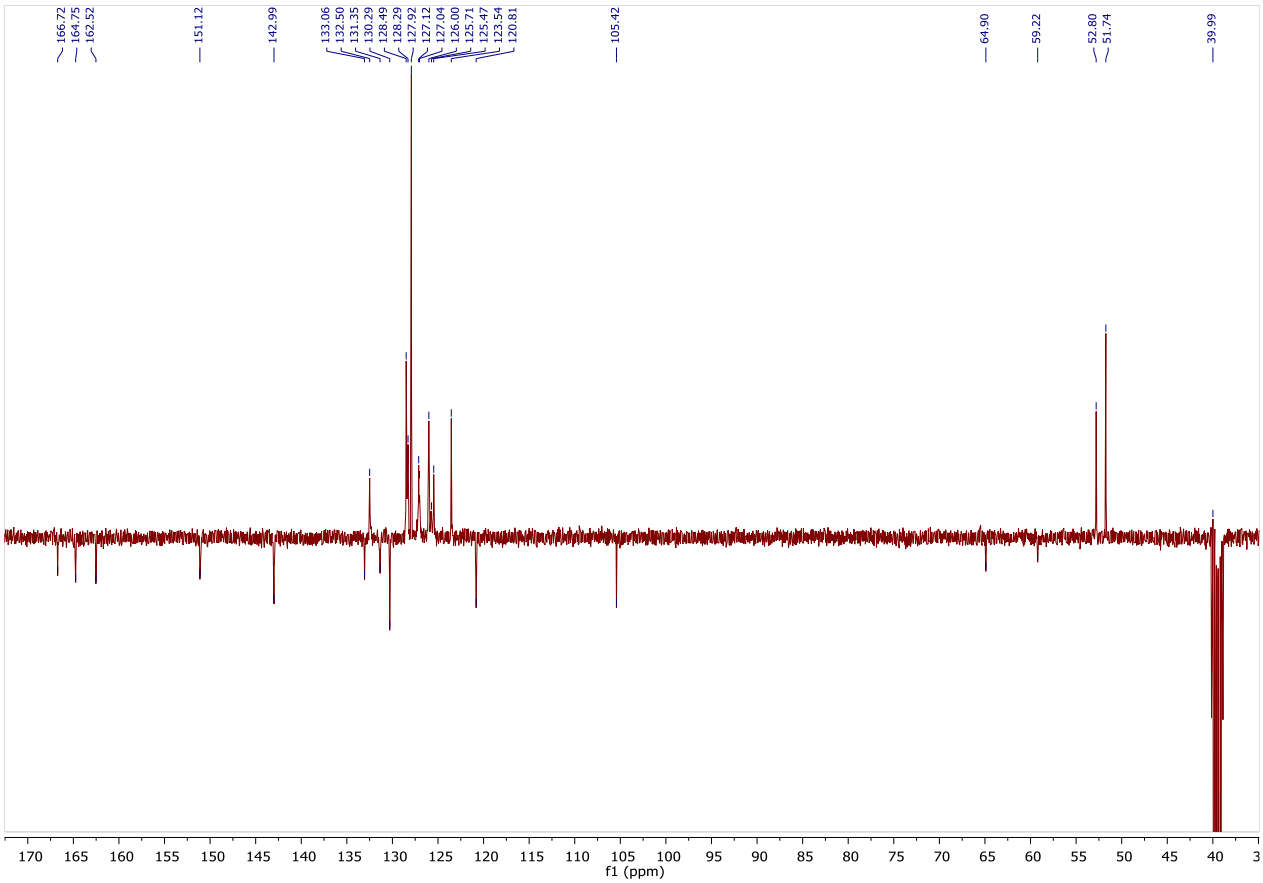
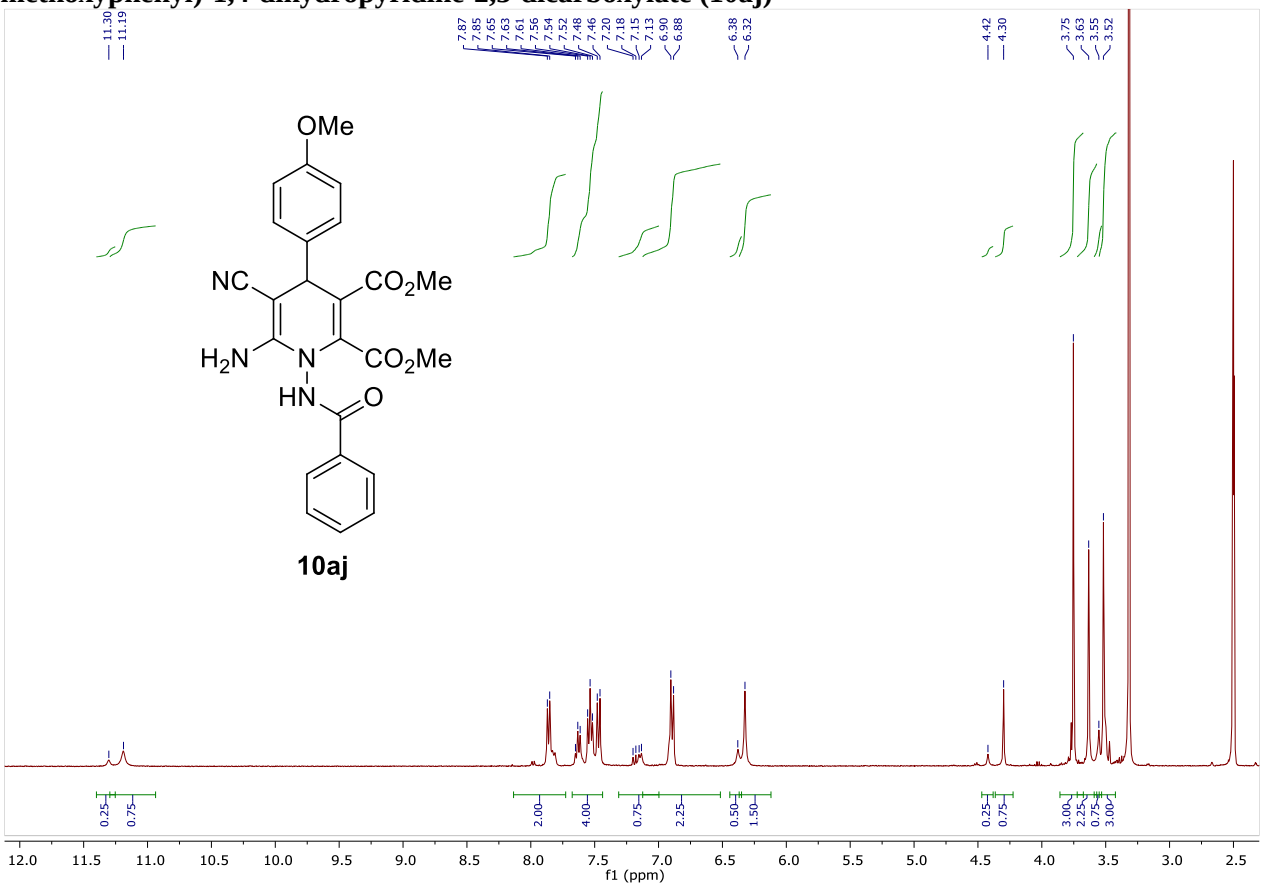



**Figure S16. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10aj)**



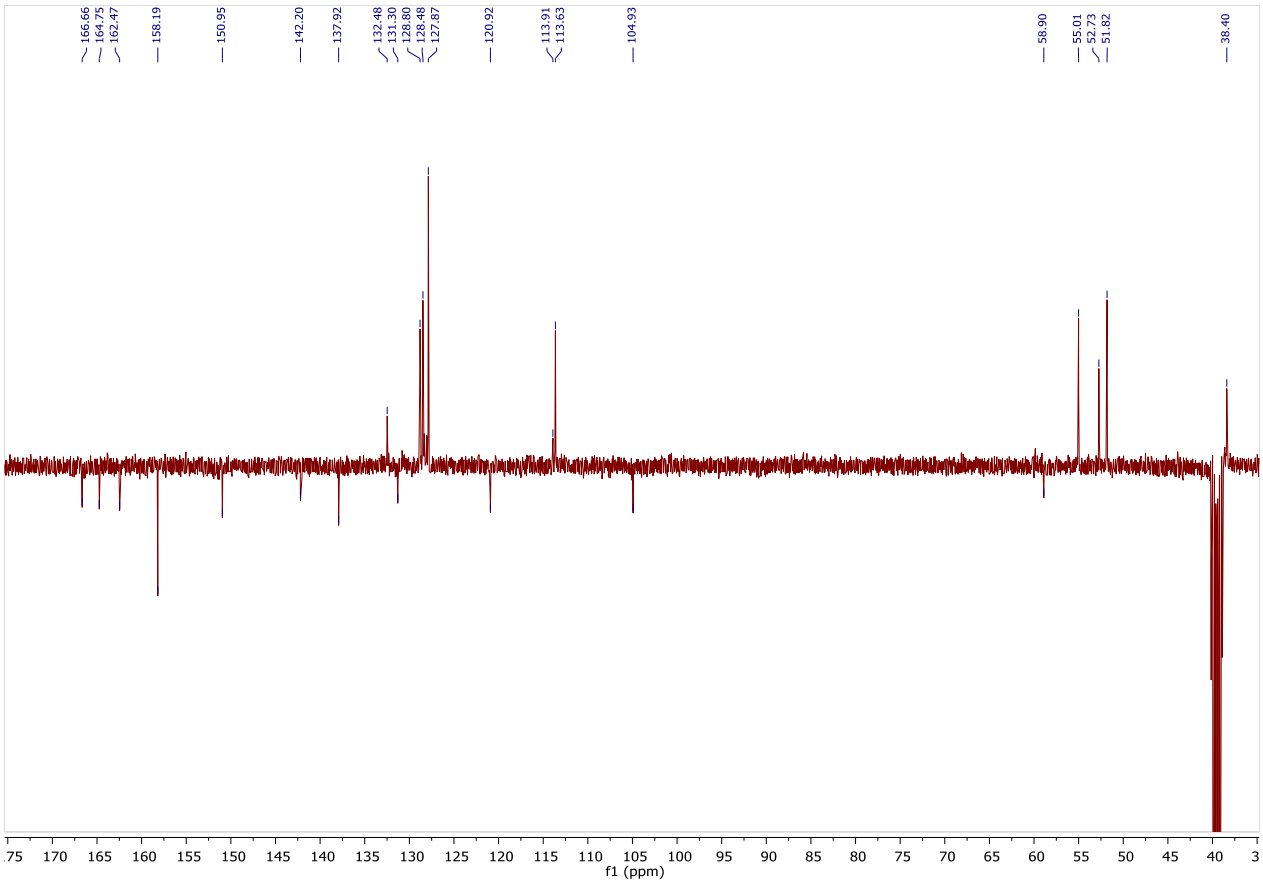



**Figure S17. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-(furan-2-yl)-1,4-dihydropyridine-2,3-dicarboxylate (10ak)**

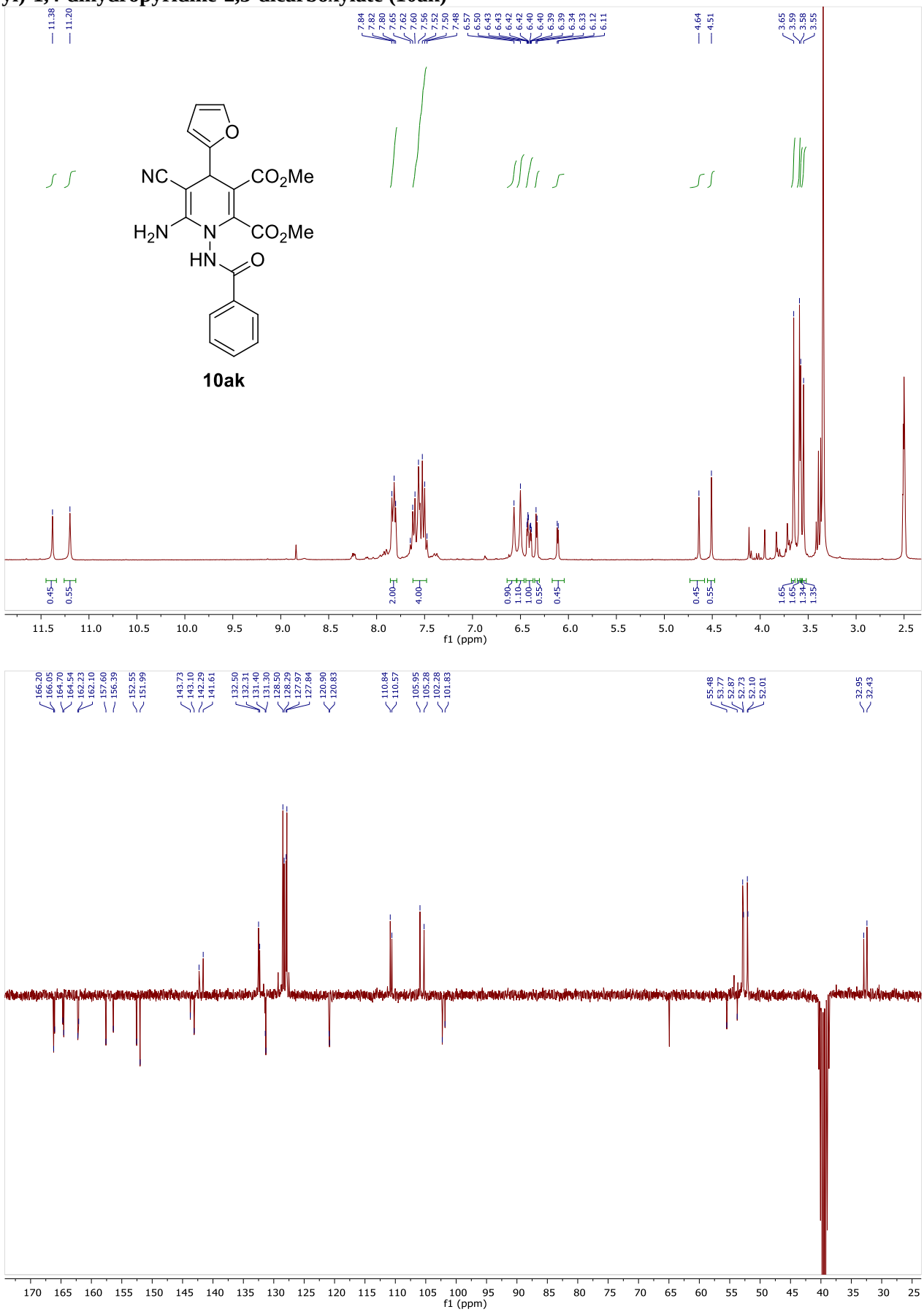


**Figure S18. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6-amino-1-benzamido-5-cyano-4-(thiophen-2-yl)-1,4-dihydropyridine-2,3-dicarboxylate (10al)**

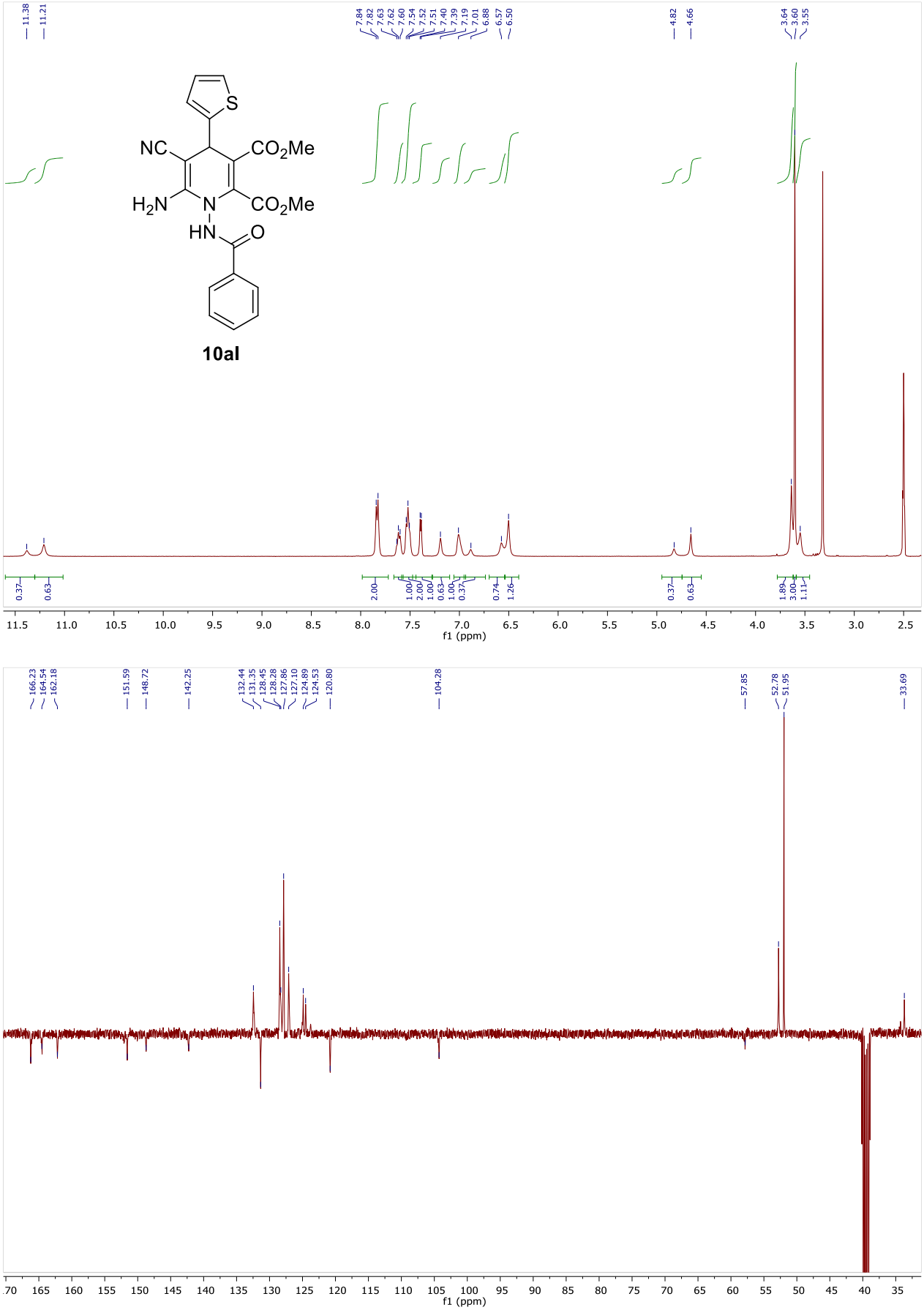
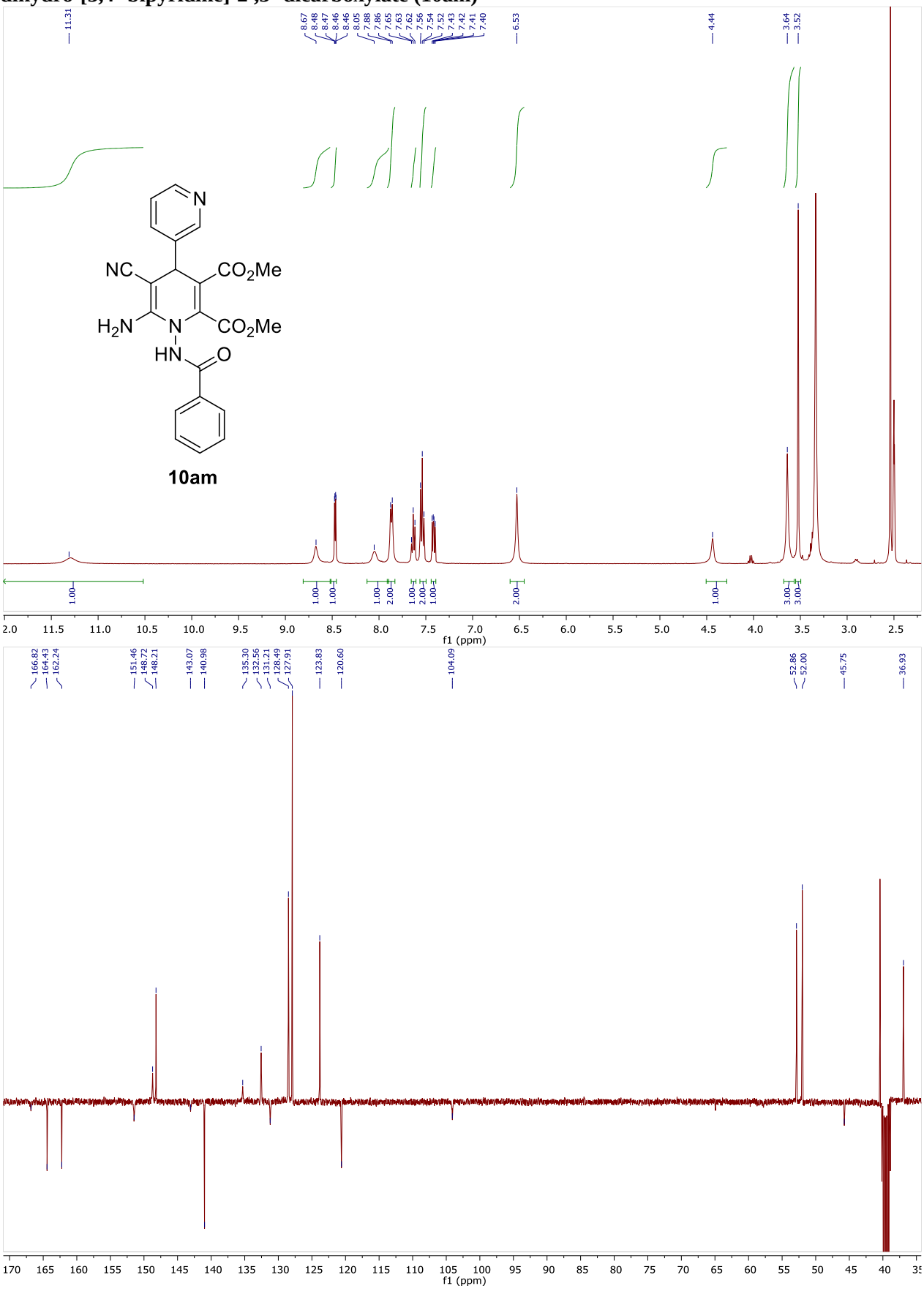
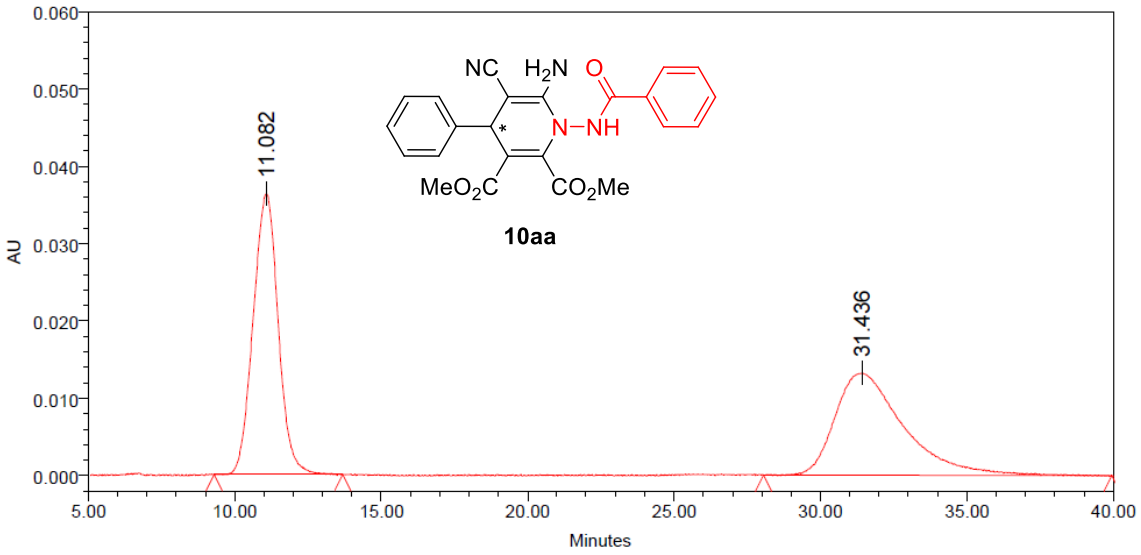


**Figure S19. $^{1}H$ and $^{13}C$-APT NMR spectra of dimethyl 6'-amino-1'-benzamido-5'-cyano-1',4'-dihydro-[3,4'-bipyridine]-2',3'-dicarboxylate (10am)**



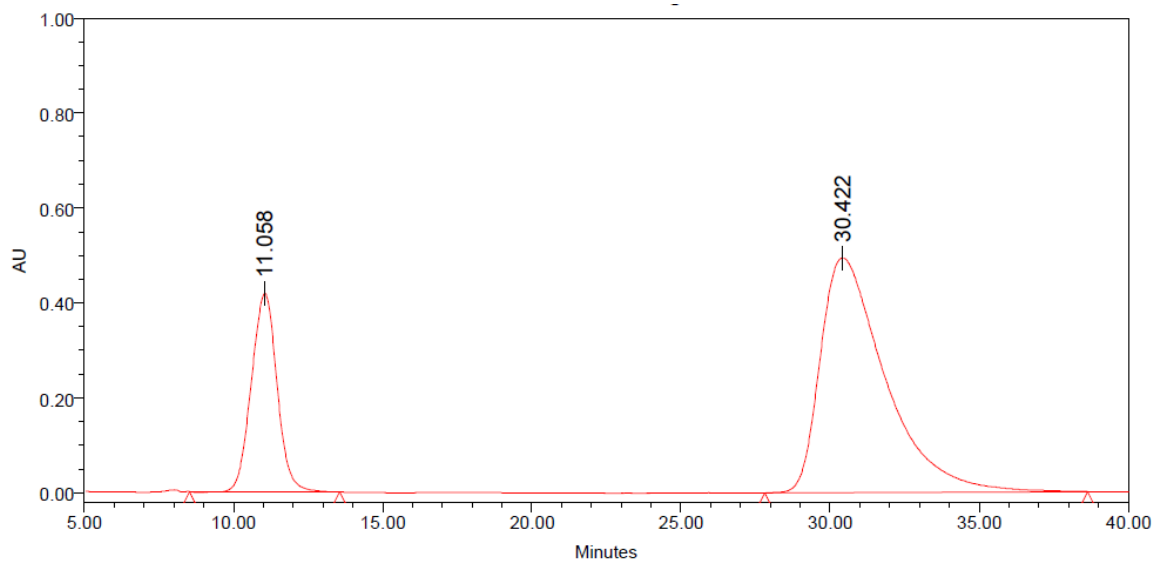
**HPLC ANALYSIS OF 1,4-DIHYDROPYRIDINES 10**




**Processed Channel: PDA 337.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 337.7 nm | 11.082 | 2158670 | 50.14 | 36296 |
| 2 | PDA 337.7 nm | 31.436 | 2146356 | 49.86 | 13164 |

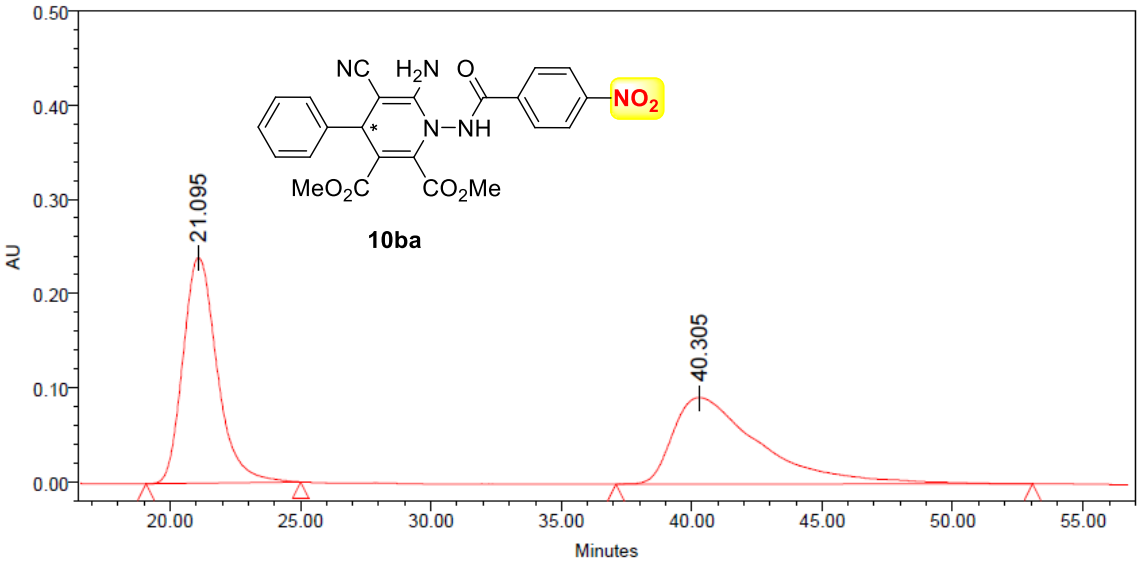
**Figure S20.** Racemic mixture of **10aa**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 11.058 | 25161769 | 25.20 | 417936 |
| 2 | PDA 237.7 nm | 30.422 | 74681844 | 74.80 | 494807 |

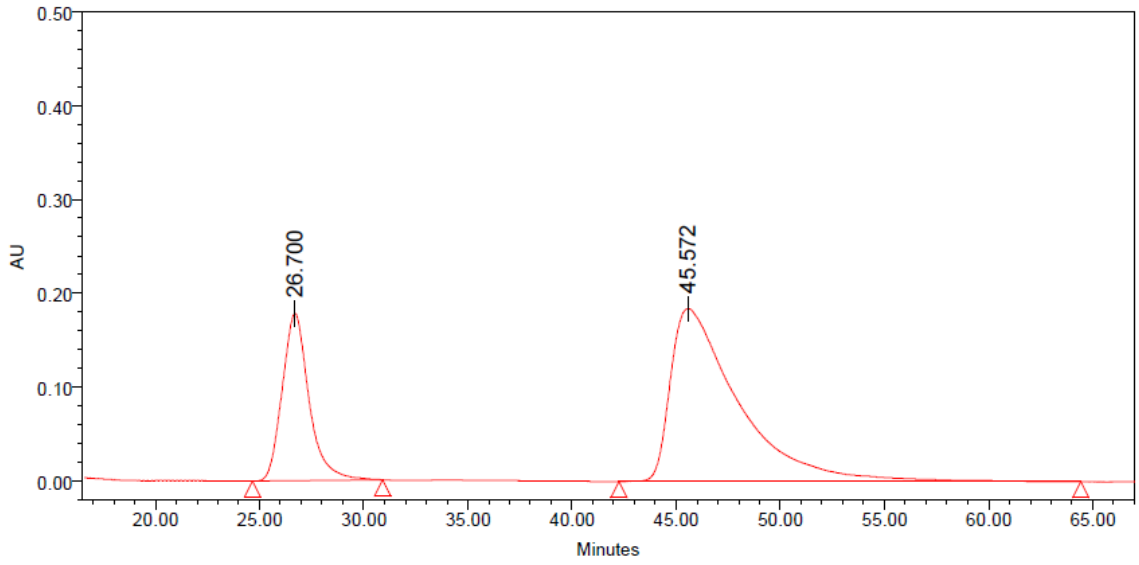
**Figure S21.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10aa)**.




**Processed Channel: PDA 249.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 249.6 nm | 21.095 | 21776897 | 50.50 | 239114 |
| 2 | PDA 249.6 nm | 40.305 | 21347894 | 49.50 | 91917 |

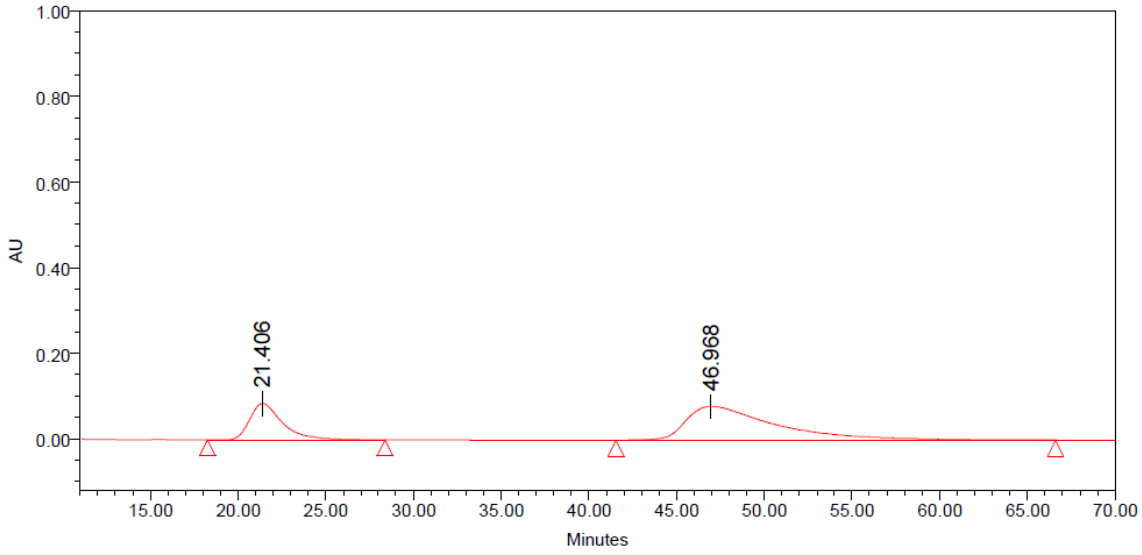
**Figure S22.** Racemic mixture of **10ba**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 249.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 249.6 nm | 26.700 | 15938249 | 27.60 | 178196 |
| 2 | PDA 249.6 nm | 45.572 | 41807602 | 72.40 | 184381 |

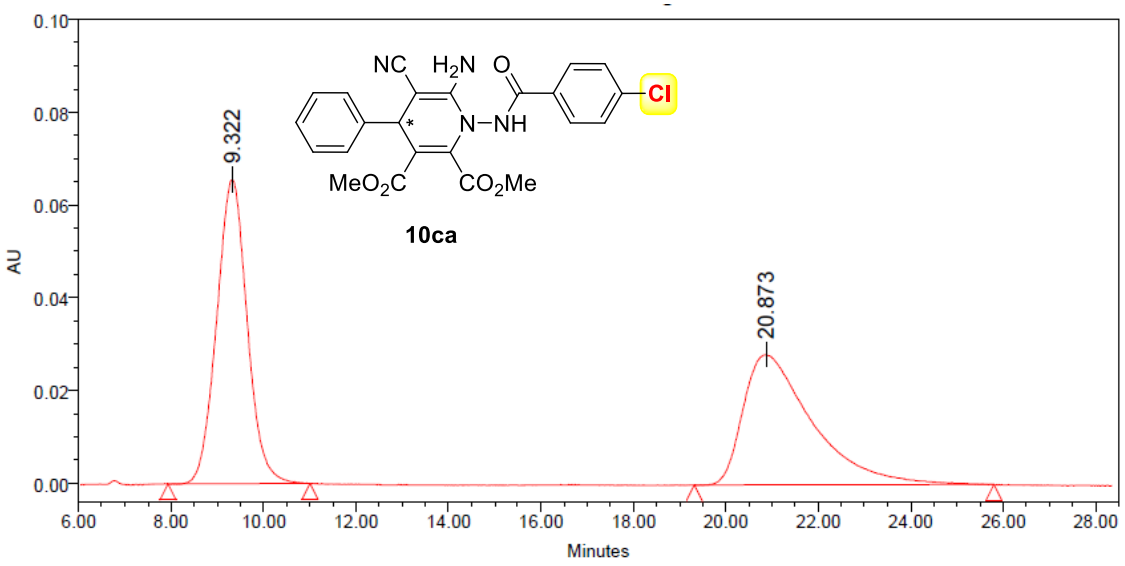
**Figure S23.** Chiral sample of **dimethyl 6-amino-5-cyano-1-(4-nitrobenzamido)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ba).**




**Processed Channel: PDA 241.8 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 241.8 nm | 21.406 | 11105207 | 28.00 | 85216 |
| 2 | PDA 241.8 nm | 46.968 | 28562492 | 72.00 | 79410 |

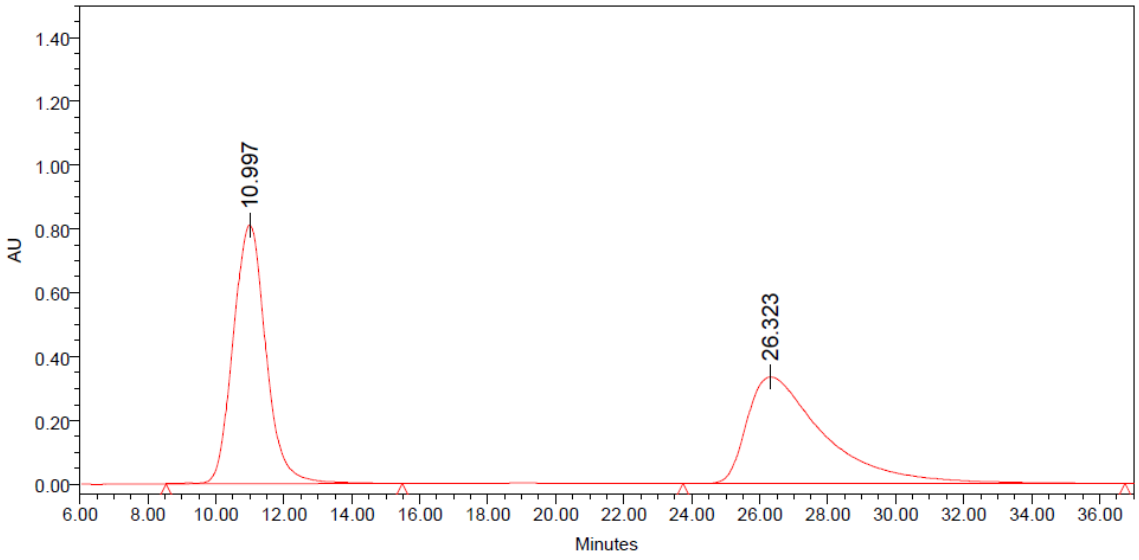
**Figure S24.** Chiral sample of **dimethyl 6-amino-5-cyano-1-(4-nitrobenzamido)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ba)** injected 3 months later.




**Processed Channel: PDA 310.5 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 310.5 nm | 9.322 | 3013526 | 50.80 | 65614 |
| 2 | PDA 310.5 nm | 20.873 | 2918428 | 49.20 | 28078 |

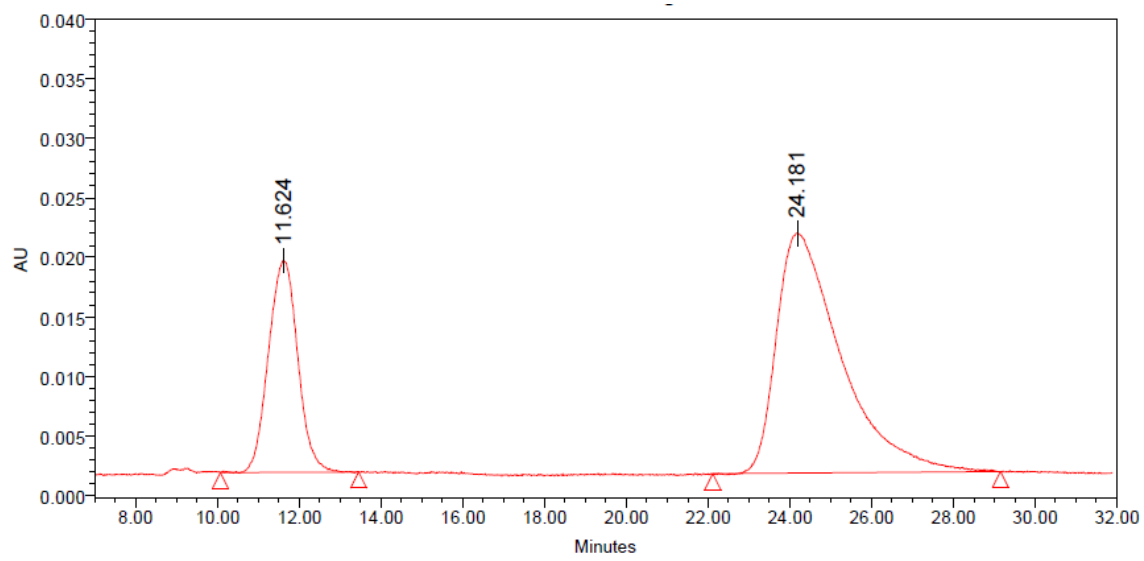
**Figure S25.** Racemic mixture of **10ca**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 254.0 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 254.0 nm | 10.997 | 54334077 | 50.83 | 810319 |
| 2 | PDA 254.0 nm | 26.323 | 52551482 | 49.17 | 334036 |

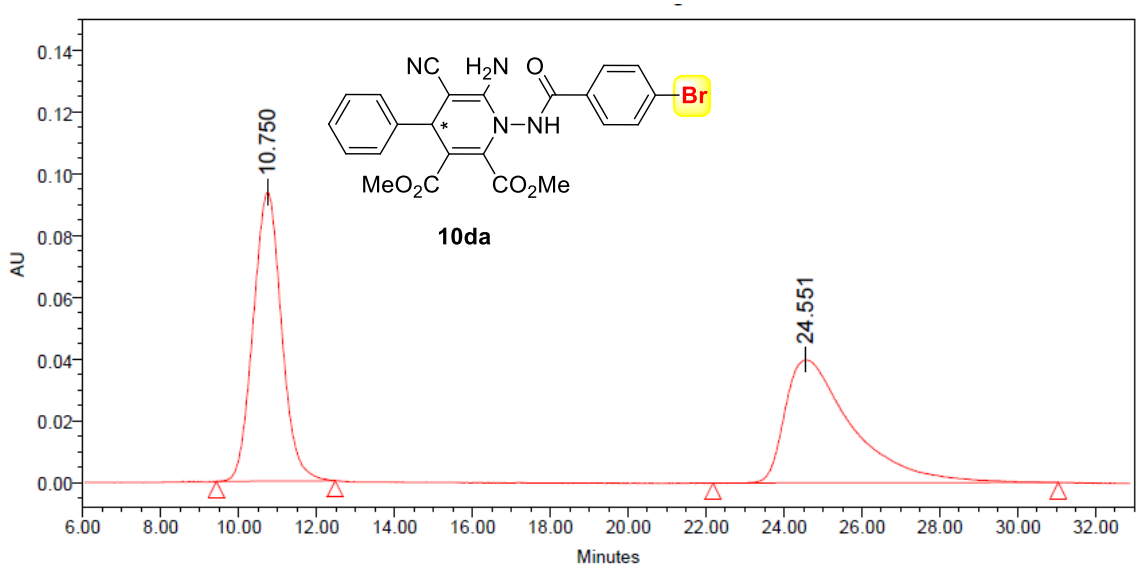
**Figure S26.** Racemic mixture of **10ca**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min) injected 3 months later.




**Processed Channel: PDA 310.5 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 310.5 nm | 11.624 | 885053 | 28.54 | 17794 |
| 2 | PDA 310.5 nm | 24.181 | 2216192 | 71.46 | 20151 |

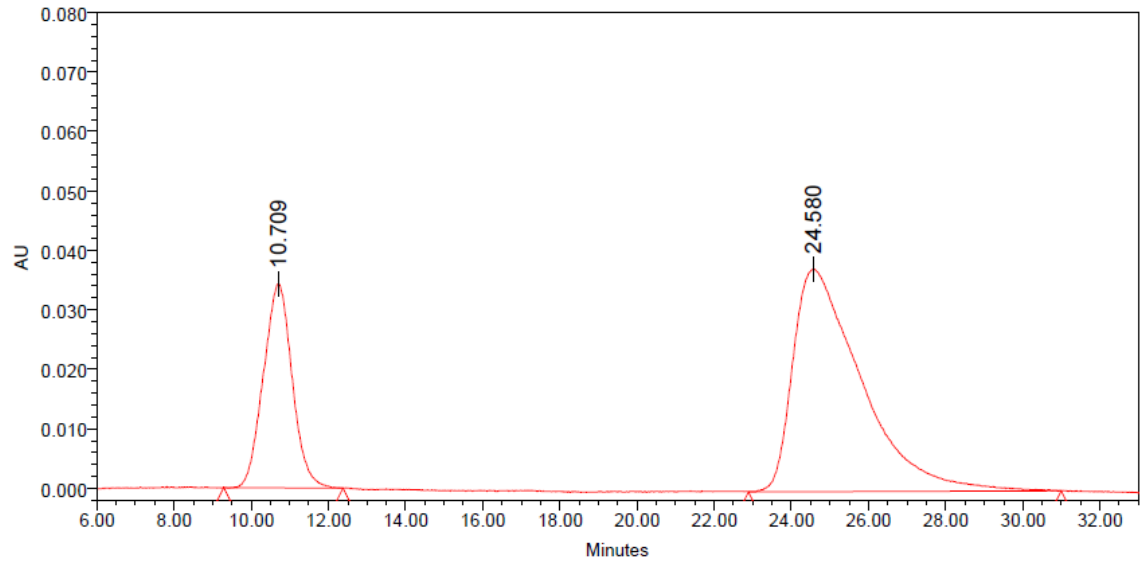
**Figure S27.** Chiral sample of **dimethyl 6-amino-1-(4-chlorobenzamido)-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ca)**.




**Processed Channel: PDA 330.0 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 330.0 nm | 10.750 | 4738746 | 49.95 | 93627 |
| 2 | PDA 330.0 nm | 24.551 | 4747889 | 50.05 | 39905 |

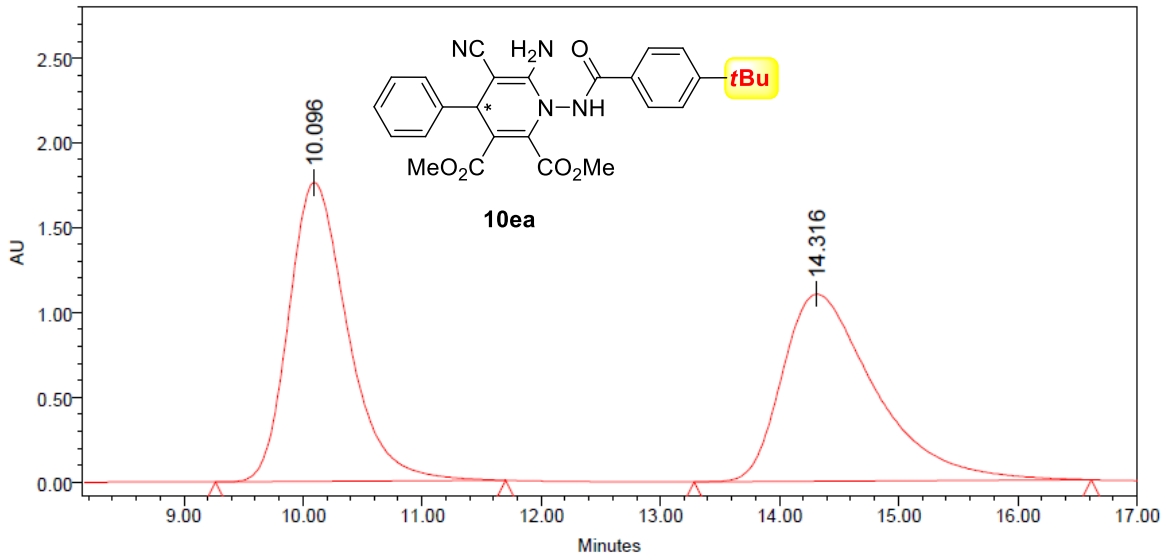
**Figure S28.** Racemic mixture of **10da**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 330.0 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 330.0 nm | 10.709 | 1776175 | 27.90 | 34259 |
| 2 | PDA 330.0 nm | 24.580 | 4590529 | 72.10 | 37376 |

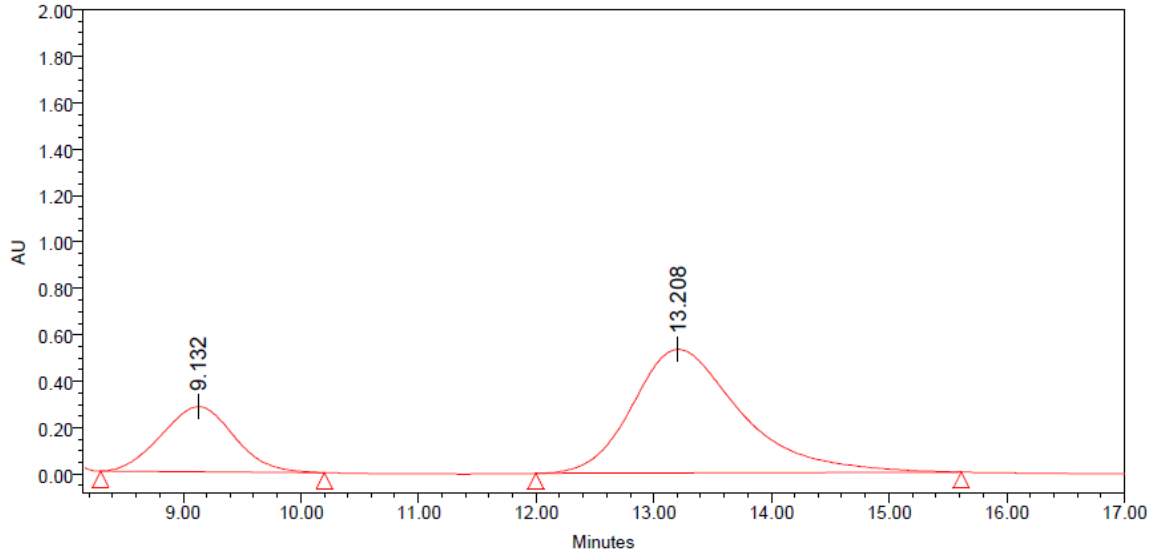
**Figure S29.** Chiral sample of **dimethyl 6-amino-1-(4-bromobenzamido)-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10da)**.




**Processed Channel: PDA 242.5 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 242.5 nm | 10.096 | 60689125 | 50.51 | 1761519 |
| 2 | PDA 242.5 nm | 14.316 | 59471736 | 49.49 | 1101201 |

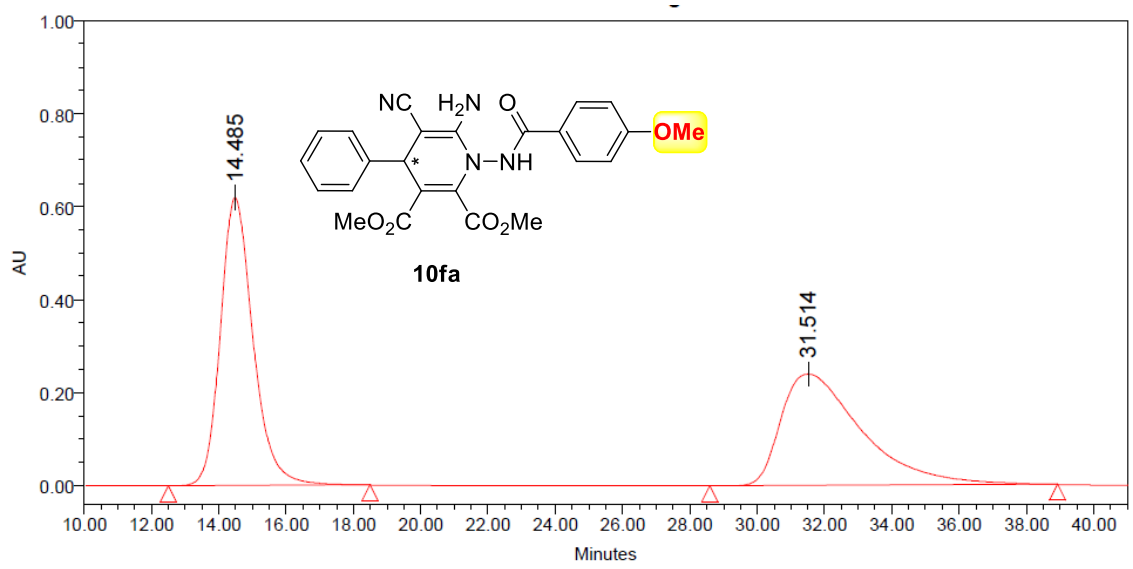
**Figure S30.** Racemic mixture of **10ea**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 242.5 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 242.5 nm | 9.132 | 12055280 | 26.06 | 280193 |
| 2 | PDA 242.5 nm | 13.208 | 34205034 | 73.94 | 533262 |

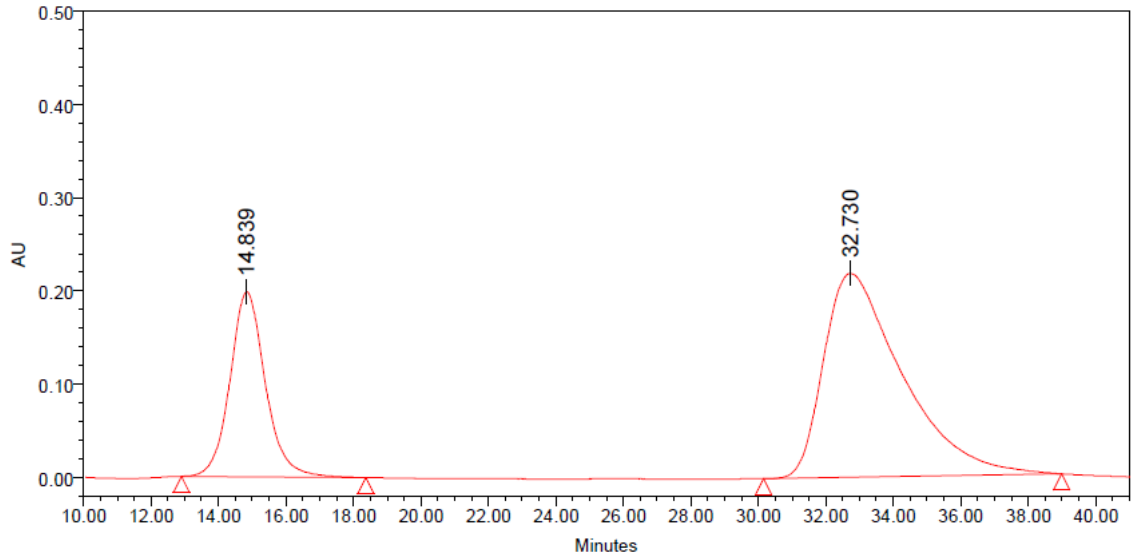
**Figure S31.** Chiral sample of **dimethyl 6-amino-1-(4-(*tert*-butyl)benzamido)-5-cyano-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10ea)**.




**Processed Channel: PDA 253.2 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 253.2 nm | 14.485 | 41736937 | 51.06 | 618777 |
| 2 | PDA 253.2 nm | 31.514 | 39997758 | 48.94 | 239602 |

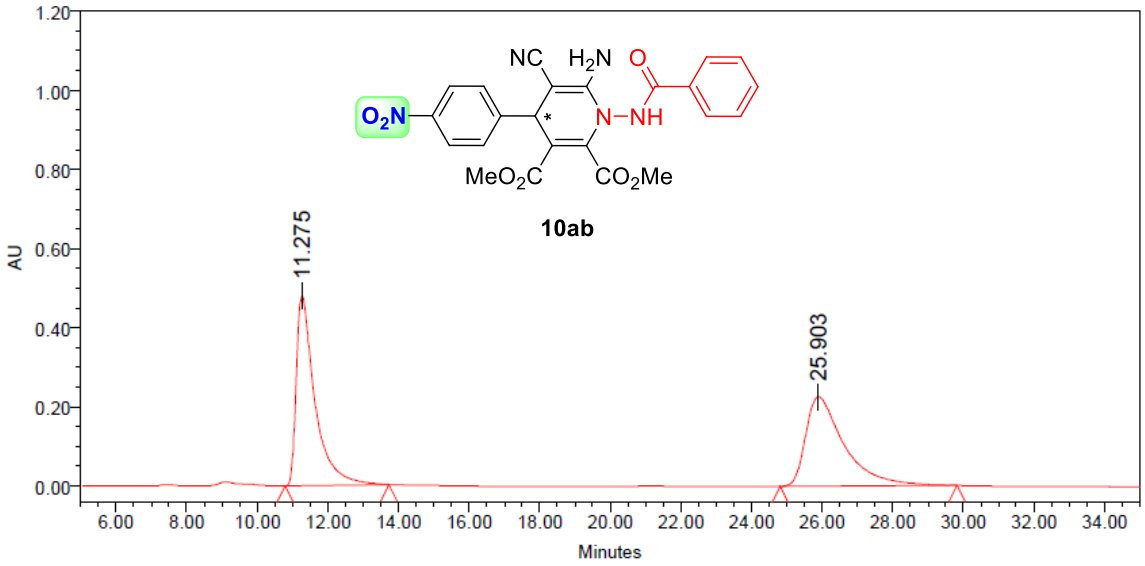
**Figure S32.** Racemic mixture of **10fa**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min) injected 3 months later.




**Processed Channel: PDA 253.2 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 253.2 nm | 14.839 | 14454503 | 28.96 | 198394 |
| 2 | PDA 253.2 nm | 32.730 | 35454138 | 71.04 | 218546 |

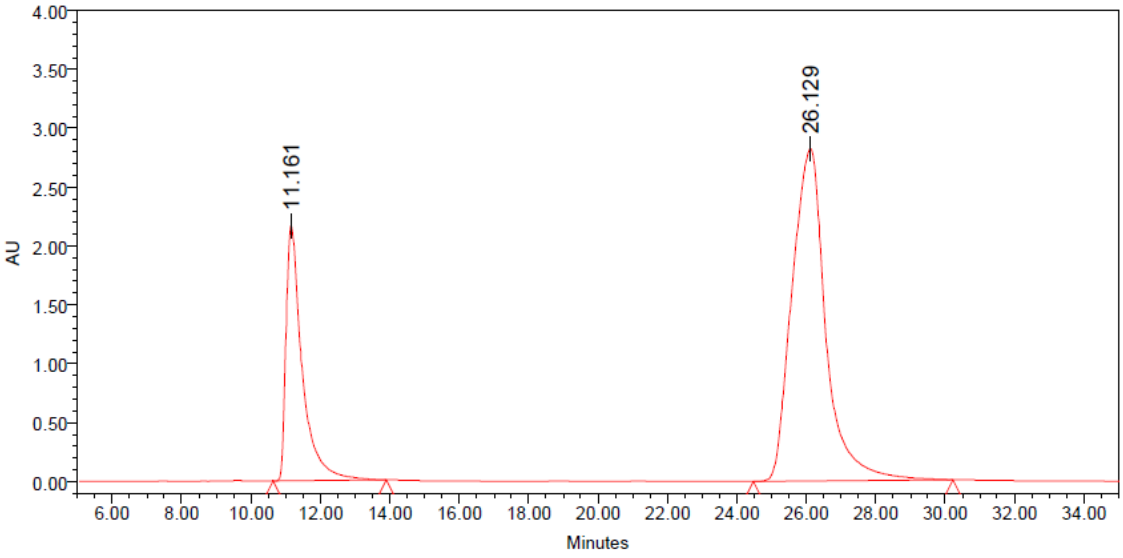
**Figure S33.** Chiral sample of **dimethyl 6-amino-5-cyano-1-(4-methoxybenzamido)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (10fa)**.




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 11.275 | 17622984 | 50.78 | 479710 |
| 2 | PDA 236.6 nm | 25.903 | 17082399 | 49.22 | 225531 |

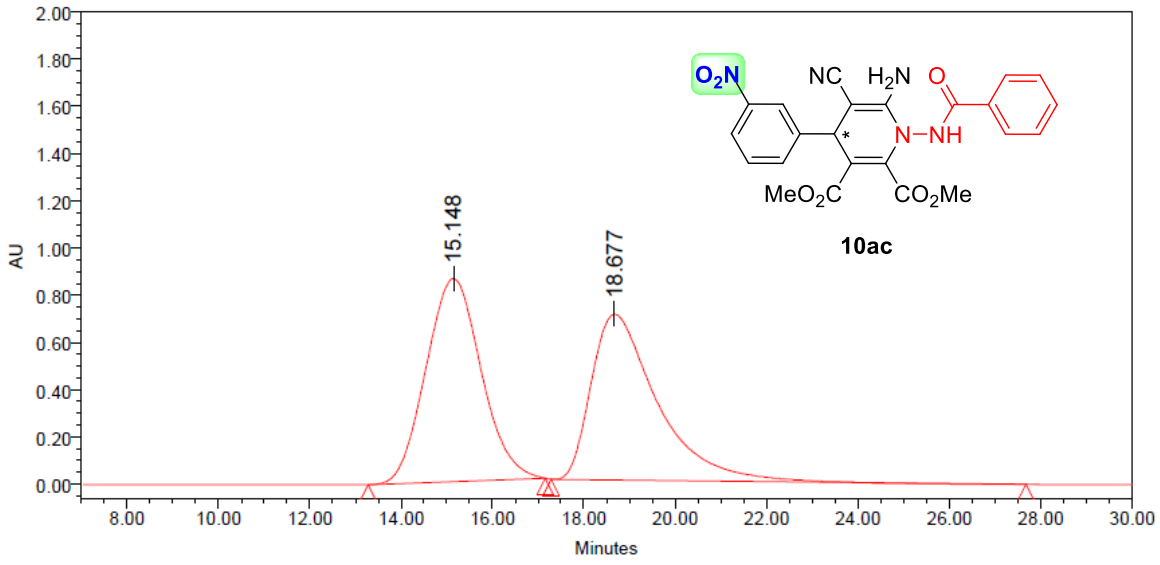
**Figure S34.** Racemic mixture of **10ab**. Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 11.161 | 70343801 | 26.94 | 2168349 |
| 2 | PDA 236.6 nm | 26.129 | 190731169 | 73.06 | 2819267 |

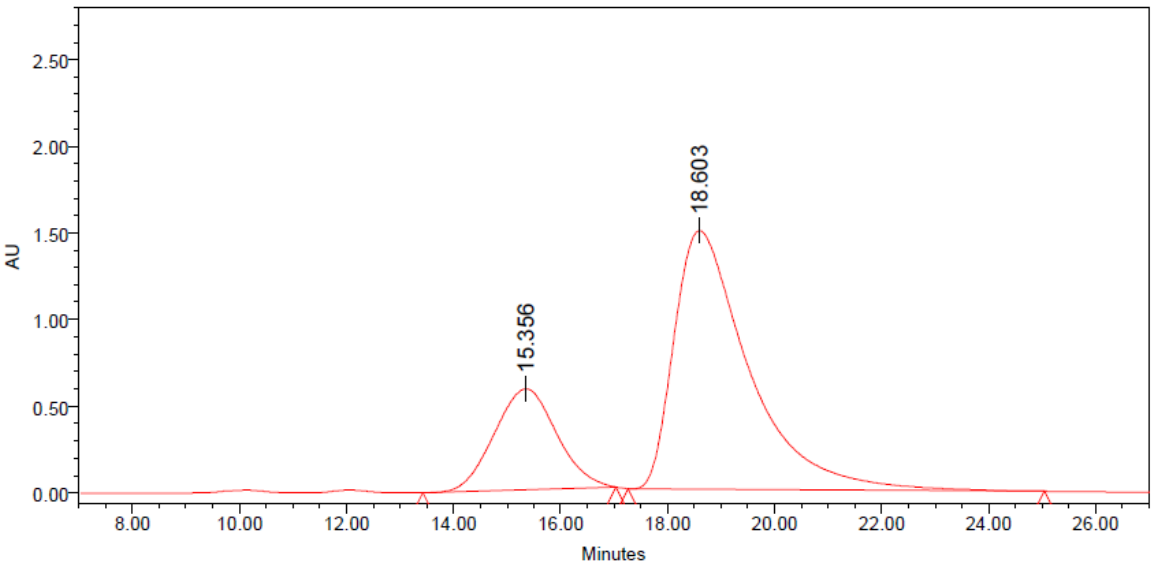
**Figure S35.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10ab)**.




**Processed Channel: PDA 238.9 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 238.9 nm | 15.148 | 72022869 | 50.49 | 859290 |
| 2 | PDA 238.9 nm | 18.677 | 70638421 | 49.51 | 700873 |

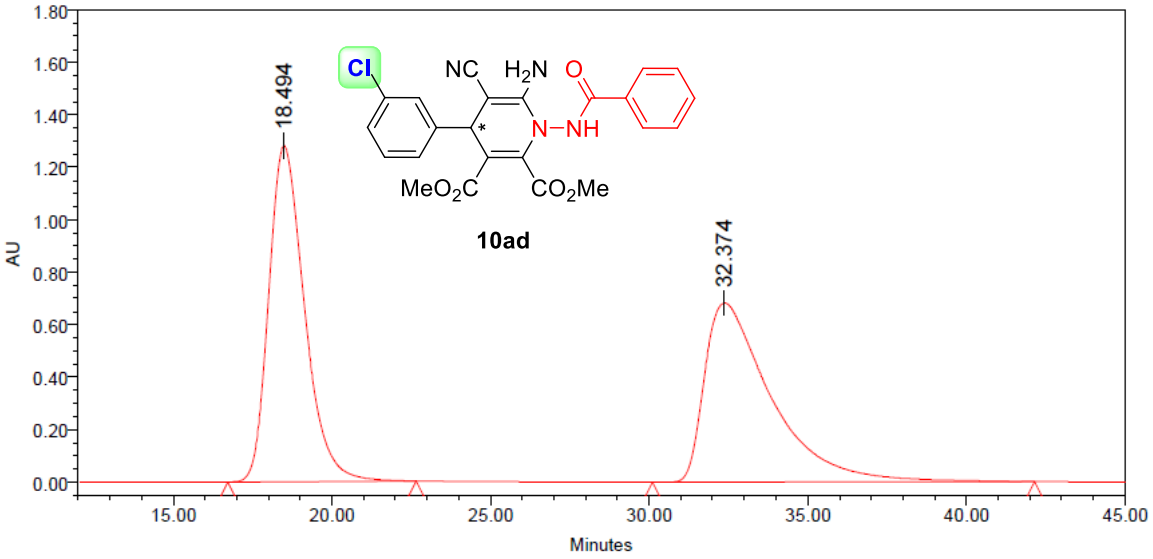
**Figure S36.** Racemic mixture of **10ac**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 238.9 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 238.9 nm | 15.356 | 47060023 | 24.46 | 581731 |
| 2 | PDA 238.9 nm | 18.603 | 145335733 | 75.54 | 1491373 |

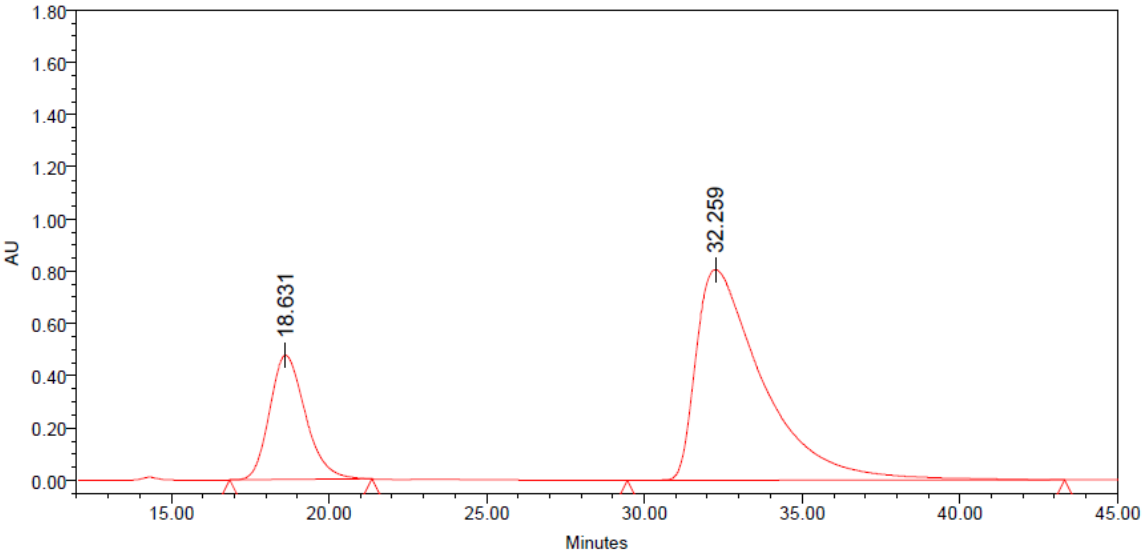
**Figure S37.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(3-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10ac)**.




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 18.494 | 100441914 | 50.09 | 1281760 |
| 2 | PDA 236.6 nm | 32.374 | 100070753 | 49.91 | 682777 |

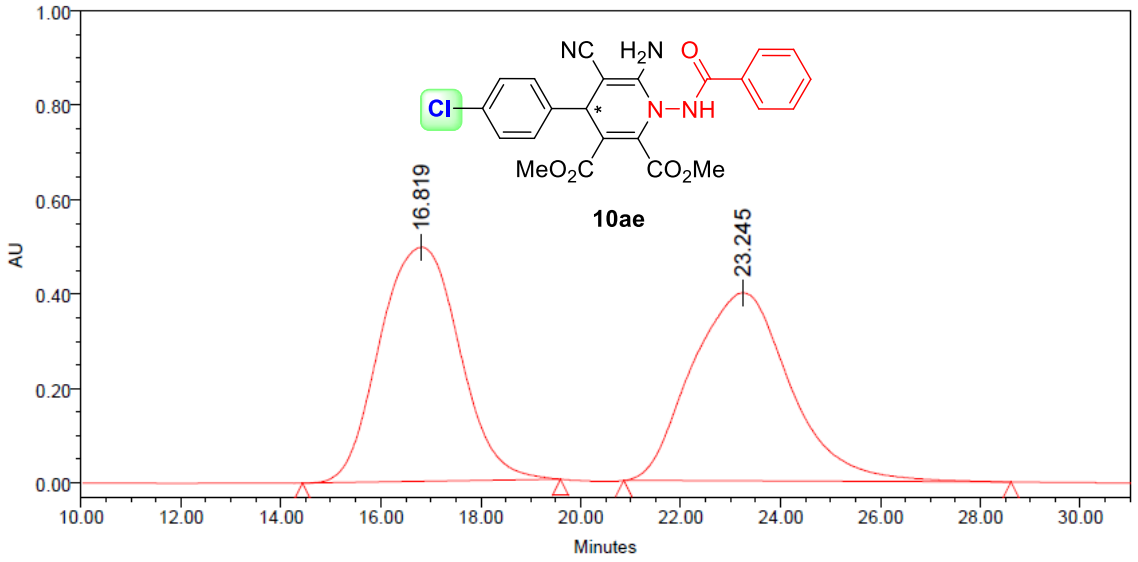
**Figure S38.** Racemic mixture of **10ad**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 80:20, flow rate 1 mL/min).




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 18.631 | 37654156 | 24.09 | 477002 |
| 2 | PDA 236.6 nm | 32.259 | 118683057 | 75.91 | 806171 |

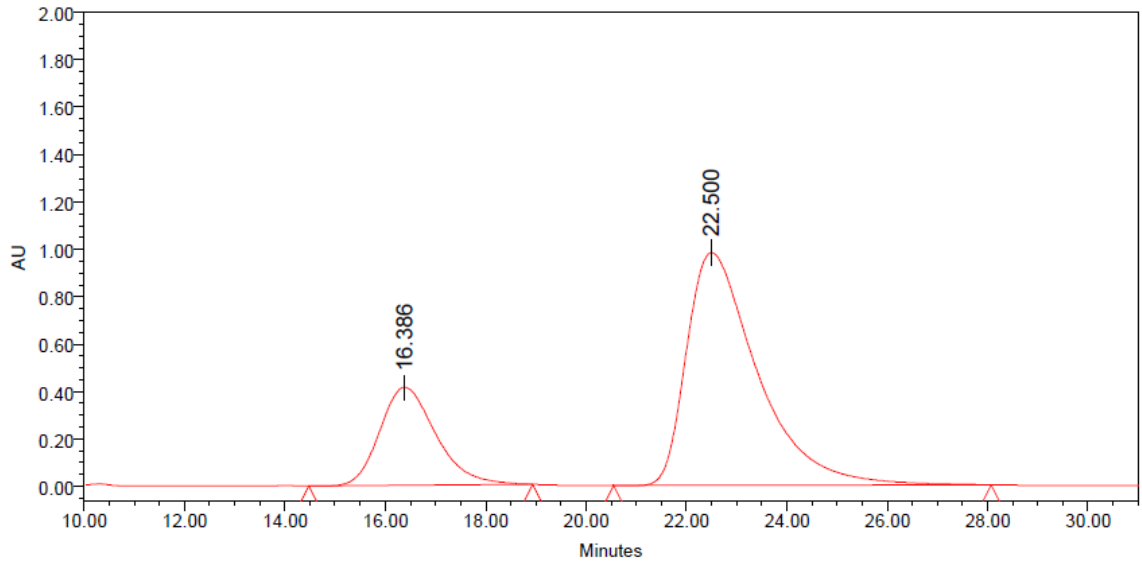
**Figure S39.** Chiral sample of **dimethyl 6-amino-1-benzamido-4-(3-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (10ad)**.




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 16.819 | 55049476 | 50.24 | 495723 |
| 2 | PDA 237.7 nm | 23.245 | 54529618 | 49.76 | 398603 |

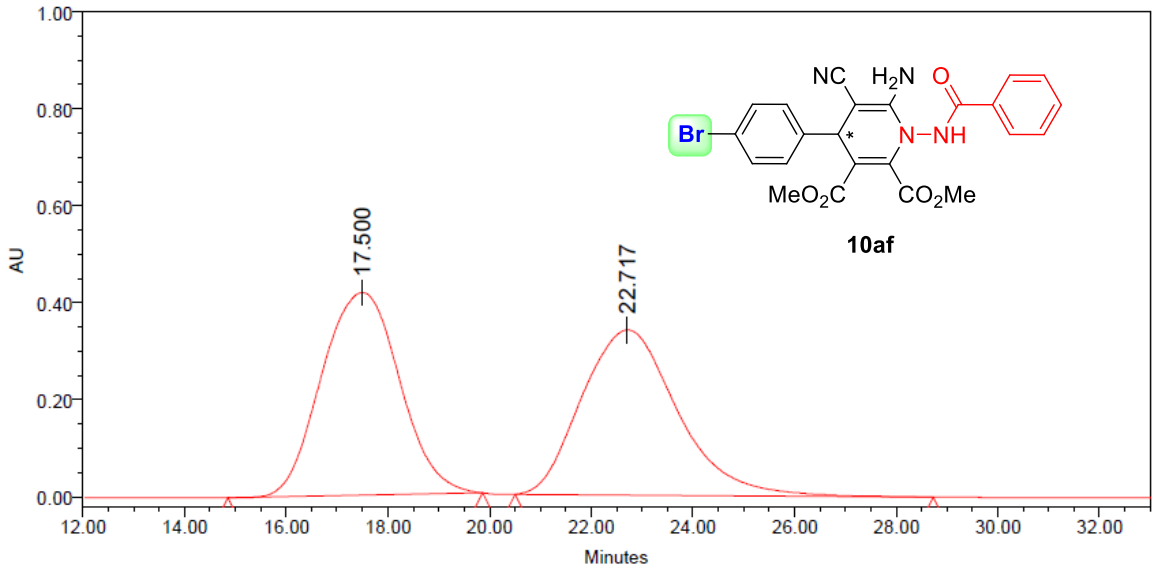
**Figure S40.** Racemic mixture of **10ae**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 80:20, flow rate 1 mL/min).




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 16.386 | 32047499 | 24.94 | 413395 |
| 2 | PDA 237.7 nm | 22.500 | 96450196 | 75.06 | 981830 |

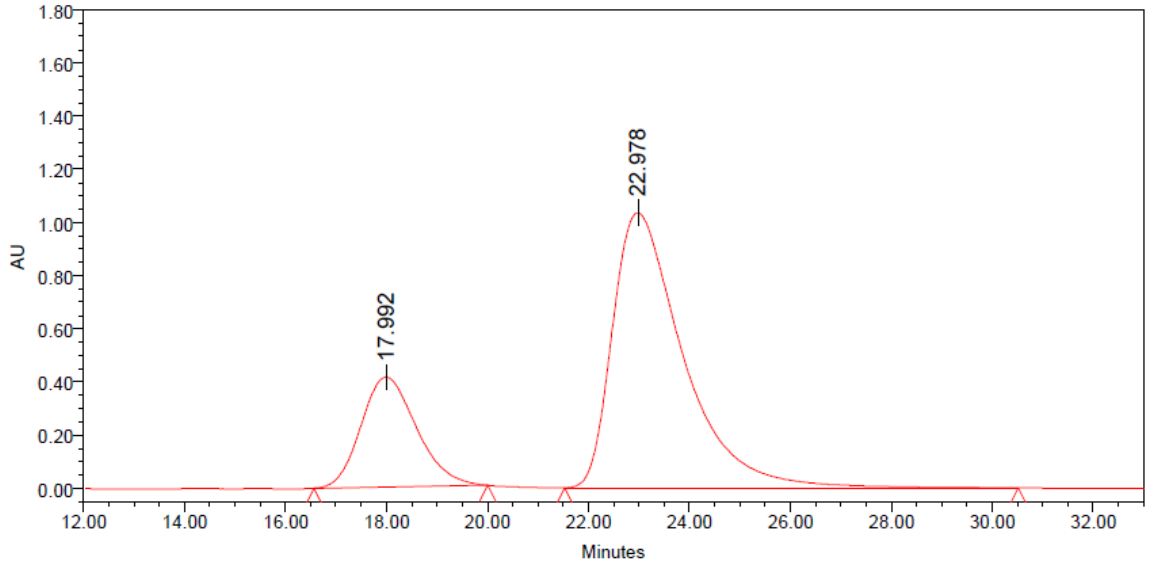
**Figure S41.** Chiral sample of **dimethyl 6-amino-1-benzamido-4-(4-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (10ae)**.




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 17.500 | 44708714 | 50.06 | 417705 |
| 2 | PDA 236.6 nm | 22.717 | 44606766 | 49.94 | 340507 |

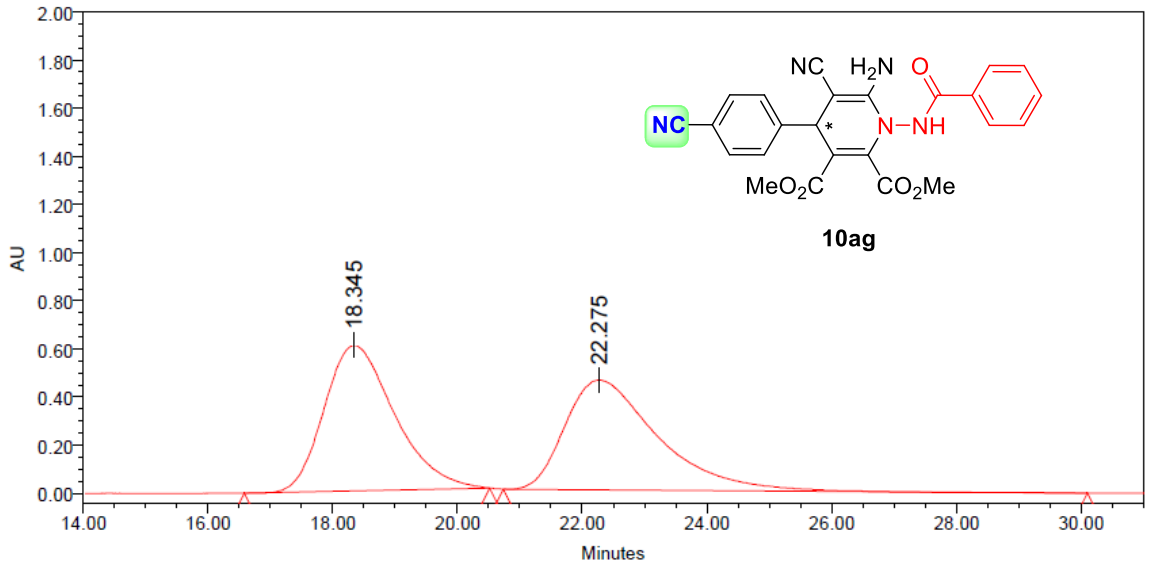
**Figure S42.** Racemic mixture of **10af**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 80:20, flow rate 1 mL/min).




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 17.992 | 31599134 | 23.88 | 413822 |
| 2 | PDA 236.6 nm | 22.978 | 100733240 | 76.12 | 1035302 |

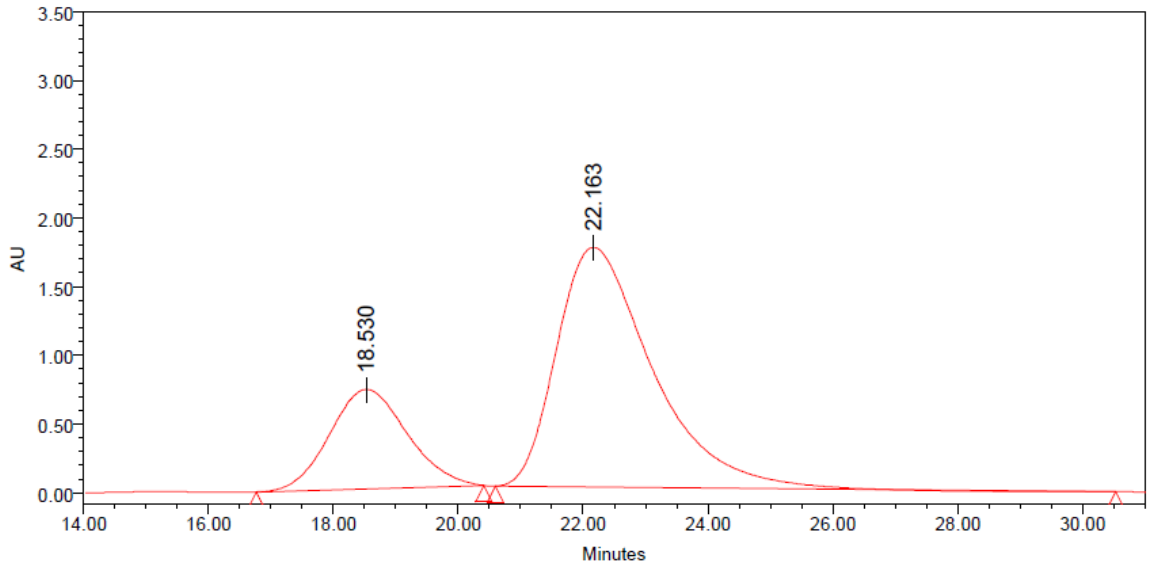
**Figure S43.** Chiral sample of **dimethyl 6-amino-1-benzamido-4-(4-bromophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (10af)**.




**Processed Channel: PDA 234.2 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 234.2 nm | 18.345 | 47416686 | 50.17 | 604355 |
| 2 | PDA 234.2 nm | 22.275 | 47099216 | 49.83 | 455713 |

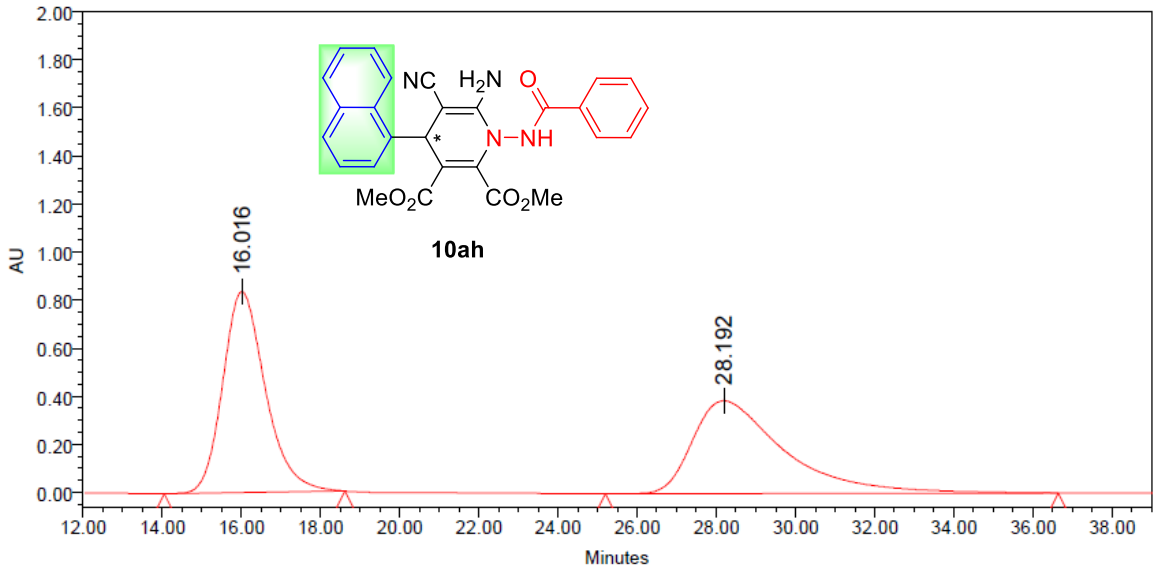
**Figure S44.** Racemic mixture of **10ag**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 234.2 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 234.2 nm | 18.530 | 62541011 | 25.05 | 724498 |
| 2 | PDA 234.2 nm | 22.163 | 187103255 | 74.95 | 1746223 |

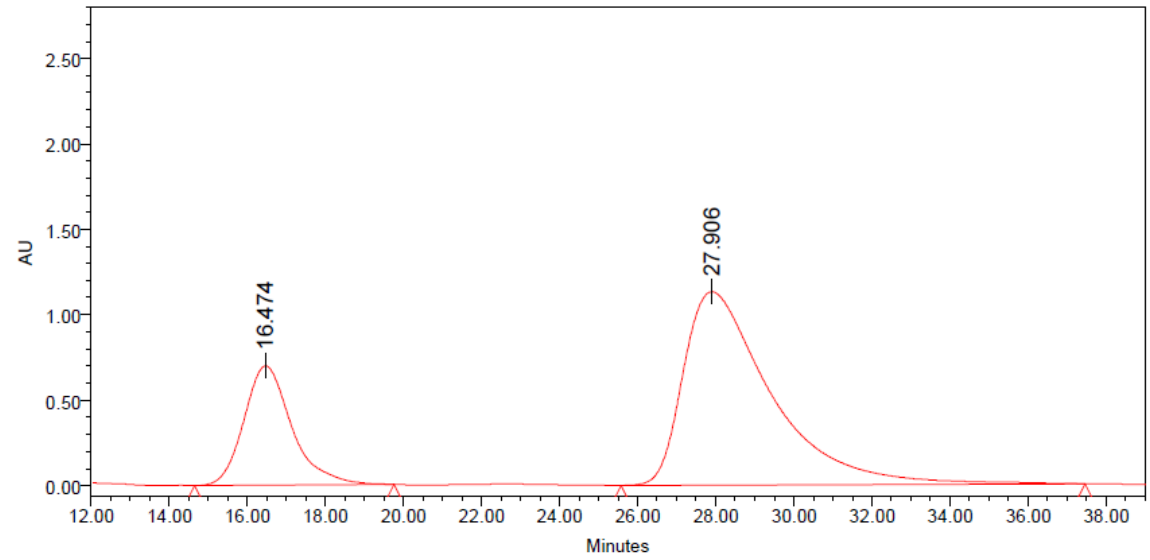
**Figure S45.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(4-cyanophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10ag)**.




**Processed Channel: PDA 221.2 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 221.2 nm | 16.016 | 62495350 | 50.32 | 836041 |
| 2 | PDA 221.2 nm | 28.192 | 61702057 | 49.68 | 385566 |

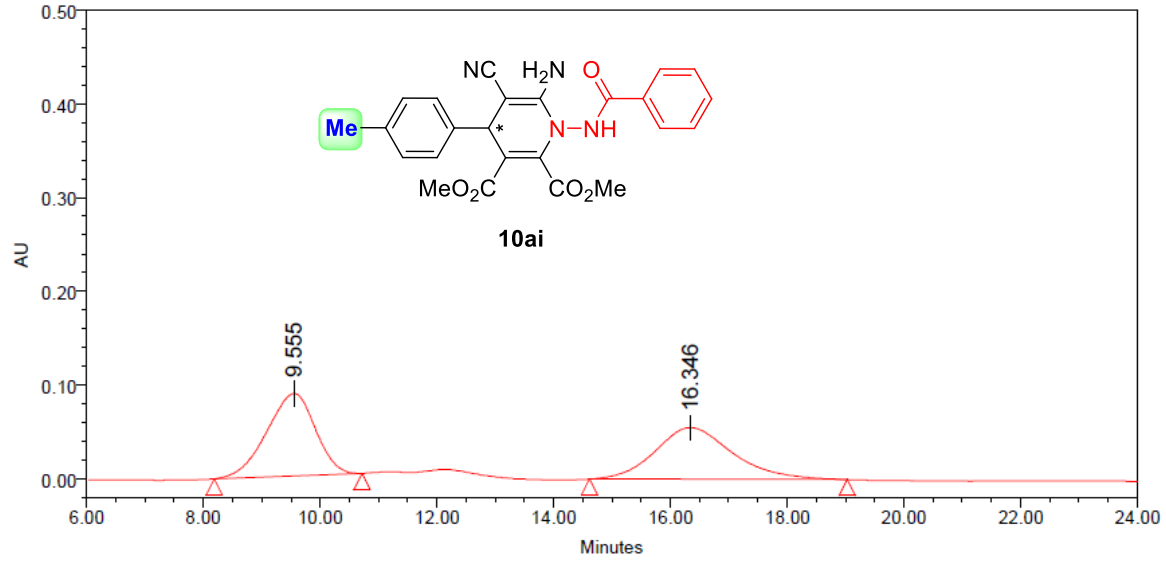
**Figure S46.** Racemic mixture of **10ah**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 221.2 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 221.2 nm | 16.474 | 59358674 | 25.17 | 697447 |
| 2 | PDA 221.2 nm | 27.906 | 176513601 | 74.83 | 1130499 |

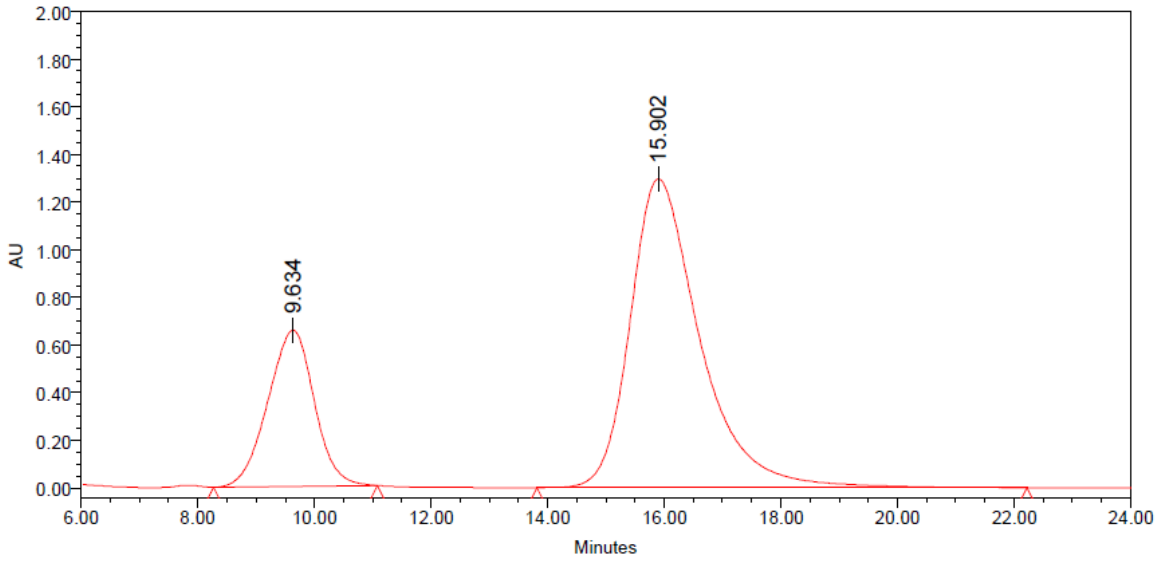
**Figure S47.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(naphthalen-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate (10ah)**.




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 9.555 | 5079543 | 49.91 | 88016 |
| 2 | PDA 237.7 nm | 16.346 | 5098577 | 50.09 | 55184 |

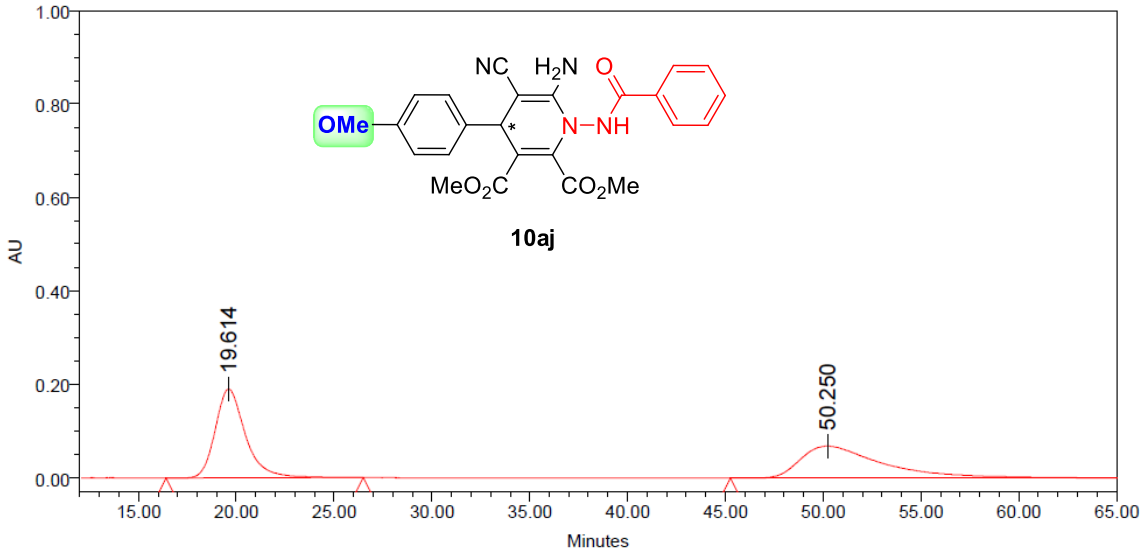
**Figure S48.** Racemic mixture of **10ai**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 9.634 | 36213748 | 25.17 | 655692 |
| 2 | PDA 237.7 nm | 15.902 | 107660471 | 74.83 | 1295935 |

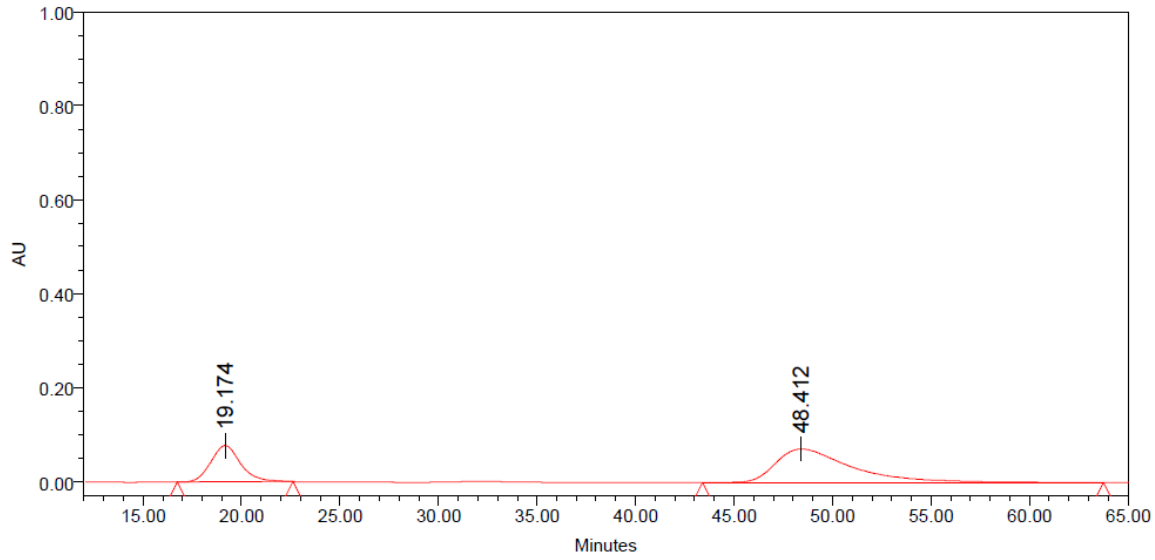
**Figure S49.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (10ai)**.




**Processed Channel: PDA 247.4 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 247.4 nm | 19.614 | 20322514 | 50.29 | 190004 |
| 2 | PDA 247.4 nm | 50.250 | 20087936 | 49.71 | 68499 |

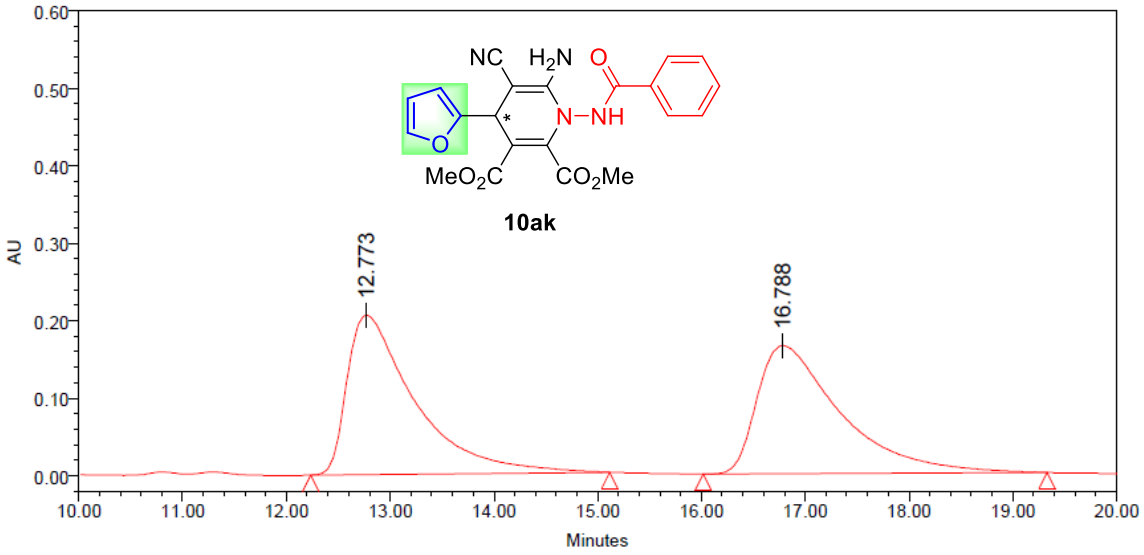
**Figure S50.** Racemic mixture of **10aj**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 19.174 | 8146189 | 29.96 | 77509 |
| 2 | PDA 237.7 nm | 48.412 | 19046679 | 70.04 | 71318 |

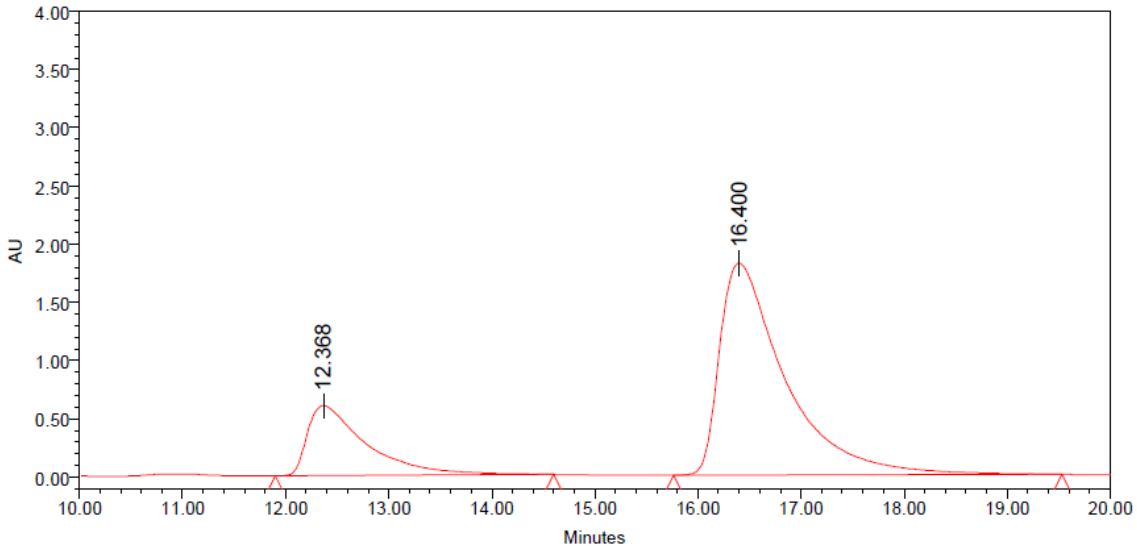
**Figure S51.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (10aj)**.




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 12.773 | 9337925 | 50.31 | 205692 |
| 2 | PDA 236.6 nm | 16.788 | 9222028 | 49.69 | 165429 |

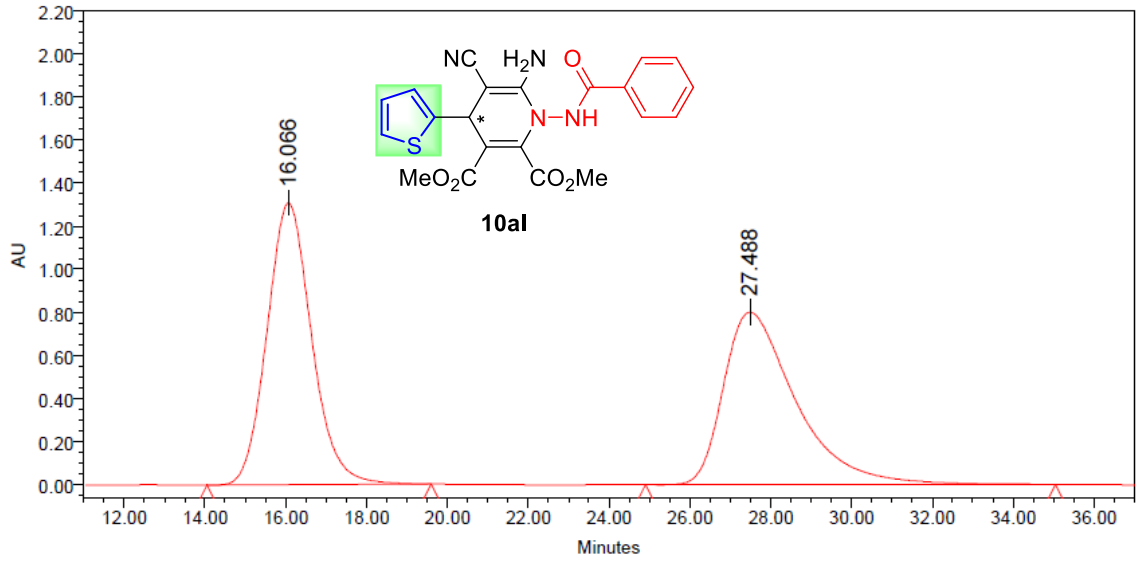
**Figure S52.** Racemic mixture of **10ak**. Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 80:20, flow rate 1 mL/min).




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 12.368 | 23993346 | 22.92 | 601900 |
| 2 | PDA 236.6 nm | 16.400 | 80675819 | 77.08 | 1822151 |

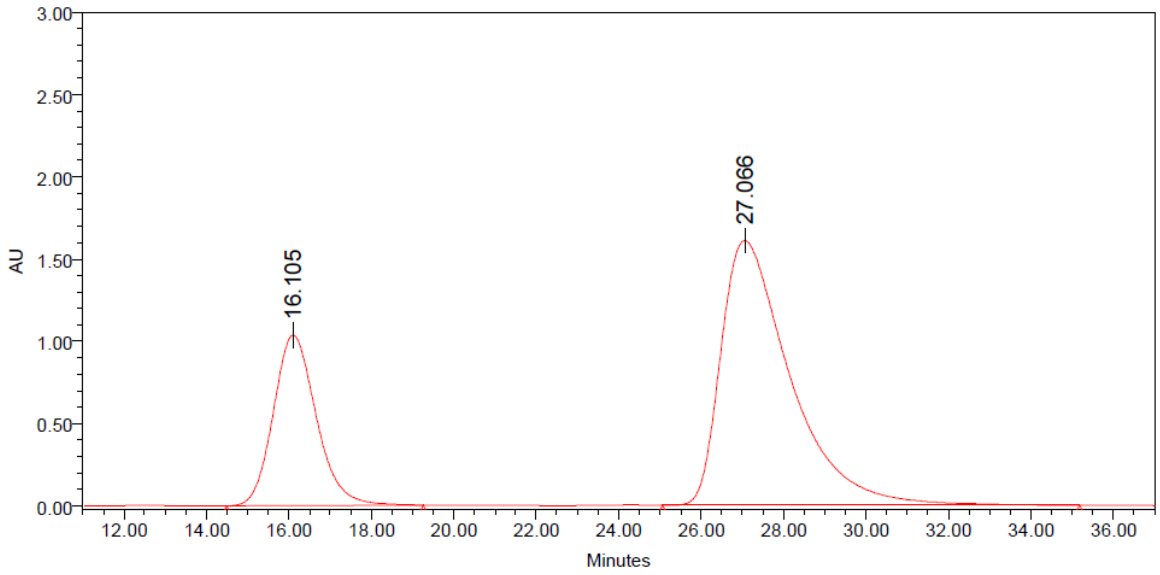
**Figure S53.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(furan-2-yl)-1,4-dihydropyridine-2,3-dicarboxylate (10ak)**.




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 16.066 | 100596140 | 50.23 | 1308641 |
| 2 | PDA 236.6 nm | 27.488 | 99663464 | 49.77 | 800792 |

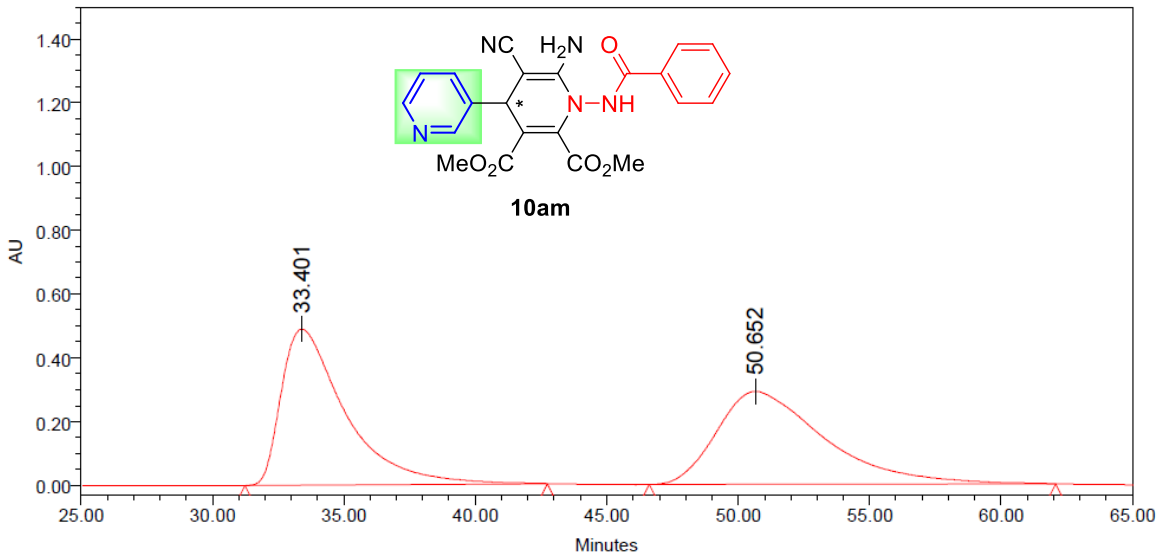
**Figure S54.** Racemic mixture of **10al**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 236.6 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 236.6 nm | 16.105 | 74932650 | 28.49 | 1035798 |
| 2 | PDA 236.6 nm | 27.066 | 188049038 | 71.51 | 1607532 |

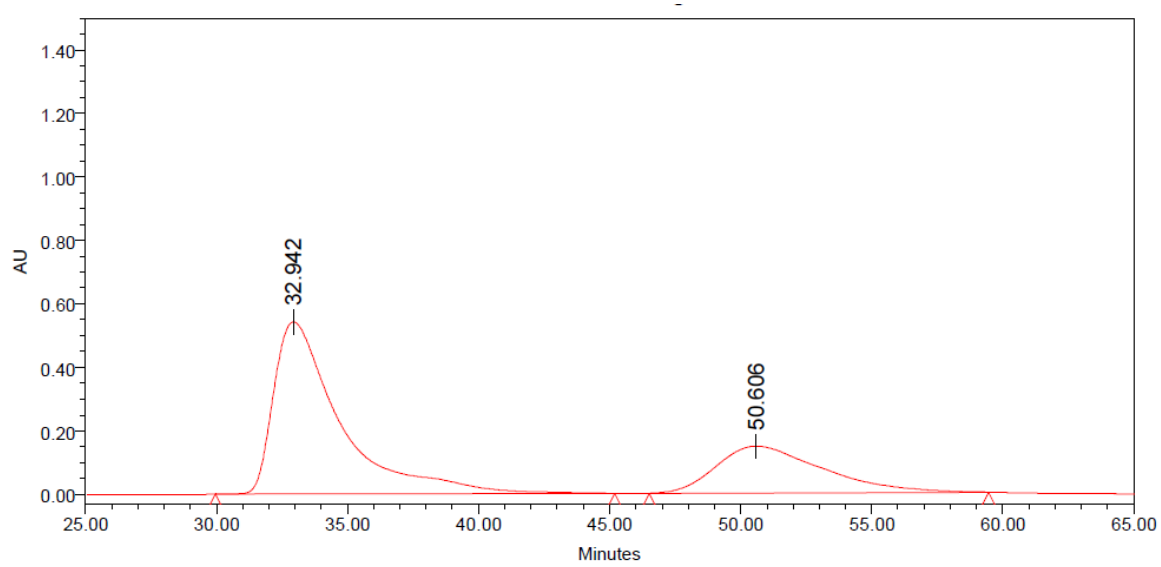
**Figure S55.** Chiral sample of **dimethyl 6-amino-1-benzamido-5-cyano-4-(thiophen-2-yl)-1,4-dihydropyridine-2,3-dicarboxylate (10al)**.




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 33.401 | 82969649 | 49.99 | 489103 |
| 2 | PDA 237.7 nm | 50.652 | 83002489 | 50.01 | 291330 |

**Figure S56.** Racemic mixture of **10am**. Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 70:30, flow rate 1 mL/min).




**Processed Channel: PDA 237.7 nm**

| | Processed Channel | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | PDA 237.7 nm | 32.942 | 95793294 | 69.83 | 542245 |
| 2 | PDA 237.7 nm | 50.606 | 41390261 | 30.17 | 146845 |

**Figure S57.** Chiral sample of **dimethyl 6'-amino-1'-benzamido-5'-cyano-1',4'-dihydro-[3,4'-bipyridine]-2',3'-dicarboxylate (10am)**.